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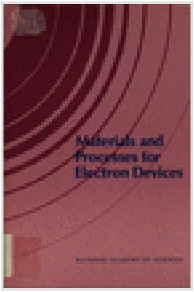

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Materials and Processes for Electron Devices

Prepared by the
Ad Hoc Committee on Materials and
Processes for Electron Devices

NATIONAL MATERIALS ADVISORY BOARD
NATIONAL RESEARCH COUNCIL

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1972

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The members of the study committee were selected for their individual scholarly competence and judgment with due consideration for the balance and breadth of disciplines. Responsibility for all aspects of this report rests with the study committee, to whom sincere appreciation is expressed.

Although the reports of our study committees are not submitted for approval to the Academy membership or to the Council, each report is reviewed by a second group of appropriately qualified individuals according to procedures established and monitored by the Academy's Report Review Committee. Such reviews are intended to determine, *inter alia,* whether the major questions and relevant points of view have been addressed and whether the reported findings, conclusions, and recommendations arose from the available data and information. Distribution of the report is approved, by the President, only after satisfactory completion of this review process.

This study, by the National Materials Advisory Board, was conducted under Contract No. DA-49-083 OSA-3131 with the Department of Defense.

Members of the National Materials Advisory Board study groups serve as individuals contributing their personal knowledge and judgment and not as representatives of any organization in which they are employed or with which they may be associated.

The quantitative data published in this report are intended only to illustrate the scope and substance of information considered in the study, and should not be used for any other purpose, such as in specifications or in design, unless so stated.

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Dedication

The untimely tragic death of DR. JACK A. MORTON *while this report was in the final editing and review process has cost the scientific and engineering community a brilliant analytical mind and a dynamic leader. The* NMAB *ad hoc Committee on Materials and Processes for Electron Devices dedicates its report to the spirit of the man to whom it owes so much in inspiration and friendly but firm guidance.*

Materials and Processes for Electron Devices
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Preface

The reader is advised that each chapter of this report is structured appropriately to its purpose. Chapter 1 sets the stage for the Committee's work. Chapter 2 gives the rationale for its operation. Chapter 3 brings together the principal problems, recommendations, and conclusions so that important managerial information is gathered in one place. The succeeding chapters deal with particular material areas and contain essential technical information as well as greater detail relating to problems, recommendations, and conclusions.

Abstract

A survey has been made of materials and processes for solid state electronic devices. Problem areas have been identified; various solutions have been considered; recommendations have been made. The approach has been to search for areas of materials and process innovation needed by the government based on the following criteria of effectiveness:

1. Adaptability;
2. Service effectiveness through basic understanding, batch processing, and partitionability.

The following material areas have been addressed: elemental semiconductors; compound and alloy semiconductors; magnetics; composite structures; inorganic dielectric materials; organic dielectrics. Conclusions and recommendations were made on approaches for materials; processes; devices; structures; system applications for short-term development (less than 5 years); medium-term applied research (5–10 years); and long-term basic research (more than 10 years).

Acknowledgments

In addition to the members and liaison representatives who participated in this study, a number of others made important contributions. The following made presentations:

Dr. Jay Zemel, University of Pennsylvania
Dr. E. D. Reed, Bell Laboratories
Dr. David Thomas, Bell Laboratories
Mr. Peter Haas, Department of Defense
Major Stanley O. Kennedy, Department of Defense
Mr. John W. Cleland, Oak Ridge National Laboratory

The Committee wishes to express its sincere appreciation of the support and contributions of Dr. Robert S. Shane, Staff Scientist, who served untiringly, creatively, and far beyond the call of normal duty, and of all the others who gave their time and energy to the work of this Committee.

JACK A. MORTON, *Chairman*
ad hoc Committee on Materials and
Processes for Electron Devices

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Contents

1 Introduction

The NMAB *ad hoc* Committee on Materials and Processes for Electron Devices came into existence pursuant to a request from the Department of Defense, Office of Director of Defense Research and Engineering (ODDR&E). The Committee's charge was to "Examine the situation in electronic materials and devices with the view toward identifying major technical issues and make appropriate recommendations."

The purpose of the Committee was seen to be a study, survey, and categorization of the use of materials in electronic devices. The Committee was to identify the status, needs, and deficiencies in materials of interest, and to suggest technical approaches for alleviating deficiencies with suitable recommendations.

It was recognized that materials must be examined against the background of their engineering use in a device. Electronic materials, however, must be evaluated in terms of adequate characterization and reliability in the real world. A study of processing was soon seen to be indissolubly tied to the materials study if useful results were to be obtained.

The client, Department of Defense (24 installations), and major DOD contractors were extensively interviewed to broaden the perspective of the current acute needs. In addition, the liaison representatives furnished a steady input relative to the Committee's need for awareness of DOD's specific needs and the government's general needs.

The following problem areas were identified as being of common interest to many DOD agencies:

Reliability Physics. An understanding is needed of the procedures for ensuring that the employment of materials will be such that the probability of achieving the design objective(s) will be maximized. Specifically, such techniques as failure analysis, failure mode, and effect analysis and predictions, acceptance testing procedures and in-service monitoring by nondestructive and non-interfering tests are meant.

Predictive Testing of Materials. This subject needs to be studied in connection with electronic materials applications.*

Low Power Semiconductor Device Materials (Ge, Si, SiC, and amorphous materials). Problems of purity, characterization, producibility, and domestic availability are apparent.

Organic Materials with long-term stability and very small gas diffusion constants are needed for substrates, coatings, and encapsulants.

Large Scale Integration (LSI) problems include but are not limited to (a) built-in second-order defects from normal manufacturing processes; (b) problems of interconnection materials such as electromigration of aluminum and other metals; (c) sensitivity to environmental interaction; (d) problems of fan-out of external conductors; (e) packaging configurations and materials.

High Dielectric Constant and/or Strength Materials are needed for small capacitors and other devices.

Aging problems need to be studied with emphasis on parameter drift as well as physical degradation by interaction with the environment. Special case environments might well be pulsed and/or steady-state radiation.

High-Density Memories with rapid retrieval. This is a group of material problems with reference to magnetics, semiconductors, interconnections, external conductors, long-term stable packaging. The impending increase in feasible chip size by an order of magnitude lends urgency to this item.

Specialty Materials. This item comprises the group of photosensitive (total EM spectrum) materials, detectors in general, piezo-electrics,

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***Report of the NMAB *ad hoc* Committee on Testing for Prediction of Material Performance in Structures and Components—NMAB-288 (1972).**

magnetostrictives, electrostrictives, etc. High speed sensors are particularly needed as well as long-term stable photoelectric materials.

The Influence of Heat on materials might have been a special case under aging (above) but thermal management is of such overriding importance in the successful utilization of electronic devices that it may be mentioned separately. Thermally conductive dielectrics, heat pipes, Peltier effect coolers, for example, are likely areas for investigation.

As will be discussed in the next chapter, most of these areas will be treated in this report—but a few are considered to be within the purview of more specialized committees, existing or recommended.

The NMAB *ad hoc* Committee on Materials and Processes for Electron Devices recognized early that other organizations were carrying on activities with which it was necessary to be *au courant*. The Advisory Group on Electron Devices (AGED) was contacted by a liaison representative, Mr. David Slater. The American Society for Testing and Materials (ASTM) Committee F-1 on Electronics was contacted by a member (Dr. W. M. Bullis). The IEEE-GNS was contacted by a liaison representative, Dr. Edward E. Conrad. Dr. Robert S. Shane contacted the other pertinent Academy Committees such as the Committee on Amorphous Materials, the Conference on Electrical Insulation and Dielectric Phenomena. Activities of other organizations of a regular and *ad hoc* nature were brought to the Committee's attention by members and liaison representatives.

Although the Department of Defense requested this study, the nature of the subject and the approach lead to the hope that the entire electronics industry may benefit from this report.

2 General Considerations

2.0 PROBLEM-POSING IN INNOVATION

As indicated in the Introduction, this *ad hoc* Committee has as its functions the identification of problems and the recommendation of potential solutions in the area of materials and processes relevant to electron devices. While problem-posing is most essential in the creative innovation process, it is by far the least expensive part. Problem-solving, once decisions are made and resources allocated to a selected potential solution, always accounts for the lion's share of total cost. Thus, problem-posers must be aware themselves of their biases, strengths, and limitations, and they are obliged to fully disclose these to the problem-solvers who may act upon their recommendations. To make sure that this understanding is mutual, let us remember that in every problem-posing exercise three elements are always present, explicitly or implicitly:

1. The *viewpoints* of the persons posing the problem;
2. A set of *potential solutions permissible* in terms of those viewpoints; and
3. *Measures of effectiveness* by which potential solutions may be

judged, so that decisions can be made as to which solution is to be pursued.

It is important to the problem-solver to fully understand all three of these elements that his problem-posers use in their studies. Only through understanding the viewpoints and criteria of the problem-posers will the problem-solver understand what has been included and excluded and thereby be able to proceed on the basis of known risks in using the recommendations of his problem-posers. To make sure that these caveats are as explicit as possible and, hopefully, to reduce the risk for the problem-solving agencies we hope to serve, the rest of this chapter will spell out the viewpoints and criteria that have guided this Committee in its efforts.

2.1 VIEWPOINTS OF THIS COMMITTEE

At an ever-increasing rate for the past half-century, electronic systems have grown in size, complexity, and versatility. Paced by previous innovations in component technology, system change is being accelerated even more by recent innovations in solid-state electronic materials, processes and devices.

Sometimes system concepts precede and stimulate component innovation. But more frequently, in recent years, new component technologies spawn new system capabilities and complexities.

In a similar way, new device ideas generate materials and process innovations. However, once a new physical concept or device invention is made, its full development and application are critically dependent upon basic advances in materials-process understanding and innovation; the "transistor effect" is certainly such a case.

In earlier years, tactical choices for innovation were few; the time interval between opportunities were long—long enough to ensure a rewarding return on R&D investment.

In recent years, the number of opportunities for materials/component innovation has grown and, indeed, is growing fantastically. They are frequently competitive with each other and with old techniques, and this rapid change elevates the risk that a new technology will become obsolete or surpassed before its development and application are complete. Today there are more opportunities to lose your shirt than to make a killing. *Short-term tactics without clear goals, ordered objectives, and long-term strategies can be disastrous.*

The component needs of the federal agencies encompass all conceivable electronic functions in widely varying and almost hostile environments. For this Committee to make tactical recommendations consistent with the shrinking resources, it had to look for viewpoints and criteria of effectiveness that would integrate these needs into broadly useful common areas, even though specific requirements may vary widely. Thus, our Committee has sought areas of materials and process innovation that, hopefully, would be generically relevant to the widest possible range of devices needed by the agencies. What, then, are the criteria of effectiveness that guided us toward such generic materials/process problems?

2.2 CRITERIA OF EFFECTIVENESS

Today's electron device and, certainly, tomorrow's depend vitally upon basic understanding and control of complex materials systems and the processes for achieving them. Investment in a new or improved technology must therefore be extensive in time, specialized manpower, and interdisciplinary coupling. To get a good return on an innovational investment any selected potential innovation must be widely applicable and long lived. It must be able to survive the changes that are sure to come in new knowledge, technology, and systems applications. "Is the proposed innovation adaptive?" is a strategic question.

To be adaptive to change, a materials-process-structure technology must first of all be understood scientifically. Only through such understanding will the materials and processes be capable of being controlled and continually improved. Only through such understanding can we hope to understand the physical mechanisms of change in materials systems when they are subjected to a variety of mechanical, electrical and radiation stresses. Only through such understanding can we hope to meet cost and reliability requirements for diversified complex systems in demanding environments.

From this viewpoint, this Committee subscribes strongly to the recommendation made by the NMAB Committee on Characterization.* The situation is well depicted in the diagram shown in Figure 2-1.

To its recommendation for strong support for this area of basic materials characterization, our Committee extends its viewpoint to the

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*"Characterization" describes those features of the *composition, structure,* and *defects,* that are significantly determined by the raw materials and processes, and which specifically determine the useful properties of that material. (NMAB-229-M)

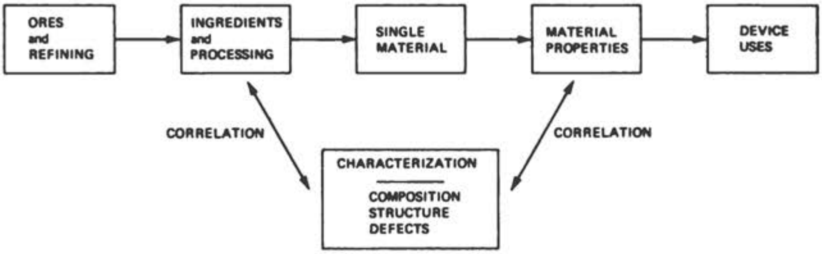

FIGURE 2-1 Characterization of single material.

material system comprising the structure of the electron device. This next level of synthesis is shown in Figure 2-2, wherein the outputs of Figure 1 become the inputs of Figure 2. Characterized single materials are formed into complex multimaterial device structures, which, in turn, have device functional properties for use in electronic systems. In our recommendations, we have been guided by the additional need for better characterization of generic material structures of devices such as metal-insulator-metal, metal-semiconductor, and metal-insulator-semiconductor structures. How are their composition, structure, and defects determined by the fabrication processes and how, in turn, does this characterization determine the useful properties of electron devices using them? The better the characterization of component materials and materials systems for devices, the more adaptive will be the technology to a wide variety of device functions and system environments. Certainly, processes such as oxide masking, epitaxial growth, diffusion, photolithography, evaporation and sputtering are adaptive processes; they are widely applicable to many different materials and device structures which, in turn, have proved their adaptability to a wide variety of system functions since 1954; and, certainly, electron and ion processing give promise of extending this adaptability

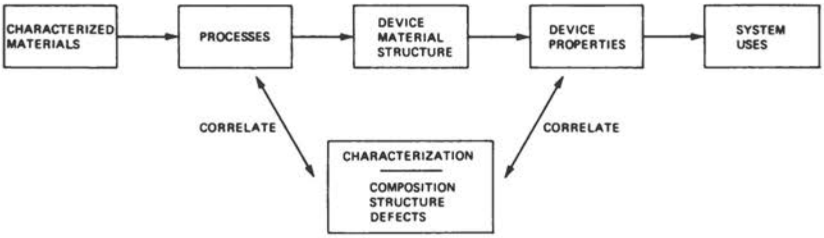

FIGURE 2-2 Characterization of material system.

as better basic understanding of their effect on materials characterization is forthcoming.

But wide applicability and scientific understanding are not sufficient conditions for long life and adaptability of materials/process technologies; they must also result in device structures and functions that are highly cost-effective for a broad range of applications.

Diffused silicon transistors and diodes were certainly most adaptive of all competing technologies until the early sixties when they reached what seemed to be intrinsic limits in performance, cost, and reliability.

But these cost-effectiveness limits were not set by the adaptability of the physics, the materials, or the processes, rather, they were limits set by a *discrete* element structure. *Batch* diffusion made thousands of elements at one time in a slice of silicon. To use them, they were cut apart, terminated, protected, tested, assembled one at a time into circuits and systems, and penalties were paid in performance, cost, and reliability. So it was asked: "Why take Humpty Dumpty apart? It is costly to reassemble him. With batch diffusion many circuits could be made at one time; *why not integrated circuits*?"

With integrated circuits, batch processing is extended to circuit intraconnection with commensurate improvements in cost-effectiveness. But one-at-a-time operations—termination, protection, test, and assembly—are still required at the circuit level. Why stop there? If some integration is good, why not the maximum?

Alas, there are hidden traps in this approach. A truly maximum level of monolithic integration means maximum area and number of process steps, and yield becomes vanishingly small. Moreover, the higher the level of monolithic integration, the more specific the design, the less applicable these will be to many different systems accompanied by less cumulative production. Low cumulative production never brings costs down the learning curve.* If one pushes monolithic integration too far, it can become less adaptive and cost-effective.

Even if all required functions can be supplied by a single material, high yield (through the learning process) requires some partitioning between identical smaller subsystems as does, indeed, adaptability.

Moreover, any single material is always limited in its functional adaptability. Silicon cannot yet provide stable, precise resistors and capacitors, nor can it provide some of the unique electronic functions of, e.g., gallium arsenide and gallium phosphide.

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*"Learning curve" refers to lowered-cost per unit resulting from gained production experience.

Thus, our strategy must recognize that, at some level in all systems, either for economy or for needed functions, all systems must become hybrid in the sense that they require the interconnection of similar and different integrated materials subsystems.

The key to economy for hybrid systems is total batch processing. It means dividing the cumulative cost of a number of process steps by the number of usable subsystems produced per batch. It also means decreasing the number of process steps per device subsystem through simplification of the materials systems and basic processes. It also means decreasing the number of unwanted defects in the component materials and device structures. All of these can be achieved only through understanding the basic relations between materials characterization and the desired properties of the device materials structure.

Finally, it means batch fabrication for all process steps, from raw material to protection and termination of each material subsystem. We also need batch assembly and intraconnection of the hybrid system. If we do not have low-cost batch fabrication at the nth level of assembly, we will always be tempted to integrate too much at the (n−1)th level of the system, with attendant lower yields and higher costs.

A key to adaptability and batch processing is flexibility in partitioning a total system into its similar and different subsystems and at the same time preserving batch assembly of those subsystems. To benefit from subsystem batch processing, we must have sufficient cumulative production of each to achieve learning-curve high yields. For easy trade-offs between subsystem costs and hybrid system assembly costs, we need complementarity and compatibility between material subsystems. Besides complementing each other in functions, for compatible batch assembly and reliability, subsystems must be well matched at their interfaces in metallurgy and topology and they must have commensurate resistance to high stress environments. If such conditions are met, the designer can partition his system optimally with regard to performance, cost, and reliability. He will be able to change his partitioning between subsystems as yields of old technologies grow, as new materials and phenomena appear, and as systems and environments change. He will have an adaptive, low-cost technology.

But low manufacturing cost per assembled system function is only a necessary condition of a cost-effective, adaptive technology; it is not sufficient. Well-controlled automated batch processes can save labor costs in manufacturing total systems. Systems must still be installed, operated and maintained for a useful service life, and these kinds of operation require skilled labor. This is service labor, not easily automated or batch processed, and its cost will continue to rise monotonically. Only by choosing an integrating criterion of effectiveness for the total costs of system service can we make sensible choices and recommendations for adaptive materials-process innovations. Viewing service, not manufactured product, as the system objective provides such an integrating measure. Service can be measured by the amount of performance per total annual dollar of expense. It can be expressed as:

$$\begin{array}{c}\text{Service}\\ \text{Measure}\end{array} = \frac{\text{Performance}}{\begin{array}{l}\text{Annualized Cost (of Manufacture,}\\ \text{Installation, Operation, Maintenance)}\end{array}}.$$

In such a total systems approach all these factors must be kept in mind. Frequently, not all costs can be minimized simultaneously. One is seeking a grand optimum; often trade-offs must be made between the various elements, as, for example, between manufacturing costs and maintenance expense in an especially hostile or inaccessible environment, such as space.

Through maintenance expense, reliability is implicitly present in this "service measure." It is rapidly emerging as a factor of major importance for large complex systems and hostile environments. Generally speaking, batch fabrication brings reliability improvements in the same way it brings manufacturing cost improvements. The opportunities for errors or defects per process step are shared for a batch of elements or subsystems; it is a fact that failure rates per integrated circuit can be as low as those for a single device chip of commensurate size. But as systems become larger and more complex and operate in more stressful environments, even this sharing is not good enough. It often happens that for critical applications, be they industrial, military, or space, there is complete duplication of electronic equipment. The economic penalties are significant; not only are manufacturing costs doubled, but building or vehicle space, installation, maintenance, and operational costs also escalate. All this is because electronic devices are not sufficiently reliable, although it would probably be more accurate to say that the reliabilities of electronic devices are difficult to predict. In fact, it has been apparent to this Committee that the determination of device reliability remains a thorn in the side of the electronics community. Since devices are being sought with failure rates as low as one or less than one in 10^9 hours, the verification of such rates is a formidably costly task. It depends partly upon the development and application of satisfactory accelerated stress-testing procedures and partly on the gathering of reliable data from the field. Both are necessary. It is particularly important that the government agencies understand that a modest but *well-organized* effort in field failure reporting could have large beneficial consequences. Provided then that there is a dedicated mechanism for rapidly reporting and analyzing the nature of these field failures in order to influence research understanding, development, and design, a critical loop will be closed, which will serve all makers and users of electron devices.

It should again be emphasized that characterization is essential to both the development of stress testing and field failure analyses and fundamental understanding of the effect of stressful environments on materials and material systems. Progress will come only from deep understanding of the physical-chemical change mechanisms in material composition, structures, and defects induced by thermal, mechanical, electrical and radiation stresses. Only when these are known can wise choices of materials and device structures, which are more resistant to particular anticipated environmental stresses, be made.

2.3 PERMISSIBLE ALTERNATIVE SOLUTIONS

Any complex problem in technology always has many alternative potential solutions differing widely in their intrinsic adaptability, cost, and effectiveness. They may range from short-term "quick fixes" to long-term approaches requiring basic research. Specific solutions may also be sought at different levels of system complexity, e.g., at the material level, through process innovations, device structures, subsystems, or the total system itself.

In the posing of problems for innovation, as we said, the viewpoints of the problem-posers are essential. They define the boundaries of permissible potential solutions and the measures of effectiveness that will serve as criteria for making choices from the range of permissible solutions.

This Committee's viewpoint is that of materials/process specialists. We are concerned primarily with electron-device problems as stated by the federal agencies, but the range of our recommended permissible solutions does not attempt to go beyond work in the basic materials, processes, and device material structures that are relevant to the device needs of the agencies. Moreover, our viewpoint seeks the widest possible applicability of the solutions. We recognize that there are a myriad of specific materials/process device problems that might be tackled, but we know that resources, even at the federal level, are limited. Therefore, in seeking the most generic solutions, we have developed criteria such as adaptability and service effectiveness through basic understanding, batch processing, and partitionability. *There will be many specific functions and areas that we have recognized but have had to pass over, not because they are not critical, but because they do not promise generic relevance, high adaptability, and, therefore, a maximum return on innovational investment*; thus:

1. The Committee has focused its work on certain classes of solid-state materials, associated processes, and device structures that promise wide applicability and high return on research and development. On the other hand, important but more highly specialized materials such as superconductors, ferroelectrics, piezoelectrics, and thermoelectrics, having critical but more limited application, have not been treated extensively. As noted earlier, these may well be the subjects of more specialized committees. For similar reasons, studies of gaseous and vacuum electronics are excluded, except as to solid-state materials employed in such structures. These include, as appropriate, those used in silicon targets, high-power devices, and phosphors, but traveling wave tubes, oxide cathodes, and vacuum devices *per se* have been excluded. Ancillary materials can be interpreted as liquids, gases, or solids, as appropriate.
2. The Committee repeatedly has considered the question of its involvement in the hardening of electron devices to radiation. However, consistent with its viewpoint and criteria, it has confined its studies and recommendations to the fundamental nature of the interaction of radiation (electromagnetic and particulate) with electronic materials. It is the purpose of this Committee to outline those problem areas that involve radiation resistance generically in materials, processes, and device material structures, but examining radiation hardening in specific devices by specific structures and processing is not consistent with our viewpoint and criteria. It should be the task of a specialized committee.

For the long run, the Committee recommends that studies ot radiation in fabrication of materials and devices be performed. An example might be in the M-I-S materials system of generic value in semiconductor devices. These devices may be fabricated with processes that produce radiation defects along with desired effects as, e.g., when sputtering, electron gun evaporation, or ion implantation are used. Important characterization studies in this area will not only advance an adaptive process for such devices but will also yield important knowledge for the design of radiation-hardened devices. As an alternative solution, new packaging techniques to produce radiation hardening may be suggested from such fundamental studies.

3. The subject of amorphous semiconductors as a class of useful device materials has repeatedly come before this Committee, sometimes in connection with radiation hardening. The Committee recognizes the presence of the NMAB Committee on Amorphous Semiconductors (sponsored by ONR) and its examination and study of the fundamentals of amorphous materials, primarily the elements and mixtures of elements from Columns IV, V, VI of the Periodic Table, and that special attention was given to electrically conducting chalcogenides.* But, consistent with its strong view on generic relevance and adaptability, particularly as based on thorough characterization, the *ad hoc* Committee on Materials and Processes for Electron Devices recommends only exploratory work at the device level (as shown in Figure 2-2) until thorough understanding at the characterization level depicted in Figure 2-1 is forthcoming.

4. A part of the overall work of this Committee, but deserving of special attention, is its concern with yield in the fabrication of widely used high-volume devices. It was agreed that this problem is certainly consistent with the Committee's viewpoint and criteria on adaptability of cost-effectiveness of generic materials, processes, and structures. Certainly, in studying characterization at both the basic materials and device structure levels, fundamental understanding of process effects on composition, structure, and defects will be an essential factor in understanding and controlling process yield. It was also recognized that process yield is a highly proprietary field and it is difficult to collect detailed and specific data. It seems likely, however, that the yield study could identify (a) certain generic yield-limiting processes and (b) the need for characterization studies in each at both levels (Figures 2-1 and 2-2). The yield study might result in recommendations for generic measurements and instrumentation aimed at establishing the desired correlations between processes and properties and the significant characterization of the material or device structure produced. Thus, through such generic recommendations and studies, the Committee hopes to provide to industry the basic tools of characterization and instrumentation that will enable it to evaluate, understand, and improve its own proprietary variations of generic materials, processes, and structures with attendant improvememts in yield and cost-effectiveness.

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*See NMAB-284, "Fundamentals of Amorphous Semiconductors."

Thus, within its viewpoints and criteria as outlined above, the Committee has organized its work into the following study panels specialized according to basic materials/process classes of high relevance and adaptability to the device objectives of the federal agencies:

1. Elemental semiconductors
2. Compound semiconductors
3. Magnetic materials
4. Composite structures
5. Inorganic dielectric materials
6. Organic dielectrics
7. Yield studies (see NMAB-290)

Within its own area, each panel attempted to evaluate the current status, limitations, trends, and opportunities with a view to identifying generic problems relevant to the agencies' device needs. Using the viewpoints and criteria discussed above, each panel then posed problems and made recommendations in any or all of the specialized areas depicted in the innovational matrix shown in Figure 2-3.

Whenever possible, the Panels attempted to identify the expected benefits and costs of such permissible solutions; but it must be realized that, in a limited study of this kind, such estimates are, at best, only

	BASIC RESEARCH > 10 Years	APPLIED RESEARCH 5-10 Years	DEVELOPMENT < 5 Years
MATERIALS			
PROCESSES			
GENERIC STRUCTURES			
DEVICES			

FIGURE 2-3 Innovational matrix.

rough guides. Much more detailed evaluation and planning would be done by any specific agency before acting on these recommendations. Our estimates should be considered only as the direction of the innovational vector, not the magnitude.

Finally, a word about committee functions is in order. Committees, however specialized or interdisciplinary, are excellent vehicles for posing problems. Through their non-involvement in action, they can bring together the different viewpoints and objectivity needed to look at all sides of a problem, establish needed criteria of effectiveness, and define alternative solutions permissible in terms of their viewpoints and criteria. They cannot and should not make specific choices and decisions as to which of the permissible solutions should be pursued with what fraction of an agency's total resources. These judgements can be made only by responsible decision-makers within line or project organizations, who will be held responsible for the effective use of their resources. Only the agencies can define their long-term and short-term goals, order their objectives in relative importance, develop a strategy for achieving those objectives, and control their tactics to match their resources. Committees are excellent for the staff function of posing problems; line or project organizations must make the choices and allocate resources to solving problems.

3 Major Problems and Recommendations

The problems listed in this chapter, together with the recommendations, have been identified and discussed in the indicated chapter, which the reader is advised to consult for completeness of understanding. In general, the format used in this and later chapters will be

1. Identification of the problem areas;
2. Recommendation, including the recommendation, the time-scale,* and the benefits that are expected to accrue from implementation of the recommendation.

3.2† PROBLEMS DISCUSSED IN CHAPTER 2

Problem

3.2.1 Materials-process-structure technology interplay must be understood scientifically.

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*2-5 years–development
5-10 years–applied research
>10 years–basic research

†Second digit refers to appropriate chapter for more information.

Recommendation

3.2.1.1 Strong support should be given not only to basic materials characterization* but also to characterization of the electron device material system. This concept should be supported at all stages of development from basic research to utilization in design. Direct benefits will accrue through vastly increased adaptability conferred by increased scientific knowledge of the materials of interest.

Problem

3.2.2 More economical methods are needed for fabrication of hybrid systems.

Recommendation

3.2.2.1 The key to economy for hybrid systems—requiring the interconnection of similar and different integrated materials subsystems—is total batch processing from raw materials to protection and termination of each subsystem. The concept should extend to assembly and intraconnection of the assembly. The batch-processing concept should be developed during applied research and applied during development. Lowered first cost by greater process yield and lowered later costs by increased reliability through greater process control will contribute maximally to lower annual service cost.

Problem

3.2.3 Make sensible choices and recommendations for adaptive materials/process innovations.

Recommendation

3.2.3.1 Choose an integrating criterion of effectiveness for the total costs of the system service. View *service,* not manufactured product, as the system objective, e.g., measure by the following equation:

$$\begin{array}{c}\text{Service}\\ \text{Measure}\end{array} = \frac{\text{Performance}}{\begin{array}{l}\text{Annualized cost (of Manufacture,}\\ \text{Installation, Operation, Maintenance)}\end{array}} \; .$$

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*See footnote, p. 6 for definition of "Characterization."

This concept should be used at all stages. The benefits come directly in improvement of decision-making process as to yield and quality of decisions.

Problem

3.2.4 Field-failure reporting and analysis has generally not been an important factor in design improvement.

Recommendation

3.2.4.1 Put in place a dedicated mechanism with modest but assured funding for analyzing and reporting the nature of failures. This concept should be brought to bear upon applied research, development, and early service life. The results of this effort would be improved research understanding, development, and design and production and test methods. Consequently, beneficial effects through lowered failure rates would ensue.

Problem

3.2.5 The important fabrication assistance of radiative methods needs extension to secure inherent benefits.

Recommendation

3.2.5.1 Encourage and put in place studies of use of particulate radiation in materials and devices for fabrication assistance and producing desired changes, e.g., by planned introduction of defects, ion implantation, sputtering electron gun evaporation, etc. This should be implemented at all stages of research. Improved fabrication methods and new materials structures may result.

Problem

3.2.6 The potentially useful class of amorphous semiconductor materials is not yet well enough understood to enable the possible benefits to be realized in a desirable way.

Recommendation

3.2.6.1 Basic understanding must be gained of those characteristics and processes that determine the fundamental behavior of devices made from these materials. Until this is done, device work is only indicative.

Basic research and some applied research should be conducted to elucidate the important aspects of the needed "Characterization."

3.4* PROBLEMS DISCUSSED IN CHAPTER 4–ELEMENTAL SEMICONDUCTORS

Chapter 4 is concerned with research and development needs for materials and processes of the elemental semiconductors. Silicon is discussed in considerable detail. Germanium, selenium, diamond, tellurium, and boron are treated briefly. Sulfur, gray tin, antimony, and bismuth are omitted simply because they offer little potential for electronic device use. Alloys such as S:Se, Ge:Si, and Se:Te are ignored for the same reason, although such alloys may become important for special application.

The broad and adaptive technology base of silicon gives it a significant advantage over potentially competitive materials for many applications. This advantage seems to grow rather than diminish; the recommendations of this report will reflect this trend. The use of silicon to make high quality TV pick-up targets, self-scanning image arrays, and electronically scanned radars probably would not have been predicted by even the most perceptive observer in 1960. All of this is not to say that support of the other materials should be completely shut down in favor of silicon, but the Committee believes that funds will most often be more effectively spent when applied to further improving silicon technology and extending its applications. There are, however, functions such as light-emitting diodes, which silicon will probably never fulfill.

Furthermore, the Committee recognizes that there are some significant gaps in our knowledge of silicon that will have to be filled before the material can attain its complete potential.

Regarding the other elemental semiconductors listed below, specialized applications exist where each can contribute. The particular applications have been isolated for future support. The Committee also recognizes that solid-state materials studies are still proceeding in many directions, trying to capitalize on some particular band structure or other phenomena of these semiconductors. These studies may result in some striking breakthrough that will change the whole picture; the government agencies should keep abreast of some of these studies and should even encourage them. However, for at least

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*Second digit refers to appropriate chapter for more information.

the next five years, we believe that the following recommendations are quite reasonable.

Silicon

Silicon is the most widely used and adaptive semiconductor material. However, the extreme requirements being placed on it have exposed a number of areas that will have to be strengthened before the material can realize its full potential. The five important broad areas are

1. Initial material
2. Processing
3. Structures
4. Devices and design
5. Packaging and testing

INITIAL SILICON MATERIAL

Problem

3.4.1 Before silicon is processed into devices or circuits, a thin slab of well-characterized material having very high crystal perfection and precise chemical composition must be produced. The problems associated with the economical production and characterization of such slices are numerous. Several of the more important ones are implicit in the recommendations below.

Recommendations

3.4.1.1 Considerably more effective methods need to be developed for determining the chemical purity and electrical characteristics of silicon at all stages of manufacture, from raw chemical input through polycrystalline deposition, single crystal growth, and epitaxial deposition. The precise measurements of epitaxial layer thickness and resistivity become progressively more difficult as the layers become thinner with advancing device technology. Rapid nondestructive methods for characterizing such thin layers would be of great value to almost all device developments. Studies of the effect of so-called nondoping impurities such as oxygen and carbon would probably clear up many anomalies observed during processing. Basic research should be supported in this area.

3.4.1.2 A thorough evaluation of the theoretical and practical limits of parameters like minority and majority carrier lifetimes, as a function of impurity content, would serve as an important guide to silicon producers and device designers. For example, a long minority carrier lifetime coupled with low resistivity would allow the fabrication of a much more efficient solar cell.

3.4.1.3 Very-high-resistivity silicon (10^3 to 10^5 Ω-cm) is being increasingly called for in infrared and visible sensing applications. Significant progress in this area will have considerably more impact on our national defense posture than on the civilian segments of the electronics market. A European source is presently supplying most of our needs for this type of material. Domestic sources of such material must be developed.

3.4.1.4 There is a continuing need for more efficient utilization of silicon. It is likely that competition between manufacturers will lead to an evaluation of larger diameter slices, but more economic slice-producing methods would still be extremely useful, for example, in large area devices such as solar cells. New methods of slice preparation would also be of great use, since present methods (saw, lap, and polish) waste more than 50 percent of the silicon. Development work in these areas is recommended.

3.4.1.5 The primary need in silicon eptiaxy is for an economical method for mass producing very thin layers. An advanced highly automated epi-manufacturing process will probably be required to bring this about. Development is recommended.

3.4.1.6 The development of an economical supply of very thin silicon on insulating supports would have significant impact on MOS and bipolar circuitry by markedly reducing parasitic capacitances and hence increasing speed. Such development is recommended.

SILICON PROCESSING NEEDS

Problem

3.4.2 As specifications of electrical parameters of discrete devices and integrated circuits have tightened during the last few years, considerable pressure has been exerted on the process engineer. This is largely the result of years of empiricism, whereby device specifications have been developed by an evolutionary process, only pausing on occasion to ask why a certain parameter is widely variable, or why parameter X is linked to parameter Y. In the following list of recommendations, the Committee has isolated only a very few of the most obvious needs.

Recommendations

3.4.2.1 Methods need to be developed to control precisely minority carrier lifetimes in device structures. This will require development of the thermodynamics of very dilute solid solutions, more knowledge of the recombination kinetics and metallurgical behavior of various impurities, and considerable effort to develop production-worthy techniques to dope silicon with lifetime controlling impurities such as Zn, Cu, Pt, Ag, Au, etc.

3.4.2.2 A great deal of support will be required for ion implantation studies before the significant potential of this technology can be fully realized. More basic and applied research and production process development are badly needed. More work on ion sources and ion beam optics would also be helpful for system design. Work should be aimed at establishing ion implantation as an efficient and economical doping process for some of the most critical device needs. A strong demonstration of its advantages will be required to break the "inertia barrier" of more traditional processes.

3.4.2.3 A wide variety of in-process control measurements should be developed. Well designed test structures on every integrated circuit slice can help identify processing difficulties. Nondestructive testing and "adjust" techniques, for example, electron beam or laser beam testing, should also receive significant support.

3.4.2.4 Improved multi-metal and refractory metal systems that are compatible with standard device fabrication, assembly, and packaging technology are critically needed. A special need exists for metal systems that can withstand high temperature processing. Improved understanding and control of Schottky barrier and ohmic contacts is also desirable.

3.4.2.5 Image technology work should also be supported, especially those methods that allow line widths of less than one micrometer to be produced. In the next few years, electron beam or, perhaps, other charged-particle technology may become a dominant force in this area.

SILICON STRUCTURES

Problem

3.4.3 Even in the presence of intense radiation environments, ever-shrinking dimensions, coupled with the greater need for complete electrical isolation, have created a need for circuits and devices to be very tightly packed and, at the same time, almost completely isolated from each other. As the structures shrink in size, dielectric–silicon interfaces become more significant; impurity and structural effects at these interfaces can dominate the electrical behavior. This problem is especially acute for radiation resistance, historically an area principally for government related application and, hence, one that did not receive a large measure of attention in commercially oriented R&D.

Recommendations

3.4.3.1 New approaches to device and circuit isolation must be sought, with a target of one micrometer between device islands and access to both top and bottom of these devices in special applications. Several orders of magnitude improvement in power-speed product may be realizable.

3.4.3.2 Studies of several types of silicon-insulator interfaces deserve support because of their extreme importance to device behavior. It is particularly important to understand the effects of the empirical processes from a more fundamental point of view.

DEVICES AND DESIGN

Problem

3.4.4 The very broad technology base of silicon makes it a candidate for a large number of uses. This includes image scanning, infrared and microwave emission and detection, and various logic schemes that involve the controlled lateral motion of charges across a slice. There are also a number of medical uses to which silicon technology might be applied. Other areas not presently utilizing silicon technology to any great extent are environmental control and optoelectronics. Recommendations are made below for the general nature of work that might be encouraged.

Recommendations

3.4.4.1 Efforts that could lead to the performance of completely new functions should be especially encouraged, for example, new logic schemes based on lateral motion of charges, and solid-state image scanning (to eliminate the necessity of electron-beam scanning).

3.4.4.2 It is desirable to develop very-high-voltage integrated circuits. These would impact systems involving cathode ray tube displays. Solid state inductors and more efficient capacitors would also be desirable for some applications.

3.4.4.3 Basic and applied studies of trapping phenomena in silicon should be supported because of their importance in existing devices and the possibility of new devices based on controlled charge storage.

3.4.4.4 A variety of medical applications seem possible. Examples of such applications are heart pacer modules, blind reader development, pressure membranes using thin silicon, ion-selective sensors, *in vivo* blood analysis and sugar control, remote heart failure warning systems, etc. Similarly, devices for applications as sensors for environmental monitoring should be developed.

3.4.4.5 Proposals for an inexpensive silicon solar cell system should be sought. A factor-of-ten reduction in cost should be a minimum goal. Military and space impact would be in the area of remote unmanned stations, but major impact would eventually be for pollution reduction by decreasing the need for fossil fuels.

3.4.4.6 Although the chance of success seems rather small, theoretical studies should be directed to the question of whether isoelectronic or other doping of silicon could lead to the development of an efficient infrared light emitter.

3.4.4.7 Theoretical studies should also be pursued to define the ultimate limits to be expected for various device and circuit structures. In particular, limitations imposed by material parameters and general physical principles should be considered for simplified but realistic structures.

3.4.4.8 Cost effective design automation is an important element in the production of integrated circuits and there is a serious need to understand the detailed relationship between manufacturing processes, device geometries, electrical performance, routing of interconnecting leads, and tests for complex circuit functions. In this connection, the reader should also refer to the report of the Panel on Yield of Electronic Materials and Devices (NMAB-290).

PACKAGING AND TESTING

Problem

3.4.5 For protective purposes, most semiconductor devices are currently packaged prior to use. However, in beam-lead-sealed junction devices this packaging is built onto the chip during batch manufacture. Packaging after front-end processing is costly and also adds another factor detrimental to reliability and yield. After packaging, the device must be tested to see if it performs the desired function. These tests are time consuming and expensive and are becoming progressively more complex.

Recommendations

3.4.5.1 Support developmental work to achieve dynamic test programs, using large computers.

3.4.5.2 Support longer term research on packageless devices and encourage the production of devices by including them in appropriate R&D programs.

3.4.5.3 Support studies of the contactless method (e.g., by electron beam) for evaluating devices.

3.4.5.4 Support efforts at solution of heat removal problems in integrated circuits and high-power devices.

Germanium

Problem

3.4.6 The use of germanium for electronic devices has shifted from broad usage in many types of devices to more specialized devices such as nuclear particle detectors and cold background IR detectors. Several laboratories are producing material with $5 \times 10^{10}/\text{cm}^3$ electrically active impurities, which ranks it as one of the purest materials ever produced.

Recommendation

3.4.6.1 Germanium device research should be encouraged in the areas of nuclear and infrared radiation detectors. A tenfold reduction in impurity content should allow replacement of inherently lithium-drifted detectors. This is a limited market at present, but large volume detectors of ultra-pure germanium would be of great interest in medical and space applications, as well as for a portable detector of general usage.

Selenium

Problem

3.4.7 The main uses of selenium are for xerography and power rectifiers. The thermodynamic properties of amorphous selenium are reasonably well known, but only phenomenological theories have been developed to explain the optical and transport properties. The trigonal form has a large refractive index and is quite birefringent. The monoclinic form converts irreversibly to the trigonal form under any type of applied field.

Recommendation

3.4.7.1 Further attempts should be made to develop fundamental theories to help define additional applications for this material. These studies should be used as a guide to any further R&D effort.

Diamond

Problem

3.4.8 Diamond is of interest because of its extreme hardness, wide bandgap, and very large thermal conductivity. Suitable chips of natural diamonds are relatively cheap, but the selection process to determine the type and preparation by grinding or cleaving is expensive. Synthetic diamonds having even higher thermal conductivities have been grown recently. Their wide bandgap makes them potentially important for light-emitting diodes although other materials such as SiC or GaN also have large bandgaps and may be more easily prepared.

Recommendations

3.4.8.1 Better methods should be sought for selecting and shaping the diamond chips, especially for heat conducting applications.

3.4.8.2 Growth studies aimed at producing high quality synthetic diamonds should be continued with emphasis on doping techniques and reproducibility.

Tellurium

Problem

3.4.9 Tellurium has been proposed for non-linear optical elements and infrared detectors. The band structure has been worked out and the mechanical properties are described in the literature.

Recommendations

3.4.9.1 Firm theoretical arguments should precede any significant effort on the above applications.

Boron

Problem

3.4.10 Boron has been proposed as a suitable material for making thermistors, neutron detectors, and acoustic delay lines.

Recommendation

3.4.10.1 The theoretical grounds on which the above applications might be based need to be examined. If these studies indicate that boron might have significant advantages over competitive materials, then work on the development of sources of high quality single crystals should be encouraged.

3.5* PROBLEMS DISCUSSED IN CHAPTER 5—COMPOUND AND ALLOY SEMICONDUCTORS AND SUPERCONDUCTIVITY

3.5.1 INFRARED DETECTOR RESEARCH

Problems

~~3.5~~.1.1 Maintaining stoichiometry, a high degree of structural perfection, purity, and chemical homogeneity for each composition in a given alloy system is a serious problem.

3.5.1.2 Control of material processing steps in fabricating integrated arrays of detectors with their interconnections is difficult.

3.5.1.3 Deleterious changes in the surface properties of these materials in storage and under different ambients are observed.

3.5.1.4 Higher yields of useful materials are required to achieve economic feasibility.

Recommendations

3.5.1.5 Present research should be concerned with improved methods of crystal growth as well as with the development of new

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* Second digit refers to appropriate chapter for more information.

thin-film synthetic techniques for depositing materials in complex and useful geometries with well characterized physical and chemical properties.

3.5.1.6 Research on surface states and their relation to crystal orientation and environmental conditions must be done to help increase device yield and performance.

3.5.1.7 Long-range research should be concerned with developing a better understanding of the photoconduction and photovoltaic effects in low bandgap semiconductors to complement the materials synthesis work.

3.5.1.8 There is need for a study of new methods for creating p–n junctions in low bandgap semiconductors. Promising techniques include (but are not limited to) annealing and particulate bombardment (protons, electrons).

3.5.1.9 If interest in infrared detectors extends beyond the 30-μm spectral range or to special applications not considered here, it is recommended that research be done in new types of thermal detectors, e.g., pyroelectric detectors, and detectors employing ternary compound semiconductor materials ($A^{II} B^{IV} C_2{}^{V}$ *) of which $ZnGeP_2$, $ZnSiAs_2$ and $CdSnP_2$ are examples.

3.5.2 ELECTROLUMINESCENT DEVICE RESEARCH

Problems

3.5.2.1 (AlGa)As, GaP and Ga(As, P) (doped with N) are presently the most efficient red, orange-yellow-green junction light sources but are costly due to problems involving chemical purity, crystal quality and limitations of suitable substrate material for epitaxial growth.

3.5.2.2 The efficiency of light emitting diodes is limited by various defects, impurities, structural properties, and interactions of these. They must be controlled more effectively for uniformity of results.

3.5.2.3 Improvement in vapor-phase and liquid-phase epitaxial growth techniques and methods of improving junction fabrication are needed.

3.5.2.4 Substrate materials are needed along with good epitaxial layers of promising new materials.

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* Roman numeral superscripts refer to the column of Periodic Table of the Elements of which A, B, and C are members.

3.5.2.5 A more detailed understanding of defect structures in substrates and epitaxial layers, including the influence of defect structure on crystal growth, impurity doping, and junction fabrication, is necessary.

Recommendations

3.5.2.6 Short-range research should be concerned with the compounds Ga(As,P) and GaP. Research is also needed on substrate materials of larger size, higher quality, and lower cost.

3.5.2.7 Immediate attention should be given to problems of vapor-phase and liquid-phase epitaxial growth techniques to achieve higher device performance at reduced cost.

3.5.2.8 A long-range research program on the development of new materials and how to prepare useful p–n junctions is needed. This effort should include a search for improved substrate materials as well as an intensive study of defect structure effects.

3.5.3 ELECTRON EMISSION DEVICES

Problems

3.5.3.1 There is need to increase the long wavelength response in photocathodes particularly at 1.06 μm for use with yttrium aluminum garnet: neodymium (YAG:Nd) lasers, and to extend the response to 1.6 μm in order to couple with the light output of eye-safe yttrium aluminum garnet: erbium (YAG: Er) lasers.

3.5.3.2 For application to imaging in the transmission mode there is need to grow thin crystal layers on suitable substrate materials which are transparent to the incident radiation; concurrent with this is the problem of growing the highest quality heterojunctions having a graded alloy region between the substrate and photocathode materials.

3.5.3.3 Need exists for a practical cathode which will operate at room temperature and at high current density.

Recommendations

3.5.3.4 Applied research on III–V compound alloy systems should continue to enhance photocathode response to 1.06 μm, and exploratory materials research to extend the response to wavelengths of about 1.6 μm should be instituted. This should result in a wider use of these devices.

3.5.3.5 For imaging devices in the transmission mode, longer-range research in the following areas should be performed:

1. Development of new synthetic tehniques or perfecting existing ones for preparing high-quality thin photocathode films on transparent substrates
2. Materials exploration and synthesis to obtain wide bandgap semiconductors in a suitable form and size for substrate crystals
3. A more definitive characterization of the role of both surface states and lattice defects at heterojunction interfaces in reducing optical and electronic losses

3.5.3.6 Long-range research is recommended to evaluate III–V compound semiconductors and their alloys for cold cathode applications, in particular, as they compare with similar devices fabricated from silicon.

3.5.4 THERMOELECTRIC RESEARCH

Problems

3.5.4.1 The major problems common to all telluride alloys relate to their poor mechanical properties and chemical instability.

3.5.4.2 Difficulty is encountered in fabricating contacts with all alloys at the hot junctions of power generating thermocouples.

Recommendations

3.5.4.3 Applied research should be directed toward improving the chemical stability of the most promising telluride alloys over the temperature range of optimum performance.

3.5.4.4 Applied research is needed on developing new materials for the semiconductor–metal contacts, particularly at the hot junction so as to extend the useful life of these devices, as well as to achieve the optimum conversion efficiency.

3.5.5 MICROWAVE DEVICE RESEARCH

Problem

3.5.5.1 There is a need for improved reliability and higher yield of GaAs devices, as well as better correlation between device performance and materials properties.

Recommendations

3.5.5.2 Advance GaAs materials characterization in areas of chemical uniformity and control of impurity doping through refinements in crystal growth techniques and through a better understanding of impurity and trapping levels. This information will lead to improved yield, reduced costs, and more efficient, less noisy, broader bandwidth devices.

3.5.5.3 Investigate new junction fabrication techniques, such as ion implantation, to extend the frequency capability and reliability of devices.

3.5.6 RESEARCH ON HIGH-POWER INFRARED LASER WINDOWS*

The dominant failure mode is the impairment of the optical quality of the window by energy absorption and thermal deformation induced by the high power laser beam.

Problems

3.5.6.1 The laser beam is initially distorted by changes in the optical properties of the window by residual heat absorption.

