Fundamentals
of Amorphous
Semiconductors

A Report of the

NMAB NATIONAL MATERIALS ADVISORY BOARD

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NATIONAL ACADEMY OF SCIENCES-NATIONAL ACADEMY OF ENGINEERING

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The study of glasses has been important historically because of their great technological usefulness. One class of these materials, amorphous semiconductors, has evoked a great deal of interest during the past few years. This interest stems in part from the fact that solid state physics, after attaining a remarkably high level of scientific understanding of crystals, can now hope for comparable achievements in connection with disordered materials. Of equal importance is the fact that the metastability of amorphous semiconductors provides them with certain unique properties that may be of considerable technological significance.

This report is intended to provide an overview of the field, its present standing, and its promise. The fundamental structural and electronic properties and the present level of understanding of these properties is of primary concern. However, much of the progress in solid state physics has traditionally been motivated by technological considerations. Therefore, the principal aspects of the physics underlying the more important amorphous semiconductor devices are discussed, as well as the technological setting in which this new field finds itself.

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FUNDAMENTALS OF AMORPHOUS SEMICONDUCTORS

Report of

The Ad Hoc Committee on the

Fundamentals of Amorphous Semiconductors

National Materials Advisory Board

Division of Engineering - National Research Council

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The study reported herein was undertaken under the aegis of the National Research Council with the express approval of the Governing Board of the NRC. Such approval indicated that the Board considered that the problem is of national significance; that elucidation or solution of the problem required scientific or technical competence and that the resources of NRC were particularly suitable to the conduct of the project. The institutional responsibilities of the NRC were then discharged in the following manner:

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

Although the reports of our study committees are not submitted for approval to the Academy membership nor to the Council, each report is reviewed by a second group of scientists according to procedures established and monitored by the Academy's Report Review Committee. Such reviews are intended to determine, inter alia, whether the major questions and relevant points of view have been addressed and whether the reported findings, conclusions, and recommendations arose from the available data and information. Distribution of the report is permitted only after satisfactory completion of this review process.

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

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Henry Ehrenreich, Chairman
National Materials Advisory Board
Ad Hoc Committee on the Fundamentals
of Amorphous Semiconductors

ABSTRACT

The study of glasses has been important historically because of their great technological usefulness. One class of these materials, amorphous semiconductors, has evoked a great deal of interest during the past few years. This interest stems in part from the fact that solid state physics, after attaining a remarkably high level of scientific understanding of crystals, can now hope for comparable achievements in connection with disordered materials. Of equal importance is the fact that the metastability of amorphous semiconductors provides them with certain unique properties that may be of considerable technological significance.

This report is intended to provide an overview of the field, its present standing, and its promise. The fundamental structural and electronic properties and the present level of understanding of these properties is of primary concern. However, much of the progress in solid state physics has traditionally been motivated by technological considerations. Therefore, the principal aspects of the physics underlying the more important amorphous semiconductor devices are discussed, as well as the technological setting in which this new field finds itself.

PREFACE

As a result of increased scientific activity and
interest in the field of amorphous materials, the Office
of Naval Research agreed that the National Materials
Advisory Board (NMAB) of the National Research Council,
National Academy of Sciences-National Academy of Engineering
initiate an appropriate committee study that would address
this challenging subject in a broad fundamental manner.
In this way, it was hoped that the study might be helpful
in organizing the presently available information about
the field, assessing its importance to physics and materials
research, and providing a perspective setting for future
investigations.

In this assignment, which was accepted in
October 1970, NMAB was requested to study those areas of
materials science and solid state physics that are pertinent
to:

(a) the unique physical properties of amorphous
materials,

(b) a characterization of amorphous materials and
the relation of physical properties to the
characterization parameters,

(c) a description of the fundamental properties of
amorphous materials,

(d) fruitful theoretical analyses of the disordered
state, and

(e) a discussion of the physics underlying amorphous
semiconductor devices.

Based on its findings, the Committee was requested to document in its final report "promising areas of research appropriate to the opportunities and problems and to suggest in this report the kind and extent of research necessary to advance amorphous materials science and technology."

Because of the nature of this request, the Committee recognized that an adequate discussion would involve placing the subject in its proper technological setting. It was felt that this could be accomplished without making definitive assessments of comparative technologies. The tutorial discussion given in Section VII should, however, provide some perspective.

In order to circumscribe the scope of the report, the Office of Naval Research suggested that the amorphous materials under the Committee's purview should include primarily elements and mixtures of elements from Columns IV, V, and VI of the periodic table and that materials like gases, liquids, plastics, liquid crystals, organic materials, structural materials such as amorphous alloys and carbon, and both silicate and oxide glasses would be excluded from extensive consideration. This delimitation of materials appeared appropriate to the Committee since the semiconducting glasses to be emphasized here are just those responsible for the great interest in this field that has developed during the recent past. As already pointed out, the oxide glasses are technologically very significant.

Electronic phenomena in amorphous oxide films are the subject of an extensive recent review (Dea 71).[*] A recent study of interest concerning the physics of amorphous materials in general was initiated by the British Science Research Council (Sr 70).

Since it is the intent here to present a reasonably concise overview of this field with regard to its present standing, its promise, and existing needs and opportunities for further research, this report obviously cannot present an encyclopedic survey even of the amorphous materials that remain after the oxide and metallic glasses have been eliminated. Accordingly, only those amorphous semiconductors of greatest fundamental and/or technological interest will be considered in any detail. These are the elemental glasses, Se, Ge, and Si and the chalcogenide mixtures As-S, As-Se, Te-Ge, and Te-As-Si. The last three have well known applications respectively in xerography and memory and threshold switching.

The NMAB Ad Hoc Committee on the Fundamentals of Amorphous Semiconductors was formed in October 1970 and conducted its first meeting in November (9-10) 1970. The full Committee held six formal two-day meetings during the

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* The convention for referencing employed in this report is explained at the beginning of Section IX which lists the literature citations. Wherever possible throughout the report, the references are to review articles rather than the original papers. Such articles are marked R in the reference section.

period November 1970-June 1971. In addition there were
several smaller sessions involving various groups of
Committee members.

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I.   INTRODUCTION

Glasses and Their Uses

It is customary to restrict the designation
"glass" to those amorphous solids that have been formed by
cooling a liquid. However, it is doubtful that "glasses"
so defined differ sharply in microscopic character from
amorphous solids with the same composition formed in other
ways. Thus the terms "amorphous solids" and "glasses" will
be taken to be equivalent in this report. Glasses can be
metallic, semiconducting, or insulating. The forces
bonding the atoms are analogous to those found in crystals.
The chemical bonding can be covalent, ionic, metallic, van
der Waals, or hydrogen bonding, or combinations of these.
Most glasses, however, fall into the predominantly covalent
category. Because of their metastability, glasses exhibit
properties that are quite unique and remarkable. They do
not undergo a first-order-phase transition at the melting
temperature. Instead, they soften gradually at sufficiently
high temperatures and pass more or less continuously into
the liquid state. The molten glass may either return to
its original state if it is cooled sufficiently rapidly,
or crystallize if it is cooled slowly. Glasses containing
several constituents may exhibit a separation into phases
having different compositions on a very minute spatial
scale. These structural transformations have a qualitative
influence on the electrical and optical properties in
various types of glasses. These are of interest not only

as phenomena in themselves but also because of their technological significance. Finally, the mere fact that glasses are structurally disordered suggests that their properties can be relatively insensitive to high-energy radiation and bombardment.

The oxide glasses are, perhaps, the most familiar. The soda-lime-silicate glasses (mixtures of Na_2O, CaO, and SiO_2) are good dielectrics, thermal insulators, and optical transmitters. Because they soften gradually with increasing temperature, it is possible to pour, mold, roll, press, and float ordinary window glass, processes that are essential in its manufacture. Many, though not all, oxide glasses are insulators with conductivities less than 10^{-8} Ω^{-1} cm^{-1}. This fact, as well as the natural tendency of metals to oxidize, makes these materials very useful in solid state device technology.

Semiconducting glasses (or vitreous semiconductors) were not investigated to any large degree before 1955. In contrast to the insulating glasses, the conductivity in these substances is electronic rather than ionic. As a result the conductivity is larger, ranging from $10^{-13}-10^{-3}$ Ω^{-1} cm^{-1}. While some of the semiconducting glasses are oxides, the most widely studied examples do not contain oxygen. Instead they contain another constituent, such as S, Se, Te of group six of the periodic table. Such elements are called "chalcogens" and the glasses involving them are known as chalcogenides. The chemical bonding in such glasses is predominantly covalent with a smaller ionic

contribution, although cases involving mixed covalent and van der Waals binding are also frequently encountered in materials such as Se.

The chalcogenide glasses have received a great deal of attention because of their established or possible importance in connection with electrophotography, infrared transmitting windows, electronic switching, and electronic and optical memory applications. Work at Energy Conversion Devices, Inc., (ECD) has particularly spurred the development of applications for chalcogenide glasses.

Elemental amorphous Se has been investigated extensively in part because it forms the essential ingredient of the photosensor involved in xerography. In practice the commercial compositions may contain some As and traces of other elements. As-Se glasses have also been studied at RCA in connection with vidicon applications. Indeed, the fundamental properties of these glasses have received considerable attention both in this country and the Soviet Union (Ko 64). The interest in technological applications of chalcogenide glasses has stimulated interest in other chalcogenide glass compositions, such as those belonging to the Ge-Te family.

Crystalline Si and Ge are among the best understood solids. Their amorphous forms are of interest particularly in connection with fundamental research directed toward exploring physical differences between the crystalline and amorphous states. The delineation of these differences would be expected to be simpler in elemental

glasses that contain only structural and not compositional
disorder.

The metallic glasses usually occur as compounds
of the form A_3B to A_5B, where A is a noble or transition
metal and B is a metalloid like Si, Ge, or P. While they
exhibit a variety of interesting properties including
radiation hardness, they have not as yet found significant
use in electronic technology. Since amorphous semiconductors
have been observed to crystallize in the neighborhood of
conventional metallic contacts, speculation has focused on
the possibility of using amorphous metal contacts on semi-
conducting glasses in order to prevent this from happening.

It should be emphasized that the study of glasses
is important, not only for technological reasons but also,
more fundamentally, because they are systems having struc-
tural and possibly compositional disorder. Until very
recently solid state physics has been concerned almost
exclusively with crystalline materials. Considerations
of disorder emphasized effects arising, for example, from
lattice vibrations, point defects, and impurities and
dislocations in small concentrations that only influence
the crystalline properties weakly. However, during recent
years, emphasis has been increasingly given to the inves-
tigation of the properties of strongly disordered materials,
such as liquids, binary substitutional alloys, and amor-
phous materials. Clearly, an increased understanding of
liquids and alloys will be of benefit to those investigating
amorphous semiconductors, just as further theoretical

insight concerning the materials considered in this report will aid those investigating liquids and alloys.

Amorphous-Crystalline Transformations

The physical, chemical, and mechanical properties of amorphous materials can all be strongly affected by the transformation to the crystalline state. The changes in electrical and optical properties have already been noted. Some examples, representative of the extent of these changes, may be useful. The room temperature resistivity of amorphous Ge and Si films can be as much as five orders of magnitude larger than that of the corresponding polycrystalline films. The extent of the change depends sensitively on the details of the film preparation. By contrast in As_2S_3 and As_2Se_3, the glasses are less resistive than the corresponding crystals. The electrical band gap, as determined from the temperature dependence of the conductivity, is respectively 0.2 and 0.55 eV in c-InSb and a-InSb.[*] In c- and a-Te, the corresponding quantities are 0.33 and 0.87 eV. The index of refraction in Te and Se decreases respectively by 40 percent and 12 percent in going from the crystalline to the amorphous state. On the other hand, in Ge the index changes but slightly in the opposite direction. The foregoing results are representative of the simplest types of measurements. As will be

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*In this report, the prefixes c- and a- will be used to specify the crystalline and amorphous states of the given material unless it is clear otherwise which is being referred to.

seen later, even the Hall effect and thermoelectric power, whose measurements represent no difficulty in many crystalline semiconductors, are still poorly established quantitatively in amorphous materials. Further citation of experimental results in the present context might therefore be misleading.

There have been qualitative observations of changes in chemical properties such as wettability, reactivity, adhesion, and solubility resulting from amorphous-crystalline transformations. Mechanical properties, such as hardness, thermal expansion, and sound velocity are similarly affected (Ov 71c).

This unique potential for change in amorphous materials is of both fundamental and technological importance. Its measurement and interpretation is a challenging and important problem for the solid state physicist and chemist; its exploitation is a challenge for the ingenious inventor. Proposals have been made to utilize these and other effects for optical mass memories, memory and threshold switches, electroluminescent displays, non-impact lithographic plates, and imaging applications including photography and copiers (Ov 71c).

As an example of how these unique properties can be utilized technologically, the memory device takes explicit advantage of the fact that glasses are energetically metastable. In the Te-based glasses, the Te rich phases tend to segregate from the rest at sufficiently high temperatures. Such temperatures can be achieved by

joule heating. Phase separation can also be achieved by
photocrystallization. Depending on the maximum tempera-
ture and the rate of cooling, the glass then settles
either into a state containing crystalline filaments or
returns to its initial amorphous state. The two differ by
orders of magnitude in conductivity. The mechanisms for
memory switching will be discussed in Section VI.

Outline

In approaching this report, the reader should
bear in mind that the field of amorphous materials is a
rapidly developing one. Some of the questions asked here
may well have been answered by the time this document
appears and others, perhaps not even alluded to, may have
taken their place. Neither should the reader expect a
comprehensive survey of the entire area, for this is not
meant to be a review in the sense the term is generally
understood by the scientific community. It can and should
be viewed as a broad survey addressed to those interested
in learning about the field, as well as the existing
incentives for pursuing investigations directed toward
either fundamental or technological ends. Not everyone
may necessarily be interested in all sections of this
report. The following outline may help the reader to find
the information he seeks. While the Committee has
assembled a fairly copious set of references, this list is
not meant to be in any sense complete. It is, nevertheless,
hoped that it will suffice to serve as an entry to various

aspects of the literature.

