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for the
COUNCIL ON MATERIALS SCIENCE
UNITED STATES DEPARTMENT OF ENERGY

November 1979

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PANEL REPORT
ON
NEW MATERIALS

Published Under the Auspices
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for the
DIVISION OF MATERIALS SCIENCE
U. S. DEPARTMENT OF ENERGY

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DECEMBER 1979

INTRODUCTION

This report is one of a series resulting from studies conducted under the auspices of the Department of Energy (DOE) Council on Materials Science. The Council was established to provide the DOE Division of Materials Sciences with in-depth studies of selected important areas of materials research and was an outgrowth of a series of overview workshops held in the Spring of 1977. The workshops were held to lay the foundation for basic materials research needs and opportunities for the then impending new energy department. Reports of these workshops were subsequently published. Professor Robert Maurer of the University of Illinois is the current Council Director.

The Council sponsored two panel studies in 1978 on High Temperature Ceramics (chaired by Professor Kent Bowen of M.I.T.) and on the Theory of Surfaces (chaired by Dr. Donald Hamann of Bell Telephone Laboratories). The panel studies of 1979 were on New Materials (chaired by Professor T. H. Geballe of Stanford University) and on Corrosion (co-chaired by Professors Robert Rapp and Digby McDonald of Ohio State University).

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PREFACE

The present report on research opportunities in new materials is the product of a diverse panel of physicists, chemists, and materials scientists. At the best, it will provide some wisdom and guidance. At the very least, the panel members themselves gained from the opportunity to exchange ideas and priorities.

The Panel was organized at the request of the Council of Materials Sciences of the U.S. Department of Energy's Materials Sciences Division to *generate a report on needs and opportunities in basic research on new materials* with the intention to provide advice which "the Division of Materials Science can use in planning future research programs." Further, it was made clear that there should be a non-tenuous link between basic research opportunities and energy-related problems facing technology. In other words, the Panel was given the license to take an uninhibited "far-out" look, but to bear in mind the mission of the Department of Energy. Any report by committee hammered together in one working session has, by its very nature, to present the consensus which prevails at that moment in time by those present. The boundary conditions, imposed by the Council of Materials Science, ensure that the panel report is timely if not scholarly. The report should be taken in the perspective through which it was prepared: a "best effort" of those present at Pajaro Dunes, California, from Sunday night, August 19, to Friday noon, August 24, 1979.

The Panel was activated in the Spring of 1979. Members were chosen with expertise in different areas. Before meeting, we prepared a list of potential topics classified by types of materials, phenomena, technique or function. In doing so, it was recognized that a built-in redundancy would result: *i.e.*, a given research opportunity might be discussed as a type of material, or a product of a developing technique, or its function. Those who read the final report will recognize that some redundancy has remained. For this, we offer no apology; in fact, the contrary: it is a plus when some research appears attractive from different points of view.

A large matrix was prepared prior to the meeting, listing all the topics on one axis and the panel members on the other. At the initial meeting on Sunday night, each panel member checked the topics of interest to him. The topics were then consolidated into subgroups which subsequently became the chapters of this report, and a coordinator was chosen for each group as noted by the superscripts on p. iv. At least one topic, ceramics, was omitted because of the comprehensive report submitted by the Bowen Panel last year on that subject. Morning and evening meetings were scheduled and afternoons were left free for informal interactions as in the Gordon Conferences. Group meetings were held in series and parallel during the five days. There were also periods where the entire panel met to hear and react to the group thinking at several stages of development.

An attempt was made by each group to structure its chapter along the following lines:

- An informative discussion of the present state of the science.
- Specific areas where research opportunities lie.

- Needs of the scientific community which, if met, would help appreciably in addressing the research opportunities.
- Needs and opportunities of technology which stand to gain if research opportunities are realized.

Each subgroup report evolved in different ways, so that in the final report a common format is scarcely recognizable. This is not surprising since each field has unique features.

Each coordinator took responsibility for consolidating and editing the rough drafts prepared by the members working on his overall topic at the meeting. The entire panel gave inputs during the meeting and during the subsequent final phases of preparation.

We hope readers accept this report in the spirit in which it was prepared: a snapshot taken in August 1979 of promising research opportunities in new materials apparent to the collective wisdom of panel members.

Council on Materials Science Panel on
NEEDS AND OPPORTUNITIES IN BASIC RESEARCH ON NEW MATERIALS
August 19 - 24, 1979

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REPORT HIGHLIGHTS

The Panel was given a broad (and diffuse) charter and responded by producing eight different chapters, any one of which could easily be expanded into a full report. The chapters are summaries of opportunities in their respective areas. The reader is referred directly to the chapter of interest to gain the perspective developed by the panel. Here, we present highlights of general interest.

1. A large number of new phases can be made without a massive effort, simply by imaginative application of a variety of state-of-the-art techniques.

New paths, beyond the traditional routes of synthesis, which have the potential of vastly increasing the number of known compounds are discussed in Chapters 1, 3 and 5. Transport of the reactants through liquid, vapor, or vacuum can be highly controlled with modern instrumentation, and feedback techniques. Film synthesis and characterization make it possible to survey phase space over a wider range of temperatures and composition and in much finer detail than heretofore.

2. Close-coupling of synthesis and characterization efforts with investigations of physical and chemical properties is highly desirable.

The ideas which flow around a closed loop of integrated research involving synthesis — characterization — investigation of properties — modification of synthesis—...generate a stimulating and vigorous environment, conducive for creative research. An example is discussed in Chapter 3 where unusual magnetic and superconducting responses to chemical substitution on certain sites are found in ternary

phases. Progress in unanticipated directions — a hallmark of basic research — can be anticipated. The discovery of cathodes for high energy-density batteries resulting from research on the superconducting properties of intercalated layered metal dichalcogenides is an example discussed in Chapter 6. The use of model systems to learn about relationships between structure, composition and properties is advocated for polymers (Chapter 2), catalysis (Chapter 7) and semiconductors (Chapter 8).

3. Amorphous materials (Chapter 4), and thin films (Chapter 5) offer a wide range of systems which can increase basic understanding and offer promise of solutions to technical problems.

Basic concepts need to be established: answers to such questions as — what is a defect in an amorphous material; what role does it play in plastic deformation, diffusion, atomic transport, or ionic conduction? What is the origin of the extreme corrosion resistance of certain amorphous alloys? How does one describe electron structures and transport phenomena in amorphous alloys?

4. Most innovative inorganic synthesis has been done in Europe with the United States playing a minor and perhaps diminishing role. University-based research efforts in the United States should be encouraged.

Until recently, Europe has provided the U.S. with well-trained solid-state chemists, and has been a source of new compounds. Table II (Chapter I), references the first synthesis of some prototype "landmark compounds." The relatively small contribution from the United States is evident. The long time intervals between the first synthesis of the prototype compound and recognition of special properties is a consequence of the fact that synthesis in Europe was done for its own sake and not closely coupled to property measurements, phenomena or theory. Recent

trends in Europe (and Japan) show more interest and effort in evaluating newly synthesized materials. The needs of the U.S. for solid-state scientists skilled in synthesis and for sources of compounds to help in overcoming materials problems in energy-related technology will require more university-based research in our country along the lines discussed in (1), (2), and (3) above. It is a challenge for the funding agencies in Washington to encourage the climate for doing so. Updated critical reviews of information scattered throughout literature (Chapter 1) would help in bringing new research to the frontiers.

CHAPTER 1

INORGANIC SYNTHESIS

INTRODUCTION

It would not be possible to calculate the ground state of 10^{22} condensed atoms, let alone a simple property such as their melting point, even if one were given the atomic wave functions, the largest digital computers, the most talented scientists available, and time since the beginning of the universe. On the other hand, a properly prepared system can be an analogue computer, or, as it is more commonly put, a reaction chamber and can provide answers in an efficient, economical way that sometimes leads to the unexpected. Materials synthesis is not likely to become an outmoded discipline in the foreseeable future.

All conceivable energy technologies are limited by material performance. It is an obvious but perhaps overlooked truism that to find better materials one first has to produce the materials. Some needs will be met by purer or better forms of known materials or by alloy additions and control of morphology, but others will require the synthesis of totally new chemical structures.

Among the undiscovered compounds some will be easily synthesized but have not yet been sought. A greater number require critical synthesis conditions, not only as regards the usual variables, but also as to the container, purity, transporting agents, "mineralizers," etc. The number

of remarkable new phases which are being discovered even in supposedly simple systems (*vide infra*) attests to the frequency with which these conditions have not been met, even in prior investigations which might have been judged as thorough. In addition, a presumably large group of materials remain undiscovered¹⁾ either because

- the rate of formation under any set of conditions is extremely slow, or
- an upper temperature limit for synthesis which is fixed by some decomposition reaction is still too low for a reasonable rate formation.

A good example is Mo_6S_8 , a conceptual predecessor of many Chevrel phases which can be made only by indirect routes; the analogous W_6S_8 and W_6Se_8 probably exist but have never been made, presumably because of low decomposition temperatures (latter case above). One can only imagine that some untried solvent, transporting agent, or vapor deposition route will make these accessible. Because of these circumstances, it can be seen that the boundaries of what is possible in the solid state are poorly defined and, correspondingly, so is one's vision insofar as applications and processes.

Some degree of synthesis by design can also be envisioned: new phases which have the combined attributes or any combination of van der Waals bonding or open structures (for easy chemical substitution and rapid ionic diffusion), metallic bonding (for electrical, thermal properties and ductility) and ionic and covalent bonding (for strength and hardness).

It is useful to recognize that the intellectual input of the synthetic component to research can vary greatly. We recognize four categories:

1. Synthesis of known materials in a specified quality, quantity, crystallinity, shape, order, etc. This effort almost always has a service component; however, it may also require creative efforts in the development of techniques and apparatus.

2. Synthesis in order to study a specific property. The effort may range from development to basic research. The phenomenological orientation may often dominate, with synthesis *per se* making a narrow contribution. Production of new structures from such synthesis efforts is rare.

3. Synthesis within a structural or related class for the purposes of exploration, extension, or extrapolation of properties. Systematic measurements of related physical properties are frequently the basis for extending predictive capabilities and for testing models. Investigations of magnetic and electronic properties are examples. This work overlaps with type 2 (above), but the role of the synthesis effort is more creative here.

4. Synthesis of entirely new types of compounds. Research of this character frequently precedes those of types 1-3 above. Success provides new solid-state structures, and with these, the promise of novel and new properties, new phenomena and new solutions for materials problems. These results also shape, redefine, and broaden our understanding and concept of the solid state. Naturally, the predictability of any result in this category may be very small.

OPPORTUNITIES FOR RESEARCH

The synthetic effort is enhanced when there is a closed loop between the synthesis, characterization, and property evaluation. Joint efforts across academic departments in universities are to be encouraged in order to benefit from interdisciplinary inputs as is done in the larger industrial laboratories. More effective understanding of the relationship between structure and various phenomena very much needs to be developed. A novel structure is often the first indication of potentially interesting properties, and conversely, measurement of an unusual property signals an unusual structure.

The search for totally new materials naturally has associated with it the highest risk, and the largest reward as well. The initial proposal must provide some good evidence or basis for believing that a particular system or type of reaction will produce a particular kind of product, bonding type or structure, although actual results often demonstrate the researcher's fallibility in predicting the unknown. A broad perspective in descriptive and structural chemistry and in solid-state physics is necessary as well as the ability to recognize and identify significant new reactions and products. Synthesis can also greatly benefit from theories which aid intuition, make predictions, and are yet rigorous enough to go beyond empiricism in aiding the understanding of structures, stability, and properties, especially of entirely new types of compounds. The nature of hydrogen in intermetallics and other inorganic phases is an example.

A number of novel materials can possibly be prepared by "high temperature" routes where one takes advantage of the unusual, often complex, molecular species which form in high-temperature gaseous systems as well as in high-temperature liquids where kinetic barriers are also minimized. Amorphous

products from quenching experiments in the liquid systems are discussed in Chapter 4. New and useful transport reactions utilizing complex equilibria may be limited by the investigator's understanding of these systems and the imagination in devising transporting agents. A proper choice of precursor species for synthesis may be invaluable. The ultimate approach in synthetic efforts, using epitaxial or molecular beam techniques to lay down reactants a few layers at a time, is discussed in Chapter 5. Molten-salt solvent systems as a synthetic means have received relatively little attention, save for unusual compounds which may be frequently separated from binary systems. Electrochemical techniques for synthesis, discussed in Chapter 3, have been only roughly explored. The choice of specific systems in which to seek new materials is the most difficult aspect and may often depend on slim leads, chemical intuition or just exploration of the unknown.

On the other hand, Category 3 (pg. 3) synthesis is more predictable. It can lead to exciting research, particularly when exploring systems with unusual structures or properties. It is almost a prerequisite to have the synthesis and property investigations and theory closely coupled. (By property here we mean any of a wide variety of physical or chemical phenomena. Examples might be elasticity, electrical conductivity, reactivity, etc.) The challenge is to establish the connection between composition and/or structure and the property(ies).

Traditional methods of support of university-based research have not actively provided a climate in which the close-coupling would thrive, in contrast to the organization of industrial and national laboratories. Thought should be given within the Division of Materials Science to ways in which better Category 3 and 4 (pg.3) type research can be made to thrive in universities.

A collection of compounds with unusual structures or properties, which offer opportunities for further research, are given in Table I. Noteworthy is the large number of highly reduced materials more or less along the interface between metals and conventional salts. Many of these have been found in supposedly "simple" binary systems, given testimony for the earlier assertion that the number of truly unusual compounds to be discovered is large indeed.

RESEARCH NEEDS

1. National effort

A broad and pervasive need for new and better materials requires that increased efforts be devoted to their creation — better examples of known materials in important applications, broad ranges of materials to aid and test our understanding of solid-state structure and properties, and totally new compounds for which applications and phenomena have not yet been conceived. The long-range future depends particularly on the last. The history of major advances in solid-state science and of significant applications and devices therefrom indicates that in nearly all cases the original prototype compound was synthesized without design for application or property, after which subsequent investigations and development led to the advance or application. An admittedly incomplete, but perhaps representative, list of such landmark advances in synthesis — usually unrecognized at the time for their significance — is given in Table II.

A continuing national problem regarding the origin of these landmark materials seems apparent; by all measures the amount and breadth of solid-state inorganic synthesis in the United States is relatively small, in contrast with the general situation in Europe and Japan. In Germany, there are 25 universities where at least one professor with inorganic interests directs research in solid-state synthesis and characterization, plus three well-integrated synthesis programs at the Max-Planck-Institute in Stuttgart.

The U.S. output of novel synthesis, at least as described in the scientific literature, reflects the fact that students in chemistry are only rarely exposed to the challenges of the solid state. Government and industrial laboratories find it difficult to find U.S.-trained personnel in solid-state synthesis and characterization. As pointed out in Chapter 6, European-trained solid-state scientists have been an important source which seems to be drying up at present. A recent survey of publications in the *Journal of Solid State Chemistry* shows that contributions from the United States have fallen from almost 50% at the beginning of this decade to less than 20% in 1979. (See letter from M.J. Sienko attached as an appendix to this chapter.)

2. National Needs: Use of state-of-art equipment

On the other hand, some optimism can be derived from the opportunities if the substantial gains in instrumentation and techniques can be realized. These new capabilities are expensive, and means should be found to increase their utilization in laboratories. Apparatus and tools which have become available or have been applied to synthesis problems only in recent years include:

- Superior containers and means for their fabrication,
- Excellent inert atmosphere facilities,
- High resolution x-ray powder techniques; automatic diffractometers,
- Improved means of analysis (microprobe, ESCA, electron microscopy, etc.).

3. Use of theory

Both ionic diffusion and phase stability are of prime importance to synthesis. Many solid-state synthesis reactions require good ionic diffusion at temperature in order to succeed; the need for a much better understanding of this process is discussed more fully in Chapter 6. The problem

of phase stability pervades many parts of this report implicitly and explicitly. Although there exist a number of empirically based predictive theories of phase stability of simple intermetallic phases, *i.e.*, of Engel-Brewer,¹⁵⁾ and of Miedema,¹⁶⁾ these have had only limited success and no applicability to a wide range of other materials which are not inter-metallic. One anticipates that new, complex, strongly-bonded materials will occur with a proper combination of transition metals and non-metals as regards size, electronegativity, electron count, admixture of covalent and metallic bonding, and qualitative band features. The search for new materials for superconducting applications, hydrogen storage, and many other energy-based uses very much needs advanced theoretical insight for guidance. Increased speed and accuracy in the calculation of electronic band structures gives some hope that such calculations may be useful for predictive as well as analytical purposes. Both empirical approximations and more rigorous calculations are badly needed to guide thinking on synthetic projects on a week-to-week basis.

4. Data collection and evaluation

Problems of phase stability are also central in discussions in later chapters. The search for new compounds with unusual properties depends upon ready accessibility to previously obtained data on the thermodynamic and physical properties of potential candidates and their analogues. "Ready accessibility" in this sense requires continuous efforts to provide and update compilations of critically evaluated data of various types. Particularly useful has been the critical evaluation of binary phase diagrams published in volumes by Hansen and Anderko (1958)¹⁷⁾ and supplemented by Elliott,¹⁸⁾ and Shunk.¹⁹⁾ For many purposes, the phase diagram

information generated in the ten to fifteen years since Shunk's review lies buried, and unused by those who need it. The lack of critically evaluated data is felt so severely that it has lead one industrial library²⁰⁾ to distribute current phase diagrams in a looseleaf format,²¹⁾ which is useful but limited by lack of completeness and criticality. The same is true of many other data needed by materials scientists, such as the alloy thermodynamic data compiled for an extended period by Hultgren and coworkers of the University of California, and other thermodynamic data formerly computed by K.K. Kelley of the U.S. Bureau of Mines. An example of a useful ongoing project is Roberts continuing non-critical, but complete compilation of superconducting data.

The Panel is aware that the need for data organization and evaluation exists over a broad range of physical science, and that this problem has been studied by a recent National Academy of Sciences committee (the Committee on Data Needs) and commented upon by other Academy committees (the Committee on Chemical Sciences and the Committee on High Temperature Science and Technology). Those committees proposed that 0.1 - 0.2% of the Federal research and development budget be specifically earmarked for critical evaluation and compilation of data in all fields of science.

TABLE I: Examples of compounds where an unusual structure or an unusual property signals a research opportunity.