3.5.6.2 Higher levels of heat absorption induce stresses that may cause mechanical failure.

3.5.6.3 Other nonlinear effects only occur when very short pulses are accompanied by instantaneous power densities in excess of 100 MW/cm^2. Most infrared laser applications do not fall in this category.

3.5.6.4 There is no obvious material choice for large, high power windows for 10.6-μm radiation to supplant the presently unsatisfactory alkali halides.

3.5.6.5 Litte work has been done on high power window properties in the 2- to 6-μm radiation range.

3.5.6.6 A high radiation environment produces color centers and carriers in optical windows at a level that causes intolerable absorption.

Recommendations

3.5.6.7 Investigate the following materials for suitability for high-power laser window material in the 10.6-μm range:

Alkali halides
Cadmium telluride

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*Also see Report of the NMAB *ad hoc* Committee on High Power Infrared-Laser Windows (NMAB-292, 1972).

Other II–VI compounds
Ternary systems
Other materials, e.g., GaAs

The following criteria should be used for each candidate material:

Low level optical absorptivity
Mechanical strength
Possibility of growing large crystal sizes
Heat conductivity and window cooling constraints
Fabrication of sintered composites without significant impairment of optical properties
Need for and compatibility with antireflection and protective coatings
Influence of impurities and radiation damage

3.5.6.8 Investigate the following materials for suitability for high power laser window material in the 2- to 6-μm range. Use the criteria of 3.5.6.7.

Alkali halides
Alkaline earth fluorides
Sapphire
Cadmium telluride
Other II–VI compounds
Ternary systems
Other materials, e.g., GaAs

3.5.7 RESEARCH ON SOLAR CELLS

Problems

3.5.7.1 The quality of bulk silicon available for this application is poor. Improvements in resistivity and the carrier lifetime of starting silicon would significantly improve cell efficiency.

3.5.7.2 Surface losses are incurred during device fabrication. If the surface recombination value could be reduced to less than 100/cm-sec, device performance would improve significantly.

3.5.7.3 The efficiency of solar cells might be increased through better characterization of new materials.

Recommendations

3.5.7.4 Research should be initiated on improving the state of the art of growing high quality, single-crystal silicon. For maximum efficiency, an order of magnitude better silicon is required compared to the material utilized in IC's and transistors. A resistivity of .01 Ω-cm and a carrier lifetime of 5 to 10 μ sec should improve cell efficiency by 50%.

3.5.7.5 There is much known about the passivation and control of surfaces in silicon for discrete devices and integrated circuit applications; a research program applying this knowledge to solar cells is in order.

3.5.7.6 There is no real promise that the efficiency of silicon solar cells will be *substantially* exceeded by other semiconductors. However, efficiencies exceeding 20% may be possible by utilizing other materials such as the III–V compound semiconductors.*

Surveillance of new developments in ongoing research in these materials should be continued, and efforts should be directed to advance the technology of these compounds for this particular application.

In particular, the development of GaAs and GaAlAs solar cells should be investigated using the modern technology of these materials developed for laser diodes.

3.5.7.7 Because of the high cost of replacing satellite systems, every effort should be made to develop Si and GaAs cells with less degradation under ionizing radiation.

3.5.8 SUPERCONDUCTIVITY

Problem

3.5.8.1 No advantage has been taken of the fact that Nb_3Sn remains superconducting with applied fields as high as 80 kG at 14°K.

Recommendation

3.5.8.1.1 Conduct applied research on the operation of existing Nb_3Sn solenoids at temperatures above 4.2°K, perhaps as high as 14°K. This may achieve potential benefits of substantial saving in weight, cost, and size of needed refrigeration.

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* J. J. Loferski, J. Appl. Phys. *27*, 777 (1956).
B. Ellis and T. S. Moss, Solid-State Electron. *13*, 1 (1970).

Problem

3.5.8.2 For full utilization of small superconducting devices (Josephson diodes and weak links) processing technology approaching that of the semiconductor industry is required (see 5.8.3.2).

Recommendation

3.5.8.2.1 Conduct fundamental and applied research on techniques for fabricating superconducting films with thin insulating barriers. Anticipated benefits are reliability, higher yield, and lower cost, in addition to performance advantages.

Problem

3.5.8.3 With few exceptions, little knowledge exists of the microscopic nature of defects that are believed to control the critical current capacity at any field strength and temperature, regardless of the synthetic technique used to prepare these superconductors.

Recommendation

3.5.8.3.1 Support fundamental research on the effect of homogeneous defect structures (grain boundaries, precipitates, dislocation nets) on the field and temperature dependence of the critical current density of Type II (carriers of high current densities below Tc) superconductors. Understanding the role of defects will permit control and lead to optimization of solenoid performance as well as permitting reduction in cost, weight, and size of copper stabilization.

Problem

3.5.8.4 Theory of superconduction fails to relate any significant parameter to the microscopic properties of the material (see 5.8.3.1).

Recommendation

3.5.8.4.1 Support fundamental research on the relationship between the microscopic parameter of transition metal compounds and the normal-to-superconducting transition temperature (Tc). From such research a theoretically guided exploratory materials effort may lead to understanding the present 21°K limit of Tc, and, hopefully, permit the next step of operation in boiling hydrogen (22°K) or neon (28°K), working ultimately toward liquid nitrogen (77.3°K) operation.

Problem

3.5.8.5 New materials and new structures are needed for low-loss alternating current, radio-frequency, microwave, and millimeter wave applications. Suitable dielectric materials for these applications are also needed.

Recommendation

3.5.8.5.1 Support an exploratory program in the area of superconducting materials, structures, dielectrics for low-loss alternating current, radio-frequency, microwave, and millimeter wave applications.

Problem

3.5.8.6 Device development of remotely controlled superconductive circuit components is needed to take full advantage of superconducting phenomena.

Recommendation

3.5.8.6.1 Support development of variable inductance, tunable resonant circuits, and relay switches for use with superconducting equipment.

Problem

3.5.8.7 New methods of information handling are possible (see 5.8.2.1) with very small power consumption at satisfactory speeds.

Recommendation

3.5.8.7.1 Support further search into new methods of information handling through use of minimum energy quantum processes operating in the "flux-shuttle" shift register. Potential benefit would be the ability to make very-large-scale memories based on superconducting weak links with orders of magnitude improvement with respect to power consumption at satisfactory speeds.

3.5.9 II–VI LUMINESCENT RESEARCH

Problem

3.5.9.1 For the II–VI compounds with bandgaps in the visible or ultraviolet, p–n junctions are unknown because the materials will form only one conductivity type showing low resistivity at room temperature. Also, all of the higher bandgap members of this family show only n-type conductivity and highly efficient hole injecting contacts to them are unknown.

Recommendations

3.5.9.2 The phenomenon of "self compensation" should be further investigated to confirm or disprove the formation of vacancies as the cause.

3.5.9.3 Experimental and theoretical studies should be carried out to find preparation conditions which will permit the formation of p–n junctions in II–VI compounds.

3.5.9.4 Theoretical and experimental investigations should be carried out to establish the necessary conditions for efficient hole injecting contacts and to find ways of utilizing these contacts in films or powders so that large area displays can be obtained.

3.5.9.5 Applied research is recommended to exploit the high internal quantum efficiency of II–VI electroluminescent compounds for multi-color emitters, in both film and powder form. This should include newer preparation techniques, such as ion implantation and radio-frequency sputtering and the use of rare earth activators.

3.6 PROBLEMS DISCUSSED IN CHAPTER 6—MAGNETIC MATERIALS FOR ELECTRON DEVICES

Much use is made of ferrites and ferromagnets for electron devices. There is no doubt that the detailed characteristics of these materials can and will be improved. This is because these materials are often inhomogeneous, polycrystalline aggregates with properties that depend upon details of the state of inhomogeneity and aggregation. With such possibilities for variation there will always be room for improvements. A new class of magnetic materials is currently under development, which is used in the so-called magnetic "bubble" technology. At present, hopes are high for finding among layers of substituted garnet, deposited heteroepitaxially on nonmagnetic single crystal substrates, the thin magnetic single crystal layers in which the bubbles may propagate. On the whole there is a sufficient bank of fundamental knowledge and experience such that commercial interests can carry on necessary research and development work at an adequate level of competence and achievement if they will. There are a few specific areas in which additional effort is required, particularly on subjects of special interest to certain agencies.

Problem

3.6.1 Ferrites, in some cases, are required in single crystal form; there are problems associated with the growth of such crystals; better material characterization is necessary.

Recommendation

3.6.1.1 Support development of generic single-crystal growth techniques. This will require better "characterization" of the materials.

3.6.1.2 This would be applied research.

3.6.1.3 Cost and product improvement would be expected.

Problem

3.6.2 The development of very-high-performance permanent magnets is needed.

Recommendation

3.6.2.1 Expand the excellent beginning on rare earth magnets to new materials for very-high-performance permanent magnets.

3.6.2.2 This would be basic research in early stages and applied research later.

3.6.2.3 An expansion of capability in areas of urgent government design need would be the benefit.

Problem

3.6.3 Materials suitable for inexpensive detection of magnetic bubbles are needed.

Recommendation

3.6.3.1 Support exploratory work on materials suitable for inexpensive detection of magnetic bubbles.

3.6.3.2 This would be basic research.

3.6.3.3 A contribution to advanced device development would result.

Problem

3.6.4 Substrates whose crystals are devoid of imperfections are needed for thin magnetic garnet layers.

Recommendation

3.6.4.1 Support development work in substrate crystal growth and characterization.

Problem

3.6.5 Surface preparation of substrate slices for subsequent epitaxial growth is not fully understood.

Recommendation

3.6.5.1 Encourage development of understanding of improved methods of surface preparation of substrate slices for epitaxial growth. Approach the work from a generic and adaptive point of view, recognizing the interaction of substrate surface character and epitaxial process.

3.6.5.2 This project is particularly attractive for increasing potential for achieving thin heteroepitaxial layers with important design benefits in speed of response, cost, and reliability.

Problem

3.6.6 There are certain other areas such as magnetic semiconductors, certain magneto-optical devices, certain catalytic processes, and, possibly, antiferromagnetic materials that involve peculiar metal-insulator phase transitions. Any of these has the potential of exploding into important use. These are all in need of fundamental understanding.

Recommendation

3.6.6.1 Continue a thoughtful program of fundamental investigations in the field of magnetic materials with particular attention to the areas listed in 3.6.6 (also see 3.7.1.1).

3.7 PROBLEMS DISCUSSED IN CHAPTER 7—COMPOSITE STRUCTURES

Problem

3.7.1 The most significant materials problems in composite structures area involve the characterization and understanding of defect and impurity interactions in insulating films and at insulator–metal, insulator–semiconductor, and insulator–insulator interfaces (see 3.6.6). The understanding and characterization of the defect and impurity interactions in insulating films and at the interfaces are addressed to the improved design and manufacture of devices containing these films and interfaces, the stability of the electrical properties of these devices during their life and the extension of this life. Temperature-induced, electric-field-induced, and radiation-induced effects must be understood, and, if not eliminated, should be controlled for optimum device performance and life.

Recommendations

3.7.1.1 Conduct an applied research effort emphasizing the chemical approach rather than the solid-state physics approach in the study of localized defects in insulating films and associated interfaces.

3.7.1.2 Investigate the localized nature of bonds in oxides and other insulators and at the interfaces to increase the control and understanding of defect and impurity interactions in insulating films and at associated interfaces. This chemical approach to the problem is expected to be more fruitful than continued efforts based on the more traditional solid-state physics approach because the one-electron model, the mainstay of the latter approach, is not completely satisfactory in dealing with wide bandgap materials.

3.7.1.3 Carry out experiments designed to reveal specific information concerning localized properties of the structure. These experiments should be performed in conjunction with electrical measurements on M-I-S structures in order to relate defect and electrical characteristics. Since the large majority of M-I-S structures use silicon, the M-I-S structures for these studies should primarily use silicon.

3.7.1.4 Exploit radiation effects studies as a very valuable experimental technique in elucidating defect properties in ways similar to their application in the field of semiconductor crystals. Understanding radiation effects in their own right will become more important not only from the viewpoint of external radiation environments, but also because of the increased use of radiation in device processing.

3.7.1.5 Undertake a basic research effort to study defects in bulk insulators. Fundamental understanding of bulk insulators is another key to the development of understanding of insulating films.

Problem

3.7.2 A particularly serious immediate aspect of the problem of impurity interaction in insulators and interfaces is the apparent strong influence of hydrogen on the characteristics of silicon dioxide.

Recommendation

3.7.2.1 Conduct an intensive, short-term effort designed to understand and control the properties of hydrogen in silicon dioxide. This problem is of great technological interest. It is a specific example of the importance of understanding impurity interactions in insulating films. The presence of small amounts of hydrogen in the ambient gas during device-annealing treatments appears to have an adverse effect on the stability of some devices, but the reasons for this are not yet at all understood. Intensive development effort is needed to solve the problem.

Problem

3.7.3 The doping at insulator-semiconductor interfaces is neither under appropriate control nor well understood. It is being increasingly recognized that greater control over the type and density of the various impurity and defect centers in semiconductors is essential in order to predict or control carrier lifetime and radiation response. Such control is even more important in device structures whose operation depends on interface characteristics.

Recommendation

3.7.3.1 Initiate basic research activity aimed at developing techniques for controlled doping at insulator-semiconductor interfaces. Long-term research directed toward solution of this problem would build on the knowledge developed both in the studies of the localized nature of defects in insulator films and in the studies of "lifetime doping control" in semiconductors and would be a logical extension of that work. Considerable basic research effort with a very-long-term payoff is required if interface doping control is to be achieved. Both greater understanding of material characteristics and improved methods for identifying and counting impurities in the insulator must be developed. This research is required so that the full potential of present M-I-S devices may be realized.

Problem

3.7.4 The effect of the metal-insulator interface on the properties of M-I-S devices is very poorly understood. Heretofore, most of the research effort on M-I-S structures has concentrated on the insulating layer and the insulator-semiconductor interface. Knowledge of the influence of the metal and the metal-insulator interface is meager. Nevertheless, the nature of this interface may affect device operation significantly.

Recommendation

3.7.4.1 Increase efforts directed toward understanding of the metal-insulator interface in M-I-S structures. Applied research as well as development efforts can be expected to be fruitful in controlling the initial properties of M-I-S devices and their stability and life.

Problem

3.7.5 Surface treatments or overcoating materials are required to control surface-charge buildup on insulating layers used for passivation of device surfaces.

Recommendation

3.7.5.1 Undertake an active search for new materials or surface treatments to control surface-charge buildup on insulating passivation layers. An applied research effort is suggested with the aim of completely eliminating this charge buildup, which leads to device instability and shortened device life.

Problem

3.7.6 Integrity of both metal and insulating films is absolutely essential for device performance. Discontinuous films may arise because of manufacturing defects, such as cracks and scratches in metal films, or pin-holes and other minute conducting paths in insulators, or they may occur subsequently, as in electromigration of aluminum stripes or chemical attack on very-thin-film nickel–chromium resistors. With the increasing use of multilayer interconnection schemes, the occurrence of conducting paths in undesired locations in the insulating layer between conductors has become particularly serious. Such conducting paths may exist even in the absence of mechanical holes. In addition, electromigration and other problems related to discontinuities in thin metal conductive or resistive films are far from solved. Intensive development efforts may be needed to solve specific problems. Since most problems of this type are very close to the manufacturer's interests, contract support is expected to be needed only where a particular problem affects a system now in the final development or procurement phase.

Recommendation

3.7.6.1 Support intensive development efforts to seek causes of and cures for lack of integrity in dielectric and metal films. Limit effort to devices to be incorporated in systems now in the final development or procurement stages. The following are among areas that may require attention: means for improving the edge profile of etched-film structures, methods for avoiding the introduction of defect regions and holes across the film thickness, techniques for reducing electromigration effects, and techniques to reduce corrosion effects in metal films, in particular in very thin nickel–chromium resistors. It is to avoid this type of "fire-fighting" in the future that other longer-range basic and applied research efforts are being recommended in the composite structures field.

Problem

3.7.7 Fundamental to the understanding of film and interface properties is the ability to measure various quantities. Measurements must be made on isolated films as well as on the structure or portions thereof. These measurements are essential to the control of the fabrication process as well as for characterization of materials and devices. Applied research on characterization methods is a traditionally neglected area.

Recommendation

3.7.8.1 Encourage the development of suitable metal film systems for specific device structures as needed. Development of specific metal systems must be tied quite closely to the particular device under development. The general principles that must be employed in studying metal systems are mechanical compatibility with adjacent materials, compatibility with processing technology (including exposure to high temperatures and corrosive chemical etchants), and electrical compatibility with the device. Because these developments are tied so closely to specific device developments, general contract support in this area should be extended only in very special cases.

Problem

3.7.9 Despite the considerable study of film growth under idealized conditions, not enough is yet known concerning the growth of thin films in practical cases. As films are prepared at lower temperatures or as film thickness is reduced, the significance of this problem increases.

Recommendation

3.7.9.1 Undertake basic research activity directed toward better understanding of film growth with principal emphasis directed toward better understanding of the sputtering process and of the morphology and characteristics of very thin films. In considering growth and nucleation problems, it is necessary to apply the studies to practical cases rather than strictly idealized cases. The important aspects are surface preparation, method of applying the film, definition of a pattern, and characterization of the resulting structure. Such research can reasonably be expected to lead to improved devices.

Problem

3.7.10 For certain desired applications, composite structures using silicon are not suitable and for certain other applications, improved performance would be expected from the use of materials other than silicon. Long-range research programs are essential to provide the materials needed to meet future system requirements. It *must* be recognized that *some* relatively undirected effort is essential to uncover new materials whose properties may be exploited in the future.

Recommendations

3.7.10.1 Undertake basic research activity directed toward the development of new materials for use in devices based on composite structures. This research should yield desirable components whose performance would be impossible to attain using silicon. Great care should be taken in encouraging research in new semiconductor materials for composite structures where the only advantage is potentially improved performance. In this latter case, the fact that silicon technology has been developed at great cost to a high degree of sophistication must be taken into account to determine whether, in fact, it is desirable to attempt to develop the new material and its technology to the point where performance improvements over silicon devices are possible.

3.7.10.2 Support long-term research programs to study silicon carbide and tin oxide, materials that may prove to be suitable for use in high-temperature M-I-S devices. One of the advantages of silicon carbide arises from the fact that silicon dioxide layers can be grown on its surface.

3.7.10.3 Undertake exploratory research programs to seek and understand other high-mobility high-bandgap materials for high temperature applications.

3.7.10.4 Undertake applied research and development work on a modest scale directed toward the development of integrated circuits with compatible electroluminescent devices such as those from gallium phosphide.

Problem

3.7.11 There is a need for an inexpensive, compact monitor to detect ambient gases and pollutants with specificity. Sensitivity to ambient gases would be a property studied in the chemical approach to investigate M-I-S structures. Such research might be expected to identify systems appropriate to the detection of certain gaseous pollutants in the atmosphere.

Recommendation

3.7.11.1 Expand applied research efforts directed toward understanding of permeability of insulator films to constitutents of ambient gases that will lead to the development of gas detectors based on the M-I-S structure. This sort of information should be explicitly sought and directed to the development of devices for atmospheric monitoring and pollution control.

Problem

3.7.12 It can be expected that a majority of future M-I-S devices will employ multilayer dielectric films in order to achieve improvements of threshold voltage, breakdown voltage, and stability that cannot be obtained with single layers. The problems of fabricating such multilayer dielectric films with highly controlled interface and other characteristics have not yet been solved.

Recommendation

3.7.12.1 Undertake fundamental research activity directed toward understanding the properties of the dielectric-dielectric interface in multilayer dielectric films. Among other things, the effects of charge accumulation at the interface must be studied and the effects of fabrication procedures determined. Although combinations of existing dielectrics such as silicon dioxide, silicon oxynitride, silicon nitride, and aluminum oxide would probably be given primary emphasis, new dielectrics for this application must also be considered.

Problem

3.7.13 A thorough assessment of the potential of charge transfer devices for fast shift registers and other M-I-S applications is urgently needed. Of interest are a determination of factors that inhibit the complete transfer of charges from one plate to the other and understanding of the dynamics of free carriers under diffusion and drift modes of motion. Trapping effects at interface states must also be considered and structures developed whereby the amount of charge lost in transfer is kept to a minimum.

Recommendation

3.7.13.1 Undertake a fundamental research program to explore the charge transfer mechanism under the field plates of charge transfer devices.

3.8 PROBLEMS DISCUSSED IN CHAPTER 8—INORGANIC DIELECTRIC MATERIALS

Problem

3.8.1 The growing need for improved methods of information storage and display make optical materials an attractive field for research and development. Active optical materials are needed for transducers, modulators, memories, deflectors and the like.

A wide variety of inorganic crystalline and amorphous materials having electrooptic, acoustooptic, photochromic, photoelastic, and similar properties are being explored, often with a particular device or function application in mind. Examples are cathodochromics and photochromics for image storage use, and acoustooptic materials to serve as light deflectors in beam-scanning systems.

As a class, these active dielectric materials all require a large effort in characterization and in the development of appropriate processing techniques. The choice of materials is so broad and the diversity of applications so great that critical decisions are necessary to avoid thinly dispersing the available research resources.

Recommendation

3.8.1.1 It is recommended that effort be applied to the ordering of priorities and the determination of choices with the greatest potential for generic solutions in the field of optical materials.

Problem

3.8.2 There is an increasing interest in the use of optical wavelengths for the transmission of information and data. The need for materials that can function efficiently in devices and circuits at these frequencies becomes important, if practical use is to be made of the inherent bandwidth and other desirable features of this segment of the spectrum.

Recommendations

3.8.2.1 Support should be given to the development of materials which can act as efficient transmission media at optical and IR frequencies. Research will be needed to characterize and understand the attenuation mechanisms in dielectrics, and to define the critical levels of purity and compositional uniformity needed. To be of greatest usefulness, materials must be available that permit signal transmission over distances measured in miles. This is probably possible only through the adaptation of composition control disciplines now found in the semiconductor industry.

3.8.2.2 A process for the fabrication of passive optical circuitry should be developed. Distributed-parameter circuitry techniques will require low and/or controlled attenuation materials in which optical properties such as refractive index may be controlled and reproduced easily. Since coherent light will frequently be the form of the signal energy, optical homogeneity must be maintained within a fraction of a wavelength.

3.8.2.3 Processes for the fabrication of active optical circuitry should be developed. Logic and switching functions capable of the highest attainable speeds will be needed. These functional devices should be compatible with passive circuitry.

Problem

3.8.3 At microwave frequencies dielectric materials have excessive loss tangents for many uses. As substrates for microstrip circuitry and as a transmission medium in dielectric antenna designs, present materials are inadequate.

Recommendation

3.8.3.1 Materials research should seek low-loss dielectrics for use in microstrip substrates and antennas. A dielectric constant of 30 to 100, good thermal conductivity, uniformity, and stability are other needed properties.

Problem

3.8.4 Filters and resonant structures at optical and microwave frequencies often depend on physical dimension as the frequency-selective parameter. The dimensional stability of the materials used will determine the device performance.

Recommendation

3.8.4.1 Effort is needed to develop materials with extreme dimensional stability over long periods of time during which they will be subject to wide environmental changes. The materials are usually used as structural elements and must be easily formable to close tolerances.

Problem

3.8.5 Dielectric substrates for the growth of single-crystal films are either unavailable or are lacking in size, perfection, and economy. Substrates permitting the growth of large area, uniform single-crystal films of good crystalline perfection would be valuable for complex semiconductor circuitry as well as in other device applications.

Recommendation

3.8.5.1 Research efforts on substrates suitable for growth of single-crystal films should be expanded, and processes for growth of the most important semiconductor films and magnetic films should be improved.

Problem

3.8.6 Substrates for thick- and thin-film circuitry are widely used, but usually fall short of desired smoothness, flatness, thermal characteristics, or other parameter.

Recommendation

3.8.6.1 Development effort should be applied to the improvement of processes for the fabrication of alumina substrates. Improvement of surface smoothness is of importance in the successful fabrication of thin-film circuitry. This must be achieved without the sacrifice of thermal conductivity.

Problem

3.8.7 Although a problem of long standing, capacitor dielectrics having sufficiently high dielectric constant and dielectric strength for use in energy storage applications are still only marginal in meeting design requirements.

Recommendation

3.8.7.1 Materials research and characterization should be carried out on dielectrics for potential use in energy storage applications. Dielectrics permitting volumetric energy densities of 1.0 joules/cm^3 or more are needed and will require work on the failure mechanisms in high-dielectric constant materials. Work should concentrate on single crystals and on high-density ceramic systems.

Problem

3.8.8 Electrolytic capacitors for circuits requiring extreme values of capacitance up to the farad range have not kept pace with the trend toward reduction of size and weight.

Recommendation

3.8.8.1 Work is needed to develop dielectric/electrode systems permitting significant improvements in electrolytic capacitor volumetric efficiency.

3.9 PROBLEMS DISCUSSED IN CHAPTER 9–ORGANIC DIELECTRIC MATERIALS

Organic dielectrics include films, sheets, coatings, fluids, gases, adhesives, composites, mixtures, and various forms of packaging or encapsulating materials. Hundreds of materials are currently used. It is not practical to list them in a summary but they may be found grouped by application in Chapter 9 of the main body of the report.

The organic material normally provides a useful function to the electronic device as a carrier, protector, container, or fastener. It must insulate, remain stable, and in no way degrade the active electronic materials under operating conditions. It should not consume energy. Presently used materials serve these functions with varying degrees of adequacy. This report considers the needs for improvement in such materials. In addition, however, there are major changes coming in the nature of the electronic components and the way they are to be made. These are described in other sections of this report. Future organic materials and their fabrication must be adaptable to these primary electronic materials and processes. Finally, it is suggested that the organic dielectric may become increasingly cofunctional in an active role with the material it serves. To these latter ends more interdisciplinary research and development work is recommended.

Some of the more generic problems or needs and suggested approaches toward their solutions are listed below. For more detailed consideration, the reader is referred to Chapter 9 of the report.

Problem

3.9.1 There is a general need to make organic dielectrics more uniform from batch to batch and to maintain properties within tighter limits in a given batch.

Recommendation

3.9.1.1 Closer control of raw materials and processes should be practiced. In some cases, this requires new means of on-line characterization.

Problem

3.9.2 Probably the most generic need expressed is for improved purity of finished materials. Ionic impurities tend to migrate in electronic device packages and cause electrical failure. Gross particulates affect mechanical properties or may make a required smooth substrate unusable. Some impurities evaporate or are boiled off in high stress areas, such as contacts, and condense in critical areas causing breakdown.

Recommendations

3.9.2.1 Develop methods for selection of pure starting materials.

3.9.2.2 Develop curing processes that do not require catalysts. Use ultra-clean processing techniques.

3.9.2.3 Perform longer-range research to develop polymers insensitive to impurities.

3.9.2.4 Investigate use of inventive systems such as circulation of fluids through filters and impurity absorbers as in transformers or capacitors, develop use of barriers or getter techniques.

Problem

3.9.3 A related problem is one of voids.

Recommendations

3.9.3.1 Develop better processing techniques.

3.9.3.2 Develop polymer systems that are free of solvents and/or catalysts.

Problem

3.9.4 There is a need for improvement of stability in various environments. Resistance to moisture and/or oxygen is an example.

Recommendation

3.9.4.1 Perform basic research to develop polymers that have greater inherent resistance to environmental attack.

Problem

3.9.5 There is need for polymers that are effective barriers to transmission of moisture and/or oxygen.

Recommendation

3.9.5.1 Develop barriers at the polymer-device interface.

Problem

3.9.6 Many applications require stability at high temperatures, or over broad temperature ranges.

Recommendation

3.9.6.1 Development of new polymers to meet this requirement should be supported.

Problem

3.9.7 Mechanical properties should not change significantly in service, e.g., a tough coating must not become brittle because of its environment.

Recommendation

3.9.7.1 New compositions or composites with improved properties should be sought.

Problem

3.9.8 Compatibility is of special importance. A coating must fit, adhere, and not react with what it is coated on. There is a wide difference in expansion coefficient between polymers and metals/semiconductors/ceramics. This can cause breaking away or other failure of the device. New low-expansion polymers are needed.

Recommendations

3.9.8.1 Conduct basic research on new materials.

3.9.8.2 Conduct basic research on surface/interfaces or coatings and substrates.

3.9.8.3 Mixtures or composites may provide partial solutions to this problem. In composites a need exists to make the expansivity as isotropic as possible.

Problem

3.9.9 The development of polymers having a high thermal conductivity is an expressed need.

Recommendation

3.9.9.1 Developing new compositions of matter involving structural approaches is worth examining, e.g., ceramic-filled polymer compositions.

Problem

3.9.10 It is desirable to make sheets, films, and coatings even thinner, without degradation of their effectiveness. We may have reached technological limits with present processes.

Recommendations

3.9.10.1 New processes such as chemical vapor deposition of various kinds are suggested for investigation.

3.9.10.2 The use of electric fields in such processes (as practiced in some automobile painting) may ensure more perfect coatings and should be investigated.

3.9.10.3 Depositing polymeric films on liquid metals, as is done in the manufacture of sheet glass, may be another approach to use and should be explored.

Problem

3.9.11 The characterization of materials at all stages of manufacture is an important need. Many current tests are macro in scale, but micro tests are needed. Reliability, with its implication of predictability, must be as high as possible.

Recommendation

3.9.11.1 Accelerated tests to predict integrity and stability of the organic material in use will have to be developed for the coming generation of devices. New micro tests should be developed.

Problem

3.9.12 There is such a wide variety of organic dielectric materials available and in use that making an intelligent choice may be difficult.

Recommendations

3.9.12.1 It is suggested that choices be made among various materials to reduce the numbers currently in service. This is a form of standardization.

3.9.12.2 It is further suggested that research and development be directed toward developing no more than a few materials that have the desired properties and characteristics outlined above, at least within specific application areas.

4 Elemental Semiconductors

4.0 GENERAL INTRODUCTION

This chapter considers research and development aimed at the needs of elemental semiconductor materials and processes. The materials are treated in order of their present-day economic significance, namely: silicon, germanium, selenium, diamond, tellurium, and boron. The materials sulfur, gray tin, antimony and bismuth are omitted simply because they are not in critical need. Alloys such as S:Se, Ge:Si, Se:Te are ignored for the same reason, although such alloys may become important for special applications.

Since silicon makes possible a technology that is exceedingly adaptive in that it has great cost effectiveness for a wide variety of functions and applications, it has, in the past, received the major technical effort, including manufacturing. The broad and adaptive technology base of silicon gives it a significant advantage over potentially competitive materials for many applications that otherwise might not be considered the bailiwick of silicon. This advantage seems to grow rather than diminish through the years.

The silicon section is divided into a discussion of five different areas:

1. initial material
2. processing
3. structures
4. device and design
5. packaging and testing

With regard to the other elemental semiconductors listed above, specialized applications exist where each can contribute. These particular applications have been isolated for future support.

4.1 INITIAL SILICON MATERIALS

4.1.1 Introduction

Need for eight major research efforts with high potential impact on initial silicon materials technology has been identified. These research areas will be discussed according to silicon manufacturing processes and not necessarily in order of importance. The first problem discussed will be the characterization techniques required for the monitoring and control of silicon quality throughout production. Consideration will then be given to the theoretical and practical limits of mobility and lifetime achievable in silicon as a function of carrier concentration. The problems remaining to be solved in the manufacture of high-purity high-resistivity silicon will be reviewed next. Problems associated with the minimization of silicon loss during reduction to slice form will be discussed with special emphasis on silicon ribbon and dendritic web growth. The technology required for processing large diameter slices will be considered next from the material and device processing standpoint. The state of low-temperature spike-free silicon epitaxy development will then be reviewed and followed by a discussion of the problems associated with continuous epitaxy. Finally, the silicon-on-insulator state of the art will be examined and suggestions for further research and development work in this field will be formulated.

4.1.2 Characterization Techniques for Silicon Production

The manufacture of high quality silicon is basically a chemical process requiring both process control and quality control. These two types of control need to be exercised on starting materials, on in-process materials, and on finished product. Process control requires a rapid characterization technique while quality control could be better supported by diagnostic characterization techniques that, by their nature, take a longer time to perform.

The type of impurity (chemical or physical imperfection) and location of the imperfection (surface or bulk) play an important role in deciding which characterization technique will be used for its determination. These are summarized in Tables 4-1 and 4-2 for input materials and silicon materials.

All input materials that are not polycrystalline or crystal silicon need only be analyzed for chemical imperfections. From Table 4-1 it is apparent that emission spectroscopy is potentially our most powerful tool for the determination of chemical impurities in these materials.

The silicon material sampling points are shown in Table 4-2. The silicon materials can be broken down into four main classes: polycrystalline material, single crystal material, polished slices, and processed slices. Each of these material classes has specific characterization technique requirements, which can be stated as follows:

4.1.2.1 POLYCRYSTALLINE SILICON

Chemical impurities and physical characteristics are of interest. A sensitive emission spectroscopy procedure could conceivably provide

TABLE 4-1 Possible Characterization Techniques for Input Materials to the Silicon Production Process

Materials	Rapid Process Control Techniques	Diagnostic Characterization Techniques
1. Gases Hydrogen Argon Helium Doping Gases Silane	1. Emission spectroscopy 2. Gas chromatography	1. Gas mass spectroscopy
2. Liquids $SiHCl_3$ $SiCl_4$ Etches Solvents Saw Coolants	1. Emission spectroscopy 2. Plasma jet spectroscopy 3. Gas chromatography	1. Classical wet chemistry
3. Solids Dopants Polishing Compounds Quartz Materials Graphite	1. Emission spectroscopy 2. Classical wet chemistry	1. Neutron activation analysis 2. Spark source mass spectroscopy

TABLE 4-2 Possible Characterization Techniques for Material from the Silicon Process

Material	Defect of Interest Chemical (C), Physical (P)	Location of Defects Bulk (B), Surface (S)	Rapid Process Control Techniques	Diagnostic Characterization Techniques
Metallic silicon				
(1) Polycrystalline	C, P	B	1. Emission spectroscopy 2. Resistivity	Neutron activation analysis Solids mass spectroscopy
(2) Single Crystal (Pulled)	C, P	B	1. Lifetime 2. Resistivity 3. Hall measurement	X-ray topography Neutron activation analysis Solids mass spectroscopy Emission spectroscopy Infrared spectroscopy
(3) Slices (Sawed and Lapped)	C, P	S	No analysis	
(4) Slices (Polished)	C, P	S	1. Photomagnetoelectric effect 2. Surface recombination 3. Lifetime 4. Spectral reflectance	Neutron activation Ion probe mass Analyzer X-ray topography Infrared spectroscopy
(5) Processed slices[a]	C, P C, P	B, S B, S	1. Lifetime 2. Resistivity 3. Hall measurement	Neutron activation Ion probe mass Analyzer Infrared spectroscopy X-ray topography

[a] Epitaxial films over either isolation (sometimes called double isolation) or buried layers (also called diffusion under the film).

a major part of the process and quality control while neutron activation and mass spectroscopy could provide the backup. Except for resistivity measurements, electrical techniques are of little value until the material is zone-refined into single crystal material. The only physical characteristic of interest is the amount of internal stress. There presently exists no sure method of measuring the stress to ascertain whether the charge will explode on heating in a puller. Very similar comments can be made in the case of thin layers of polycrystalline silicon. No analytical technique exists at the present time to characterize their resistivity and internal stresses. Such characterization techniques are needed to ensure process control and high yield of dielectrically isolated material.

4.1.2.2 SINGLE CRYSTAL SILICON

At this point in the process, physical as well as chemical imperfections become important. These are primarily bulk imperfections.

Rapid process control techniques become imperative at this point. All present characterization techniques, with the possible exception of emission spectroscopy, serve as diagnostic methods. Electrical characterization techniques are the key to the problem. Contactless lifetime and resistivity measurements on each rod and perhaps on several slices cut from each rod would be of significant value in determining the concentration and nature of electrically active imperfections. These measurements would be especially valuable if these quantities could be measured locally. Laser beam and electron beam scanning come to mind in this regard, but quantitative techniques remain to be worked out. Localized infrared absorption in the far IR might also be useful for such measurements, but detection techniques would have to be greatly improved.

4.1.2.3 SLICES

Since all sawed and lapped slices come from the crystals discussed above, the only impurities that could be introduced are on the surface. Presumably, all single crystal rods were 100% inspected and all slices will see subsequent polishing. Characterization of surface mechanical damage and/or contamination resulting from the sawing operation would help to ensure a high quality finished product. The mechanically and chemically polished slices require extensive quality and process control.

Both chemical and physical imperfections are of interest in determining slice quality. However, unless the slices go through a heat treatment (see 4.1.2.4) most imperfections will be restricted to the surface. We do not know any rapid process-control techniques that are currently available for slice inspection. Since the number of samples is likely to be large, it is apparent that electrical or optical techniques, such as those listed in Table 4-2, should be applicable. Here again there is diagnostic backup, but not nearly as much as is needed for surface analysis. The proposed ion-probe mass analyzer should perform well in this area.

4.1.2.4 PROCESSED SLICES

These are silicon slices that have undergone heating so that the chemical and physical surface imperfections are distributed in the bulk. Even more than in 4.1.2.3 there is a dearth of rapid process-control techniques. Electrical techniques appear to be the most applicable.

Existing diagnostic techniques are sparse. Considerable development work is required in this area.

In summary, it appears that emission spectrographic techniques for $SiHCl_4$ and silicon need to be developed to utilize the ultimate sensitivity of this technique. We currently have semiquantitive procedures for silicon but need to lower the detection limits and quantify the procedures.

Computer-controlled Hall effect or Van der Pauw techniques for resistivity measurement and rapid process control on silicon single crystal rods needs to be developed. Rapid process control and diagnostic characterization techniques for evaluation of surface imperfections on mechanically and chemically polished silicon need to be developed and evaluated. Certainly a radically new approach is needed for the electrical evaluation of epitaxial material. Both transmission and reflection infrared techniques have not been fully exploited and these procedures need further investigation.

The probability of success for new characterization-technique development is high but the estimated time for completion of a project appears to be from five to ten years. Increased effort would certainly accelerate achievement of goals, possibly by two to five years.

Improved material-characterization techniques would support the development of higher quality materials. These, in turn, should result in better device-manufacturing yields and, perhaps, devices with new performance capabilities.

4.1.3 Theoretical and Practical Limits of Mobility and Lifetime

The operation of many silicon devices involves conduction and recombination within diffused regions. Proper device design requires the consideration of how these processes occur in materials having carrier concentrations or impurity concentrations as high as 10^{19} cm^{-3}. Although the principal mechanism that limits the mobility in heavily doped materials is probably scattering by ionized impurities, the usual (Brooks-Herring) theory will not be valid in this case for a number of reasons. In uncompensated material, carrier-carrier scattering is expected to become important, while in compensated material, conduction in band-tail states and impurity bands must be considered; the treatment of scattering by an individual impurity as an independent event is probably not correct. The role played by band-tail states and impurity bands is probably even more important in the cases of carrier lifetime, because recombination very likely proceeds by way of these states. The conservation of momentum that normally limits interband recombination is probably relaxed when recombination occurs between band-tail states.

The generation of defects during the diffusion process is a complicating factor that depends critically on the thermal cycling involved. The role of these defects in limiting mobility and lifetime must also be considered. Although carefully controlled experiments are still needed, this general area is one in which theory has lagged behind experiment.

The first step toward an adequate theory might be to abandon the periodic lattice potential and to develop a theory of band states along the lines presently being investigated for disordered materials. Once the band structure has been determined, adequate theories for transport and recombination might follow. The program envisioned here is a long-term basic investigation, based on experimental work, which could lead to an improved understanding of transport and recombinaation in heavily doped regions, thereby permitting more precise device design. Improvements in solar cell efficiency might also result from such a program if a material were developed with high carrier concentration and long carrier lifetime.

With proper support, it is expected that results from this work would impact in two to three years.

4.1.4 High Resistivity Silicon

Ultra-pure, high-resistivity (9-15 Kohm-cm), long minority-carrier lifetime silicon is required to produce high speed IR detectors for laser energy sensors. Slightly lower resistivity (500-5000 ohm-cm) silicon is used to produce nuclear radiation detectors. Other possible applications include microwave transistors, high voltage rectifiers, and various light detection devices.

A common method of producing polycrystalline silicon is hydrogen reduction of trichlorosilane at elevated temperatures. A second method is to use silicon tetrachloride as an alternate starting material. Pyrolysis of silane or dichlorosilane is a third method of making polycrystalline silicon. The most practical method of producing 9-15 Kohm-cm long lifetime silicon is by control of the purity of starting materials in order to produce polycrystalline silicon with very low (p-type) contamination, preferably $\leqslant 0.06$ ppba.

Increased resistivity is attained by reducing the n-type impurity content of polycrystalline silicon with multiple float zone passes in vacuum.

Contaminants that degrade lifetime must be avoided. Unfortunately, a practical method of reducing boron (p-type) impurities is not known.

Although material of the required quality is being produced in limited quantities, many problems exist for improvement of yields and reduction of production costs. Starting materials should be improved. The preferable starting reagent (silicon tetrachloride, silane, dichlorosilane, trichlorosilane) should be ascertained as well as the preferable reactor construction materials and the optimum reagent purification method (distillation, chelation, oxidation, or combination).

Finally, analytical methods capable of detecting less than one part per billion of impurity (carbon, boron, phosphorus, etc.) in starting reagents should be developed. Deposition process should be optimized by the determination of preferable construction materials for vaporizers and reactors and the determination of the effect of deposition parameters on purity.

The vacuum float zone process should be improved by optimizing the silicon container material, since it is felt that the choice of material used at this point is critical in avoiding introduction of "lifetime killers."

Detailed studies to determine the effect of vacuum float zone parameters, rate of zone pass, and number of passes on purity should be performed. The development of a method for removing boron from silicon should be undertaken.

Contamination-free material handling and preparation methods should be developed, together with the development of more accurate and reliable methods and equipment for measuring resistivity, minority-carrier lifetime, and electrical type.

Some engineering effort is presently being directed to the problems listed with the exception of the development of analytical methods capable of detecting less than one part per billion of impurity and development of a method of removing boron from silicon.

Although a number of applications for high resistivity silicon exist, the total material quantity presently produced and used is small compared with more conventionally prepared silicon. If such applications are to become important, additional support is needed to encourage effort in this new technology area.

4.1.5 Minimization of Silicon Loss During Reduction to Slice Form

One of the major sources of loss in the manufacturing process for producing silicon in a form suitable for electronic device fabrication is that of slicing single crystals. Conventional industry practice is to use a diamond coated blade 0.008 to 0.009 in. thick. The process results in kerf loss equivalent to approximately 0.011 in. of crystal length for each pass of the saw. Thus, for each slice cut to 0.015-in. thickness, 0.026 in. of crystal is consumed. This means that the maximum yield for this operation would be 58%. Of somewhat lesser significance is the crystallographic damage generated during the sawing operation. Although the effect of this crystal "work damage" on slice quality can be minimized by proper etching and polishing procedures, additional silicon is consumed, thereby further reducing maximum yield possible for this operation. Typically, for a finished polished slice thickness of 0.015 in., a sawed slice of 0.021 in. is required. Including kerf loss, the maximum yield for the slicing/polishing operation would be 47%.

Over the years, the major industry effort directed to solving this problem has been concentrated on techniques to reduce the kerf loss, e.g., thinner blades, thin-wire sawing, and, more recently, some attempts to use laser cutting techniques. None of these approaches have resulted in an economical solution to the problem. Thinner blades have been produced; however, slice quality has deteriorated when such blades have been used unless saw speed is greatly reduced and blades changed much more frequently. String sawing has met with similar disadvantages. Laser techniques using thermal energy to vaporize the silicon have been completely unsuccessful for large diameter crystals. Although cleaving silicon crystals to form slices has been suggested, the control necessary would cause one to question the feasibility of this approach.

The most obvious approach is to grow the silicon in the proper thickness originally. Although numerous approaches have been suggested, only two appear to have a reasonable probability of success. These are single-crystal ribbon growth and silicon web growth. (Although casting silicon sheets on a molten substrate in a manner analogous to making plate glass would have economic potential, the technological problems related to finding a suitable nonreacting substrate and in developing a means for conversion to single crystal form are formidable.)

Feasibility has been demonstrated for both ribbon growth and web growth; however, truly economical manufacturing techniques have not been developed for either process. Both approaches have met with considerable resistance, primarily, because of industry reluctance to modify photolithographic processes. Consequently, a desirable program would be to develop a complete manufacturing process using these techniques from crystal growth through diffusion and device fabrication. The crystal growth difficulties are minor compared with those when the Teal-Little modification of Czochralski crystal growth was developed. If a concerted effort were applied, the probability of success would be high. Depending on the level of effort, a successful process might be a reality in two to three years. Specifically, techniques must be developed for growing ribbon or web at least 2 in. wide with yields comparable to those achieved presently in large diameter, pulled crystals.

Slice polishing techniques and photolithography techniques would have to be developed concurrently. Epitaxial deposition and diffusion techniques already use horizontal-type reactors that would be required for a rectangular form. Processing in these areas would require optimization.

Because of the magnitude of the problems involved in developing a complete processing system, it is likely that the support at the current level will not offer a viable solution in the near future.

4.1.6 Problems Associated with Larger Diameter Slice

The microelectronics industry has matured to the extent that uniformity of product and reproducibility are now key economic considerations. The requirement for larger area slices, however, may be expected to result in an initial relaxation of these specifications within the conventional technology followed by the development of new processing concepts to recover tight specifications. In the present case, emphasis will be placed upon 3-in. diameter crystals, although the slab concept will also require further consideration.

The growth of 3-in. diameter (and larger) dislocation-free crystals by the Teal-Little technique is expected to result in a greater radial resistivity variation than is currently present in 2-in. diameter slices. Such an increase will have an adverse effect in slices produced to narrow resistivity specifications as for metal oxide-semiconductors (MOS). We believe the solution to this and related problems will require a basic crystal growth research program (three to five years) to relate the influence of macroscopic crystal growth parameters to the development of various chemical and structural microinhomogeneities in the crystal.

The quality of the mechanical shaping of the crystal into slice form has a predominant effect on the crystalline perfection of the slice and can strongly influence subsequent device performance. Crystals grown by computer techniques appear to be of sufficient diameter control so as not to require centerless grinding operations. Nevertheless, the nature of the residual surface and the peripheral crystalline damage introduced during the sawing of 3-in. diameter slices need to be investigated. This is essential in order to establish the post-slicing processing steps required to remove the various surface damage sites. Otherwise, the thermal stresses associated with subsequent high-temperature processing may activate the residual surface dislocation sources and cause their propagation throughout the initially dislocation-free slice volume. In that case, the anticipated benefits of growing dislocation-free silicon may not be realized.

The bow developed during sawing will create array registration problems during subsequent photolithographic processing as well as add difficulty to dielectric isolation. Therefore, the development of an economical novel slicing process to avoid the introduction of extensive surface damage and to minimize slice bow is clearly desirable.

The uniformity and quality of the polished surface across the 3-in. diameter slice is anticipated to pose a general, though not substantial problem. The residual surface work damage due to the final polish, however, will become more significant as the devices become shallower and the chips become larger and more complex.

The ability to produce large area photomasks with minimal defects is dependent upon the development of improved photosensitive coatings. Current films such as emulsion and photoetched chrome have some residual defects. A defect-free coating system needs to be developed.

Additional materials development concerns the glass substrate. The glass must be extremely flat in order to maintain optical focus and to ensure that the patterns will be in the proper registration. Current techniques for producing such glass are far too expensive.

The use of large arrays will make the registration of successive pattern levels more difficult as well as increase the problem of focus and slice-to-mask contact. New technologies and new device design concepts that minimize registration requirement will be required. Photoresist material characteristics such as coating-thickness uniformity, photographic sensitivity, and reproducibility will also be much more important than in the case of 2-in. diameter slices.

Automated techniques for mask alignment and photomask inspection are essential. Indeed, conventional inspection of a complex, large area photomask will be more expensive than the cost of the mask itself. Contact printers will require improved illumination systems and more reproducible contact than is currently achievable for 2-in. slices. Projection printers for 3-in. fields, furthermore, will have a shallower depth of focus than for 2-in.-diameter slices; techniques for the conservation of all available depth of focus will need to be investigated. Finally, electron beam exposure for both slice printing and mask production will become more important and a resist with high sensitivity compatible with electron beam technology will be required. The finer line resolution and greater depth of field available with electron beam techniques will permit greater density and help to overcome the problems of nonsmooth surfaces.

The uniformity of epitaxial layer thickness and resistivity across a 3-in. diameter slice is not expected to be a major problem using current epitaxial reactors. The development of larger reactors, however, in order to increase capacity, will require a one-year development program in order to minimize potential problems such as excessive thermal gradients.

Slip may be activated during high-temperature processing due to the presence of thermal stress fields. In this regard, the ratio of the slice diameter to furnace diameter is an important parameter. A program is needed to determine the engineering requirements for 3-in.-diameter, dislocation-free slice processing; a simple "enlargement" of current manufacturing facilities will not be sufficient. Parameters investigated during such a study should include both oxide thickness and sheet resistance uniformity across the slice.

In sum, support is essential for several programs discussed above. For example, consider the reproducibility of a particular silicon crystal specification. Electronic device characteristics are essentially an expression of our modification of a grown silicon material in a predetermined manner. The reproducibility of such devices, however, is controlled by incoming material characteristics as well as by subsequent device manufacturing operations. While computer-controlled crystal growth is a beginning toward reproducibility, a detailed study of the influence of macroscopic crystal growth parameters on the development of various chemical and structural microinhomogeneities is, it appears to us, essential for the control of material parameters.