Section II is concerned with the fundamental
ideas, already touched upon here, that underlie the
structure and the thermodynamic properties of glasses.
Such basic concepts as the "ideal" glass, the metastability
of the amorphous state, the parameters such as the glass
temperature which characterize a given material, and the
bonding forces are given detailed attention. These ideas
are of central importance because they lead to an under-
standing of effects, like phase separability and photo-
crystallizatioi. that are unique to the amorphous state.

The third section presents an overview of some
of the basic methods used to prepare amorphous materials
in either film or bulk form. The fourth section deals
with experimental tools that should be useful in charac-
terizing a glass. The delineation of parameters that must
be measured, in order to specify a given sample sufficiently
uniquely that it can be duplicated either at the same
laboratory or elsewhere, is of great importance. Unfor-
tunately, however, amorphous materials as prepared in the
laboratory are sufficiently complicated that it is
impossible to specify a set of such parameters completely
at the present time.

The fifth and longest section of the report is
concerned with the fundamental properties of some of the
extensively studied amorphous semiconductors, the inter-
pretation of these properties in terms of simple physical
models, as well as some of the basic approaches that may
be useful in the development of ab initio theories.

This section, which will be of principal interest to those
engaged in basic research, consists of several parts dealing
respectively with optical, electrical, magnetic, and lattice
properties, physical models, and basic theories. Of these,
the first four emphasize the experimental aspects of the
subject. An attempt is made to appraise the present state
of knowledge in terms of opportunities available for
further research. However, it must be realized that because
many experiments have not yet been done sufficiently
reproducibly on well-characterized samples, such an assess-
ment of opportunities is frequently based cn rather scant
information.

The remaining parts of this report are addressed
to the more device-oriented scientists. Section VI is
concerned with device physics and presents an overview of
the phenomenology used to describe some of the more
familiar applications of amorphous materials, such as the
threshold switch, and the electrical and optical memories.
For completeness, some perspective comments concerning the
electronic applications of oxide glasses are made here.
Section VII attempts to survey the technological setting
in which the amorphous semiconductor technology finds
itself. In particular, it discusses some of the other
available or suggested technologies, whose products perform
functions similar to those seen as promising in amorphous
semiconductor devices. Very few, if any, attempts will be
made to provide a relative assessment since this can be
done meaningfully only with access to proprietary information,
and because it is not the Committee's function to provide
such an appraisal. A broad-brush survey is included here

to present as complete a picture as possible of the
amorphous semiconductor field.

Section VIII contains summary and perspective
statements as well as a variety of recommendations. Some
of these concern further research in various areas, which,
in the opinion of the Committee, might profitably be
pursued in the future. These recommendations should be
viewed in the context of the discussion contained in the
body of the report. Section IX is devoted to literature
references.

II. STRUCTURE AND BONDING IN AMORPHOUS SOLIDS

Macroscopically, the amorphous solid is distin-
guished from the fluid by its high resistance to shear
deformation, i.e., by its relatively high-shear viscosity.
Practically, we consider a body solid (Con 54) when its
shear viscosity, η, exceeds 10^{15} poise though the "glass
temperature," T_g, is taken to be the temperature at which
$\eta = 10^{13}$ poise. It is often found that the time constant,
τ, for changes in molecular configuration within an
amorphous system, scales roughly as the shear viscosity.
According to this scaling law, τ should be of the order of
20 minutes at the glass temperature, and one day at
$\eta = 10^{15}$ poise.

Microscopically, the basic distinction between
solids and fluids might be made in terms of the nature of
the molecular motions (Tu 69b); a substantial fraction of
these motions is translational or "diffusive" in a fluid,
while in a solid, whether amorphous or crystalline, the
motions are almost wholly oscillatory. Thus, in contrast
with the fluid, in the solid there exists a well-defined
set of positions about which the molecules oscillate.
These positions are characterized by translational
symmetry in the crystal, but in an amorphous solid their
pattern is aperiodic. In the crystal, interpositional
changes of molecules occur without alteration of the
position pattern. Such interpositional exchanges do alter
the pattern in an amorphous material near its glass temper-
ature, but it is possible that they would not change the

pattern in the hypothetical "ideal" glass.

It has not been proven theoretically that the state of minimum energy of any substance is crystalline rather than amorphous. However, experiment has shown that nearly all pure substances are more stable in some crystalline than in an amorphous solid form. It has been pointed out (Tu 69b) that this generalization may not hold for some systems that are constrained to be compositionally disordered. However, it follows that to form an amorphous solid, the ordering processes (crystallization in the case of simple pure substances; compositional ordering followed by crystallization for some mixtures) that are favored thermodynamically must somehow be bypassed. This might be accomplished, for example (Tu 69a), by cooling the liquid at a sufficiently rapid rate or by various deposition (vapor, electro, etc.) techniques.

When glass is formed by cooling a liquid, it is often observed (Kau 48) that the heat capacity and thermal expansivity drop sharply in the vicinity of T_g, as defined above. However, the temperature at which these abrupt changes occur is lower for lower cooling rates, and it simply marks the point below which the amorphous system is no longer in internal configurational equilibrium. That this equilibrium is not achieved in the glasses of ordinary experience is to be expected in view of the very large time constants noted earlier for configurational changes at $T < T_g$. Also, it is not likely that amorphous solids formed by the various deposition techniques are in internal

equilibrium. It follows that, at the same temperature and pressure, two amorphous solid specimens with the same compositions may still differ somewhat in internal structure. This behavior is quite analogous to that of a compositionally disordered crystalline alloy at temperatures where the time constant for interpositional exchanges is very long. An amorphous solid, if constrained from crystallizing, would presumably relax after an infinite time to an "ideal" amorphous state of minimum enthalpy and entropy (Gi 58, Coh 60,64). The structural characteristics of ideal glasses are considered later.

If we classify condensed materials according to the type of bonding responsible for their coherence, i.e., covalent, metallic, ionic, van der Waals, or hydrogen, every class contains some members that can be put into the amorphous solid form (Tu 69a). In general, the tendency to amorphous solid formation is greatest in some covalently bonded materials, and least in most ionic and metallically bonded materials.

The problem of whether the structure of amorphous solids is, in general, distinct and unique, or only trivially different from that of a crystalline solid, has persisted for a long while without being resolved definitively. The continuous random models for amorphous structure, of the type developed by Zachariasen (Zac 32), Bernal, and others (Be 59,60a,60b,OW 70a), seem to be uniquely different from crystal structures. At the other extreme, there are the models based on the idea that the amorphous

solid is an assembly of randomly oriented microcrystallites.
For the microcrystallite models to be meaningful, it appears
that the crystallite dimension should equal or exceed two
unit cell dimensions. At this dimension, most of the
material in the system would lie on crystallite boundaries,
and the atomic configurations across these boundaries
would be more important than those within the crystallites
for the over-all description of the amorphous structure
(War 37). Model studies indicate that the atomic config-
urations connecting highly misoriented crystallites are
quite similar to some of the configurations in the contin-
uous random models; for example, pentagonal arrangements
are often seen. This suggests the interesting possibility
that the structure of a microcrystallite assembly might
degenerate to a continuous random structure when the
crystallite size falls below a certain limit.

Dense Random Packing (DRP) of Hard Spheres

The coherence of those amorphous solids, with
which this study is primarily concerned, is due mostly to
covalent bonding, as in amorphous germanium; a mixture of
covalent and van der Waals bonding, as in amorphous
selenium; or a mixture of covalent and ionic bonding, as
in the soda-lime-silicate glasses. However, it may be
instructive to consider first the nature of the Bernal
dense random packed structure (DRP structure) of uniform
hard spheres. This structure has a density about 86
percent that of crystalline close packing. It has been

characterized by the distribution of its Wigner-Seitz
cells (voronoi polyhedra) amongst a small group of ideal
forms from which the actual forms of the cells can be
derived by small distortions. From this standpoint the
structure can be viewed as an admixture of crystallographic
cells and non-crystallographic cells (such as pentagonal
dodecahedra). The unique feature of the structure is these
non-crystallographic elements. When short-range inter-
atomic interactions dominate, as in the condensation of
attracting uniform hard spheres, packing to form tetra-
hedral holes (e.g., rather than octahedral) will be
preferred. This should almost always lead to a randomly
packed structure, an expectation that was confirmed by
Bennett (Ben 70) in a study of computer-generated hard-
sphere structures.

Structure of Covalently Bound Amorphous Systems

In covalently bound systems, the analog of the
DRP structure is the random network type of structure that
was first proposed by Zachariasen (Zac 32). Recent model
studies have shown that these structures can account
remarkably well for the pair distribution functions,
densities, and configurational entropies of tetrahedrally
coordinated amorphous systems. The models are constructed
according to the following general procedure (Eh 70):
(1) the number of nearest neighbors, their average spacing,
and the dispersion of these spacings around the average is
made the same as in the corresponding crystal; (2) a

certain distribution of distortions of the bond angles
from their ideal crystal values is allowed; (3) the surface
density of dangling bonds is kept constant during the
building of the model. In this way an "ideal" amorphous
structure is formed, which can be enlarged indefinitely
without the development of prohibitive strains. It has
been shown (Bel 66,Ev 66) that such a model satisfactorily
accounts for both the pair distribution function (PDF) and
density (97 percent of crystalline) of fused silica with
average distortions of $\pm 15^{\circ}$ (maximum $\pm 30^{\circ}$) from the
average Si-O-Si bond angle taken to be 150°. Bell and
Dean also showed (Bel 68), by considering the options
available in enlarging the model according to the described
procedure, that the configurational entropy should fall
within the range of the observed values (ca.$\frac{1}{2}$ k/molecule) for
the transition from cristobalite to fused silica. The
described rules were used by Polk (Pol 71) to build a
random network structure for the tetrahedrally coordinated
elements (see Fig.1). Average distortions of $\pm 10^{\circ}$
(maximum $\pm 20^{\circ}$) above the ideal tetrahedral bond angle
were allowed. The structure so formed had a density
97 ± 2 percent of that of the crystal, and its PDF is in
excellent agreement with that of amorphous silicon as
determined by Moss and Graczyk (Mos 69). The local config-
urations in random network structures can also be charac-
terized by a small number of ideal forms, in this case
rings, from which the actual forms can be derived by small
distortions. As with the random sphere packing, it is
found that the amorphous structure viewed in this way is
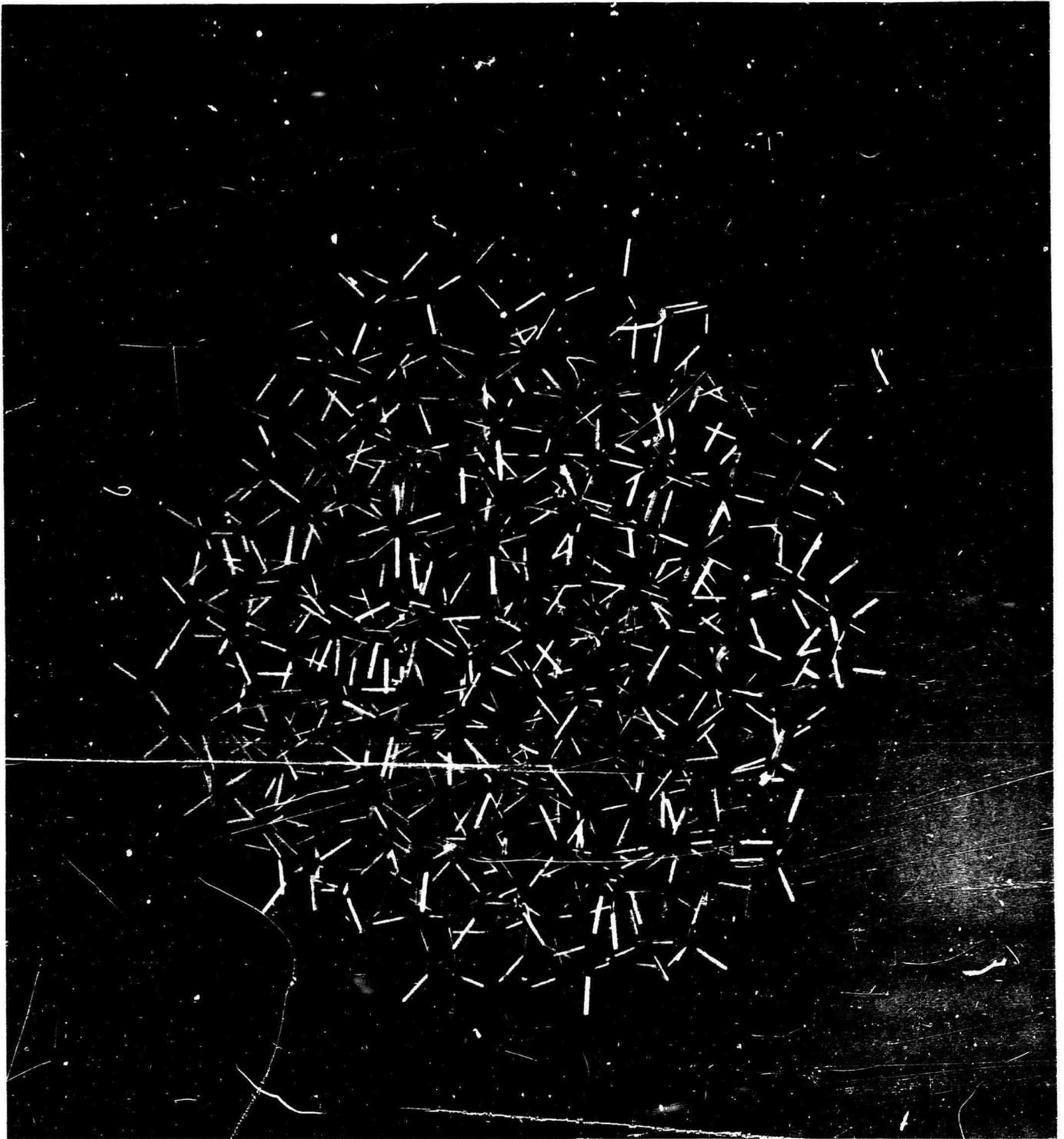
Fig. 1. Random network model for an ideal amorphous
structure of a tetrahedrally coordinated element (Pol 71).

an admixture of non-crystallographic and crystallographic elements; for example, the Polk structure for amorphous Ge and Si can be described as an assembly of 5- and 6-membered rings. Similar structures have been generated recently by computers (Sh 71, Hen 71).