COMPOUND	UNUSUAL FEATURE	More detailed discussion in literature
Nb_5Se_4	Infinite chains of M_6X_8 -type clusters sharing faces	Ref. 2
Cs_{11}O_3 , Cs_7O	Nonmetal structure in a metal array; photoemission	Ref. 3
Ta_2S	Strongly bonded columns of metal polyhedra	Ref. 4
NaMo_4O_4 , Sc_5Cl_8	Infinite chains of metal octahedra, high stability	Ref. 5, 6
ZrCl , ZrBr	Infinite, strongly bound double metal sheet structure	Ref. 7,
SmB_6 , SmS	Mixed valency (5d, 4f)	Chapter 3
$(\text{RE})\text{Mo}_6\text{Se}_8$	Cluster compound/high critical field	Chapter 3
Nb_3X $\text{X}=\text{Al}, \text{Ge}, \text{Si}$	High critical current	Chapter 3
$(\text{RE})\text{Rh}_4\text{B}_4$	Coexistence of superconductivity and magnetism	Chapter 3
$\text{M}(\text{Ch})_2$	Layered chalcogenide charge density waves,	Chapters 3, 6
Li_3N	High ionic conductivity	Ref. 8
Te_2Cl_2 , BiI ,	Unusual metal chains	Ref. 9, 10
$\text{Hg}_{3-x}\text{AsF}_6$	Infinite linear strings of Hg	Ref. 11
$\text{Ca}_{11}\text{Bi}_{10}$, Na_3Hg_2 , KSn	Heavy metal clusters in intermetallic phases.	Ref. 12
$(\text{Ag}_6\text{O}_8)\text{AgNO}_3$	Superconducting, ionic clathrate	Ref. 13
PdSi (amorphous) and derivatives	Soft magnetic materials, corrosion resistance	Ref. 14
PVF_2	Piezoelectric polymer	Chapter 2

TABLE II: Some inorganic syntheses leading to landmark developments in solid-state science.

PROTOTYPE COMPOUND	FIRST REPORTED BY	COUNTRY	YEAR	SUBSEQUENT DEVELOPMENT
$K_{0.5}MoS_2$, $LiMoS_2 \cdot 0.6 NH_3$	Rudorff	Germany	1959	Battery cathodes (Li_xTiS_2)
KC_8	Fredenhagen	Germany	1926	Metallic graphite, high-energy batteries
β -alumina (Mg,Ca, (Na))	Rankin Stillwell	U.S.A. U.S.A.	1916 1926	Solid electrolyte
$ZrO_2(Y_2O_3)$	Nernst	Germany	1900	O_2 sensor
$ZrO_2(CaO)$	Ruff	Germany	1929	O_2 sensor
V_3Si	Wallbaum	Germany	1939	A15 high-temperature superconductors
$SnMo_6S_8$	Espelund	Norway	1967	Superconductors- very high fields
$(Mo_6Se_8) M^{II}Mo_6Ch_8$	Chevrel	France	1971	
$K_2[Pt(CN)_4]x_{0.3}$	Krogmann	Germany	1968	One-dimensional metals by oxidation
$Bi_2(MoO_4)_3$	Zambonini	Italy	1915	Oxidation catalyst
H_xMoO_3	Glemser	Germany	1951	Electrochromic displays, proton mobilities in solids
$BaTiO_3$	Tammann	Germany	1925	Ferroelectrics
$LiNbO_3$	Süe	France	1937	Piezoelectric, non- linear optics
$BaFe_{12}O_{19}$	Adelsköld, Schrewelius	Sweden	1938	Ferrites, memories
InP	Thiel	Germany	1910	III-V semiconductors
(RE)Ni ₅	Klemm	Germany	1943	Strong magnets
Synthetic zeolite	Barrer	England	1948	Many catalysts
Amorphous Si	König	Germany	1944	Solar cells

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Journal of Solid State Chemistry

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13.

October 16, 1979

Prof. T.H. Geballe
Department of Applied Physics
Stanford University
Stanford, California 94305

Dear Ted:

We have just completed an analysis of the papers published in the Journal of Solid State Chemistry in connection with planning for 1980 and 1981. The results clearly show that there has been a decline in the percentage of papers originating in the U.S. The apparent gainers are France, Germany, and Japan. Here are the relative percentages, comparing the 3-yr periods 1970-72 and 1976-78. Also included are the results for the first 9 months of 1979.

	<u>1970-72</u>	<u>1976-78</u>	<u>1979 (9 mos.)</u>
Australia	8.4%	3.3%	4.4%
England	2.8%	5.9%	3.7%
France	15.6%	25.7%	25.7%
Germany	3.1%	5.1%	9.6%
Japan	1.1%	7.4%	7.4%
Netherlands	7.8%	4.2%	8.1%
U.S.	47.2%	25.6%	19.1%
all others	14.0%	22.8%	22.0%
total number of papers published	358	544	136

According to the French members of my Editorial Advisory Board, the enhanced publication rate of the French laboratories is a direct result of increased government support for solid state chemistry research in France. The actual explosion of French publication in this area is even bigger than our figures indicate since we need to take into account that the French have started two materials journals in the French language since 1972.

Sincerely yours,

Mike

M.J. Sienko, Editor
Professor of Chemistry

MJS/by

CHAPTER 2

BASIC RESEARCH ON NEW POLYMERIC MATERIALS

INTRODUCTION

The importance of polymer materials to the major energy technologies is clearly illustrated by the many programs currently being funded by the Department of Energy. Most of these programs are of a short-range nature and depend on the use of, or modification of, current state-of-the-art polymer materials.¹⁾ It is the purpose of this section to define various areas of polymer research which could lead to new materials which combine properties critical to future DOE needs. This is not intended as a comprehensive overview for polymer research; but rather, five areas enumerated below have been selected for particular consideration because of the specific backgrounds of the "authors." These include:

- High temperature polymers
- High strength-modulus polymers and composites
- Radiation sensitive/stable polymers
- Impervious/semipermeable/soluble polymers
- Electrical properties of polymers.

In considering these five topics, there are several themes that seemed to be common to all of the areas. Hence, these are discussed in these opening paragraphs.

We identified as a very important requirement the need to closely wed research on fundamental polymer phenomena to strong synthetic programs.

In all of the proposed programs the need to better understand structure-property relationships was clearly evident. For example, in conducting polymers, structural requirements associated with the development of conducting electrons is not yet understood. Conceptual approaches to combine the unique electrical conductivity features with desired rheological properties have as yet not been defined. With high-temperature polymers, structural features deemed necessary for thermal stability are still not clearly understood, let alone the complex mechanisms of degradation observed under different environments. In the case of high strength-modulus polymers and composites there is virtually no understanding of the rheological and morphological characteristics of thermotropic (rigid, rod-like) polymers which would provide a basis for understanding their unusual behavior. Work on developing new higher strength-modulus reinforcing agents for use in composites is at a standstill because of the lack of insight as to the strength-limiting features in filaments with glassy, polycrystalline or ribbonlike morphologies. In the area of radiation stable (sensitive) polymers this field remains more an art than a science. Fundamental understanding of mechanisms of reactions of polymers when exposed to different types of radiation including neutron, electron beam, x-ray, deep UV and near UV is desperately needed, since polymer scientists working in these areas are forced to operate on an empirical basis. With respect to permeability of gases through films, some understanding as to the mechanisms has been developed but as yet little progress made on devising new, more impervious films or semi-permeable membranes based on these concepts.

One very important concern identified by this study group, which in part may explain the slow rate of progress on developing new polymers, is the almost complete absence of strong polymer synthetic capabilities in the universities. Thus, while most polymer groups in universities have brought together scientists with outstanding skills in polymer characterization for study of structure-property relationships, the complementary effort in synthesis is lacking. Historically, this balance was maintained primarily through the very strong synthetic efforts in industry; however, during the past decade the chemical industry has shifted its focus from developing new polymers to improving existing systems and processes. Hence, a large void now exists in the area of new polymer synthesis.

Another point which is common to all of the indicated programs is the need to design into polymer structures those features which permit ease of rapid melt processing into the myriad of forms such as injection molded parts, extruded films and fibers coatings, etc. Those polymers which are processed from solvents are clearly less desirable, not only because of the energy required to evaporate the solvent but also because of the need to eliminate solvent wastes from effluents. Finally, it is apparent to this group that the potential to develop new and unusual polymers which combine unique properties tailored to specific goals is just in its infancy. This versatility is an attractive feature of polymer materials and the need for highly trained polymer synthetic scientists will increase sharply in the coming years.

HIGH TEMPERATURE POLYMERS

With respect to basic studies directed at high temperature polymers, there is considerable information of an empirical nature which has built up over the past 20-25 years on this subject.²⁾ Unfortunately, there is considerable confusion as to the limitations of present materials, and, in particular their mechanisms of degradation. Thus, elastomers such as silicones, polyphosphazenes and carborane polymers are thought to degrade in the range of 200°C. A program aimed at defining the exact limitations can be designed around using available materials. A second approach to high temperature elastomers involves synthesis of new perfluoro polymer structures which can be readily cross-linked to yield useful elastomeric properties. The optimum design for such structures as well as their mechanisms of degradation would appear to be of considerable scientific interest. Finally, another approach which may be of value is to take advantage of the high temperature polymer technology developed over the past 25 years. Thus, by modifying these various structures to reduce their T_g below $\sim 150^\circ\text{C}$ could yield a material which behaves as an elastomer at temperatures above 175°C .

The design of high-temperature polymers which incorporate the desired melt rheology features combined with extremely high strength-stiffness features represents a major challenge to polymer scientists. Basic studies on morphology, rheology and new synthetic approaches must be pursued to realize this goal.

The significance of the above programs to long-range needs is clearly illustrated by considering the following applications. Thus in

geothermal energy requirements, there is a need for new elastomers as gaskets and sealants which are stable to 275°C and resistant to brine and H₂S. Similarly, polymer-concrete composites designed as corrosion-resistant structural materials will require development of polymers stable to 400°C. Easily fabricated high-temperature polymers with significantly superior properties over light and refractory metals are needed for many areas concerned with energy conservation. Other programs pertinent to energy conservation include high temperature solid lubricants and laminating resins for high performance composites.

HIGH STRENGTH- HIGH MODULUS MATERIALS

In this section studies on both rigid, rod-like polymers will be considered along with needs for improved reinforcing agents. Work on rigid rod-like polymers has focussed almost completely on the development of lyotropic systems that are spun from solutions into filaments (e.g., Kevlar).³⁾ As such, a considerable body of knowledge has developed on such materials with respect to their rheological and morphological characteristics. On the other hand, thermotropic polymers (*i.e.*, they can be processed from the melt) are just now being described in the literature⁴⁾ and there is essentially no basic understanding as to their morphology and rheology. Thus there is a great need to develop a far better knowledge base as to the fundamental behavior of these melts consisting of rigid rod-like structures, since they offer a far greater degree of versatility in terms of fabricating a wide variety of forms with outstandingly high mechanical properties. To date, only certain aromatic polyesters

have shown these unique features and it is critical that the key structural features associated with thermotropic behavior be identified permitting optimization of the aromatic polyesters and development of new systems.

The topic of new or improved reinforcing agents is considered here because of its importance to high performance composites. It is especially critical in light of the almost total lack of research in this area since the late 1960's, at which time the Air Force and NASA shifted the focus of research on new reinforcing agents to prototype studies.⁵⁾ One of the most important questions is to determine the strength limiting features in carbon filaments with the goal of increasing the strength by three to four times. This kind of research should be directed to a basic understanding of the internal stresses in carbon fibers which arise from differences in crystalline orientation across the fiber diameter. A similar problem may exist in high strength-modulus BN filaments and basic studies on this material would be highly desirable. Studies to develop ceramic composites reinforced with high strength-modulus filaments and designed to withstand temperatures far in excess of 1000°C represent a major challenge for the materials scientist. Candidate systems that might fulfill these requirements include B_4C or SiC filaments embedded into a SiC or Si_3N_4 matrix. Research studies to characterize the high temperature mechanical properties of the candidate filaments and especially the interface with the matrix material would appear basic to progress in this area. As one looks to the next generation of reinforcing materials, studies should be directed to development of new planar reinforcing materials, based on single crystal flakes with aspect ratios of 100/1. Exploratory studies indicate that

lightweight composites with planar modulus values of 30-40 Msi can be fabricated, which represents a two to three times increase over values obtainable with fiber reinforced structures.

The above programs would appear to present a number of important advantages to the Department of Energy, particularly in the areas of energy conservation and energy storage. Thus rigid, rod-like polymers would provide a high-temperature high-strength material significantly improved over light metals such as aluminum with the additional advantage of being fabricated by injection molding and possibly extruded into films. Flywheels fabricated from new higher strength graphite fibers would provide a three times increase in the figure of merit for flywheels. High temperature composites reinforced with filaments stable to 1300°C would provide a meaningful alternative to the inherently brittle ceramic which are currently being developed for use as high-temperature turbine blades.

RADIATION SENSITIVE/INSENSITIVE POLYMERS

Systematic studies to understand the nature of the interactions between polymer structures and different types of radiation sources has yet to be carried out. A large body of empirical knowledge has been generated on photodegradation of polymers resulting in partial solutions through use of stabilizers.⁶⁾ Clearly more basic studies are needed to develop a predictive capability with respect to behavior of polymers in neutron, electron beam, x-ray, Deep UV and Near UV radiation. Programs which undertake to elucidate the degradation mechanisms in polymers on exposure to these various types of radiation should be closely tied to corresponding

research on the effects of radiation on the optical and mechanical properties of films and coatings. With this kind of understanding it would then be possible to design stabilizers tailored to screen against those wavelengths to which a given polymer is particularly susceptible. Another area of particular interest are those polymers which display reversible responses on exposure to specific wavelengths in the UV. Thus, crosslinked polymeric tribenzopyran or cis-biphenylazo structures in the form of films can display one-to-four-percent expansion and contraction in the plane of the film.⁷⁾ This unusual phenomenon appears to depend on reversible ring opening/closing reactions or on cis-trans isomerization which are induced photochemically. Basic research to better understand this phenomenon and to synthesize new systems which can display larger volume changes with a high level of reversibility would seem highly desirable. Of a far more speculative nature is basic research directed at development of new polymers which mimic the features of semiconductors for use in photovoltaic systems.

The above programs, especially on photodegradation reactions in polymers, is of very high priority to both the solar thermal energy conversion and photovoltaic energy conversion programs, particularly with respect to the glazings, concentrators and receivers. A basic understanding of the mechanisms of interaction of polymers with various forms of radiation (particularly electron beam, x-ray and Deep UV) is critical to developing future lithographic processes required for one-micron-and-smaller circuitry for high density microelectronic devices. At present, research in these areas is pursued primarily by the intuitions of the experimenter with very

little fundamental knowledge as a guide. Development of polymers resistant to neutron fluxes would have major impact in the development of cryogenic insulation for fusion reactors.

BARRIER FILMS - SEMIPERMEABLE MEMBRANES - WATER SOLUBLE POLYMERS

In the work on characterizing permeability and diffusivity of polymers to moisture and corrosive gases much progress has been made in defining the role of free volume, degree of crystallinity and nature of polymer functionality. More recent studies have begun to elucidate the effect of stresses on permeability and the tendencies for certain mixed gases to facilitate diffusion. With this relatively broad knowledge base it would seem highly desirable to initiate basic research programs directed at developing new polymer films which incorporate the features of crystallinity with minimal free volume and low functionality. With respect to semipermeable membranes, basic studies to better characterize the mechanisms of hydrogen ion transport through films of sulfonated perfluoropolymers would appear highly desirable, particularly in the search for improved systems. A similar argument could be made for developing new high molecular weight, water soluble, polymers with rheological and functionality features tailored to minimize interreactions with different ionic environments; however, the basic research aspects are not as clear since these studies are far more meaningfully carried out in small scale field tests.

Development of films and coatings with improved barrier properties would have great consequences not only to most of the solar technologies but in many areas of commercial importance. By inhibiting transfer of corrosive

gases through polymer coatings, a major step would be made in reducing the degradation of the polymer-substrate interfaces and greatly extending lifetimes. The development of a sulfonated perfluoropolymer known as "Nafion" has provided a major advance in the electrolytic process for hydrogen production from hydroelectric sources. Thus electrolyzers with efficiencies of 85-90% have been achieved using this polymer as a solid polymer electrolyte compared to commercial electrolyzers which function at an efficiency of 65%. With respect to water soluble polymers for use in enhanced oil recovery, the urgency for pushing research in this area derives from the potential of recovering 280 billions barrels of oil which were previously thought to be unrecoverable.

CONDUCTING POLYMERS

Since the discovery of metallic and superconducting properties in the inorganic polymer $(\text{SN})_x$ ⁸⁾ it has been found that similar properties characterize several organic polymers based on polyacetylene,⁹⁾ polypyrrole¹⁰⁾ and polyparaphenylene.¹¹⁾ Unlike $(\text{SN})_x$ or brominated $(\text{SN})_x$ these organic polymers are not intrinsically metallic nor do they exhibit superconductivity; they are in fact closed shell insulators which become conducting to the degree they can be oxidized or reduced. Polyacetylene, for instance, is an insulator whose electrical conductivity can be varied from $\sim 10^{-9}$ to $10^3 \Omega^{-1} \text{ cm}^{-1}$ by treatment with oxidizing agents such as AsF_5 , I_2 , Br_2 , Ag^+ , etc. or reducing agents such as the alkali metals. Similar properties characterize the polyparaphenylene based polymers. The electrochemically prepared polypyrrole tetrafluoro-borate is somewhat different. In this case oxidation is achieved electrochemically during the synthesis

rather than by "doping" existing material as is the case for polyacetylene powder or molded pellets. The conductivity of the polypyrrole films can presently be varied between 10^{-3} and $10^2 \Omega^{-1} \text{ cm}^{-1}$ by incorporation of controlled amounts of N-methyl pyrrole into the films.

The progress during the last four years reflects the fact that the area has attracted and sustained the cooperative interdisciplinary efforts of the chemists and physicists, both crucial to meeting the challenges of this complex field. Today the field remains exciting scientifically and continues to show promise technologically. Though current successes have led to the stressing of the electrical properties of polymers, efforts should also be directed toward developing polymers which show associated properties such as high thermal conductivity and magnetic behavior.

RESEARCH OPPORTUNITIES

As is to be expected in a relatively new, primarily materials led field, the research opportunities and needs are numerous in order to achieve a basic understanding of conducting polymers comparable to the classical metals and semiconductors.

1. New Polymers

In the area of new polymers significant technological benefits would derive from polymers which besides displaying conducting properties also possess the attractive physical properties of plastics, e.g., processability and stability. Further attempts should be pursued to prepare new conducting polymers, from monomers, where the polymerization is initiated by the Lewis acid or the Lewis base required to induce conductivity. The role of electrochemistry in the field needs more emphasis — not only in

producing new polymers but also in helping define oxidation and reduction potentials of existing polymers. In this latter context, it is of particular importance to find new polymers capable of being doped n-type if the junction properties of polymeric semiconductors are to be capitalized on. Again, in developing guidelines for new polymer systems, it is important to define the importance of polymer geometry. The search for other properties in polymers should be sought, e.g., thermal conductivity and magnetism.