Applied projects such as sawing and photolithography are just as important, however, in view of their possible degradation effect on the high-perfection grown silicon crystal. Photomasks and photolithography are currently the principal limiting factors in device speed, complexity, and manufacturing yields. Because many of the problems affecting photomasks and photolithography have already been identified and defined, work in these areas can be expected to yield significant benefits relatively quickly. Again, reference should be made here to the Panel on Yield of Electronic Materials and Devices Report (NMAB-290).

4.1.7 Low-Temperature Spike-Free Epitaxy

Before considering details of the process, let us review the status of silicon epitaxial technology. This is shown in Table 4-3. One sees, for example, that the deposition temperature has lowered somewhat, but not significantly, though layers of acceptable quality can now be grown at temperatures in the 850-900°C range, providing a high-temperature vapor-phase etch precedes the deposition. Lower temperatures are particularly desirable for depositing thin layers; this reduces substrate out-diffusion, but unless the temperature of subsequent operations is also lowered, there is little net gain. Further, the deposition rate has remained essentially constant since 1963. This has not been from choice since rates from near zero to 14 μm/min have been reported, but rather because 1 μm/min provides a time adequate for accurate control, but not so long that it causes economic problems. Moving up the table, we can see that the thickness and resistivity control improved substantially between 1963 and 1964, but since then, it has remained nearly constant. Dislocation, stacking fault, and spurious

TABLE 4-3 Silicon Epitaxy Technology Status and Trends

	1963	1964	1965	1970	Comments
Surface protrusions	85% free	90% free	$\simeq 1/\text{cm}^2$	$\simeq 1/\text{cm}^2$	Must be removed for good photolithography definition
Dislocation density (per cm^2)	8,000	2,000	2,000	2,000	Adequate
Stacking faults (per cm^2)	10,000	100	10–100	10–100	Adequate
Thickness control	±25%	±5–15%	±5–15%	±5–15%	Not adequate for some components
Resistivity	±25%	±10–20%	±10–20%	±10–20%	Inadequate for many components
Slice diameter	7/8 in.		1.5 in.	2 in.	Trend is larger for economic reasons
Slices/reactor	4		20	40	
Deposition rate	1 μm/min		1 μm/min	1 μm/min	Deposition rates of up to 14 μm/min have been reported
Deposition temperature	1200–1250°C	1200–1250°C	1200–1250°C	1050–1200°C	Function of rate—can be as low as 850°C

growth densities were radically reduced in 1963 with the introduction of substrate etching. As long as considerable care is taken in substrate preparation, and diffusion damage for those epitaxial layers utilizing local diffusion before deposition is carefully controlled, the film quality is minimally acceptable. *Any* surface protrusions can cause difficulties in subsequent masking operations, particularly as dimensions become smaller and smaller. Current practice seems to be physical removal of the more obvious of these defects but, if economically feasible, they should be prevented.

Summarizing, most process parameters achieved thus far are marginal but still acceptable to most users. Consequently, any improvements have been toward increasing reactor capacity rather than for meeting tightly controlled product specifications. This is illustrated in that portion of the table showing slice diameter and slices per reactor. It should be noted that the capacity in total surface area has increased by at least a factor of 50 since 1963.

Conventional epitaxy proceeds from the thermal decomposition of silicon tetrachloride at temperatures in the range 1200 to 1250°C. The high temperature, the nature of the reaction components, and the reversible nature of the reaction create basic difficulties in closely controlling the parameters of layers grown by this method. In practice, layer thickness and resistivity cannot be controlled more closely than ±15% if realistic yields are required. Of equal importance for this discussion is that layer properties for any particular run depend significantly on the immediate past history of the reactor. This poses an almost insurmountable difficulty if the present urgent need of the industry for automatic control of the epitaxial process is to be satisfied.

It has been recognized for some time that the high temperature and the nature of the chemical reaction of the silicon tetrachloride process provide less than ideal conditions for close control of the deposition process. The use of silane as a silicon source has been considered recently by various industrial laboratories. Epitaxial processes operating at temperatures slightly above 1000°C have now been implemented in various places throughout the country. The processes have resulted in greatly improved film thickness and resistivity tolerance. Maximum variation of ± 5% can readily be achieved.

The needs of the device engineer for even thinner films with predetermined, accurately controlled resistivity are such that even the abovementioned processes are often inadequate. Development of silicon epitaxy at temperatures well below 1000°C is required in order to produce devices such as avalanche diodes, step recovery diodes, and IMPATT diodes with a high yield. Such a process should result also in surfaces of high quality. Early experiments on silane epitaxy have shown that deposition tends to concentrate on sites of a surface distortion or impurity, producing a rapid local growth often referred to as "spike." Such spikes are detrimental to the photolithographic masks used to produce the fine patterns required in modern devices.

A possible approach to the solution of this problem is to pursue the study of silane epitaxy at lower temperatures than presently used. The possibility of silane as a silicon source is attractive, since its decomposition proceeds readily (yielding only silicon and hydrogen at 700°C) and is essentially irreversible.

No serious problem with the homogeneous gas phase reaction is expected since preliminary evidence indicates that acceptable growth rates occur at temperatures below 1000°C. The more difficult problems are crystalline perfection and surface quality. Solution of these two problems will involve the development of an *in situ* slice-cleaning technique in order to achieve an ultrahigh level of cleaniness at all deposition stages. Such a level of cleanliness is required if one wishes to obtain epitaxial films free of any spurious growth. Low-temperature vapor etches, ion bombardment, and reverse rf sputtering are *in situ* cleaning techniques that should be investigated. The required anticipated level of cleanliness is beyond that available in current epitaxial manufacturing operations.

The probability of success for this new technology can be estimated as high. A large amount of preliminary work has already been done toward establishing a process operating between 900°C and 1000°C. Development of a process below 900°C will involve basically new concepts, and, as a result, its probability of success will be rated as low.

Present thickness characterization techniques are not applicable to thicknesses less than 1 μm. The situation for resistivity characterization techniques is even worse. Only the spreading resistance probe can be used to measure the resistivity of films thinner than one micrometer. This technique is destructive since it necessitates the formation of a bevel. Success of low-temperature thin-film epitaxy will necessitate the development of nondestructive resistivity and thickness characterization techniques applicable to films thinner than 1 μm.

The impact of controlled low-temperature epitaxy on device manufacture would be great. An ability to obtain thin epitaxial layers with controlled resistivity with these processes implies that one could achieve layers with predetermined impurity profiles, a feat not possible by conventional diffusion processes. Such an advantage would, in fact, affect especially the domain of microwave devices where large impurity gradients are often required. Devices requiring such large gradients are often devices with the largest efficiencies.

Controlled low-temperature epitaxy is expected to be available in the next five years, provided that the current level of effort is maintained.

4.1.8 Advanced Silicon Epitaxial Manufacturing Processes

Reactor design itself has changed very little in the past several years; increased capacity has been achieved primarily by scaling up some of the original designs. There are no continuous reactors reported in commercial use. Various feedback loops have been inserted to control some parameters during batch processing but the fact remains that the basic parameters, i.e., epitaxial layer thickness and resistivity, must still be individually evaluated after the process is finished. The problem with silicon epitaxy is that there have been few improvements in its quality level during the past five years and that level is barely adequate to meet current requirements.

The first requirement is to develop better knowledge of the gas flowrate effect and the kinetic rate constant of epitaxial deposition so that a system can be designed that will give a uniform deposition rate (both for Si and dopant) over a large enough area to be economically feasible. The second requirement is to improve the technology of reactor design so that a cleanliness level adequate for surface-defect-free depositions can be maintained.

It is not clear whether the approach should be a large-scale continuous reactor, a large batch reactor, or a multitude of small low-volume high-deposition rate reactors. For example, were a continuous reactor to be employed, corrective actions could only be applied to following slices and thus would not represent true feedback. The limiting item is lack of appropriate sensors. It seems quite feasible to devise a thickness monitor that will continuously record the thickness of the layer but the control of resistivity will very likely always remain an after-the-fact procedure. There are no sensors for monitoring the surface quality of the layer during deposition; and, in fact, no really good sensors for precisely determining perfection even after slices are removed from the reactor.

The third requirement is to develop either in-line sensors or a totally integrated control of inputs (temperature, flow rates, etc.) such that, when combined with the first requirement above, material parameters themselves can be adequately controlled. Finally, after this is done, a logical decision can be made with respect to which route of reactor development to follow.

Taken in sequence as described, the probability of producing a system to simultaneously reduce slice cost/unit area by 50%, eliminate surface protrusions, cut thickness, and resistivity variation by 50%, and increase the size of slices as required should be about 90%.

All classes of devices and circuits which use or attempt to use the epitaxial layer as a base will be affected by such a program. These devices and circuits include various complementary bipolar integrated circuits (IC's) and field effect transistors (FET's) and some power transistors. Dielectric isolation needs that require double polycrystalline structures would be helped, as would any discrete circuit or IC that is designed to have the layer width and collector-base space charge width at breakdown closely matched.

It is expected, based on these considerations, that the above discussed problems should impact the industry in two to four years, although the current level of effort is hardly adequate as judged from the lack of progress over the last five years.

4.1.9 Silicon-on-Insulator Structure

Parasitic capacitances in metal oxide-semiconductors (MOS) and bipolar circuits limit maximum frequencies of operation. These parasitics can be reduced orders of magnitude by utilizing silicon-on-insulator substrates. Several approaches have been developed to date to accomplish such structures. Extensive work has been deveoted to the development of silicon heteroepitaxy on sapphire or magnesium aluminum oxide spinel; relatively little effort has been directed toward preparation of chemically or electrochemically thinned silicon on silica or polycrystalline silicon substrate. The above approaches have been used successfully for MOS applications only. Results have been low cost, high quality material for MOS. High quality material at any cost is not presently available for bipolar applications.

Another approach to solving the problem of preparing silicon-on-insulator is to use very thin single-crystal silicon slices on which insulator material has been deposited in an appropriate fashion. Silicon slice thickness required for this approach can be readily achieved by electrochemical thinning techniques. Although this technique has been found successful in some laboratories, it has not been developed to the extent of the first-mentioned technique.

The probability of success for MOS is good while bipolar development will be more difficult and will require considerable effort. An improved speed-power product in both MOS and bipolar areas would result from such an effort. (Definite DOD product improvements would be possible with cost tradeoffs–a necessary consideration.)

The development work will very likely not be completed without increased support. The time to impact appears to be one to two years for MOS (high cost), two to four years for MOS (low cost), and two to five years for bipolar transistors if effort beyond the present level is applied.

4.2 SILICON PROCESSING NEEDS

4.2.1 Introduction

The national needs for reliable, sophisticated semiconductor electronic components require innovation in manufacturing process technology to ensure availability with required performance at a reasonable cost. This section addresses the requirement in several selected areas for additional research and development efforts. These are (a) precise lifetime control, (b) low-temperature dielectric formation, (c) in-process measurements, (d) ion implantation, (e) metallization systems, and (f) image technology.

Beyond the specifics to be discussed, there is a need for highly controllable, automated silicon process technology in the overall scope. This requirement exists as regards the national need to ensure processed-in reliability. The elements of this integrated manufacturing process remain open to question, but an example of a possible approach is described by Burger and Donovan.[1]

4.2.2 Precise Lifetime Control

GENERAL DESCRIPTION

Silicon can be obtained with any desired resistivity between 10^{-4} and 10^4 ohm-cm. However, the minority-carrier lifetime is often unspecified or is only required to exceed some particular value. Yet this parameter can vary (often unaccountably) from 10^{-9} to 10^{-3} sec. It is also often the dominant factor in determining reverse leakage, dark current, switching time, and many other device parameters. There is a partic-

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[1] R. M. Burger and R. P. Donovan, Solid State Technol. *12*, No. 10, 58 (1969).

ularly strong need for *precise* control of lifetime in power devices such as bipolar transistors, silicon control rectifiers (SCR's), and triacs, since the minority-carrier lifetime controls the switching time, on-state-voltage, gating current, and current gain.

APPROACHES

It is possible to control the lifetime by diffusing Au at precise temperatures so that the amount introduced is controlled by the Au solubility at that temperature. However, this requires exorbitantly long diffusion times in the desired temperature range.

There are many impurities that could be used for lifetime doping, but production-worthy processes have not been worked out for any except Au. The following list summarizes the various tasks that should be pursued in this general area:

1. Production-worthy methods of reducing the chemical activity of Au at high temperatures
2. Production methods of introducing impurities such as Au, Co, Ni, S, Ag, Pt, etc.
3. Cross section and emission time measurements of these impurities in various charge states
4. Range of stability during heat treatment for impurities for which production-worthy introduction processes are developed
5. Effect of heavy doping on solubility of these impurities
6. Diffusional properties of these impurities as affected by dislocation density, sample history, and heavy doping
7. Other methods of lifetime modification, such as radiation damage and ion implantation, impurity pairs, or other combinations
8. Localized lifetime modification methods for integrated circuits and other devices, either during the introduction process or by device-by-device modification after an initial introduction step
9. Characterization of native defect clusters and various types of dislocations as "lifetime killers"
10. Characterization of isoelectronic traps (C, Ge, Sn, Pb) and isoelectronic impurity pairs (III–V, II–VI, etc.) as lifetime modifiers and possible efficient luminescent centers

PROBABILITY AND TIME OF IMPACT

All of the above items appear feasible and profitable with the possible exception of Item 10. Items 1, 2, and 4 would have immediate impact on today's devices. Item 3 is essential for effective pursuit of a number of new device concepts, especially those based on trapping phenomena in compensated high-resistivity materials. Item 7 is probably the only hope of obtaining minority carrier lifetimes shorter than 10^{-9} sec. Thus, for those device types requiring lifetime killers for speed, there is a natural barrier of about 10^9 Hz.

Devices on a single slice are often required to have widely different switching times. Item 8 would respond to this need and also open up the possibility of new types of circuits. Item 10 could lead to an efficient infrared light emitter from Si. This would have important ramifications in optoelectronics.

IMPACT

The nature of most of the above tasks is such that industrial R&D laboratories have generally not undertaken them seriously, primarily because the economic benefits were not believed to be immediate. However, the Committee believes that R&D effort is highly leveraged in several of these areas, especially where successful implementation would allow completely new functions to be performed. Higher yields in the area of power devices would have the highest impact on a short-term basis.

4.2.3 Low-Temperature Dielectric Formation*

GENERAL DESCRIPTION

Silicon devices are typically encapsulated in complex packages to provide protection from the environment. The ability to passivate the device directly would greatly ease the problem of packaging. In order to provide this passivation on a finished device, one must avoid temperatures at which the device metallization undergoes degrading reactions with the silicon in contact or active areas. For example, aluminum alloys with silicon at an appreciable rate at 500°C. Shallow junction devices such as microwave or emitter coupled logic (ECL) devices can suffer extensive emitter-base shorting after a 30-min 500°C treatment. Therefore, a dielectric passivation layer should be capable of being applied at temperatures below 450°C.

The passivation layer must protect the device or array and the metal

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*Some of these same problems are discussed from a broader viewpoint in Chapter 7 on Composite Structures. Also, see 4.3.2.

interconnection from degradation due to ambient attack or contamination. There are several identified modes of device degradation:

1. Migration of foreign ions to active areas of the silicon surface
2. Corrosion or attack of the metal interconnections caused by chemical attack or electrochemical corrosion
3. Formation of spurious leakage paths on, in, or through the surface silicon oxide layer of the device

These problems can be solved or at least minimized by the formation of dielectric passivation layers over the surface of a finished semiconductor device.

APPROACHES

The three dielectrics being investigated at this time are silicon nitride, doped silicon oxide, and aluminum oxide. Each of these is discussed separately in the following. The impact of such passivation technology will be assessed in the conclusion of this section.

Silicon Nitride. Most of the current work on silicon nitride has been done on films formed by chemical vapor deposition (CVD) at temperatures in excess of 700°C. The silicon nitride films are usually deposited directly on the device oxide surface before the metallization is applied. Silicon nitride acts as an effective diffusion barrier to ions such as sodium and to water molecules. However, the metallization is not protected from chemical or electrochemical corrosion and the silicon nitride films are usually not thick enough to prevent the formation of inversion layers on the silicon surface. (However, in the beam lead sealed junction technology the metallization needs no protection against sodium ions, and a combination of silica and silicon nitride prevents inversion from occurring.) Thus, there is need for applied research in the area of low-temperature deposition techniques along with extensive film characterization. The present contenders in the area of low temperature deposition techniques are radio frequency (rf) sputtering and rf-induced vapor deposition. It is not clear whether silicon nitride films deposited at low temperatures will retain the useful properties of CVD silicon nitride films.

Doped Silicon Oxide. Silicon oxide films heavily doped with phosphorous or boron form glasses that act as "getters" for impurity ions such as sodium. The doped oxides can be formed using CVD at temperatures in the range of 300° to 450°C. Glassy films can also be applied using spray or spin-on techniques followed by a firing at 400° to 450°C. These films can be applied over the device metallization without causing severe degradation. These films are fairly effective ion barriers and are somewhat effective in retarding chemical and electrochemical corrosion, although water vapor can slowly penetrate the silicon matrix, particularly under the influence of a favorable temperature gradient or voltage bias. This area is being fairly well covered by the semiconductor industry. A good compilation of available techniques and data would be useful.

Doped silicon oxide films can also be deposited by rf sputtering or evaporation techniques. These vacuum-deposited films are generally not as effective as passivation films laid down by CVD. However, these films may be useful as diffusion sources for the common dopants in silicon.

Aluminum Oxide. Aluminum oxide films show promise of being effective ion barriers and less permeable to water vapor than silicon oxide films. Aluminum oxide films can be formed by CVD techniques at temperatures above 400°C. They can also be made by converting aluminum to aluminum oxide by means of anodization. By the anodization technique, the aluminum thin film interconnects can be imbedded in and overcoated with aluminum oxide. The aluminum interconnects are thereby "hermetically" sealed in a protective coating of their own oxide, providing an excellent corrosion barrier. At this time, however, the effects of absorbed polar molecules are not known and no quantitative data are available for ion migration. Applied research in these areas is needed.

PROBABILITY AND TIME OF IMPACT

Improved deposition techniques on any of the above three dielectrics would have significant short-range impact (1 to 2 years). The first two are already widely used and the third is being seriously considered for several applications. The characterization of the physical properties is inadequate in all three cases, but it would be of particular benefit in the case of aluminum oxide, since it has received much less attention.

Basic studies of the mechanisms of film deposition would also have significant impact. Most of the present processes have evolved from a purely empirical base. A sound theoretical understanding of the effect of various parameters on plasma deposition, anodization, and other low-temperature deposition processes would lead to significant advances in the general field of film deposition.

IMPACT

If an effective low temperature passivation layer were developed, the reliability of semiconductor devices could be markedly improved, and, at the same time, packaging cost could be lowered. In particular, surface sensitive devices, such as MOS, ECL, and high-voltage diodes and transistors would benefit. However, many of these advantages are available in the beam lead sealed junction technology at the cost of more process complexity. Moreover, such low-temperature dielectric deposition techniques would not be limited in application to silicon devices.

4.2.4 Ion Implantation

GENERAL DESCRIPTION

Present device fabrication methods are performed at high temperatures, typically 1100° to 1200°C, such that dopants diffuse into the crystal as a result of energy ($kT \simeq 0.1$ eV) supplied to the lattice. Dopant profiles are restricted to those resulting from Fick's law. In addition, the high-temperature processing steps often cause material degradation due to introduction of gross lattice defects and chemical contaminants.

Ion implantation is a method of overcoming these limitations. Implantation allows precise quantities of ionized, isotopically pure dopants to be injected at high energies, typically 10^4 to 10^7 eV, into a crystal held at almost any temperature. After implantation, additional heating, at 500° to 900°C, is generally used to remove lattice damage and cause the implanted dopant to take up substitutional lattice sites to provide electrical activity. In addition to doping crystals, implantation techniques coupled with backscattering measurements and nuclear reactions are powerful diagnostic tools for impurity and crystal defect analysis.

One of the major barriers to the development of ion implantation to its full potential is the lack of equipment designed and built for semiconductor production applications. In particular, the stability and operating lifetime of ion sources for large-scale production of semiconductor devices are problems that affect cost. A second consideration is that of beam handling between the ion source and slice target chamber. It is highly desirable that the system used be simple and reliable.

In addition, the elimination of neutrals is of great significance. In this connection, a third area of concern is the accuracy of the dose measurement in the target chamber. It is of prime importance that this measurement be accurate and reproducible. Also, for production purposes, the through-put capability of any chamber design is important.

The use of ion implantation to form junctions in silicon has not yet been completely characterized or evaluated. Empirical data have been developed but a detailed understanding of the mechanism of annealing and impurity activation would be very useful. In particular, the behavior of the elements of interest, such as boron, phosphorus, arsenic, oxygen, nitrogen, etc., have not been well characterized. The role of crystal damage in annealing, junction formation, and resulting device characteristics is at best only partially understood.

The use of ion channeling has not been widely studied with a view to device application; its utility in this area remains an open question. In addition, channeling in conjunction with backscattering measurements, nuclear reactions, and x-ray fluorescence can provide a valuable tool to detect impurity atoms for analysis, provide information on crystal damage profiles and precisely locate impurity atoms in the host lattice. For backscattering work, proton and alpha measurements are particularly useful; giving depth resolution to about 50 Å and atom position resolution to about 0.2 Å for elements heavier than the Si host lattice. For elements lighter than Si, such as boron, the (p,α) and (p,γ) reactions and stimulated fluorescent x-ray emission are very useful for impurity layer and defect analysis. However, at this time, direct application of these techniques to semiconductors is not widespread in industry.

APPROACHES

Applied and developmental research is necessary to develop equipment that would provide a production base for implanted semiconductor devices. This is particularly important if a true semiconductor manufacturing system is to become available. Some basic work on ion sources and ion beam transport would be helpful for system design.

More applied work on implanted layer formation, annealing, and damage analysis should be carried out. Basic work should be done in these areas as well, particularly with a view to understanding and modeling the process well enough to predict the process effects on device characteristics. The use of backscattering, nuclear reactions, and x-ray emission for the analysis of implanted layers and damage profiles may prove indispensible to understanding and, as such, should receive both basic and applied research support.

Development of specific device types will require applied research effort both from the standpoint of device design as well as process development. Since implantation offers process capability, not available by other means, new device concepts and designs are possible; this may require basic device understanding as well as product development work.

PROBABILITY AND TIME OF IMPACT OF IMPLANTED SEMICONDUCTORS

With the data presently available, the probability of success in several application areas appears to be very high. The requirements for precise control of shallow doped layers and high resistance regions in smaller geometric patterns will provide a major incentive for implementation. The rate at which it becomes widely applied will depend critically on the level of effort supplied. The problems are extremely diverse and complicated, however, and progress will be slow unless major resources are committed to both research and development in the field of ion-implanted semiconductors.

IMPACT

Implantation processing is amenable to automation since control of ion energy governs the depth distribution of injected dopant and control of ion beam current and time governs the total quantity of dopant. A variation in ion energy of 1% may cause a variation in the depth of peak impurity concentration of only ~ 125 Å. Typically, energy may be reset to within 0.1%. State-of-the-art equipment is capable of maintaining beam current stability to one part in 10^4. Modern current-monitoring devices are capable of resolving 1 pa, i.e., 6×10^6 ions/sec. Therefore, the total quantity and distribution of injected impurity can be very precisely controlled. The resulting reproducibility could have a very large effect on the yield and cost of processing semiconductor devices. Specific examples of potential improvements to particular device types are discussed below.

For MOS devices the most immediate impact would be the arbitrary adjustment of threshold voltage made possible by implantation. Not only are several threshold voltage values on a single chip now possible for p-channel enhancement-mode devices, but enhancement/depletion-mode combinations are also possible. This means that a true single power supply MOS system with a larger speed-power product can be built for a variety of memory applications. Structures with no gate overlap also become possible using implantation to tailor the source/drain areas. Of longer-term significance is the use of implantation to fabricate n-channel devices.

Implantation can be used to produce very-high sheet resistivity (up to 100 kΩ/□) which means that very-high-value precision resistors can be fabricated using only a small silicon chip area. This has an impact on several integrated circuit areas, but particularly on linear circuits where the total circuit chip area can be drastically reduced with attendant cost and yield improvements.

The precise tailoring of impurity profiles will be important for several device and circuit applications. The control of very shallow junction depths and control of the base profile and doping level under the emitter of a bipolar transistor will provide increased speed-power product in high frequency microwave devices used in high-speed logic circuits.

Another application of impurity profile tailoring is the tuning diode. The desired retrograde profile can provide a high capacitance ratio. This, coupled with the potential for integrating other devices such as high-value resistors and MOS devices with the diode, could provide a family of voltage tunable rf circuits for communication systems. Another possible application is the fuse circuit area.

Visible light sensors with high quantum efficiencies can be fabricated using implantation to form the junction required. This capability could be extended into the uv region as well.

Using implantation as a technique to introduce impurities into a localized region of the crystal, buried (and surface) dielectrics can be formed. Since these regions can be precisely located and controlled, the fabrication of radiation-hardened circuits could potentially be greatly simplified.

This is not intended to be a complete list, but rather an indication of the broad potential that ion implantation has for device application. Some immediate impact areas are already clear, e.g., MOS threshold voltage adjustment, but since the techniques are relatively new, the long-range impacts could be much greater than even now anticipated.

SUPPORT REQUIRED

Support for device application is essential if the broad applicability of the implantation process is to be fully realized. This is particularly true for new device concepts that could provide step-function improvements at the system level. In addition, many of the applications will not be economically realized if a sufficient process data base or adequate production equipment is not developed. Thus, it is equally important that support be provided for both implantation process research and equipment development.

4.2.5 In-Process Measurement Applied to Silicon Materials in Device Fabrication

GENERAL DESCRIPTION

To achieve high performance in today's complex microelectronic systems, it is necessary not only to have good design, but also manufacturing processes that do not adversely affect the products. It is known that in silicon the presence of lattice defects can influence electrical properties such as mobility and minority carrier lifetime. Similarly, chemical impurities introduced during fabrication can affect both surface and bulk properties of silicon devices. The direct effects of these imperfections on the products are sometimes weak, but strong indirect effects, such as dislocation impurity interactions, often result in poor products and system performance, as well as reliability problems. Consequently, it is imperative that one characterize the silicon "in-process" material and monitor the processes through the fabrication of devices and subsystems. Only by knowing and controlling the material quality by in-process measurements can one hope to make a reliable electronic system.

APPROACHES

In the semiconductor components industry, the determination of physical properties and imperfections is carried out on control slices at the conclusion of each manufacturing step. However, one rarely measures the physical dynamic effects in progress. For instance, in the growth of an epitaxial silicon film one does not measure the nucleation center density, the growth rate, the diffusion layer thickness, or even the true silicon surface temperature. The development of appropriate sensors and techniques for such measurements would allow us to build much more sophisticated products than is now possible.

At present, key developments are needed in the following areas:

1. An effective method for characterizing epitaxial layer quality prior to device fabrication
2. *In situ* measuring techniques for determination of structural defects in production environment (thermally stimulated current, plasma resonance, spreading resistance, etc.)
3. Sensitive methods for characterization of impurities such as carbon, nitrogen, and oxygen
4. Combined use of process monitor test patterns and computer modeling to understand the kinematic nature of defects related to processing conditions

For the longer term, the type of goals that should be pursued are listed below:

5. Continuous correlation of material properties, processing parameters, device characteristics, and circuit operation, with rapid feedback loops in the manufacturing process
6. New and/or improved measuring techniques for the determination of structural defects in high complexity, multilevel devices and products made by new technology
7. Rapid nondestructive device and circuit function measuring techniques, preferably with ability to test and fix iteratively. This would include electron beam and scanning light beam measurements.

PROBABILITY AND TIME OF IMPACT

Since the know-how and technological groundwork of the suggested areas of process-parameter interrelation are available, the probability of success is rather high. Depending on the amount of support, the impact should be readily visible in a one-to-two-year time frame. The establishment of scientifically based analysis of production process on a routine basis would be of continuing value.

IMPACT

The impact of an organized program to make in-process measurements could be truly immense. All aspects of the electronics industry would be upgraded by higher yields, quality, and reliability. The increased understanding of device processing would allow pursuit of goals that are presently unattainable because of geometrical or reliability limitations (microwave, displays, memories, etc.).

4.2.6 Metallization Systems

Metals are used in semiconductor devices as intraconnecting paths between devices on monolithic chips, as interconnections between devices and the outside, and as active device components such as Schottky diodes. Different metallization systems may be required to satisfy various requirements of each of these different uses, but all systems utilized must be mutually compatible and must be compatible with standard device fabrication, assembly, and packaging technology.

The status of metallization systems for each of these three applications is discussed separately in the following.

INTRACONNECTION METALLIZATION SYSTEMS

The predominant metal presently used for intraconnection of silicon devices is aluminum. The advantages of aluminum for this purpose are its low resistivity and its adherence to silicon and silicon oxide surfaces. Aluminum forms low resistance ohmic contacts with heavily doped p- and n-type silicon, and it is compatible with a widely-used interconnection technique–ultrasonic bonding of aluminum wire. The processes required for its deposition (vacuum evaporation) and delineation (chemical etching) exist, even though they may be relatively cumbersome and expensive. The disadvantages of aluminum are many: It is soft and easily damaged mechanically; it corrodes readily in nonhermetic packages; it forms undesirable electrochemical cells with gold, which is often used as an interconnection metal; it is metallurgically incompatible with gold; it is susceptible to electromigration; because of its low temperature eutectic with silicon, it is incompatible with high-temperature processes used for forming insulating and passivating dielectrics; it can act as a diffusion sink for silicon with adverse effects on shallow-junction devices; and it requires a relatively expensive deposition technique.

Other metals, such as gold, appear to possess one or more overwhelming disadvantages so that no other single metal appears satisfactory for intraconnections. This has led to the development of several multimetal systems, such as titanium/platinum/gold, molybdenum/gold and titanium–tungsten/gold. These systems all suffer from the added complexity of depositing and delineating a series of different metals.

The research and development required in this area includes:

1. Techniques of improving the properties of aluminum intracon-

nections; improvements in the metal properties, and improvements in passivation techniques

2. Continued development of the multi-metal systems listed above, both in improving the properties of the systems and in reducing the complexity of the processing. Very careful studies of the metallurgy of these systems together with silicon are required, as well as measures of resistance to corrosion and electromigration.

3. Development of other systems, such as refractory and noble metal silicides, emphasizing compatibility with silicon device processing

INTERCONNECTION METALLIZATION SYSTEMS

Essentially three general types of systems exist to connect devices with the exterior world: (1) wire-bonds; (2) beam leads; and (3) bumps, both solder-reflow and aluminum. Considerable development has gone into each of these systems, and the advantages and disadvantages of each are too complex to list here. Essentially two criteria are placed on each system: (1) It must be metallurgically and electrochemically compatible with the intraconnection metallization on the device die; (2) it must be compatible with the exterior system requirements of the user, metallurgically, electrically, and economically. It is obvious that development of interconnection systems must be based on a specified device and upon a specified end use. It therefore follows that interconnection metallization development programs should be considered an integral part of specific device-system development programs.

SCHOTTKY BARRIER AND OHMIC CONTACTS

Within the last few years, significant advances have occurred in the Schottky barrier area in that there are a number of commercial discrete devices and integrated circuits incorporating Schottky barriers to take advantage of their fast switching and low forward voltage drop characteristics. The nature of ohmic contacts is now better understood, and it is generally accepted that high surface-carrier concentration is necessary to achieve low resistance contacts. However, there are a number of problem areas that have to be solved before reproducible and reliable Schottky barriers and ohmic contacts can be readily made on semiconductors:

1. Surface cleaning: Good Schottky barriers and ohmic contacts can only be formed if the semiconductor surface is sufficiently free of

oxide, impurities or dielectric films, etc. Chemical cleaning and vacuum sputtering methods have been tried, but better methods are needed for production. It should be noted that for complex large system integration (LSI), poor ohmic contact formation is one of the serious causes of yield loss.

2. Contact to shallow structure: Most of the metals used to form Schottky barriers and ohmic contacts, such as Al and Pt, react with Si; therefore, they are not suitable for shallow device structures. The Al-Si system has been employed for these contacts but other metal systems less reactive with silicon and perhaps more easily deposited should be investigated.

3. High temperature Schottky barrier system: Most of the metal systems employed cannot be processed at very high temperatures due to rapid diffusion of these metals, e.g., Al ($T<577°C$); Pt ($T<1000°C$). Development of high-temperature metal systems not only makes possible the use of lower cost packages but also considerable process flexibility.

4.2.7 Summary

In the areas discussed above, research and development support is required as summarized below:

A. Precise lifetime control
    1. Production methods for using impurities other than Au for lifetime control
    2. Investigation of other techniques for lifetime control
B. Low-temperature dielectrics
    1. Silicon nitride–low-temperature deposition techniques and film characterization
    2. Silicon oxide–data compilation
    3. Aluminum oxide–film characterization, ion migration studies, effects of absorbed polar molecules
C. Ion implantation
    1. Process research
    2. Equipment development
D. In-process measurements
    1. Characterization and measurement techniques and instruments
    2. Nondestructive test and "adjust" techniques, e.g., electron beam
E. Metallization systems
    1. Development of improved multimetal and refractory silicides

    2. Improved methods of connecting devices to exterior world
    3. Schottky barrier and ohmic contact studies
F. Image technology

In addition to the areas described above, a brief description of needs in image technology for silicon microelectronics is also appropriate.

The required geometries for sophisticated electronic components, (e.g., microwave devices) are such that the resolution capability of near ultraviolet optical technology is inadequate. Electron beam technology for mask making and direct, computer-controlled exposure of photoresist (more appropriately, electroresist) is evolving. Additional support is required to speed the maturation of the approach as a production technology. Support should also be provided for research directed at probing the geometric definition limits of this technology; the present approach appears limited by available electron-sensitive resists, etching technology, etc., to approximately 0.1 μm line definition.

There has been a historic trend in silicon processing technology toward the use of larger silicon slices. Projection of the capability of current technologies toward larger (3 in. or greater) slices requires considerable development of equipment, particularly in the case of image technology. Larger photomasks, the necessary contact or projection printing equipment to hold 2 μm or less line width, and separation capability across the large slice are needed.

4.3 STRUCTURES

4.3.1 Dielectrically Isolated Structures

4.3.1.1 DESCRIPTION OF PROBLEM

Dielectrically isolated semiconductor integrated circuits require both performance and economic improvements. Reduction of parasitics is needed to improve the speed-power product. Greater tolerance to ionizing radiation is also desirable. Both the reduced parasitics and increased radiation tolerance could be achieved by development of techniques for reducing the dimensions of the dielectrically isolated regions and the size of devices fabricated within these regions. Smaller dimensions would also allow the complexity of MSI or LSI arrays to be increased. Smaller base width, increased base dopant concentration, and thinner epitaxial regions would improve the neutron tolerance of bipolar transistors.

Improvements in the yield of good isolated pockets on each slice would result in reduced cost and extend the applications of such structures.

4.3.1.2 RESEARCH AND DEVELOPMENT NEEDED

Reduced Device Dimensions and Spacing

The capability of fabricating dielectrically isolated device structures with smaller dimensions and closer spacing is needed. This includes achievement of very thin dielectrically isolated layers containing extremely shallow epitaxial films with sharp concentration gradients. The ability to characterize resistivity and thickness of ultrathin epitaxial regions is a prerequisite to the control of these processes. Additionally, the capability of defining very narrow vertical openings (as low as 0.5 μm) is needed to reduce the area and spacing of the dielectrically isolated regions.

Some reduction in layer thickness of dielectrically isolated layers may be achieved by improved control of mechanical and chemical thinning. However, new approaches are needed for substantial reductions. High surface quality must be maintained to allow the resolution required of the small area devices. Low-temperature diffusion and oxidation processes must be developed and/or improved in order to maintain sharply defined epitaxial layers and reduce surface damage.

Improved Yield and Economy

Processes must be simplified and the yield of acceptable dielectrically isolated pockets on each slide must be increased to reduce the cost of dielectrically isolated devices.

Basic Studies

Material properties should be investigated for potential improvement of device characteristics achievable in dielectrically isolated structures. For example, crystal orientation affects properties of both bulk and surface.

4.3.1.3 PROBABILITY OF SUCCESS

1. Reductions in dimensions of dielectrically isolated regions would unquestionably result from a comprehensive program in this area. The

probability of reducing area by a factor of 10 and thickness by a factor of 2 is greater than 50 percent. Significant improvements in the ability to characterize ultrathin regions will require development of new concepts.

2. Significant improvements in yield and cost of dielectrically isolated slices are expected. The probability of reducing the number of defective pockets on each slice by a factor of 2 is 50 percent. Since the basic studies (c) are not clearly defined at this point (See a, b, and c under 4.3.1.5), the probability of success cannot be estimated. However, improved understanding would contribute to the success of (a) and (b).

4.3.1.4 IMPACT

Reduction of dimensions leading to improved speed-power product and increased radiation tolerance will result in systems of smaller size and weight with lower power requirements. Increases in yield and hence lower cost will extend the range of applications of dielectrically isolated structures, for example, into linear circuits.

4.3.1.5 TIME TO IMPACT

The expected time to impact production devices for the three areas of research and development are as follows:

a. Reduced device dimensions and spacing: 2–3 years
b. Improved yield and economy: 1–2 years
c. Basic studies: 3–5 years

Since nearly all of the interest in radiation resistance involves government applications, it receives little attention in commercially oriented R&D. Federal support is essential if this aspect of the work is to be accomplished.

4.3.2 Silicon-Insulator Interfaces

4.3.2.1 DESCRIPTION OF PROBLEMS

The development of planar device technology has given a frame of reference for understanding and control of the characteristics of the real silicon surface. Since that development, the silicon dioxide–silicon system has become the most studied and best understood of the solid–

solid interfaces. However, in practice, the control of device surface characteristics is still largely art. Manufacturing procedures for surface control are a maze of empirically developed and poorly understood chemical and thermal treatments.

Fundamentally, the insulating films on silicon surfaces affect the electrical characteristics of those surfaces through (a) their bulk charge density, which controls the silicon surface potential and, hence, carrier densities; (b) interfacial structure and impurities that control surface lifetime or carrier generation rates; and, (c) mobilities. The conceptual link between the specific chemical species, reactions, and structure at, or near the insulator–silicon interface and the resulting electrical behavior of the underlying silicon surface, which is vital to intelligent process design, is largely forged from hypotheses drawn from various experimental results. The range of validity of the resulting models is thus limited to the unique sample preparation procedures used for those experiments. Work in various laboratories has established the generality of many of the results, but independent characterization techniques have not been developed to sufficient levels of sensitivity to establish the validity of the models. Physically and chemically specific models for structural dependence of the electrical behavior of the insulating films usable for devices is a requirement for, as well as the co-product of, the development of new surface-oriented device concepts.

In addition, the establishment of silicon device manufacturing processes has not always been supported by sufficient process characterization data so that results of empirical surface control process development have sufficient generality to permit application to the manufacture of other device types, or for comparison of results with existing or proposed surface models.

Surface effects play a role in virtually all devices. This role is constantly increasing as the devices become smaller (larger periphery-to-area ratio) and shallower (a larger proportion of active device volume subject to surface and interface phenomena). The M-I-S device family (MOSFET's, memory cells, and charge coupled devices) depends completely upon surface control for their operation. Research to increase understanding of surface effects and to render manufacturing processes more responsive to surface technology will not only permit fabrication of new device types, but affect yields of existing device processes.

4.3.2.2 RESEARCH AND DEVELOPMENT NEEDED

Specifically, additional work seems appropriate in three areas. First, a basic understanding needs to be achieved of structure and impurity effects in thermally grown and deposited SiO_2 films and other materials found to be useful in device fabrication, e.g., silicon nitride and aluminum oxide. This could include development and application of optical absorption and reflectance techniques (including electroreflectance) as well as resonance techniques, e.g., electron spin resonance (ESR), that can contribute evidence of bonding phenomena and leading to usable energy band diagrams for the materials. Fabrication process studies are required; sample preparation is very important if results are to be applicable in device processes. Results should be related where possible to electrical behavior of some device-like test structure, to establish extrapolability of the data. An example of a well-known effect that needs more complete analysis is the strong effect of hydrogen, introduced at various temperatures, on the electrical behavior of the oxide–silicon interface.

A second area, closely related to the first, involves charge transport and storage effects in insulating films and the control of these characteristics by film fabrication, by applied electric fields, or temperature. These effects are already of prime importance in various memory cell devices currently being developed. They also affect stability and reliability of other planar devices. Needs in this area could be met through support of (a) characterization studies of materials involving theoretical and experimental work on dc conduction and thermally stimulated currents, and (b) development programs on novel devices, e.g., multi-insulator memory cells, amorphous semiconductor devices, and charge-coupled devices.

The third area relates to the establishment of better controlled, better understood manufacturing processes. These processes are usually developed under strong economic pressures, and control of surface effects is often done through parameters only indirectly related to surface behavior. If manufacturing processes were adequately characterized from the point of view of the basic surface-oriented parameters, they could become more responsive to advances in surface control technology, and could, themselves, contribute to the development of that technology.

4.3.2.3 PROBABILITY OF SUCCESS

The probability of obtaining significantly increased understanding of and control over silicon surfaces and silicon–insulator interfaces is 100 percent.

4.3.2.4 IMPACT

Control of silicon interfaces will result in increased manufacturing yields of silicon-integrated circuits leading to lower costs and will increase the reliability of these circuits. Increased yields will also permit advances in the complexity possible in circuits.

4.3.2.5 TIME TO IMPACT

The impacts described will not occur as step functions, but rather in a continuous manner as studies proceed. Effects on manufactured devices will begin to occur approximately one year after studies commence. The total program length will be of the order of three to five years. Funding to stimulate development of more sensitive characterization techniques and to foster their application together with those already on hand to yield thorough and usable material, process, and device models will have a unifying effect that cannot otherwise be achieved.

4.4 NEW WAYS TO EXPLOIT SILICON (SEE TABLE 4-4)

By almost any standard applied, silicon technology is far ahead of any other materials technology, semiconductor or otherwise. Most of the present day uses are electronic in nature, although limited use occurs in the optical industry for infrared windows and lenses. In this section an attempt is made to delineate other possible uses for Si, in the electronic fields and in others such as medical, environmental control, and optical.

4.4.1 Electronic Applications

Silicon is already widely used to make discrete electronic components and integrated circuits of many types. However, there are still many electronic functions that are performed more efficiently using other technologies. These include, for example, image scanning and infrared emission. Other possibilities for exploitation are frequency division, microwave emission and detection, and various logic schemes that involve moving charges laterally across a Si slice. Several of these are discussed in more detail below.

TABLE 4-4 New Ways To Exploit Silicon

	Time Scale[a]	Effect on U.S. GNP [b]	Effect on U.S. Defense Posture[b]	Ecological Effects[b]	Social Impact[b]	Activities in Aero-space[b]	Success Probability[c]	R&D Location[d]	Gov't. Support[e]
Charge coupled devices and bucket brigade	2–5	3	4	2	2	3	3	I	2
Passive image scanning	2–5	1	5	3	2	5	3	I, U	2
Trapping phenomena	2–5	1	4	3	1	3	3	U, I, G	2
High voltage IC's	2–5	4	5	3	4	4	4	I	3
Solid state inductor	1–3	4	4	3	4	5	2	I, U, G	2
Medical applications	2–10	4	3	4	5	5	4	I, U, G	5
Inexpensive solar cell	3–10	5	3	5	5	5	3	I	4
Infrared light emitter	2–5	3	5	3	2	4	2	U, I	2
Crystallographic applications	2–5	1	4	4	2	4	3	U, I, G	2

[a] In years before impact felt.

[b] Impact rating 1-5; 5 most important.

[c] Probability of 1 is 0.0, probability of 5 is 1.0.

[d] U,I,G, denote university, industry, and government laboratories, respectively.

[e] 1 denotes a little (~$\$10^5$) government support would be effective; 5 denotes larger expenditure (>$\$10^7$). Note that this applies only to the annual level of support, not the relative importance of the program.

The recent development of charge transfer devices, exemplified by the new analog MOS shift registers, the charge coupled devices (CCD), the bucket brigade (BB), is important since much greater simplicity, higher device densities, and lower cost are possible. Their application in medium, and perhaps large, serial storage, as well as several other electronic functions, heretofore only marginally feasible, appear possible. One such application is in analog-matched filter signal processing and another is a flat silicon imager that does not require an electron beam for read-out. Present self-scanned solid state imagers based on the phototransistor do not compete with the electron-beam-scanned Si diode vidicon tube, mainly because of fundamental limitations of sensitivity, noise, and bandwidth as well as yield problems. However, the extreme simplicity of CCD's and BB's hold promise for both high yield and high resolution and could be utilized in inexpensive, rugged, miniaturized Si cameras in the near future.

Another general area that looks fruitful is that involving trapping phenomena in high-resistivity silicon. Efficient infrared sensors, frequency dividers, high-current pulse generators, counters, and other devices have already been made using these concepts, but no one has developed them to the point where they look commercially attractive. Government agencies should be especially alert to possible applications in this area because the potential payout is extensive and cost-effective.

High-voltage integrated circuits are needed in many civilian and military display systems. There are no technological reasons why high-voltage rectifiers, power transistors, and other devices could not be monolithically integrated using the latest dielectric-isolation methods. However, a great deal of development work would be required before this could be realized.

A solid-state inductor is still badly needed, especially one that can be readily integrated with present circuits. Possibilities of performing this function using Si should be investigated.

4.4.2 Medical Applications

There are numerous ways that Si could be used in the fields of medicine. These applications would be especially accelerated by government support since the economic benefits of such developments would not be realized for several years. The sociological benefits of such programs could be truly immense. We will only list a few examples here:

1. Microprobes (*in vivo*)
2. Pressure membranes using thin Si
3. Semi-permeable membranes
4. Heart pacer integrated circuits
5. Image sensing arrays (blind reader, etc.)
6. Ion-selective sensors
7. *In vivo* blood analysis, sugar control, etc.
8. Remote heart failure warning systems

4.4.3 Environmental Control

An important aid in environmental control would be the development of an inexpensive solar cell. This would allow partial replacement of conventional power sources, which presently use fossil fuels to produce over 90% of the electricity generated in this country. The cost-per-unit area would have to be about 1 percent of that of present solar cells in order to compete with conventional power sources. However, considering the great availability of Si and the relative simplicity of the solar cell, such price reduction may indeed be possible.

4.4.4 Optoelectronic Applications

Silicon is used for infrared windows and optical elements. It is also used widely to sense visible and near infrared light. It has not yet been used as an infrared light emitter because of the indirect nature of its bandgap. However, this problem has been circumvented in GaP by using isoelectronic dopants. Relatively inexpensive theoretical studies would probably tell whether efficient emitters could be made from Si using a similar approach. Development of such a device would greatly enhance the penetration of Si in the expanding optoelectronics field.

The extremely high crystal perfection of Si and the availability of very large single crystals open up many other possible areas of application. For example, the fields of x-ray and neutron spectroscopy are already benefiting from the use of large Si crystals. Government agencies should be especially alert for other applications that utilize the unique size and perfection of Si crystals.

4.4.5 Cost-Effective Design Automation as an Aid to Silicon Usage

The use of silicon technology is greatly enhanced by cost-effective design automation. The current state of the art in design automation has already greatly increased the custom use of silicon by decreasing the cost and time associated with the design effort. It is clear that custom applications increase as the costs become lower.

Three major areas that limit design automation presently are:

1. The relationship between process, geometries, and electrical performance
2. Theories of minimal area placement and routing
3. Test generation for complex functions

4.4.5.1 RELATION OF PROCESS AND GEOMETRY TO ELECTRICAL PERFORMANCE

One essential ingredient in the application of design automation to electrical design in silicon technology is the availability of models. A model must be sufficiently accurate and it must be possible to obtain the model parameters economically. Furthermore, the technique of modeling must be basically general, so that it is not subject to rapid obsolescence.

In their attempt to produce a new design, engineers must presently make use of the measured electrical properties of previously used geometries and processes. At best, the electrical properties are predictable only for slight variations in geometry and process. Usually, the designer interpolates between two similar designs, whose properties bracket the desired performance characteristics. This approach requires extensive testing of individual devices and the maintenance of elaborate files; these are costly.

A modeling technique that would be particularly useful in alleviating this problem in integrated circuits is the process model. Such a model accepts the basic process parameters and geometries as input and predicts the electrical performance of the device. A process model would allow the designer to evaluate the performance of a new geometry-process combination with the aid of computer programs without actually building and characterizing the device. The process model combats obsolescence and eliminates the expensive file-building and maintenance operations, otherwise required.

4.4.5.2 BARRIERS TO FULL UTILIZATION OF DESIGN AUTOMATION IN SILICON TECHNOLOGY: AUTOMATIC LAYOUT CAPABILITY, FUNCTIONAL TEST TECHNOLOGY

At present there is no economical automatic layout capability for components with various sizes, shapes, and orientations on a single slice. There are no techniques or algorithms available to perform this task while ensuring an economical production slice size and connectivity. The current methods are:

1. *Manual* – Manual methods are expensive, error-inducing, and slow. Tomorrow's slice sizes will be simply too large for application of manual techniques.
2. *Man-Machine Interaction [Graphic cathode ray tube (CRT)]* – Graphic CRT methods are expensive and slow, although errors may be automatically flagged. CRT size and the amount of distinguishable information storable on the tube limits the slice size that can be practically handled.
3. *Semi-Automatic*–Slice sizes designed by this technique are excessively large for producing large volumes of slices economically. This method normally requires costly and error-inducing manual intervention.