Perhaps the most interesting and significant feature of these random network structures is that, in contrast with the DRP hard sphere structure (density 86 percent that of crystalline close packing), they exhibit densities closely approaching those of the corresponding crystals. If the energies associated with distorting the bond angles are not too large, this means that their energies will be only a little larger than those of the crystals, as is indeed observed. The question of the dependence of energy on bond angle is an important one for the relative stability of amorphous Ge and Si and it merits further investigation.

The random network structures that have been discussed, containing no internal dangling bonds, represent ideal structures, which may be more or less closely approached by actual amorphous structures, and which might be the end states of the thermal relaxation processes discussed above. Depending upon their conditions of formation, the actual structures may contain considerable numbers of internal dangling bonds and voids. Even so, the structure of the greater part of the amorphous body might approximate the ideal according to a "swiss cheese" model (Eh 70).

A somewhat different view of the amorphous
structure of the tetrahedrally coordinated elements had
been proposed by Grigorivici and coworkers (Gr 68,69b).
In this model the 5- and 6-membered rings are little
distorted from their ideal forms and incorporated into the
structure so that only "staggered" and "eclipsed" config-
urations of two connecting tetrahedra appear. This scheme
would appear to minimize any energy due to bond distortions
but it does not permit indefinite enlargement of the
structure without prohibitive strains. The actual structure
would have then to be an assembly of more or less discrete
amorphous clusters or "amorphons" ccntaining a high concen-
tration of dangling bonds. Also, it appears that there
must be a substantial density deficit associated with such
an assembly but this problem seems to have been largely
neglected.

The problem of the inter-domain boundary volume
contribution is also a troubling one in the application of
the microcrystallite models (War 37). It was considered
by Cargill (Car 70) when he tested these models with the
structures of metallic glasses but it appears to have been
largely ignored in the interpretation of covalently bound
glass structures in terms of the model. Cargill showed
that a deficit of 1/4 to 1/3 monolayer at the boundaries
would lead to a very large decrease in bulk density at the
crystallite sizes required to account for the x-ray inter-
ference function.

Experiment suggests that in amorphous semi-conductors generally, as well as in tetrahedrally coordinated systems, the nearest neighbor coordination required by the generally accepted chemical valence, usually as specified by the 8-N rule, is mostly realized. The "ideal" covalent amorphous structure is considered to be one in which every atom is bonded to the proper number of nearest neighbors to satisfy its valence requirements. The definition may also include limits on the permissible deviations of bond lengths and bond angles from their crystalline values. An actual amorphous material will, in general, contain, besides the defects noted earlier, a number of unsatisfied valences.

The group V elements, e.g., As and Sb can crystallize into a 3-coordinated network in which each atom is at the apex of a pyramid formed by the bonds to the three atoms with which it coordinates. These groups are bound together in puckered 2-dimensional layers that are stacked, partly by van der Waals binding, to form the crystal. A random network, which can be a fully connected 3-dimensional one, can be formed from such a 3-coordinated system by distortions of the ideal A-A-A bond angle (about 98° for the arsenic structure). The As_2S_3 and As_2Se_3 amorphous structures might be regarded as having been generated by the insertion of S or Se atoms between each As-As closest pair of the amorphous As structure. The SiO_2 and Si amorphous structures may be related similarly.

In 2-coordinated systems, such as Se and Te, an amorphous structure can be formed without any bond distortions by rotation of neighboring chain segments randomly relative to each other. In this way, a long chain takes the form of a random coil. In an actual system, these coils will interpenetrate and there will be strong van der Waals interactions between neighboring segments of a coil. It is now believed (Lu 69) that in addition to coils, amorphous Se contains quite a large admixture of rings, primarily 8-membered, which are bound into the structure by van der Waals forces, and possibly by interlocking with coils.

Mott (Mo 67b) suggested that in amorphous semiconductor solutions, in contrast with crystalline solutions, the chemical valence of each constituent atom is everywhere satisfied. This view seems to be supported by most of the experimental evidence. In glasses formed by slow cooling of melts, there probably is enough time for the achievement of this chemical valence satisfaction when it is energetically preferred. However, as Mott noted, this ideal chemical bonding might not be fully realized under some conditions of amorphous solid formation by vapor quenching. Strong evidence for the attainment of local valence satisfaction by covalent bonding was obtained for the Te-Ge amorphous system by Bienenstock and coworkers (Bi 70). In the Te rich alloys, the tetrahedral coordination of the Ge results in the cross-linking of the Te chains into an amorphous 3-dimensional network.

Phase Separation and Crystallization of Amorphous Systems

To this point we have considered only the forma-
tion and structure of a single amorphous solid phase. As
we noted, such a phase is not the thermodynamically most
stable one and so it may evolve in a variety of ways into
a thermodynamically more stable polyphase system. A complete
characterization of the structure then requires information
about the spatial distribution of the several phases, as
well as of the molecular configuration within each phase.
To discuss this characterization, it will be helpful to
define the various temperatures that are pertinent in the
structural evolution. The glass temperature, T_g, has
already been defined. The thermodynamic crystallization
temperature, T_{tc} (often designated T_m), is the temperature
at which the liquid coexists in equilibrium with one or
more crystalline phases; it lies well above T_g. Liquids
containing two or more components often are prone to
separate into two liquid phases. The temperature at which
phase separation becomes thermodynamically possible at a
given composition will be denoted by T_{tp}. Often liquid
immiscibility gaps open only in the temperature range where
the liquid would be undercooled; i.e., T_{tp} falls well below
T_{tc} for many liquids.

The isothermal time constants for both crystal
growth and phase separation in covalently bound systems
are usually found to scale roughly as the shear viscosity
(Tu 69a). Consequently, the rate of structural evolution
in an amorphous system usually becomes very sluggish and

often imperceptible at temperatures below T_g. Crystalliza-
tion of amorphous phases may, under certain conditions,
occur fairly rapidly at temperatures between T_g and T_{tc}.
Sometimes a term, kinetic crystallization temperature, T_{kc},
is used to denote the temperature at which the crystalliza-
tion rate becomes very rapid. However, this term can be
quite misleading since the crystallization rate depends
critically on the seed (nucleation center) density and may
be substantial over a considerable temperature range (Tu 69a).
It is probable that most covalent amorphous solids,
especially films on substrates, already contain a consid-
erable density of nucleation centers so that their crystal-
lization may be governed primarily by the crystal growth
rate, u. This rate is generally described as the product
of two factors, $u = f_1(\Delta T) \; f_2(T)$; one, $f_1(\Delta T)$, is a
thermodynamic factor which increases at a moderate rate
with the undercooling $(T_{tc} - T = \Delta T)$, and $f_2(T)$ is a
kinetic factor which decreases sharply with decreasing
temperature, T (Tu 69a). In covalently bound systems, the
possibility exists that the kinetic factor in crystal
growth can be sharply increased by extraneous effects such
as trace impurities (Tu 58) or photon absorption, which
might lead to the breaking of covalent bonds. Such effects
seem fairly well documented in the crystallization of
amorphous selenium. For example, halogen additions
markedly reduce the viscosity of liquid selenium and
increase the crystal growth rate (Ke 67), presumably by
breaking bonds and thus reducing the length of the selenium
chains. Also, Dresner and Stringfellow (Dr 68) have

demonstrated a marked photoenhancement of the crystal growth rate in amorphous selenium. More recently, Feinleib, et al (Fe 71), have reported a marked photoenhancement of the crystallization rate of Te-Ge based glasses.

As we have noted, a liquid consisting of two or more chemical components often has a very strong thermo-dynamic tendency to separate into two liquid phases when it is undercooled to the vicinity of its glass temperature. The reason for this is that T_g is quite low, relative to the coherence energy of the system, so that there is little entropic stabilization of the glass solution. Further, most glass compositions will not correspond to any of those most favored energetically (Morr -). These are likely to be the pure components or a pair of ordered solutions, each with some simple stoichiometric ratio (e.g., As_2Se_3 or $GeTe_2$). From this point of view, as was shown by Morral and Cahn (Morr -), the thermodynamic tendency toward some kind of phase separation will be greater the more compon-ents there are in the solution. Further, the interfacial tension between two amorphous phases is relatively small and it vanishes altogether at the consolute (critical solution) temperature (Ca 68). Consequently, at wide departures from equilibrium, phase separation in amorphous solutions can occur on a very fine spatial scale; e.g., a few tens of angstroms. Since the distances over which diffusion must occur are so very small, phase separation is very rapid and difficult to suppress even when the viscosity of the system is as high as, for example, 10^6 to 10^7 poise. However, at this viscosity the phase

separated structure, once formed, is likely to persist
(i.e., gravity segregation of the separated phases will be
very slow) when the system is cooled into the glass state.
This means that there is a high probability that any
multicomponent glass formed by cooling its melt will be
separated into two phases, often interdispersed on a very
fine spatial scale. Indeed, this phase separability
characteristic is, perhaps, one of the most unique and
valuable properties of multicomponent glass-forming systems.
It can be and has been exploited to achieve phase inter-
dispersion with much smaller periods than is possible by
other methods. Further, it often happens that one of the
liquid phases separating in this process can crystallize
very rapidly because it is more fluid and/or more under-
cooled than the parent liquid (Mau 64). This leads to a
body in which one of the interdispersed phases is crystal-
line. When phase separation occurs by a spinodal mechanism
(i.e., by amplification of periodic composition fluctuations)
(Ca 68,Hil 68), the two phases will be initially inter-
connected (Ca 65). Phase interconnectivity also can be
established, following a nucleation and growth-phase
separation, Ly a coalescence process (Hal 65,Se 68). The
sequence of processes considered here may be summarized
as follows:

Homogeneous viscous liquid $\xrightarrow[\text{phase separation}]{T < T_{tp}}$ $\begin{matrix} \text{A liquid} \\ + \\ \text{B liquid} \end{matrix} \twoheadrightarrow \begin{matrix} \text{A glass} \\ + \\ \text{B crystal} \end{matrix}$

The rate of phase separation increases quite rapidly as $T-T_{tp}$ increases. If one of the phases is easily crystallizable, it may appear that the initial kinetic crystallization temperature is almost indistinguishable from that at which phase separation occurs.

III.   PREPARATION

The basic goal in preparing amorphous materials
is to freeze them into a metastable state characterized
by the absence of long-range order. This can be accomplished
by a large number of methods that can be grouped into two
basic categories. One is to introduce disorder by thermal
methods, then to quench from the liquid or vapor to below
T_g sufficiently rapidly to prevent the achievement of
internal configurational equilibrium. The other is to
create the disorder in a solid below the temperature at
which it can regain long-range order in the time scale ot
the experiment. Different methods may or may not give
equivalent films for a variety of reasons which are often
difficult to determine.

While the causes of non-reproducibility among
samples may be determined by application of the character-
ization techniques discussed in the next section, it is
during the preparation steps that it is created and the
possibility of control exists. Although glasses may
approach an "ideal" metastable non-crystalline state
(Sec. II), they can be quenched into many other metastable
states making structure and properties preparation depen-
dent. Control over composition and purity is also poorer
than with crystalline materials since the potential for
impurity rejection or leveling during crystal growth is
lost.

The glasses of interest here represent a broad

range of preparative challenges. Se and the As-Se glasses are easy to form by quenching and have been prepared from the melt and vapor. Experimental evidence indicates that the quenched glasses retain the local coordination of the liquid, which, in turn, is closely related to the molecular structures of the crystalline forms (My 67). Ge has not been quenched from the melt. X-ray studies (Kr 69) (Br 71b) show the glass structure to be closely related to the crystalline form in contrast to the liquid which has very low viscosity and shows metallic conduction. Amorphous Ge has been prepared by (Br 71b) evaporation, sputtering, glow discharge, electrolysis, ion implantation, transformation of a high-pressure-crystalline polymorph (Bu 71), and phase separation from a Ge-GeO$_2$ solution (deN 71). While a-Ge films prepared by various techniques appear to be structurally similar, their properties vary widely.

Quenching

The most common preparative method is quenching from the melt or vapor. Melt quenching rates extend from $\sim 10^{-2}$ °C/second in an annealing furnace, to $10^3 - 10^4$ °C/second in strip furnaces, to $10^5 - 10^7$ °C/second by the more complex splat cooling techniques (Sa 68). Vapor quenching rates overlap the high end of this range and rates as high as 10^{15} °C/second have been reported (No 69). The choice of method is usually dictated by the material of interest since the faster quench rates are achieved at greater experimental complexity and cost. The number of nucleii and crystal growth rate determine the minimum required quench rate (Tu 69a).

1. Vapor Deposition

Vapor deposition is the most commonly used
technique for materials considered in this report. A
number of special techniques have been developed and will
be mentioned here in the context of advantages or disad-
vantages in the preparation of amorphous semiconductors.
Numerous reviews on thin-film preparation are available
for further information on specific systems, techniques,
and materials (Ch 69) (Mai 70).

All vacuum deposition systems consist of several
basic elements, a vacuum chamber, a source of the material
to be deposited, a substrate and associated fixturing. A
most significant factor is the amount and nature of contam-
inants, including the ever present atmospheric gases,
available for incorporation into the material of interest.
All pumping systems except cryosorption contribute some
foreign material, e.g., hydrocarbons, Ti, and Hg. Fortunately,
mercury pumps are rarely if ever used in this application
since some materials, such as Se, are excellent getters
for Hg vapor. In addition, systems vary in their pumping
speed for various atmospheric gases, in effect concentrating
certain species. The surface of the film being deposited
is exposed to sufficient background gases to condense $\sim$ 4
monolayers per second at 10^{-5} Torr and at 10^{-9} Torr
$\sim$ 4 x 10^{-4} monolayers/sec. What, if any, material is
incorporated, how it is incorporated and its effect must
be individually considered. It is frequently noted that
it becomes more difficult to quench an amorphous film at

higher vacuums indicating a stabilizing effect of impurity incorporation.

The substrate temperature during sample preparation is a particularly important parameter. Too low a temperature results in low-density films with poor adhesion. At higher temperatures there may be sufficient mobility only to allow complete replication of the substrate, while slightly above this there is sufficient flow to provide very smooth surfaces and higher densities. At still higher temperatures, crystallization begins and the ability to quench an amorphous phase is lost. Since physical and molecular structure can be affected by quench rate and annealing, other measured properties may vary with substrate temperature at preparation.