2. Polymer characteristics

Polymers in general, and the present insoluble, poorly crystalline conducting polymers in particular, present significant barriers to their characterization. It is important to learn how to adapt current techniques to these materials and also to develop new techniques. A second approach is to develop new polymers which are soluble or well crystalline which would be more amenable to standard characterization techniques.

Although considerable progress has been made in interpreting the semiconductor ideas, it is necessary to learn more about the physics and chemistry of defects and traps in these materials and their influence on the conductivity needs to be evaluated. In particular, the search for experimental evidence for solitons in these materials should be extended. It is also critical that we learn more about the nature and distribution of the dopant species, particularly in the semiconducting region.

3. Technological possibilities

It is too early to realistically assess the technological implication of conducting polymers. For many applications the technological aspects would be strongly positively impacted by the demonstration that these conducting properties could be obtained in polymers possessing the attractive properties of plastics, e.g., plasticity, elasticity, low density chemical and thermal stability. However, in view of the progress in this area it is not unreasonable to speculate a commercial future for organic conductors in the same way organic photoconductors have begun to compete with their inorganic analogs.

4. Piezoelectric polymers

Polyvinylidene fluoride (PVF₂) is a semicrystalline polymer which is currently of great interest in a variety of research areas because of its high piezoelectric and pyroelectric coefficients, and because of its large nonlinear optical coefficient and high dielectric breakdown strength. The polymer chain composed of CH₂CF₂ monomer units exhibits a strong transverse dipole moment which is responsible for most of its interesting properties. However, charge injection and trapping also occur, and there is currently some controversy as to which effect is the dominant mechanism. Fundamental questions such as the role of the amorphous region in charge trapping, charge conduction, and dielectric loss have not been addressed.

The opportunity to answer these questions exists by variations in synthesis and processing. Several avenues are currently being studied, including copolymerization with nonpolar species such as tetrafluorethylene (C₂F₄), and low temperature homopolymerization which reduces chain defects

such as head-to-head linkages. The crystalline-to-amorphous ratio in the latter material is considerably enhanced over commercial material due to its lower defect density, and some variation in properties has been achieved.

The bulk of the studies have been oriented toward characterization and application of commercially available film. Their most serious handicaps are that, at the present time, there is no domestic source of electroded and poled films having a wide range of properties. One very important application, the nondestructive testing of materials and structures by acoustic imaging using conformable PVF_2 transducers, has been identified. This application would benefit greatly from films having increased piezoelectric modulus and reduced loss tangent.

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CHAPTER 3

INTERMETALLIC COMPOUNDS

INTRODUCTION

Free energies of formation of intermediate phase compounds often are small — but their physical properties — strength, hardness, corrosion resistance, hydrogen storage capacity, superconducting properties, magnetic properties, etc., can all be vastly different, and in favorable cases can be applied to solve technologically important problems.

A great deal has been learned about binary phase diagrams in the past using the techniques of thermal analysis, powder metallurgy, optical microscopy, and x-ray diffraction. However, there remains an even richer field of intermediate phases with three or more types of atoms per unit cell which are sometimes called ternary phases. Under favorable conditions, as already pointed out in Chapter 1, these phases can have the combined attributes of partial van der Waals bonding or open channels (for easy chemical substitution), metallic bonding (for electrical properties, ductility), and ionic and covalent bonding (for strength, hardness). There further remains an uncharted field of intermediate phases which have not been reached by traditional methods of preparation because of

n.b.: The term *intermetallic* has come by general useage to include compounds between metals and metalloids as well as between metals only, which a literal meaning of the term implies. In the report we go along with general useage. MBM/THG

kinetic limitations at the relatively low temperatures at which they become stable. Vapor or liquid phase quenching as well as new solvent systems under the appropriate conditions have been used to circumvent the need for macroscopic diffusion and thus to prepare new phases.

Once a new phase has been properly prepared there can, in favorable cases, follow a splurge of new science, and occasionally of technology. Active fields in solid-state science which depend heavily upon synthesis include the study of metal-insulator transitions, mixed valency, superconductivity, and magnetism. A good example of how technology benefits is provided by the rare earth-cobalt permanent magnets, which were only synthesized for the first time two decades ago, and make it possible to design lightweight motors.

In the section immediately below, we discuss four examples, all superconductors, which have and are providing new insights into the properties and possibilities of intermetallic compounds. Superconductivity is of interest for the technological reasons mentioned in the section on technology needs (below), but also because it is a very sensitive probe of structure, composition, order, and morphology, which in turn relate to many other important technological problems. A case in point is how investigations of the superconducting properties of the intercalated transition metal dichalcogenides led to new battery cathodes (discussed in Chapter 6 on Solid State Ionic Conductors).

OPPORTUNITIES, BASIC RESEARCH

1. Classes of materials which afford an opportunity for systematic investigation of various physical phenomena

a. *A15 compounds*

The highest transition temperature superconductors form in the A15 phase. The compound Nb_3Sn which is stable and easily formed from the elements by diffusion is likely to serve as the "copper" and the "silicon" of superconducting large-scale-technology. More remains to be learned about its superconductivity: the nature of defects and their role in flux pinning, the nature of surface barriers to the entry and exit of flux, and the superconducting and mechanical performance when incorporated in the composite structures needed to produce high magnetic fields for rotating machinery and fusion containment magnets. The opportunity exists for studying the effect of well defined physical and chemical changes upon its macroscopic superconducting properties such as critical current and critical fields. There is a need to develop *quantitative* theories. This approach will directly bear upon the technological need for higher performance superconducting magnets.

The compound Nb_3Si , which may turn out to be the highest T_c A15 phase superconductor, has been prepared as a metastable A15 phase only by vapor phase quenching, and then only as Nb-rich as discussed later in this chapter. Its synthesis is a more extreme challenge than the synthesis of the presently known three highest-temperature-superconductors, Nb_3Al , Nb_3Ge , and Nb_3Ga , none of which has been properly prepared as a pure ordered phase. Understanding the conditions which favor the stabilization and strong electron-phonon coupling may lead to the synthesis of even-less-stable pseudo-binary ordered A15 phases, none of which is presently known.

The marked susceptibility of Al₅ compounds to radiation damage not only needs to be well understood for technological reasons but affords an opportunity to generalize the results and extend them to different classes of intermetallic compounds which combine partially covalent, metallic and ionic bonds. The severe degradation of the superconducting properties is easily removed by simple annealing. Some analyses show that there is a large redistribution of charge and atomic motion within the unit cell upon being irradiated which may be understood qualitatively at least in terms of the formation of covalent bonds. An equally important and probably related problem is the strong dependence of the physical properties upon stoichiometry. Tunnel junctions have recently been prepared with adequate characteristics to permit the application of the powerful technique of electron tunnelling spectroscopy to unravel the microscopic parameters.¹⁾

b. *Layered and quasi-one-dimensional compounds*

Much progress has been made in the past several years in understanding the relation between the electronic and lattice degrees of freedom, particularly in low dimensional phases such as TaS₂, NbSe₃ and TTF-TCNQ. Van der Waals forces hold sheets or chains together giving the structures a quasi one- or two-dimensional character which is reflected in the physical properties. The ability to synthesize compounds where composition can be varied in a well-defined way permits properties to be related back to band structure. For instance, lattice instability in TaS₂ varies with substitution of Ti for Ta in a way which clearly establishes the driving force as a charge density wave which derives from a particular wave vector spanning the Fermi surface.²⁾ The interaction

and coexistence of charge density waves with superconductivity provides valuable experimental data for understanding both phenomena.³⁾

When two-dimensional superconducting crystals based upon TaS_2 are intercalated with organic molecules the resulting superconducting transition temperatures are above 3K and upper critical fields with H parallel to the crystal layers have slopes, $(\frac{dH}{dT}c_2) > 200 \text{ kOeK}^{-1}$, several times higher than any other superconductor. These intercalation compounds are extreme examples of ternary compounds and have some features in common with the Chevrel and rare earth rhodium boride phases discussed below. The conduction band is well localized within the metallic layers of the unit cell. Metallocene radicals incorporating 3d elements with uncompensated spins (see Chapter 6 on Solid State Ionics, p. 93) can be introduced with little apparent effect on the superconducting properties indicating an as yet uninvestigated example of the coexistence of magnetism and superconductivity.

c. *Ternary molybdenum chalcogenides (Chevrel phases)*

The ternary molybdenum chalcogenides, or Chevrel phases, $\text{M}_x\text{Mo}_6\text{X}_8$ have been and remain promising candidates for investigations of superconductivity, magnetism, and the interplay of these two phenomena. The component M ranges throughout the periodic table of the elements (alkali metals, alkaline earths, transition metals, s-p metals, rare earths and actinides), the X atoms can be either S, Se or Te, or, in part, Br or I, and the value of the index x generally lies within the range $1 \leq x \leq 4$. The compounds have rhombohedral symmetry and consist of Mo_6X_8 units or "clusters" and channels into which the M atoms can be inserted. Some of the Chevrel phase compounds exhibit superior superconductive

properties with critical temperatures T_c as high as ~ 15 K ⁴⁾ and upper critical fields H_{c2} approaching 70 T. ^{5,6)} Although it is generally believed that the extremely high values of H_{c2} (the highest known for any material) can be traced to the "cluster" character of these compounds, a fundamental understanding of the origin of the high H_{c2} values is lacking and systematic studies are clearly called for. In addition, experiments yielding knowledge of the electronic band structure and phonon characteristics would be very useful. The Chevrel phases may represent a successful means of avoiding the electron-phonon instability, *i.e.*, by allowing very anharmonic behavior associated with the M element, while containing these degrees of freedom by rather rigid Mo_6X_8 cages. Information about the electronic structure of these materials may accrue from the exploration of mixed ternary systems and may possibly lead to increases of T_c and H_{c2} above their present limits. The preparation of more dense polycrystalline and, in some instances, single crystal specimens, has recently been accomplished, and should be extended in order to make contact with theoretical studies of the electronic band structure and lattice dynamics. In particular, it should be possible to address the long-standing questions concerning the coexistence of superconductivity and various kinds of magnetic order. Efforts directed towards understanding critical phenomena involving coupled order parameters should be pursued. Apparently, the reason that the ternary rare earth (RE) molybdenum chalcogenide cluster compounds, and other ternary RE cluster compounds, are so well suited to this type of investigation is twofold:

- The periodic disposition of RE ions with partially-filled 4f electron shells and corresponding magnetic moments leads to

long-range magnetic ordering via the RKKY interaction. As a result, the magnetic ordering temperature T_M is well-defined and the features in the physical properties at T_M are sharp (e.g., λ -type anomaly in the specific heat at T_M).

- The clusters that are apparently responsible for some of the remarkable superconducting properties are relatively isolated from the rare earth ions. Consequently, the overlap between the conduction electron and localized 4f electron wave functions is rather small, leading to a small value of the conduction electron spin-RE magnetic moment exchange interaction parameter J of the order of 0.01 eV, nearly an order of magnitude smaller than in typical rare earth metallic compounds.

Recent experiments on various $RE_xMo_6S_8$ and $RE_xMo_6Se_8$ compounds have yielded several examples in which superconductivity and antiferromagnetic order coexist;^{7,8)} and one example, $Ho_{1.2}Mo_6S_8$,⁹ in which superconductivity is destroyed at a second lower critical temperature by the onset of ferromagnetic order.¹⁰⁾

Further systematic studies of superconductivity and magnetism in these compounds will also shed light on the electronic structure of a class of complex intermetallic compounds that may be prototypes for catalysts in important chemical reactions.

d. *Ternary rare earth rhodium borides*

The ternary rare earth (RE) rhodium borides constitute another class of cluster compounds which exhibit a rich interplay between superconductivity and magnetism. In these materials, the free energies of the superconducting and magnetically ordered states achieve a delicate balance as reflected in the original report by Matthias *et al.*¹¹⁾

that some of them were superconducting (those with RE = Nd, Sm, Er, Tm and Lu), while the others were ferromagnetic (those with RE are Gd, Tb, Dy and Ho). In ErRh_4B_4 , superconductivity is reentrant¹²⁾ due to the onset of ferromagnetic order,¹³⁾ while in the NdRh_4B_4 ¹⁴⁾ and SmRh_4B_4 ,¹⁵⁾ superconductivity and magnetic order coexist. In these compounds, the role of crystalline electric fields appears to be central and needs to be elucidated. Since these materials have tetragonal symmetry, single crystal specimens would be particularly valuable in achieving a detailed understanding of their remarkable behavior. Some pseudoternary RE rhodium boride systems have been investigated. Systematic studies may lead to other systems of ternary rare earth cluster compounds.

Radiation damage studies have been initiated on ErRh_4B_4 and $(\text{Er},\text{Ho})\text{Rh}_4\text{B}_4$ pseudoternaries¹⁶⁾ and have revealed some surprising results. This appears to be a promising technique that may prove as useful in investigating cluster compounds and superconducting-magnetic interactions as it is in the A15 compounds.

These compounds represent a challenge to solid-state theory since a description of the ground state of the coupled superconducting and magnetic system goes beyond the Bardeen, Cooper, and Schrieffer theory of superconductivity. Further theoretical and experimental work is needed to clearly identify the important features of these compounds.

e. Other cluster compounds

In view of the striking superconductive properties exhibited by the ternary molybdenum chalcogenides and rare earth rhodium borides, some of which arise from the interplay between superconductivity and long-range

magnetic order, it seems worthwhile to look for other systems of cluster compounds. It can reasonably be anticipated that in addition to superconductivity and magnetism, new cluster compounds will be discovered that have other unusual and useful properties such as mechanical strength, resistance to corrosion, catalytic activity, phase transitions, superionic conduction, etc., and conceivably, new phenomena (see Chapter 1).

f. *Intermediate valence rare earth compounds*

During the past several years, there has been a great deal of interest in a certain class of metallic rare earth (RE) compounds which exhibit an intermediate or nonintegral valence of the RE ion constituent. In such compounds, it is generally believed that the 4f electron shell fluctuates between two configurations $4f^n$ and $4f^{n-1}$, accompanied by the emission and absorption of an electron by the RE 4f shell. The RE ions that have been found to exhibit this type of behavior include Ce, Sm, Eu, Tm and Yb, and examples of materials of this type include α -Ce, CePd₃, SmB₆, SmS in its collapsed metallic phase, EuCu₂Si₂, TmSe, YbCuAl₂, etc. The materials have striking and unusual properties such as nonmagnetic behavior of the magnetic susceptibility below a characteristic temperature $T_0 \sim 10^2$ K which is related to the valence or interconfiguration fluctuation lifetime $\tau \sim 10^{-13}$ s; other characteristics include a large electronic specific heat coefficient, a peak in the thermoelectric power near T_0 , and various types of anomalies in the electrical resistivity near T_0 . This class of materials has also been studied by means of Mössbauer and XPS techniques which support the basic picture of temporal fluctuations between two 4f configurations. In view of the unique electronic structure of these materials, more experimental work to document and

classify their striking physical properties would seem to be in order. Moreover, a completely adequate theoretical description, particularly one that incorporates the role of the phonons, has yet to emerge. Comparison with the behavior of 4f-related compounds should prove illuminating. These materials may also have other interesting properties that are applicable to catalysis.

2. Innovative synthesis

a. *Metastable and kinetically-limited equilibrium phases by vapor phase condensation*

Intimate mixtures of species can be obtained by condensation from the vapor. The reaction product which follows is not limited by kinetic factors and diffusion. Equilibrium, or metastable equilibrium states, are readily achieved. While the above ideas are not new, the hardware and techniques which have been developed in the past few years make for a possible major increase in the number of known compounds.

In the simplest application, the co-deposition technique can be compared to powder metallurgy where the size of the powder has been reduced to a single atom or molecule. Solid-state reactions, which at low temperatures require months or longer, can occur in seconds. Thus, portions of phase diagrams involving a refractory metal as one component can be explored below, say, 1000°C. Likewise, materials with low or very incongruent melting points can be prepared with facility well below these points, as can phases which become highly disordered or defect-laden at temperatures necessary for classical synthesis.

In more sophisticated applications, the number of different species, their sequence and rate of arrival at the substrate, their kinetic

and internal energy, the interface energy and epitaxy with the substrate, the substrate temperature, the presence of trace gases which can affect surface mobility during growth are all controllable deposition parameters which can be used to obtain stable and metastable phases that normally cannot be isolated. The superstructures of GaAs-GaAlAs, which have been grown by MBE techniques and described in Chapter 5 on Thin Films, represent an extreme example which is perhaps only the tip of the iceberg.

Perhaps a more representative example is the case of Nb_3Si . The elements react at elevated temperatures to form a stable compound with the Ti_3P structure. It has been found that films deposited below 850°C form in the A15 structure, the phase desirable because of potentially strong superconducting properties.¹⁷⁾ Classical metallurgical techniques alone would never be able to isolate the A15 phase of Nb_3Si , but once the necessary conditions for obtaining it have been established from among the multi-infinity of possible trajectories in parameter space, other methods of fabrication may become possible.

The use of two, three, or even more independently controlled sources permits the deposition to be carried out over a range of composition. This makes it possible to investigate the compositional dependence and to synthesize new phases in a systematic way. The rapid development of new sputtering sources, evaporation and vacuum techniques makes the synthesis of new compounds from the vapor phase a promising and open-ended approach.

Vapor transport is an established technique for the growth of single crystals and often makes use of volatile halides of the component

elements, if they exist, or if they form in requisite amounts during the growth process. The Nb_3Sn single crystals have been grown by chemical vapor deposition and served as the source of many important investigations. The use of organometallic compounds for growth from the vapor phase offers another degree of choice and it is an area that has not been looked into for vapor phase growth of intermetallics.

Vapor phase condensation (or electrodeposition) offers the possibility of fabricating layered composites. With a technique such as Rutherford backscattering such composites can be used as diffusion couples in which the diffusion of A into B can then be measured, and compound formation can be detected at much lower temperatures and in shorter times than conventional techniques permit. Ion implantation followed by pulsed annealing offers the possibility of producing new compounds at surfaces which can be selected to have desirable properties for wear, corrosion resistance, etc.

b. *Single crystals and new phases by molten salt electrodeposition*

Techniques have been developed for the growth of single crystals of LaB_6 ¹⁸⁾ and PrB_6 by the electrolysis of suitable molten salt solutions in the 700-800°C range. Large centimeter-size crystals were produced at low current densities (approximately 20 mA/cm²). Examples of other compounds synthesized by these electrolysis techniques include Zr_3B_4 , TiB_2 , VB_2 , MnB , Ni_2Ge , Mn_5Ge_3 , Cr_3Ge , VB_4 and a range of Cr-B compounds including Cr_3B_4 , CrB_4 , Cr_5B_3 , Cr_2B , Cr_3B_2 , and Cr_4B . One can recognize that the range of possibilities for preparing new and unusual compositions by this method is extremely broad.

c. *Synthesis of new materials and growth of single crystals from low melting liquid metals*

Although the flux growth of high melting oxide crystals (e.g., garnets) and the growth of semiconductor single crystal alloy layers from liquid metal solutions for semiconductor devices are well established laboratory and technological processes, little has been done on the synthesis and growth of intermetallic compounds from low melting metallic or salt solutions.