A completely automatic system for the layout of components of a slice would provide fast error-free designs. It would eliminate the need for expensive graphic CRT equipment for this application and provide placement and routing tools (planar routing techniques) also applicable to other technologies.

The development and application of functional test technology to the problems of silicon technology requires effort in the three major areas discussed below:

1. Problems in test generation technology–Effort should be directed toward automatic test sequence generation for (a) asynchronous circuits and (b) circuits requiring very long test sequences, such as those containing counters.
2. Designing digital circuits for testability–Many problems in test generation can be avoided if considered during the design phase. Logic design rules to improve testability without sacrificing design flexibility need further study. Particular areas of investigation should include the

problems of logic partitioning, test point selection, and minimization of the use of asynchronous circuits.

3. Problems in fault diagnosis–Implementation of automatic procedures for fault diagnosis requires a computer-driven test set having considerable storage capability. For effective diagnosis of circuit failures for either repair or failure analysis, development of a tester and the associated software for utilizing diagnostic test sequences is necessary.

4.4.6 The Ultimate Performance of Si Devices Based on Materials and General Physical Principles

After designing solid-state devices to optimize desired characteristics, there will always be fundamental limitations on their ultimate performance. These are set by materials properties such as saturated drift velocity and lattice thermal conductivity, as well as general physical principles.

Well-known examples of such limits are the $Pf^2 \approx$ constant relation (P = maximum power output, f = frequency) for microwave transistors and that the least amount of energy to change a logic state is $\Delta E \approx kT$ (k = Boltzman's constant, T = temperature). The latter then leads to minimum switching speeds given by $\Delta t = \Delta E/K = kT/K$ using Heisenberg's uncertainty relation, i.e., typically, 0.01 psec. However, both of these calculations are somewhat unrealistic. For instance, if a device changed its logic state by tunneling from one state to another at low temperatures, then the lower bound on the energy required to switch would not be kT, but would be set by the tunneling process. Likewise, the Pf^2 = constant law is derived without reference to even a simple device structure and does not properly account for items such as the Kirk effect, which will modify this conclusion. It is believed that device modeling should be closer related to actual device structures including their input and output loads. For instance, the switching time of a transistor is not limited by the Heisenberg uncertainty principle, but by the amount of capacitance on the output.

Another instance of needed work is on ohmic contacts; the models for tunneling do not apply in the case of a heavily doped semiconductor, nor do the models treat the real case of an alloyed contact on an oxidized Si surface.

Silicon technology is quite advanced; however, the studies suggested should provide realistic goals for further technology advances. Most of the advances described would probably be in the 10–20 percent range rather than a factor of two or more. This increase would be significant for certain types of devices such as rf power sources or integrated circuits. For instance, if the area of the ohmic contacts could be reduced, then the number of active elements on an IC chip could be increased significantly.

4.5 PACKAGING AND TESTING

4.5.1 Packaged Devices

4.5.1.1 DESCRIPTION OF PROBLEM

Increasing power density, due to smaller-sized components and higher packing density, makes heat removal from packaged devices a major problem.

4.5.1.2 POSSIBLE SOLUTIONS

The design of more efficient high-speed devices and the design of improved packages are two obvious lines of attack. More thermally conductive substrates, e.g., beryllia, would improve the heat sinking. Successfully passivated devices (see below) would allow direct liquid-phase cooling.

4.5.1.3 PROBABILITY OF SUCCESS

The probability of improvement through device and package redesign is high, about 80–90 percent. Obviously, some improvement must result from use of more thermally conductive substrates but the extent may be small. The successful application of liquid cooling is considerably more doubtful; 20 percent may be a fair estimate of success.

4.5.1.4 IMPACT

A significant increase in packing density and a lowering of power demand would result.

4.5.1.5 TIMING

The design changes and substrate material substitution would be relatively short-term: in the one- to three-year time period. The liquid cooling program is relatively long-term: three to five years.

4.5.1.6 IMPORTANCE OF SUPPORT

In view of the importance of packing density and power requirements to many of the military and space programs, some encouragement of these developments would seem desirable.

4.5.2 Packageless Chips

4.5.2.1 DESCRIPTION OF PROBLEM

All semiconductor devices are currently packaged for protective purposes prior to use. This manufacturing step is costly and, in addition, adds another factor in reliability and yield.

4.5.2.2 POSSIBLE SOLUTIONS

The most demanding specifications are those of the military. Two technologies offer the possibility of meeting these. The first, which is already in the development stage, consists of the deposition of thin adherent passivating layers onto the device to provide protection from the ambient. This requires some packaging in that a framework is required to support the chip and leads. An alternative approach uses chips which are sufficiently thick to allow direct insertion into printed circuit boards; leads are brought to the chip edge and inserted into a connector or bonded to leads. An existing technology, beam leads, is a step in this direction, but does not yet offer maximum cost economy.

4.5.2.3 PROBABILITY OF SUCCESS

Both technologies have a high probability of success. The thin adherent passivating layers could be either alumina or silicon nitride, and both have a better than a 90 percent chance of success. The thick silicon technique is probably a little less certain but may be as high as 60% for larger chips.

4.5.2.4 IMPACT

A significant improvement in reliability can be expected together with a marked reduction in size and weight. Costs should decrease dramatically.

4.5.2.5 TIMING

A successful completion of these programs could make an impact very rapidly. The thin adherent passivating layers could be available within one to two years; the thick silicon is somewhat longer term, probably about four years.

4.5.2.6 IMPORTANCE OF SUPPORT

At present, the main industrial thrust is toward the thin passivating layers; additional effort would be required to implement other approaches, such as thick silicon.

4.5.3 Dynamic Testing

4.5.3.1 DESCRIPTION OF PROBLEM

Historically, the device manufacturer has designed test equipment with the objective of analyzing manufacturing problems. The user, however, is more interested in how the device functions in his product and how it reacts dynamically in solving the problem his equipment was designed to meet.

Currently, the number of functions per device is increasing at an almost exponential rate. For example, a year ago a device might be a 2-input NAND, this is now a subset in a 4-bit ADDER with look-ahead. Equipment for testing such a device is very expensive and the computer programs which must be generated are extremely difficult, time-consuming, and error-prone. Consequently, their availability is limited.

4.5.3.2 POSSIBLE SOLUTIONS

The provision of economical test hardware is primarily an engineering problem. The complexity of the test program is beginning to stabilize although some problems associated with device-tester interactions have not been completely solved, e.g., the case in which the device generates its own timing sequences such that the tester must slave itself to the device. The industry now generally accepts the grading and sorting random test patterns to verify device operation (often with less than 100% operational assurance), whereas such patterns should be generated from the logical function to be performed.

A test plan developed by translating output conditions to internal device requirements is important to decrease the test time required and increase the assurance of complete device evaluation. In order to implement this philosophy, a more adept communication language between the test program generator and test equipment is required. This will further serve as a mechanism to improve the productivity of communication between the device manufacturer and end user.

As silicon device dimensions decrease (through better computer-aided design, projection photolithographic printing of circuits on slices, or any of the various microdefinition approaches on the technical horizon) causing increased functional density, new approaches for both contacting and exercising devices must be developed. There are several emerging techniques for device testing for which additional basic research is required. These approaches are not consistent with current classical test instrumentation but could provide lower cost in-line evaluation of device characteristics such that the Quality Assurance function can be included as an integral part of the manufacturing process. Examples of these techniques include directing beams of energy (either electrons or optical) into a device causing it to function. The beam approach eliminates test sockets and satisfies rapid programmability. There is further evidence that, using the absorption and transmission characteristics of silicon exposed to radiant energy, devices could be inspected during the manufacturing process to ensure gross compliance to performance characteristics. A composite three-dimensional image of the device could be obtained and compared in an optical computer to the model image. Anomalies and defects within the device would be detected as deviations from the model.

4.5.3.3 PROBABILITY OF SUCCESS

The successful development of suitable test instruments has a high probability dependent only on investment of time and money. The complexity of testing is beginning to stabilize; this should result in the equipment exhibiting a cost-reduction trend. The generation of test programs requires the use of a large computer.

4.5.3.4 IMPACT

The test problems facing device manufacturers are not insurmountable. However, there is the possibility that silicon technological developments may further outpace test development much the same as has already happened in MOS. If this occurs across the industry, it may be extremely difficult for end users to find second sources, to establish definite reliability criteria, or to realize potential lower costs to implement the more complex devices of the future.

4.5.3.5 TIMING

As suggested under 4.5.2.5, this could become critical. The applied research and development is likely to take at least three years.

4.5.3.6 IMPORTANCE OF SUPPORT

A subsidy to equipment and/or device manufacturers could affect the development of specifications.

4.5.3.7 RECOMMENDATIONS

1. Support developmental work in the generation of test programs for dynamic testing through large computers.
2. Support the longer-term research in packageless devices and encourage the production of such devices by including them in appropriate R&D programs.
3. Support studies of the contactless methods (e.g., electron beam) for evaluating devices.
4. Support efforts at solution of heat removal problems in integrated circuits and high-power devices.

4.6 GERMANIUM

In recent years the application of Ge semiconductor properties has moved on from transistors, diodes, IR detectors, etc., to more specialized devices. The accelerated advancement of silicon technology in planar geometry and integrated circuitry has contributed strongly to this trend. In addition, new, highly specialized detector materials such as PbSnTe and HgCdTe have emerged recently as strong competitors to extrinsic germanium IR detectors. This has been due principally to the less severe cooling requirement of these materials.

The main thrust of germanium semiconductor device research today is toward solid-state semiconducting detectors of electromagnetic or particle radiation. These are among the most important and widely used instruments in nuclear physics today. Such devices have virtually replaced gaseous ionization or scintillation detectors in nuclear spectroscopy by virtue of their superior energy resolution and have contributed to a better understanding of fission, structure of nuclei, and many analytical problems of interest to biology, geology, mining, criminology, and industrial processing.

Germanium or silicon is employed as the base material in many types of such detectors, and significant advances have been made in the active volume, energy resolution, and counting rate in recent years. The ultimate limit of performance, however, depends on the efficiency of charge collection and the removal of charge-trapping states or noise-generation mechanisms. The perfection of the material as regards single crystallinity, carrier concentration, chemical impurity content, chemical impurity compensation, uniformity of impurity distribution, dislocation content, and internal strain are only some of the variables that affect charge collection and trapping efficiency.

Major attention has been given in the past to growing large, pure, uniform, low-dislocation-content single crystals, mainly of germanium, by the pulling process. Similar attention has been given to compensating the remaining impurities by the technique of lithium drifting to provide material that is electrically intrinsic. Less attention has been given to the problem of identifying and removing those chemical impurities or lattice defects that remain after normal crystal growth conditions, and even less attention has been given to (a) purposeful doping with chemical impurities to achieve carrier compensation, or (b) alternative forms of compensation, such as radiation-induced lattice defect states.

Several laboratories have recently started a program that is designed to further purify the germanium starting material and each succeeding generation of pulled single crystals, toward an ultimate goal of a large single crystal ingot section with an electrically active impurity concentration of less than 10^{10} atoms-cm^{-3}. A major object is to achieve an active volume for charge collection without the necessity of any compensation of existing impurities by preferential doping, lithium drifting, or radiation-induced compensation.

Total elimination of the procedure of lithium drifting to achieve compensation would also eliminate the present problem of lithium precipitation, which occurs if detectors are ever permitted to warm to ambient temperatures. The present requirements of lithium drifting to achieve compensation and detector storage at liquid nitrogen temperature to prevent precipitation are time consuming and expensive; elimination of this requirement would be of great benefit to both manufacturers and users. Of course, the demand for ultimate perfection as regards such variables as quality and uniformity remains and will continue to be of major importance, even if the total impurity content is reduced.

The present status on ultrapure germanium is that several laboratories are producing materials with $\sim 5 \times 10^{10}$ cm^{-3} impurities. Devices of 6-cm^3 volume and 0.5-cm depletion depth have been achieved, and 50 mm diameter devices with 1 cm depletion depth may be available by December 1972. The International Atomic Energy Agency has demonstrated a traveling detector (1.5 cm^3 volume) that has been cycled from liquid nitrogen to ambient temperatures ~ 50 times, and still gives 1 KeV resolution at 122 KeV.

A factor-of-three reduction in impurity content is anticipated within a year, and a factor-of-ten reduction in impurity content should be sufficient to replace almost all need for lithium-drifted detectors. A major problem is that the impurity concentration varies along the ingot length, and radial inhomogeneities limit the maximum cross section to date. However, there is no obvious reason why these problems cannot be solved. Limited user experience suggests an improved performance of ultrapure detectors over lithium-drifted detectors. Much more experience is required, but there has been a spectacular advance in the purity and quality of germanium detector material in the past several years, and further advances may be anticipated in the next several years.

It must be recognized that detectors pose extremely high demands on materials, but the market is limited at present. Continued improvement in germanium may provide 60-cm^3 devices and energy resolution that will permit detector operation at temperatures that can be achieved by thermoelectric cooling in about 5 years. Such devices would be of great interest in medical and space applications, as well as providing a portable detector for general usage. The best effort to date on GeSi alloys, CdTe, and even more exotic compounds for ambient temperature storage and operation, is such that that ultrapure germanium is expected to remain the material of most importance for some years.

Of the other specialized germanium devices, perhaps the most notable are the cold background infrared detectors. These probably will continue to be used for some time due to the near ideal location of impurity levels appropriate to IR detector wavelength requirements and to the present high state of development of germanium materials.

Germanium transistors and integrated circuits function well at very low, cryogenic temperatures. Under present conditions of limited, experimental use, however, efforts are being made to use the more readily available off-the-shelf silicon devices; some success has been had in finding techniques for using such devices. If, on the other hand, superconducting circuitry increases strikingly in importance, as some think it may, the situation may change and the cryogenic use might then develop into a unique application area for germanium.

4.7 SELENIUM

Selenium occurs in three different physical forms: (a) amorphous; (b) trigonal (hexagonal); and (c) monoclinic. The amorphous form is stable at room temperature but transforms to trigonal at temperatures greater than about 50°C. This crystallization temperature may be raised appreciably by the addition of certain impurities. The light-sensitive properties of amorphous selenium have been used for a number of years in xerography and in the manufacture of vidicons. Trigonal crystals are stable up to the melting point at 217°C. The semiconductor properties of trigonal Se have been applied to the manufacture of power rectifiers. Studies have been undertaken to adapt trigonal Se to nonlinear optical systems. The monoclinic form is metastable, converting to the trigonal form under any type of applied field, and has no practical application in the electronics industry.

4.7.1 Amorphous Selenium

The thermodynamic properties of amorphous selenium have been studied extensively; quantitative values of the important parameters are available in the literature. Quantitative values of the constants which define the mechanical, optical, and transport properties are also available. The atomic arrangement of this amorphous material is very complicated and consists of at least two structural units: (a) helical chains and (b) eight-membered rings. For this reason, only phenomenological theories have been developed to explain the known experimental facts. Further attempts should be made to develop fundamental theories that will be useful in developing additional electronic applications for this important material.

4.7.2 Trigonal Selenium

The birefringence properties of trigonal selenium suggest that these crystals may be useful in nonlinear optical devices. They transmit all wavelengths between 0.4 and 20 μm. The refractive index in the visible spectrum is greater than 3.5 and the ratio n_e/n_o is exceptionally large. Early attempts to use these crystals as tunable parametric oscillators and amplifiers indicated that the available crystals were nonhomogeneous, had high absorption coefficients, and suffered damage when irradiated at high optical energy densities.

An effort should be undertaken to grow high quality trigonal crystals of selenium with emphasis on their mechanical, optical, and transport properties.

4.8 DIAMOND

Diamond is of interest because of its extreme hardness, wide band gap, and very large thermal conductivity. The hardness of diamond surpasses that of any other material and is by definition 10 on Moh's scale. The band gaps in eV are ~ 5.5 (indirect) and ~ 7.3 (direct), respectively. The thermal conductivity of certain natural diamonds is greater than that of any other element and reaches a maximum (≈ 150 W/cm deg) at 80°K in type IIa crystals. The optical properties of diamond have been classified on the basis of type I, IIa, and IIb. Type IIa diamonds have fewer defects and therefore fewer absorption bands above the short wavelength cut-off at 2300 Å. Diamond is useful for windows throughout the ultraviolet and visible regions and well into the infrared. A strong absorption band at 0.35 eV has been attributed to aluminum. Other levels of absorption have been identified as due to boron (0.0029–0.87 eV), manganese (2.25 eV), and nitrogen (0.16 eV). The transport properties of diamond crystals depend on their perfection, but, in general, the mobility of both holes and electrons is about 1000 cm^2/V sec at room temperature. The large energy gap makes diamond useful for constructing devices to be used at high temperatures. Ion implantation has been successfully used to prepare p–n junctions and more work along this line is encouraged.

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A continuing study on the growth of synthetic diamond crystals has been carried on for a number of years, particularly at the General Electric Company. The problem is difficult due to the high pressures and high temperatures involved. High quality crystals up to 0.2 gm in size are now grown routinely. Doping techniques have been developed so that either high purity crystals or those containing certain impurities can be grown at will. Type IIa synthetic diamonds have been grown which exhibit even higher thermal conductivities than the best natural specimens. High quality p–n junctions have not been grown due to difficulties in n-type doping which arise from the Jahn-Teller effect. The problem has been analyzed theoretically and it is hoped that future effort will result in junctions with useful electrical properties.

The large thermal conductivity of type IIa diamonds has led to their use as heat sinks for small electronic devices. Although suitable chips of natural diamonds are available and relatively cheap, the selection of type by optical methods and the preparation of the chip by cleaving or grinding is expensive. Better methods should be sought for these two processing steps.

4.9 TELLURIUM

The only crystal form of tellurium is trigonal and this is stable up to the melting point at 450°C. Good quality p-type crystals have been grown with hole concentrations as low as 10^{16} cm^{-3} and mobilities around 1000 $cm^2 V^{-1} sec^{-1}$. Te can be doped with Sb to obtain carrier concentrations as high as 10^{18} cm^{-3}. Measurements have been made that delineate the phonon, transport, and optical properties of these crystals. The band structure of tellurium has been worked out and the mechanical properties are described in the literature. The impurity levels are yet to be determined.

The most important device applications are in the areas of nonlinear optics and infrared detection. Tellurium transmits at wavelengths between 3 and 20 μm. There is an absorption band at 10 μm that arises from valence band splitting. The change in electrical conductance under light excitation at 10 μm results from a change in the mobility of the carriers rather than an increase in number. Since the phenomenon is due to transition of electrons between valence bands, the time constant is very short and, as derived by theory, should be of the order of 10^{-11} sec.

Although tellurium crystals have been grown which have better quality than selenium, the same recommendations for future work apply here as given above. In addition, impurity level studies should be made to assist in the design of very-high-speed infrared detectors.

4.10 BORON

Boron is a potentially useful material for making numerous electronic devices including thermistors, neutron detectors, and acoustic delay lines. Commercial application is lacking, however, due to difficulty in producing suitable material. A number of polymorphic forms of boron have been reported in the literature. Those that have been definitely established are α-tetragonal, α-rhombohedral, and β-rhombohedral. Further improvement in crystal quality is required before boron can become of practical use in the electronics industry.

However, before any major efforts on improving crystal quality are undertaken, first priority must be given to theoretical predictions and reasonable estimates of probability of success for the various proposed applications.

5 Compound Semiconductors and Superconductivity

5.0 INTRODUCTION

This chapter is primarily concerned with an assessment of materials and process research in compound semiconductors for a wide variety of electronic devices. It addresses itself to what we are doing and why we are doing it; where we are going and how we are going to get there; and, finally, what we must do to advance and broaden the technology. The detailed reports, therefore, will contain an introduction describing applications, present state of materials and process research, major problems, and recommendations for applied and basic research.

The assessment is confined to III-V*, II-VI, IV-IV, and IV-VI compounds and their alloys, since the preponderance of device research involving transistor-like structures has centered on these materials classes. It is also confined predominantly to those device applications that are in a very active stage of research or may already be classified as a technology. These include electron emission devices, electroluminescent diodes, laser diodes, microwave devices, infrared detectors, solar cells, high-power infrared laser windows, and power-generating

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*Roman numeral denotes column in Periodic Table of Elements.

thermocouples. Therefore, it is acknowledged at the outset that this chapter is not all-inclusive.

In this assessment, it was also considered proper to place compound device research and technology in its proper perspective with regard to the dominant position of silicon with its rapidly advancing materials technology and associated processing techniques. This was done wherever appropriate, as in the case of microwave devices, solar cells, and power generating thermocouples. In this connection, it is also noteworthy from the device applications that the emerging III–V and II–VI components technology is largely based on those devices that cannot be made with silicon.

For purposes of completeness, this chapter also includes a review of metal alloys and intermetallic compounds for superconducting applications.

Finally, it is only proper to note that the information contained in this chapter is a direct result of discussions with researchers in organizations and contract administrators in a number of government research centers, as well as with researchers in educational institutions.

5.1 INFRARED DETECTOR RESEARCH

5.1.1 Introduction

The field of infrared detectors is still in an early stage of rapid growth. Applications range from geographic mapping to medical diagnostics. However, it is generally agreed that present research and development efforts, stimulated largely by government needs, have been concerned with reconnaissance applications, such as detection of troop or vehicle movement in jungle terrain either by day or night. Here, the background viewing temperature is that of earth (300°K), although some space applications would involve much lower temperatures. The detectors themselves are operated below room temperature, usually between 50°K and liquid nitrogen (77°K). This is dictated by requirements of high signal-to-noise ratio. IR detectors are also used for laser receivers. These require high speed operation (~ 50 MHz) for large bandwidth communications or short pulse (10–50 ns) for radar.

The special range of major current interest is 0.5 to 14 μm with particular emphasis on the 8–14 μm range and 3–5 μm range. These two ranges correspond to regions of negligible atmospheric absorption (atmospheric windows).

5.1.2 Present Status

The materials research on infrared detectors is concerned with semiconductors exemplified by the following compounds or compound alloy system: PbS for the 1-3 μm range; (PbSn) Te for the 8-14 μm range; and the (Hg, Cd) Te alloys for the entire 1-14 μm range. There is also some recent exploratory research on InAs for the 15-30 μm range and on In (As, Sb) alloys for anti-pollution spectroscopy.

Good PbS detectors have been fabricated and are now in commercial use. They have been made from polycrystalline-thin films prepared by chemical deposition from lead acetate solutions, and also by chemical vapor deposition. The latter, however, are not as reliable. No large arrays of detectors have been made of PbS films, primarily because of the difficulties encountered in preparing stoichiometric material with uniform chemical and physical characteristics. Moreover, the photoconduction phenomena in this material is still not well understood.

Good individual detectors have been made with InSb single crystals for the 3-5 μm range. Some suppliers have experienced difficulty in making multielement linear areas having uniform performance with this material. The crystals of InSb are made by the Czochralski and Bridgman techniques of growth from the melt. Material with uniform impurity composition and low-defect structure over large areas can be achieved with these techniques. Attempts at integrating these devices in arrays has clearly revealed the need for developing better processing techniques for the necessary interconnections between detectors and switching circuitry.

(Pb, Sn) Te detectors are made from single crystals prepared by a modified Bridgman technique and by a vapor-phase growth technique. Outstanding figures of merit ($D^* = 10^{12}$ cm Hz$^{1/2}$ watt at 10 μm radiation) (see Table 5-1) have recently been achieved with these detectors operating at 20°K and viewing a background temperature of 20°K. However, materials which give these values are not easily reproducible. In fact, they have been achieved in one instance by a special technique of Bridgman growth requiring a month. These detectors operate as photovoltaic diodes requiring p–n junctions made by diffusion techniques. To date, no good detectors have been made in the photoconduction mode. For background-limited (Pb, Sn) Te photoconductors much smaller carrier concentrations are theoretically needed than with (Hg, Cd) Te in order to compensate for the much shorter life-

TABLE 5-1 Present State of Research in IR Detectors

Material	Growth Technique	λ Range (μm)	D^*_λ $\frac{\text{cmHz}^{1/2}}{\text{watt}}$ [a]	$T_{\text{Operation}}$	Mode of Operation
PbS	Chemical deposition	1–3	2×10^{11} (3 μm)	77°K	PC [b]
InAs	Melt growth (Czochralski)	1–3	7×10^{11} (3 μm)	77°K	PV [c]
InSb	Melt growth (horizontal Bridgman, Czochralski)	3–5	1×10^{11} (5 μm)	77°K	PV
(Hg, Cd) Te	Melt growth (vertical Bridgman, zone leveling)	0.5–20	5×10^{10} (10 μm)	77°K	PC
(Pb, Sn) Te	Vapor deposition Vertical Bridgman	8–14	2×10^{10} (10 μm)	77°K	PV

[a] All D* values are for 295°K background temperature and 2π sterad. field of view.
[b] Photoconductive
[c] Photovoltaic

time in (Pb, Sn) Te. These small carrier concentrations have not yet been achieved.

(Hg, Cd) Te crystals, prepared either by a modified Bridgman growth or by a quench-recrystallization anneal technique, have provided the best photoconductive detectors in the 8–14 μm range. In fact, theoretical performance ($D^* = 6 \times 10^{10}$ cm Hz$^{1/2}$ watt) (see Table 5-1) has been achieved, operating the detector at 77°K and viewing a 300°K background. Moreover, by varying the alloy composition it should be possible to extend operation over the 1–30 μm range. Significantly, large linear arrays of hundreds of elements have been fabricated with good performance. This suggests that these alloy crystals are amenable to hybrid integrated circuit techniques involving metal interconnections. Some detectors in the photovoltaic mode have been made with these alloys but, in general, their performance has been inferior to the photoconductive devices.

In all of the above materials and applications there is the question of the advantages of the photovoltaic vs the photoconduction mode of operation. The former operation, though providing faster responses and somewhat higher theoretical figure of merit, does require a more advanced technology, since single crystals and high quality p–n junctions are involved. It is presently believed that for single detectors or small linear arrays of elements the photovoltaic mode may be the more desirable, particularly when speed of response is the criterion; whereas for large two-dimensional arrays the photoconduction mode of operation will be chosen in view of the materials considerations involved.

Table 5-1 serves to summarize the present state of research and development in infrared detectors.

5.1.3 Major Problems

Problems common to all of the research on detectors involve materials and materials processing. In these compounds, there are the problems of stoichiometry, growth of crystals with high degree of structural perfection, purity, and chemical homogeneity; this is also the case for each composition in a given alloy system. There is also the problem of material processing in fabricating integrated arrays of these detectors and their interconnections. Finally, there is the problem of undesirable change in the surface properties of these materials spontaneously in storage and by interaction with different ambient environments.

Associated with these materials problems is the question of economics. A higher yield of useful material is required, as well as improved methods of fabricating arrays of detectors in a hybrid or integrated circuit approach. Operations of detectors should be at as high a temperature as possible to minimize refrigeration costs.

5.1.4 Recommendations

Present research should be concerned primarily with improved methods of large single crystal growth as well as development of new thin-film synthetic techniques for depositing materials in complex and useful geometries with well-characterized physical and chemical properties. In this connection, it would be highly advantageous if a single synthetic technique could provide the single crystal for the detector, either in the photovoltaic or photoconductor mode, as well as the interconnections required to assemble many of these detectors in two-dimensional arrays. Further, it would be very desirable if one semiconductor alloy system could satisfy as broad a spectral range as possible, even though each specific alloy composition must be regarded as material with unique problems of growth, purification and processing. Finally, research in these compounds and their alloys on the surface states and their relation to crystal orientation as well as response to changes in environmental conditions to help increase device yield and performance must be conducted.

Long-range research efforts should be concerned with a better understanding of the photoconduction and photovoltaic effects in low bandgap semi-conductors to complement the materials synthesis work. This should include studies of impurity and trapping levels, and the relation of these levels to important transport properties, e.g., carrier lifetime and mobility. In addition, a better definition of band structure may be required. There is also a need for exploring new methods of creating p–n junctions (e.g., by annealing or proton bombardment) in the low bandgap semiconductors. Finally, it would appear that there is no urgency for exploratory research for new materials, since existing ones give outstanding figures of merit over the present spectral ranges of highest interest. This would not be the case if the spectral range of interest extends beyond 30 μm or to applications not revealed to this Committee. Above this wavelength, consideration might be given to new types of thermal detectors such as pyroelectric detectors. In addition, exploratory research in the class of ternary compound semiconductors with the generalized formula: A^{II}, B^{IV}, C_2^{V} could be fruitful.* Examples are $ZnGeP_2$, $ZnSiAs_2$, and $CdSnP_2$. These materials can provide a range of energy bandgaps to cover a desired higher detectivity against low-temperature backgrounds than possible with existing materials.

5.2 ELECTROLUMINESCENT DEVICE RESEARCH

5.2.1 Introduction

Since 1962 p–n junction electroluminescence has evolved rapidly from the laboratory stage to medium-scale manufacturing. Major impact on electronic systems is just beginning to be felt, since it has only recently become possible to manufacture practicably efficient diodes for production of infrared and visible light at costs which permit wide-scale utilization. The present state-of-the-device art is the result of extensive fundamental and applied research in III–V compound material preparation and advances in characterization of their

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*Roman numeral superscripts refer to column of Periodic Table of the Elements. of which A, B, C are members. Subscripts have usual chemical formula significance.

radiative properties. The material development potential is far from exhausted. Significant advances that will further increase the use of electroluminescent diodes may be expected. These devices, as a class, comprise incoherent light emitters and laser diodes that emit coherent light.

The principal present and anticipated uses of incoherent *visible*, light emitting diodes (LED) are:

1. Non-contact printing for computer terminals
2. Indicator lights
3. Numeric displays
4. Character recognition
5. Cathode-ray tube replacement

The principal applications projected for *infrared* LED's are:

1. Communication links
2. Card readers
3. Components in high impedance switching
4. Triggers for light-sensitive devices such as silicon controlled rectifiers
5. Variable wavelength sources for spectroscopy as in the case of gas detection

Semiconductor laser diodes have been made from a large variety of semiconductors covering a spectral emission range from the red to the far-infrared (0.63 μm to 34 μm). Applications of such diodes include:

1. Infrared illuminators for night vision and vision through fog and smoke
2. Ranging devices such as altimeters, range finders, and proximity fuses
3. Communication system links
4. Optical sources for very-high-resolution spectroscopy
5. Hologram readout
6. Memory devices

The basic properties of electroluminescent diodes that make them attractive for all of the above applications are:

1. Low voltage requirements

2. Relatively low cost per element
3. Small size

The reliability of the components depends on the choice of material, the method of material processing in device structures, and the mode of utilization. In general, the present or potential life of these devices is as good or better than that of competing components, such as incandescent light bulbs.

5.2.2 Present Status

5.2.2.1 INCOHERENT LIGHT SOURCES

Present device technology is based on the compound semiconductors GaAs, GaP, Ga (As, P) alloys, and (Ga, Al) As alloys. The latest data on the characteristics of light-emitting diodes made from these materials, as well as their method of crystal growth, are given in Table 5-2.

GaAs is the most widely used material for infrared diodes; very high efficiencies (10–30 percent) have been obtained at room temperature by using special geometric configurations in device fabrication. Extensive material and process research have been conducted on this compound. GaAs-based devices have been in production for some years. There has also been work reported on diodes emitting further in the infrared, using alloys of GaAs, most notably (In, Ga) As. However, there are no well-defined needs at present for such light-emitters, and the fact that they must operate below room temperature is a distinct disadvantage.

The most widely used base for visible light-emitting diodes comprises the Ga (As, P) alloys. This group of materials has neither reached the maximum of its potential in brightness nor its minimum cost. Doped with nitrogen, light-emitting efficiency can be greatly increased; as yet, this development is in its infancy and requires further

TABLE 5-2 Characteristics of Light-Emitting, Spontaneous Diodes (dc Operation, 300°K) Based on Most Advanced Device and Materials Technology

Material	Impurity Additions	λ(A)	Color	Quantum Efficiency (%)	Growth Method
GaP	S + N	~5600	Green	0.1–0.4	LPE, VPE[a]
GaP	Zn + O	~7000 (broad)	Red	2–7	LPE
Ga(As, P)	Zn, Te or Se, N	9000–6000	IR to yellow	2–0.3	VPE
(Ga, Al)As	Zn, Te, Ge or Si	9000–6800	IR to red	7–0.5	LPE
GaAs	Si	9700–8900	IR	32–3	LPE

[a] LPE—liquid-phase epitaxy; VPE—vapor-phase epitaxy.

work. Presently Ga (As, P) is the most suitable material for the mass production of individual red-, orange-, and yellow-emitting diodes and small numeric displays. This is because the active material can be deposited by vapor phase epitaxy (VPE) on GaAs single crystal substrates and it has a brightness suitable for many applications. Many wafers can be grown simultaneously with a relatively well-understood but not fully developed technology. Furthermore, increasing the size of the GaAs crystal substrates is definitely feasible by well-developed techniques of crystal growth from the melt, such as the Bridgman and Czochralski methods. Thus, even lower cost per element can be forecast, not to mention the greatly increased performance recently made possible by the introduction of the N isoelectronic trap in Ga(As, P).

GaP technology in recent years has made impressive advances. Both red- and green-emitting diodes can be made with a single fabrication technology, and with a red-emitting efficiency higher than Ga(As, P) alloy (see Table 5-2). The recent development of Czochralski-grown GaP by the flux-encapsulation technique has opened the possibility of mass production; large single crystal substrates are now possible. Because of its higher luminous efficiency, the green emission from GaP is about 10 times brighter than the typical Ga(As, P) red emission. There is, as yet, little understanding of the nonradiative processes in GaP; the present efficiency of the green emission is believed to be far from the maximum theoretically possible. This is also true of N-doped Ga(As, P) in the red-orange-yellow. Therefore, the potential exists that GaP, as well as N-doped Ga(As, P), will be made with much higher levels of brightness than is now available. This would have an impact on making possible larger displays because the drive current per element would be reduced. Furthermore, it would increase the speed of nonimpact printing machines. In this connection, it should be noted that available photosensitive paper coatings are considerably more sensitive in the green and ultraviolet than in the red.

Light-emitting diodes of (Al, Ga) As alloys can be made with brightness comparable to that of ordinary Ga(As, P) alloys but do not have immediate promise of improvement via addition of an isoelectronic trap. In addition, the necessary use of liquid-phase epitaxy in manufacturing is a further disadvantage from a cost standpoint.

Other materials for visible incoherent light-emitting diodes are being explored. (In, Ga)P alloys are theoretically very attractive since they remain direct bandgap to 2.2 eV; this is substantially higher than either Ga(As, P) or (Al, Ga) As. Thereby, a more efficient red-, orange-, or yellow-emitting diode should be possible. The major drawbacks of this ternary crystal are the present lack of convenient techniques for the growth of "defect-free" material and some difficulty in forming high-quality p–n junctions in it. The main reason for this is that the lattice constant mismatch between InP and GaP is larger than that between GaP and GaAg, or between GaAs and AlAs. This has a profound impact on the defect structure of the material, the ease with which it can be made into p–n junctions, and, hence, on the efficiency of the radiative processes. It is believed that significant progress is possible with this material; but, this will require substantial research effort.

Blue-emitting diodes would be most desirable since this would make possible three-color displays and indicators to increase the information content. Presently, there is no efficient electroluminescent source comparable in brightness to the red-yellow-green LED's. Phosphor-coated GaAs diodes have been fabricated wherein a blue-emitting phosphor is excited by the infrared light emitted from the GaAs diode. These devices, however, are inherently inefficient because of the quadratic upconversion processes required to achieve blue emission from the phosphor. GaN, which is a direct bandgap material, is the most promising of the available III–V compounds for blue emission. Blue-emitting GaN diodes were reported at the 1971 International Electron Device Conference.*

It should be pointed out that the only semiconductor material from which blue, green, yellow, and red light-emitting diodes have all been made is the IV–IV compound, SiC. Although the materials and device technology of SiC is not as far advanced as GaAs, GaP, and Ga(As, P) alloys, it is ahead of such exploratory III–V compounds as GaN. Fair light-emitting junctions have been fabricated in SiC crystals by many techniques including grown junctions, liquid- and vapor-phase epitaxy, and ion implantation. In view of the yield problems in the areas of crystal growth and device processing, it is doubtful that SiC diodes will ever be competitive with Ga(As, P) and GaP, for example, in combined efficiency and cost for red-yellow-green incoherent diodes.

It is generally believed that the reliability and performance of present GaP, Ga(As, P), and (Al, Ga) As materials are adequate for single element indicators where a red, orange, yellow, or green color can be used. With improved process technology, reductions in cost will occur

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*M. Jones, private communication.

and thereby widen the use of these LED's not only as replacements for filamentary light sources, but also in areas where light sources are not presently used. For example, LED's will be widely used as functional indicators in circuit subsystems, greatly facilitating the maintenance of complex industrial and consumer equipment including such widely used equipment as automobiles and trucks.

The design use of gas discharge and filamentary numeric indicators is already practical for applications requiring small readouts. It may be safely predicted that with further reductions in material cost, digital panels will increasingly replace meters. The size of the display element that is economically feasible with LED's will increase as material costs go down and reflection light pipe techniques are further developed. Here, GaP and, to a lesser extent, certain Ga(As, P) alloys have a distinct advantage, because they do not self-absorb and, therefore, with a small emitting area, can illuminate a larger reflector.

Displays large enough to compete with cathode ray tubes are believed to be some time off because of the problems connected with individually addressing 10^5 or more elements. Aside from the material costs, if single crystal diodes are required, the circuitry appears to be too costly at this time except for highly specialized applications. It is clear that the addressing problems represent a major limitation which may be overcome only by suitable integrated circuit technology. The general feeling is that cathode ray tubes are going to be hard to replace by light-emitting diodes except in selected applications.

5.2.2.2 COHERENT LIGHT SOURCES (LASER DIODES)

Research in semiconductor laser diodes for room temperature operation is now concentrated in the GaAs–(Al, Ga)As alloy technology, since this alloy family is the only material system presently capable of fabrication into reproducibly good heterojunctions–an absolute necessity for efficient room temperature operation. Room temperature characteristics of laser diodes fabricated from this materials system are shown in Table 5-3.

The material and process technology for these coherent light-emitting sources is relatively advanced at this time. Lasers emitting light at a wavelength between 8000 Å and 9000 Å at room temperature are now in commercial production. These devices are well suited for

TABLE 5-3 Room-Temperature Characteristics of Light-Emitting, Coherent (Laser) Diodes Based on Most Advanced Device and Materials Technology

Material	Threshold Current Density (A/cm^2)[a]	Impurity Additions	λ (A)	Differential Quantum Efficiency (%)
GaAs	1000–8000[b]	Zn, Si, Ge	9000	43–60
(Al, Ga)As	1000–8000	Zn, Te	7100–9000	10–50
	3000	Zn, Te	7400	30

[a] Continuous wave operation is easily achieved at room temperature for threshold current densities below ~3000 A/cm^2; above this threshold diodes operate in the pulsed mode.

[b] Here the threshold current density range reflects device design; it does not take into account operating parameters, such as diode life.

ranging and illumination, but are limited for holographic and communication requirements. For the holographic application the achievable resolution is limited by the broad spectral width of the emission; in the area of communications the limitation is associated with atmospheric absorption. Newer device structures based on multiple epitaxial layers and heterojunctions are capable of higher duty cycle operation than present production devices; this includes continuous wave operation. This new generation of devices with their more complex epitaxial and heterojunction structures should be developed further in the near future.

Efficient visible laser diodes ($\lesssim$ 7000 Å) are available at this time only if operated below room temperature. The bandgap energy of (Al, Ga)As becomes indirect in the range 1.92-1.95 eV, limiting the lasing range in these alloys. While higher bandgap alloys are available, e.g., (In, Ga) P, it will probably be difficult to incorporate good quality heterojunctions which will sufficiently confine the optical field and the carriers for satisfactory low threshold lasers.

The narrow bandgap semiconductor alloys (Pb, Sn) (Te, Se) and (Hg, Cd)Te are the most advanced materials for infrared sources up to 30 μm. Such sources are tunable over a narrow wavelength range and, hence, are useful for spectroscopy, as in gas analysis. However, these materials must be operated below 77°K, which tends to limit their applicability. Moreover, the technology of synthesis and processing is still in its infancy; there is insufficient material characterization and low device yield.

5.2.3 Major Problems

5.2.3.1 INCOHERENT LIGHT SOURCES

Since GaP and Ga (As, P) (with N-doping) presently provide the most efficient red-yellow-green sources, most of the problems are concerned with growth and processing of these compounds for improved device performance at lower cost. The starting materials, gallium, phosphorus, and arsenic, are not as pure as one would like; larger substrate crystals of GaP and GaAs [for Ga(As, P)] are required for broader applications and lower processing costs. There is inadequate understanding of the structural, defect, impurity, and other limiting factors controlling the efficiency of these light-emitting diodes, as well as the complex nature of degradation processes occurring during their operation. Also, the various processes for forming p–n junctions are not entirely satisfactory or necessarily compatible with high performance and low cost. Finally, mass production capabilities based on liquid-phase or vapor-phase epitaxial growth of GaP must be explored to achieve lower cost with no loss in diode performance.

There is also the problem of obtaining suitable substrate material for exploring the device potential of promising new materials, such as the (In, Ga)P alloys. Unsolved in some cases is the general problem of amphoteric doping for junction formation, as is the case of GaN, which so far cannot be made high conductivity p-type.

5.2.3.2 COHERENT LIGHT SOURCES

There are several significant problems in connection with the science and technology of laser diodes. First, there is the question of reliability under stringent high duty-cycle operation; hence, extensive work is required to develop devices appropriate for high rate data communication. Second, there is presently no *visible* coherent light source at room temperature. Finally, there is the problem of developing sufficiently small bandgap materials and technology for infrared spectroscopy. This need is emphasized by growing interest in gas analysis in connection with monitoring air pollution. In general, there is the problem of expanding development of epitaxial and heterojunction structures beyond the present system GaAs–(Al, Ga)As.

5.2.4 Recommendations

5.2.4.1 INCOHERENT LIGHT SOURCES

Short-range research should be concerned primarily with the compounds Ga(As, P) and GaP. There is general agreement that cost reductions and improved performance in red-orange-yellow-green diodes can and will be achieved. As already mentioned, this will require research to achieve: suitable substrate materials of larger size and lower preparation cost, a more detailed understanding of the defect structure in the substrates and epitaxial layers, and the knowledge of the relationship of defect structure to crystal growth, impurity doping, and diode processing methods. All these parameters are vital factors in design of high-performance devices and in establishing requirements for mass production capabilities. Immediate research is also needed in determining those fundamental factors limiting the light-emitting efficiency of Ga(As, P) and GaP diodes (from red to green). Effort should be directed toward further elucidation of the dependence of diode operating failure mechanisms upon materials processing technology.

Long-range research on the high bandgap III–V semiconductors should include a general study of impurity effects, such as amphoteric doping, isoelectronic traps, and bandtailing. Some attention should be given to those materials capable of extending light emission into the blue portion of the spectrum such as GaN and SiC. Moreover, the role of various dopant impurities on the luminescent properties of these compounds is still not well understood; in this connection, studies of solid solubilities and precipitation effects would be desirable.

Long-range research is required on heterojunction structures that emit light at or near interfaces between semiconductors of different energy bandgap. Such complex structures could significantly improve the carrier injection efficiency and transmission of emitting light; examples of such variable bandgap material systems for heterojunction fabrication are (Al, Ga)P–GaP and (Al, Ga) (As, P). Finally, exploratory research for new compounds and compound alloys is recommended in order to either extend the light-emitting spectrum, or provide higher efficiencies at currently available wavelengths as might be possible in the case of (In, Ga)P. This will require studies of crystal growth techniques, impurity doping, alloy homogeneity, and changes in energy band structure with alloy composition. In addition, all the usual fundamental properties of a new material must be studied, as well as the various issues peculiar to introducing p–n junctions.

5.2.4.2 COHERENT LIGHT SOURCES

Applied research is recommended on the physics of failure relating to crystal compositional changes, lattice damage, and change in defects in the active region of laser diodes. While some of the factors governing reliability are now better understood, much more research is required to achieve a high degree of device reliability.

Long-range research should be concerned with development of heterojunctions in the (In, Ga)P alloys since the band structure of this alloy system could provide an efficient laser in the visible spectrum at room temperature. Principal emphasis should be on fabrication of good heterojunctions with few interface states associated with lattice mismatch and strain and/or impurity defect interactions.

Finally, in the area of infrared spectroscopy for gas (pollution) analysis, there should be research on better characterization of low bandgap semiconductors as regards crystal growth, ohmic contacts, and device processing.

5.3 ELECTRON EMISSION DEVICE RESEARCH

5.3.1 Introduction

Two important processes, which lead to the emission of electrons into vacuum from solid surfaces, are photoemission and secondary emission. In each of these processes, electrons are excited to sufficiently high energies to be ejected from the solid material. In the case of photoemission, the excitation process involves the absorption of light, while with secondary emission, the excitation results from bombardment with high energy primary electrons. These two processes form the basis for the operation of key components in devices such as photomultiplier tubes. In this device, photoemission is used to detect light by generating an electron at the photocathode; this current, in turn, is multiplied by a series of secondary emitters, also known as *dynodes*. Such devices have been common for almost fifty years. They have generally been used as sensitive light detectors in systems such as scintillation counters and spectrometers.

It has only been in the last decade that a detailed understanding of physical principles underlying the operation of photocathodes and dynodes has been obtained. This understanding has led to the design, from essentially basic concepts, of electron emission devices that far outperform anything in the prior art and, at the same time, represent a novel marriage of solid-state technology with vacuum-tube technology. This advance can largely be attributed to the utilization of the principle of effective negative electron affinity (NEA), in the fabrication of the photocathodes and dynodes. This principle effectively makes the emission of electrons into a vacuum much more efficient in the operation of both of these device components. The surface activation procedures necessary to provide significant NEA were, at the outset, most compatible with selected III–V compound semiconductors in simple structural geometries. Moreover, the ready availability of the sophisticated materials technology required for the syntheses of these compounds led to rapid advances in the development of these superior electron-emitting devices, now commercially available. Future device improvements will depend on the ability to prepare complex heterojunction structures; this ability requires further advances in materials synthesis and processing. There are some indications that the negative electron affinity state can be achieved in heterojunctions without use of thin surface films of alkali metals.

5.3.2 Present Status

The negative electron affinity effect has been achieved in a variety of III–V compound semiconductors, of which the most important are GaAs, GaP, and alloys of Ga(As, P) and (In, Ga)As. This effect, as noted above, results from depositing on the surface of these semiconductors a thin film of an alkali metal, usually cesium (Cs), which serves to alter the band structure at the surface of the semiconductor so as to facilitate electron emission into vacuum.

Certain important characteristics in both single crystal and polycrystalline structures are required to make best use of the NEA effect. These are great crystalline perfection, high chemical purity and homogeneity, controlled alloy composition and reproducible, predictable impurity doping profiles–all of which are necessary, *inter alia,* to provide the required long electron diffusion length and high surface escape probability. These vital materials properties are most readily achieved in thick epitaxial layers, which are prepared by either vapor-phase epitaxy (VPE) or liquid-phase epitaxy (LPE). Moreover, these layers imply electron emitter operation in the reflection mode. This means that in the case of photocathodes, the photoexcited electrons are emitted from the same surface on which the light is incident; while in the case of secondary emitters, the secondary electrons escape from the same surface bombarded by the primary electrons.

Photomultiplier tubes sensitive to radiation at 1.1 μm, 1.06 μm, 1.0 μm, and 0.92 μm use photocathodes of cesiated (In, Ga)As alloys, while tubes sensitive to 0.75 μm radiation utilize photocathodes of a cesiated Ga(As, P) alloy. In addition, all of these photomultiplier tubes are made with secondary emission dynodes of cesiated GaP. Some typical operating characteristics of these photomultiplier tube components fabricated from these III–V compounds and their alloys are given in Table 5-4. In general, the performance of these devices represent an order of magnitude improvement in every aspect (efficiency, gain, dark current, stability, and noise) over their more conventional counterparts such as the S-1, S-11, and S-20 photocathodes. As indicated, these device components operate in the reflection mode; a principal application of electron emission is thereby excluded. This is the application to imaging.

Imaging devices require a "semitransparent" cathode which operates in a transmission mode; i.e., the electron image is emitted from the photocathode surface opposite to that on which the light image is incident. For semitransparent operation, the substrate material, on which the photocathode is epitaxially grown in single crystal form, must have an energy bandgap larger than that of the photocathode it-

TABLE 5-4 Some Typical Operating Characteristics of Photomultiplier Tube Components Fabricated from III–V Compounds and Their Alloys

	Photocathode			
Material	λ(Å)	Efficiency	Secondary Electron Emitters: Gain	Synthesis Techniques
GaP	–	–	30→300	VPE[a] Poly-xl[b] (Cs-activated)
GaAs	9000→UV	30% (visible region)	–	VPE
Ga(As, P)	7500→UV	30% (visible region)	–	Single crystals
(Ga, In)As	16000→UV	30% (visible region) 2% (106 μm)	–	(Cs-activated)

[a] Vapor-phase epitaxy.
[b] Polycrystalline.

self in order to provide an optical window for the incident radiation. This necessitates the growth of compound semiconductors in heterojunction structures; these may include regions having a graded alloy composition. This is to avoid excess lattice strain and defect generation in the transitional interface between the substrate and the photocathode material. Moreover, this interface or heterojunction must be very thin (several micrometers) so as not to significantly absorb the incident light before it reaches the photocathode.