The classical method of providing a vapor of the desired material at the substrate is evaporation. The sophistication comes in the choice of heating methods. Simple resistance or RF induction heating of a source is appealing because of its simplicity, but introduces problems of contamination and fractional distillation (Ef 69) in multicomponent materials. The first problem can be minimized by proper choice of crucible material or eliminated by using the material as its own crucible. The most common method for this is electron bombardment where a focused electron beam causes evaporation from a small heated region on the surface of a larger piece of the material of interest. Such localized heating can also be accomplished by energy absorbed from a laser source which

is physically located outside the vacuum chamber. If the
source material is sufficiently electrically conducting,
exploding wire and arc methods are also possible although
more commonly used for metals and refractory materials.
These methods all subject the evaporating material to high
energies and high local temperatures, which may produce
different vapor species then simple thermal sources.

The problem of fractional distillation is
commonly circumvented by coevaporation or flash evaporation
techniques. In coevaporation, different components are
fed into the vapor stream from separate sources. Stoichi-
ometry is controlled by the temperature or surface area of
each source. Feedback control of deposition rate by source
temperature is possible, but independent source calibrations
may not be valid due to vapor phase reactions and different
accommodation coefficients of the actual film. While
uniform distribution of the major components can be achieved,
impurities may still fractionally distill from each source
resulting in their concentration at one or both film
surfaces.

In flash evaporation, material is continuously
fed into a source at a rate slow enough to prevent the
buildup of a pool of molten material so that the instan-
taneous average composition of the vapor is that of the
feed material. This method is slow, inefficient, and
usually results in films with numerous defects due to
spatter of solid and liquid material from the source. A
variation uses continuous feed to a pool of molten material

with the rate controlled so that the vapor is of constant composition, although different from that of the feed material.

The source temperature controls the evaporation rate and may affect the vapor species and, by means of radiant heating, the film temperature. The condensation rate is also dependent on the evaporation rate but subject to some independent control through substrate temperature. Film properties may be affected by the deposition rate in several ways. Fast deposition favors low-density films since there may be insufficient time for surface mobility processes, while slow deposition allows more time for reaction with and incorporation of residual gas species present in the vacuum chamber.

Sputtering is another method that can avoid fractionation effects and is finding ever wider application, including commercial use at ECD (Nea 70b). The surface of the material to be deposited is the target of bombardment by energetic ions which sputter target material free to be collected on the substrate. The ions can be inert, Ar being the most popular, or reactive where the desired deposit is a compound of the target material, and a second component such as O or S is introduced with the sputtering gas.

The basic characteristics that make sputtering attractive are many. A clean substrate can be prepared by using it as a target and sputtering away surface contaminants before deposition. The sputtered species are

themselves highly energetic and provide dense and highly adherent films, providing the target is maintained at a sufficiently low temperature to prevent sublimation processes. Uniform film composition matching that of a multicomponent material target is the rule rather than the exception, although target bulk diffusion, decomposition, surface reaction, or widely varying sticking coefficients on the substrate, can cause problems. Large areas of uniform thickness can be prepared with high efficiency, although there may be problems with target preparation. Targets should have an area about twice that of the film desired. The deposition rate is easily kept constant and can be controlled by gas pressures and accelerating voltage.

The method is, of course, not without disadvantages. The sputtering gas provides an additional potential film contaminant as well as a contaminant carrier. Although avoiding the localized intense heating of a thermal source, the plasma discharge heats large areas with resultant outgassing. The high-energy species lead to new contaminants through reaction with other parts of the system and cracking of hydrocarbons. Deposition rates are slow compared to thermal methods. The additional cost and complexity of the system may also be a factor.

Many variants of the basic process have been developed. The substrate can be DC or asymmetrically AC-biased to provide some bombardment cleaning of absorbed gases, which would otherwise be trapped at an obvious loss in efficiency. The systems normally operate at 20-100m

Torr to sustain a discharge. Cleaner films can be obtained by sputtering at lower pressures using a magnetic field to increase ionization efficiency, an auxiliary source of electrons or ions, radio frequency excitation, or a combination of these. Reasonable deposition rates at pressures as low as 10^{-4} Torr are possible. RF sputtering also provides the cleanest method of removing the surface charge from an insulating target making sputtering of insulators possible and significantly increasing the rate for low conductivity materials. Even under optimum conditions, sputtering is a relatively slow process. Rates are generally less than 10 Å/sec. compared to 10-1,000 Å/sec. for thermal sources.

Chemical vapor methods requiring heat, such as vapor phase pyrolysis or highly exothermic reactions, may not be suitable because unavoidable heating of the substrate and depositing film results in crystalline deposits. Thermal pyrolysis of silane above 800°C is used to grow epitaxial crystalline films of Si. Vapor phase decomposition of silane in a glow discharge occurs at low temperatures and, although slow, results in a-Si films reported to have dramatically different electrical properties from those prepared by other methods (Br 71b).

2. Liquid Quenching

For ready glass formers, the techniques of melt quenching are relatively straightforward and well documented in the oxide glass literature. Large samples of As-Se, Ge-As-Se, Ge-Sb-Se (Ta 71) and other glasses of excellent

optical quality are commercially available. Important
precautions include assuring complete reaction and
chemical homogeneity of multicomponent glasses, vacuum
outgassing, and preventing high-temperature reaction with
crucibles, ampul materials, and ambient atmospheres.
Sample mass and geometry, heat capacity, and thermal con-
ductivity control the achievable quench rate. The basic
parameters involved and methods of predicting required
quench rates have been studied but will not be further
discussed here (Sa 68) (Tu 69d). However, when reporting
quenchability of a glass, actual cooling rates or data
defining sample mass, surface area, etc., should be reported
since the ease of quenching and, therefore, definition of
glass-forming compositions is sample dependent.

Splat cooling (Du 70) is less frequently used
since it often produces samples that are strained and of
an unsuitable geometry and perfection for most measurements.

Other Methods

Solids can be transformed to a disordered state
in a solid-state reaction with the energy provided by
radiation (neutron, α particles, etc.), shear, or chemical
reaction in processes often referred to as amorphization
(Ro 70). The chemical reaction need not be completely
solid state; in fact, reaction with, or evolution of, a
vapor in an oxidation, reduction, or disproportionation
reaction is often involved.

A variety of other chemical methods are also

used to prepare glasses. In addition to the vapor and vapor-solid reactions previously mentioned, there are numerous solution processes such as electroplating, electroless plating, anodization, and polymerization. In general, films prepared by chemical processes are subject to wide property variations due to trapped impurities, poor stoichiometry control, and inhomogeneities resulting from incomplete reactions.

Sample Environment

In addition to the preparation of the amorphous layer, one must consider the total sample including substrate, electrodes, and free surfaces.

The choice of a substrate is generally determined by the measurement to be made but must be consistent with a set of secondary restraints. Matching thermal expansion coefficients is important, especially if measurements are to be made as a function of temperature or if deposition is at a temperature far from ambient. Glasses are brittle below T_g and will crack easily, especially under tension. Sample flow may also occur during measurements above T_g resulting in lack of reproducibility due only to a new film thickness.

A second consideration is chemical reactivity. Reaction of the depositing vapor or liquid with the substrate or adsorbed films, or slower diffusional processes, can result in alloy or compound formation. In addition, gas diffusion through the sample and reaction with the electrode is possible. If electrical measurements are to

be made, the electrodes, including the substrate if it serves as an electrode, may be chosen for their blocking or injecting characteristics. Chemical reactions with the layer or diffusing gases may result in an electrode with entirely unexpected behavior (Ut 71). It has recently been suggested (Br 71a) that only noneutectic forming metals should be used for electrodes and that much earlier data need reexamination. The substrate can also serve as a source of nucleation sites for crystal growth in the sample.

Chemical reaction of a free surface with the ambient atmosphere is another possibility. The surfaces of As-Se films have been shown (Tr 69) to oxidize in air at room temperature yielding crystalline As_2O_3 and a surface glass layer rich in Se.

One must never forget that these materials are in a metastable state with respect to a crystalline or phase separated form. Transformations may occur slowly but continuously without external stimulation, or more rapidly when external influences are present. The crystallization of Se in the presence of light (Dr 68) or water vapor (Chi 67) is one example. Many problems can be avoided by storing samples at low temperatures, in the dark and in an inert atmosphere. Encapsulation may be considered where practical.

IV.   CHARACTERIZATION

The importance of materials characterization has
been recently addressed in the report of the MAB Committee
on Characterization of Materials (MAB 67). It states,

> Clearly, much of solid-state research
> is concerned with th. effort to under-
> stand properties, in terms of a particular
> composition and structure, but it cannot
> be emphasized too strongly that a substantial
> fraction of this effort is of marginal value
> because it is carried on without a clear
> understanding of the true nature of, and
> need for, characterization, and it fails
> to distinguish between property studies on
> characterized and uncharacterized materials.

One has only to leaf through a collection of current
papers in the field of amorphous semiconductors to be con-
vinced that the problem exists here. While a majority
of the experimental papers give some preparative information,
few report any attempt at characterization outside the
specific measurement to which the paper is addressed, and
certainly none to the standards proposed in the MAB
report. It is characteristic of the field that in approxi-
mately 2000 pages (Ch 69, Mai 70) reviewing the preparation
and properties of thin film less than 40 are devoted to
struc.are and composition, and nearly half of these discuss
diffraction techniques not generally applicable to amorphous
films.

This lack of attention is not surprising for
several reasons. Materials ch.racterization is difficult,
time-consuming, and expensive. Existing characterization

tools and sampling techniques may not be directly applicable
and, in some cases, new tools may have to be developed.
Much work in this field is carried out presently by individ-
ual investigators in academic laboratories while an in-
dustrial scientist in a more established field may have
the direct support of as many as 2-3 other workers in
materials proparation and characterization.

The MAB Committee evolved as a working defini-
tion (MAB 67):

> Characterization describes those features
> of the composition and structure (including
> defects) of a material that are significant
> for a particular preparation, study of
> properties, or use, and suffice for the
> reproduction of the material.

A particularly important fact is that major attention to
amorphous semiconductors is recent and consequently it is
usually unknown what compositional and structural features
directly and unambiguously define a material. While it
would be of great value for this report to specify a mini-
mum characterization to insure reproducibility, this is
not yet possible except in a limited way for a few specific
materials. Certainly any characterization must address
the three important questions of chemical composition,
whether or not the specimen is truly and completely
amorphous, and whether or not there are multiple phases
present. In the latter case their composition and distribu-
tion must be specified. In addition, while glasses may
approach an "ideal" metastable noncrystalline state, they
can be quenched into many other metastable states which
may be changed by annealing. Measurement of the true bulk

density or the heat capacity over a very limited temperature range can serve to characterize a sample without altering it. Measurement of thermal characteristics over a wide temperature range by, for example, differential thermal analysis (DTA) or scanning calorimetry (Mu 70) can yield significant further information but may be a destructive test causing crystallization, phase separation or allowing the sample to relax to a new state. These are relativcly easy, but important, measurements and provide necessary data to test structure models.

The practical question of what must be specified to insure reproducibility deserves comparable attention to the more fundamental determinations of composition and structure. An example of evolving property-structure-cómposition relationships is provided by the current controversy over the properties of a-Ge and Si. A large part of the early nonreproducibility is now attributed to differences in deposition temperature or post deposition annealing. A model has evolved (Br 71b), largely from radial distribution functions, small angle x-ray scattering, density and ESR data, which incorporates small voids into an otherwise dense amorphous matrix. The effect of voids on electrical and optical properties is modified by annealing. It is not yet clear just how annealing influences the voids since the gross film density does not change (Th 71). While further structural studies are conceived and contemplated to understand these effects, other experiments can be carried out and reproduced by carefully controlling and reporting deposition conditions and subsequent annealing.

The remainder of this section will concentrate on composition and structure, tools available for their measurement, and some specific problems associated with the amorphous semiconducting materials.

Composition

Although questions concerning molecular species, valence states and clustering might be considered compositional, they will be discussed in the part devoted to structure below. The principal concern here is chemical purity and stoichiometry.

In the literature, the question of sample purity is often ignored, or dismissed with a statement concerning the use of 5-9's or 6-9's pure elements. This may in part be due to the widespread belief that amorphous materials are impurity insensitive. In some instances there is good evidence to support this belief. There are also many reports of the dramatic effects of a few parts per million (ppm) to a few percent of impurities, for example the electrical effects of S, Te, As, Cl, Tl, Bi, Ge (Sc 70), and O (La 70) in Se, the optical effects of O in Se (La 70), As-Se (Va 70), As_2Se_3 and GeAsTe (Sav 65), SiAsTe (Hi 66), Ge (Ta 71) and GeSe (Va 70), the physical effects (e.g., T_g, microhardness) of I and Ge on As_2Se_3 (Ko 62), and modification of the crystallization rate of Se by Sb and Te (Dz 67), to list a representative few.

Use of the designation 6-9's purity may also be misleading since for most elements it is of questionable validity. To extablish that a material contains less than

1 ppm total impurities requires analysis for about 100
elements to a sensitivity and accuracy of less than 10 ppb
each. The technique most commonly used is emission
spectroscopy which can detect approximately 70 elements
with a sensitivity of the order of 1-10 ppm. Even if
materials of this purity are obtainable, maintaining this
level through sample fabrication is also demanding and not
generally addressed unless proven necessary.

Elements common to the amorphous semiconductors
considered in this report range from Ge and Si which can
be purified to these high levels, to Se which is relatively
impure. Selenium purification processes are limited by an
inability to zone refine, ease of compound formation includ-
ing organoseleniums, and the ease of generation and extreme
toxicity of H_2Se. In addition fractional distillation
during thin film preparation and slow diffusion during melt
quenching may result in local concentrations of these im-
purities, especially at surfaces, where their concentration
is sufficient to affect property measurements but too low
on average to be detected by conventional chemical analyses.