Synthesis from low melting solutions offers several advantages over conventional methods including the possibility of single crystal growth. For example, intermetallic compounds of basic and technological interest generally contain transition elements and exhibit such high melting points that inert crucibles are not available. The intermetallic compound may contain one component that is volatile and thus requires a low temperature synthesis technique.. Compounds of interest may form incongruently from the melt and the formation of a single phase material may only be made via growth from solution. Finally, synthesis and crystal growth from a novel solvent system offers the possibility of obtaining a more pure phase if the impurities in the solutes segregate into the host liquid during growth.

Recently, the rare earth (RE) borides (REB_4 and REB_6) were synthesized from liquid Al.¹⁹⁾ There are, of course, other low melting elements and many eutectic alloys and Al-Ga mixtures²⁰⁾ and this opens an opportunity for the synthesis of many new three and four component intermetallics, particularly those that might contain stoichiometric amounts of the flux components. However, you need an etch

to remove the solidified flux from grown crystals, and this may limit the fluxes used. The solution growth process offers the opportunity for growth of large single crystals of important materials for fundamental studies of intrinsic properties. Synthesis from molten salt systems (other than the parent binary melts) has been little explored.

d. *Composite materials and Technological configurations*

Fundamental research on materials systems is usually carried out on samples which are, as far as possible, homogeneous and defect-free across the bulk of the material. Materials technology, however, frequently necessitates the deliberate introduction of a controlled variation of either composition or imperfections on various scales at the surface or in the interior of materials. A few outstanding examples of this include the semiconductor p-n junction, precipitation hardened alloys for great mechanical strength, fiber-reinforced plastics for lightweight structures and fine filamentary superconductors for high field magnets and electrical machines. The last-mentioned example represents a rapidly developing technology of intermetallic compounds. This will be discussed in more detail in order to illustrate the great potential of composite intermetallic compounds.

High field, high current density superconductors were discovered about twenty years ago. It was immediately apparent that these materials could be used to construct zero loss electromagnets of great value to an important group of energy technologies including electric power, MHD and fusion generators. The actual development of superconducting magnets then revealed that the superconducting wire could not be used in bulk form. This was due to magnetic instabilities or "flux jumps".

which occurred during any changes of current or field within the magnet. These instabilities caused an uncontrolled normalization of the magnets during excitation.

To overcome the magnetic instability problem, composite conductors were prepared in which the superconductor consisted of a large number of fine filaments embedded in a good normal conductor such as copper. This procedure reduced the large flux jumps to a lot of small ones which released less energy per unit volume. Further advances included further segmentation of the copper with alloy zones to reduce electromagnetic losses.

At present, fine filamentary, composite superconductors are produced by a multistep, repetitive process of bundling copper and superconductor bars together and drawing down to small sizes. This is an expensive process. It lends itself very well to certain alloy superconductors, for example, niobium-titanium alloys. These alloys have rather low critical temperature ($\sim 10^\circ\text{K}$) and maximum upper critical fields around 10 T. Magnet designers would prefer to use other materials in particular the A15 intermetallic compounds, for which T_c and H_{c2} are roughly double the values of niobium-titanium. Unfortunately, the A15 compounds are brittle and cannot be drawn down in fine filamentary form in their native state.

One solution to this problem is to draw down one of the components of the A15 compound, e.g., niobium, within a matrix of bronze and then to form the A15 intermetallic at the end of the drawing process by a high temperature diffusion step. This has been quite successful, but it has certain disadvantages. The most serious one is the high impurity level in the copper stabilizer.

Looking to the future application of superconducting materials, it seems likely that intermetallic compounds will provide the highest superconducting critical temperatures and critical fields. Therefore, we must find other novel methods of making these materials in finely-divided form combined with high conductivity normal metals. A number of approaches have been suggested. For example, high speed quenching techniques, such as are used to produce amorphous metals, can also produce finely divided crystalline systems. Alternatively, small grain composites can be produced by chemical vapor decomposition carried out in a plasma-arc reactor. Precipitation of dendrites or filaments from a solvent compound is a third approach.

These unconventional approaches may also be used to produce finely-divided forms of metastable intermetallic compounds which cannot be attained by a diffusion reaction process. Metastable intermetallics, as discussed previously, offer promise of major improvements of the basic superconducting parameters T_c , H_{c2} and J_c .

In summary, we recommend that new emphasis be placed on seeking out radically new methods of preparing intermetallic-metal-alloy composite systems of controlled geometry and structures extending down to the 100 Å scale. Innovation in this area will give the materials designer new opportunities to attain novel performance in the electrical, magnetic, mechanical and physical performance of materials.

BASIC RESEARCH NEEDS

1. Experimental methods of determining defect structures

Although there has been a rapid advance in the development of new tools for establishing deviations from ideal crystal structures of complex intermetallic compounds, the application of these advanced techniques needs to become more widespread. This is particularly crucial in the more complex intermetallic compounds since the physical properties are dependent on small deviations from stoichiometry or long-range order.

Noteworthy among the new techniques are:

- High resolution electron microscopy including electron energy loss analysis or lattice imaging
- Ion beam analysis techniques such as Rutherford scattering, channeling, and nuclear resonance scattering
- Extended x-ray absorption fine structure (EXAFS) and diffuse scattering
- Neutron techniques including diffuse scattering.

Advances in the above techniques for the study of defect structures are expected as atomic resolution imaging becomes practical in scanning transmission electron microscopy and with the availability of high intensity synchrotron sources of x-rays and with intense pulsed neutron sources.

2. Higher resolution electron state spectroscopies

It would be very desirable to develop higher resolution spectroscopies for characterizing electron states in narrow band systems. Materials of current interest include Al₅ compounds, ternary cluster compounds, and intermediate valence RE compounds. An energy resolution approaching 0.01 eV would be particularly useful.

TECHNOLOGY NEEDS

Intermetallic compounds already play a vital role in present-day technology. Examples include their use as dispersion hardening agents in steels, the very extensive use of the refractory carbides for grinding and machine tools where extreme hardness is essential and permanent magnet materials such as Alnico and the rare-earth-cobalt compounds which have recently become prominent because of their very high magnetic energy products.

As we look to future applications of intermetallic compounds, it appears that they will enter into almost every phase of advanced energy technology, including production, conversion, storage, distribution, and utilization of energy. It should be noted that from an electrical conductivity viewpoint the metallics cover an almost continuous spectrum from pure metallic through semiconductor properties, with extension into the low resistivity insulator region. Hence, much of our comment here is equally applicable to semiconductors as to metallic properties. We see the following major functions and roles to be played by intermetallics in future energy technology:

- There will be an increasing demand for hard or refractory coatings resistant to erosion, corrosion and ablation at a variety of temperatures. Such protective coatings will be needed in coal liquefaction and gasification plants, breeder reactors, magneto-hydrodynamic power generators and in deep geothermal systems. They will be put in place by plasma spraying, chemical vapor deposition and probably ion implantation. Research on new methods of surface coating is vital.

- There will be a need for new composite or multi-component high strength, refractory material systems for turbine blades in gas and steam turbines. These materials will enable higher inlet operating temperatures and thus greater efficiency in power plants.
- High temperature materials will be needed to withstand extreme nuclear radiation environments in the fuel system of breeder reactors and in the first wall of fusion reactors. These materials must retain strength and be resistant to swelling caused by intense neutron bombardment. Intermetallic compounds seem to offer the best candidates for these applications.
- New magnetic intermetallic compounds are vitally needed for application to electrical machinery. In particular, ways must be found of replacing cobalt in the rare-earth-cobalt systems because of the scarcity and high cost of cobalt. If these systems can be cost reduced or a higher B·H product attained, they will find wide application in reducing losses in electrical motors and generators. Possibly, high saturation rare-earth compounds can also be applied to magnetic cooling or heating systems for heat pumps.
- Superconducting technology is in the process of moving out of the laboratory to prototype manufacture in electrical power generators, ship propulsion systems, and fusion magnets. In all cases, the great attraction is greater efficiency or energy saving. To accelerate the progress in this new technology, we need better superconducting properties (T_c , H_{c2} , J_c) combined with high mechanical strength and electromagnetic stability. Intermetallic

compounds of the Al₅ and related structures offer the best avenue of progress to these goals and intensified research on these superconductors is essential.

- The forthcoming decline in crude oil production and the substitution of alternative hydrocarbon resources to supply the fuel and petrochemical needs of the United States will require new chemical reactions which will, in turn, place severe demands on the availability of suitable catalysts. Many compounds, particularly the compounds of metals with unfilled d and f bands, are of interest as potential catalysts in the future.
- Many compounds exhibit solid-state phase transitions in which major changes in physical properties may occur over a narrow range of temperature. Steep variations in electrical conductivity, dielectric constant, or magnetic susceptibilities will often occur at these phase changes. Such property changes provide an excellent basis for new sensor development. Sensors are required to provide critical temperature rise signals in power equipment or in some cases to provide direct feedback to limit electric currents or voltages to the device. Alternatively, there is a need for new solid material sensors to detect the concentration of various gases in combustion systems, e.g., O₂, CO₂, CO, SO₂, etc. This type of sensor is vital to improving the efficiency of combustion and for control of undesirable emission.

- For the future development of hydrogen as a fuel, possibly coupled with its direct generation in solar photo-electro-chemical cells, there is a need for better means of storing hydrogen gas to replace compressed gas cylinders. Many solids, for example palladium, absorb hydrogen very well but cannot be considered as bulk storage materials because of cost. There is a need for low cost intermetallic compounds to perform this function.
- Recent research on intercalated graphite compounds has suggested that it may be possible to synthesize conductors with electrical conductivity at room temperature higher than that of metallic copper. There are some difficulties connected with extreme anisotropy in such materials, but the importance of a breakthrough of this type to the electrical power industry is great enough to warrant further study.

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CHAPTER 4

AMORPHOUS SOLIDS

GLASS FORMABILITY AND STABILITY

To discuss glass formation by melt quenching it will be convenient to allude frequently to the following parameters:

$$T_{rg} = T_g/T_\ell, \quad T_\ell/\bar{T}_m, \quad (T_{kc} - T_g)/T_g, \quad T_N$$

where:

T_{rg} is the reduced glass temperature

T_g is the actual glass temperature

T_ℓ is the thermodynamic liquidus temperature

$\bar{T}_m$ is the average/atom of the thermodynamic crystallization temperatures of the glass constituents when pure

T_{kc} the "kinetic crystallization temperature," is the temperature of rapid crystallization onset when the glass is reheated

T_N is the onset temperature at which the homophase crystal nucleation rate reaches measurable values when a liquid is undercooled.

Experience indicates, with no exception we know of, that $T_{rg} < 1.0$.

That is, all glasses, and more generally amorphous solids, are less stable

than *some* crystallized state of the material; this statement is based on the proviso that chemical bonds may be broken and re-formed in the crystallization process.

Those nonmetallic liquids, e.g. silica and o-terphenyl, which can be slow cooled in large continuous masses to glass form, all exhibit $2/3 \leq T_{rg} < 1.0$. Further, the frequency of homophase crystal nucleation in these materials appears to be negligible; they devitrify only if seeded.

In contrast, for the metallic alloy glass formers so far identified^{1,2,3)} $0.45 \leq T_{rg} \leq 0.70$.

Generally the liquidus of these glass formers is greatly depressed^{1,2,4,5)} relative to $\bar{T}_m$. In particular, $0.40 \leq T/\bar{T}_m \leq 0.79$. The displacement of T_{kc} from T_g is usually small;^{1,3)} it is sometimes negative so that the glass transition is obscured, and only a few alloys have exhibited

$\frac{T_{kc} - T_g}{T_g}$ greater than 0.10 to 0.15. No simple correlation for T_g of alloy glass formers seems to have been found. For many such alloys $T_g/\bar{T}_m \sim 0.39 \pm 0.03$ but there are some marked exceptions.

BASIC RESEARCH OPPORTUNITIES

1. Characterization and measurement of crystal nucleation rates in alloy glass formers.

- Is nucleation homophase or heterophase?
- If homophase, how does the nucleation rate depend on undercooling and T_{rg} .

There seems to be no proof for the occurrence (or non-occurrence) of homophase nucleation in undercooled alloy glass forming melts. However, there are scattered observations which suggest that $(T_N/T_g) < 0.80$ [for

most pure metals ($T_N/T_m < 0.75$]. From this behavior it would seem that the frequency of homophase nucleation in those alloy glass formers for which $T_{rg} \geq 0.60$ ought to be negligibly small at all cooling⁶⁾ so that they could, if freed of heterophase impurities, be slow cooled in bulk to the glass state. The potential technological impact might be processes for making useful alloy glasses in massive form.

Alternatively, if crystal nuclei are formed copiously at relatively slow quench rates either by homophase nucleation or by secondary nucleation processes starting from heterophase impurities, it may be possible to obtain by varying quench rates, in addition to a completely amorphous structure, the following types of microcrystalline structures:

- High density of microcrystallites dispersed in an amorphous matrix. This structure would have high mechanical strength. If the amorphous matrix were transformed by some means to a superconductor, the microcrystallites would serve as flux pinning centers.
- A completely microcrystalline structure which, e.g. depending on the composition, might exhibit outstanding mechanical strength or high critical currents in superconduction.

We note that NASA and ONR are supporting some research in these areas but the magnitude of the effort is small relative to that in other fields of amorphous metal research.

2. Extension of composition ranges of glass formability by more rapid quenches

It appears that quench rates of 10^{12} °C/sec or greater may be attained in very thin, e.g. < 0.1 micron, molten metal layers by picosecond

laser pulsing. This capability would seem to offer the opportunity to markedly extend the composition range of glass formation by melt quenching and so obtain glasses with T_{rg} well below 0.45.

3. Development of understanding of the role of impurities in amorphous solid metal formation

a. *Theory for dependence of T_g on alloy composition*^{1,2,4)}

There are some empirical correlations of T_g with various parameters but none appear to be wholly successful. There is no satisfactory microscopic theory for T_g . If we had either a successful phenomenological or a microscopic theory, we might be able to identify alloys with $T_{rg} > 0.7$ and so have a greater potential for bulk glass formation.

b. *Characterization of and theory for effect of impurity admixture on amorphous solid formation in melt quenching or condensation.*

How low in impurity content can we go in either of these processes and still obtain an amorphous solid? There seems to be no clear answer to this question from either theory or experience.

STRUCTURE AND DEFECTS:

1. Research opportunities

a. *Structural studies*

The physical and electronic properties of amorphous materials depend to a great extent on the atomic scale structure of these materials. The nature and extent of chemical and topological short-range order are of fundamental importance. X-ray, electron, and neutron diffraction methods give useful information in the form of atomic pair correlation functions.⁹⁾

There is a need to obtain more detailed information not available from conventional diffraction studies. The use of NMR and Mössbauer spectroscopy has not been fully exploited. Little use has been made of recently developed EXAFS techniques¹⁰⁾ which promise to yield considerable information on the atomic-scale chemistry of amorphous materials. Small angle x-ray scattering (SAS) offers a rather unexploited means of studying defect structures in these materials. Internal friction measurements and possibly Raman spectroscopy may also be a useful means of detecting defect structures.

The concept of a defect in amorphous materials needs further clarification. In amorphous semiconductors, defects can be identified by their influence on electron transport and optical properties. In amorphous metals, defects appear to govern the plastic deformation behavior of the materials. Other material properties are likely influenced by defect structures and this area of research should be explored.

b. *Comparative studies*

Various methods are presently used to prepare amorphous materials. These include vapor deposition, sputtering, electrodeposition, laser melting, and melt quenching methods. The same material prepared by different methods is frequently found to exhibit rather different properties. Again the concept of defects may well prove to give useful insight into this problem. Do materials prepared by different methods relax to a common structure upon thermal aging? Can the various materials be described by their variation from an ideal structure?

c. *Radiation effects*

Radiation damage provides a controlled means of altering the atomic scale structure of amorphous materials. Little has been done to

determine the nature and effect of neutron, heavy ion, and electron damage on various properties. This is particularly important since existing data^{11, 12)} suggest that many properties of amorphous metals are highly insensitive to radiation damage. Many possible applications of amorphous materials in the area of fusion technology seem promising. They include inner wall materials, structural materials, and superconducting magnets. More extensive study of the effects of irradiation is clearly very desirable.

d. *Surface structure*

Finally, little or no attention has been paid to the structure, composition, and short-range order of surface and interface regions of amorphous materials. Since this is of importance for such areas as corrosion, wear, and catalysis, it would seem that opportunities exist to utilize recently developed surface techniques on amorphous materials. Nearly nothing has been done in this interesting and important area.

ATOMIC TRANSPORT AND TRANSFORMATION BEHAVIOR.

The following are the frequencies, reciprocal time constants, for some of the important atomic transport processes in liquids and glasses:

k_{η} : frequency of flow or shear relaxation process; proportional to $1/\eta$, where η is the shear viscosity

k_D : frequency of diffusive transport process; proportional to the atomic mobility

k_u : frequency of interfacial rearrangement process in crystal growth; proportional to crystal growth rate

k_v : frequency of volume relaxation process; proportional to volume viscosity, η_v .

In nonmetallic glass forming liquids these constants often, but not always, scale together. Such scaling is very useful and often permits fairly reliable estimates of k_D , k_u and k_v , which are fairly difficult to measure, from shear viscosities, which can be measured fairly easily to very high accuracies. When these scaling relations are fulfilled, the rates of crystallization, phase separation and volume relaxation, as well as of shear relaxation, become negligible at temperatures only a few degrees below the glass temperature.

1. Basic research opportunities

a. *Characterization of atomic transport coefficients in alloy glass formers*¹³⁾

There is evidence that in some alloy glass formers, appreciable crystal growth and impurity transport occur at temperatures as low as 100 to 150° below T_g . Also there seem to be no reported measurements of volume relaxation rates in metal glasses. There is opportunity as well as great need to characterize these transport coefficients more fully and definitively. Such measurements will permit tests of the validity of the scaling relationship for alloy glasses as well as information on the stability of these glasses at T below T_g .