Both vapor and liquid-phase epitaxy have been used with some success in an effort to satisfy the foregoing requirements of materials and processes for constructing transparent photocathode structures. While LPE offers advantages with regard to preparation of suitable substrate surfaces prior to crystal growth and in the quality of the graded alloy interface region, it does not appear to have the flexibility of VPE in choice of materials for the substrate-heterojunction-photocathode materials system or the facility to grow large area photocathodes. In this early stage of materials technology development for imaging devices, where feasibility, reliability, and cost are concerned, it is not clear that either technique offers any overwhelming advantage over the other. It should be noted here that imaging tubes have already been constructed from cathodes in the reflection mode (Photoreflectronix image tubes); however, they are so cumbersome in this geometrical configuration that their application will be greatly limited.

Since a need exists for a practical cathode that will operate at room temperature and at greater current densities than normally used in photoelectric cathodes, exploratory research has been under way to evaluate III-V compounds for this electron emission application. Presently, the best candidates are GaAs, using a direct p–n junction structure, and GaAs–(Ga, Al)As heterojunction structures, optoelectronically coupled. Both of these approaches make use of cesium-coated, negative electron affinity surface. It should be noted that Si negative electron affinity cold cathodes have already yielded encouraging results as regards stability and high current density operation, and hence must be considered a top contender for this application. The presence of alkali metal vapor films on cathodes may limit their life as a function of current density and/or the type of device in which the cathode may be employed.

5.3.3 Major Problems

Photomultiplier tubes, with photocathodes and dynodes constructed from III–V compounds and their alloys, are now commercially available with high yield and outstanding operating characteristics over a wide spectral range of sensitivity. One notable exception is the need to increase the long wave length response in photocathodes and particularly at 1.06 μm for use with yttrium aluminum garnet: neodymium (YAG:Nd) lasers and to extend the response to 1.6 μm in order to couple with the light output of the eye-safe yttrium aluminum garnet: erbium (YAG:Er) lasers. This could lead to widespread use of these devices in a variety of consumer operations.

Most of the other problems with electron emission devices are concerned with their application to imaging. For the transmission mode, the photocathode epitaxial layers of these compound semiconductors must be thinner than 5 μm; the layers must be prepared so that the important transport properties, such as diffusion length, are comparable to those in bulk single crystal layers on suitable substrate materials which are transparent to the incident radiation. Concurrent with this is the problem of mastering the materials and process technology for growing the highest quality heterojunctions with a graded alloy region between the substrate and photocathode materials. Moreover, in order to be useful in imaging, the area of the photocathode layer should be at least 250 cm^2; in fact, it is desirable that the area be 2500 cm^2 or larger for broader viewing.

Finally, it should be noted that the secondary emitter dynodes could serve as a gain stage in imaging devices operating in the transmission mode. The formidable problem here is that the secondary emitters would have to be prepared as free-standing large area films, a few micrometers in thickness.

5.3.4 Recommendations

Applied research should continue in an effort to enhance photocathode wavelength response in photomultiplier tubes at 1.06 μm and to extend the response to wavelengths of about 1.6 μm.

For imaging devices operating in the transmission mode, longer-range research is required in the following areas:

1. Development of new synthetic techniques or perfection of existing techniques for preparing high quality thin photocathode films on transparent substrates
2. Materials exploration and synthesis to obtain wide bandgap semiconductors in a suitable form and size for substrate crystals

3. More definitive characterization of the role of both surface states and lattice defects at heterojunction interfaces in reducing optical and electronic losses

Finally, research should continue to evaluate III–V compound semiconductors and their alloys for cold cathode applications and, in particular, as they compare with similar devices fabricated from silicon. Heterojunction materials that are not dependent on cesiated surfaces for negative affinity electron effects should also be studied.

5.4 RESEARCH ON THERMOELECTRIC POWER GENERATION

5.4.1 Introduction

There has been an extensive program of material research in the field of thermoelectric power generation for the past two decades. This effort was stimulated by the desire to achieve high-energy conversion efficiencies in devices having no moving parts, silent, and requiring little or no maintenance. At the present time, conversion efficiencies up to approximately 10 percent have been achieved by using two or more semiconductor alloys joined electrically and thermally in series to form segmented branches in the thermocouple arrangement. In general, efficiencies of 5 to 7 percent have been attained in practical devices.

In spite of the high cost and low efficiencies of thermoelectric generators, numerous applications involving remote, unattended power sources have evolved. These include, unattended terrestrial power in remote locations such as for telephone repeaters, unattended lighthouses and navigation buoys, and auxiliary power for space satellites including unattended sources for powering scientific instruments on the lunar surface.

5.4.2 Present Status

Semiconductors do not, in general, exhibit optimum thermoelectric properties over temperature ranges sufficiently large to ensure high power generating efficiencies (~10 percent). Consequently, research has been directed toward developing materials having high conversion efficiencies or material figures of merit over relatively narrow temperature ranges (see Table 5-5). Devices could then be constructed in

TABLE 5-5 Materials for Thermoelectrical Power Generation

Material	Conductivity Type	Temperature Range (°C)	Material Figure of Merit[a] ($\times 10^{-3}/°K$)	Growth Technique
Bi_2Te_3-Sb_2Te_3	P	25–250	2.6	Vertical Bridgman
Bi_2Te_3-Bi_2Se_3	N	25–250	2.2	Vertical Bridgman
PbTe	P	100–600	1.1	Vertical Bridgman
PbTe	N	100-600	1.3	Vertical Bridgman
PbTe–SnTe	P	100–600	1.0	Vertical Bridgman
PbTe–GeTe	N	100-600	1.7	Vertical Bridgman
Si–Ge	P	400–1000	0.6	Zone leveling
Si–Ge	N	400–1000	0.8	Zone leveling

[a] Averaged over indicated temperature range of operation.

$$\text{Figure of Merit} = \frac{(\text{Seebeck coefficient, v/°K})^2}{(\text{electrical resistivity, ohm-cm})\ (\text{thermal conductivity, w/cm-°K})}$$

which the material is selected to provide optimum performance over a specified temperature range. In addition, the temperature range and, consequently, power generating efficiency could be increased by constructing thermocouple branches in a sandwich-type arrangement. The materials are placed electrically and thermally in series such that an envelope of their thermoelectric properties represents the best average figure of merit over the entire operating temperature range.

The attainment of optimum performance from thermoelectric power generating devices not only depends on the optimization of thermoelectric material parameters, but also requires suitable electrical contacts at the hot and cold junctions. Reliable methods of contacting semiconductor thermoelements at low junction temperatures have been devised; these have the necessary electrical and mechanical properties for service over extended time periods. However, difficulty has been encountered in providing materials suitable for contacting thermoelements at elevated junction temperatures. Presently available materials for contacting semiconductor thermoelements are found, in many cases, to form poor metallurgical junctions. This leads to high electrical and thermal resistance at the semiconductor–metal interface. In addition, chemical changes of junction characteristics have been observed for several types of material. These changes lead to ultimate device failure.

Of the many candidate semiconductors that have been examined, the most promising that demonstrate power-generating capability accompanied by reasonable efficiency are Bi_2Te_3-base alloys for temperatures up to 250°C, and Si-Ge alloys up to 1000°C. Pertinent thermoelectric properties of these materials for power generation are summarized in Table 5-5.

The Bi_2Te_3-base alloys (Bi_2Te_3-Sb_2Te_3 and Bi_2Te_3-Bi_2Se_3) are usually prepared from the melt by a vertical Bridgman technique. Powder metallurgy techniques (pressing and sintering) have been used to improve the poor mechanical strength of this class of semiconductors. This, however, leads to some deterioration of electrical properties. These alloys are not useful above 250°C due to the onset of intrinsic conduction in these small energy gap materials. Decrease in the thermoelectric figure of merit results.

The PbTe-base alloys (PbTe-SnTe and PbTe-GeTe) exhibit high figures of merit for temperatures up to a little above 600°C. However, instability of the operating parameters of these materials, due to the volatility of tellurium, limits their long-life usefulness at operating temperatures above 550°C. This problem is particularly severe in a vacuum environment, as encountered in outer space. The loss of tellurium at these elevated temperatures causes high resistance at the semiconductor-metal contacts, decrease in mechanical strength, and, therefore, need for encapsulation of the thermocouples. These alloys are usually prepared by a vertical Bridgman technique or by a quench-anneal procedure. Thermocouple elements have been prepared by standard powder metallurgical techniques to improve their mechanical strength; there is some sacrifice in the material figure of merit of these Pb-Te base alloys as for the Bi_2Te_3-base alloys above.

The Si-Ge alloys were developed for efficient thermoelectric power generation at temperatures in excess of 600°C. The alloys are chemically stable and exhibit excellent mechanical strength. The alloys are prepared from the melt by a zone leveling technique to provide a high degree of chemical uniformity both as regards alloy composition and impurity distribution. The chemical composition and physical properties of these alloys are well characterized as regards achieving the optimum figures of merit over the required temperature range of operation.

5.4.3 Major Problems

As pointed out above, the major problems common to all telluride alloys are their poor mechanical properties and compositional instabilities. In addition, difficulty has been encountered in the area of semiconductor-metal contacts at the hot junction of the power generating thermocouple. These problems are manifested by an abnormally high resistance at the junction interface due to a metallurgically poor metal–semiconductor bond, or a catastrophic failure resulting from chemical reactivity at the interface over a period of time.

In the case of the Si-Ge alloys, the major problem is associated with the life of the metal–semiconductor contact at the hot junction. Long-term missions at temperatures in the neighborhood of 1000°C require extremely stable, nonreactive contact material.

5.4.4 Recommendations

Applied research should be directed toward improving the compositional stability of the most promising telluride alloys over the temperature range of optimum performance. For example, this might involve studies of techniques for encapsulating these materials to retard or prevent loss of a volatile component. Applied research is also recommended in developing new materials for the semiconductor–metal contact, particularly at the hot junction, so as to extend the useful life of these devices, as well as to achieve the optimum conversion efficiency.

Long-term research might well be directed toward the development of semiconductor materials having unique and desirable characteristics, e.g., for operation in various chemically aggressive environments and under conditions of either thermal or mechanical extremes. However, it does not appear that a broad exploratory research program for new thermoelectric semiconductors is warranted at this time, since the probability of achieving figures of merit significantly higher than those of presently available materials up to 1000°C is low. It would seem more appropriate to advance the characterization and device technology of the available materials.

5.5 MICROWAVE DEVICE RESEARCH

5.5.1 Introduction

Solid-state devices for microwave applications play an extremely important role as compact power sources, amplifiers, mixers, and demodulators for both military and commercial systems, such as radar, communications, navigation, intrusion alarms, and auto collision avoidance. The compound semiconductor, GaAs, with its negative differential mobility has created a major impact in the microwave field because a broader variety of devices is now possible. At the present time, silicon transistors and trapped-plasma-avalanche-transit-time (TRAPATT) oscillators can satisfy a number of microwave system requirements of frequencies up to 4 GHz. At higher frequencies GaAs devices are more suitable in terms of noise, power, bandwidth, efficiency, or combinations thereof, and they currently supply the need up to the millimeter wave (~30 GHz) portion of the spectrum. These devices include the transferred electron oscillators (TEO) in both the domain (Gunn Effect) and limited space-charge accumulation (LSA) modes, as well as the Schottky barrier (SB) avalanche and transit time (IMPATT) oscillators. In spite of this generalization, in view of the rapidly advancing materials processing technology of silicon, it is possible that within the next few years there will appear silicon power transistors and impact devices operating up to 10 GHz.

5.5.2 Present Status

In the fabrication of most GaAs microwave devices, severe requirements are placed on the preparation, purity, crystal perfection, and processing of the material. It is necessary to prepare thin (generally 0.5 to 20 μm) layers of single crystal GaAs in a state of high purity so that they can be controllably doped, by suitable incorporation of impurities during growth, to the desired carrier concentrations with little variation over the active area of the device. The control of thickness and doping concentration of the layers must be done while depositing the epitaxial layer on a GaAs single crystal substrate, which, depending on the device, must be either heavily doped or semi-insulating. In either case, the substrate must have a low density of crystal defects so as to avoid their propagation into the epitaxial grown layer. It is further necessary to prepare either low resistance planar ohmic contacts or non-ohmic ones depending on the requirements of the particular device.

It would appear that much progress has been made to satisfy most of these requirements by the Czochralski melt-growth of the substrate material and by both liquid-phase and chemical vapor-phase techniques for growth of the epitaxial layers. However, it should be noted that difficulties have been experienced in some device fabrication due to variations in the doping density within a single epitaxial layer, as well as from one epitaxial layer to another grown from similar substrate material. The same applies to variations in the defect density of the substrate material, particularly with high doping concentration. However, difficulties in the substrate material can be largely overcome by suitable choice of doping impurity. Despite these variations in material properties, many GaAs microwave devices with outstanding characteristics have recently been fabricated. These are summarized in Table 5-6. For comparison, the best combined properties of some silicon microwave devices are included at comparable frequencies.

TABLE 5-6 Present State of GaAs Microwave Devices, Including Some Silicon Devices for Comparison

Frequency (GHz)	Power Output (Watts)	Efficiency (%)	Duty Cycle Seconds, cw-Continuous	Mode
		GaAs Transferred Electron Oscillators		
1.0	117	32	10^{-2}	Domain
2	200	29	10^{-3}	Domain
4	2000	–	–	LSA
5	0.6	3	cw	Domain
9	600	10	6×10^{-6}	LSA
10.5	1.4	10.8	cw	Domain
18	0.35	11	cw	LSA
28	0.125	2.3	cw	Domain
34.5	0.19	7.4	cw	LSA
40	0.06	3.0	cw	Domain
50	0.02	0.7	cw	LSA
88	0.02	2	cw	LSA
		GaAs Avalanche Oscillators		
4	5	9	cw	S.B.[a] IMPATT
5	4.7	10	cw	S.B. IMPATT
6	2.9	13	cw	S.B. IMPATT
8	7.0	14	cw	S.B. IMPATT
9.6	0.6	17	cw	S.B. IMPATT
10	2.5	9	cw	S.B. IMPATT
14	1.0	10	cw	S.B. IMPATT
17	0.6	9	cw	S.B. IMPATT
		Si Avalanche Oscillators		
1	1200	25.6	10^{-3}	TRAPATT
3	100	26	10^{-3}	TRAPATT
5	40	15	10^{-3}	TRAPATT
9.6	50	6	10^{-3}	TRAPATT
18	0.8	4	cw	IMPATT
50	1	14.2	cw	D.D.[b] IMPATT
92	0.14	5.2	cw	D.D. IMPATT

[a] Schottky barrier.
[b] Double drift.

GaAs transferred-electron oscillators, operating in the domain mode, have been gradually replacing klystrons as local oscillators in microwave equipment. These devices, operating up to 10 GHz, have excellent low noise characteristics and low voltage supply requirements with efficiencies as high as 10 percent for continuous wave (CW) operation (see Table 5-6). These improved efficiencies and, hence, improved power outputs have resulted from corresponding improvement in materials preparation and processing.

GaAs transferred electron oscillators in the LSA mode are being considered for high-power pulse sources in beacons, distance measuring equipment (DME), and other transponder equipment. It can be seen from Table 5-6 that such devices have produced kilowatts of power at lower microwave frequencies, and should ultimately produce such power up to 16 GHz with efficiency exceeding 20 percent. Such devices will require variation of less than 2 percent in the doping density of the epitaxial layer; this is presently most difficult to achieve reproducibly.

Schottky-barriers GaAs avalanche diode oscillators (SB-IMPATT) have shown higher power and efficiency than any silicon IMPATT in the 4–10 GHz region. Although, the IMPATT devices are more efficient than the GaAs TEO devices, they require higher voltage power supplies for operation in the 2–16 GHz region. The IMPATT can also be operated as a negative resistance amplifier with higher power output than the TEO devices, but does not have the linearity and bandwidth of the TEO. It is expected that power levels of the GaAs Schottky-barrier IMPATT device will double during the next year with major improvement in efficiency.

It is apparent from Table 5-6 that silicon double drift (DD) IMPATT devices take over in the millimeter-wave spectrum (>30 GHz). This is largely due to the increasing sophistication in materials processing technology for silicon devices. As similar advanced technology becomes available to GaAs, this situation, i.e., silicon device dominance at these high frequencies, may change in favor of GaAs.

Exploratory work on GaAs field effect transistors (FET) has shown that these devices can operate at frequencies as high as 40 GHz. By contrast, silicon FET devices have achieved an operational capability of only 12 GHz. GaAs field effect transistors are needed as broadband, low-noise microwave rf and if amplifiers. In addition, there is some interest in the use of these transistors as fast switches for high rate data communications; switching response times of less than 2×10^{-10} sec have been obtained.

GaAs mixer diodes are used throughout the microwave and millimeter portions of the spectrum. GaAs Schottky-barrier mixer diodes are comparable in performance to silicon diodes in the 2–10 GHz region, but at millimeter frequencies they are used exclusively because of their superior noise- and conversion-loss characteristics. It would appear that there are no major problems in the fabrication of these mixer diodes. The same can be said for GaAs tunnel diodes.

GaAs variable capacitance (Varactor) diodes have already been used as low noise rf amplifiers or as nonlinear elements in frequency multiplication channels for digital communications systems. A more recent application under consideration for these diodes is for television UHF tuning, particularly because they have a significantly lower insertion loss than their silicon counterpart. GaAs varactor diodes have been fabricated by vapor phase growth techniques which result in the best combination of reverse breakdown voltage (80–100 V) and cut-off frequency (150–250 GHz) at −6 V and a junction capacitance of 0.3 to 0.7 pf. This may be compared to typical values of 40 V and 160 GHz with diodes made from GaAs crystals grown from the melt, subsequently processed to produce rectifying junctions by conventional diffusion techniques. These superior characteristics can be directly attributed to accurate control of the electrical properties of the material in the diode structure, as well as to the preparation of defect-free and abrupt rectifying p–n junctions that minimize the effect of microplasma discharge.

5.5.3 Major Problems

As already indicated, GaAs microwave devices are in direct competition with silicon devices over the entire microwave frequency spectrum. Therefore, one of the major problems is the fast-moving target of silicon processing technology in the areas of epitaxial crystal growth, subtractive processes by selective etching and machining, solid state diffusion, and surface chemistry and material technologies with are so powerful in making sophisticated device structures with superior performance, high yield and eventually lower cost. The double drift IMPATT oscillator, which cannot yet be made with GaAs is a classic example of this. Thus, GaAs materials technology is still far behind; and there is a need to close the gap if one is to capitalize on the superior intrinsic electrical properties of GaAs. Resources should be allocated to those applications (a) where the GaAs devices would provide a very significant improvement in performance over silicon devices, e.g., low noise or improved efficiency suffice to justify any additional device cost over silicon, or (b) where GaAs devices possess a unique material property or processing advantage providing gains in performance, reliability, and cost as in the Schottky-barrier avalanche oscillators, or (c) where one just cannot make the desired device with silicon, as in the case of transferred electron oscillators and amplifiers.

In addition to the above competitive consideration, it would appear that the most pressing material problem in designing and fabricating GaAs microwave devices is not one of feasibility of performance of a given device, but rather one of reliability and high yield. Thus, crystal growth techniques for producing the substrate material, the active epitaxial layers, and ohmic contacts have not been refined to ensure adequate control over such important material parameters as crystal defect density, impurity concentration, and electrical junction profiles and characteristics. Moreover, there is a problem of insufficient data on correlation between device performance and materials properties.

5.5.4 Recommendations

The most pressing materials problems where current research is needed are in the areas of compositional uniformity and control of impurity doping. These are directly concerned with refinements in crystal growth techniques and material purity and perfection. Associated with these problems is a need for better understanding of band structure and, in particular, impurity and trapping levels. This information can lead to improved characterization and uniformity of materials resulting in higher breakdown voltages. Control of impurity concentration will improve yield and reduce costs, and provide improved device efficiency, lower noise figures, and broader bandwidth capability. As already indicated, underlying all of these immediate goals is a need for a definitive correlation of device performance with the properties of both the GaAs substrate and epitaxial layer. This correlation is complicated by the difficulty of comparing devices made by different methods currently used by fabricators of these devices.

Long-range research is needed in the exploration of new materials as well as in further advancing GaAs materials and process technology. A very interesting new microwave material is the In(As, P) alloy system, which has two potential areas of application. The first is TEO devices with larger peak-to-valley ratios and, hence, higher efficiencies. Alloys with 80–100 percent InP have peak-to-valley ratios exceeding those of GaAs, and, because of their 3-level band structure, could provide a new transferred-electron mode independent of transit time. The second application is in high frequency FET devices. Here the saturated drift velocity in a 60 percent InP-40 percent InAs alloy exceeds those of GaAs and Si by factors of 2.5 and 5, respectively, with a corresponding increase in the upper frequency limit.

In the area of advancing technology, new junction fabrication techniques such as ion implantation could extend the frequency capability and reliability of GaAs devices. Moreover, the new techniques could enhance the prospect of fabricating microwave devices (such as double drift) not presently possible with GaAs, and might well lead to monolithic integration at millimeter-wave frequencies.

5.6 RESEARCH ON HIGH-POWER INFRARED LASER WINDOWS*

5.6.1 Introduction

With the advent of the very high optical powers associated with lasers, damage problems due to laser beam interactions with matter became evident, and as even higher laser powers have become available, the problems have become acute. High powers are now available at fixed frequencies in the 2–6 μm range (e.g., from CO), and optical parametric oscillators offer promise of high power and tunability over the 2–6 μm wavelength range. Various forms of CO_2 lasers provide even higher powers at 10.6 μm. Therefore, problems have arisen with regard to damage to laser windows, or to beam degradation in lossy windows in this frequency region. It should be noted that in using parametric oscillators to generate radiation from 2–6 μm, the most severe materials damage problem is in the nonlinear crystal itself, rather than in the laser windows and other optical components.

5.6.2 Present Status and Problems

The damage caused by infrared laser beams can be traced under most circumstances to residual heat absorption. In the first place, this leads to optical distortion of the laser beam. At higher levels of absorption, the induced thermal stresses may lead to mechanical failure. Only in the case of very short pulses where instantaneous power densities exceed 100 megawatts/cm^2 might other nonlinear effects such as stimulated Raman and Brillouin scattering and self-focusing play a role. Most infrared laser applications will not be operated in this latter regime.

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*Also see Report of NMAB *ad hoc* Committee on High-Power Infrared-Laser Windows (NMAB-292, July 1972).

An intensive study, both experimental and theoretical, of window materials at 10.6 μm is under way. The materials include several alkali halides, germanium, several III-V and II-VI semiconductors, both in single crystal and sintered forms. In semiconductors with small bandgaps or shallow impurity levels, "thermal runaway" is a problem. As the material is heated, more carriers are created, leading to increased absorption, etc. This problem is present in germanium and GaAs. It is completely absent in alkali halides. These crystals have low mechanical strength and are subject to attack by water vapor. Much work needs to be done on ternary systems or sintering techniques to improve mechanical properties without impairing optical characteristics. The same holds for the design and fabrication of coatings. These are necessary to provide protection from the environment and for reduction of reflection losses. It is not clear, at the present time, which material would be most suited for large, high-power 10.6 μm windows. The sizes contemplated are such that the world supply of gallium is a serious negative factor in considering GaAs as a candidate. The fabrication of windows of large sizes is a major problem. Only alkali halide crystals have been grown in the required sizes.

Little work has been done on high-power window properties in the 2–6 μm range. Here one has the advantage of utilizing other candidates such as sapphire and alkaline earth fluorides.

There can be little hope of operating the optical window in a high radiation environment. The production of color centers and carriers will produce intolerable absorption. One may only hope to anneal and bleach out the radiation damage effects as rapidly as possible to restore the original optical properties.

5.6.3 Recommendations

A wide variety of materials need to be investigated as to their suitability for high-power windows in the wavelength ranges about 10.6 μm and 2–6 μm. These materials should include, among others, the alkali halides, CdTe and other II–VI compounds as well as ternary systems. In the 2–6 μm range, fluorides of alkaline earths and sapphire should be added to the list.

The following points should receive attention for each material:

1. Low level residual optical absorptivity
2. Mechanical strength
3. Possibility of growing large crystal sizes
4. Heat conductivity and window cooling arrangements

5. Fabrication of sintered composite without impairing optical properties
6. Antireflection and protective coatings
7. Influence of impurities and radiation damage

5.7 RESEARCH ON SOLAR CELLS

5.7.1 Introduction

The solar cell has been one of the most critically important devices of the U.S. space program. Over 600 U.S. satellites have already been powered by such cells. Over ten million cells will be required during this decade to power satellites, some of which will require 50 to 100 kw of onboard electric power.

It is also becoming evident that solar cells may play an increasingly important role in the generation of electrical power for terrestrial purposes. As power requirements increase, so does the danger of pollution, and the direct conversion of sunlight into electricity does not generate any pollution, whether it be thermal, gaseous, or particulate.

The main deficiencies of solar cells for space applications are efficiency and radiation resistance, while for terrestrial purposes the main drawback is high cost. Cost reductions of about two to three orders of magnitude would make solar cells very interesting for terrestrial application.

5.7.2 Present Status

Silicon has been the most important material used in solar cells to date. All American space satellites have been powered by silicon solar cells. It is estimated that about 10 million silicon cells of either 1 × 2 cm or 2 × 2 cm have been sold. These cells exhibit about 11 percent conversion efficiency for outer space sunlight at 25°C. They will operate at temperatures up to 125°C and in radiation fluences up to about 10^{16}, 1 MeV electrons. Such cells cost about $100 per watt of electricity.

Over the last 10 years silicon solar cell efficiencies have improved only by about 20 percent. This is considerably short of the theoretical expectations. Very little research effort has gone into attempts to improve cell efficiency. Much work has been carried out on silicon solar cell material synthesis and device fabrication techniques for cost effectiveness. Such approaches as the use of silicon dendritic crystals, thin deposited silicon films, and ion implantation have been tried without any improvement in cost or performance. In addition, considerable effort has been expended for arrays and systems and toward understanding and improving the radiation resistance of silicon cells. Several dozen research contracts have been awarded in the lithium–silicon material system; the fabrication of these lithium cells is now understood, as well as the environmental factors necessitating them.

The II–VI compound semiconductor, CdS is the second most studied material for solar cells. Its major advantage is the fact that cells with respectable performance (5 to 7 percent efficiency) can be made by relatively simple material processing technology. Single crystal cells have been made; but, even more important, polycrystalline cells, made by evaporating CdS, are almost as efficient as the single crystal cell and are far less expensive to make. The CdS solar cell promises to be a very low cost cell, easy to fabricate in large areas with considerable savings in weight. Indeed, the cost of the CdS cell may be several orders of magnitude lower than a comparable silicon cell; therefore, it could be attractive for terrestrial applications. Unprotected CdS cells are not very durable in normal ambients, especially in the presence of water vapor; but, much progress is being made in understanding and controlling this problem. Moreover, the photovoltaic nature of cell operation has not been clearly elucidated in the material. The cell probably is a copper sulfide, cadmium sulfide heterojunction, where the copper sulfide is the active material. Cells have been made by a wide variety of techniques, but they all seem to end up with the same properties and operational characteristics.

Considerable research has also been done on the II–VI compound, CdTe; at present, most of this work is going on in France and the Soviet Union. The cell does not appear to be as complicated as the CdS cell; however, the electrical properties are not quite as good, and there is still the problem of operational instability. In general, solar cells made from II–VI compounds will probably be used for terrestrial applications and not in space.

Solar cells have also been fabricated from the III–V compound semiconductor, GaAs. Work on these cells has gone on sporadically during the past 15 years. Theoretically, GaAs should be a more efficient material than silicon, although results to date do not support this. Quantities of 1 × 2-cm GaAs solar cells have been made with efficiencies as high as 10 percent. The cost of these cells would be at least ten times that of silicon in production quantities. GaAs solar cells exhibit two other properties that may be important to specific space applications.

One such property is improved radiation resistance; the other is higher operational temperature capability (up to 250°C). The slow degradation of silicon cells in space, typically 10% loss of efficiency per year, limits the use of silicon solar cells in satellites intended for long operation. For such satellites, for solar probes, or for other high temperature usage, GaAs cells or Ga–As–GaAlAs heterojunction cells should exhibit important advantages.

5.7.3 Major Problems

5.7.3.1 SILICON

Two major sources of inefficiency exist in silicon solar cells. One has to do with the bulk silicon quality and the other, the surface losses. The silicon cell is a simple device structurally and is easy to make using existing silicon technology. However, for maximum efficiency, an order-of-magnitude better-quality silicon (compared with the material required for integrated circuits or transistors) is required for improved solar cells. It has been estimated that to improve cell efficiency by 50 percent, raw material silicon is required with about 0.01 ohm-cm resistivity and with a carrier lifetime of 5 to 10 μ sec. There is insufficient materials research directed toward the improvement of silicon to this degree (cf. Chapter 4).

Even when such ultrapure silicon is available, very careful material processing must still be developed to preserve the desirable properties during fabrication. Controlled diffusion is a primary need. Gettering techniques must also be applied. Every effort must be expended to obtain the lowest reverse saturation current in the final p–n junction. This parameter is several orders of magnitude off from the theoretically predicted Shockley I_0. Also, the exponential or so-called A or λ factor should be unity and not 2, as is generally observed in solar-cell junctions. It is believed that these deviations are caused by energy states, probably due to impurities or defects in the barrier or bulk regions of the cells. Improved starting material and processing might correct the situation.

With respect to the surface properties of silicon cells, if the surface recombination value could be reduced to less than 100 cm/sec rather than the 10^5 cm/sec that appears at the top surface, appreciable improvement in performance could be realized. There is much known regarding the passivation and control of surfaces in silicon. This kind of research has not been applied to solar cells; if it were, improved response in the ultraviolet portion of the spectrum could be realized as well as increased resistance to short circuit currents.

Finally, long-range requirements for cost reduction involve improved automation of cell manufacture and a much cheaper process for growing single-crystal silicon. Silicon solar cells must use single crystal material; and the limiting cost factor is that involving silicon growth. Any major (order of magnitude) cost improvement will necessitate a revolutionary low-cost growth method.

5.7.3.2 II-VI COMPOUNDS (CdS, CdTe)

CdS or CdTe solar cells are the only present day hope for truly low cost cells, since single crystal material is not needed and the materials involved are not expensive. However, a better understanding of cell operation is required to achieve high reliability. The role of the copper sulfide upper layer has to be better understood. It may be that before stability is achieved, other upper layers need to be investigated. A degree of stability in this type cell can be achieved by plastic encapsulation; however, this is considered to be an unsatisfactory long-range solution.

5.7.3.3 GaAs

New techniques of crystal growth such as liquid phase epitaxy (LPE) and vapor phase epitaxy (VPE) could be applied to improving GaAs solar cells. The use of (Ga, Al)As alloy window to remove the surface from the GaAs cell could improve performance. A great deal of study of the surface properties of GaAs is necessary in an effort to reduce the recombination velocity value from the present 10^5–10^6 cm/sec. This improvement will slowly evolve from work on existing devices, such as the GaAs field effect transistor. Work on high-temperature contacts is also needed if the high-temperature cell is to be practical. The major problem of cost may not be solved, so that GaAs should only be considered in applications where this is not a limitation, or where it is competitive with other system costs.

5.7.4 Recommendations

5.7.4.1 An appreciable improvement in the efficiency of silicon solar cells is technologically feasible. Therefore, a research and development effort should be initiated towards the development of a 20–22 percent (room temperature and AMO) efficient silicon solar cell.

5.7.4.2 The main impediment to attaining the above goal resides in the quality of the silicon. Therefore, materials research should be initiated on increasing the diffusion length of highly doped silicon. A goal of 50 μm diffusion length (10 μ sec lifetime) in silicon of 0.01 ohm-cm resistivity is feasible. Before this work is carried out, a study of the state of the art of high-quality single-crystal silicon should be undertaken.

5.7.4.3 Studies should be initiated in two other areas of importance to achieving high-efficiency silicon solar cells. These areas are appreciably improved surface recombination properties at the front surface and better quality of the junction current-voltage characteristic as measured by the A factor. Surface recombination velocities of 100 cm/sec and A factors near unity should be the goal.

5.7.4.4 It appears that efficiencies greater than 20 percent in such materials as III–V compounds are theoretically possible. However, there is no promise that the actual silicon efficiency will be substantially exceeded by other materials; the cost associated with the development of any new material to the actual production of solar cells will probably be very high. Nevertheless, exploration of promising new ideas and close surveillance of new developments in ongoing research in these materials should be carried on.

5.7.4.5 Thin-film photovoltaic cells do not seem to offer the possibility of high efficiency solar energy conversion. They do, however, promise a substantial cost advantage over single crystal cells, and, therefore, research should be continued on such cells for possible terrestrial applications.

5.8 SUPERCONDUCTING DEVICE RESEARCH

5.8.1 Introduction

Of all the phenomena of solid-state research, superconductivity is perhaps the most striking. Below a critical temperature (T_c), superconductors exhibit zero resistance and can carry current densities in excess of 10^5 amp/cm^2 in magnetic fields well above 150 kilogauss. Moreover, the superconducting state exhibits a macroscopic ordering of electrons such that it has unique quantum mechanical coherence properties.

Application of these unique properties leads to two distinct groups of devices, which may be characterized as *low-current* and *high-current* devices. High-current devices serve to generate high magnetic fields and also to store and transport large amounts of electromagnetic energy. The required cooling of high-current systems is a basic disadvantage, but this disadvantage is outweighed in many systems by the great reduction of power losses in high-field magnetic systems, in linear accelerators, and in specialized motors constructed during the past decade. The situation is quite different for low-current–low-power superconductor systems where the cooling is used to reduce the intrinsic noise level of the system. Many of the nonsuperconducting devices, such as infrared detectors and parametric amplifiers, are cooled for the same purpose. Well-designed superconductive receivers or sensors come much closer to the theoretical noise limits.

The emergence of compact, automated closed cycle refrigerators, first used for masers and semiconductor devices, has greatly relieved the cooling problems of superconductive systems.

5.8.2 Present Status

It is beyond the scope of this discussion to go into applications in any detail. They run the gamut from small elegant devices for measurement of small fields and voltages to large-scale systems that owe as much to cryogenic engineering as to superconductivity. The following sections are intended to merely illustrate the range and diversity of superconducting applications. For further details, the reader is referred to the biannual conferences on applied superconductivity whose proceedings are published in the *Journal of Applied Physics.*

5.8.2.1 WEAK-LINK AND JOSEPHSON DEVICES

These represent the most direct use of quantum mechanical coherence. The nonlinearities and magnetic field sensitivity of these devices have their major use in the detection of small changes in magnetic flux voltage standards, and in extremely fast switches. Point contact "Josephson" diodes (weak links) have shown frequency response beyond 10^{12} Hz, noise equivalent power better than 10^{-13} watts, and response time better than 10^{-9} sec. The SQUID weak link devices (superconducting quantum interferometer devices) can measure field changes of less than 10^{-9} gauss/sec. The SLUG (superconducting low inductance undulating galvanometer) device is capable of detecting 10^{-17} volt under optimum conditions. The switching characteristics of Josephson tunnel diodes can be used to construct computer flip-flops; it has been shown that the switching time is less than 10^{-9} sec. Ladder-like superconductive thin-film configurations, with weak links in the rungs, can be used as "flux shuttles" or magnetic shift registers. These superficially resemble the "magnetic bubble" memory configurations discussed in Chapter 6, but with the very important difference that in the superconducting case the "bubble" represents just one quantum of magnetic flux. The energy required to shift a bubble one step is reduced by many orders of magnitude and approaches the theoretical limit based on the temperature of the memory. Very-large-scale memories based on superconducting weak links promise orders-of-magnitude improvements with respect to power consumption while attaining satisfactory speeds. These new computer concepts are not to be confused with earlier other non-quantum devices with long response times.

5.8.2.2 HIGH Q CAVITIES AND TRANSMISSION LINES

High-purity high-T_c superconductors, such as Nb, can have a microwave surface resistance smaller by a factor of 10^6 to 10^7 than that of Cu. This low resistance is preserved in rf or d-c currents in magnetic fields smaller than the lower critical value (H_{c1}). This observation led to the concept of superconducting resonant cavities and transmission lines with unloaded Q values up to 10^{11} at microwave frequencies. At the lower frequencies, losses are usually higher because of the dielectric support structures required. A 150-m linear accelerator utilizing Nb microwave cavities cooled to 2°K is now being built at Stanford University. Nb with a T_c of 9°K and an H_{c1} of about 1800 gauss is by no means optimum for such an application; one can envision more extensive uses of superconductors when materials with higher T_c and comparable or higher H_{c1} are used. Nb_3Sn with a T_c of 18°K and an H_{c1} of about 700 gauss at $T = 0°K$ is one possible candidate for high-temperature operation of high Q cavities.

5.8.2.3 HIGH FIELD SOLENOIDS

High-field, large-volume solenoids are the major application of superconductivity today. The enormous increase in superconducting research in the early sixties was engendered by industrial and government interest in this application. Unfortunately, despite the advances in technology, research on new materials is now greatly reduced. Initial solenoids utilized two materials: Nb-Zr alloys and the intermetallic compound Nb_3Sn. Both materials were discovered prior to the theory of Type II superconductivity. As shown by the theory, certain superconductors, designated Type II superconductors, are characterized, among other things, by their ability to support high current densities below their critical superconducting transition temperature (T_c) and critical magnetic fields (H_{c2}). Alloys of Nb-Ti, have since been added to the list. With a few exceptions, these materials were optimized for performance at 4.2°K and below, and little attention has been paid to the advantages of higher-temperature operation.

Early solenoids exhibited a gap between the anticipated and actual performance of a given material. This departure was given the "useful" nomenclature of "degradation." It was ascribed to instabilities in the current distribution in a given solenoid, which led to the creation of normal regions, and current quenching due to the high available energy densities. Analysis of the behavior of superconducting solenoids before and after an instability emphasized the fact that superconductors in the normal state are poor solenoid materials due to their high resistivity and low thermal conductivity. Furthermore, there is a multiplicity of current paths in a superconducting solenoid, and at any point the actual current density, particularly at low fields, can be considerably larger than that implied by the current inserted through the leads.

From these and other observations on solenoid degradation, it was apparent that the use of some good conductor in a solenoid was desirable. A good conductor such as copper could eliminate or reduce hot spots, could carry some of the current load by transformer action if a normal region should form, and, in contact with the superconductor, could bypass a normal region until the superconducting state is restored. This last configuration appears paradoxical until it is noted that at dc, normal metals are equivalent to insulators relative to a superconductor. These concepts were carried to the limit with fully stabilized solenoids where sufficient copper is available to carry *all* the current with a rise in temperature less than T_c. In this manner, predictability and absolute safety are achieved at the expense of current density and additional size, cost, and weight. Fortunately for large volume, low-field applications, current density is not crucial.

An additional advantage of stabilization is that it made possible the use of material such as Nb-Ti; such alloys had optimum metallurgical and superconducting properties despite their low T_c ($\sim$9°K), but "degradation" prevented their use in practical devices. With stabilization these alloys have completely replaced Nb-Zr alloys in solenoids. Above 80 kgauss, current density is important, and fortunately Nb_3Sn can be utilized successfully with only partial stabilization. In the case of Nb-Ti, billets of the alloy are inserted in copper cylinders and the wire drawn to size. Twists have been inserted recently in the drawing process, and this leads to better performance under rapid changes in the field. For Nb_3Sn partial stabilization is achieved by plating or soldering copper to the wire or ribbon, which is usually in the form of a thin layer of Nb_3Sn on a steel or niobium substrate. The Nb_3Sn can be deposited either by a vapor phase transport technique, or by plating the substrate with Sn from a melt followed by a diffusion reaction.

Other materials of current interest are V_3Ga prepared by a diffusion process, and sputtered layers of NbN. Both compounds support high current densities up to 200 kgauss. The ternary system $Nb_3(Al, Ge)$ exhibits critical field values (H_{c2}) of 200 kgauss at 10°K, and the data suggest critical fields as high as 400 kgauss at 4.2°K. A new potentially low-cost superconductor for medium field solenoids has been formed by impregnating porous glass with a lead-bismuth alloy.

To give some indication of the current state of the art, it is only necessary to interpolate in volume and field between 150 kgauss 6-in. bore solenoid made of chemically transported Nb_3Sn on a Hastelloy ribbon substrate, and the 18 kgauss 12-ft bubble chamber at Argonne National Laboratory made of wire drawn Nb-Ti. In the first case, superconductivity provides a savings in space and capital cost; at the other extreme the savings is largely in running costs (power losses). For magneto-hydrodynamic power applications and fusion power programs, superconducting solenoids are crucial for the economic utilization of the generated power.

A wide-bore superconducting solenoid stores a substantial amount of electromagnetic energy. For energies above 10^4 J, such "inductive" storage leads to a system that is more compact and lightweight than an analogous capacitive system. Losses during the discharge of a superconductive inductor can now be reduced by using twisted multifilament conductors with low ac losses and by switching with superconducting high current relays.

High-speed vehicles can be "levitated" above a metal-lined roadbed by means of the magnetic field from a superconducting solenoid aboard the vehicle. Various configurations are under study for the development of high speed trains.

5.8.2.4 ELECTRICAL POWER LINE GENERATORS AND MOTORS

High-field magnets can be adapted for use in electrical power generators and motors with very large increases in power per unit volume and significant gains in efficiency. Moreover, the cost of large machines with superconducting field sources is anticipated to be significantly less than that of conventional machines, even including the burden of refrigeration. These advantages render superconducting generators and motors attractive for commercial utility operation, shipboard and airborne applications.

The feasibility of the basic concepts has been amply demonstrated by the 80 KVA ac machine recently constructed by H. H. Woodson and collaborators at MIT. At the present time, construction of a 1 MVA generator at Westinghouse is nearing completion, and design plans have been made by the MIT Group for a 1,000 MVA machine, a capability comparable to the largest conventional generators currently in use by utility companies.

Estimates of design engineers indicate that 10^4 MVA generators are within reach using presently available materials; further improvement depends on superconducting materials development. The capital costs of such a system, including refrigeration, is more than compensated over a five- to ten-year period by the reduction in power losses.

Where large amounts of power must be conducted through limited cross sections (for example, underground), superconducting power transmission lines, ac or dc, may become economically favorable in five years. Recent proposals contemplate use of niobium plated copper lines with current capacity such that the peak field is below the lower critical field H_{c1}. Appreciable savings in refrigeration costs would be obtained if Nb_3Sn were used with operation at 14°K rather than 4.2°K. In the case of power transmission the relatively low H_{c1} of Nb_3Sn ($\approx$600 gauss at 0°K) can be offset by conductor geometry.

5.8.2.5 MISCELLANEOUS APPLICATIONS

To conclude this section on present status, it appears worthwhile to list the following additional applications of superconductivity:

1. Levitated persistent current rings are now in use in plasma research. Here a superconducting ring in a sealed dewar is levitated in a

vacuum to supply symmetrical field without supports for long-lived plasmas in fusion research.

2. Levitated superconducting spheres have been proposed as gyroscopes with low values of drag for accurate measurements of position in space.

3. By applying the principles of flux conservation, superconducting pistons and cylinders can be utilized to concentrate flux. Flux conservation can be used with a superconducting Faraday disk configuration, for example, to charge solenoids or other devices with current by the repeated passages of a normal spot through the current containing flux.

4. The ability of a superconductor to shield an external field together with flux quantization should permit the creation of a *zero* field region of macroscopic dimensions. Superconducting shields around audio or rf circuits can provide a high degree of isolation or decoupling not obtainable by other means.

5. Superconducting coils have the potential to provide active cosmic ray and solar flare shielding of personnel in space flight at a great reduction in weight compared to passive shielding.

6. The low thermal conductivity of the superconducting state, as compared to the normal state, permits the fabrication of a magnetically-controlled low-temperature heat switch.

5.8.3 Major Problems

5.8.3.1 MATERIALS

The fundamental problem underlying all superconducting applications is that of the costs associated with refrigeration. Despite the clear advantage of existing superconducting devices operating at 4.2°K, large savings in refrigerating costs and size could be achieved by operation at 20°K or 40°K. For example, refrigeration costs would drop to about 10 percent of present levels if operation at 40°K were possible. To understand the force of this observation it must be realized that, at present, there is no theoretical indication that transition temperatures (T_c) above 21°K *cannot* be obtained. Unfortunately, the empirical evidence, with only one superconductor above 20°K, is discouraging.

The absence of a theoretical limit on T_c is accompanied by theoretical inadequacies with regard to the critical field of superconductors (H_{c2}). Again the theory fails to relate a quantity of practical significance to the microscopic properties of the material. For example, the large increase of H_{c2} observed for Nb_3Al (≈30 percent) was an *unexpected* consequence of an increase in T_c of about 10 percent.

Finally, if one surveys the materials now in practical use in high-field, high-current devices, one discovers that all but one of them were discovered prior to 1957 and that all of them have been optimized for performance at 4.2°K. Thus, no advantage has been taken of the fact that one of those materials (Nb_3Sn) remains superconducting with applied fields as high as 80 kilogauss at 14°K. Furthermore, with few exceptions, we have little knowledge of the microscopic nature of defects which are believed to control the critical current capacity at any field and temperature, regardless of the synthetic technique used to prepare the superconductors. Consequently, there has been insufficient optimization of current capacity. Inherent instabilities have been avoided by massive additions of a normal conductor, or geometrical control rather than through microscopic understanding and control of flux-pinning impurities.

5.8.3.2 DEVICE PROCESSING

The small superconducting devices (Josephson diodes and weak links) are of technological value because of their unique performance. However, the fabrication of such devices is limited by low yield and poor reliability due to inability to control the dimensions and quality of insulating barriers. In almost all such devices, metallic oxides (naturally grown) are the key contributor to performance; and in all cases, control, uniformity and life are only poor to fair. For full utilization of these unique storage elements, switches, magnetometers and high frequency detectors, a processing technology which approaches the sophistication of that existing in the semiconductor area is required. Thin films prepared either by sputtering or vacuum deposition are a logical and economic form for these devices. Photoresist techniques already exist for integrated arrays. However, control and optimization of thin tunneling and insulating barriers are lacking.

5.8.4 Recommendations

5.8.4.1 Applied research is recommended on the operation of existing Nb_3Sn solenoids at temperatures above 4.2°K, perhaps as high as 14°K. There are presently only limited data on the high-temperature performance of solenoids, and there are potential appreciable savings in the weight, cost, and size of required refrigeration.

5.8.4.2 Fundamental and applied research should be carried out on techniques for the synthesis of superconducting films with thin insulating barriers. In addition, the application of existing integrated circuit technology to superconducting devices should add reliability, yield, and low cost to their already apparent advantages in performance.

5.8.4.3 Fundamental research is required on the effect of homogeneous defect structures (grain boundaries, precipitates, dislocation nets) on the field and temperature dependence of the critical current density of Type II superconductors. The understanding and control of defects will permit optimization of solenoid performance as well as permitting a reduction in the weight, size, and cost of copper stabilization.

5.8.4.4 Fundamental research on the relation between the microscopic parameters of transition metal compounds and the normal-to-superconducting transition temperature (T_c) is needed. Of the six superconducting systems that achieve T_c above 18°K, all of them are niobium based; five of them are in the A-15 (β-W) crystal structure. A good starting point for such a program is theory and experiment on well-characterized niobium-based A-15 structures. From this research a theoretically guided exploratory materials effort has a chance of understanding the present 21°K limit of T_c and hopefully extending operations to the temperature of boiling hydrogen (22°K) or boiling neon (28°K).

5.8.4.5 A search for new materials and new structures with low losses for ac, rf, microwave, and millimeter applications is also recommended, as well as concurrent search for low-temperature dielectrics for supporting and for capacitive elements.

5.8.4.6 Further development is needed for remotely controlled superconductive circuit components, such as variable inductance, tunable resonant circuits, and relay switches.

5.8.4.7 Further search is required into new methods of information handling through use of minimum energy quantum processes operating in the "flux-shuttle" shift register.

5.9 II–VI LUMINESCENT DEVICE RESEARCH

5.9.1 Introduction

The luminescent properties of the II–VI compounds are many and extremely varied. The response of these materials to excitation by ultraviolet light, x rays, and high energy particles has been known for many years, in some cases dating back to the last century. The more recent research on these materials has been principally directed toward their potential use as efficient electroluminescent sources, particularly in the visible region of the spectrum.

For this application, attention has been directed toward the (Zn, Cd) (S, Se) alloy systems, since they show excellent photoluminescent and cathodoluminescent efficiency in this frequency range.

5.9.2 Present Status

At present (Zn, Cd)S solid solution alloys activated with Cu or Ag and coactivated with either chloride or aluminum are used in cathode ray tubes (TV kinescopes, radar, and oscilloscopes) and in x-ray intensifier screens. In the latter use, luminescent materials constituted of heavier atoms such as tungstates, tantalates, and rare earths, with better stopping power for x rays, are being investigated and are replacing the II–VI materials. The largest use of the II–VI luminescent materials, at present, is in cathode-ray tubes of various sorts. A rough estimate of the amount of material used annually is about 10^3 tons. These II–VI alloys are the most efficient cathodoluminescent materials known, and can be made to cover the whole visible spectrum in their emission color by suitable formulation.