The importance of chemical analysis cannot be
overstated. Experimenters interested in preparation or
property measurement should be aware of the actual purity
range of the starting materials, the importance of impurity
effects in related materials or measurements and the avail-
able analytical tools which might give meaningful informa-
tion. Little can be said here about the actual methods.
Chemical analysis is an active field with methods ranging
from older established wet chemistry through ever more

rapid and reliable instrumental techniques. Reviews of methods, their precision and sensitivity, and unique features are available. For example, the state of the art is reviewed biennially (even years) in a special issue of Analytical Chemistry (AC 70). In general the application to amorphous semiconductors is straightforward. If the glass is easily melt quenched, large samples can be available for analysis. In the case of thin films or splat quenched glasses only a few milligrams may be available and simple compositional analysis takes on the complexity of a trace element determination in macro samples. Such samples also have very high surface areas and bulk analyses may be difficult due to the large influence of surface contamination.

The determination of compositional gradients on a micron or submicron scale, for example, those resulting from distillation effects in thin-film preparation by vacuum evaporation (Ef 69), or local inhomogeneities due to phase separation, also challenge the state of the art. Recent developments such as the electron probe microanalyzer (microprobe) (Cam 70), ion microprobe massanalyzer (IMMA) (Evan 70), microfocus x-ray (milliprobe) (Cam 70), and Auger spectroscopy (Harr 68) are having a major impact and hold considerable promise for the future.

Structure

Structure, as defined here, ranges in scale from macroscopic defects (e.g., cracks and bubbles) which are important if experimental data is to be meaningful to atomic bonding and molecular structure which are more

important for theoretical understanding and modeling.
Phenomena such as crystallization and phase separation can
span the range from visible to the unaided eye to the
Angstroms limit of the most powerful microscopes available.
Obviously no single tool can be recommended for all
characterizations.

1.   Macroscopic (≥ 10Å)

Optical microscopy (Coc 70) remains a primary
tool. Gross defects such as bubbles, cracks, foreign
inclusions, surface contamination and reaction products,
as well as crystallization and phase separation down to
about 1μ can often be easily identified. For other than
very thin films or surface effects an infrared microscope
is required for many materials (Va 68). The scanning
electron microscope (Fish 70) overlaps optical microscopy
and extends its range down to less than 100Å. Using the
standard secondary electron mode, surface defects can be
studied throughout this range. Other modes of operation,
such as conduction, backscattering and cathodoluminescence
can give additional information on surface and/or bulk
properties (Fe 71). Density is another measurement sensitive
to the presence of voids or inclusions, and is capable of
quite high sensitivity. It cannot alone, however, describe
the nature or size of the inhomogeneity.

Phase separation may involve a crystalline phase
of the same or different composition or a second amorphous
phase of different composition. The former is usually
determined by x-ray (Pf 70) or transmission electron
diffraction (Fish 70). Reflection electron diffraction can

reveal the presence of a crystalline phase on the surface typical of the bulk or possibly due to a reaction product such as an oxide. Selected area diffraction, taking advantage of a focused x-ray or electron beam, may offer further sensitivity advantages. These techniques not only establish the presence of a crystalline phase but can generally give positive identification as well. As the size of the individual crystallites decreases and/or strain increases, the diffraction peaks spread. In the 20-50°. region, interpretation is controversial.

The presence of two or more amorphous phases may be detected by optical or electron microscopy. The advent of high energy electron microscopes (MeV) makes transmission electron microscopy applicable to thicker films without requiring sample thinning procedures which may themselves affect the structure. However, identification of the phases is generally accomplished through high resolution x-ray fluorescence. Current electron probe microanalysers (Cam 70) can do quantitative chemical analysis, for all elements with atomic number 5 or greater, on a micron scale. The scanning electro microscope can also be equipped for x-ray analysis and offers somewhat higher resolution. Auger spectroscopy (Harr 68) offers high sensitivity for the light elements. Small angle x-ray scattering is a technique, frequently applied to polymers, which can detect repeat distances of 10-10,000 Angstroms and thus can characterize phase separations with domains in this size region. If the two phases differ significantly in other properties such as conductivity, optical absorption or

reflectivity, dielectric constant or loss, etc., then detection and identification may be accomplished more readily or with greater sensitivity by methods based on such a property.

2. Microscopic ($\leq 10\overset{\circ}{A}$)

The greatest handicap to structural characteriza-tion of amorphous materials is that the absence of long-range order precludes complete structure determination by standard x-ray, electron and neutron diffraction methods. The scattering which is observed can be used to determine a radial distribution function (RDF) from which the number and distance of at least the first and second nearest neighbors of an average atom can be determined. Recently Mozzi and Warren succeeded in greatly improving the resolu-tion of the x-ray method by using procedures which minimized the Compton modified scattering (Moz 69,70). Even if the RDF calculated for a model structure matches the experimental RDF, there is still no guarantee that the model structure is unique. At least a dozen studies of a-Se can be found in the literature. Using similar experimental data, nearly half that number of different structures including 2 and 3 dimensional chains, 8-500 atom rings, 6 atom packets and combinations of these have been proposed (Gr 69a, Bre 69). Similarly, proposals have been made to the effect that the structural units of a-Si involve distorted tetrahedra, pentagonal dodecahedra, or diamond-like microcrystallites (Mos 69). a-Se is found to have 2 neighbors at $2.34\overset{\circ}{A}$ and 8 at $3.72\overset{\circ}{A}$ identical to both trigonal and monoclinic Se, and a-Si 4 at 2.35 and 12 at 3.86 again identical to the

crystal form. Therefore, one must depend on data at larger
interatomic distances where resolution is poor due to the
overlap of many peaks and is also subject to large experi-
mental errors. In the case of a glass with two or more
elements of significantly different scattering power, for
example,GeTe, it is possible to gain additional information
with respect to a preference for Ge-Ge, Ge-Te or Te-Te
bonding (Bi 70) In general, however, it is safer at
present to complement RDF data with information from other
experimental techniques to choo\. among possible structures.

Additional information about nearest neighbors
can be obtained by any effect characteristic of the chemical
bond involved. Principal among these are the various forms
of optical spectroscopy (Cr 70) There is often sufficient
carry-over of spectral features from the crystalline form
or forms to permit the formulation of convincing arguments.
IR has been used (Lu 69)to determine the presence of both
ring and chain molecules in a-Se corresponding to the mono-
clinic and trigonal crystal forms respectively. Raman
spectra of As-S glasses (In 69) have shown the presence of
S-S and As-S bonds in both the molecular forms found in
Realgar (As_4S_4) and Orpiment (As_2S_3). Electron (He 70) and
x-ray spectroscopy (Cam 70) are capable of describing the
atomic bonding of the elements present and can also be
useful in these determinations.

Localized unpaired electrons can be detected by,
for example, ESR (Kon 70) or static susceptibility (Ta 70b)
measurements (Mul 70) and may provide useful information.
NMR (Ese 70) can also describe the environment of atoms of

those elements for which probes are available (e.g., As^{75}, $Sb^{121,123}$, Bi^{209}, Cl^{35}, Se^{77}) (Pe 68).

The question of molecular species, particularly macromolecules, has been addressed by numerous indirect measurements. While these are not usually considered as part of the characterization procedure, property measurements have been shown to be directly related. The presence of Se_8 rings and Se_n chains can be demonstrated using IR spectra. Their relative abundance and the average chain molecular size have been determined by differential solubility (Bri 29), viscosity vs. halogen concentration (Ke 67), magnetic susceptibility (Ma 64) and Raman spectroscopy (Wa 69). In some binary systems, structural arguments can be developed from thermodynamic (My 67), viscosity (Ne 63), elastic constants (De 69), microhardness (Ko 62), solubility (Bo 69) magnetic susceptibility (Ci 70), and other measurements (Ts 71), made as a function of composition.

The specific use of a material may also suggest further characterization tools such as Schlieren techniques (Va 68) to detect local compositional variation in optical windows and electron beam current measurements to detect local electrical inhomogeneities in vidicon applications.

At the present, it is likely that optimum application of these techniques will still result in a less certain characterization than for comparable crystalline materials (Ka 70). This emphasizes the initial admonition quoted from the MAB report which was largely addressed to

crystalline substances. More rapid progress in under-
standing the properties of amorphous semiconductors is
possible if these characterization methods are intelligently
applied, new tools are constantly sought, and the importance
of the relation and sensitivity of properties to structure
and composition is widely acknowledged.

V. FUNDAMENTAL PROPERTIES OF AMORPHOUS SEMICONDUCTORS

General Concepts

Because the understanding of amorphous semi-
conductors is strongly influenced by the body of knowledge
concerning crystalline systems, it is appropriate to
review first some of the key features of the electronic
states in crystalline semiconductors (Kit 66,Zi 64).

1. A perfect crystalline semiconductor at 0°K has
an empty conduction band of states, separated by an energy
gap from a filled valence band. The states in the two
bands may be regarded roughly as derived from antibonding
and bonding orbitals respectively, but the states are
much more free-electron-like than is implied by a tight-
binding description.

2. In a pure, non-vibrating crystal, and in the
one-electron approximation, the wave functions in the two
bands may be written in the Bloch form, i.e., as the
product of a plane wave of definite wavevector, $\vec{k}$, and a
function having the periodicity of the lattice.

3. In any real crystal there will be defects (e.g.,
impurities, vacancies, interstitials, dislocations), which
scatter the Bloch waves, so that the wavevector, $\vec{k}$, is
only an approximate quantum number characterizing the
states. Scattering is also produced by phonons, and at
high energies or finite temperatures, by electron-electron
interactions. In addition, defects can give rise to
states within the energy gap of the perfect crystal.

4.   At low temperatures, the Fermi level of a perfect
semiconductor lies halfway between the bottom of the con-
duction band and the top of the valence band. The number
of charged carriers (electrons in the conduction band and
holes in the valence band), and hence the electrical
conductivity at low temperatures, is proportional to
$e^{-E_a/kT}$, where the activation energy, E_a, is one half the
energy gap, E_g. This form for the conductivity is called
the "intrinsic" conductivity of the material. In any real
material, however, at sufficiently low temperatures, the
very small intrinsic conductivity will be dominated by the
contribution of carriers associated with impurities or
other defects, which give rise to states in the gap, and
generally cause the Fermi level to be closer to one or the
other side of the energy gap. The conductivity then
depends strongly on the number and kind of defects present,
and is called "extrinsic." In general, the more imperfect
the material, the larger the value of the extrinsic conduc-
tivity, and the larger the temperature range over which
the extrinsic conductivity is seen.

5.   The principal optical absorption band in a
crystalline semiconductor is associated with transitions
of an electron from a state in the valence band to a state
in the conduction band having the same wavevector as the
initial state. The fundamental optical absorption edge
occurs at the gap energy, E_g. For crystals where the
lowest state in the conduction band occurs at a different
point in the Brillouin zone than the top of the valence

band, optical absorption near the fundamental edge requires the aid of a phonon or crystal defect to conserve wave-vector. In a real crystal, absorption well below the threshold, E_g, can occur because of transitions from a filled defect level inside the energy gap to the bottom of the conduction band, from the top of the valence band to an empty defect level, or from one defect level to another. In a crystal with a small density of defects, one would see a number of sharp thresholds in the absorption, corresponding to transitions between the isolated defect levels and the edge of the conduction or valence band. In a crystal with a large density of defects, or many kinds of defects, one would find only a relatively featureless tail in the optical absorption below the fundamental edge. An absorption tail below the fundamental edge can also result from interaction of the electronic states with lattice distortions (phonons). The position of the funda-mental absorption edge is also lowered somewhat by the electron-electron interaction, which leads to a series of electron-hole bound states (excitons) just below the continuum of states beginning at E_g.

Many features of the crystalline semiconductor persist in the amorphous. There will again be a filled valence band, roughly derived from bonding orbitals, and an empty conduction band derived from antibonding orbitals. In the amorphous material, $\vec{k}$ is not a good quantum number for the electronic states. Some remnants of $\vec{k}$-conservation may persist, however, in that states in a given energy range may contain predominantly wavevectors associated

with particular portions of the Brillouin zone of the ordered structure.

Remnants of $\vec{x}$-conservation in the optical absorption spectrum would be manifest as enhanced matrix elements for optical transitions between states associated with the same portion of the Brillouin zone. Thus, in a crystal with impurities or phonon scattering, transitions that conserve wavevector are generally much stronger than indirect transitions, where the initial and final states are associated with different parts of the Brillouin zone. This should be distinguished from non-direct transitions, which occur when the remnants of $\vec{k}$-conservation are negligible. In the latter case, the optical absorption reflects a simple convolution of the densities of states of the valence and conduction bands. Non-direct transitions have, in fact, been evoked to explain photoemission results in a number of crystalline materials as well as in amorphous Ge (Sp 67,Sp 70).

The rough features of the density of states will generally be the same in the amorphous material as in the crystalline, provided the short-range ordering of the atoms is similar for the two cases (Io 60). Sharp features of the crystalline density of states, arising from critical points in the Brillouin zone, where there is a vanishing of the gradient of the energy value with respect to wave-vector, would, of course, be considerably smoothed out in the amorphous system. Corresponding to the energy gap in the crystal, there will be a quasigap in the amorphous

material, where the density of states is much smaller than
in the valence and conduction bands (see Fig.2). Although
an ideal covalent amorphous structure might still possess
a true energy gap with zero density of states, there will
always be a finite state-density in real materials. The
states in the quasigap are believed to be localized in
space, and may be associated with a particular defect or
cluster of defects, or with a statistical fluctuation of
the parameters of the material in some limited region of
space. Electrons in these states have very low mobility
at low temperatures.

The electronic states in the body of the valence
and conduction bands are probably extended throughout the
material. These states will have a much higher mobility
than states in the quasigap, although their mobilities
will be very much smaller than the mobilities of free
carriers in crystalline semiconductors. The more or less
sharp transition between these states of relatively high
mobility and the states of low mobility is called the
mobility edge.

The general picture of amorphous semiconductors,
presented above, is that underlying the theories
developed by Mott, by Cohen, Fritzsche and Ovshinsky, and
others (Mo 67b,Coh 69,71b,Gu 63,Ba 64). Some of the more
detailed models used to explain the properties of amorphous
semiconductors will be discussed below.