The atomic diffusivities in alloy glasses are in the range 10^{-18} $\text{cm}^2 \text{sec}^{-1}$ and lower.¹³⁾ There is need for further development of experimental techniques for measurement of such small diffusivities.

b. *Further exploration for and characterization of liquid-liquid phase separation in alloy glasses.*

The occurrence of liquid-liquid phase separation upon reheating to the glass transition range after melt quenching has been demonstrated.^{14,15)} However, the exploration for such separation as well as the characterization of it has been quite limited. We might expect that its occurrence in ternary glass forming alloys might be as widespread as in silicate systems provided crystallization were avoided. The onset of crystallization can be minimized by careful selection of annealing temperatures and times. Also it is evident that the larger is $(T_{kc} - T_g)/T_g$ the easier it will be for $\ell - \ell$ phase separation to be exposed.

Liquid-Liquid phase separation can be carried out in a way such that two phases are interdispersed on a spatial scale as small as 30 to 50 Å. Such structures might be exploited, e.g. in the following ways:

- Formation of porous metal membranes by selective dissolution of one of the phases,
- By crystallization to form a high density of flux-pinning centers in a superconducting alloy.

SUPERCONDUCTING MATERIALS

Amorphous superconductors are a unique class of metastable materials which exhibit high critical fields,^{16, 17)} high strength, and ductility. The microscopic origin of superconductivity in these materials and the parameters which determine T_c are of interest. The systematics of T_c in

amorphous transition metals have been shown to differ substantially from those of the corresponding crystalline materials.^{16, 17)} These differences reflect the fundamental influence of disorder on the electronic structure of d-band metals and alloys. Atomic-like properties appear to have a far more dominant influence on superconductivity in the amorphous state. A fundamental understanding of this behavior should enhance our understanding of the role of long-range order in crystalline superconductors.

In some sense, amorphous superconductors are the extreme example of metastability. Starting from an amorphous material, a variety of other metastable materials are obtainable by thermal treatment. These include composite materials which contain both an amorphous and a crystalline superconducting phase interspersed in a highly refined morphology.¹⁸⁾ Such structures are promising as practical high field magnet materials. In such composites, one can exploit both the desirable mechanical properties of the amorphous phase together with the high T_c and high H_{c2} of the crystalline phase. Finally, amorphous superconductors offer a novel method of synthesizing high T_c crystalline superconductors with high refined grain size through complete crystallization of the amorphous matrix.¹⁹⁾

ELECTRONIC PROPERTIES AND MAGNETISM

The understanding of the electronic properties of amorphous metals poses a unique challenge to solid-state theory. As yet, no comprehensive theory of electronic transport in amorphous metals has emerged.²⁰⁾ Among

the variety of phenomena observed are the anomalous temperature dependence of electrical resistivity,^{21, 22)} Kondo-type anomalies,²³⁾ a positive Hall coefficient in some amorphous alloys a negative magnetoresistance. As yet little experimental information is available on other transport properties such as the thermoelectric power.

Much effort has been devoted to the study of the 3D transition metal alloys (Cr, Mn, Fe, Co, and Ni base materials). These alloys have been fairly well characterized and are now being developed for technical applications. Several important problems remain in spite of considerable research. Magnetostrictive effects in these materials are still poorly understood, and pose a serious obstacle to practical use in transformer cores. The effect of thermal relaxation on magnetic properties is another technically important problem which deserves further study. Magnetic alloys containing rare earth metals have only recently been studied extensively. The nature of magnetic interactions among rare earth ions in amorphous alloys is not well understood. The RKKY interaction which mediates this interaction is presumably attenuated by the strong electron scattering²⁴⁾ in the amorphous state as suggested by deGennes.²⁵⁾ The effect of magnetic ordering on superconductivity in the amorphous state has not been studied at all. Several opportunities in basic solid-state physics exist in all of the above mentioned areas.

CORROSION, DEFORMATION BEHAVIOR, HARDNESS AND COATINGS

1. Research opportunities

a. *Development of a theory of passivation*

Several investigations have now indicated that certain Fe-Cr-metalloid alloys are much more resistant to corrosion when in amorphous

as opposed crystalline form.²⁶⁾ It appears that this exceptional corrosion resistance of amorphous alloys derives from their extraordinary compositional and structural homogeneity on a spatial scale greater than a few angstroms, and thus the composition and structural singularities which provide the preferred points of corrosive attack on passive films are largely lacking.

The research opportunity is not restricted to the behavior of passive films on amorphous metals. Rather it is to understand the mechanism of passive resistance generally. This is an old problem but an attack on it by highly qualified structural metallurgists and inorganic chemists in concert might be fruitful. It appears that the dissolution of the passive film is an interface (film-solution) limited process and that the problem is to characterize the dissolution kinetics and the role of structural irregularities thereon.

b. *Microscopic theory for mechanical strength and ductility of amorphous alloys*

The microscopic theory for the exceptional strength and considerable ductility of a large number of glassy metal alloys is still far from clear.²⁷⁾ However the problem has attracted widespread attention, and there is now a large effort to characterize and explain the mechanical properties of alloy glasses.

c. *High hardness, wear resistance*

A number of amorphous metallic alloys have been found to exhibit Vicker's Hardness in the range from 1000 to 2000 Kg/mm.^{28, 29)} The homogeneous nature of the amorphous phase, together with the high hardness and

strength, suggest possible use of these materials as protective wear-resistant coatings. Hardness, together with high resistance to corrosion, makes such a possibility extremely attractive.

2. Technological needs

A wide variety of technologies, including deep-well oil drilling, corrosion resistant high hardness bearings, and solar photovoltaic arrays, will obviously benefit if reliable economic methods of producing appropriate amorphous coatings are developed.

AMORPHOUS OXIDE AND CHALCOGENIDE MATERIALS

1. Research opportunities

It has recently been shown that the crystalline octahedrally coordinated ferroelectric materials, LiNbO_3 , LiTaO_3 , and BaTiO_3 ,^{30,31)} can be quenched from the melt to form amorphous dielectrics. A unique unexplained feature of these materials is the fact that their dielectric constants are much larger than their crystalline counterparts. Very large dielectric anomalies also appear on heating prior to the onset of crystallization, and the microscopic nature of this effect is also not understood. Other properties, such as the pyroelectric effect, suggest that amorphous LiNbO_3 and LiTaO_3 are amorphous ferroelectrics, but ferroelectric domains have not been observed.

Amorphous LiNbO_3 and LiTaO_3 exhibit room temperature ionic conductivities of $10^{-5} \Omega^{-1} \text{cm}^{-1}$, six orders of magnitude greater than their crystalline counterparts.

There is a need to develop an understanding of local atomic structure and bonding levels for heavy metal ions in silicate glasses. Research should be devoted to understanding cation diffusion mechanisms in the glasses. What types of defects are introduced by ionizing radiation?

2. Technological opportunities

There is a technological need to develop small all-solid-state high-energy density thin-film batteries for microcomputers. Films of amorphous LiNbO_3 and LiTaO_3 and other octahedral coordinate glasses could serve as the basis of solid electrolytes for Li secondary batteries. Solid electrolytes based on amorphous polyolefin alkali thiocyanates are being considered by the French.

The metallic layered crystalline dichalcogenides, such as TiS_2 and VS_2 , are being used as cathode materials in the development of high-energy density Li/ TiS_2 , VS_2 nonaqueous batteries (as discussed in Chapter 6 below). There is evidence in the case of MoS_2 that the amorphous electrode can reversibly intercalate significantly more Li than the crystalline electrode, thus increasing the capacity of the cell. This result suggests that the capacity of other metallic cathode matrices, such as the vanadium oxides, might be increased by making them amorphous.

3. Nuclear waste storage of fission products (Many elements in the periodic table).

Development of a basic understanding of incorporation and resistance to leaching in silicate glasses is a need. This work is to be done with a view toward developing *new* complex glasses for incorporating radioactive elements which would be stable, resistant to leaching, and protected from breakdown due to ionization.

SUMMARY OF OPPORTUNITIES IN RESEARCH

1. Characterization and measurement of crystal nucleation rates in alloy glass formers.
2. Extension of composition ranges of glass formability by more rapid quenches.
3. Development of understanding of impurity role in amorphous solid formation.
4. Experimental characterization of nature and extent of short-range order in amorphous solids.
5. Effect of irradiation on structure and properties of amorphous solids.
6. Comparison of amorphous solids of the same composition prepared by different techniques.
7. Use of new techniques to characterize the surface of amorphous materials.
8. Characterization of microscopic parameters which lead to superconductivity in amorphous alloys.
9. Characterization of atomic transport coefficients in glassy materials.
10. Further exploration of liquid-liquid phase separation in alloy glasses.
11. Studies of amorphous or amorphous-crystalline composite materials for superconductivity and other areas.
12. Develop a comprehensive theory of electronic transport in amorphous solids.
13. Magnetic interactions in amorphous alloys containing rare earth elements. Magnetostriction.
14. Development of a theory of chemical passivation of surfaces.

15. Development of a microscopic theory of mechanical strength and ductility of amorphous alloys.
16. Development of a theory for electronic behavior of amorphous oxide glasses and other non-metallic amorphous solids.
17. Development of a theory of atomic scale structure and bonding levels of metal ions in amorphous oxides; also understand ionic conduction, etc.

SUMMARY OF POTENTIAL IMPACT ON TECHNOLOGIES

1. Soft magnetic materials for electrical power applications are now being commercially developed by General Electric, Allied Chemical, and some foreign companies. Device scale applications in magnetic memory are also under development.
2. Temperature stable resistors and other device components.
3. Materials for use in high radiation environments.
4. High strength fibrous and lamellar composite structural materials.
5. Corrosion and wear-resistant coatings for many specialized technologies.
6. High-strength formable conductors for superconducting magnets.
7. Semiconducting materials for photovoltaic device applications.
8. Porous metal membranes for filtration, osmosis and catalysis.
9. Solid-state thin-film batteries for microcomputers.
10. Containers for nuclear waste storage.

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CHAPTER 5

THIN FILMS

INTRODUCTION

The field of thin film research^{1,2)} has progressed extremely rapidly in the past twenty years, largely due to the incentive of technological applications, particularly circuits initially comprised of discrete devices and now demonstrating great complexity of function on a single substrate. It is only realistic to assume that the future of the field will again be strongly influenced by the progress expected in semiconductor and magnetic bubble integrated circuitry, with their associated techniques of pattern generation by photo, e-beam and x-ray resist lithography.

However, strides in thin film research have primarily occurred in materials, techniques and instrumentation strongly influenced by the semiconductor industry; other aspects of the field remain at a stage where ample opportunity exists for research at a fundamental level. An example is amorphous and polycrystalline silicon (to be discussed in detail in Chapter 8 dealing with semiconductors) where it is clear that knowledge is rudimentary compared to the artistry of an integrated circuit in single crystal silicon. Preparative methods not commonly used by industry have been neglected, and may be more interesting from a research point of view and more valuable for other emerging applications. For these reasons, although we realize that the greatest progress in the field of thin films in the future will probably be associated with semiconductor circuitry, we will be brief when dealing with that aspect of the field. A recent report³⁾ outlines the research that will be required to support the future of the electronics industry.

THIN FILM PREPARATION

To help in later discussion, we briefly summarize the common methods of thin-film preparation, and note the peculiarities of each.

1. Evaporation

Using a single source heated resistively or with an e-beam, this method is primarily useful only for elements.* Using multiple sources, compounds and alloys can be prepared. Molecular beam epitaxy (MBE)⁴⁾ is the growth of single crystal material by multiple source evaporation. In addition to evaporation of the elements comprising the compound, impurities can also be introduced as dopants.⁵⁾ Multilayer structures, with each layer being a few monolayers of a given compound, have been grown.⁶⁾ Thus MBE can be regarded as the most carefully controlled thin film growth to date.

As evaporation is a high vacuum process, all the tools developed for surface science can be utilized and *in situ* surface studies of the growing film can be carried out, but in practice this is rarely done except in MBE.

2. Sputtering

By bombarding a target with energetic ions from a discharge, films can be prepared whose composition generally matches that of the target. Thus this method is ideal for alloys and compounds. A dc discharge is often enhanced by confinement by a magnetic field (magnetron heads)⁷⁾ or by an electron source (triodes), and insulators can be sputtered with r.f. However, typical gas pressures are 1-100 μ , thus gas incorporation is very likely and high vacuum surface tools cannot be used during deposition. The use of focussed ion beams⁷⁾ allows some improvement in the vacuum level. "Getter sputtering",⁸⁾ in which a liquid-nitrogen cooled container is placed around

* Certain compounds deposit stoichiometrically when evaporated, e.g. CdS; molecular solids also.

the discharge target and substrate, reduces the partial pressure of active impurity gases.

3. Chemical vapor deposition⁹⁾

Chemical vapor deposition is carried out by reacting gases over a substrate, usually in a heated tube. Different CVD processes such as the halide or organometallic methods depend upon the composition of metal-bearing gas. *In situ* surface analysis is not possible, but growth rates are large and thick ($> 10 \mu$) layers can be prepared.

4. Liquid phase epitaxy¹⁰⁾

Liquid phase epitaxy is growth from a melt saturated with elements of the material of interest. It has been used particularly for semiconductors such as GaAs and GaAlAs and doping of the individual layers can be carried out.

5. Organometallic vapor deposition

It has recently been shown¹¹⁾ that the thermal decomposition of organometallics to form solid solution, lattice matched submicron semiconductor layers will result in devices exhibiting properties comparable to those produced by liquid phase epitaxy and chemical vapor deposition. The use of organometallics should be applicable to the synthesis of thin films of many materials, particularly intermetallic compounds. In addition, it has recently been demonstrated that dissociation of organometallic compounds can be accomplished by laser-induced photodissociation and this offers another possibility of accomplishing controlled growth of thin films.¹²⁾ It may also be possible to produce alloy films from two or more volatile compounds, e.g. an alkyl compound in interaction with a chloride to produce the alloy with elimination of alkyl chloride.

6. Electroplating

Electroplating can take place from aqueous solutions at room

temperature, or from molten salts at quite high temperatures, say $\sim 600^{\circ}\text{C}$.

In general, evaporation and sputtering are the means most commonly used to prepare thin metallic films; the other techniques above are more specifically applied to certain materials such as semiconductors.

A COMMENT ON TECHNIQUES

As a means of material preparation, thin film methods are unusual in that much of the required equipment, both for attaining vacuum and for film deposition, can be purchased commercially, as can the surface analysis tools that may be added to the same system. There appears to be a danger that basic research in thin films will be partially dictated by what equipment is most easily available, and thus the field will lack variety and novelty. We suggest that unusual approaches to pumping systems, deposition methods and film characterization should be encouraged whenever possible. As an example we cite the work of Thompson,¹³⁾ who cools an entire vacuum chamber to liquid helium temperatures. The operating pressure is orders of magnitude lower than in conventional systems at room temperature.

OPPORTUNITIES FOR RESEARCH

Compared to other methods of material preparation, thin film deposition has some unique advantages and disadvantages which offer opportunities for basic research. To utilize these fully, thin film growth itself should first be understood in more detail.

1. Thin film growth

Although this problem has been considered in the past, the full power of modern vacuum techniques, *in situ* surface studies and characterization by, for example, high resolution electron microscopy, has not yet been

brought to bear except in isolated cases. For example, new electron microscopes ¹⁴⁾ working at $\sim 10^{-9}$ Torr will allow *in situ* structure studies and energy loss spectroscopy of a growing film. There is a need for fundamental investigations of the detailed atomic scale mechanisms by which films, both crystalline and amorphous, form and grow. Such understanding will allow greater control over thin film composition, morphology, microstructure and electronic properties, and could also lead to new selective techniques to produce films of unusual chemical composition and atomic structure. Research of this type is also closely allied to other problems in modern surface physics and chemistry; crystal growth, amorphous film formation from the vapor, epitaxy and coatings in device production, corrosion and other gas-surface reactions. Interesting possibilities for research include combining kinetic measurements with detailed observation and characterization of incipient films during their early growth stages. Such studies could be carried out as a function of vapor chemical constituents, of surface temperature and composition and of overall incident flux. Deliberate changes could be made in the vapor molecular structure and effects on film growth studied (e.g. atomic As versus As₄). Lasers and other techniques (plasmas, energy transfer) allow selective (optical) electronic and vibrational excitation of the condensing molecules. Another rich area involves looking at the production of films from low energy ions, from very complex, high temperature vapors where one has unusual molecular aggregates, and under conditions where molecules are excited (optically or perhaps by electron impact) while they are on the surface (e.g., by focussing a laser on the growing film and comparing film formation in the illuminated region with that outside). At high laser powers, this process would become an *in situ* annealing of the growing film (which might

allow improvements of crystallographic order at low overall substrate temperatures). We note that there is a high level of current interest in laser annealing of semiconductor films¹⁵⁾ after preparation. Irradiation of various kinds during growth, as proposed above, would seem to offer more opportunity for observation of unusual growth effects. Laser annealing of completed films other than semiconductors should also be studied as a method of producing metastable phases.

2. Surface modification

There are a number of ways in which the surface of a bulk (or film) material can be modified to produce more desirable properties: for example, resistance to corrosion, erosion and wear, or improvement in conductivity or oxidation characteristics.

The formation of a surface compound by reaction of a deposited layer with the bulk is a relatively simple process (and is commonly used to produce transition metal silicides on silicon). The mechanical properties of such surface layers in particular should be investigated.

Ion implantation is a way of introducing impurity ions into the surface of a material, the depth of implant extending to $\sim 1\mu$ and being variable with ion energy. It is widely used to dope semiconductors and compound formation can occur. It has produced metastable compounds (e.g., there is a strong increase in superconducting T_c of Pd with H implantation at low temperatures). In addition to implantation, sputtering and damage of the surface occurs. It has been reported¹⁶⁾ that this strongly changes the corrosion resistance and oxidation rates of the implanted/damaged part of the surface. Much further work is required in this field to understand the relative importance of the nature of the implanted ion, its energy, compound formation, sputtering and damage on these surface properties. This

is an area where surface tools can be used to advantage, and *in situ* studies in high resolution electron microscopes, including energy loss spectrometers, should be possible.

In some situations, for example in a fusion reactor first wall, materials will be at elevated temperatures and subjected to intense radiation. The interaction of this displacement producing radiation with metallic alloys gives rise to the formation of nonequilibrium phases (or phase distributions). The kinetics and morphology of this microstructural evolution can now be studied using high resolution analytical microscopy. Since the process is phenomenologically understood¹⁷⁾ as the preferential binding of one alloy component to one of the mobile radiation produced defects (e.g. interstitial atom-silicon atom binding in Ni-Si alloys) that tend to annihilate preferentially at defect sinks (e.g. dislocation loops, grain boundaries, and surfaces), this phenomena needs basic research efforts in understanding defect-defect, defect-solute, and defect-sink interactions.