The synthesis of the (Zn, Cd)S cathodoluminescent phosphors is carried out by the precipitation of the sulfides from aqueous solution. To these precipitates are added the activators of either copper or silver and the coactivators of either chloride or aluminum in such ways as to obtain uniform mixtures. These mixtures are then subjected to a high temperature treatment to produce the phosphor. The heat treatment avoids oxidation of the sulfides by the use of closed containers or controlled composition atmospheres. After firing, the phosphors are comminuted and usually coated with such material as silicates or phosphates so as to produce free-flowing powders whose particle diameter falls in the range of 5 to 20 μm. The phosphors are then ready for the fabrication of a luminescent screen. During the formation of the screen, the efficiency of the phosphors is somewhat downgraded, the extent being dependent on the particular processing steps used. Problems of screen fabrication have prevented selenium from being used as a constituent of these phosphors, since selenium-containing phosphors are very seriously degraded during screen fabrication.

Presently, most workers in the field are of the opinion that little improvement is to be made in the intrinsic efficiency of (Zn, Cd)S cathodoluminescent phosphors except for the newer rare earth activated variety. However, for most cathode-ray tube applications, some increase in the finished screen efficiency is to be obtained by improvements in the processing techniques of these phosphors.

In the area of electroluminescence, II–VI phosphors are known that operate under different types of excitation, one being ac excitation and the other dc excitation. For ac excitation, the phosphors comprise Zn(S, Se, Te) solid solutions. They are activated with copper or manganese and coactivated by either one of the halogens or one of the Group III cations. These systems are the most efficient electroluminescent materials in the blue-to-yellow region of the spectrum. They are capable of up to about 2 percent power efficiency. However, they have short peak life. Even the best materials degrade to half brightness in less than 10^4 hours under constant voltage, although recent results indicate that their lifetime is considerably greater under constant power.

The foregoing phosphors contain copper in excess of the solubility limits, the limit being determined by the particular method of coactivation. The generally accepted model is that the excess copper precipitates as Cu_2S along imperfection lines of the crystals to form conductive spikes. No widely accepted model exists for the injection of charge carriers from the Cu_2S conductive spikes into the luminescent material. The phosphors are synthesized by techniques quite similar to those outlined above for cathodoluminescent phosphors. After synthesis, excess copper sulfide, which has precipitated on the external surface of the crystallites, is removed by washing in cyanide solution. This leaves only the internal precipitates to couple with the ac field and cause injection to take place. The powder thus produced is imbedded in a dielectric, such as a plastic or glass, and fabricated into a sandwich cell, one of whose electrodes is transparent. These ac materials have had some limited practical use in instrument panels and night lights.

In the area of dc electroluminescence, the phosphors, so far, show poor efficiency because efficient means of injection for both carrier types have not yet been demonstrated. The higher band gap II–VI's (ZnS, ZnSe, ZnTe, CdS, and CdSe) are not easily doped to show either p- or n-type carrier behavior according to dopants. Of the above named compounds all are easily made n-type with the exception of ZnTe which shows p-type conductivity. Only the low bandgap CdTe and (Cd, Hg)Te alloys show amphoteric doping characteristics. For this reason, those materials capable of visible luminescence have not yet been prepared with well-defined p–n junctions. Therefore, highly efficient electroluminescence has not been obtained via the p–n homojunction route. Research efforts are presently under way to try to prepare p–n junctions in ZnSe and CdS.

Besides the p–n junction approach, d-c electroluminescence can be achieved in ZnS, ZnSe, ZnTe, and CdS by heterojunction injection. In Al-doped ZnS, blue emission from single crystals has been obtained with In and Cu contacts. In ZnS powders and films doped with Mn and/or rare earths, dc visible electroluminescence has been obtained from junctions employing Cu_2S; in fact, powders of Mn-doped ZnS coated with Cu_2S have shown power efficiencies of up to 0.3 percent in the yellow accompanied by very-high-quantum efficiency. These powders and films are highly resistive, which accounts for the large difference between the power efficiency and the quantum efficiency. Similar effects, but with lower efficiency, have been observed in ZnSe materials. Research is proceeding currently on more sophisticated heterojunction configurations.

5.9.3 Major Problems

The major potential use of the luminescent II–VI materials lies in the area of visible electroluminescence. From all that is known about these materials after several decades of research, it appears certain that all of the luminescent recombination processes are very efficient; on the other hand, the carrier injection processes leading to recombination through the efficient centers is very inefficient. The direct approach to solving this problem is via the fabrication of p–n junctions; but this route is very difficult, since the high bandgap II–VI compounds (ZnSe, CdS, and ZnTe) do not readily form both conductivity types. This lack of p- and n-type doping has been ascribed to the property of self-compensation, wherein a native defect is formed to compensate for one type of doping impurity, thereby allowing only one conductive type to form. This widely believed explanation is more in the realm of theory than in the established existence of the defects; much work needs to be done in establishing the exact mechanism for the lack of both conductivity types. Another approach to d-c electroluminescence in II–VI compounds is to achieve the necessary carrier injection by a heterojunction technique. Many heterojunction approaches have been tried in the II–VI materials, and many have shown the emission of visible light but only with poor efficiency.

The visible emitting II–VI compounds ZnS, ZnSe, and CdS and their alloys are well known as efficient phosphors in powder and polycrystalline film form. This property makes them attractive for broad area, reasonably efficient, low-cost display and lighting elements. However, the injection problem still exists in these polycrystalline systems; it must be solved before highly efficient devices can be obtained.

In the field of broad area devices ac electroluminescence may also be an attractive approach, particularly since it is known that the ac-excited phosphors show comparatively great brightness per unit volume. Furthermore, new multilayer film techniques have resulted in high contrast devices even without optimum brightness. The main problem, therefore, is to obtain high brightness regions in a larger fraction of the available volume, thereby increasing efficiency and reducing power drain. In addition, there is a need to lengthen the effective operational life of these ac electroluminescent materials. Greater density of high brightness regions is presumably associated with the form and distribution of Cu_2S precipitates. The control of these precipitates by the techniques used in eutectic alloy formation could be a promising approach to this problem.

5.9.4 Recommendations

5.9.4.1 Basic research in the area of dc, visible electroluminescent II–VI compound semiconductors is needed for better characterization of the self-compensation phenomenon which prevents the formation of efficient p–n junctions by simple impurity additions. A better understanding of injection into these same materials by heterojunctions could also lead to highly efficient electroluminescence.

5.9.4.2 Applied research is recommended to develop the best carrier injection technique applicable to appropriate II–VI semiconductor compounds in powder and polycrystalline film form for broad area application. Also in broad area devices, applied research is needed to characterize the form and distribution of Cu_2S precipitates as they relate to the brightness and life characteristics of ac electroluminescent materials.

5.9.4.3 Applied research is recommended to exploit the high internal quantum efficiency of II–VI electroluminescent compounds for multicolor emitters, both in film and powder form. This should include newer preparation techniques, such as ion implantation, rf sputtering, and the use of rare earth activators.

5.10 BIBLIOGRAPHY

5.10.1 Infrared Detector Research

1. P. W. Kruse, "InSb Photoconductive and PEM Detectors," In *Semiconductors and Semimetals*, Vol. 5, R. K. Willardson and A. C. Beer, eds (Academic Press, New York, 1970), pp. 15–83.
2. I. Melngalis and T. C. Harman, "Single Crystal Lead-Tin Chalcogenides," In *Semiconductors and Semimetals*, Vol. 5, R. K. Willardson and A. C. Beer, eds (Academic Press, New York, 1970), pp. 111–174.
3. D. Long and J. L. Schmit, "Mercury-Cadmium Telluride and Closely Related Alloys," In *Semiconductors and Semimetals*, Vol. 5 , R. K. Willardson and A. C. Beer, eds (Academic Press, New York, 1970), pp. 175–225.
4. E. H. Putley, "The Pyroelectric Detector," In *Semiconductors and Semimetals*, Vol. 5, R. K. Willardson and A. C. Beer, eds. (Academic Press, New York, 1970), pp. 259–285.

5.10.2 Electroluminescent Device Research

1. H. C. Casey and F. A. Trumbore, "Single Crystal Electroluminescent Materials," Mat. Sci. Eng., *6*, 69 (1970).
2. H. Kressel, "Semiconductor Lasers," In *Lasers*, Vol. 3, A. Levine and A. DeMaria, eds (Marcell Dekker, New York, 1971).

5.10.3 Electron Emission Device Research

1. B. F. Williams and J. J. Tietjen, "Current Status of Negative Electron Affinity Devices," Proc. IEEE, *59*, No. 10 (Oct. 1971).

5.10.4 Research on Thermoelectric Power Generation

1. F. D. Rosi, "Thermoelectricity and Thermoelectric Power Generation," In *Solid State Electronics*, Vol. 11 (Pergamon Press, New York, 1968), pp. 833–868.

5.10.5 Microwave Device Research

1. B. E. Berson, "Transferred Electron Devices," Proc. 1971 European Microwave Conf., *1*, Aug. 23–28 (1971).
2. F. Sterzer, "Transferred Electron (Gunn) Amplifiers and Oscillators for Microwave Applications," Proc. IEEE, *59*, (Aug. 1971), pp. 1155–1163.
3. R. Edwards, "Recent Advances in Avalanche Diode Microwave Sources," Proc. 1971 European Microwave Conf., *1*, Aug. 23–28 (1971).
4. S. M. Sze and R. M. Ryder, "Microwave Avalanche Diodes," Proc. IEEE, *59*, (Aug. 1971), pp. 1140–1154.
5. W. G. Matthei, C. K. Kin, "New Gallium Arsenide IMPATT Diode Results," Abstr. Cornell Conf. High Frequency Generation and Amplification: Devices and Applications, Cornell Univ., Ithaca, New York, Aug. 17–19 (1971).

6. D. J. Coleman, Jr., J. C. Irvin, G. E. Mahoney, and H. H. Wade, "Recent Improvements of GaAs IMPATT Diode Performance," Abstr. Cornell Conf. High Frequency Generation and Amplification: Devices and Applications, Cornell Univ., Ithaca, New York, Aug. 17–19 (1971).
7. J. C. Irvin, D. J. Coleman, Jr., W. A. Johnson, I. Tatsuguchi, D. R. Decker, and C. N. Dunn, "Fabrication and Noise Performance of High-Power GaAs IMPATT's," Proc. IEEE. *59*, (Aug. 1971), pp. 1212–1215.

5.10.6 Research on High Power Infrared Laser Windows

1. F. A. Horringan and R. I. Rudko, "Materials for High Powered CO_2 Lasers," Final Tech. Rep. Contr. No. DA-AH01-69-C-0038, AD 693311.

5.10.7 Research on Solar Cells

1. P. Rappaport, "Photovoltaic Power," reprinted from J. Spacecr. Rockets, *4*, No. 7, (1967), pp. 838–841.
2. J. J. Loferski, "Theoretical Consideration Governing the Choice of Optimum Semiconductor for Photovoltaic Energy Conversions," J. Appl. Phys. *27*, 777 (1956).

5.10.8 Superconducting Device Research

1. B. Matthias, Amer. Sci. *58*, 80 (1970).
2. B. Matthias, Phys. Today *24*, 21 (1971).
3. John Clark, Phys. Today *24*, 30 (1971).
4. J. Hulm, D. J. Kasun, E. Mullan, Phys. Today *24*, 48 (1971).
5. P. G. deGennes, *Superconductivity of Metals and Alloys,* (Benjamin, New York, 1966).
6. B. B. Goodman, Rep. Progr. Phys., *29*, 445 (1966).

5.10.9 II–VI Luminescent Device Research

1. M. Aven, "II–VI Semiconducting Compounds," In *Electroluminescence in II–VI Compounds, 1967 International Conference,* D. G. Shomos, ed. (W. A. Benjamin, Inc. (Menlo Park, Calif., 1967), p. 1232.
2. F. F. Morehead, "Physics and Chemistry of II–VI Compounds," Chapter 12 in *Electroluminescence,* M. Aven and J. Prener, eds. (North Holland, 1967).
3. A. G. Fischer, "Luminescence in Inorganic Solids," Chapter 10 in *Electroluminescence in II-VI Compounds,* P. Goldberg, ed., (Academic Press, New York, 1966).

6 Magnetic Materials for Electron Devices

6.0 INTRODUCTION

Magnetic materials are of tremendous importance to electron devices. A clear expression of this importance was the recent award of a Nobel Prize to Louis Néel of the University of Grenoble in France. His award "for fundamental work and discoveries concerning antiferromagnetism and ferrimagnetism which have led to important applications in solid-state physics" was the first award in the area of solid-state physics since Shockley, Brattain, and Bardeen shared the prize in 1956.

Certain parts of the field of magnetic materials are in a fairly advanced, even mature, state of development; however, as this report will describe, there are still exciting and important discoveries being made that make possible, for instance, new high-performance permanent magnets or magnetic bubble devices. In addition, there is potentially important research work. Possibly, antiferromagnetic materials such as V_2O_3 will play a part in devices in which there is a phase change between a metal and insulator. Nearly ferromagnetic materials such as $ZrZn_2$, Pd, Pt, $PrPt_5$, have possible futures. There are scientific reasons, now understood, explaining why some of these materials are good catalysts. Other such materials will help in attaining very low temperatures for scientific studies. One should, therefore, continue to support a thoughtful program to help fundamental work in this field as well as work of immediate interest for devices.

6.1 MATERIALS FOR MAGNETIC "BUBBLE" DEVICES

Recently a new class of magnetic devices has been described that may have considerable impact on techniques used to store and manipulate information. These devices use small magnetic domains ("bubbles") to represent bits of information. These domains are formed in a thin plate of magnetic material and can be moved around in a controlled manner. The domains interact with each other, so logic functions can be performed. In principle, the processing associated with making these devices is simpler than it is for semiconductor devices. It may be pointed out here that these bubble devices are extremely resistant to the effects of radiation. They have been exposed to massive doses (up to 10^7 rads) of γ-radiation without deleterious effects.

The material in which the bubbles are contained must have certain minimum requirements:

1. It must be available in nearly defect-free single crystal plates, or films, with a unique magnetic axis of easy magnetization perpendicular to the plate or film. It has been established that domains do not propagate in polycrystalline films.
2. The material must be optically transparent. While there is nothing in the operation of a memory that requires it, there is presently no way of setting up a memory device without watching the domains. Future development may waive this requirement, but for the present it is necessary.
3. The domains must have a useful size. A diameter of 0.3 mils (about 8 microns)* will allow a storage density of about 10^6 bits per square inch, a very attractive density. A diameter of 3 mils, however, will reduce this by a factor of 100. On the other hand, domains cannot be made arbitrarily small. As the size is reduced, circuit elements become increasingly difficult to prepare and detection problems rise.

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* 1 mil = 0.001 inch
1 micron (μ) = 10^{-6} meter

Equilibrium domain diameter, *d*, depends upon the magnetic properties of the material in the following way:

$$d \approx \frac{(AK)^{1/2}}{4\pi M^2}$$

where A is the magnetic exchange constant, K is the anisotropy constant, and M is the saturation magnetization. Since M and K depend on temperature, it can be seen that for domain size to remain constant either the temperature must be controlled, or $\sqrt{K}$ and M^2 must have similar temperature dependence near room temperature.

4. The domains must be mobile. For a given size, mobility determines the bit rate at which a memory may be operated. Although domain mobility can be traded to some extent for smaller domain size, a goal of a megacycle bit rate will require a mobility of at least 100 cm/sec Oe for a 0.3-mil domain. In addition, coercivity must be low.

5. The magnetic properties of the bubble domain material must not be so temperature-sensitive as to change the size of the domains during operation. If domain size varies too much the domains will not move reliably among the circuit elements.

Given these requirements, the presently available magnetic materials that fulfill them are few. The requirements for materials that are transparent in thin sections and possess a magnetic moment at room temperature restrict us to the following:

1. Hexagonal ferrites $M^*Fe_{12}O_{19}$
2. Spinels MFe_2O_4
3. Orthoferrites (R.E.†) FeO_3
4. Garnets $(R.E.)_3Fe_5O_{12}$

The hexagonal ferrites have been investigated sufficiently to establish that they have very-low-domain mobilities and are difficult to prepare as large, high-quality single crystals.

Spinels have received little attention because they are cubic; i.e., they have no uniaxial magnetic properties. (However, the experience with "cubic" garnets, to be related below should be kept in mind, together with possible strain effects.) In addition, the perfection of available crystals is inadequate.

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* M–metal ion

† R.E.–rare-earth ion

Although the first hopeful results were obtained with orthoferrites, today these are not attractive materials. This is because the bubbles are normally so large that devices with useful storage capacities cannot be made. Various tricks may be played to increase the saturation magnetization, M, or to decrease the anisotropy, K. However, extreme temperature-sensitivity results, which again does not allow practical devices to be built. Thus, in spite of their original promise, use of orthoferrites in bubble-domain devices will probably be limited by the necessity to compromise on domain size or temperature control to highly specialized, small memories.

At present, the most promising materials are based on the garnet structure. Until recently, no one suspected that the garnets would be at all suitable for this purpose. This was because everyone knew that garnets were cubic crystals and so should not show the necessary magnetic anisotropy. The discovery of growth-induced anisotropy in mixed rare-earth iron garnets led to the exploitation of this versatile family of materials. However, simple garnets by no means provide satisfactory properties. As an example of the methods used to achieve a useful composition consider the following situation:

It is again necessary to achieve temperature-insensitive characteristics. Garnets with flat magnetization versus temperature curves near room temperature can be prepared by using rare earths, which form iron garnets with compensation points in the $4\pi M_s$ versus T curve. The compensation points arise because the net magnetization of the iron-containing sublattice opposes the magnetization of the rare-earth sublattice. When the temperature dependence of the sublattice magnetization is such that the moments exactly balance each other, the net moment becomes zero. This occurs at different temperatures for different rare earths.

Halfway between the compensation point and the Curie temperature, the magnetization curves are quite flat. Thus, a garnet with a low compensation point whose maximum in $4\pi M_s$ above that point is near room temperature will have little temperature sensitivity. However, the room-temperature magnetization must have the right value to yield the desired bubble size. This can be achieved in a variety of ways. For example, the position of the compensation point can be adjusted not only by the simple choice of a rare-earth garnet, but by employing solid solutions as well. For instance, the substitution of gadolinium into yttrium iron garnet introduces a compensation point where one is normally absent, and the temperature of this compensation point depends on the amount of gadolinium added.

The magnitude of the magnetization may be adjusted in other ways. The magnetization of rare-earth garnets with compensation points low enough to give a flat magnetization curve at room temperature also have a $4\pi M_s$ of several hundred gauss. The uniaxial anisotropy in garnets is low enough that domain diameters are too small to detect unless the magnetization is around 150. Thus, nonmagnetic ions, gallium or aluminum, must also be added to replace some of the iron ions in the garnet to lower its moment. However, this moves the compensation point toward room temperature again. To achieve temperature insensitivity, a nice balance must be struck between the species of rare earths on the dodecahedral sites and the concentration of nonmagnetic ions on the tetrahedral and octahedral sites.

Furthermore, like all such devices relying on domain wall motion, the best operation occurs when the effects of nonuniform strain are minimized. Here again, with a detailed knowledge of magnetostrictive coefficients it is sometimes possible to choose a combination of rare-earth ions such that the magnetostriction is zero.

It is such considerations as these that require for the correct bubble size, temperature and strain insensitivity, compositions such as:

$$Y_{1.85}Eu_{0.18}Gd_{0.50}Tb_{0.47}Fe_{4.4}Ga_{0.6}O_{12}$$

Moreover, there is the question of why the cubic garnets show anisotropy at all. There is no doubt that anisotropy is in some way built in during growth and is associated with facets of the growing crystal. Thus, only certain regions of a crystal show the effect—in fact, the crystals have to be "mined," i.e., the critical regions must be located and exploited. It is very likely that it has to do with the nonrandom distribution of the different rare-earth ions on the dodecahedral sites, associated with the faceted growth of the crystals.

Preparation Techniques

Single crystals have to be used for bubble materials. The methods that have been used up to the present are as follows:

1. Growth from molten salt (flux)
2. Growth from melt
3. Epitaxial growth
    a. Chemical vapor deposition
    b. Liquid phase epitaxy
    c. Hydrothermal

1. The growth from flux is the method which yielded most of the useful crystals for the early device experiments. However, in spite of this success, it must be recognized that the technique, with all its flexibility, is time consuming and expensive. Runs take two or three weeks to complete, yields are uncertain and crystals tend to be flawed. Crucibles cost many thousands of dollars. For all but experimental purposes other methods are more attractive.

2. Growth from the melt is a simple way of growing crystals and is used, of course, for silicon. Unfortunately, for orthoferrites and garnets the melting points are high, and at the melting points decomposition often occurs. It has been possible to grow from the melt one orthoferrite, yttrium orthoferrite, using the Bridgman technique under one atmosphere of oxygen; in fact, several other rare earth orthoferrites have been grown recently by the float zone technique under higher oxygen pressure. However, orthoferrites are not very useful, and the method does not seem to be applicable to the magnetic garnets.

3. Even if satisfactory methods were available to grow large single crystals, there remains the very considerable task of cutting them up and polishing slices to a thickness of only a few microns. It would clearly be preferable to grow the thin crystals directly on a substrate using epitaxial techniques.

In the garnet system, despite the fact that rather complex materials are being deposited, and also that one usually uses heteroepitaxy rather than homoepitaxy, rather remarkable progress has been made in thin-film deposition.

An important step forward was the Czochralski growth of nearly perfect substrate crystals. These are R.E. gallium garnets. They may be gadolinium, dysprosium or samarium gallium garnets or their mixed crystals. This is very convenient as lattice parameters can be adjusted to fit a particular iron garnet.

Deposition on the substrates is brought about using several methods:

1. Chemical vapor deposition (CVD) relies on the reaction of several gas streams. Deposition of garnets takes place near 1200°C.

2. In another technique, liquid phase epitaxy (LPE) occurs from a flux—a tipping method has been used, although more recently a method in which the substrate is dipped into the flux and then withdrawn has proved to be very convenient. Temperatures near 900°C are used. Uniform growth is obtained by deposition from the supercooled flux.

3. Hydrothermal epitaxy has also been employed. This occurs at

much lower temperatures (near 400°C) but at present appears to be only of academic interest.

To varying degrees, all of these methods have succeeded, in that regions of single crystal films have been produced in which bubbles are mobile. The LPE "dipping" technique is most highly developed at the present time. Using this method, films have been grown of various mixed garnet compositions which have areas of the order of one square centimeter with no defects that impede bubble motion. Thickness, magnetization and other bubble parameters are constant to within 10 percent. Bubble shift registers with 10,000 steps have been operated on these films. With further development, the CVD method should provide films of comparable quality.
Problems still under investigation include the following:

1. Defect-free areas must be larger
2. Uniformity of thickness and magnetic properties must be improved
3. Reproducibility from film to film must be improved
4. Compositions that give rise to optimum device performance must be developed. Improvements in speed, operating margins, and temperature sensitivity are required.

The magnetic anisotropy of some epitaxial garnet films is induced by a growth mechanism that is similar to that in the bulk flux-grown garnets. These heteroepitaxial films will generally be in a state of stress at room temperature. It seems quite certain that in some cases, at least, this stress is responsible for the magnetic anisotropy. Thus, bubbles have been seen in holmium iron garnet, $Ho_3Fe_5O_{12}$, when grown on a substrate. Since this compound has only one species of rare-earth atom it cannot derive its anisotropy from the nonrandom inclusion of the cations.

At present, our knowledge of strain-induced anisotropy is rudimentary. Information is required about lattice dimensions and thermal coefficients of expansion and also a detailed knowledge of any compositional gradients that may occur at the interface between substrate and crystalline film. Strain-induced anisotropy could be valuable since we might be able to tailor material systems to device requirements. It is, in effect, another variable that we can manipulate to produce a desired material property. The presence of both types of anisotropy gives additional flexibility to the garnet system.

One must not forget that when the bubble crystal problem is solved, there will still be problems in defining with sufficient precision the magnetic metallization pattern on the crystal surface, i.e., the metallized pattern that is used to propagate and control the motion of the bubbles. This will be a pattern with much detail on a very fine scale. In addition, there is the problem of detectors of the bubbles in the crystalline film. There are reasons to believe that these problems will yield to steady engineering pressure.

In summary, we see the need for intensive materials and process work to support the magnetic bubble devices. We need understanding of many phenomena, we need knowledge of many parameters, and we need much effort to devise good engineering methods for crystal growth under a wide variety of conditions, including those which will take these devices out of the laboratory stage and into a production environment. Nevertheless, progress has been so rapid and the options are so numerous that it seems almost certain that satisfactory solutions will be found in the reasonably near future.

6.2 FERRITE MATERIALS

Ferrites are magnetic materials that are also insulators. In them the magnetic moments of atoms of one kind are directed antiparallel to the moments of other atoms (antiferromagnetic coupling); however, the cancellation is not complete and a net magnetic moment results. They have wide application to electronic devices and may be discussed under the following headings.

6.2.1 Square Loop Ferrites

The primary use of these materials is for memory applications in computers. They are generally used in the form of discrete cores that are threaded with wires in a variety of organizational arrangements termed 2½D, 3D, etc.). We do not see this method of assembly being replaced by new batch techniques. If cores are to be replaced it will be by semiconductor memories, or possibly by magnetic bubbles, and, indeed, computers will soon be sold using bipolar semiconductor devices for the main frame memory.

The development of higher squareness ratios and faster switching times have been the goals for square loop ferrite work. The materials have been in an advanced state of development since about 1960 and recent improvements only came about through brute force techniques. Even today there is not complete understanding of how squareness is maximized; the problem is a complex one involving, as it does, the surface properties and imperfections of granular material. Switching times are influenced by (a) domain wall motion which has an inherent speed limitation, and (b) the coercive force of the material that is influenced by composition and processing.

The industry uses MgMn and Li ferrites usually doped with Ni, Mn and/or Zn. Although MgMn(Zn) ferrites have faster switching times, Li ferrites are used for core sizes less than 20 mils O.D. for reasons of strength. Today, systems may use 16 mil O.D. cores and one megabit memories, and achieve read-rewrite memory cycle times of about 500 ns using 2½D or 3D wire organization. In Japan, a 300,000 bit memory with a cycle time of 300 ns is being developed using 12 mil O.D. cores and 2½D, 3 wire organization. In America, a 1,000,000-bit memory with a 250 ns cycle time using a 2 core per bit, partial switching, and linear select mode of operation has been advertised.

As a measure of progress in this field one may note that 5 years ago it was reported by the electromagnetics subpanel of the MAB that 14 mil O.D. cores were providing switching times of 300 ns and were tested in manufacture at a rate of 10/second. Today 12 mil O.D. cores are in use, 200 ns switching times have been achieved, and testing speeds are approaching 30/second.

6.2.2 High Q Ferrites and High Permeability Ferrites

The former are used mostly in frequency selective coils or transformers; the latter principally for broadband transformers. For the broadband use, high permeability is desirable since it minimizes the number of turns required for transformer action at low frequencies, and this reduced parasitics at high frequencies.

For high Q materials MnZn ferrites are used below 1 MHz, and NiZn(Co) ferrites between 1 and 100 MHz. In the absence of an economical and sophisticated quartz filter technology, some telecommunication concerns have found it important to develop the low frequency MnZn ferrites. At present the Japanese appear to lead in this field with "Neferrite" in manufacture, with μ (permeability) = 2000 and $\mu Q = 600{,}000$ at 100 kHz. "Super Neferrite" has also been developed by the Japanese but is not yet in manufacture; it has $\mu = 2000$ and $\mu Q = 1{,}200{,}000$ at 100 kHz. Thus, Q values of 600 have been achieved; 5 years ago Q values were reported to be in the range 250 to 300. These advances have come through much detailed process work, in this case the key was the use of highly reactive ferrite powder prepared by coprecipitation techniques. For frequencies above 1 MHz there have been needs for inductors with high Q and good temperature stability. NiZn(Co additive) ferrites have been developed that are of superior quality for this application. The function of the cobalt is to tie down the domain walls because of its high uniaxial anisotropy, with the result that there is less domain wall motion and so lower hysteresis losses.

For high permeability, the anisotropy and magnetostriction must be minimized and this is done primarily by composition, although low magnetostriction is aided by processing that produces large and uniform grain size with low internal strains. Again, the Japanese appear to be leading with material of a permeability of about 10,000 that has been in manufacture since 1966. It is, however, anticipated that given the will, fairly modest efforts by a competent organization could equal this performance. Increased attention may however be necessary in manufacture to mechanical finishing, for the Japanese appear to be well ahead in the art of ferrite grinding.

6.2.3 Microwave Ferrites

These materials are used for tunable isolators, circulators, modulators, switches, etc., in microwave circuits, and have been in a mature state of development for several years. Since 1965 most of the work in this field has revolved around modification of specific materials to make them suitable for particular devices.

The most commonly used microwave ferrites are the yttrium and rare earth garnets, with yttrium iron garnet, YIG, receiving the most attention as it has about the narrowest resonant line width of all the ferrimagnetic materials. Its magnetic moment is often modified by the substitution of Al or Ga for some of the iron. There is, however, need for materials with higher intrinsic anisotropy and narrow line width ($\Delta H < Oe$) which will allow microwave tuning of mm wave frequencies with comparatively weak external biasing fields.

Microwave devices are also made from ferrites with the spinel structure. These often contain some divalent iron and do not sinter to a very high density, and so generally do not have as narrow a resonance line width as the polycrystalline garnet ferrites with their simple single-phase structure. Thus, spinels are only used in less demanding applications that do not require the more expensive YIG.

It is hoped that the calcium, vanadium, bismuth iron garnet system will prove to be more economical and, in certain applications, have better performance than YIG or the rare-earth garnets. However, there appear to be great difficulties in the preparation of dense, reproducible, single-phase polycrystalline parts. Nevertheless, this type of material could be used in large quantities in microwave-phased arrays to produce significant system weight savings by elimination of need of heavy cumbersome rotatable antennas. For example, one system may use several thousand units that together weigh some hundreds of pounds. Further efforts to prepare these materials will, if successful, be most worthwhile.

Five years ago, temperature stability of polycrystalline ferrites was a problem, but with present-day technology, control of the temperature stability of these materials is well developed.

One might add that such modified garnets may also be useful for magnetic bubble devices employed for optical displays. The figure of merit of this material, used this way, is roughly an order of magnitude better than the closest competitor known today.

Usually the garnets are used in polycrystalline form, but occasionally single crystals are required. An example is for variable filters in electronic countermeasure equipment or for microwave preselectors in microwave instrumentation. For these purposes crystalline spheres only about 0.1 in. in diameter are required, and such crystal sizes are not hard to obtain from material grown from a flux. Larger crystals would not be easy to grow. Furthermore, larger YIG crystals might be useful for magneto–elastic delay lines, and for lasers that might have interesting properties that could be modified with magnetic fields. It would seem worthwhile to press for improved crystal growth methods. One objective might be to engineer properly the flux growth method. For instance, it should be possible to develop a seeded flux growth apparatus to work near 1300°C so that a controlled single crystal could be grown from a flux rather than an ill-defined collection of several crystals. It might even be possible with sufficiently good engineering control to pull crystals from a flux. It must be recognized that these are very difficult crystal growing problems that have already received some attention, and, so far, this attention has had few useful results. If more work is to be initiated, careful account should be taken not only of the objectives but also of the competence of the organization supported.

6.2.4 Summary of Ferrites

The ferrites generally are in a mature state of development. There is no doubt that improvements will come with time as people pay more attention to materials and process problems. These improvements will be derived from a consideration of such things as grain size, controlled addition of impurities, annealing schedules, composition of the atmosphere during heat treatment, grain orientation, and so forth. The principles of the game seem to be well understood, and one gains the impression that a competent manufacturer can usually get what he wants without excessive development costs. There may be need for increased single-crystal growth efforts, and perhaps for sustained effort in the endeavor to understand all the details, for instance, of the reasons for squareness in the square loop ferrites, or perhaps why the garnets do not have low loss at low frequencies.

6.3 FERROMAGNETIC MATERIALS

It is convenient to classify ferromagnetic materials into three groups:

1. Permanent magnetic materials with a coercive force $Hc > 300$ oe
2. Semihard magnetic materials with $10 \text{ oe} < Hc < 300$ oe
3. Soft magnetic materials with $Hc < 10$ oe

6.3.1 Permanent Magnets

These are used for biasing fields in microwave systems, for focusing devices for electron beams, for dc electric motors, and so forth. Until recently, certain Alnico alloys had the highest energy products available at reasonable cost, with values somewhat below 10×10^6 gauss-oersteds. We do not see significant improvements in this figure for Alnico alloys or in the coercivity that can be achieved, as this is already approaching the limit set by coherent rotation. Improvements in the magnetic properties of ferrites, such as barium ferrite, are considered to be even less likely as we are approaching the limit set by saturation magnetization.

For the very highest-energy products certain PtCo alloys have been used, for instance, with values of 9.2×10^6 gauss-oersted. These alloys are very expensive. Recently, there has been a big step forward with the discovery of rare-earth-containing materials such as $SmCo_5$.

Energy products as high as 25 × 10^6 gauss-oersted have been achieved in laboratory magnets by use of some of these materials when prepared by special powder metallurgy techniques. The coercivity of these materials is also very high.

There are several purposeful projects under way with the objective of defining manufacturing methods for the fabrication of rare-earth–cobalt magnets in production quantities. A number of sintering techniques with and without sintering aid additions have been developed that are suitable for the routine manufacture of rare-earth–cobalt magnets with energy products exceeding 15 × 10^6 gauss-oersteds. These powder metallurgy techniques are employed to permit control of the metallurgical microstructure of the magnets, to eliminate the structural damage imparted to the particles during grinding, and to prevent chemical degradation. Both small grain size and the degree of preferred crystal texture and critical microstructure are factors in the production of high-energy product magnets. Techniques other than the powder metallurgy approach are also being explored with encouraging early results. The production of magnets by sputtering or by mechanical working methods such as extrusion and swaging appear to be reasonable production process candidates for the manufacture of the large number of magnet shapes and sizes required by the variety of applications for high energy, permanent magnets of the rare-earth–cobalt type.

As noted above, rare-earth–cobalt magnets offer many advantages over existing materials, particularly their high-energy product and very high coercive force. In certain permanent magnet applications, the reduction in the quantity of permanent magnet material that is required in a given device may result in system cost savings when rare-earth–cobalt magnets are substituted for cast Alnico 5 magnets. An example might be magnets used in satellites. At the present time, the cheapest high-energy products, high coercivity permanent magnet materials, are cast Co-Cu-Ce-rich mischmetal* alloys; powder metallurgy techniques to prepare these magnets are not required.

The high residual induction and very high coercive force of the magnets offer greatly increased freedom from device design and performance limitations imposed by the required magnet shape and size of demagnetization characteristics. The high reliability of permanent magnet devices and the advantageous design factors of rare-earth–co-

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***Mischmetal–An alloy of rare-earth metals containing about 50 percent cerium, with 50 percent lanthanum, neodynium, and similar elements.**

balt magnets have initiated a number of new device developments. In electronics, the primary applications are in microwave amplifier tubes and sources of compact, low cost, light weight, reliable bias fields for solid-state microwave devices or other solid-state devices including magnetic "bubble" devices. At the present time, electrical and mechanical functions for the new magnets are more numerous than the electronic. Some of these applications such as gyros and accelerometers, motors and generators, or magnetic bearings and seals are often components of a total system that contains extensive electronic components. The rapid rate of development of the magnets and the promise of additional energy product gains of up to 100 percent is stimulating an increasing amount of new permanent magnet device development activity, which suggests a considerable increase in the role of permanent magnets in the advancement of technology.

Presently, there is a considerable effort in this field of activity directed at empirical improvements of the state of technology. There is, however, a great need for an improved understanding of the whole subject. The basic reasons for the high-energy products and high coercivities are not really understood, and the reasons why casting methods, which offer real economic advantages, are not successful, remain a mystery.

6.3.2 Semihard Magnetic Alloys

These have been developed for situations requiring coercive force control, high squareness, and high saturation magnetization. Examples of applications are permanent and electrically alterable memories, miniature switches, and hysteresis motors.

The distinguishing feature of work with the semihard magnetic alloys has been the development of means of controlling coercive force within close limits while maintaining high values of squareness and saturation magnetization. For example, the electrically-alterable piggyback twistor memory makes use of two alloys, FeCoAu and NiFeMo, in tape form for information storage and information sensing. The compositions of these alloys and the manner in which tapes are formed from them must be adjusted so that specific closely controlled values of coercive force and squareness can be simultaneously produced in them by a short-duration heat treatment.

Further development of semihard magnetic alloys will likely continue for applications where device feasibility depends critically on the close control of several magnetic properties. While we expect no new breakthroughs in this area, the successful development of new alloys will depend upon the investigation of compositional and structural dependence of basic magnetic properties.

6.3.3 Soft Magnetic Materials

These are widely used, for instance, as transformer cores or in certain memory devices. Again, no great breakthroughs are expected here, although specific advances will come as they are needed. Materials have been available for several years with initial permeability of nearly 200,000, maximum permeability of approximately 1,000,000, and, in grain-oriented form, squareness ratio of about 0.90. Improvements have been slow to come; for instance, permalloy has been developed for piggyback twistor memories with a squareness ratio of 0.95 in place of 0.90. In fact, improved alloys are available for this use, but they have not yet been employed for there is no commercial market pull for their adoption.

While tremendous advances over the last 50 years have been made in the Fe-Si alloys for use as transformer cores, it is not likely that this will continue, and so there are no requirements for large-scale additional support here.

An area that is still under active development is one that involves the thin-film deposition of materials such as Ni-Fe (permalloy). These films may be deposited on a planar structure or as plating on a wire. They have application as computer memories, for switching times are not limited by the film but rather by the rise time of the drive current. Domestic and Japanese manufacturers are using plated wire, but we do not expect this to be a technology that will gain the ascendancy over other magnetic memory systems. Most of the development effort goes into process and metallurgical control. Such control is very important, for the information is written into a continuous medium where there is the possibility of interaction of the bits of information. Unless the material is very homogeneous, this interaction can lead to errors. We believe that this is one reason why the tendency in magnetic memories is toward discrete magnetic elements such as ferrite cores.

6.3.4 Summary of the Ferromagnetic Materials

It seems that while certain major advances are being made, such as the rare-earth magnets, and while there is still the need for increased understanding in certain areas, generally, as with the ferrites, we have a mature technology. Advances will come from materials and process work, but such work should be inspired by specific device requirements, not by general hope that something good inevitably will come from it.

6.4 MISCELLANEOUS APPLICATIONS

6.4.1 Magneto-Optics

1. Certain ferromagnetic materials have been discussed as being useful for modulating light beams by means of the Faraday effect. This could be used for display of memory devices.

Varying magnetic fields will alter the Faraday effect in YIG; devices have been built to operate at room temperature at several hundred megacycles. The crystals only transmit satisfactorily in the infrared, but this could be useful particularly for chopping the emission from GaAs lasers. Presumably, the search should go on for materials with useful magneto-optical properties in the visible part of the spectrum. Such devices, if discovered, would then be in competition with electro-optic modulators.

2. Films of magneto-optical materials are being investigated for memories with thermomagnetic write-in and magneto-optical read-out. These show promise for high-storage-capacity, erasable memories with fast accessing. The films are maintained in the presence of a biasing field not large enough to reverse the magnetization of the film. If a spot on the film is heated above the Curie temperature—for instance, by a laser beam—when the spot cools it will have the opposite magnetization, and can now be detected optically.

A variety of film materials have been used, for instance, garnets, EuO, and a metallic film of MnBi. Improvements in the materials could come through optimizing parameters such as the Curie temperature, anisotropy, magnetization, Faraday rotation, and optical absorption. Alloys such as CrTe, Mn_5Ge_3, and MnAlGe are being considered to achieve these improvements.

While improvement in magnetic materials will help in this field, it should be noted that improvements are also required in laser, light deflectors, and light valves before this class of device is likely to come into widespread use.

6.4.2 Ferromagnetic Semiconductors

Ferromagnetic semiconductors (rare earth chalcogenides and chromium spinels) have been of considerable theoretical and experimental interest. The large effects of magnetic fields on the electronic and optical properties of these materials have been studied, but do not seem to be useful at present. The low Curie temperatures of most of these materials and the inherent temperature sensitivity of the large effects will probably limit their utility. In fact, there seem to be easier ways to affect electrical and optical properties by a magnetic field if that is what one wants to do. There has always been hope of combining in some way electronics and permanent magnetic memory in the same material, using these magnetic semiconductors, but so far no one has thought of a practical way of doing it.

6.5 PROJECTED NEED FOR FURTHER WORK (TABLES 6-1, 6-2, 6-3)

6.5.1 Materials (Table 6-1)

1. Work on surface properties and granular perfection, precise composition, fabrication techniques such as coprecipitation, spray drying, freeze drying
2. Larger single crystals, and growth technique for new materials
3. Slight effort at increased understanding

TABLE 6-1 Projected Need for Further Work–Materials [a]

	Basic Research, >10 Years	Applied Research, 5–10 Years	Development, <5 Years
Square loop ferrites			1
High Q and high permeability ferrites			1
Microwave ferrites	3	2	1
Hard ferromagnets	4		5
Soft ferromagnets			
Magneto-optics		6	
Magnetic semiconductors	7		
Magnetic bubble domains	8	9	

[a] See 6.5.1 for explanation of numbers in columns.

4. Increased understanding of rare-earth–cobalt permanent magnet materials

6. Slight effort—better materials could help but other advances are necessary

7. Basic research in the hope of combining the performance of magnetism with the ease of access of semiconductors

8. Higher bubble mobility needed

9. Improvement of substrate and epitaxial materials

6.5.2 Processes (Table 6-2)

10. Optimization of heat treatment, atmospheric control during firing, cleanliness, surface preparation

11. Work needed on preparation and magnetization; e.g., pulverization and alignment, dispersion in molten copper, and alignment during solidification

12. Some work to support plated-wire memory

13. Processes associated with gas-phase and liquid-phase epitaxial growth and surface preparation are in need of support

6.5.3 Devices (Table 6-3)

Devices will benefit from improved rates of assembly and testing of ferrite cores in memory arrays

14. Innovative design is needed for microwave-phase shifters and, indeed, for generally integrated microwave technology

TABLE 6-2 Projected Need for Further Work—Processes[a]

	Basic Research, >10 years	Applied Research, 5–10 years	Development, <5 years
Square loop ferrites			10
High Q and high permeability ferrites			10
Microwave ferrites			10
Hard ferromagnets		11	11
Soft ferromagnets			12
Magneto-optics			
Magnetic semiconductors			
Magnetic bubble domains		13	13

[a] See 6.5.2 for explanation of numbers in columns.

TABLE 6-3 Projected Need for Further Work–Devices [a]

	Basic Research, >10 Years	Applied Research, 5–10 Years	Development, <5 Years
Square loop ferrites			Devices
High Q and High permeability ferrites			
Microwave ferrites		14	
Hard ferromagnets			
Soft ferromagnets			
Magneto-optics		15	
Magnetic semiconductors			
Magnetic bubble domains	16	16	16

[a] See 6.5.3 for explanation of "Devices" and numbers in columns.

15. The device needs for magneto-optics are for more reliable and economical lasers and for means of addressing the laser beam

16. The device needs for successful use of magnetic bubble materials include good detectors for the bubbles and, to go along with these, good low-level amplifiers

7 Composite Structures

7.0 INTRODUCTION

The presence of two or more chemically dissimilar materials in semiconductor device structures generally introduces additional problems which must be considered during design, production, and service phases. In this chapter, the problems arising from a number of the more widely used combinations of materials are considered.

There is considerable controversy regarding a convenient descriptive term for structures made of such combinations of materials. Although the term "composite" suggests to many people fibrous or other mixed structural materials rather than electron devices, composite is the correct adjective for the present case* and its use in the term "composite structures" is preferred by the Committee.

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* From Webster's New International Dictionary, Second Edition:

"COMPOSITE, COMBINATION, COMPOUND are here compared only in their adjective uses as elements in the names of certain appliances, apparatus, or manufactured products. COMBINATION suggests an object designed or constructed to serve more than one use or function; as, a *combination* bicycle, car, pedal, plane. COMPOSITE suggests an object made by combining different, sometimes heterogeneous parts; as, a *composite* photograph, beam, ship, carriage. COMPOUND stresses the complexity of the component parts; as a *compound* microscope, lever, steam engine, locomotive."

All solid-state devices are, in fact, composite structures. In the simplest case, the semiconductor or other active material is connected to the external circuit by means of attached metal conductors. In more complex situations, an interface between two dissimilar materials may form the active region of the device.

The following composite structures are considered:

1. Metal–insulator–semiconductor
2. Metal–semiconductor
3. Metal–insulator
4. Semiconductor–insulator
5. Metal–diamagnetic insulator–nonmagnetic insulator

In many of these structures, the metal is in itself a composite of several elements sequentially deposited to ensure adhesion to the substrate, to inhibit unwanted reaction with the substrate, and to ensure reliable interconnection.

Uses of these structures in electronic components are described, trends in the usage of these structures are projected, problem areas related to the presence of two or more dissimilar materials or an interface are identified, and actions to solve these problems to advance the state of knowledge in this area are recommended.

7.1 USES OF COMPOSITE STRUCTURES IN ELECTRON DEVICES

7.1.1 Metal–Insulator–Semiconductor (M-I-S) Structures

This combination of materials is widely used in diverse types of solid-state devices. Three types of interface active devices have been identified. Best known is the insulated-gate, field-effect transistor, variously described as IGFET, MOSFET, and MISFET, a majority carrier device usually constructed of aluminum, silicon dioxide, and silicon. Several semiconductors other than silicon have been investigated for use in this application. These include gallium arsenide, cadmium sulfide, silicon carbide, and tin oxide. The criteria for selection of semiconductors for this application include high carrier mobility and a low charge-density at the interface with a compatible high-quality insulating film. At present, lowest interface charge-densities are obtained with oxide films grown on silicon. Of the other materials listed, an insulating film can be grown directly only on silicon carbide.

Besides silicon dioxide, aluminum oxide and silicon nitride have been extensively investigated as insulator films for IGFET's. A desirable insulator must have a low interface charge and a high dielectric constant. To reduce susceptibility to radiation damage, a short electron range and a high degree of preradiation perfection are desired.

Metals other than aluminum have not been extensively used for IGFET's; some other metals now being considered are chromium/gold, titanium/platinum/gold, tungsten, and tungsten/molybdenum.

Recently, a new device based on the M-I-S structure was announced. Charge-coupled devices, based on minority carrier storage and transfer, can be used for imaging, memory, and other functions. Despite design and operational differences, the requirements for the insulator–semiconductor interface are similar to those of IGFET's. First devices were fabricated from silicon and silicon dioxide with chromium/gold metal electrodes.

The third interface active device is a memory device based on charge storage at the interface between the two insulators in an aluminum-silicon nitride–silicon dioxide–silicon structure.

Another major application of the metal–insulator–semiconductor structure is in the passivation of silicon devices constructed by the planar process. Silicon dioxide, sometimes covered or combined with silicon nitride, is the most widely used insulator; interconnections are almost always aluminum. In this application, the insulating film whose primary use is passivation of the semiconductor separates the semiconductor from the conducting metal. The thin insulating film must be of high resistivity, impervious to the ambient atmosphere and without conducting paths.

To a much lesser degree, passivation layers of this type have been used in other semiconductors such as germanium, gallium arsenide, or gallium phosphide. The insulating film is generally chemically vapor-deposited or sputtered silicon dioxide.

7.1.2 Metal–Semiconductor Structures

Metal films are used to make ohmic contacts and Schottky barriers on semiconductors. Aluminum is the principal contact material for silicon devices. Platinum silicide is used in special cases for ohmic contacts. Gold is frequently used for eutectic die attachment. Aluminum-germanium is being investigated as a low-Z substitute for gold die attachment.

Silicon and gallium arsenide are both used in Schottky barrier devices. Metals are chosen for the desired Schottky barrier height. Some common materials used on silicon are molybdenum, platinum silicide, nickel, and aluminum; gold is commonly used on GaAs.

7.1.3 Metal-Insulator Structures

Metal-insulator structures where the fact that the insulator is on a semiconductor substrate is pertinent to device performance are covered in section 7.2.1. In this section, metal–insulator structures, such as capacitors, resistors, interconnections and crossovers, whose operation is independent of the substrate are covered. The principal discrete film capacitor is tantalum–tantalum dioxide. Film resistors of nickel-chromium alloys and various silicides are common. As mentioned previously, aluminum is the most widely used interconnection material; molybdenum–gold, titanium–platinum–gold, molybdenum, aluminum–silicon, gold–copper, and aluminum–copper are among the metal combinations being investigated for this application. Recently, a metal–metal oxide-metal structure has been investigated as a mixer in the millimeter wave and infrared regions. A number of material combinations have been tried; best results to date have been achieved with a tungsten point on a nickel alloy base.

7.1.4 Semiconductor–Insulator Structures

Semiconductor films epitaxially deposited on insulating substrates offer a number of advantages for many applications. The most widely investigated systems are silicon on sapphire and silicon on magnesium–aluminum spinel. Layers of gallium arsenide have also been deposited on magnesium–aluminum spinel and on the semi-insulating forms of gallium arsenide. Heteroepitaxial growth of one semiconductor on another also frequently offers advantages. This type of structure is considered in the compound semiconductor section of this report.