We close this section concerning general concepts
with a warning. Many terms such as effective mass, n-type,
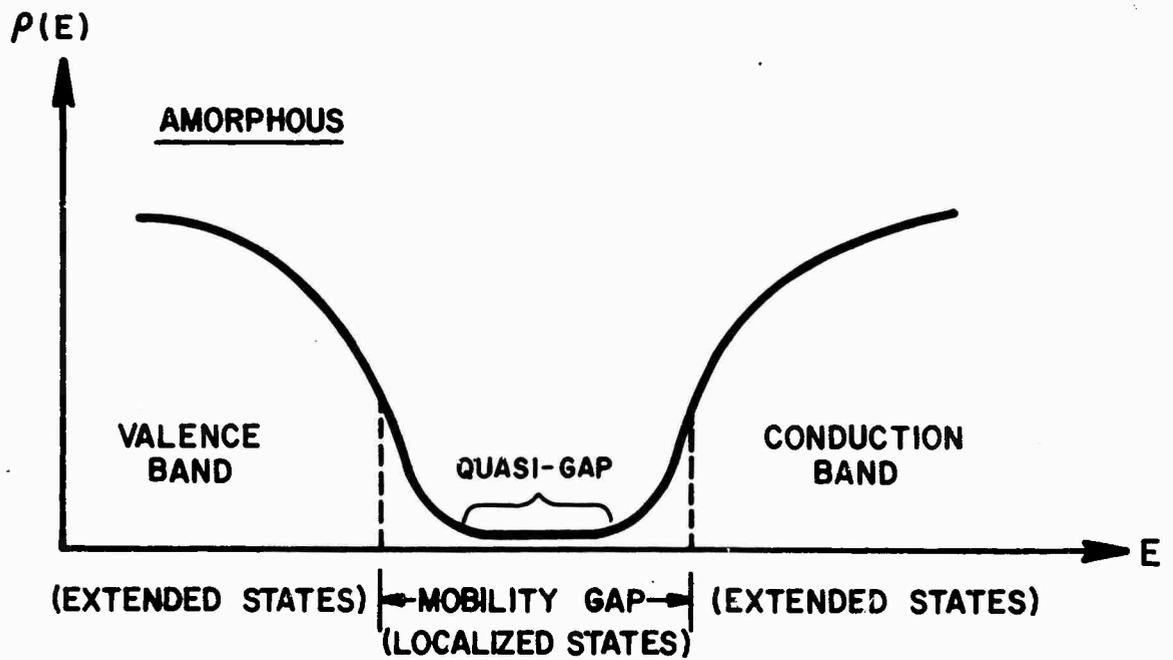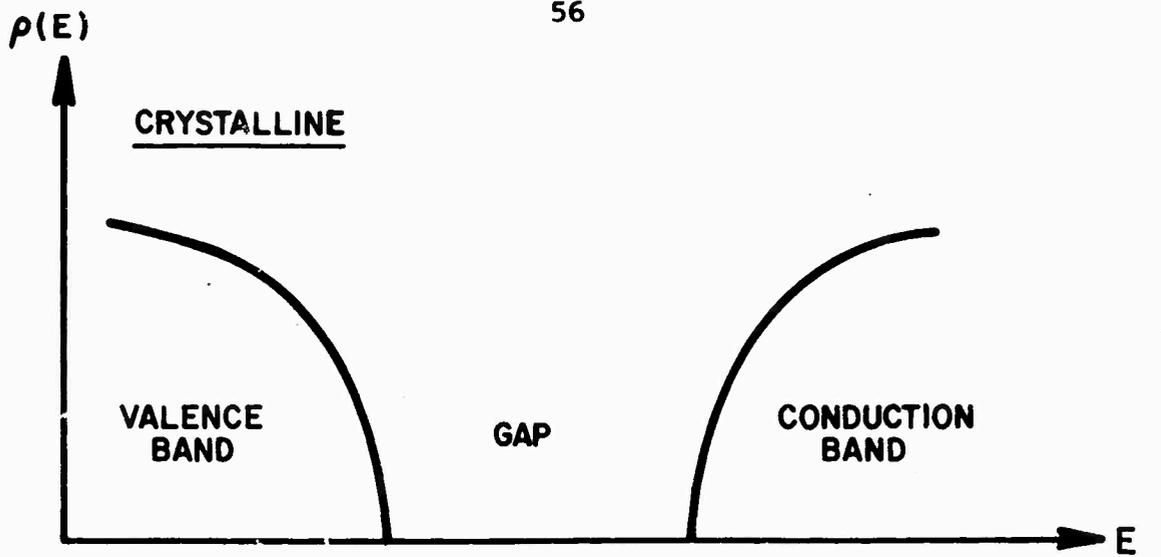
Fig. 2. Schematic density of states for a crystalline and an amorphous semiconductor.

p-type, intrinsic, extrinsic, etc., have been borrowed
from crystalline semiconductor theory and used to describe
phenomena in the amorphous materials. It is important to
remember, however, that the applicability of these ideas
to the amorphous state is not always very well established
and that, in any case, the precise meaning of the terms
may be somewhat different than in the crystalline case.

Optical Properties

The scientific and technological interest in amorphous semiconductors stems mainly from their electrical and optical properties. Usually, the optical properties are easier to interpret and we discuss them first. Optical absorption reflects essentially the density of states, more or less modified by the transition probabilities between the states. In crystals, it has been possible to obtain much information about the electronic and phonon state structures from the optical measurements, and similar methods have been applied to amorphous solids (Ta 70a, St 70a, St 70b, Ta 71).

Measurements

The precision of measurement is often severely limited by macroscopic inhomogeneities of the samples producing light scattering. The determination of the optical constants of films from transmission and reflectivity measurements meets with an additional difficulty. The optical constants are calculated from complicated equations which take into account interference effects. It often happens (in particular at low-absorption levels) that a meaningful determination of the optical constants requires not only a precision of measurement which is difficult to attain, but also an extremely uniform thickness and homogeneity of the film (Do 70). At high-absorption levels, the optical constants are determined from the measurement of the reflectivity and Kramers-Kronig analysis. As in crystals, one is concerned with

the quality of the surface. In addition, there is the difficulty that the shape and position of the broad structure in the optical constants observed in amorphous materials is more sensitive to the arbitrary extension of the reflectivity data beyond the range of actual measurements than in crystals.

Principal Optical Absorption Band

A typical example of the difference in optical properties between crystalline and amorphous solids is shown in Figure 3. The principal absorption band of a-Ge is situated approximately in the same energy range as that of c-Ge, but it lacks the sharp structure characteristic of crystals. This is easily understood: with the loss of the long-range order, the k-vector ceases to be a good quantum number and is only partially or not at all conserved during optical transitions. In this case, the broad features of the spectra are determined by the convolutions of the band state densities rather than the joint band state densities whose singularities are responsible for the structure of crystalline spectra. The electroreflectance method, which is particularly sensitive to these singularities, appears to be less useful for the amorphous semiconductors. Recent work (Fi 71a) has shown that the previously reported electroreflectance in a-Ge is probably an artifact.

The simplest assumptions that the matrix element for the optical transitions is constant for the whole absorption band, and that the band state densities are
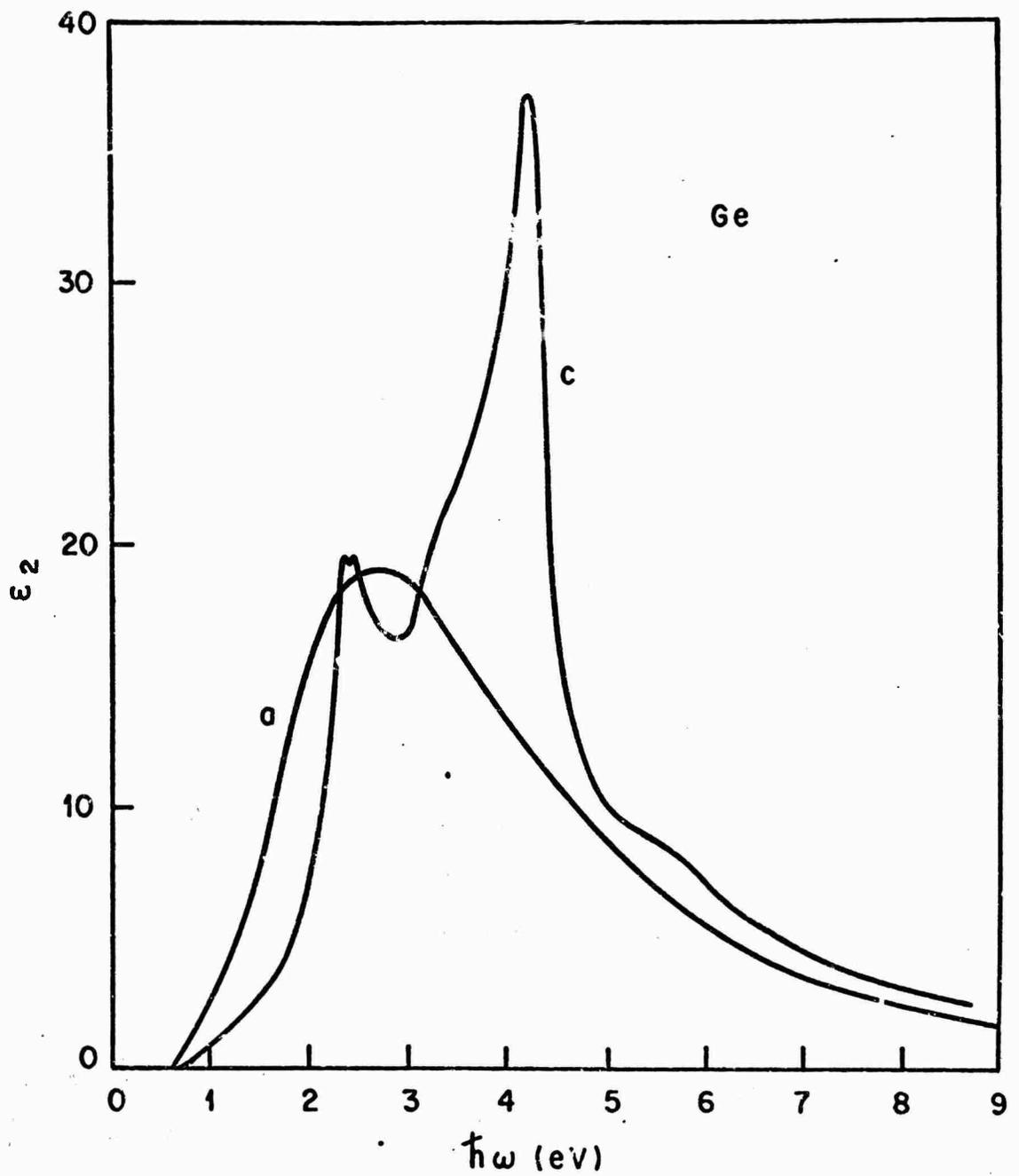
Fig. 3. Principal optical absorption band of a-Ge (curve a) and c-Ge (curve c).

little different from crystalline values have been checked for a-Ge and found to be unsatisfactory. Simple suggestions were tried to explain the shift of the principal absorption peak at 4.4 eV, dominating the spectrum of c-Ge, to 2.7 eV in a-Ge, based either on the change of the band state densities or the energy dependence of the matrix element (Br 69). The latter explanations appear to contradict the results on external electron photoemission (Sp 70) from amorphous Ge, which are consistent with the shift of the valence band state density toward the top of the band.

Only small differences in the principal absorption bands were observed in crystalline and amorphous forms of As_2S_3 and As_2Se_3 (Za 71), if we disregard the disappearance of the sharp structure in the amorphous form. In Se and Te, a large shift of the absorption edge toward higher energies is observed in amorphous as compared to trigonal forms. This is probably due to the disturbance of the interaction between the helical chains by disorder, and/or the appearance of the rings in the amorphous form.

Index of Refraction

From the available data, it appears that the electronic part of the index of refraction at low frequencies, $n(0)$, changes only moderately (at most ten of percent) if the short-range order of the amorphous form is the same as in the corresponding crystalline form. This is the case for the network structures such as Ge, 3-5 compounds, As_2S_3, and others. This is consistent with the view that the average gap depends only on the short-range order.

A large change of n(0) is observed if the short-range order (character of the binding) changes as, e.g., in GeTe. GeTe crystallizes in a distorted rock-salt structure (coordination number 6). a-GeTe has a mixed coordination number of 4 and 2 for Ge and Te respectively. The binding is predominantly covalent (Bet 70). The values of n(0) are 6 and 3.3 in c-GeTe and a-GeTe (Br 70).

The two-fold coordinated structures, Se and Te, exhibit a large change of n(0) in accordance with the large shift of the band edge. The same effect is observed in some systems containing Te (such as $Ge_xTe_{1-x}X$), where X is some other constituent, from which tellurium rich phases crystallize out during the amorphous-crystalline transition. These systems have a higher kinetic crystallization temperature than pure Te and are potentially useful materials for electro-optical memory devices.

Although n(0) of a-Ge is close to that of c-Ge, it has been shown to be somewhat greater by 0 to + 10 percent depending on the method of preparation, substrate temperature during deposition, and annealing (Th 71). It has been suggested that this is due to vacancies that disappear (or conglomerate into larger voids) during annealing. Electron-spin resonance observed in amorphous Ge has been associated with states at internal surfaces of voids (Br 69). The pressure dependence of n(0) of amorphous Ge and Si is comparable to that observed in crystalline forms (Co 71).

Absorption Edge

In contrast to the principal absorption band, the shape and energy of the absorption edge often depends on the preparation and thermal history of the samples (a structure-sensitive property), in particular, in thin films. Figure 4 shows the dependence of the absorption constant of a-Ge in the region of the absorption edge on the temperature of annealing (Th 71). The pressure shifts of the edge in amorphous Ge and Si are different from the shifts of any of the gaps in the crystal (Co 71).

Similarly, as in crystalline semiconductors, the definition of the absorption edge energy, E_g^{opt}, requires some knowledge or at least some theoretical assumptions about the absorption processes in the region in question. It appears that in many amorphous semiconductors it is possible to distinguish between the high energy part where the absorption constant varies as

$$\alpha \sim (\hbar\omega - E_g^{opt})^r/\hbar\omega \qquad \alpha \stackrel{>}{\sim} 10^4 \text{ cm}^{-1}, \qquad (1)$$

the exponential part, where $\alpha \sim \exp(\hbar\omega/E_c)$, and the weak absorption tail, where $\alpha \sim \exp(\hbar\omega/E_t)$ with $E_t \gg E_c$ (for $\alpha < 1 \text{ cm}^{-1}$). Here ω is the photon frequency and E_t, E_c are characteristic energies.