3. Materials preparation

The conventional evaporation and sputter techniques can be utilized in novel ways to prepare materials, or to rapidly search for new phases and physical properties within a given alloy or compound system.

a. *Use of Phase Spread*

By controlling the rate of two evaporation sources, and placing substrates above and parallel to the line between them, a fraction of the phase diagram of the two evaporating constituents can be produced. Likewise a gradient in substrate temperature can be introduced. Amorphous films can be prepared at lower temperatures. Thus the structural, mechanical

and electrical properties of every part of the phase diagram can be rapidly surveyed. This method has been used with success recently for Al₅ superconductors and structure, lattice constant, T_c and the energy gap determined as a function of composition.¹⁸⁾ It should be noted that in some cases the phase diagram will differ from that of the bulk, in that film deposition can produce metastable phases, Nb₃Ge being one example.

Sputtering from multiple sources can be used similarly and, as the substrates can often be placed closer to the sources, practically the whole phase diagram can be produced in a single deposition.¹⁹⁾ Use of magnetron heads appears very desirable, in that their deposition rate is high, rate can be set by the sputtering current, and unwanted heating of the substrates is small.

By using three sources, ternary phase diagrams can be produced. This method was employed to search for magnetic films for bubble circuits.²⁰⁾

It is clear that this multiple source deposition method, although demonstratedly powerful in the production of materials, is being used only in isolated cases and for particular phenomena such as superconductivity and magnetism. We feel it should become much more widespread, one example being in producing amorphous and polycrystalline semiconductor films. Mechanical properties of films produced by this method should be studied; for example, it has been found by chance that films of Mo₅Ru₃ and W₃Ru₂ being made for superconductivity studies²¹⁾ exhibited unusual hardness and corrosion resistance.²²⁾

b. *Metastable phases*

Film deposition is often regarded as a rapid quench process to the temperature of the substrate. This has allowed the preparation of

metastable phases which cannot be made by conventional bulk methods as in the case of Nb_3Ge where T_c in films has reached 23 K²³⁾ compared to an onset of 17 K in bulk arc-melted, quenched and annealed samples. Also, by the use of substrate temperature down to 4 K if necessary, amorphous materials can be readily produced in a form ideal for *in situ* electrical and structural characterization. With change in substrate temperature the amorphous-crystalline transition can be readily studied in a controlled manner.

4. Surfaces and interfaces

Full advantage should be taken of the opportunities offered by thin film preparation, in that a fresh clean surface is produced (at least momentarily) and that an interface, or multiple interfaces, can be readily prepared.

a. *Surface roughness*

For one material, variation of substrate temperature, deposition rate and gas pressure can result in films with a surface which is optically smooth, or so granular that it appears black. This variation in growth should be better characterized, particularly in systems of interest as solar absorbers. It is obviously related to the understanding of thin film nucleation and growth, as discussed above.

b. *Epitaxial growth*

Epitaxial growth of a film on a fresh surface of an underlying film or on a substrate has been demonstrated in a limited number of cases, MBE of GaAs/GaAlAs layers being the primary example. In other cases, lattice matching, but not single crystal growth, is achieved. By deposition of Nb_3Ge on the stable compound Nb_3Ir it was shown that the A15 phase of

Nb_3Ge could be extended beyond its equilibrium composition.²⁴⁾ An amorphous silicon layer, deposited on a grooved silica substrate and subsequently laser annealed, became single crystal with an orientation determined by the grooves.²⁵⁾ As the grooves were $\sim 2\mu$ wide, which is huge on an atomic scale, this suggests that the initial nucleation and growth of thin films might be controlled in a predictable way by suitable preparation of substrate surfaces.

c. *Interface compounds and multilayers*

The use of "diffusion couples" to measure interdiffusion and compound formation is well known. However, multiple source deposition allows the formation of films with alternating components where the individual layers become very thin (a few atomic layers). These structures would allow not only the study of very slow diffusion rates but, more importantly, the interface regions can become a large fraction of the total film. Thus the chance for observing unusual compounds stabilized by interfacial energies is optimized. Again, *in situ* studies of such films as a function of annealing temperature, by x-ray or electron scattering and Rutherford backscattering at low angles, should be encouraged.

d. *Other*

The clean surface of a film is ideal for the subsequent preparation of tunnel junctions, which can be a most useful probe of the properties of superconductors and semiconductors,²⁶⁾ and also for making Schottky barriers and metal-insulator semiconductor barriers now of interest as photovoltaic devices.

5. Novel geometrical materials

The thin film geometry can be made as small as desired in one dimension, although uniformity of the film may be hard to achieve. When

combined with modern lithographic techniques, it is possible to make two or even all three of the dimensions of a film small, i.e., $\geq 1000\text{\AA}$, and thus approach the electronic wavelength, at least in semiconductors and semimetals. This offers the opportunity of the most fundamental studies, particularly of electronic properties of materials, and also of preparing new materials by "molecular engineering" (or at least "molecular layer engineering"). The use of molecular beam epitaxy in the GaAs-GaAlAs system where repetition of monolayers or placement of dopant impurities into specific layers has been achieved can serve as an example of what might also be done in many other systems given sufficient understanding and control of the growth process. This monolayer engineering is not restricted to semiconducting systems: already work on magnetic/non-magnetic²⁷⁾ and on superconducting/normal metal²⁸⁾ multilayers has been reported.

6. Dielectrics

The success of silicon integrated circuitry relies heavily on the insulating properties of silicon oxide. However, many other useful semiconductors (such as GaAs) do not grow a thermal oxide of a quality suitable for device use. When integrated circuitry utilizes linewidths $< 1\ \mu$, oxide insulators will become thinner than at present. There is at present little basic understanding of the limitations of evaporated dielectrics as insulators. Research is required into the effects of nonuniformity and defects, nonstoichiometry, ionic and electronic conduction and interface reactions with metals and semiconductors. These studies should not be restricted to inorganic compounds such as oxides, fluorides, nitrides, etc., but polymeric thin films should also be considered. The formation of single crystal polymer monolayers should be

possible using techniques of epitaxial growth, plasma polymerization, vapor deposition, liquid crystal orientation and spin coating. Basic questions to be answered include the effect of the substrate on orientation, the limits of film thickness to achieve insulating (and other) properties, morphology and the nature of metal-polymer interactions and interdiffusion. In addition to insulating properties, the corrosion resistance, wear resistance, adhesion strength to metals and photosensitivity and radiation sensitivity should be determined.

7. Cermet, nonhomogeneous and granular films

By codeposition of metals and insulators, or of a metal in oxygen, films have been prepared which exhibit electrical behavior ranging from metallic to insulating.²⁹⁾ Considerable work has been carried out on such systems but recent interest in the general nature of localization in 1-, 2-, and 3-dimensions is already giving new insight into their behavior. The optical properties of such materials are also of interest, in that their absorption can be made to peak at different wavelengths depending on the volume fraction of metal. A promising class of selective solar absorbers derives its absorption characteristic from a two-phase metal/oxide structure. Particle size and thickness of these "black chrome" or "black cobalt" films lie below optical wavelengths, but their structure and arrangement are not known in detail. Therefore, the theoretical basis is missing for directed efforts to prepare such films and to prevent their degradation at operating temperatures.

8. Film characterization

Thin film research has been, and still is, plagued by nonreproducibility of films made under "the same" conditions. This is due to the

many parameters affecting the film, some of which may not be controlled or even appreciated. Gas impurities can be incorporated from the source, the vacuum system, or from the substrate; metallic impurities from the source, from the chamber walls or the masks near the substrate. The film structure is sensitive to substrate temperature, gas pressure (in sputtering systems) and the nature of nucleation on the substrate. If full understanding of the materials is to be achieved, and complete utilization of thin film methods in the preparation of materials such as amorphous silicon or superconducting Nb_3Ge , a much better characterization of the completed films must be carried out and their properties related to deposition parameters. Much more widespread use of *in situ* surface analysis tools would be a major step forward, in that growth parameters could be varied and their effect observed immediately. At present, such studies are fairly common only in semiconductor MBE. This either requires that traditional thin film scientists learn and appreciate the use of available surface tools, or that surface scientists become interested in a much wider variety of materials and interface systems than they have to date.

9. Deposition method characterization

Given the progress in thin film characterization and the relationship between film properties and deposition parameters outlined in (8) above, an aim would be to characterize the limitations and advantages of each deposition method so that for a given material property the method could be chosen to optimize this characteristic. Two examples, both poorly understood at present, are that sputtering seems to yield Nb_3Ge with a higher T_c than evaporated material, but sputtering of polycrystalline silicon yields material which is unsuitable for device fabrication.

10. Theory

Surface physics theory has in large part dealt with a very limited number of solid-vacuum interfaces, particularly the crystal faces of silicon. Thin film research deals with less ideal materials and interfaces. To contribute to many of the research problems outlined in (1) - (9) above, theory should begin to consider semiconductor-dielectric and metal-dielectric interfaces, and the contact between dissimilar metals, particularly its electrical resistance. In many cases there is no lattice matching in such interfaces; perhaps an understanding of the defects and grain boundaries generated in such cases will even lead to prediction of interface and surface compounds.

RESEARCH NEEDS

In addition to the control of deposition process, and characterization of the resulting film by existing surface and bulk methods, it is often of interest to look at the electronic properties, impurity content and structure at a given depth within a film. Many methods accomplish chemical analysis by destruction of the film by ion milling. There is a need to identify and develop nondestructive tools which accomplish this and give structural and electronic information as well. Rutherford backscattering is of value (but the depth resolution is generally $\sim 100\text{\AA}$ unless low angles are used) and specific nuclear reactions can be used to profile hydrogen and oxygen. Electron microscopy has good lateral resolution but is not very specific in depth. The scanning acoustic microscope should be valuable for film and interface studies.³⁰⁾

RESEARCH OPPORTUNITIES FOR TECHNOLOGY

In a field which has been stimulated largely by technology, the division between basic and technological research is somewhat arbitrary and there is strong overlap with the recommendations made above. We have attempted to arrange this section in order of decreasing importance to energy needs.

1. Spectrally selective solar absorbers

Selective absorbers are films and surfaces whose absorbance (α) for solar radiation is high, but is low for their own thermal re-radiation in the infrared (then, by Kirchoff's law, their emittance (ϵ) in the i.r. is also low). One group of selective absorbers are composites of an i.r. reflecting metal substrate coated with a thin absorber layer (semiconductor, metal-dielectric interference stack, granular metal-oxide film). The second important group comprises simple metal films with high α/ϵ , or metal substrates covered with small particles of the same material. Particularly for this latter group, practical limits to α/ϵ need yet to be determined.³¹⁾

2. Photovoltaics

Photovoltaics will be discussed in Chapter 8. Although the semiconductor-semiconductor crystalline junction is most efficient at present, other considerations (cost of materials, energy cost of production, etc.) make it worthwhile to examine other heterojunctions. Already the semiconductor-metal and semiconductor-oxide-metal junctions are receiving attention. It would be worth determining, perhaps from carrier lifetime estimations alone, whether the metal-oxide-metal junction can ever be a useful photovoltaic cell.

3. Interface stability

In photovoltaic cells, and in all thin-film circuitry, interfaces between different materials are subjected to electric field and current

flow. The stability of these interfaces, in particular their composition profile and defect distribution, should be investigated. Again, unusual compound formation at the interface might be possible.

4. Surfaces for specific environments

Given the number of preparative methods of films and surfaces of alloys, intermetallic compounds and amorphous materials mentioned so far, it should be possible to produce surfaces having desirable properties for a given application. Many films based on transition or rare earths metals are very hard, exhibit corrosion, erosion and wear resistance, and some do not oxidize to produce an insulating coating. However, interest in these films is often for another characteristic, such as superconductivity or magnetism, and the mechanical properties are generally not measured or published in any detail. Some way needs to be found to encourage those in the thin film field to be more aware of the importance of such characteristics. Similarly, dielectrics, which have been mentioned above, should be considered as passivating and protecting layers for photovoltaics.

A self-replenishing low Z coating for a fusion reactor first wall is required, as are corrosion resistant structural materials for fission and fusion reactors.

5. High T_c superconductors

The highest T_c superconductor Nb_3Ge is easily made in thin film form by evaporation, sputtering or CVD. Ways to use this compound, Nb_3Al , $Nb_3(Al_xGe_{1-x})$ and also the Chevrel phases (with even higher critical field) in useful conductor form should be devised.

6. Microstructures

Although the physics and applications of microstructures will probably be more important commercially than all the above, we comment only briefly in view of an earlier report. However, mechanical properties of materials made on the scale of 1000 Å, such as diffusion, electromigration, and strength as well as interface stability, should be considered. It is often a useful scientific approach to consider limiting behavior, and such studies of extremely small structures might shed light on failure mechanisms which occur, but less frequently, in semiconductor devices and metallizations of more conventional size. Thermal boundary resistances between different materials (and to liquids and gases) will also become important as semiconductor circuitry shrinks in size, and in solar power applications.

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CHAPTER 6

SOLID STATE IONICS

INTRODUCTION

Solid-state ionics is the science related to how the ionic properties, and in particular ionic motion, affect the overall properties of a solid. Little is really known about how ions diffuse in solids — why some solids show ionic conductivities orders of magnitudes higher than others, what is the effective size of the ion as it moves through the lattice potential, what can be predicted about diffusion in a solid even of known structure, and how can one molecularly engineer a solid to give the desired level of ionic mobility, be it high or zero? Ionic mobility is critical in a large number of technologically important areas, including corrosion of metals, hydrogen embrittlement, semiconductor construction, solar cell junctions, hydrogen storage materials, oxidation catalysts, battery electrodes and electrolytes, electrochromic devices, sensors for automobile pollution control, etc. Even slight improvements in our knowledge in this one area could have major societal impact.

OPPORTUNITIES, BASIC RESEARCH

In this section the opportunities (and needs) for basic research will be briefly described, followed by an in-depth discussion of work in one area, intercalation compounds, to exemplify where opportunities might be found generally and the approach taken in this one case. This approach, particularly as related to lithium incorporation in solids, is

directly applicable to the understanding of reactions occurring between hydrogen and various solids. At the present time the scientists in these two areas are not communicating, which is to the neglect of the high potential synergism.

In order to generate new materials exhibiting the desired ionic motion (properties) there is a need for a broadly applicable theory of ion transport at the atomic level. Such a theory should be able to explain which lattice defects are important for diffusion within a solid of its constituent ions and also of the probability of incorporating foreign ions/molecules (guest species) into the host lattice. Data are now beginning to be collected on diffusion in solids in the bulk state, on surfaces and at grain boundaries, so that the time is ripe for a coordinated theory or model of ion transport to be generated. Closely related to such a model would be an understanding of the driving force behind intercalation-type reactions: — what are the thermodynamics, what is the bonding? For the latter, a few specific questions come to mind: what is the ionicity of hydrogen in solids? It is clearly H^+ in H_xWO_3 , but only partially ionized in PdH . What is the ionicity in $LaNi_5H_6$? And even more interesting, how does the electronic nature change as the ion diffuses? Related questions include: what happens as the electronic properties of the host change (metals vs. insulator; and what role is the bonding in molecular intercalates and how does that affect diffusion; and what role does electron transfer play in determining the electronic and optical properties of the compound formed (i.e., how much chemical manipulation of these properties can one hope to achieve)?

Sufficient compounds have now been studied that it should be possible to elucidate the role of the crystal structure in determining the magnitude of the ionic mobility. Particularly, what is the relation between the ionic size of the mobile species, the diffusion path size and the ionic mobility, and what role does the dimensionality of the lattice (1-, 2-, or 3-D) play? In addition, does electron delocalization in the host lattice favor diffusion, i.e., reduce the potential wells, over that in an electronic insulator? An understanding here would allow in the ideal case the synthesis of materials with pre-determined properties, and in any event, give guidance to the synthetic chemist or the device engineer. Diffusion is important in many preparative reactions besides the obvious intercalation reactions (e.g., battery reactions); examples include the formation of oxides and sulfides by reaction of their metals with oxygen or sulfur (also important in corrosion), where in many cases the metal must diffuse through the product layer to react — in these cases product morphology is controlled by the diffusion process, e.g., TiS_2 , VS_4 pipes¹⁾; $\text{Hg}_{3-8}\text{AsF}_6$ is also apparently formed²⁾ by the transportation of mercury along the mercury-atom chains in the crystals; and the doping of many semiconductors is performed by diffusing the foreign ion into the host lattice. Diffusion resulting in the formation of an intercalation compound may possibly be the precursor to a whole new set of composites at the molecular level; an example might involve the incorporation of a monomer into a structure followed by a polymerization step. Growth of novel zeolites is also being accomplished through construction of the inorganic lattice around long-chain molecules; these molecules are subsequently removed leaving channels of predetermined size and with minimum defects.³⁾

In the next few pages some aspects of intercalation compounds will be discussed to exemplify the opportunities available for materials of this type. Intercalation compounds may be defined as those compounds formed reversibly between guest and host species in which the host structure is essentially maintained; they may be 1-, 2-, or 3-dimensional. Typical examples of these are shown in the table below:

<u>Hosts</u>	<u>Guests</u>
Sulfides: e.g., TiS_2 , $\text{V}_{(1-x)}\text{Fe}_x\text{S}_2$, NiPS_3 , MoS_3	Metals, organic electron donors
Oxides: e.g., WO_3 , MoO_3 , FeOCl , V_6O_{13}	Metals, 'oxygens', molecules
Metals: e.g., LaNi_5	Hydrogen
Clays	Organics (+ ion exchange)
Graphite/Boron nitride	Metals, halogens, Lewis Acids

1. Intercalation compounds

The intercalation compounds of graphites and of the transition metal dichalcogenides — both alkali metal and molecular compounds — were first synthesized in Europe, as is the case with so many of the novel materials now the subject of research in the United States. The alkali metal intercalates of graphite have been known since 1926,⁴⁾ whereas those of the dichalcogenides were not reported until 1959.⁵⁾ Both classes of compounds were rapidly enlarged by U.S. efforts driven by an interest in novel superconducting compounds and phase transitions in two-dimensional materials. The initial hopes of finding higher temperature superconductors or evidence for non-phonon mediated

superconductivity were not realized. However, research on the simple binary chalcogenides and their alkali metal intercalation compounds has been extensive because of the discovery of charge density waves in the unintercalated compounds and the discovery of highly energetic electrochemical intercalation of lithium in TiS_2 and its resulting potential for high energy density, reversible, ambient temperature batteries.