7.1.5 Magnetic Epitaxial Layers

A structure recently under investigation for magnetic bubble applications consists of one or more layers of garnet epitaxially grown on nonmagnetic garnet with a metallic pattern deposited on top. This structure is considered in the chapter on magnetic materials.

7.2 TRENDS

7.2.1 Future Device Requirements

Need for a wide variety of new or improved device structures is anticipated for future electronic systems. Although discovery of new phenomena or interactions may shift emphasis and requirements in the future, presently projected device needs are based on concepts that have been previously developed. Many of these needs cannot be met with existing materials, processing techniques, and designs.

In the composite structures area, several specific device and processing requirements have been identified:

1. Radiation-hardened IGFET's
2. Improved memory devices
3. Improved device passivation
4. Detectors for ambient gas constituents
5. Improved contacting, interconnection, and isolation
6. Electroluminescent devices compatible with IC technology

7.2.2 Materials Projections

Because of the advanced state of its technology, silicon appears to be the logical choice for all applications for which it is suitable. Even though devices based on silicon and related materials are expected to serve for many applications, improvements in radiation hardness and resistance to pulse burnout as well as reduction in life-cycle costs, size, and power consumption are desired. Some of these objectives cannot be met without the application of some new materials, preferably compatible with silicon technology. Silicon devices are not suitable for very-high-temperature applications or for some specialized functions, and new materials will have to be developed to fill these needs.

This suggests that emphasis should be placed both on improved yield and better understanding of silicon-based structures and on investigation of less widely used materials. Some of the thrusts in the first area, such as improved process control techniques and larger, more defect-free silicon crystals at reduced cost, are considered in the chapter on elemental semiconductors. From a composite structure viewpoint, the need is for improved characterization and control of insulators, metals, and the various interfaces now being employed in devices.

Good semiconductor–insulator interface properties can be achieved with silicon if thermally-grown silicon dioxide is used as the insulator. This system leaves much to be desired with respect to sealing the interface from the external atmosphere. Hence, overcoats and other insulators are being actively investigated. Properties of the silicon–insulator interface are not the only concern. It is also necessary to consider the interfaces between metals and the insulator and any insulator–insulator interfaces that may exist in the structure.

Requirements for metal films are perhaps even more specialized so it is difficult to lay down universal rules in any detail. In any instance, mechanical, electrical, and technological compatibility are necessary. Improvements in characterization and understanding are essential to place the search for new metal/metal combinations on a more solid footing in addition to determining the adequacy and usefulness of known metal/metal combinations.

The question of new semiconducting materials for various applications is considered in the chapters on elemental and compound semiconductors. Here it is necessary to consider the impact of such new materials on composite structures. Insulator and metal films suitable for use on these materials will be needed. One particularly difficult requirement is that of good interface properties at the semiconductor–insulator interface. These are particularly difficult to achieve unless the insulator is grown on the semiconductor.

Another perhaps more basic application of composite structures is in the rapid examination of new materials. The advent of semiconductor alloys has raised a host of difficult questions requiring substantial experimental and theoretical research. It has been increasingly apparent that epitaxy provides a versatile way of growing single crystals for both science and technology. The two basic approaches, liquid epitaxy, and gas-phase epitaxy, have found applications for different materials in different ways. For example, sublimation works for the IV–VI compounds but fails almost completely for the group IV semiconductors. Conducting initial experiments on single-crystal films allows the investigator to get first-cut knowledge of material properties and thereby reduce the time and effort needed for deciding which alloys have properties of potential interest.

7.3 Problem Areas

7.3.1 Defect and Impurity Interactions

The most significant materials problem in the composite structures area involves the characterization and understanding of defect and impurity interactions in insulating films and at insulator–metal, insulator–semiconductors, and insulator–insulator interfaces. Control and understanding of defects and impurities is instrumental in meeting the first four device requirements listed in 7.2.1, as well as a portion of the fifth.

This problem is complex and has many facets. Temperature-induced effects include diffusion and reactions at interfaces and electrodes. Electric-field-induced effects include ion migration and surface charge buildup. Radiation-induced effects may arise from in-process radiation (such as electron-beam deposition of metal films, sputtering, or ion implantation) as well as from weapon or space radiation.

A particularly serious, immediate aspect of this problem is the apparent strong influence of hydrogen on the characteristics of silicon dioxide. Another aspect concerns the interface states between the silicon nitride and silicon dioxide layers in a memory device structure. Additionally, successful identification of more radiation-tolerant insulating films cannot occur without better knowledge of defect-impurity interactions.

7.3.2 Continuity of Deposited Metal and Insulating Films

Integrity of both metal and insulating films is absolutely essential for device performance. Discontinuous films may arise because of manufacturing defects, such as cracks and scratches in metal films or pinholes and other minute conducting paths in insulators, or they may occur subsequently, as in electromigration of aluminum stripes or the chemical attack on very-thin-film nickel–chromium resistors.

One important problem occurs because of the existence of steps in the surface of the structure. This problem is particularly serious in integrated circuit structures with multilevel interconnection schemes. Integrity of both metal and insulating films becomes more difficult to achieve if the steps cannot be made with sloping sides. Another important problem is the integrity of crossovers of metal films.

The opposite problem also occurs in making multilevel interconnections because it is essential to form small conducting ("via") paths between layers at the desired points. A high resistance or open path can render the circuit inoperative.

Adhesion of dissimilar films can also be a significant problem. Die attachment and bonding pads are particularly critical points. A related problem is the stress set up in such combinations or in heteroepitaxial films as a result of temperature changes during fabrication or operation.

One problem of this type has been solved recently. The difficulties with gold-aluminum connections, long thought to be associated with colorful but brittle intermetallic gold-aluminum compounds and known by names such as "purple plague" and "white plague" have been traced to voids associated with the formation of the intermetallic compounds. Conditions which enhance or retard void formation have been identified, and it is possible to avoid failure from this cause if suitable precautions are observed.

7.3.3 Film Preparation

Despite the considerable study of film growth under idealized conditions, enough is not yet known concerning the growth of thin films in realistic cases. As films are prepared at lower temperatures or as film thickness is reduced, the significance of this problem increases.

Characterization techniques necessary to control film properties are not yet fully developed. In many cases, problems are increased multifold when the specimen to be characterized is a thin film, particularly if it is on a substrate or another film that interferes with the measurement.

7.3.4 Effects of Organic Encapsulants

Organic encapsulating materials on devices present a different sort of interface problem. The organic material may stress the device as it cures, constituents of or impurities in the organic material may corrode or affect the electrical properties of the device, or the organic material may allow the passage of undesirable atoms. These problems are taken up in Chapter 9, Organic Dielectrics.

7.4 RECOMMENDATIONS

The recommended research and development for composite structures is summarized in Table 7-1. The recommendations are described below.

TABLE 7-1 Research and Development Matrix for Composite Structures [a]

	Basic Research	Applied Research	Development
Materials	Control of properties of insulator or interface (interface doping) 7.4.3	Chemical approach to study of localized defects in insulator films 7.4.1	Metal films for specific devices 7.4.9
	Study of defects in bulk insulators 7.4.1	New materials to control surface-charge build-up on passivation layers 7.4.5	Integrity of dielectric films 7.4.6
	Control of dielectric-dielectric interfaces in multi-layer dielectric films 7.4.12	Effect of ambients on exposed insulator films 7.4.8 Characterization techniques 7.4.7	Hydrogen in SiO_2 7.4.4
Processes	Greater understanding of sputtering process 7.4.11 Growth mechanisms in real cases–application to very thin films 7.4.11	Process control techniques 7.4.7	
Structures	High-temperature M-I-S systems 7.4.10	Metal–insulator interface properties 7.4.2	
		Methods for characterizing properties of composite structures 7.4.7	
Devices	I-C/Electroluminescent device compatibility 7.4.10 Charge-transfer mechanism under the field plates of charge transfer devices 7.4.13	Gas detectors 7.5.8	

[a] See appropriate paragraph for details of conclusions and recommendations.

7.4.1 Emphasize the Chemical Approach

Emphasize the chemical (localized) approach rather than the solid-state physics approach in the study of insulating films and associated interfaces.

To increase the control and understanding of defect and impurity interactions in insulating films and at associated interfaces, it is necessary to investigate the localized nature of bonds in oxides and other insulators and at the interface. This chemical approach to the problem is expected to be more fruitful than continued efforts based on the more traditional solid-state physics approach because the one-electron model, the mainstay of the latter approach, is not completely satisfactory in dealing with wide bandgap materials.

Experiments designed to reveal specific information concerning localized properties of the structure should be carried out. These experiments should be performed in conjunction with electrical measurements on M-I-S structures in order to relate defect and electrical characteristics.

Radiation effects studies would be expected to be a very valuable experimental technique in elucidating the defect properties in ways similar to their application in the field of semiconductor crystals. In addition, understanding of radiation effects in their own right will become more important not only from the viewpoint of external radiation environments, but also because of the increased use of radiation in device processing. Fundamental understanding of bulk insulators is another key to the development of understanding of insulating films.

Both intermediate and long-range efforts must be undertaken. A critical short-term effort is discussed separately (see Recommendation 7.5.4). Two critical long-range areas of fundamental research are also discussed separately (see Recommendations 7.4.12 and 7.4.13).

7.4.2 Metal–Insulator Interface in M-I-S Structures

Increase efforts directed toward understanding of the metal-insulator interface in M-I-S structures.

Heretofore, most of the research effort on M-I-S structures has concentrated on the insulating layer and the insulator–semiconductor interface. Knowledge of the influence of the metal and the metal–insulator interface is meager. Nevertheless, the nature of this interface may affect device operation significantly. Short- and intermediate-range efforts can be expected to be fruitful.

7.4.3 Techniques for Controlled Doping at Insulator–Semiconductor Interfaces

Initiate directed long-term research activity to lead to techniques for controlled doping at insulator–semiconductor interfaces.

It is being increasingly recognized that greater control over the type and density of the various impurity and defect centers in semiconductors is essential in order to predict or control carrier lifetime and radiation response. Such control is even more important in device structures whose operation depends on interface characteristics. Long-term research directed toward solution of this problem would build on the knowledge developed both in the studies of the localized nature of defects in insulator films and in the studies of "lifetime doping control" in semiconductors and would be a logical extension of that work. Considerable basic research effort with a very-long-term payoff is required if interface doping control is to be achieved. Both greater understanding of material characteristics and improved methods for identifying and counting impurities in the insulator must be developed.

7.4.4 Understand and Control the Properties of Hydrogen in Silicon Dioxide

Conduct an intensive, short-term effort designed to understand and control the properties of hydrogen in silicon dioxide.

An immediate problem of high technological interest is the influence of hydrogen on the characteristics of silicon dioxide. This is a specific example of the importance of understanding of impurity interactions in insulating films. The presence of small amounts of hydrogen in the ambient gas during device-annealing treatments appears to have an adverse effect on the stability of some devices, but the reasons for this are not yet completely understood. Intensive, short-range effort is needed to solve the problem.

7.4.5 New Materials To Control Charge Buildup on Insulating Layers

Search for new materials to control surface-charge buildup on insulating layers.

The principal requirements imposed on films used for passivation of device surfaces are that they be high-resistivity, impervious to the ambient atmosphere, and without conducting paths. A major need for such films is the development of surface treatments or overcoating materials that will act to control the buildup of surface charge.

7.4.6 Causes of and Cures for Lack of Integrity in Dielectric and Metal Films

Encourage intensive, short-term efforts to seek causes of and cures for lack of integrity in dielectric and metal films.

With the increasing use of multilayer interconnecting schemes, the occurrence of conducting paths in undesired locations in the insulating layer between conductors has become particularly serious. Such conducting paths may exist even in the absence of mechanical holes. In addition, electromigration and other problems related to discontinuities in thin metal conductive or resistive films are far from solved. Intensive short-term efforts may be needed to solve specific problems. In particular, means for improving the edge profile of etched-film structures, methods for avoiding the introduction of defect regions and holes across the film thickness, techniques for reducing electromigration effects, and techniques to reduce corrosion effects in metal films are needed. Additional research on gold-aluminum compound formation, "purple plague," etc., is not required. Since most such problems are very close to the manufacturers' interests, contract support is expected to be needed only where a particular problem affects a system now in the final development or procurement phase. It is to avoid this kind of "fire fighting" in the future that other longer-range basic and applied research efforts are being recommended in this chapter.

7.4.7 Develop Suitable Methods for Characterizing Composite Structures and Their Constituent Parts

Undertake intermediate-range efforts to develop suitable methods for characterizing composite structures and their constituent parts.

Fundamental to the understanding of film and interface properties is the ability to measure various quantities. Measurements must be made on isolated films as well as on the structure or portions of it. These measurements are essential to the control of the fabrication process as well as for characterization of materials and devices. Research and development on characterization methods is a traditionally neglected area. Increased support of these activities on a medium to long-range basis is needed to provide adequate techniques in a timely manner.

7.4.8 Gas Detectors Based on M-I-S Structure

Expand efforts directed toward understanding of permeability of insulator films to constituents of ambient gases that will lead to the development of gas detectors based on the M-I-S structure.

Sensitivity to ambient gases would be a property studied in the chemical approach to investigating M-I-S structures and such research might be expected to identify systems appropriate to the detection of certain gaseous pollutants in the atmosphere. This sort of information should be explicitly sought and directed to the development of devices for atmospheric monitoring and pollution control.

7.4.9 Metal Film Systems for Contacts and Interconnections

Encourage the development of suitable metal film systems for contacts and interconnections on specific device structures as needed.

Development of specific metal systems must be tied quite closely to the particular device under development. The general principles that must be employed in studying metal systems are mechanical compatibility with adjacent materials, compatibility with processing technology (including exposures to high temperatures and corrosive chemical etchants), and electrical compatibility with the device. Because these developments are tied so closely to specific device developments, general contract support in this area should be extended only in very special cases.

7.4.10 New Material Development

Undertake fundamental research activity directed toward the development of new materials for use in devices based on composite structures.

Long-range research programs are essential to provide the materials needed to meet future system requirements. Silicon carbide and tin oxide are materials that may prove to be suitable for use in high-temperature M-I-S devices. One of the advantages of silicon carbide arises from the fact that silicon dioxide layers can be grown on its surface. There is also need for considering other high-mobility, high-bandgap materials for high-temperature applications. Another area that can be identified now is the development of integrated circuits with compatible electroluminescent devices such as those from gallium phosphide. Finally, it must be recognized that some relatively undirected effort is essential to uncover new materials whose properties may be exploited in the future.

7.4.11 Better Understanding of Film Growth

Undertake fundamental research activity directed toward better understanding of film growth.

In considering growth and nucleation problems, it is necessary to apply the studies to realistic cases rather than strictly idealized cases. The important aspects are surface preparation, method of applying the film, definition of a pattern, and characterization of the resulting structure. Principal emphasis should be directed toward better understanding of the sputtering process and of the morphology and characteristics of very-thin films.

7.4.12 Control of the Dielectric–Dielectric Interface in Multilayer Dielectric Films

Undertaking fundamental research activity directed toward understanding properties of the dielectric–dielectric interface in multilayer dielectric films.

It can be expected that a majority of future M-I-S devices will employ multilayer dielectrics in order to achieve combinations of threshold voltage, breakdown voltage, and stability that cannot be obtained with single layers. Problems of fabricating such multilayers with a high degree of control of interface and other characteristics over a wide range of thicknesses must be studied and the effect of charge accumulation at the dielectric–dielectric interface be determined.

Combinations of existing dielectrics such as silicon dioxide, silicon oxynitride, silicon nitride, and aluminum oxide would probably receive primary emphasis at first, but consideration must also be given to new dielectric materials.

7.4.13 Charge Transfer Mechanism under the Field Plates of Charge Transfer Devices

Undertake a fundamental research program to explore the charge transfer mechanism under the field plates of charge transfer devices.

This study is urgently needed to permit a thorough assessment of the potential of charge transfer devices for fast shift registers and other M-I-S applications. Of interest are a determination of factors that inhibit the complete transfer of the charges from one plate to the other and understanding of the dynamics of free carriers under diffusion and drift modes of motion. Trapping effects at interface states must also be considered and structures determined where the amount of charge lost in transfer is kept to a minimum.

8 Inorganic Dielectric Materials

8.0 INTRODUCTION

It is not easy to give a coherent picture of the field of inorganic electronic materials. There is no unifying theme or continuous history to allow presentation in a logical or even a chronological order. For certain applications, these materials could be defined as high-resistance semiconductors, an area to be covered in another chapter. Some applications may fall in the field of physical electronics. The approach chosen here has been to present as broad a spectrum of inorganic electronic materials as possible in the hope that few critical and unconventional areas will be overlooked.

The classification method chosen is far from ideal and is certainly not the only one possible. We have chosen to categorize by application rather than, for example, by material property, feeling that this will be more useful in the task of recommending research priorities. The broad subdivisions are according to the segment of the electromagnetic spectrum being used.

Because of the breadth and diversity of material types to be classified, we have attempted to condense the information into several tables (Tables 8-1, 8-2, 8-3). Thus, while we have listed and commented on each material category in the text, it is possible for the reader to scan the tables for an abbreviated summary of the materials and related significant information.

In the tables, the classifications are listed under the heading *Functions*. To clarify the material classifications a list of *example materials* is included. These are not necessarily intended to represent materials recommended for further research, but simply materials existing today that have been explored and/or put to use in the corresponding applications.

The remaining columns in the tables are intended to summarize in very abbreviated form the technical status, difficulty, and urgency associated with the respective material and function. A few words are given under *Technical Problems* pinpointing key property or processing difficulties that have been encountered. *Scale in Use* gives a rough index of the commercial status–laboratory level or production scale, followed by a column giving an estimate of the time to reach satisfactory level of commercial application. Finally, an indicator is given of economic effectiveness of the processes now used or contemplated for the corresponding material group, which bears some relationship to the priorities of work needed.

8.1 FUNCTIONAL CLASSIFICATION TABLES

8.1.1 Optical Frequencies

8.1.1.1 FIBER WAVEGUIDES

These devices offer potential for economic high information rates in communications. There are problems in controlling attenuation and developing handling, installation, etc., techniques for small fibers.

8.1.1.2 MULTIMODE WAVEGUIDES

Conventional fiber optics, or multimode waveguides, require improved transmission for many uses. Transmission in the blue and infrared regions of the spectrum is particularly poor. Added strength is necessary for enduring imposed mechanical stresses.

8.1.1.3 FILM WAVEGUIDES

Coherent optical processing could utilize miniature film circuits somewhat analogous to integrated circuits today. The whole technology for these compact, fast devices needs to be developed.

TABLE 8-1 Applications of Inorganic Dielectric Materials–Optical Frequencies

Functions	Examples of Materials	Technical Problems	Scale in Use[a]	Years R&D Required	Process Cost-Effectiveness
1.1 Fiber waveguides	Glass	Attenuation	L	3-10	High
1.2 Multimode waveguides	Glass	Attenuation	L-P	3-5	High
1.3 Film waveguides	Glass	Patterning, attenuation	L	3-15	Medium
1.4 Windows	Hot-pressed II–VI's, glass, germanium	I.R. and U.V. transmission, chemical durability	P	3-5	High
1.5 Interference filters	ZnS-MgF_2, CeF_4-ThO_2	Control of transmission, optical damage	P	3-5	Medium
Active devices - incoherent light					
1.6 Photochromic	Silver-doped glass, iron-doped titanates	Sensitivity, bleaching	P	3-10	Medium
1.7 Cathodochromic	Iron-doped titanates	Sensitivity, fatigue	S	3-10	Medium
1.8 Phototurbid	Crystallizable glasses	Speed, range of wavelength sensitivity	L	3-10	Medium
1.9 Photomagnetic	Europous compounds, MnBi	Speed, range of wavelength sensitivity	L	3-10	Medium
1.10 Phosphors:					
U.V. sensitive	Doped ZnS	Efficiency	P	3-5	Low
X-ray sensitive	Doped ZnS	Efficiency	P	3-5	Low
Electron beam-sensitive	Doped $BaSiO_3$, YVO_4	Efficiency, transparency	P	3-10	Medium
Electric field charge sensitive	Doped ZnS	Efficiency, frequency sensitivity, fatigue	P	3-10	Medium
Infrared to visible sensitive	Rare earth doped crystals	Efficiency, range of wavelength sensitivity	L	3-10	Medium
1.11 Photocathodes	Bi, Sb, alkalis	Uniformity of sensitivity, lifetime, control	P	3-5	Low
1.12 Secondary electron emitters	Cu:BeO	Uniformity of sensitivity	P	3-5	Low
1.13 Thermopiles and bolometers	Coated copper-constantan, Pt	Speed, sensitivity	P	3	Low
1.14 Pyroelectric detectors	Ferroelectric crystals	Sensitivity, speed	L-S	5-8	Medium
Active devices – coherent light					
1.15 Waveguide logic	Electrooptic crystal substrates, etc.	Design, patterning, efficiency	L	5-10	Medium
1.16 Electrooptic modulators, beam deflectors	$LiNbO_3$, $BaNa(NbO_3)_3$	Speed, power, resonances, optical quality, damage	S	5-10	Low
1.17 Photoelastic beam deflectors and modulators	Sapphire glass, alpha iodic acid, water	Speed, sensitivity	S	3-5	Medium
1.18 Bistable electrooptic displays, memories	PZT[b] ceramic, $Bi_4Ti_3O_{12}$	Speed, optical quality, fatigue	L	5-8	Medium
1.19 Second harmonic generators	Potassium dihydrogen phosphate	Optical damage, optical quality	S	5-8	Low
1.20 Parametric amplifiers	$LiNbO_3$	Optical damage, optical quality	S	5-10	Low

TABLE 8-1 *(Continued)*

Functions	Examples of Materials	Technical Problems	Scale in Use[a]	Years R&D Required	Process Cost-Effectiveness
1.21 Glass lasers	Nd^{3+} doped glass	Thermal conductivity, optical damage, photoelastic effect on optical quality	S	3-5	High
1.22 Crystal lasers	Nd^{3+} doped YAG[c]	Optical quality	S	3-5	Low
1.23 Liquid lasers	Nd^{3+} doped $POCl_3$	Retention of optical quality, efficiency, liquid corrosiveness	L-S	5-8	High

[a] L = laboratory, S = semiproduction, P = production.
[b] PZT = Lead zirconium titanate.
[c] YAG = yttrium aluminum garnet.

8.1.1.4 WINDOWS

Chemically and physically durable materials are needed, especially for the infrared. The region around 10 μm is important.

8.1.1.5 INTERFERENCE FILTERS

This class of materials includes an important subgroup in nonreflecting coatings. Abrasion-resistance and cost need improvement. Development of processes with good uniformity and reproducibility is also needed.

8.1.1.6 PHOTOCHROMIC MATERIALS

All photochromic materials could profit from greater speed (more absorption per darkening photon). In organic materials, undesirable fatigue is shown. Recycling is accomplished by utilizing either thermal fading or optical bleaching. Both techniques are awkward in many applications and selective erasure is not possible.

8.1.1.7 CATHODOCHROMIC MATERIALS

There is a marked similarity between cathodochromic and photochromic materials. Most of the shortcomings above apply to both.

8.1.1.8 PHOTOTURBID MATERIALS

Materials that change their scattering properties, or turbidity, under photoexcitation are similar to photochromics that change their absorption. Few such materials now exist and new ones may suffer in reversibility. However, it presently seems that uses would be similar to photochromics.

8.1.1.9 PHOTOMAGNETIC MATERIALS

This useful effect depends on thermal heating. As such, sensitivity and speed will probably continue to be drawbacks.

8.1.1.10 PHOSPHORS

Considerable effort has been devoted to improving and utilizing phosphors; therefore, the marginal efficiency of further research is considered to be low. Electroluminescent phosphors offer so much benefit, if improved, that they are somewhat exceptional in this regard. Infrared or visible phosphors are also an exception. Being nonlinear, these do not have an easily defined "efficiency." However, their output under any usual excitation is disappointing. This and the use of pumping could be productive lines of research.

8.1.1.11 PHOTOCATHODES

Perfected to a large degree, the wavelength range of sensitivity could still be extended with benefit. Some of the main problems lie in controlling the properties.

8.1.1.12 SECONDARY ELECTRON EMITTERS

Much work has revolved around the use in photomultipliers. A new area has arisen in channel multipliers. Process improvement and control is especially important in this latter case.

8.1.1.13 THERMOPILES AND BOLOMETERS

These thermally sensitive detectors are useful because they operate where other detectors cannot. The thermal principle will limit both sensitivity and speed.

8.1.1.14 PYROELECTRIC DETECTORS

These devices are similar to 8.1.1.13 but their property-change under thermal excitation is more amenable to signal generation.

8.1.1.15 WAVEGUIDE LOGIC

Little has been done in this field. There is a large area of needed research in learning how to accurately make such small devices and in improving their performance in switching optical signals and controlling optical power.

8.1.1.16 ELECTROOPTIC MODULATORS, BEAM DEFLECTORS

These devices have great potential but have been retarded by the small size of the electrooptic effect in most materials and the lack of optical homogeneity. The speed could be higher than photoelastic deflectors noted below, but capacitative effects and resonances are limiting factors.

8.1.1.17 PHOTOELASTIC BEAM DEFLECTORS AND MODULATORS

The more important of these two uses is the deflector. For many applications, photoelastic deflectors are today's preferred solution. Problems of speed and sensitivity (which lead to power consumption) are important. Materials and device design responding in the GHz region especially need improvement.

8.1.1.18 BISTABLE ELECTROOPTIC DISPLAYS AND MEMORIES

Optical readout of stored information is the projected area of application for this class of ferroelectrics and other electrooptic materials. The disadvantages of present materials are aging on storage and loss of sensitivity with repeated interrogation.

These perennial disadvantages of known ferroelectrics in most applications would seem to warrant a more serious attack and search for alternative material classes.

8.1.1.19 SECOND HARMONIC GENERATORS

Of limited use, the primary benefit is in infrared-to-visible conversion. In this context, parametric amplifiers (8.1.1.20) offer more flexibility at somewhat greater cost in complexity.

8.1.1.20 PARAMETRIC AMPLIFIERS

The ability to provide a coherent, tunable source is a highly desirable goal. Problems now include homogeneity of the material, sensitivity to ambient temperature, optical absorption, and optically induced damage.

8.1.1.21 GLASS LASERS

Glass lasers are chiefly useful for high-peak powers (note: *not* for average power). This will probably limit them to use as triggers, special ranging situations, etc. Damage at high-peak power is a problem and warrants work. High-power effects, in general, are an entirely new field that presents opportunity and problems. The reader is directed to NMAB-271 "Fundamentals of Damage in Laser Glass" for a fuller discussion than is possible here.

8.1.1.22 CRYSTAL LASERS

These are the most promising of the lasers using solid dielectric materials. Problems are the same as those in parametric amplifiers (8.1.1.20) but to a lesser degree. Devices with low power consumption (high efficiency) are needed and work on compatible sources that have more efficient pumping (such as diode sources) should be encouraged.

8.1.1.23 LIQUID LASERS

Liquid lasers have not lived up to promise. Many of the superficial advantages, such as material homogeneity, are not real. The difficulty of handling the corrosive liquids is severe. Research should be limited to ideas of demonstrable merit.

8.1.2 Microwave Frequencies

8.1.2.1 SUBSTRATES, STRIP LINE DIELECTRICS

A relatively high dielectric constant, greater than 10, preferably about 30 to 40, and upwards to 100, is the most important feature differentiating strip transmission line substrates used at microwave frequencies from substrates used at lower frequencies. This requirement is related to the reduction in size of transmission lines obtained with increasing dielectric constant of the substrate. Almost equally important are low loss tangent, temperature stability of the dielectric constant, and high thermal conductivity–as a means of minimizing local heating. Good surface finish and mechanical strength are requisites common to

TABLE 8-2 Applications of Inorganic Dielectric Materials–Microwave Frequencies

Functions	Examples of Materials	Technical Problems	Scale in Use[a]	Years R&D Required	Process Cost-Effectiveness
2.1 Substrates, stripline dielectrics	Al_2O_3, sapphire, titanate ceramic	To obtain high K-low loss tang., low TC,[b] surface finish	L-S	3-5	Medium
2.2 Acoustic delay line, bulk wave devices	Special glasses, crystals	Acoustic losses, delay, time, TC,[b] glass quality	P	2-4	Medium
2.3 Surface wave devices and circuits	Piezoelectric films, substrates PZT,[c] $LiNbO_3$, ZnO	Coupling coefficient, losses, delay time, TC,[b] surface quality	L-S	5-8	Medium
2.4 Transducers, piezoelectric resonators	Thin films of CdS ZnO, $LiNbO_3$	Control of geometry, homogeneity, structure	L-S	3-8	Low
2.5 Resonant cavities	Low thermal expansion material	Machinability, connections, strength	L-S	2-5	Low
2.6 Lenses, antennae	Foam glass	Low density, homogeneity, density-gradient control	L-S	4-6	Medium
2.7 Transparent electrical shielding	SnO_2 or gold-coated glass	Transparency, conductivity	L-S	2-4	Medium

[a] L = laboratory, S = semiproduction, P = production.
[b] TC = thermal coefficient of expansion.
[c] PZT = lead zirconium titanate.

thin film substrates. It is not likely that a single material will be found to meet all requirements.

8.1.2.2 ACOUSTIC DELAY LINE

These devices are based on the propagation and multiple reflection of acoustic waves in a bulk solid. This results in a time delay between the input and output signal. Low velocity of propagation, small attenuation of acoustic waves, and little temperature dependence of these properties are prime requirements. New glass or crystal materials may offer a better combination of these properties; improved homogeneity may result from better forming methods.

8.1.2.3 SURFACE WAVE DEVICES, CIRCUITS

Surface waves are generated by interlocking film electrodes deposited on a piezoelectric body or on a piezoelectric film formed on a passive substrate. Electrode spacing and other dimensions determine R-L-C characteristics. Very small interelectrode spacings are required for high frequency in microwave applications, so that good photolithography is one of the important requirements. The piezoelectric crystals or films should have a high piezoelectric coupling coefficient, a low temperature coefficient, a low temperature coefficient of time delay, and low losses. The delay characteristics are used in pulse expanders or compressors, readers and decoders, matched digital filters, etc. Because of easy access to surface waves, direct coupling to silicon integrated circuits appears to be possible.

8.1.2.4 TRANSDUCERS, PIEZOELECTRIC RESONATORS

In this range of frequencies, the transducer has to have the shape of a very thin crystal or a thin film deposited on the interacting substrate. Property requirements are otherwise similar to other transducers.

8.1.2.5 RESONANT CAVITIES

Materials of very low thermal expansivity could lead to very stable frequency reference sources for microwave systems. Materials that hold dimensional tolerances better than one part in 10^7 per degree could greatly simplify microwave communication equipment designs.

8.1.2.6 DIELECTRIC ANTENNAE

Lightweight low-loss inorganic dielectrics (e.g., foamed dielectrics) have promise in refractive microwave antenna system. Materials with controllable dielectric constant, good strength, and long-term stability over wide temperature ranges are needed.

8.1.2.7 TRANSPARENT ELECTRIC SHIELDING

In some microwave-powered equipment, such as cooking ovens, good visibility is required simultaneously with adequate shielding of the microwave radiation. Glasses provided with a currently available transparent conductive coating do not provide a satisfactory solution.

8.1.3 High–Low Frequency, dc and Power Applications

8.1.3.1 SUBSTRATES FOR EPITAXIAL FILMS

This is one of the most important areas of application in this chapter. Insulating substrates are required for making epitaxial films of silicon, compound semiconductors, and magnetic garnets. Besides these

TABLE 8-3 Applications of Inorganic Dielectric Materials–High-Low Frequencies, dc and Power Applications

Functions	Examples of Materials	Technical Problems	Scale in Use[a]	Years R&D Required	Process Cost-Effectiveness
Substrates, Dielectric Films					
3.1 Substrates for epitaxial films	Sapphire, garnet, Mg-spinel, etc.	Matching structure process	L-S	3-10	Low
3.2 Substrates for thin-film hybrid circuits	Sapphire, Al_2O_3, BeO ceramics	Surface quality, bonding strength, HF-resistivity	L-P	4-6	Medium
3.3 Thin-film capacitors for hybrid circuits	Ta_2O_5, Nb_2O_5, TiO_2, La_2O_3	Wet process step, defects, porosity, reliability	L-S	3-5	Low
3.4 Substrates for hybrid thick film and multilayer circuits	Ceramics: 94–96% Al_2O_3, BeO	Shrinkage, high firing temperature incompatible with many metals, dielectrics	L-P	4-5	High
Capacitive Devices					
3.5 Screen printable crossovers, capacitor films	Lead glasses, glass-ceramics	Firing condition different K-values, dielectric strength	L-P	2-4	Medium
3.6 High Q capacitors	Mica, glass, titanates (NPO)[b]	Volume efficiency, cost versus reliability	P		Medium-high
3.7 High K capacitors	Titanates, niobates	Cost-reliability, aging, ferroelectric effects	P	3-5	Medium-high
3.8 Electrolytic capacitors	Anodized Al, Ta foil, porous slug	Equivalent series resistance, limited operating temperature, size	P	3-5	High
3.9 Solid tantalum capacitor	$Ta/Ta_2O_5/MnO_2$	Anodizing efficiency, yield, frequency limit	P	3-5	High
3.10 Energy storage capacitors	High-density ceramics, crystals	Volume efficiency, dielectric strength, thermal stability	L-S	3-5	Medium
3.11 Capacitive thermometry for cryogenic temperature	Titanate glass-ceramics	Limited high sensitivity range	L-S	2-4	Medium
3.12 Voltage tunable capacitors	Ceramic ferroelectrics	Dielectric breakdown, temperature stability range	L-S	3-4	High
Transducers and Miscellaneous					
3.13 Transducers	Poled ferroelectric ceramics (PZT[c]), crystals	Coupling efficiency, mech. strength, energy losses, polar degradation	S-P	5-6	Medium
3.14 Resonant filters and coupling devices	Poled ferroelectric ceramics, crystals	Coupling efficiency, energy losses, stability	P	3-5	Medium
3.15 Voltage generators	Poled ferroelectric ceramics	Coupling efficiency, polar degradation	S-P	3-5	Medium
3.16 Ferroelastic devices	Gd-molybdate	Crystal size, quality, aging	L-S	5-8	Low
3.17 Thermistors (PTC) TANDEL devices	$BaTiO_3$:La,$SrTiO_3$, Cu-Co-oxide, etc.	Reproducibility, temperature stability	L-P	3-4	Medium
Power Transmission					
3.18 Glass-metal, ceramic-metal seals	Matched pairs	Variety for all uses, strength	S-P	5-8	High

TABLE 8-3 (*Continued*)

Functions	Examples of Materials	Technical Problems	Scale in Use[a]	Years R&D Required	Process Cost-Effectiveness
3.19 High voltage insulators	Ceramics, glasses	Strength, surface resistivity, corrosion resistance	P	5-8	High
3.20 Coatings and Packages	Ceramics, glasses	Need lower processing temperatures	L	5	High

[a] L = laboratory, S = semiproduction, P = production.
[b] NPO = very-low thermal coefficient of capacitance change (Negative-Positive-Zero).
[c] PZT = lead zirconium titanate.

areas of immediate interest, there is need for substrates for ferroelectric and piezoelectric films required for surface acoustic wave and related devices, optical memories, thermal imaging systems, etc. The choice of substrate material depends on lattice constant, thermal expansivity and chemical compatibility with the deposited film. Surface quality is equally critical. Sapphire, various spinels, and gadolinium-gallium garnet are the most used materials. Materials research and characterization, surface preparation for devices, and development of low-cost production processes are all rated as top priority subjects.

8.1.3.2 SUBSTRATES FOR THIN-FILM CIRCUITS

Because of the need for high thermal conductivity and strength—as well as good dielectric properties—alumina and, in exceptional cases, beryllia are the best choice for this application. Surface quality, e.g., flatness, smoothness, and bond strength to the epitaxial layer as well as cost and process reproducibility represent some of the problem areas. For tantalum circuits, resistance to hydrogen fluoride etch is also desirable.

8.1.3.3 THIN-FILM CAPACITORS

There is a definite need for a thin-film dielectric that can be made by vacuum or vapor deposition methods. Ta_2O_5 is the best available to date, but requires anodic oxidation (a wet process) and MnO_2 "self-healing" electrodes. Limitations to the applied voltage are severe and reliable large area units are expensive. Research has the highest priority rating.

8.1.3.4 SUBSTRATES FOR HYBRID THICK FILM AND MULTILAYER CIRCUITS

The tape process and lower-grade alumina (94 percent) are generally used. Surface is less critical whereas cost is very critical in this case. The future lies in multilayer assemblies. Only metallization by molybdenum-manganese alloy or tungsten will endure the necessary firing conditions. The problems encountered in these alumina-based circuits are relatively high resistance of conductors, low resistance of resistors (both caused by the reducing firing), and limited capability to incorporate capacitances in the multilayer circuit. While some of these shortcomings of multilayer circuits may be relieved by R&D on materials and techniques, the main emphasis in effort should be on process improvement.

8.1.3.5 SCREEN-PRINTABLE CROSSOVERS, CAPACITORS

These are applied usually at a temperature below 1000°C to be compatible with silver or gold metallizing. A variety of glasses and glass-ceramics were developed with different dielectric constants. Some of these "frits" may need improvement in dielectric properties, such as higher dielectric strength and a larger choice of dielectric constant values, including greater than 1000.

8.1.3.6 HIGH Q CAPACITORS

Mica and glass capacitors are being increasingly replaced by NPO-type ceramics. These are made by mixing two materials, one with negative, the other with positive temperature coefficient of capacitance, so that a compensated, near-zero value of the temperature characteristic of capacitance is obtained. Sintered (multilayered) "monolithic" construction, used recently, helps the volume efficiency problem. This component is likely to be replaced by either thin- or thick-film technology.

8.1.3.7 HIGH K CAPACITORS

This group comprises very cheap disk capacitors and high-volume efficiency, relatively reliable monolithic capacitors. Cost is largely dependent on the electrode metal (Ag, Au, Pd, etc.). Good temperature characteristics at relatively high K-values (2000-3000) are obtained by mixing ferroelectric ceramics with different peak temperatures. However, undesirable voltage effects and piezoelectric phenomena remain. Another principle controls temperature effects by restricting grain growth, using additives, pressure, or glass-crystallization techniques. These methods are liable either to increase cost or to decrease the K-value. On the other hand, voltage rating is improved and ferroelectric side effects are, to a large extent, eliminated. Effort on a medium priority level is recommended.

8.1.3.8 ELECTROLYTIC CAPACITORS

These units provide the highest capacitances and cannot be replaced by solid-state capacitors. Besides elimination of the corrosive liquid, there are other needs for improvement: lower series resistance and smaller size are desirable; these are considered to be of medium priority.

8.1.3.9 SOLID TANTALUM CAPACITORS

The solid tantalum capacitor is a very successful product; its present-day performance is generally accepted. Still, the process is inefficient; the anodizing potential is 3–4 times larger than the rated voltage. Improvements may be possible to decrease ac and dc losses. A limited research effort is recommended.

8.1.3.10 ENERGY STORAGE CAPACITORS

Improvements are needed in volumetric efficiency and temperature stability. Ceramics, or crystals, can be used with advantage over plastic foil, if the dielectric strength exceeds 800 Kv/cm and dielectric constants over 100 can be realized. Potential distribution at high electric fields (over 10^5 V/cm) in insulating ceramics and crystals becomes nonlinear and is dependent on defects, grain boundary phenomena, electrode configuration, etc. More studies in this area are needed in single-crystal and high-density ceramic systems. Advances made here could also be extrapolated to increase the reliability of other components.

8.1.3.11 CAPACITIVE THERMOMETRY FOR CRYOGENIC TEMPERATURES

The large temperature dependence of the dielectric constant of certain ferroelectrics can be used with advantage in thermometry, especially near liquid helium temperature, because of small power dissipation and insensitivity to magnetic field effects. Materials should be optimized for various temperature ranges and instrumentation developed, as indicated by the cost-effectiveness ratings.

8.1.3.12 VOLTAGE TUNABLE CAPACITORS

Some ferroelectrics with a Curie temperature near 25°C have a dielectric constant that varies by a factor of 5 or more with applied voltage. Key problems are dielectric breakdown strength, frequency, and temperature stability. Some effort in this area appears to be desirable.

8.1.3.13 TRANSDUCERS, RESONANT FILTERS, VOLTAGE GENERATORS

Materials are needed with higher mechanical strength, higher coupling coefficients for different frequency ranges, higher stability, lower losses, and other more specialized characteristics required for a very wide field of applications. These devices can be classified in two groups: single crystal and ceramic transducers. Cost-effectiveness estimates are the same for both transducer and filter applications, somewhat lower for voltage generator uses.

8.1.3.14 FERROELASTIC DEVICES

Whereas in piezoelectrics, including poled ferroelectrics, the materials have an equilibrium state at zero field, ferroelastics are morphologically bistable as well as possessing electrical (remanent polarization) and optical (birefringence) bistability. This could lead to interesting memory-coupled electromechanical–optical devices. Work along this line has been intensive in Japan while it has just been started in the United States. Research and development should receive high priority.

8.1.3.15 THERMISTORS (PTC)–TANDEL DEVICES

Ferroelectric titanates in the semi-insulating state, having very high ac and/or dc losses, are used in positive temperature coefficient (PTC) thermistors and other temperature-compensating devices. This characteristic, obtained by doping with n-type substitutional impurities, is potentially useful and should be better understood as one of the few electrical grain boundary phenomena observable in polycrystalline materials.

8.1.3.16 GLASS-METAL, CERAMIC-METAL SEALS

A wider variety is needed and more strength and/or reliability should be achieved.

8.1.3.17 HIGH-VOLTAGE INSULATORS

Certain problem areas such as strength, surface resistivity, and corrosion resistance need further attention.

8.1.3.18 COATINGS AND PACKAGING

Inorganic hermetic packages and dielectric coatings with low-processing temperatures have received considerable attention for several years, but remain a need in the electronics industry.

8.2 DISCUSSION OF RESEARCH PRIORITIES

8.2.1 Optical Frequencies

Optics presents a significant opportunity for fruitful research because of two needs. The first is the increasing human desire to assimilate information visually. This opens a large area in displays, printing, etc. The second is the increasing need to process information electronically. The high optical frequency has the potential of permitting high data-transmission rates while the short wavelength implies a small diffraction limit with the potential of spatially dense information storage.

The first group of devices, labeled "passive devices," involves no single overall deficiency. These devices build upon materials technology that has previously been employed in optics and hence requires only improvement. In some cases, required improvements may be so extensive that they require entirely new approaches, as in optical fibers.

Active devices encompass a group using diverse optical materials. Many of them exhibit nonlinear effects and/or transformation properties, converting energy from optical to other forms, or the reverse.

Many uses and new effects have arisen, and will arise in the future, from nonlinear effects in materials. Excitation by more than one simultaneous electrical force is used in modulators, transducers, etc. Nonlinear phenomena excited by a single electrical force can sometimes be of interest, such as in infrared-to-visible convertors or parametric amplifiers.

A second important category of effects is what might be named photosensitive effects to denote changes of state under optical excitation. Examples are induced optical absorption, photoconductivity, etc. When these persist after optical excitation, wider use is possible. The temporal stability after excitation will vary from application to application, but the range of properties in such materials is presently greatly restricted.

Basic research in these fields should include exploratory studies to uncover large effects and theory to provide both guidance and control. To serve such a role, those aspects of the theory that connect with experiment should be emphasized. Studies of lattice dynamics and their influence on electronic properties will contribute to the fields mentioned above. These studies can also be connected with some order–disorder aspects to link structure with properties not only for lattice dynamics but for static lattices of semiamorphous structures, thin films, etc.

Nonlinear optical materials, intended primarily for use in optical memories, will probably depend on coherent light to achieve high storage densities. Absence of imperfections, absorption of light in films as thin as possible, as well as maximum change of properties under minimum excitation will be important.

Another group of materials evolves light under various types of excitation. All devices could benefit from increased quantum efficiency. The last phenomenon, electroluminescence, has great potential but has been subject to considerable research effort without resulting improvement.

Devices utilizing coherent light only must, by definition, retain coherency through the active volume. This imposes the requirement of optical homogeneity within a fraction of wavelength. Lastly, coherent light permits the attainment of high light flux densities and hence optical damage will be a prevalent problem.

8.2.2 Microwave Frequencies

As a general trend, microwave devices are gaining in importance and their commercial application is broadened. In the past, microwaves were mostly used in radar and other military systems. Now, applications are being extended to communications in general and to power sources. This has been made possible by the discovery of methods and devices for making microwave systems smaller and more efficient. Most new active devices are made from semiconductor materials, and therefore, are not discussed here. Some other devices, significantly, new methods based on the concepts of integrated circuits are a result of research and development in inorganic dielectrics. The status of these efforts and future needs are outlined in Table 8-2 and in the preceding chapter. Here, their relative importance and approaches to problem-solving are discussed.

Substrates for strip transmission lines are one of the top priority items listed in this group. The size of a stripline is reduced approximately in proportion to $\sqrt{\epsilon}$. Characteristic impedance and attenuation coefficient are the other important parameters. Various tradeoffs between device size, temperature stability, and/or acceptable power level are possible. Requirements also vary in terms of frequency; therefore, the frequency dependence of these properties is important. Considering these varying requirements, it is unlikely that one material could satisfy all needs. R&D should be devoted to the microwave properties and device applications of several dielectrics such as alumina and beryllia ceramics, sapphire crystals, titanate ceramics, some composite materials, and methods of preparation.

The dielectric used in a device based on acoustic wave propagation serves both as a substrate and as an active device. One can distinguish bulk- and surface-wave devices. The second is very important because of ease of access for control or for coupling to other devices such as silicon-integrated circuits. Surface acoustic waves (SAW) are nondispersive and propagate at velocities of about 3 km/sec. The key advantages of SAW lie in the ability to be tapped, sampled, and modified at any plane normal to the surface of the piezoelectric solid. Progress in these devices relies on research and development on piezoelectric crystals and ceramics. Here again, various sets of the properties listed in Table 8-2 (2.3) can be defined as useful. The piezoelectric material is either the substrate or a thin film deposited on a passive substrate. In the latter case, some film properties such as thermal expansion can be controlled by the substrate. Piezoelectric films can also be used for local excitation of surface or bulk waves in substrates. On the whole, there should be equal emphasis on new materials, film deposition techniques, making of high-density ceramics, and growth of good quality crystals.

Resonant cavities are used for special application; the requirements are listed in Table 8-2 (2.5). As suitable new structural materials become available, these should be tested for the present application.

Foam glass lenses and antennae are gaining in significance as higher power needs in microwave transmission and communication systems are emerging. New methods and materials should be investigated to satisfy the needs listed in Table 8-2 (2.6).

Improved conductive coatings to provide optically transparent shielding from microwave energy are needed. Such improvement could be either a material or a method differing from what is available today. The improved coating would also have applications in other areas, particularly for electrooptic devices.

8.2.3 High-Low Frequencies

Some of the most familiar applications of dielectrics belong to this section together with some challenging problems and a few new devices. The whole group is described in Table 8-3 and related comments. The device functions are subdivided into four groups:

1. Substrates and dielectric films
2. Capacitive devices
3. Transducers and miscellaneous
4. Power transmission

Single crystal substrates of an insulating material suitable for the deposition of single crystal films of semiconductor or piezoelectric substances represent one of the most urgent needs. Sapphire crystals may satisfy a very wide range of requirements related to dielectric and thermal properties, strength, surface finish, and chemical compatibility. Since variation of lattice parameters is generally needed, other single crystal substrates such as spinels and garnets should receive attention.

Polycrystalline alumina is widely used for thin-film circuitry because of economy and good thermal properties. For many film systems, surface finish as well as flatness is inadequate. Single crystal sapphire as a thin-film substrate is an interesting possibility but use is severely limited by available size and cost. Work on the solution of these and related problems would be of importance.

For thick-film circuitry, lower grade alumina satisfies most requirements. Beryllia may have use in special applications where high thermal conductivity at temperatures under 200°C is important.

In the area of capacitive devices, there is need for investigation of failure mechanisms in ceramic and glass-ceramic dielectrics. Basic knowledge could lead to development of capacitors of greater volumetric efficiency and higher voltage ratings. Dielectrics must be improved for use in film circuitry as well as for discrete components. Of particular interest is the development of materials and processes to be used in energy storage capacitors for very high electric field gradients.

Also important is the problem of gaining greater volumetric efficiency in very-large-value capacitors. Electrolytic capacitors remain as a bulky component in circuitry that is otherwise rapidly diminishing in size and weight. Techniques should be found for producing capacitance values to a farad or more in small volume components.

In addition to these more conventional uses, many special forms of capacitor dielectrics would be useful in particular applications. Ferroelectric ceramics having wide excursions of dielectric properties with temperature show promise in temperature measurements, radiation detection, bolometers, etc. Materials with closely controlled dielectric properties as a function of temperature are needed in compensation and stabilization circuits. With the definition of such application problems, work should be encouraged on materials research since many opportunities remain to find useful solutions.

8.3 TRENDS AND RECOMMENDATIONS

Prediction of future direction and choice of priority in a field as dynamic as electronics is difficult, but the following would seem to be desirable directions for research in the inorganic dielectrics:

There is an increasing need for electronic display techniques to meet diverse environmental and operational situations. Two strong thrusts are evident in present display research—interactive and digital displays. Both will require dielectric materials support. The difficulty of constructing an efficient interactive display forces either novel or complicated solutions. This makes it unclear what particular role dielectric materials will play but the situation ensures that it will be an important one. The study of inorganic dielectric materials for interactive displays requires support if success is to be achieved.