The high energy part is often used for the definition of E_g^{opt}. For some materials, it is found close to E_g^{opt} in the corresponding crystal. In other materials, shifts in either direction have been observed. E_g^{opt} can be smaller or larger than the electrical gap determined

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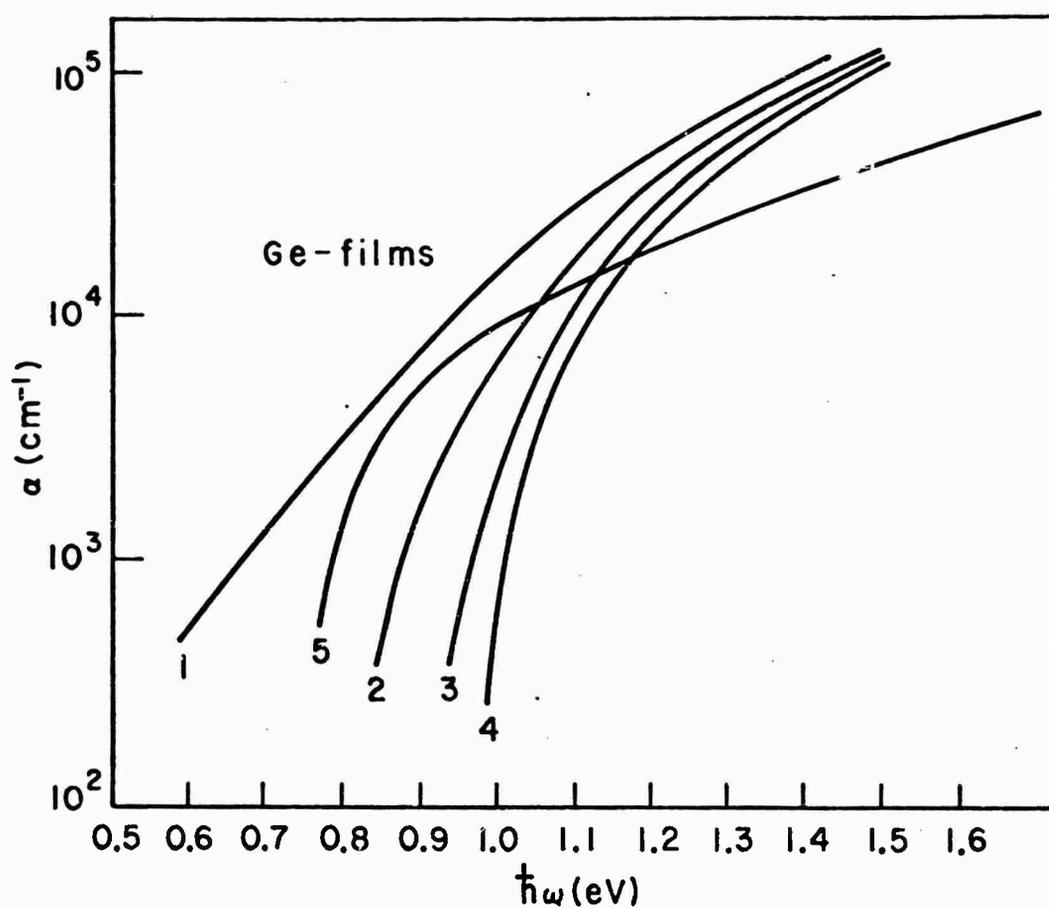
Fig. 4. Dependence of the absorption edge of a-Ge on the
temperature of annealing (Th 71). Curve 1:
deposited at 20°C, non-annealed. Curves 2,3,4,5:
annealed at 200,300,400,500°C respectively.
During the annealing at 500°C the sample crystallized.

from the temperature dependence of electric conductivity.
This may indicate that the Fermi-level is not necessarily
in the middle of the gap. For the exponent, r, one often
finds r = 2 (As_2S_3, As_2Se_3, GeTe, $GdGeAs_2$, Si and others);
sometimes r ≈ 3 (in complicated chalcogenide glasses such
as $Si_5Ge_{15}As_{25}Te_{55}$). In amorphous Se, the data indicate
that r = 1 (Da 70).

Below $\alpha < 10^4$ cm^{-1}, the absorption edge is
generally not as sharp as predicted by the formula
$(\hbar\omega - E_g^{opt})^r$. In some cases, the broadening may be due to
absorption associated with the states in the gap. This
appears to be the case for amorphous Ge films which often
show broad edges that can be sharpened by annealing
(cf.Fig.4). Some methods of preparation give a sharp edge
(Do 70). In many compound semiconductors, α, in the range
of about 1 to 10^4 cm^{-1}, is proportional to $\exp(\hbar\omega/E_c)$ with
the constant, E_c, in the range of 0.05 to 0.08 eV at room
temperature. Lowering the temperature keeps E_c almost
constant. At higher temperatures, E_c increases unless
annealing processes take place, which may reduce E_c. This
exponential part of the absorption edge behavior is similar
to the Urbach tails observed in crystals, as discussed in
the section on Models below.

Below the exponential absorption tail of compound
amorphous semiconductors, one observes weak absorption tails
with a considerably smaller slope (Ta 70b,Wo 71). The
absorption in these tails depends very much on sample
preparation and purity. It has been shown experi-
tally that this absorption is not an artifact produced by

light scattering. This absorption tail has been associated with the states in the energy gap. From the available experimental data (Ta 70b), it appears that the optical absorption cross-section of these states is a few orders of magnitude smaller than the cross-section observed for localized states in crystals. Pure semiconducting glasses are highly transparent in the range below the absorption edge and above the lattice absorption bands.

Free carrier absorption is generally not observed even at high temperatures. Glasses are, for this reason, much more transparent at high temperatures in the infrared region than crystals with the same energy gap. However, in a relatively highly conducting glass, $Tl_2SeAs_2Te_3$, an absorption that may be ascribed to free carriers has been observed (Mi 71).

In the infrared spectrum of amorphous Ge, one observes a band at 0.23 eV, which may be interpreted as evidence for a peak in the distribution of the gap states. These states may arise from defects (Ta 70c).

In some chalcogenide glasses, a photoluminescence band has been observed at low temperatures (Ko 70,Fis 71) at energies well below the optical gap. This is not necessarily evidence for a peak in the localized state density in the gap as suggested originally, but can be explained on the basis of uniformly decreasing density tails and plausible assumptions about the competition of the radiative recombination process with the relaxation process.

Electrical Properties

Investigations of the electrical properties
of amorphous semiconductors lean heavily on the procedures
and analyses used in studies of crystalline semiconductors
like Ge, Si, and the III-V compounds. However, exploration
of amorphous semiconductors encounters many unusual aspects
and difficulties (some of which are already apparent in
work on low-mobility materials like oxides):

1.   The preparation of well-defined samples for
electrical measurements is a cumbersome and often impossible
task. Besides foreign impurities and other traps, specimens
contain uncontrolled compositional and positional inhomo-
geneities, which may give rise to charge accumulations and
potential fluctuations.

2.   The resistivity of an amorphous semiconductor or
semi-insulator is often several orders of magnitude larger
than that of its crystalline counterpart (Ow 70a).

3.   Charge carrier concentrations are hard to obtain
because of the difficulties in measuring and interpreting
the Hall coefficient.

4.   Mobilities are small and their magnitudes are
difficult to evaluate. The determination of the Hall
mobility depends on one's ability to measure the Hall co-
efficient. The drift mobility may be trap-limited and in
any case is measurable only in sufficiently good samples.

5.   The effects of impurities on electrical properties
are hard to assess.

6.   Many amorphous semiconductors show switching-type I-V curves and other non-linear effects.

Experimental Techniques

Because of the inherent difficulties listed above, measurements on amorphous solids have the tendency to be ambiguous. Hence experiments are more convincing when they have been performed under a number of different conditions (a variety of substrates, sample thicknesses, substrate temperatures, quenching rates, electrical contacts, and, if possible, different sample geometries). In most cases, the geometry of sample and electrodes is much different from that used with crystalline specimens. Often samples can only be prepared in the form of thin films. Considering the high resistance of most amorphous semiconductors, it seems difficult to use anything else than the capacitor geometry. Frequently, this leads to uncertainties about the homogeneity of the applied electric field as a result of possible barrier layers at the electrodes. In dealing with relatively well-conducting amorphous materials, it should be possible to apply four electrodes and use the potentiometric method (at the same time being careful to avoid surface conduction). The capacitor geometry is also objectionable in determinations of the Seebeck coefficient. In this case, one measures the temperature difference between the electrodes, which will be quite different from that across the sample if sizable temperature drops occur at the metal-semiconductor interfaces.

Another aspect that has to be considered is the matter of contacts. In general, metal contacts on small gap (E_g < 1.5 eV) amorphous semiconductors are believed to be ohmic and have low resistance. On the other hand, problems arise with electrical contacts between metals and wide-gap amorphous materials (Fr 71a). In the latter case, both blocking and rectification have been observed.

Quite extensive studies have been made concerning contacts on amorphous Ge and Si (Eos 70). The conclusion reached is that the noble metals cause alloying and crystallization at temperatures as low as 100-200°C. In contrast, refractory metals do not cause such effects until much higher temperatures are reached.

D. C. Conductivity

Studies of a variety of amorphous semiconductors indicate that the temperature behavior of the conductivity depends on the type of bonding. For example, the purely covalently bonded amorphous Si and Ge show different electrical properties from amorphous Se and Te in which there is mixed covalent and van der Waals bonding. The chalcogenide glasses with their cross-linked network structures have again another kind of conductivity-temperature relation.

Most important is the fact that the temperature dependence of amorphous Si and Ge (ln σ vs 1/T) cannot be analyzed in terms of an exponential increase (not even over a limited temperature range). In other words, the

conductivities of amorphous Si and Ge do <u>not</u> show a single
activation energy (Br 71b,Cl 70). Recently it has been
reported that the conductivities of amorphous thin films
of Si, Ge, and also carbon below room temperature follow
an $\exp(bT^{-\frac{1}{4}})$ relationship rather accurately, in accordance
with a tunneling mechanism suggested by Mott (Mo 69a). (See
discussion further on in this section.)

The effect of impurities on the conductivity of
amorphous Si and Ge differs considerably from that on
crystalline samples of the same elements. Crystalline Si
and Ge are strongly influenced by impurity concentrations
as low as 10^{14} or 10^{15} cm^{-3}, while amorphous thin films do
not seem to be affected before levels of 10^{18} - 10^{19} cm^{-3}
have been reached.

On the other hand, it has been pointed out in
the discussion of the preparation of thin-film samples
that amorphous semiconductors like Ge and Si are very
susceptible to the temperature of the substrate, to temper-
ature cycling (annealing) (Br 71b), and to the presence of
even very small residual gas pressures (Wal 68).

The two-fold coordinated semiconducting glasses
like Se and Te show a simple exponential behavior of the
conductivity over a wide temperature interval extending
without any discontinuity into the liquid range (St 70a).
The activation energies derived from these transport
measurements agree roughly with one half of the optical
energy gaps of the two materials measured on amorphous
films. However, as remarked previously, this agreement

may be coincidental. Amorphous Se and Te, which possess
ring and chain structures, are much more sensitive to
small impurity concentrations; amounts of the order of
10^{17} cm^{-3} appreciably alter the electron and hole mobilities
(Fr 71a).

The conductivities of amorphous films of the
chalcogenide alloys follow, in general, the same patterns
of a well-defined exponential temperature dependence as
discussed above for Se and Te. However, the conductivity
changes more rapidly near the glass temperature, T_g.
Cooling from temperatures around T_g, one finds in some
amorphous films at lower temperatures different $\ln \sigma$-vs-$1/T$
curves depending on the rate of heating and cooling (Fr 71a).
Rapid quenching tends to increase the activation energy at
low temperatures. In glasses containing several constituents,
there may be phase separation upon heating to temperatures
above T_g; if this occurs, the effect on the electrical
properties is considerable.

In summary, for the chalcogenide glasses, plots
of log (conductivity) vs. reciprocal temperature often
show a high-temperature segment which can be retraced in
successive runs, and low-temperature branches which depend
on previous history. In crystalline semiconductors, one
would call these two parts "intrinsic" and "extrinsic."
However, in the case of amorphous semiconductors these
terms are not well defined. Perhaps it would be better to
refer to the high- and low-temperature portions of the
conductivity curves as structure-insensitive and structure-

sensitive branches, respectively.

Hall Effect

As mentioned before, measurements of the Hall coefficient are difficult and only very few have been performed. This situation is illustrated by the results of two experiments on amorphous Ge (Cl 67,Nw 68): The authors agree on the order of magnitude (10^{-2} cm^2/V-sec), but not on the sign. More reliable figures can be quoted for relatively well-conducting compounds such as As_2Te_3. Tl_2Se (Ko 60) and As_2SeTe_2 (Mal 67). In amorphous films of these materials, the Hall coefficient is negative; Hall mobilities are about 10^{-1} cm^2/V-sec and rather independent of temperature.

Drift Mobility

This parameter has been studied so far only in amorphous samples of Se (Tab 68), As_2Se_3 (Sch 70), and As_2S_3 (In -). Photocurrents were produced by very short light pulses. Transit times of the carriers were measured as a function of film thickness, wavelength, applied field strength, temperature, and light intensity. It was possible to separate drift mobilities and lifetimes; for Se the results indicate electron drift mobilities of the order of 6 to 8 x 10^{-3} cm^2/V-sec, while hole mobilities have surprisingly larger values of about 0.15 cm^2/V-sec.

Field Strength

In measuring electrical properties of amorphous semiconductors, one has to pay close attention to the strength of the applied field. Many of the samples used are thin films and hence the fields are large. Most semiconducting glasses show ohmic behavior up to fields of the order of 10^4 V/cm and increasingly larger deviations from linearity above this field. The latter can be traced back to two possible causes: electrode effects, and bulk effects (Fr 71a). The former result from injection at a metal-semiconductor contact. Although it is still somewhat of an open question whether injection can occur in most amorphous semiconductors, it is widely believed that carriers can be injected in films of chalcogenide glasses thinner than 1μ, and that the switching in such films depends on the resulting space-charge effects. Hence the electrical current will be space-charge limited and will depend on the applied voltage, because both the number of carriers and their drift velocity are proportional to the field. The presence of large numbers of deep traps will suppress the build-up of any space-charge-limited current.