The existence of independently variable, interpenetrating, interacting sublattices offers not only clear technological opportunities to discover new physical phenomena or to study well-known phenomena in controllable systems. An example of this is found in the compounds Li_xTiS_2 ($0 \leq x \leq 1$) where the Li array acts as a two-dimensional lattice gas with a tendency to order at certain rational values of x .⁶⁾ An understanding of this phenomenon on a fundamental level appears possible and is now the subject of research at a number of universities. Such an understanding will be important beyond the Li_xTiS_2 compounds and should be useful in identifying some of the key features which control the freedom of ions in ionically conducting solids.

Perhaps the most significant implication of the Li/TiS_2 cell discovery is that reversible, rapid, highly energetic redox chemistry is possible at ambient temperature. Henceforth, a good deal of research could profitably be directed toward the search for other examples of a similar nature. This would be a search for compounds which undergo a similar reaction; that is, for compounds containing transition metals in a reasonably high oxidation state within a structure which can accommodate alkali ions (Li, Na) without the necessity of breaking covalent bonds or radically altering the host structure. Some progress has been made in

in this area but no candidates for battery cathodes have been identified which are significantly better than TiS_2 . A need exists for a clearly enunciated theory or set of principles to guide this research. Recent work⁷⁾ suggests that a profitable turn in the search for high energy systems might be found in amorphous transition metal sulfides like MoS_3 .

Alternatively, graphite intercalates such as C_8AsF_6 , C_8AsF_5 , etc. might be combined with suitable electrolytes to give a battery approximating an alkali/halogen system. Although many such graphite intercalation compounds are now known, only in a few instances are the guest species well defined. Typically, there is confusion concerning the extent of charge transfer between host and guest, lack of definition of the guest species (e.g., whether it is AsF_5 or $1/3\text{AsF}_3 + 2/3 \text{AsF}_6^-$), lack of knowledge of the placement of the guest species with respect to the host lattice and ignorance of the impact of the guest on the host structure. An added attractive feature of many of these intercalates is that there is very little change in crystalline structure during reaction, thus minimizing swelling/contracting and disintegration of the electrode.

Since the early and mid-twenties, research on molecular intercalation complexes has been conducted at a low level in a few places. This is in part because progress in this area requires the more traditional chemical skills sorely lacking in the materials science community in the United States and, more recently, because the hoped-for effects on the superconductivity of the layered host were not observed. Most recently, work⁸⁾ in Germany has made significant steps in elucidating the nature of the bonding in certain of these systems, relating it to that of the simpler ionic compounds. The technological opportunities for molecular

intercalation complexes are not clear at present. They do represent scientifically interesting systems however, and the ability to alter the electronic and other solid-state properties of these materials in subtle and not so subtle ways by the applications of the traditional notions of molecular manipulation argues well for an interesting future for these compounds in the hands of imaginative chemists and physicians.

A particularly interesting subset of these materials is that which results from the insertion of the metallocenes dicyclopentadienyl cobalt and dicyclopentadienyl chromium between the layers of the dichalcogenides. The resulting compounds, $\text{TaS}_2^-(\text{Cp}_2\text{Co})_{1/4}^+$ and $\text{TaS}_2^-(\text{Cp}_2\text{Cr})_{1/4}^+$, are superconductors even though the chromium ions carry a local magnetic moment. Such complexes may have interesting catalytic implications.

Another subclass of molecular compounds of interest is those in which a long chain amine is inserted between the layers. These yield compounds containing a molecular bilayer specifically similar to those in cell walls. These layers are undoubtedly liquid-like and undergo "crystallization" as the temperature is decreased. Thus, sandwiched between metallic layers 6 Å thick, one has a solvent where solution chemistry and diffusion should be of some interest. The liquid-like character of this region should be enhanced by the introduction of disorder via admixture of chains with double bonds and side groups. All in all, such compounds appear to offer an interesting, unusual, and variable electrochemical environment which could prove fascinating to explore, but as yet no known technological application.

Part of the difficulty associated with the study of intercalation is the failure of researchers to prepare crystals suitable for a single

crystal structure work on any intercalation compound, be it of the layered dichalcogenides, graphite, or other host. This has been of lesser concern for the structurally simpler metallic intercalation compounds than it has been for the molecular compounds where it tends to preclude progress in elucidating the nature of the guest host bond. The greater application of electron diffraction and EXAFS should help solve these problems.

BASIC RESEARCH NEEDS

As discussed earlier, one of the success stories in solid-state science encompasses the class of materials called *Intercalation Compounds*. Progress in this area came about through a basic science drive rather than from a technology need. Such intercalation compounds, particularly of the layered disulfides, were first reported in the German literature in 1959. They were then studied to see how intercalation affected their physical properties, in particular superconducting.⁹⁾ Out of a study to determine the exact chemical composition of the highest superconductor, a potassium compound,¹⁰⁾ the high free energy of formation of these intercalates was discovered which led to the battery application.¹¹⁾ In this battery program, a synthesis effort was originated to prepare TiS_2 economically. One technique found¹²⁾ here gave sulfides of high surface area which in turn allowed a study of the catalytic properties of all the transition metal sulfides. These catalytic studies, which involved predominantly amorphous compounds, then led to the finding that amorphous materials were active as battery cathodes.⁷⁾ It is such an interdisciplinary approach to a broad class of compounds that is most likely to uncover new materials of unusual properties that may in the future have important energy implications.

What is needed are a few more broad synthesis/characterization studies of this type.

More specific needs in this area include an expansion of synthesis capabilities; for example, greater emphasis might be given to low-temperature reaction routes or to the application of electrochemical tools. To meet this need, the academic community should place a greater emphasis on synthesis. This will also increase the general synthesis expertise and the resources available to the next generation. At the same time, students get a training in the basics of structural characterization; it is surprising how many times a piece of work is reported where the simplest x-ray evidence for the phases discussed has not been obtained. (The advanced structural tools are now becoming more broadly available, and are not felt to be an impediment to progress in the solid-state sciences.) This need for chemists trained in the synthesis and elementary characterization of solid compounds is critical to all studies of new materials. The major synthetic efforts of this sort are in Europe, particularly Germany, the United Kingdom and France. More support for this kind of work in the United States would facilitate a more effective national effort. In the past, immigration policies permitted the United States community to advance by absorbing Europeans into the research effort here with little difficulty. Such an approach is not possible under current immigration practice. If these research efforts are to continue, the U.S. would do well to foster the growth of such activities in its own university system more than it has.

TECHNOLOGY NEEDS

Ionic or molecular motion in the solid state is critical in a wide range of technologies. This impact is not only found in the materials during actual use, but also in the formation and degradation of key components. The technology needs are described here in several rather broad categories and are not all inclusive but tend to cover what were felt to be the presently conceived needs.

BATTERIES

In a society relying progressively more on electrical energy, there is a need for storing this energy, particularly in a mobile form. Batteries are one way of doing this. A battery consists of three active components: the anode (reducing electrode), the electrolyte (the medium through which the charged ions, but no electrons, are transferred from one electrode to the other), and the cathode (oxidizing electrode). In addition, there are various inert components, for example current collectors, separators and containment materials. Other related electrochemical devices, such as electrochromic displays (H_xWO_3) and oxygen sensors (ZrO_2), have similar components/properties and will not be considered. In batteries of interest in the energy field, solid materials play differing roles depending on the configuration of the particular system as high discharge rates preclude solid/solid interfaces so that these cells tend to have either both electrodes solids with a liquid electrolyte, e.g. $LiAl/molten\ salt/FeS$, $Li/organic/TiS_2$ or both electrodes liquids with a solid electrolyte, e.g. $Na/\beta\ alumina/S$. The various components will now be considered.

1. The Anode

The need here is in the understanding and perfection of the electrodeposition of metals, which is critically important in re-charge of cells using lithium and zinc anodes. In these cases, dendritic, or even non-metallic, deposition is life determining. Electrodeposition is an art not a science at the present time, and a fundamental understanding of the critical parameters would be important not only in energy storage but also in the energy intensive metal electrowinning industry and in the electrosynthesis of new compounds (that might have impact in the energy area as well as elsewhere). One way around this problem is to use alloy anodes such as LiAl where dendrites cannot form under proper voltage control; however, this approach incurs both weight and voltage penalties but is worthy of further study particularly for high lithium content alloys, e.g., those with silicon.

2. The Cathode

New materials can have a marked impact on the energy storage capacity of batteries and particularly on the numbers of discharge/charge cycles that can be obtained. In the case of lithium cells, most work has been performed on titanium disulfide;^{13,14)} and on transition metal oxides, for example, V_6O_{13} .¹⁵⁾ There is still need for new inorganics that still have higher energy densities without significant changes in the voltage during discharge. Although several new compounds come close to TiS_2 in actual storage capacity, none show significant improvements from capacity/cost/availability/electronic conductivity (over whole range of discharge)/reversibility/or rate of discharge point of view. A whole new class of cathode materials that are just now being investigated are those that are amorphous in structure, e.g. MoS_2 , V_2S_5 , MoS_3 ,⁷⁾ V_6O_{13} .¹³⁾

It should, however, be emphasized that the cathode is no longer the rate-controlling step in the development of advanced lithium batteries, and the fundamental understanding of their mode of operation is in pretty good shape. It is therefore recommended that most support be aimed at the understanding of the other parts of the system, e.g. anode materials (alloys/plating, etc.), and on the properties of electrolytic solutions which are the limiting steps (not materials science *per se*).

3. The Solid Electrolyte

Much excellent work has been reported on the β aluminas since their ion conducting properties were reported in 1967 at the Ford Motor Company.¹⁷⁾ Subsequently, the Lincoln Laboratory Group¹⁸⁾ have discovered through a basic understanding of the structural needs of ionic mobility a number of comparable materials which are isotropic in their properties. Such isotropic materials help both the ionic conductivity and the mechanical properties. Ideally, higher conductivities are needed at lower temperatures to reduce corrosion problems associated with the present high temperature sodium/sulfur cells. Preferably, one would want to operate cells at temperatures sufficiently low, $\sim 200^\circ\text{C}$, where plastic components can be used. However, if such electrolytes are discovered, then an alternate cathode will be needed because of the solidification temperature and high viscosity of sulfide melts which restricts the use of the present sodium/sulfur cells to a lower temperature limit of about 300°C .

Various fluorite-type materials containing non-bonding valence pair species such as Bi^{3+} exhibit high anionic conductivity and could conceivably lead to electrochemical devices involving oxide or halide

containing cathodes or batteries of the type alkali/alkali⁺ and fluoride⁻/fluorine material. A fundamental understanding of the diffusion process in such materials is highly desirable, and might be accomplished by high resolution electron microscopy combined with synthetic chemistry.

4. Separators

There is a need in many systems (batteries, electrolysis cells, fuel cells, etc.) using liquid electrolytes for separators that are stable at the same time to both highly reducing and oxidizing environments. In many cases these are preferably ion-selective; an example is Nafion (DuPont product), but this is too expensive for many large applications. Another example of a system where development progress is being held up for the lack of a suitable material is the high-temperature lithium molten-salt battery (Argonne National Laboratory); in this case a separator is required to replace the expensive boron nitride now in use.

CATALYSTS

Catalysis is at the heart of petroleum refining and will become more critical as the feeds become heavier, as such crudes whether from traditional sources or from shale, tar sands, coal, etc., will require much greater conversion. Particularly important is the ability to both break down large carbonaceous molecules and to remove undesirable species such as sulfur, nitrogen, oxygen and various metals, in particular vanadium and nickel. It is quite likely that petroleum crudes will become the nation's largest single source of vanadium.

The diffusion of ions and molecules is important in several areas of catalysis. These include: the sintering of metallic particles, of

compound catalysts and of the supports themselves; the migration of oxygen ions in oxidation catalysts, which is critical in their operation; and the diffusion, or non-diffusion as the desire may be, of molecules into shape-selective catalysts prior to reaction. In this last case there is a need for a strong long-term activity in these shape-selective catalysts in terms of synthesis, structure and characterization. Such catalysts are one hope in significantly improving the selectivity of reactions, thus both reducing feed wastage and potentially environmentally unacceptable byproducts. These catalysts may be of application both in the petroleum and chemicals area, e.g., in the conversion of $\text{CO} + \text{H}_2$ obtained from coal gasification to petroleum, and the conversion of xylenes to the para isomer. There is very little synthetic materials work (outside Mobil/Union Carbide) to create compounds with specific structures (molecular engineering), be they zeolitic in nature, clay based, or use transition metal layer or tunnel structures (including clathration reactions).

In the case of oxide oxidation catalysts, evidence is mounting that ionic mobility coupled with a variable oxygen composition is critical to their operation. The oxygen used to oxidize the organic comes from the oxide lattice not from the gaseous oxygen; the latter merely re-oxidizes the oxide. Apart from the early work of Winter, who showed that the oxide oxygen could be readily exchanged throughout the whole lattice with gaseous trace oxygen, there is no direct measurement of the diffusion of oxide ions in these lattices under catalytic conditions.

One of the predominant ways that catalysts sinter and thereby lose activity is by the surface diffusion of atomic/ionic species. Here

again there is very little actual diffusion data to guide the engineer. Various ways have been found to minimize diffusion, e.g. by increasing the interaction between catalysts and support,¹⁹⁾ or to undo its effects, e.g. by redispersing the catalyst.

METALLURGY

Diffusion of ions/atoms are important in several areas of technological importance to metals. These include corrosion (diffusion of oxygen or metal ions), hydrogen embrittlement (hydrogen diffusion), and hydrogen storage materials (again, hydrogen diffusion). In the first, means for minimizing the diffusion of the ions in protective films are needed. In the other cases the requirements are opposites to one another. Thus, to minimize hydrogen embrittlement both the solubility and diffusion coefficient need to be minimized, whereas for storage these need maximizing. What is learned in studies in the one will surely help in advancing the other. The specific needs for hydrogen storage media, be they metallic or inorganic in nature, are high and reversible incorporation of hydrogen coupled with light weight and low cost; the temperature and pressure at which this should occur depends on the application in mind. Some intercalated graphites show metallic conductivity and are highly resistant to oxidizing agents, and so may displace metals as electrodes in electrochemical synthesis, e.g. C_8AsF_6 in fluorine reactions.

SEMICONDUCTORS

A better understanding of the diffusion of atomic species should assist in enhancing the utilization of diffusion techniques for producing and doping semiconductors; these could be crystalline, amorphous, bulk or thin film in nature. In addition, critical to the operation of so many semiconductor devices, e.g. solar photovoltaic cells, is the minimization of diffusion of species across interfaces which can degrade the device. One material where diffusion data would be very useful is amorphous silicon, SiH_x , where very little is known about the mobility of the hydrogen.

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CHAPTER 7

CATALYSIS

Heterogeneous catalysts currently play a major role with energy in many different ways, and it can be confidently predicted that this role will become increasingly more important. Improvements in catalysts which might appear minor have already had dramatic impacts on the energy situation. For example, the replacement of part of the amorphous alumina silica cracking catalyst with a crystalline alumina silicate (a zeolite) saves this country more than two-billion dollars per year by converting a larger fraction of crude petroleum into gasoline.

The number of different chemical reactions which require catalysts is too large to enumerate here. There are hundreds of such reactions, and all can be related to energy in various ways. Furthermore, catalysts can serve critical roles in terms of solving pollution problems and conserving raw materials. In coal conversion, catalysts are important for liquefaction, gasification, and the CO/H_2 reaction. Photocatalysts may play an essential role in utilization of solar energy. Electro-catalysts are important both for producing electricity in fuel cells and for efficiently using electricity in electrolysis cells of various kinds.

There are many ways in which a catalyst advance could be successful from a technological point of view. Generally the more important considerations are higher activity, better selectivity to a desired product, and longer life. Potentially, the most dramatic advance would be the discovery of a catalyst which would catalyze a reaction which had never before been effectively catalyzed, e.g., the oxidation of methane to methanol.

Heterogeneous catalysts have become very advanced materials by a largely empirical approach. A big problem in suggesting future directions for improved or new catalysts is that we do not know where we are now. That is, we know very little about some of the most successful and important catalysts that are presently in use. Therefore an area which should receive special emphasis is the application of state-of-the-art materials characterization techniques to important catalysts. A critical characterization tool would be electron microscopy with microprobe and microdiffraction. Examples of other useful techniques are EXAFS, XPS, UPS, AUGER, NMR, ESR, IR and Raman.

Catalysts frequently have several different stages of life. The phases present in a material may change dramatically when it is used as a catalyst. For example, cobalt molybdate is converted to a mixture of cobalt and molybdenum sulfides when used as a hydrodesulfurization catalyst. All catalysts eventually degrade with use, and sometimes they can be regenerated. Thus, the characterization of catalysts should include the fresh, activated, deactivated and regenerated stages. Once current catalysts become better characterized, ideas will naturally emerge for new and improved catalysts.

The importance to surface studies of catalyst characterization cannot be overemphasized. Surface studies may not be relevant to catalysis unless they are performed on the phases and the crystallographic faces actually present in real catalysis. Frequently, such information is lacking even for very important catalysts.

There is good reason to believe that the highly empirical approach to new catalysts is no longer successful enough to be encouraged.

Further advances are most likely to occur if a systematic approach is stressed. Such studies would combine and correlate careful synthesis, characterization, and reactor studies. For the synthesis part the composition, structure, and synthesis technique would be systematically varied. Materials prepared would then be characterized by techniques such as x-ray diffraction, adsorption measurements and electron microscopy. Reactor studies should be carried out over a wide variety of conditions, and an attempt should be made to derive kinetic expressions. There are many possibilities for both materials and reactions. An example would be the study of Chevrel phases ($A_xMo_6S_8$) where A can be Pb, Sn, rare earths, etc. for hydrodesulfurization.

Selective oxidation catalysts are continually being reduced at one type of surface site and being reoxidized at a different site. There must be an effective method of passing electrons from the site of catalyst reduction to the site of its reoxidation. Valence degeneracy is involved, and detailed knowledge of the electronic structure of the catalyst may be very important in certain types of catalysis. This should be further studied.

Bulk, as well as surface diffusion, is of great importance in catalysis. It is believed that high mobility of oxygen anions is a characteristic of some of the best catalysts for selective oxidation. However, there are no reliable data on oxygen mobility in such materials as molybdenum trioxide and bismuth molybdates. The selectivity obtained with zeolite catalysts is generally assumed to be related to diffusion of molecules in the zeolite pores. More and better diffusion data for molecules in zeolites would improve our understanding and point the way

to better catalysts and processes. Many catalysts deactivate due to sintering. A study of diffusion in such catalysts could suggest methods of improving catalyst life.

Many important catalysts consist of several phases. The catalytic properties of this mixture are clearly superior to those of any of the individual phases. One example is the cobalt sulfide/molybdenum sulfide mixture used as a hydrodesulfurization catalyst. The nature of the synergistic mechanism is not known in such catalysts, and there should be increased effort in this area, particularly to look for replacements for cobalt.