A similar situation exists for digital displays, regardless of whether dot matrix or other geometrical forms are used for the information portrayed. However, in this case many workable solutions are at hand and these can serve as indicators of what will come in the interactive case. Dielectrics in digital displays are always important as structural elements and sometimes are the active light sources. When used as structural elements, machinability, high-field dielectric strength, and sealability are desirable properties for dielectrics. When used as light sources, low operating voltage, strong nonlinearity for x-y address, etc., are needed properties in dielectrics. In addition to the main research trends, contrast and brightness in cathode ray tubes continue to be improved by research in phosphors, tube face coatings, etc.

Optical effects in materials are becoming increasingly more important in both storage and read-out memory functions. The trend to optics stems from the potential for speed and high informational packing density, as well as from the need for storage of images and patterns taken directly from the optical domain. No one information storage material yet possesses all the desired traits of speed, high resolution, nonvolatility, erasability, and homogeneity. Information storage also requires improvement beam deflectors and modulators.

Optical read-out was stated in Chapter 6 to be useful for storage media other than optical, i.e., magnetic bubbles. For read-out, a strong need exists for larger modulation effects on the probe light so that sufficiently low probability of error can be obtained.

For both memory functions and the display devices noted above, the family of ferroelectric-like solids deserves special mention. This group includes materials with an enormous diversity of properties and cross-coupling of physical effects. There would seem to be a good likelihood of finding important new solutions to device problems through research in this field.

There is an important trend in electronics toward higher frequencies and higher speeds in communications systems. The forcing factor is the apparently endless growth in the transfer of information and data of all sorts. The resulting emphasis on devices and materials useful in satisfying these needs will certainly continue. An example is the exploration of optical frequencies to exploit their potentially wide modulation bandwidth. This application demands new devices and new materials and poses research objectives of considerable importance.

Dielectric transmission media having low loss at microwave and/or optical wavelengths are vitally needed. Not only must such materials be developed, but it must be learned how to process and form them with great uniformity and homogeneity, and to incorporate them in devices that can stand the hazards of practical use.

Considerable progress has been made in the past few years toward the development of materials with low attenuation optical wavelengths. In the inorganics, glasses have been examined. They show promise at the present research stage of facilitating development of signal-carrying lines with such high transmission efficiency that long distance applications can be considered. Such lines may have attractive properties (e.g., freedom from electromagnetic noise; electrical isolation) in addition to their potentially broad bandwidth, but much additional work will be required before application and use.

Just as families of equipments have evolved over time for the transmission of information at lower frequencies, it will be necessary to develop the system components appropriate for optical signals. The inorganic dielectrics whose properties cross-link the optical and electrical domains will be important in the functions of amplification, modulation, etc.

The trend toward miniaturization will certainly continue. It is not only a product of our interest in space, it is another facet of the increased personalized use of electronics and the increased complexity of devices and equipment, and it is responsive to the need for economy. The impact on inorganic materials is diverse but is exemplified by the need for improved dielectrics that permit the miniaturization of wave-guiding and wave-containing structures at microwave frequencies. Miniaturization through the development of high dielectric constant strip-line structures requires use of materials that are not only low in loss but are also homogeneous and mechanically superior. To date, no materials have been found that exhibit a combination of high dielectric constant (K of 10 to 100) and low loss at microwave frequencies. As a consequence, virtually all of the miniaturization microwave circuitry (strip-line) today makes use of alumina—with a sacrifice in volumetric efficiency—as the substrate.

In addition to the need for substrates capable of supporting microwave circuitry, several forms of passive substrates needed in electronics fall short of the ideal. Improvements in these applications are vital in lowering costs and improving the performance and reliability of electronic circuitry and systems. Film circuitry remains important in many cases where monolithic circuitry is inappropriate. Alumina ceramic is the almost-universally-used substrate. In the case of thin-film devices, compromises are necessary in the dimensional tolerances of circuit patterns and in the choice of films to be used, because of an inability to achieve adequate surface smoothness. Alternative materials (e.g., certain glasses or glaze coatings), while having desirable surface properties, fail to meet requirements of thermal expansion, chemical inertness, and/or thermal conductivity. This problem is worthy of further research; the solution may require the use of composite materials.

Other passive substrates are needed to support single crystal films. In semiconductor device development, much work has been done seeking high quality single crystal films of silicon, germanium, gallium arsenide, or other semiconductor on an insulating substrate. More recently, work on moving-domain magnetic memories has focused attention on single-crystal films of ferrites, garnets, etc. Little success has been achieved in the growth of such films on noncrystalline substrates, although this remains an attractive objective. Much more likely in the near term is the growth of large-area (several cm^2) active crystal films, strain-free, and with a high degree of perfection.

In the foregoing cases, materials choices are closely constrained by the need for matching of lattice parameters between substrate and films, as well as the requirement for easy and economical processing of large sizes with a high degree of perfection.

Some success has been achieved in recent years in the development of materials with low coefficients of dimensional change with temperature, time, and other environmental factors. The inorganic dielectrics have proven to be more stable in some cases than the best of the known stable metals and alloys.

With the increasing use of microwave and optical frequencies for which distributed-parameter circuitry is typical, the dimensional stability of a circuit structure can be an important consideration. As a complementary technique to the traditional use of mechanically-resonant crystal for frequency selection and filtering, distributed-parameter resonators, filters, guides, and other circuitry, making use of stable materials, can serve the same functions with advantages in many cases.

Dielectric materials are available today with dimensional stability better than one part in 10^8 per degree centigrade. Improvements in this, as well as improvement in understanding of long-term structural changes in dielectrics are needed if the aforementioned application techniques are to become useful.

The more conventional applications of dielectrics in capacitors are still of great importance. Many problems remain to be solved in achieving the capacitive volume efficiencies and the energy densities needed in future devices. Special attention should be given to the study of defect structures and failure mechanisms affecting life and reliability in dielectric materials. Understanding of

- Dielectric properties in high electric fields
- Effects of aging
- Effects of radiation

would contribute importantly. Investigation of such phenomena should be extended to single crystals, polycrystalline thin films, and ceramic bodies. Band theory, proved to be extremely useful in the past in describing the properties of semiconductor crystals, is now being applied with some success to amorphous and to simple polycrystalline systems. Better understanding of the effect of traps and space charges in insulators could help greatly to outline the scope and limits of dielectric applications.

Several processing techniques such as hot pressing and glass-crystallization have been used with success to make high density, often transparent, ceramic bodies exhibiting both high dielectric constant and dielectric strength. Studies of the electric field distribution in these composite systems, often exhibiting electrical surface phenomena related to fine particle structure and usually containing a second phase and/or residual porosity, should lead to optimization of their energy storage capability and to improved reliability.

A very exciting problem is the development of solid or semiliquid electrolytes with high room-temperature conductivity. Such electrolytes, in contact with some conductors of large surface area, form an electric double layer. Capacitances of the order of 100 farad/gram can be obtained in this manner. Exploitation of this effect for a variety of energy storage devices for low voltages is promising. These include batteries, fuel cells, and high-value, electrolytic-type capacitors.

This brief list is by no means all-inclusive and is subject to the opinions and biases of the Committee. It should be taken together with the earlier more complete outline of applications and problems in this very broad class of materials. However, devices and applications included in this discussion of trends are certain to have an important impact in the field of electronics, and many suffer from deficiencies in available materials.

As a final comment, while the understanding of structure has progressed enormously in recent years for crystalline materials, the same cannot be said for amorphous, or for composite crystalline/amorphous materials. Many of the useful dielectrics fall in these latter classes and would benefit from fundamental work aimed at an improved understanding of structure and conduction mechanisms. This might well be an outfall from characterization studies accompanying amorphous semiconductor device development.

9 Organic Dielectrics

9.0 INTRODUCTION AND GENERAL SUGGESTIONS

The area of organic dielectric materials is exceedingly broad, covering hundreds of materials. The information presented herein is a compilation of opinions of experts in the field. It is arranged in a manner designating materials or composites as they are generally known in the industry. Current materials are first listed followed by needs for both materials and processes. Tables at the end of the report summarize properties of current materials.

In nearly all cases, research needed includes both basic and applied, with periods of time to achieve desired ends estimated between 1 and 7 years. Where new materials must be synthesized, or properties much beyond the state of the art are needed, "basic" research is called for with periods in excess of 5 years. Where new processes must be developed or inventive modifications of materials are proposed, shorter periods are suggested, averaging 2 to 5 years. It is suggested that users of this report look for current materials listed for each class, refer next to their properties, and use this as a basis to derive meaning from the suggestions of needs for the particular class in question. A reading of the pertinent "lower dissipation factor" in a film, which is a generality, becomes specific when the dissipation factors of current materials are examined.

Perhaps most important for future development of organic dielectrics is the consideration of the probable future for electronic materials, devices, and processes reported elsewhere in this document. In Chapter 2, stress was given to the ideas of batch fabrication and adaptability. The organic materials developers will need to keep such trends foremost in their thinking since their products are generally subservient to the other materials in devices and systems. Thus, the organic encapsulant serves to protect the device. If the device is batch fabricated, then the organic must be amenable to the fabrication process as well as provide its protective function.

A further kind of consideration involves interaction of materials. Suggestions made elsewhere in the report include passivation of active components or clever design of devices to relieve the need for super-encapsulants. For example, barrier layers against ion migration into an active device might minimize the need to make organics free of ionic impurities, as frequently suggested.

Many needs expressed were for highly special applications. Obviously, not all organics for electronics need to be stable at 400°C. Reality and economics will dictate limits on such requirements. Environment will dictate choices of materials. Mechanical, chemical, and thermal stresses become as important to consider as electrical properties.

Nevertheless, there is a common suggestion by most contributors that stresses the need for better control of properties of organic materials. This includes both tolerance limits for a given property of a material and its uniformity from batch to batch. Another general need is for more perfect materials. Since polymers and elastomers are made of relatively random atomic structures, they accommodate imperfections and impurities that contrast sharply (and often detrimentally) with the perfection of the components they house.

The high electrical resistivity associated with organic polymer materials has made it very difficult to obtain an understanding of the conduction process. The high mobility and large lifetime associated with carriers in some contemporary semiconductors has enabled the researcher and engineer to make meaningful electrical measurements and, in turn, to arrive at the necessary criteria for material improvement. In contrast, there are very few organics, with the exception of anthracene, whose carrier mobilities are known in terms of magnitude or sign.

The polycrystalline or amorphous nature of organic materials currently used for encapsulation or as capacitor dielectrics has led to theories of polaronic or hopping conduction, but these theories are very difficult to test. Various forms of radiation, optical or nuclear, have been used to generate a sufficient number of free carriers to raise the conductivity to a conveniently higher level; but, then it is found that the conductivity is dominated by very complicated trapping processes that arise from the high concentration of spatial and chemical impurities. Those concerned with synthesis need more fundamental information about transport mechanism in organic polymers. The need for organic liquids and solids with (a) improved resistance to dielectric breakdown and (b) resistance to transient conductivity, induced by ionizing radiation, may be met if greater effort is expended in the production of purer organics or synthesis of new organics designed for such resistance. These are needed both as large single crystal and as ultrapure liquids. Once the mobility, lifetime, and quantum yield of free carriers in "pure" materials is established, the deleterious effects of specific impurities or imperfections can be assessed and criteria can be established for the production of more reliable insulators.

It is suggested that a less passive role may be increasingly in order for organics. A simple example is the organic encapsulant for a light-emitting diode which also serves as a lens. Perhaps organic materials may, themselves or with additives, become electronically cofunctional with the active or passive device materials. It is beyond the scope of this assignment, but there exist many potentially active roles for organics. Semiconductors, liquid crystals, dye lasers and photoconductors are but a few examples. Of great importance in current processes are the photopolymers as positive and negative resists that serve an active role to achieve an end. The development of active or coactive organic materials and processes for electronics is a real challenge to the chemist.

Finally, there remain to be made many inventive combinations of materials for dielectric functions. Reinforced plastic laminates are examples of such functional composites. Additives of particulate dielectric inorganics to plastics have been developed. Perhaps a shape factor for the particulate needs to be considered, or consideration given to its surface as presented to the resin. Deliberate additives that migrate to a desired location on curing of the composite may form needed barriers or provide adhesion, or resistance to a particular environment. Solid–liquid combinations, plastic–plastic, plastic–ceramic, plastic–metal, and many others should be investigated. All these may be as useful as the development of superior new polymers.

9.1 FILMS, SHEETS, PAPERS

9.1.1 Current Materials

Cellulose acetate (H4-1)
Cellulose acetate butyrate (H4)
Cellulose acetate propionate (1)
Cellulose acetate nitrate
Ethyl cellulose
Nylon 6/6
Polyallomer
Polycarbonate, 40% glass reinforced
Polyester, rigid
Polyethylene, medium density
Polyimide
Polypropylene
Polystyrene
Polyvinyl chloride
TFE-fluorocarbon
Vinylidene chloride
Kraft papers

9.1.2 Needs

9.1.2.1 DENSE FILMS

1. Synthesis of films with properties:
   a. High temperature capability* (500–800°F) for 1000 hours
   b. Low dielectric loss ($< 1 \times 10^{-3}$ radians at 500°F)
   c. Moisture-resistance
   d. Higher dielectric constant for capacitors
   e. Capacitance stability
   f. Lower dissipation factor

2. Processing
   a. Making defect-free films (voids, particulates)
   b. Making thinner ($< 0.1 \times 10^{-3}$ inch) films of a wide range of polymer materials
   c. Developing extrusion or casting or other processes for materials that are not readily made as films
   d. Uniformity of batches of high-performance polymer films

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* Perhaps only very special applications. Most applications will be at lower temperatures.

9.1.2.2 POROUS FILMS, PAPERS

1. Synthesis of porous films, foams
   - a. Replacing cellulosics
   - b. Higher mechanical strength
   - c. Temperature operation up to 400°F
   - d. Impregnable with low loss fluids (alternate: dense films embossed)
   - e. Low dielectric constant (< 3)
   - f. Low dielectric loss ($< 1 \times 10^{-3}$ radians at 300°F)
   - g. Impregnated foams with low dielectric constant (< 1.5) to line wave guides
2. Processing
   - a. Thin ($0.3\text{–}1.0 \times 10^{-3}$ inch) films are needed
   - b. Uniformity of porosity, density, (10–30% porosity range)
   - c. Freedom from defects
   - d. Means of making uniform $<$ 1-mil foams in tubular form for wave guides

9.1.2.3 RESEARCH NEEDED

1. Basic, applied, development
   - a. Synthesis of new compounds 5–10 years
   - b. Improvement of properties of current materials 2–5 years
   - c. Processes 1–7 years

9.1.3 General Remarks—Films, Sheets, Papers

There is a trend away from kraft paper to plastic films because of the increased electric strength and lower dissipation factor of these films. For use in high-voltage capacitors, these films must be impregnated with a dielectric liquid to fill the voids and increase the corona starting voltage. Since these films are relatively nonporous, they have been embossed or used in combination with kraft paper to allow a convenient means of impregnation. There is a need for other methods of making void-free high voltage capacitors.

The thinnest commercially available plastic film dielectric is polycarbonate, which is made as thin as 0.00008 inches. There is a need for thinner films made from other materials.

There may always be a demand for materials of higher dielectric constant. Work has been done on the addition of metallic oxide powders to plastic films, but this results in a degradation of electric strength.

There is a continuing need in specialty capacitors for improved values of temperature coefficient, capacitance stability, and dissipation factor. There may be a small need for improved high temperature dielectrics, although the great bulk of capacitors are used at temperature ratings of 85°C and 125°C for continuous service.

9.2 COATINGS

9.2.1 Current Materials, Wires, Components, Connections, Parts

Acrylics
Alkyds
Chlorinated polyether
Depolymerized rubber
Diallyl phthalate
Epoxies
Epoxy-polyamid
Phenolics
Polyamide
Polyimides
Polyesters
Polyethylene
Polymethyl methacrylate
Polystyrene
Polyurethanes
Polyvinyl butyral
Polyvinyl chlorides
Copolymer of PVC and vinyl
Acetate
Polyvinyl formal
Polyvinylidene fluoride
Polyxylylenes
Silicones
Nylons and co-polymers
Polyamide-polymide
Polyalkene
Polytetrafluoroethylene

9.2.2 Needs

1. Materials
    a. Increased compatibility of insulation components and their environment
    b. Flexible, moisture resistant materials/system capable of continuous operation at up to 900°F
    c. Thin wall extrudable high strength insulation materials, e.g., polyimides
    d. Nonburning coatings in oxidizing atmosphere
    e. Corona resistance combined with toughness
    f. Low outgassing in sealed environments

  - g. Higher purity
  - h. Adhesion to a wide variety of surfaces

2. Processes
    - a. Application methods which avoid air inclusions
    - b. Improved adherence
    - c. Rapid evaluation techniques
    - d. Low temperature curing (radiation, e-beam, uv).
    - e. Ultrapure, ultrathin coatings (CVD, gaseous free radical polymerization)

9.2.3 Research Needed

Basic, applied, development
1–3 years

9.2.4 General Remarks—Coatings

Comments are given for magnet wire, varnish, and ground insulation. The main problems are the compatibility of insulation components. This is described in IEEE 70 CP 55-PWR. The second most important problem is the method of rapid thermal evaluation in order to get rapid feedback to materials people. (Note IEEE 71 CP 238-PWR.)

Solving these problems should:

1. Increase reliability of components and systems
2. Decrease the cost of component development
3. Decrease the cost of system development
4. Reduce laboratory testing of trivial developments
5. Give constructive guidance to materials manufacturers

9.3 FLUIDS, CAPACITORS

9.3.1 Current Materials

Chlorinated aromatic hydrocarbons
Mineral oils
Synthetic hydrocarbons (butene derivative)
Fluoro inert liquids

9.3.2 Needs

1. Synthesis of new fluids
   a. Replace aromatic hydrocarbons to avoid pollution
   b. Polar liquids, nonflammable
   c. Dielectric constant 5–7 at 50 Hz and 200°F
   d. Dielectric loss $< 1 \times 10^{-2}$ at above specifications
2. Processing
   a. Removal of impurities in use (absorbing circulating system)
   b. Maintenance of low conductivity in use ($< 10^{-12}$ ohm-cm^{-1})

9.4 FLUIDS, TRANSFORMERS

9.4.1 Current Materials

Oils
Chlorinated aromatic hydrocarbons
Mineral oils
Synthetic hydrocarbons (butene derivative)
Fluoro inert liquids

9.4.2 Needs

1. Synthesis of fluids: (similar to capacitors, above, but lower dielectric constant 2–4)
   a. Long-term stability (years) to high temperature, corrosion
2. Processing:
   a. Need for degassing in use (or controlled gassing of preferred material)
   b. Gas and water-free fluids
   c. Minimum impurities, especially those that react with environment to form gas or water
   d. Development of encapsulated transformers

9.4.3 General Remarks—Fluids, Transformers

It is difficult to generalize on some of the real problems involved in insulation in transformers today, because they involve so many different properties which are intermingled in use. The various materials in oil-immersed transformers are relatively on a par as far as their functional characteristics are concerned.

A general enhancement of long-term life at high temperatures in all of the various materials is needed.

Although there has been considerable activity in the area of encapsulated materials for distribution, and some products placed upon the market, there has been difficulty in putting laboratory developments into production. It is very difficult to obtain a void-free product in its final form and to maintain it in such form under severe heat-cycling which occurs in use without getting some cracking or introduction of weak spots in the dielectric system. The next area of real advancement in the smaller transformers will be in the area of encapsulated transformers, compared to the present units using the paper insulation system. This will require a much higher level of reliability. It will also require, along with the increased electrical and mechanical strengths and durability, the reduction of the cost of these materials. At present, the production of such encapsulated transformers entails additional costs, both in materials and production processes which result in a higher final cost.

9.5 GASES

9.5.1 Current Materials

Sulfur hexafluoride
Fluorocarbons
Mixtures with rare gases

9.5.2 Needs

1. Synthesis of new gases with the following properties:
    a. High electric strength
    b. Insensitive to impurities
    c. Insensitive to moisture
    d. Good heat transfer capability
    e. Stable to high temperatures (consistent with temperatures of advanced electronic systems)
    f. Low toxicity
    g. Low cost
2. Processing
    a. Means of containing gases
    b. Integrated filling systems for cables, connectors
    c. Self-sealing techniques

3. Research
   a. Basic and applied 3 to 7 years

9.6 ADHESIVES

9.6.1 Current Materials

Pressure Sensitive Adhesives (PSA)

Acrylics
Acrylates
Silicones
Natural Rubber
Styrene Butadiene
Butyl Rubber
Butadiene
Acrylonitrile
Polyisobutylene
Ethylene/propylene/butadiene
Neoprene
Polyvinyl acetate
Polyethylene copolymers
Resins, general
Polyterpenes
Hydrocarbons, general
Esters
Phenolics
Polyurethanes

Structural Adhesives (SA)

Epoxies
Polyurethanes
Rubber/polymers
As above

9.6.2 Needs

1. PSA that are solvent-free systems for high vacuum and populated area usage
2. PSA and SA for low-energy surfaces, e.g., surfaces wetted with oils, water, etc. Desired types include polyethylene, polypropylene, polytetrafluoroethylene, and silicones
3. Adhesives resistant to diesters and polyesters
4. Oil-resistant PSA and SA, e.g., resistance to hydrocarbon oils, phosphate ester, hydraulic fluids, transformer oils
5. Modification of ethylene/propylene/butadiene or development of means to get adhesion of ethylene/propylene/butadiene to polymer and metallic substrates
6. Structural adhesives for applying electrical devices to concrete and plaster

7. Improvement of peel and shear adhesion at higher temperatures and high-stress environments, e.g., thermal cycling and corrosive media

9.7 CIRCUIT SUBSTRATES

9.7.1 Current Materials

This covers a wide range of plastics and laminates, most of which are listed in Tables 9-1, 9-2, 9-3, and 9-4.

9.7.2 Needs

9.7.2.1 MATERIALS/PROCESSES

1. Low-cost reinforcement without defects of cellulosics (moisture sensitivity, temperature limitations, and poor dimensional stability)
2. Isotropic reinforcement (avoid current problems of nonuniformity for machining binder and filler, nonuniform expansion/contraction)
3. Avoidance of wicking of moisture or processing chemicals at reinforcement/resin interface
4. Flame retardance
5. Stability at high temperatures, 300°F (including nonoxidation and dimensional control, especially creep or flow)
6. Better control of dielectric constant of substrate (range and tolerance) and precise circuit line patterns
7. For microwave circuits, a homogeneous organic of low dielectric loss and a dielectric constant above 9
8. For flexible circuitry, a mechanically strong, dimensionally stable film with little moisture sensitivity

9.7.2.2 RESEARCH

Basic, applied, development
  1–5 years

9.7.3 General Remarks—Circuit Substrates

It is possible to define theoretically a nearly ideal dielectric substrate for a wide variety of uses. In essence, this material would be a low cost, mechanically strong, tough, easily machinable, homogeneous,

TABLE 9-1 Dielectric Properties of Major Plastics[a]

Plastic/Reinforcement	Arc Res,[b] sec	Dielec Const[c]		Dielec Str,[d] vpm	Dissip Factor[c]		Vol Res,[e] ohm-cm
		60 cps	10^6 cps		60 cps	10^6 cps	
ABS, high impact	–	2.8–3.2	2.7–3.0	350–440	0.005–0.007	0.007–0.015	1–4 × 10^{16}
ABS-Polycarbonate	96	2.74	2.69	500	0.0026	0.0059	2.2 × 10^{16}
Acetal copolymer	240	3.8	3.7	>400	0.005	0.004	1 × 10^{14}
Acetal homopolymer	129	3.7	3.7	500	0.0048	0.0048	1 × 10^{15}
Acrylic, high imp	–	3.5–3.9	2.5–3.0	400–500	0.03–0.04	0.01–0.02	2.0 × 10^{16}
Alkyd, glass reinf	180	5.2–6.0	4.5–5.0	300–350	0.02–0.03	0.015–0.022	10^{14}
Allyl diglycol carbonate	185	4.4	3.5–3.8	290	0.03–0.04	0.1–0.2	4 × 10^{14}
Cellulose acetate (H4-1)	–	3.5–7.5	3.2–7.0	250–600	0.01–0.06	0.01–0.10	10^{10}–10^{13}
Cell acet butyrate (H4)	–	3.5–6.4	3.2–6.2	250–400	0.01–0.04	0.02–0.05	10^{11}–10^{14}
Cell acet propionate (1)	–	3.7–4.0	3.4–3.7	300–450	0.01–0.04	0.02–0.05	10^{11}–10^{14}
Cellulose nitrate	–	7.0–7.5	6.4	300–600	0.09–0.12	0.06–0.09	10–15 × 10^{10}
Chlorinated polyether	–	3.10	2.92	400	0.011	0.011	1.5 × 10^{16}
Chlorinated PVC	–	3.08	3.2–3.6	1250–1550	0.02	0.02	10^{15}
Diallyl phthalate (DAP), glass reinf	130	–	–	350–430	–	0.015	1–5 × 10^{10}
Ethyl cellulose	–	–	2.8–3.5	350–500	–	0.010–0.060	10^{12}–10^{14}
Epoxy, cast, rigid	86	4.02	3.42	400+	0.005–0.04	0.04–0.06	6.1 × 10^{15}
Ethylene ethyl acrylate (EEA)	–	2.8	–	550	0.001	–	2.4 × 10^{15}
Ethylene vinyl acetate (EVA)	–	3.16	–	525	0.003	–	0.15 × 10^{15}
Ionomer	–	2.4	–	1000	0.003	–	10^{16}
Melamine, cellulose elec.	70–135	6.2–7.7	5.2–6.0	350–400	0.026–0.192	0.032–0.12	10^{12}–10^{13}

Nylon 6/6, 30% glass reinf	148	4.0	3.5	400	0.018	0.017	5.5×10^{15}
Phenolic, glass reinf	60	7.1–7.2	4.6–6.6	200–370	0.02–0.03	0.02	$7\text{–}10 \times 10^{12}$
Polyallomer	–	2.3	2.3	500–650	<0.0005	<0.0005	$>10^{16}$
Polycarbonate, 40% glass reinf	120	3.80	3.58	475	0.0006	0.0007	1.4×10^{15}
Polyester, rigid	115–135	2.8–4.4	2.8–4.4	300–400	0.003–0.04	0.006–0.04	10^{13}
Polyethylene, medium dens	–	2.3	–	480	<0.0005	–	$>10^{15}$
Polyimide	50–180	5.01	4.91	500	0.0034	0.0090	9.2×10^{15}
Polyphenylene oxide	75	2.58	2.58	500	0.00035	0.0009	10^{18}
Polyphenylene oxide, mod	75	2.64	2.64	550	0.0004	0.0009	10^{17}
Polypropylene, glass reinf	73–77	2.3–2.5	2–2.5	320–475	0.002	0.003	1.7×10^{16}
Polystyrene, 30% glass reinf	28	3.1	3.0	396	0.005	0.002	3.6×10^{16}
Polysulfone, 30% glass reinf	114	3.55	3.41	480	0.0019	0.0049	10^{17}
Polyvinyl butyral	–	2.7–3.3	2.6–2.8	400–480	0.0050–0.0065	0.013–0.027	$>10^{14}$
PVC, nonrigid-elec	–	6.0–8.0	–	24–500	0.08–0.11	–	$4\text{–}300 \times 10^{11}$
PVC-acrylic	80	3.86	3.44	429+	0.076	0.094	1.5×10^{13}
Polyvinyl formal	–	3.2–3.5	2.7–3.1	310–450	0.008–0.010	0.018–0.023	–
Silicone, glass reinf	240	4.34	4.28	–	0.01	0.004	9×10^{14}
TFE-fluorocarbon	200+	2.1	2.1	400–500	0.0002	0.0002	$>10^{18}$
Vinylidene chloride	–	3–5	–	–	0.03–0.15	–	$10^{14}\text{–}10^{16}$
Urea, cellulose filled	85–110	7.2–7.3	6.4–6.5	340–370	0.042–0.044	0.027–0.029	$5\text{–}8 \times 10^{10}$

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[a] Data from Materials Engineering's 1970 Materials Selector. Printed with permission from Reinhold Publishing Corporation (*Materials Engineering Magazine*, September 1970, p. 36).

[b] ASTM D495.

[c] ASTM D150.

[d] ASTM D149.

[e] ASTM D257.

TABLE 9-2 Dielectric Properties of Reinforced and Filled Laminates[a]

Plastic/Reinforcement	Arc Res,[b] sec	Dielectric Constant[c]			Diel Str,[d] vpm	Dissipation Factor[c]			Vol Resist., ohm-cm
		60 Hz	1 kHz	1 mHz		60 Hz	1 kHz	1 mHz	
Diallyl phthalate laminates									
Cotton fabric base	130	5.1	–	4.8	390	0.015	–	0.018–0.040	–
Glass fabric base	150	4.3	–	4.1	530	0.013	–	0.015	–
Epoxy laminates									
Cellulose paper base	30–100	4.0–6.0	–	4.0–4.6	475–750	0.010–0.025	–	0.30–0.035	7×10^{15}
Glass fabric base	15–180	4.2–5.3	–	4.5–5.3	400–750	0.003	–	0.010–0.025	10^{15}
Glass nonwoven filament	60	5.9	5.6	5.4	450	0.005	0.007	0.018	3.3×10^{13}
Melamine-formaldehyde laminates									
Asbestos paper or fabric	–	–	–	8.0–9.6	50–150	–	–	0.12–0.22	–
Cellulose paper base	100	–	7.9	6.4–8.5	400–700	–	0.057	0.035–0.05	–
Cotton fabric base	120–186	7.5–8.6	7.3–8.3	6.2–8.0	200–450	0.06–0.15	0.03–0.09	0.03–0.07	–
Glass fabric base	175–200	6.5–10.0	6.1–9.5	6.0–9.0	200–500	0.04–0.10	0.012–0.03	0.011–0.025	–
Glass mat base	170–200	4.5–6.5	4.2–6.0	4.2–7.5	300–450	0.004–0.05	0.004–0.05	0.006–0.08	–

Phenolic laminates									
Asbestos fabric base	4	–	7.5	5.5–10.0	50–100	–	0.06–0.10	0.10–0.15	–
Asbestos paper base	4	–	7.0	5.2	160–250	–	0.15–0.20	0.08–0.14	–
Cellulose paper base	4–75	4.5–7.5	4.2–6.0	3.6–6.0	300–1000	0.02–0.10	0.03–0.07	0.02–0.08	10^{10}–10^{13}
Cotton fabric base	4	5.0–10	4.2–6.5	5.0–7.0	150–600	0.04–0.50	0.04–0.09	0.05–0.10	10^{10}–10^{12}
Cotton web base	Tracks	–	–	5.5–7.0	200	0.10–0.5	–	0.06–0.50	–
Glass fabric base	Tracks	4.0–10.0	4.8–6.3	3.7–6.6	300–700	0.01–0.10	0.015–0.042	0.005–0.05	2.5×10^{10}
Nylon fabric base	10	3.7–6.0	3.6–4.1	3.3–4.5	360–600	0.02–0.06	0.01–0.02	0.015–0.040	7×10^{13}
Wood fiber base	Tracks	–	–	5	75–500	0.20	–	0.05	–
Polyester laminates									
Cotton base	70–85	–	–	2.9–3.6	300–500	–	–	0.02–0.04	–
Glass fabric base	80–140	4.0–6.0	–	3.0–4.0	250–700	0.02–0.04	–	0.007–0.03	–
Glass mat base	100–185	4.4–6.0	4.2–5.0	3.0–6.0	300–500	0.005–0.05	0.004–0.04	0.007–0.04	10^{6}–10^{12}
Paper Base	28–75	5.1	–	3.0–4.2	600–800	0.1	–	0.02–0.03	10^{13}
Silicone laminates									
Asbestos fabric base	–	–	–	–	50–150	–	–	–	–
Glass fabric base	150–250	3.7–4.3	3.7–4.3	3.7–4.3	180–480	0.0005–0.0055	0.0006–0.0035	0.0015–0.0050	–
TFE-fluorocarbon laminates									
Ceramic nonwoven fiber	190	2.5–2.7	–	2.4–2.5	150–250	0.002–0.003	–	0.001–0.003	>10^{7}
Glass fabric base	180+	2.6–2.8	2.6–2.8	2.6–2.8	300–750	0.0005	0.0004	0.0006	>10^{6}
Glass nonwoven fiber	180	2.2	2.2	2.2	300	0.004	0.0001	0.0005	>10^{7}

[a] Data printed with permission from Reinhold Publishing Corporation (*Materials Engineering Magazine*, September 1970, p. 36).
[b] ASTM D495.
[c] ASTM D150.
[d] Short-time, 1/8 in. thickness, ASTM D149.

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TABLE 9-3a Properties of Elastomers for Electrical Insulation [a]

Property	Natural	GR-S	Butyl	Neo-prene	Nitrile	Polysulfide	Silicone
Dielectric strength	H	H	MH	M	M	L	M
Power factor	M	M	M	MH	H	VH	M
Resistivity	H	M	VH	L	L	VL	M
Dielectric constant	M	M	M	MH	M	VH	M
Abrasion resistance	H	H	MH	VH	MH	M	L
Flexibility	H	H	H	MH	MH	H	H
Res to compr cutting	MH	MH	M	M	MH	M	L
Cold flow at room temp	L	L	L	L	L	M	MH
Cold cracking temp	VL	M	L	M	MH	MH	VL
Sunlight resistance	MH	MH	H	H	M	H	H
Ozone resistance	L	M	H	H	MH	H	H
Corona resistance	M	M	M	H	M	–	–
Heat resistance	MH	H	VH	MH	MH	H	VH
Flame resistance	VL	VL	VL	MH	VL	L	M
Water resistance	H	H	H	M	M	M	H
Oil resistance	VL	VL	VL	M	MH	H	M

[a] Comparative ratings based on best attainable values. VH = very high; H = high; MH = medium high; M = medium; L = low; VL = very low.

TABLE 9-3b Properties of Elastomers [a]

	Volume Resist, ohm-cm	Power factor, %	Dielectric Strength, vpm
Excellent:			
Silicone	10^{14}	1	600
Fluorocarbon	10^{13}	4	500
Good:			
Butyl	10^{16}	2	600
Natural rubber	10^{16}	5	500
Chlorosulfonated polyethlyene	10^{14}	3	600
SBR	10^{13}	7	500
Fair:			
Urethane	10^{12}	4	500
Polysulfide	10^{12}	30	250
Neoprene	10^{11}	20	350
Acrylic	10^{9}	20	350
Poor:			
Buna-N	10^{3}	30	350

[a] Data printed with permission from Reinhold Publishing Corporation (*Materials Engineering Magazine*, September 1970, p. 36).

TABLE 9-4a Dielectric Strength of Coatings[a]

Coating	Dielectric Strength volts/mil
Acrylic	450-550[b]
	350-400[c]
	1700-2500[d]
Alkyd	300-350
Chlorinated polyether	400[b]
Chlorosulfonated polyethylene	500[b]
Diallyl phthalate	450[c]
Diallyl isophthalate	420[c]
Depolymerized rubber (DPR)	360-380
Epoxy	650-730[e]
	1300[f]
Epoxy, modified	1200-2000[d]
Neoprene	150-600[b]
Phenolic	300-450
Polyamide	780[g]
Polyamide-imide	2700
Polyester	250-400[b]
	170[c]
Polyethylene	300[b]
	500[b]
Polyimide	3000[i]
	4500-5000[j]
	560[b,k]
Polypropylene	750-800[b]
Polystyrene	500-700[b]
	400-600[c]

Coating	Dielectric Strength volts/mil
Polysulfide	250-600[b]
Polyurethane (one component)	3800[l]
Polyurethane (two component, 100% solids)	275
	750[m]
Polyvinyl butyral	400
Polyvinyl chloride	300-1000[b]
	275-900[c]
Polyvinyl formal	860-1000
Polyvinylidene fluoride	260[b]
	1280[b]
	950[c]
Polyxylylene	
Parylene N	6000[c]
	6500[b]
Parylene C	3700[b]
	1200[c]
Parylene D	5500[b]
	4500[c]
Silicone	550-650[o]
	800[p]
	1500[d]
TFE fluorocarbon	400[h]
	480[b]
	430[c]
	3000-4500[g]
FEP fluorcarbon	4000[r]

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[a] All samples 125 mils thick unless otherwise noted.
[b] Short-time method.
[c] Step-by-step method.
[d] 2 mils thick.
[e] Cured with anhydride-castor oil adduct.
[f] 10 mils.
[g] 106 mils.
[h] 60 mils.
[i] Pyre-M.L., 10 mils thick.
[j] Pyre-M.L. (RC675).
[k] 80 mils.
[l] 1 mil.
[m] 25 mils.
[n] 8 mils.
[o] RTV
[p] Flexible type.
[q] 1-4 mils.
[r] 1.5 mil.

flame retardant, low loss, dielectric constant 2 to 3, dimensionally stable material with adequate resistance to processing chemicals and good bond strength to copper foil and deposited copper. Preferably, it would be only semirigid so that 1/16-in. thick sheets could be deformed around a 6-in. radius, 0.010-in. thick material could be bent 180° at least once, and 0.002-in. material would be a strong, flexible film.

TABLE 9-4b Dielectric Constants of Polymer Coatings (at 125°F)

Coating	60–100 Hz	10^6 Hz
Acrylic	–	2.7–3.2
Cellulose acetate butyrate	–	3.2–6.2
Cellulose nitrate	–	6.4
Chlorinated polyether	3.1	2.92
Chlorosulfonated polyethylene	6.19	~5
Depolymerized rubber (DPR)	4.1–4.2	3.9–4.0
Diallyl isophthalate	3.5	3.2
Diallyl phthalate	3–3.6	3.3–4.5
Epoxy-anhydride–castor oil adduct	3.4	3.1
Epoxy (one component)	3.8	3.7
Epoxy (two component)	3.7	–
Epoxy-polyamide (40% Versamid 125, 60% epoxy)	3.37	3.08
Fluorocarbon (TFE)	2.0–2.08	2.0–2.08
Phenolic	5–6.5	4.5–5.0
Polyamide	2.8–3.9	2.7–2.96
Polyamide-imide	3.09	3.07
Polyester	3.3–8.1	3.2–5.9
Polyethylene	2.3	2.3
Polyimide-Pyre-M.L. enamel	3.8	3.8
Polypropylene	2.22–2.28	2.22–2.28
Polystyrene	2.45–2.65	2.4–2.65
Polysulfide	6.9	–
Polyurethane (one component)	4.10	3.8
Polyvinyl butyral	3.6	3.33
Polyvinyl chloride	3.3–6.7	2.3–3.5
Polyvinyl chloride-vinyl acetate copolymer	3–10	–
Polyvinyl formal	3.7	3.0
Polyvinylidene chloride	–	3–5
Polyvinylidene fluoride	8.1	6.6
Polyxylylene		
Parylene N	2.65	2.65
Parylene C	3.10	2.90
Parylene D	2.84	2.80
Shellac (natural, dewaxed)	3.6	3.3
Silicone (RTV types)	3.3–4.2	3.1–4.0
FEP	2.1(10^3 Hz)	–
TFE	2.0–2.2(10^3 Hz)	–
Wax (paraffinic)	2.25	2.25

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The only immediate obvious need that could not be met by the "ideal substrate" is for microwave materials with higher dielectric constants. Almost all other applications could use the same material.

Mechanical properties are of such predominant importance in the large majority of uses that all rigid organic substrates are reinforced, with the exception of some very-low-loss materials for microwave applications. The common reinforcements are cellulose paper and glass

TABLE 9-4c Dissipation Factors of Polymer Coatings (at 125°F)

Coating	60-100 Hz	10^6 Hz
Acrylic	0.04-0.06	0.02-0.03
Alkyd	0.003-0.06	–
Chlorinated polyether	0.01	0.01
Chlorosulfonated polyethylene	0.03	0.07 (10^3 Hz)
Depolymerized rubber (DPR)	0.007-0.013	0.0073-0.016
Diallyl phthalate	0.010	0.011
Diallyl isophthalate	0.008	0.009
Epoxy dip coating (two component)	0.027	0.018
Epoxy (one component)	0.011	0.004
Epoxy (one component)	0.008	0.006
Epoxy polyamide (40% Versamid 125, 60% epoxy)	0.0085	0.0213
Epoxy polyamide (50% Versamid 115, 50% epoxy)	0.009	0.0170
Epoxy cured with anhydride-castor oil adduct	0.0084	0.0165
Phenolic	0.005-0.5	0.022
Polyamide	0.015	0.022-0.097
Polyester	0.008-0.041	–
Polyethylene (linear)	0.00015	0.00015
Polymethyl methacrylate	0.06	0.02
Polystyrene	0.0001-0.0005	0.0001-0.0004
Polyurethane (two component castor oil cure)	–	0.016-0.036
Polyurethane (one component)	0.038-0.039	0.068-0.074
Polyurethane (one component)	0.02	–
Polyvinyl butyral	0.007	0.0065
Polyvinyl chloride	0.08-0.15	0.04-0.14
Polyvinyl chloride, plasticized	0.10	0.15
Polyvinyl chloride-vinyl acetate copolymer	0.6-0.10	–
Polyvinyl formal	0.007	0.02
Polyvinylidene fluoride	0.049	0.17
Polyxylylenes		
Parylene N	0.0002	0.0006
Parylene C	0.02	0.0128
Parylene D	0.004	0.0020
Silicone (Sylgard 182)	0.001	0.001
Silicone, flexible dielectric gel	0.0005	–
Silicone, flexible, clear	0.001	–
Silicone (RTV types)	0.011-0.02	0.003-0.006
FEP dispersion coating	0.0002-0.0007	–
TFE	0.00012	0.00005

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cloth. The principal disadvantages of cellulose paper are moisture sensitivity, dimensional instability, and limited operating temperature. Glass cloth is the standard reinforcement where dimensional stability and high strength are required.

Reinforcing layers produce anisotropic and variable electrical properties, interfaces for wicking of moisture and processing chemicals, and nonuniformity in machining characteristics between binder and filler. By restricting edgewise expansion, reinforcement increases the transverse expansion, which jeopardizes the integrity of plated-through

TABLE 9-4d Properties of Coated Wires[a]

Coating	Thermal Rating, °C	Advantages	Limitations
Formvar	105	Toughness, high dielectric strength, compatibility, heat shock resistance	Crazes in polar solvents
Polyesters	155	Toughness, dielectric strength, chemical and cut-through resistance	Hydrolyzes in moist, sealed atmosphere
Polyurethane	105	Dielectric strength, chemical resistance, compatibility, solderable without stripping, moisture and corona resistance	Reduced abrasion resistance
Nylon	105	Dielectric strength, solvent resistance, solderability, toughness, windability	Moisture absorption, high electrical loss at all frequencies
TFE	180	Thermal stability, chemical stability, dielectric strength, low dielectric constant	Abrasion, gas permeability, cold flow, adhesion
Formvar–nylon	105	Solvent resistance, toughness, windability, heat shock	Nylon portion subject to same limitation as nylon above
Formvar–nylon	105	Bondable, dielectric strength, heat shock resistance	Vibration, high mechanical stress
Polyurethane–nylon	105	Solderability, solvent resistance	Moisture absorption, high-frequency losses
Polyimide	220	Thermal resistance, chemical stability, radiation resistance	Stripping difficulty, solvent crazes
Polyimide/fluorinated ethylene propylene	200	Good mechanical, physical, electrical, and high-temperature properties	
Cross-linked polyimide–polyamide	150	Good mechanical, physical, electrical, and medium-temperature properties	
Polyvinylidine fluoride	135	Good mechanical and physical properties	Poor electrical (K = 7.7), fair temperature properties
Cross-linked polyalkene	150	Good mechanical, physical, and electrical, medium-temperature properties	
Polytetrafluoroethylene	250	Good physical, excellent electrical and temperature properties	Poor mechanical
Polyvinyl chloride	105		Poor mechanical, fair physical, poor electrical (K = 5.7) and fair temperature
Silicone rubber	200	Good electrical and high-temperature properties	Poor mechanical, fair physical

Note: A prebake at 125°C for 2 to 4 hr after winding relieves film stress so that crazing does not subsequently occur during varnish or resin encapsulation.

[a] Data printed with permission from *Materials Engineering Magazine* (September 1970, p.36), Reinhold Publishing Corporation.

holes and causes undesirable changes in propagation characteristics for microwave signals.

A good example of the difficulty of providing an improved substrate is polyphenylene oxide (PPO). The only superficially apparent disadvantage of PPO is its high cost. It has the desirable characteristics of homogeneity, good-to-excellent electrical properties, thermal stability, flame retardance, dimensional stability, and low water absorption. Its mechanical properties are adequate in thickness of 1/16-in. and over (thinner when supported). These properties make PPO a more ideal substrate for microwave stripline circuitry than TFE-glass. Yet, PPO has only limited success to date because of sensitivity to solvents and tendency to stress crack. There are also reports that it is not sufficiently insensitive to moisture and that it oxidizes on long-term heating at 150°C or above. Designers of microwave circuitry who have started with PPO commonly switch to the apparently less desirable TFE-glass laminate because it can be processed and is mechanically reliable.

A better substrate is not the only need for computer circuitry. In multilayer circuits for high-speed logic interconnections, control of circuit impedance is becoming critical. Holding circuit impedance to required tolerance demands control of both dielectric constant and circuit dimensions (line width and dielectric thickness). Present bonding layers for constructing multilayer circuitry consist of glass impregnated with B-stage epoxy, which flows unpredictably under heat and pressure and causes mechanical and electrical variations. New bonding layer materials that bond without significant flow are needed.

In the microwave area, ceramics may become the dominant material for microstrip substrates. The controlling factors here are dielectric constant which can be precisely controlled at values of 9 and above, and also substrate thickness which can be precisely controlled by grinding. It is presently possible to achieve dielectric constants of 8 or 9 with titania-loaded polytetrafluorethylene (TFE) which could be produced in large sheets at relatively low cost. The problems are thickness control and dielectric constant control. Basic research seems unlikely to turn up homogeneous organic material with a low dielectric loss and a dielectric constant of 9. Therefore, needed R&D appears to be in the areas of better binders for the high dielectric constant filler and of processing techniques to control composition and thickness.

No presently available polymeric films are entirely satisfactory for flexible circuitry. Improved moisture resistance and the ability to maintain high insulation resistance in moist atmospheres are substantial needs both for the base materials and for the finished circuit. The water absorption of polyimide film is probably its most serious deficiency not only because it degrades the insulation resistance, but also because it causes dimensional changes. A strong dimensionally stable film with very low moisture sensitivity would be a good research goal.

9.8 MICROELECTRONIC PACKAGES, POTTING, ENCAPSULANT MATERIALS

9.8.1 Current Materials

Silicone transfer molding resins
Epoxy transfer molding resisn and potting resins
Phenolics
Diallyl phthalate transfer molding resins

9.8.2 Needs

9.8.2.1 MATERIALS

1. Elimination of ionic impurities from the resins (major cause of electrical failure)
2. Improved moisture resistance or means for protection (better or defect-free bonding)
3. Reduction or elimination of shrinkage on resin curing
4. Decrease of thermal expansion coefficient to be more in line with those of active and passive components (major need)
5. Increase of thermal conductivity (major need)
6. Uniformity of materials, batch to batch
7. Constancy of physical properties
8. Development of suitable materials for injection molding
9. Better control of dielectric constant
10. Elimination of catalysts which will react with circuit components
11. New thermosetting polymers

9.8.2.2 PROCESSES

1. Decrease the time for molding in the transfer molding process
2. Eliminate sticking in molds

3. Lower the resin viscosity in the transfer molding process
4. Develop an injection molding process
5. More automation

9.8.2.3 RESEARCH

Basic, applied, development
1–7 years

9.8.3 General Remarks—Packages, Potting, Encapsulation

The majority of materials used for potting and the like are either epoxy or silicone polymers (one estimate of current usage within RCA is a quarter million pounds per year). They are used for a wide variety of applications. Users are pretty much at the mercy of the manufacturers, as far as specific properties are concerned. This is likely because, until now, sophisticated uses of these materials have represented a small fraction of the overall market; the manufacturers have not been motivated to research and formulate small batches of specialized products. With the expected rapid growth of plug-in circuit modules for home instruments and the need to encapsulate an increasingly diverse number of miniature circuits composed of exotic materials, the situation is bound to change. Manufacturers will have to concern themselves with producing highly refined materials, free of trace impurities. Batch-to-batch uniformity of behavior of these materials must improve. It will not be possible to leave to luck the question of interaction of components and catalysts in these substances with various materials and components likely to be found in miniature circuits. The dielectric constant will have to be a controllable property as potted elements are used at higher frequencies. Uses in components for military and aerospace will require materials which retain a constant set of physical properties over a wide range of temperature. In some applications, shelf life of the materials before use has been a problem. Quicker-setting materials are needed in some operations. In brief, to meet the demands of an industry of growing sophistication, the manufacturers will have to produce a set of these substances with properties of a matching degree of sophistication.

An important new approach to volume production of potted circuits is the concept of *injection molding* the encapsulant. This would, in principle, permit the fabrication of the container and the placing of the protective mass of encapsulant in a single, rapid, cost-saving operation. Aside from the purely mechanical problems this approach poses, a class of thermoplastic (curable) molding compounds with the above-mentioned qualities will have to be developed which can be processed at temperatures below the point at which solders melt or circuit elements degrade.