Many oxides have acid sites which are critical to their catalytic properties. There have been many attempts to characterize such sites by chemical adsorption with molecules such as ammonia and by spectroscopic techniques such as IR. However, none of these techniques have been completely satisfactory, and there is a need for the development of a better method to characterize surface acidity.

Many of the conclusions reached in the *Panel Report on High Temperature Ceramics* (Dept. of Energy, January, 1979) are highly pertinent to catalysis. For example, a rational synthesis of a catalyst generally depends on an understanding of the physics and chemistry of particulates; also, defects in materials can strongly influence catalytic properties and lifetime of catalysts.

Recent advances in catalysis have come about primarily from research activities in industrial laboratories. Frequently, information is not made available on the actual composition or the optimum synthesis method for advanced catalysts. This presents a problem for those outside

a particular company who desire to carry out research on a relevant catalyst. However, this problem cannot be allowed to inhibit progress in this critical field. Industrial laboratories will generally welcome more research on catalytic materials by scientists in academic and government laboratories, and they would certainly be willing to identify many of the important materials relevant to catalysis. Examples of simple, but very important, catalysts are:

- Silver metal for oxidation of methanol to formaldehyde and for the oxidation of ethylene to ethylene oxide
- Co/Mo/S for hydrodesulfurization reactions
- $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ for the oxidation of propylene to acrolein, for the ammoxidation of propylene to acrylonitrile, and for the oxidation of 1-butene to butadiene.

CHAPTER 8

SEMICONDUCTORS

INTRODUCTION

Semiconductors are the key materials of the second industrial revolution. They are able to act as switches, and as detectors and emitters of light at high functional densities. Thus semiconductors afford inexpensive intelligent machines that have begun to pervade nearly all aspects of industrial economies.

The importance of a sound research base in semiconductors was recognized early. Vigorous and continuous research, in fact, has contributed to making the United States the world leader in electronic information processing and in communication. Improved information technology contributes to energy conservation; thus can be considered energy technology in a broad sense. Studies of future research needs in these areas include pertinent materials aspects.¹⁾

This chapter covers aspects of bulk semiconductors for all applications, all materials and some device aspects for solar cells, and some aspects of thermoelectric converters.²⁾

STATUS OF SEMICONDUCTOR TECHNOLOGY, WITH EMPHASIS ON SOLAR CELLS

Because of the existing and at present more economic alternatives for producing energy, the potential of semiconductors in terrestrial photovoltaic conversion did not receive adequate attention until the mid-1970's.

There are now substantial applied research and engineering programs under way in the United States,³⁾ and to a lesser degree in other countries.

These programs are justified through economic analyses that indicate a realistic chance for photovoltaics to replace/substitute conventional electric generating capacity.⁴⁾

Three types of technology are pursued currently to obtain photovoltaic converters for economic production of electricity: concentrators, flat plate silicon, and thin film arrays.

In concentrators, the semiconductor cell area may be ten to ten-thousand times smaller than the system aperture. Cells can be comparably expensive (approximately \$1000/m²) but must be highly efficient ($\geq 30\%$)⁴⁾. The best research results to date are 20.5% in silicon cells,⁵⁾ 25% in cells based on gallium arsenide,⁶⁾ 28% in a converter that employed spectral splitting for more efficient conversion by a pair of silicon and gallium-arsenide based cells,⁷⁾ and 26% for a silicon thermophotovoltaic cell designed to convert radiation from a black body at 2000°C (ultimately to be heated by sunlight).⁸⁾ Device theory, materials, and cell fabrication are closely related to those employed in conventional semiconductor technology.

Flat plate silicon arrays represent the only current commercial technology, drawing on twenty years of development for small-scale applications primarily in spacecraft. Conventional single crystal silicon is used as the starting material but alternatives, such as coarsely polycrystalline (multigrain) cast materials, are in sight. One principal barrier to the rapid introduction of cast and other non-single-crystal silicon is the lack of understanding of growth, electronic properties, and processing of polycrystalline semiconductors and junction devices. For silicon cells, a specific fabrication technology, distinct from those employed in microcircuit

production, has been developed over the years. Due to the small size of the market, processing steps have evolved incrementally. The challenge now is for rapid introduction of efficient and highly automated production of pure silicon, its crystallization, device processing, and module fabrication.

Cost (less than 70¢ per peak watt generating capacity), performance (10% efficiency) and operating life (20 years) of thin film modules have been well defined, but no such cell has been demonstrated in the laboratory. This lack of an obvious candidate which combines minimal materials consumption with acceptable performance in a device and module structure that is highly amenable to automation explains the very broad "screening" programs carried out at present. These programs are severely hampered by the absence of elementary information about optical (e.g., energy gap) and electronic (e.g. conductivity type) properties of the majority of materials of interest. Moreover, the constitution of these materials ranges from amorphous to polycrystalline, but adequate information on device theory, processing characteristics, or aging behavior does not exist.

Thin film modules more expensive than 70¢/W_p or less efficient than 10% can address limited but still substantial markets. Commercial production is imminent for cuprous sulfide/cadmium sulfide modules for solar applications. The production of small cells based on amorphous silicon-hydrogen alloys for incorporation in watches has been announced for early 1980.

Emphasis on inexpensive thin-film devices likewise will provide the motivation for the screening of candidates for solar thermoelectric converters. Here new materials such as the amorphous silicon-hydrogen alloys or polyacetylene will be characterized for the three properties that

contribute to the figure of merit: the Seebeck coefficient, the electrical and the thermal conductivity.

OPPORTUNITIES FOR BASIC RESEARCH

1. Preparation and understanding of perfect crystals

The group IV semiconductors silicon and germanium have been prepared as more perfect crystals and with higher purity than any other material. This quest for materials with ideal properties that can be compared with theoretical predictions has generated advanced purification, crystallization and measurement techniques. These techniques, as well as the better theoretical understanding of crystalline solids, has been valuable in controlling the properties of a wide range of materials of use in the energy field. Moderately funded but long-range work in the growth of silicon or germanium crystals with zero dislocation density and with minimum content of low Z impurities (carbon, nitrogen, oxygen) is recommended.

2. Interaction between defects

Numerous properties of solids (plastic behavior, electronic conductivity in semiconductors, impurity diffusion) can be dominated by defects rather than by the matrix material. Since more methods for analysis can be brought to bear on semiconductors than on most other classes of materials, defect studies can attain a scope and a degree of complementarity difficult to reach elsewhere. Efforts should be undertaken to promote comprehensive understanding of interactions between point defects, line defects, and surfaces/interfaces. These studies should cover structural, electronic thermodynamic (equilibrium) and kinetic (transport) aspects. Examples are the theory and experiments on the energetics of point defect

interaction, or the correlation of electronic with metallurgical (e.g., chemical activity) properties at high concentrations of impurities.

3. Relation of bulk to surface properties.

Much of current surface research focusses on aspects of surfaces that differ from the bulk. It would be desirable, however, to come up with guidelines that permit prediction of surface properties from known bulk data. Clearly, this must be a theoretical effort carried out with a large base of reliable experimental data. Examples of questions are:

- How do surface layer space charges and the associated field superpose on bulk properties?
- Are surface and bulk electron affinities identical?
- Are bulk thermodynamic data applicable to surface reactions?

4. Electronic structure and optical properties of polycrystalline semiconductors.

With a few notable exceptions, fundamental research on polycrystalline semiconductors for junction devices has been carried out only during the past two or three years.⁹⁾ Electronic equilibrium and transport properties, the segregation of impurities and the formation of phases in the grain boundary, grain boundary diffusion and passivation (the reduction of grain boundary effects on carrier transport), and the effects of intersecting grain boundaries and p-n junctions require advances in basic understanding. Very fruitful studies could be carried out in the following areas:

- Explanation of the known differences between group IV, III-V, and II-VI semiconductors, in majority carrier transport across grain boundaries

- Measurement of the electronic band structure at grain boundaries and comparison to the at least four existing models
- Using present high lateral and depth resolution surface analysis methods to study the mechanism of formation and segregation of impurity phases within grain boundaries, and
- Applying controlled preparation techniques in conjunction with methods for structural study to identify the relative uptake of strain by grain boundary and grain.

5. Nucleation and growth

Structures with preferred grain orientation, and coatings are needed in a number of energy technologies to perform a variety of tasks. Polycrystalline and thin film cells depend on controlled nucleation and growth with specified grain dimensions. Progress in cell research depends on practical solutions addressing particular combinations of materials. Guidance from a better theoretical understanding of nucleation and growth could shorten the recurring and wasteful but entirely empirical search for proper conditions for grain growth. It has been shown recently that nucleation and growth phenomena also affect the structure, and apparently the electrical characteristics, of hydrogenated amorphous silicon.

In this context the question of directional solidification in a low technology environment does merit attention. A number of techniques for the preparation of polycrystalline bulk or sheet silicon would benefit from quantitative guidelines.

Because of the wide applicability of a useful theory of nucleation and growth this area is ranked among the opportunities for basic research.

6. Amorphous Semiconductors

The discovery that hydrogenated amorphous silicon can be doped n- and p-type¹⁰⁾ and the subsequent demonstration of a photovoltaic device based on $\alpha\text{-SiH}_x$ ¹¹⁾ has stimulated substantial research activity. This material, a challenge to theorists and experimenters alike, is under investigation in university, government and industrial laboratories because it is regarded as a candidate for "breakthroughs" both in basic physics and in device applications.

Research on amorphous semiconductors does not appear in need of extra support. However, a brief listing of recognized problems is presented to provide a better balance to this chapter on research opportunities. It should be mentioned that $\alpha\text{-SiH}_x$ is considered primarily as a candidate for an inexpensive thin-film solar cell, but that applications as a selective solar absorber or as a thermo-electric material also have been discussed.

$\alpha\text{-SiH}_x$ can be made by d.c. or a.c. glow discharge in silane, reactive sputtering of silicon in the presence of hydrogen, chemical vapor deposition from silane, and a number of less used techniques such as electrodeposition, ion plating, ion implantation and evaporation. The properties of the product film are affected by a large number of growth parameters including the deposition geometry. The effect of the respective technique, e.g., plasma deposition, on the film properties is not understood. In response to this situation, several laboratories are augmenting their diagnostic capabilities.

The role of dopant impurities (boron, phosphorus) and of so-called modifiers (fluorine) is not understood, neither is the creation of new defects upon the introduction of the p-type dopant, boron. There is no

theoretical framework for understanding and interpreting charge transport. Moreover measurement techniques for carrier lifetime and diffusion length are difficult and controversial. The determination of the residual density of states within the band gap also is difficult. There is no routine technique for the precise determination of hydrogen content.

Needless to say, fabrication of junction devices with $\alpha\text{-SiH}_x$ identifies additional opportunities for thin films oriented materials research.

7. Interaction of energy beams with semiconductors

Yet another area which is receiving much current attention from physicists, materials scientists, and electrical engineers is the processing of semiconductors with laser or electron beams. For instance, heavily damaged ion-implanted semiconductor layers have been recrystallized with a single laser pulse. Ion-implanted solar cells have been rendered electrically active with one electron pulse covering a 3-inch diameter wafer.

The mechanisms of recrystallization, the distribution of impurities in the temporarily liquid phase, and the nature of residual defects under conditions of extremely rapid cooling should be studied. Basic understanding of these issues is likely to lead to new techniques of treating and processing surface layers.

NEEDS FOR BASIC RESEARCH

1. Exploratory preparation of new semiconductors

Particularly in the area of thin film photovoltaics, a continuous search for new semiconductors would be welcome to broaden the choice of available materials. This search need not be carried out in the context of a separate program. Instead, support could be provided to all pertinent

synthesis groups in the country for the measurement of the optical absorption edge (between one and two electron volts), the conductivity type (preferably both n and p) and the conductivity of a new compound.

Guidelines for exploring new semiconductors or analogue compounds of known semiconductors could be of value. Such guidelines, possibly derived from semi-empirical theory, should indicate the nature (direct or indirect) and the magnitude of the energy gap.

2. Refractory materials

Since the performance of semiconductor devices is highly susceptible to impurities, nonreactive materials for containers, reactors, and substrates are important. However for fabrication temperatures above 500°C, the number of available refractories is so limited as to be restrictive. In essence, fused silica and graphite are used for crucibles and shaping dies, fused silica for reactors, and alumina, mullite, carbon, tungsten, and molybdenum as substrates. A program on new refractory materials as well as on the mechanisms of wetting and reaction will be useful not only to semiconductor and solar cell research but also to other energy conversion technologies.

3. Classification of preparation techniques

A large number of preparation techniques has been used to produce device-quality semiconductors. These include crystallization from the melt or from liquid solutions, evaporation, chemical vapor deposition, sputtering and related techniques, ion or neutral beams, electrodeposition, spraying, screen printing, etc. Patterns have begun to emerge on the applicability of these techniques. For instance, II-VI semiconductors can be screen printed while group IV or III-V's do not yield useful material.

Sputtering has shown little promise with conventional semiconductors (as opposed to α -SiH_x), apparently on account of concomitant radiation damage and of difficult control of grain growth. A survey of published literature on this question could provide very useful guidelines to the experimenter and could avoid unnecessary duplication.

4. Theories for mass and heat transfer during solidification and condensation

Two areas in semiconductor preparation require improved mass and heat transfer theories: crystallization of sheet silicon, and deposition of films from vapors. A drawback, common to current silicon sheet growth techniques, is the need for extensive instrumentation and highly trained operators to prevent or rectify instabilities that develop easily at the solidification front. Improved theoretical support in the design of film shaping parts and of crucible, heater, and heat-shield geometries could contribute substantially to cost reduction. In chemical vapor deposition, the problems of non-uniform deposition over the length of a reactor, and of efficient use of reactant gases need to be addressed, the former in the interest of improved device yield, the latter as a means of materials conservation.

5. Methods for simultaneous structural, electrical, or chemical analysis

The most promising techniques for characterizing defects in semiconductors appear to be those combining structural or chemical analysis with electrical measurements. For instance, electron beam induced currents produced in a scanning transmission electron microscope have provided the first direct observation of the electrical activity of

semiconductor interfaces.¹²⁾ Other techniques that could produce useful fundamental information are:

- Characterization of electrical and of chemical properties on a lateral scale of 10 nm
- Direct measurement of space charge or of the associated field with an energy resolution of better than 0.1 eV.

6. Theories of deep level, interfaces, and of carrier recombination

Although the performance of most junction devices is limited by carrier recombination or generation at deep levels (within the energy gap) or at surfaces, no adequate predictive theories exist. At present it is not possible to calculate the energy level of a given impurity, the density of states within the gap at a surface or interface, or the rate of carrier generation and recombination which proceeds by these defects. Therefore the effect of introducing impurities or of an interface cannot be predicted quantitatively, nor can one put limits on the ultimate performance of devices.

7. Photoexcitation and charge separation

Photovoltaic processes different from charge excitation across a band gap and charge separation by a space charge layer do exist. Examples can be found in the photosynthetic apparatus which employs molecular levels and tunnelling, and in metal-insulator-metal structures that can exhibit internal photoemission albeit with low efficiency.¹³⁾ Tunnelling barriers (1-5nm) are typically more than one order of magnitude narrower than semiconductor space charges (100 nm). Hence, the materials saving for tunnelling converters would be significant. Provided that very highly absorbing materials ($\alpha \geq 10^{-5} \text{ cm}^{-1}$) can be employed, fundamental research

on alternative excitation and separation processes could lead to less expensive photoconversion technologies.

TECHNOLOGY NEEDS

1. Materials needs

a. *Semiconductors*

Semiconductor technology depends on continued advances in the preparation of crystals and crystalline films of known and well characterized materials. Silicon, gallium arsenide, indium phosphide, and alloys of III-V and of II-VI compounds with high purity and crystalline perfection are needed for high-performance devices such as concentrator cells and other optoelectronic devices, and for microcircuits.

Preparation and purification techniques need to be explored for "solar grade" silicon. This is a yet undefined material containing more impurity than silicon used in microelectronics. Solar-grade silicon should be inexpensive but exhibit adequate photovoltaic performance. Demands on purity may vary with the method that is used for silicon crystallization. For instance, polycrystalline material may offer better opportunities for impurity rejection (into grain boundaries and grain boundary phases) than single crystals.

Thin small grain polycrystalline films (of direct gap materials) for photovoltaic conversion have been plagued notoriously with non-uniform crystalline size and porosity with the effect that these films have to be grown much thicker (20 to 30 μm) than what is thought to be economically acceptable (2 to 5 μm). Here, technology needs to encompass the selection of proper substrates, control of nucleation and

growth, as well as growth techniques that make efficient use of the starting material. In this context, thought should be given to the recycling of unused reactants.

The need for controllable and scaleable techniques for the deposition of hydrogenated amorphous silicon films has been emphasized earlier.

A separate category of semiconductors demanding material development is electrodes for photoelectrochemical conversion. Here, the need is for stable electrodes inert against dark and photocorrosion with band gaps low enough for substantial solar absorption.

b. Ancillary materials

Inexpensive or reusable substrates and containers should be explored with emphasis on the principles governing introduction of impurities, materials losses, and reactivity in the case of re-use.

New transparent, electrically and thermally conducting, materials such as tin oxide, indium tin oxide, and cadmium stannate should be developed for application in contacts or in connecting layers, with emphasis on low contact resistance.

A clear need does exist for inexpensive contact metallization to reduce the demand for silver, and possibly gold. Stable intermetallic compounds that do not release impurities into the semiconductor are required, or metals that form a diffusion barrier upon initial reaction with the underlying semiconductor.

2. Growth and processing

Non-conventional, potentially cheaper methods are needed for the fabrication of device grade materials. The search for such methods

that have not been adequately explored are spraying, screen printing, casting of sheets, melt-spinning, horizontal growth, and electrodeposition.

Processing techniques that are amenable to automation need to be explored. Examples of such techniques are sheet growth, sputtering techniques, and energy beam techniques for annealing or recrystallization.

The problem of grain boundary passivation should be examined in a systematic fashion. In polycrystalline silicon, promising results have been obtained by introducing hydrogen and by in-diffusion of phosphorus (the dopant for the top layer in the solar cell). The mechanisms of passivation are under dispute. Preferential oxidation at grain boundaries has been demonstrated in polycrystalline gallium arsenide films.

Two device-oriented materials problems that also fall in the domain of thin film research are the preparation of reproducible and stable tunnelling barriers, and the very general quest for cell structures that are compatible with polycrystalline materials. With polycrystalline semiconductors, junction formation at low temperature (by producing a Schottky barrier) may be preferable to high temperature techniques (in-diffusion of a dopant) to avoid shorting or shunting of cells along grain boundaries.

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