Strongly non-ohmic behavior has been observed also in cases where electrode effects do not play a role. The rapid increase of the current at high fields is then a bulk effect, which has been attributed to the lowering of a coulombic barrier by the action of an applied electric field, e.g., the Poole-Frenkel mechanism (Fr 71a, Jo 71, Bag 70).

A. C. Conductivity

A possibly fruitful technique for probing electrical properties of amorphous (and other low mobility) semiconductors is the measurement of the a.c. conductivity. A partial list of materials that have been explored by this method includes: Se, As_2Se_3, As_2Te_3, Te_2AsSi, and SiO (Fr 71b). Most measurements cover a frequency range from 10^2 to 10^8 Hz. At high frequencies ($\omega > 1$ MHz), the conductivity usually increases like ω^2 and is independent of temperature. Below 1 MHz, the frequency dependence of the a.c. conductivity is often somewhat less than linear: $\sigma \sim \omega^n$, where $0.7 < n < 1.0$. The latter behavior, which shows a small temperature dependence, has been compared with the a.c. response of Ge at very low temperatures (impurity range) (Po 61), where the ω and T dependence was interpreted as phonon-assisted hopping between trap sites.

One should realize that hopping is only one of many possible loss mechanisms that can occur in a semi-conductor or semi-insulator. Besides charge carrier diffusion (corresponding to d.c. conductivity, which is ω-dependent), there are several other sources of dielectric losses (relaxation or polarization effects) such as inhomogeneities, dipole layers, surface barriers, ionic dipoles, etc. In most cases there is not one but a series of relaxation mechanisms, each with its own relaxation time.

Austin and Mott (Au 69) have derived an expression for the a.c. conductivity in amorphous semiconductors

assuming the hopping mechanism. This will be discussed
below in the part of this section devoted to models. Their
expression contains the density of states at the Fermi
level ρ_o., A.C. conductivity measurements have been used to
obtain values of ρ_o for various materials. The result,
however, is somewhat suspect because of the ambiguity of
interpreting the a.c. loss and the uncertainty about the
magnitude of several other parameters in the hopping
mechanism.

It may be helpful to study very simple glasses,
where one can isolate, hopefully, a single Debye peak.
Studying such a peak under a variety of different external
circumstances (electric field, photo-excitation, different
dopings, etc.) might provide the key to an understanding
of the distortions and reorientations that take place in
the glass. One should realize, however, that any conclu-
sions reached concerning the mechanism responsible for
a.c. conduction behavior do not necessarily extrapolate
to the d.c. case.

Photoconductivity

The exploration of photoconductivity in amorphous
semiconductors has produced a host of interesting relations
between the photocurrent and such experimental variables
as wavelength, intensity and duration of the exciting
light, temperature of the sample, or applied field.
Explanations of these effects are usually in terms of
phenomenological models.

Photoconductive effects of widely varying magnitudes have been observed in a-Ge and Si (Gr 67, Fi 71b), in a-Se, in a-GeTe, and in chalcogenide glasses (Jo 71). In Se, the photoconductive threshold appears 0.6 eV above the absorption edge. The smaller value of the strong absorption is identified with a localized exciton of the Se_8-molecules, while the larger threshold for the photoconductive process is associated with transitions between one-electron band states (Lu 70).

As_2Se_3 and other chalcogenide glasses do not show a well-defined photoconductivity threshold. In these materials, carriers seem to be excited from one-electron states extending well into the forbidden energy gap. Experiments have concentrated on the dependence of the photocurrent on light intensity and temperature, and on transport effects. In order to explain the results of these measurements, several investigators (We 70,Ho 70) have assumed recombination or cross-section edges located between the mid-gap and the mobility edges. The recombination edge, E_K (or cross-section edge), is defined as that energy where recombination occurs at the same rate as thermalization.

Two other photo-effects have been observed in chalcogenide glasses (Fa 70). The first is known as steady-state photoconductivity: Illumination of a thin film at nitrogen temperature produces an excess current, which decays extremely slowly after cessation of the exciting light. The other effect is the generation of a

thermally stimulated current after brief exposure to pair-
producing radiation at 77°K. These phenomena may contribute
to our knowledge of electronic states (traps and tail-
states) within the pseudo gap.

Seebeck Coefficient

As mentioned before, data concerning this
parameter are rather uncertain because of the difficulties
involved in the measurement (especially in the case of
thin films). If one takes the results at face value, it
appears that qualitatively the temperature dependence of
the Seebeck coefficient is not very different from that of
crystalline semiconductors (St 70a,Ow 70b). The Seebeck
effect is a first-order effect in non-degenerate semi-
conductors; hence an analysis of the effect requires a
rather exact knowledge of the density of states, the loca-
tion of the Fermi level, and the nature of the scattering
mechanism. Unfortunately, such information is practically
unavailable.

For a series of chalcogenide glasses, the Seebeck
coefficient is positive, indicating hole conduction, while
Hall coefficient measurements on the same samples show
negative values, implying that conduction is by electrons.
In a complicated system, however, these two measurements
need not be related in a simple way.

Piezo- and Magneto-Resistance

The piezoresistive and magnetoresistive effects have been measured for a few amorphous semiconductors (St 70a). In all cases, the effects are very small ($\leq$ 1%) and negative. From the experimental point of view, some warnings should be expressed. It is not clear that external stress is meaningful when the amorphous sample is already heavily strained. A negative magnetoresistance could be the result of inhomogeneities or internal barriers (Her 60). Furthermore, one should realize that transport properties depend on a host of material parameters, which makes any analysis of experimental results extremely difficult.

Very recent measurements of electron tunneling into a-Si (Sau 71) show promise for obtaining information concerning the density of localized states.

Magnetic Properties

The magnetic susceptibility of glasses is generally diamagnetic and constant at high temperatures and exhibits a superimposed Curie-term at low temperatures (Ta 70c). The glasses are always more diamagnetic than the corresponding crystals. A satisfactory theoretical explanation of this fact is not available. From the Curie term, the concentration of free spins can be estimated. One assumes that they correspond to highly localized states in the gap because such states may be expected to be singly occupied. Their concentration in some chalcogenide glasses was

found to be of the order 10^{18} cm^{-3}. By measuring the same sample of As$_2$S$_3$ in its crystalline and amorphous forms, it was shown that these states are due to disorder (Ta 70b).

It has been possible to measure electron-spin resonance in films of amorphous Si, Ge, and SiC. The spin concentration in non-annealed samples was found to be of the order 10^{20} cm^{-3} and diminished with annealing (Br 69). The resonance was ascribed to states on internal surfaces associated with voids. Recently ESR has been observed also in chalcogenide glasses (Smit 71).

Faraday rotation has been measured in amorphous Se at the absorption edge. The results were found to be interpretable in terms of non-direct transitions (Mort 71).

Lattice Vibrations

Because of the absence of k-vector conservation, the phonon spectra, both infrared (Ta 70c) and Raman (Sm 71), reflect essentially the phonon state densities. In amorphous Ge, Si, and 3-5 compounds, it appears from the experimental data that these densities are similar to those observed or calculated in crystals. In a-Se and compound semiconductors, reststrahlen bands are observed also in the amorphous state; however, the bands are broadened and the weaker ones often disappear.

The relaxation of the k-vector conservation often leads to disorder-induced bands, such as the appearance of one optical phonon absorption band in a-Ge (Ta 70c),

which is forbidden in c-Ge. Another example is a broad absorption band observed between 1 and 300 cm^{-1} in oxide glasses, which has been tentatively ascribed to single acoustical phonon absorption (Am 69); these bands have not yet been studied in amorphous semiconductors.

Inelastic scattering of neutrons on polycrystalline and amorphous Se has shown little difference between both spectra (Kot 67). The authors conclude from this that the phonon state density is determined predominately by the short-range order.

Localized vibrations of impurities and defects have been observed in semiconducting glasses. In a-Ge, bands probably associated with vibrations of oxygen-defect complexes have been reported (Ta 70c). The presence of oxygen may severely limit the infrared transparence of chalcogenide glasses because of vibrations due to oxygen bonds (Va 70).

In connection with long wavelength acoustical phonon excitations, crystalline as well as non-crystalline solids may be regarded approximately as elastic continua. The use of glasses in ultrasonic applications is therefore often convenient. Recently, some semiconducting glasses (such as $Ge_{30}As_5S_{65}$) have been shown to exhibit very low acoustical losses (Kra 70). This makes them attractive materials for acoustic delay lines and also for acousto-optic devices.

Thermal conductivity of glasses is due to phonons since the electronic contribution is generally negligible.

At room temperature the thermal conductivity is much
smaller than in crystals. This is explained by the very
small mean-free-path of thermal phonons, of the order of
interatomic distances. However, at very low temperatures
much longer mean-free-paths have been observed (Ze 71).

The specific heat at very low temperatures in a
number of semiconductor and oxide glasses shows a deviation
from the Debye law. Between $0.1^{\circ}K$ and $3^{\circ}K$ it has been
observed to vary as $AT + BT^3$ (Ste 71). This departure
from the expected behavior may possibly be generally
characteristic of the amorphous state and is sufficiently
remarkable to warrant further investigation. Its origin
is not yet understood.

Models

Density of States and Optical Properties

Various models have been used to apply the
experience with the band structure and optical properties
of crystalline semiconductors to the problem of obtaining
a quantitative understanding of their amorphous counter-
parts. Comparison with the crystalline case is most
likely to be useful for the extended states of the amor-
phous material.

For a substance such as Se, which occurs in
several crystalline forms, one approach has been to
approximate the density of states and optical properties
of the amorphous form by some weighted average over the

crystalline forms (St 69). A related approach is the work
of Rudge and Ortenberger (Ru 71) who used the OPW method
to calculate the band structure and optical properties of
hypothetical crystals of Ge in the 2H (wurtzite) and 4H
structures, as well as for the actual cubic (diamond)
structure. They then compared the observed dielectric
function of amorphous Ge with an average for the various
crystals, achieving at least partial success in explaining
the differences between the observed spectra of a-- and c-Ge
shown in Figure 3.

Henderson (Hen 71) has constructed a periodic
tetrahedrally coordinated lattice having 64 atoms per unit
cell with the local atomic arrangements simulating an
amorphous array, whose radial distribution function is in
reasonable agreement with the electron diffraction results
for a-Ge (see Section II). If it is possible to calculate
the energy levels of such a system, we should gain consid-
erable insight into the nature of the electronic states in
the bulk of the conduction and valence bands in a-Ge, and
we might hope to reproduce with considerable accuracy the
density of states and the optical absorption spectrum in
the region of band-to-band transitions.

Another class of models that has been used to
understand amorphous systems starts from the wave functions
or pseudopotential appropriate to the periodic system, and
then introduces the effects of disorder as a more or less
ad hoc scattering process. Examples of this approach are
the calculations of Kramer (Kram 70) on a-Se and the work

of Brust (Bru 69) on a-Ge.

A rather different approach to understanding amorphous semiconductors was taken by McGill and Klima (Mc 70). They calculate the "reaction matrix" for a cluster of eight tetrahedrally coordinated carbon atoms in a staggered and in an eclipsed configuration, using a muffin-tin approximation for the atomic potentials. Multiple scattering theory then yields a density of states for a hypothetical amorphous diamond, the system being treated as a gas of randomly distributed eight-atom-molecular scatterers.

A qualitative understanding of the optical properties of semiconductors, amorphous and crystalline, can be obtained from the Penn model of an isotropic semiconductor (Pen 62). In this model, the electronic properties are characterized by two parameters: the density of valence electrons, and an average energy gap, Δ, which corresponds to the average energy gap along the faces of the Jones zone in the crystalline case (Hei 69). Perhaps more sophisticated theories based on this model will be able to deal with detailed differences between amorphous and crystalline materials. Phillips' theory of chemical bonding in semiconductors, which emphasizes the dielectric constant of the materials, the density of electrons, and the electronegativity of the atoms, has had remarkable success in systematizing optical properties, heats of formation, and elastic constants of the tetrahedrally coordinated crystalline semiconductors (Ph 70a). This

approach may also prove useful for the amorphous case.

Attempts to understand the form of the optical absorption near and below the fundamental absorption edge have been generally less concerned with explaining the features of particular materials than with elucidating the widespread occurrence of certain forms. The common occurrence of an imaginary part of the dielectric constant proportional to $(\hbar\omega - E_g^{opt})^2$ (cf. Eq [1]), just above the fundamental absorption edge, can be explained as either an indirect or a non-direct transition between a valence band and conduction band having the usual square-root dependence of the density of states at the band edges (Ta 65). It has been remarked that the magnitude of the absorption edge in amorphous Si, relative to the indirect edge in crystalline Si, can be simply explained assuming a mean-free-path of 10A in the amorphous form versus 350A in the crystal (Eh 70). Davis and Mott (Da 70), however, explain the absorption just above the fundamental edge in terms of transitions from extended states in the valence band to localized states at the edge of the conduction band, or vice versa. The quadratic dependence then arises from the convolution of a finite density of extended states at the mobility edge, and a density of localized states which they claim to be roughly a linear function of energy. Cases where the quadratic law does not hold (e.g.,Se) are explained in terms of peculiarities in the densities of states for these substances.

Localized states in the pseudogap pose rather

different problems than the states in the bands. For the
localized states, the kinds of defects or fluctuations
responsible for the binding of the states must first be
identified, the binding energy associated with particular
kinds of defects must be calculated, and the expected
probability for finding the various kinds of defects must
be understood on a statistical basis.

If a localized state is tightly bound to a single
defect such as a foreign impurity atom, a vacancy, etc.,
it may be possible to estimate the binding energy or range
of binding energies possible for the state by considering
the experimentally observed binding energy of a similar
defect in a crystalline semiconductor. To the best of our
knowledge, good first-principle calculations of the binding
energy of a deep trap in a crystalline semiconductor have
never been done. These should be possible with presently
available techniques. The study of defect states in a
quasi-amorphous lattice, such as the Henderson model
mentioned above, might also be very enlightening. Estimates
of the numbers of various kinds of defects are difficult
to make, but experimental measurements of various kinds,
such as density, magnetic resonance and susceptibility,
Raman scattering, diffraction, etc., may be useful in
deciding between different statistical models.

For localized states bound to a large cluster of
defects, or to a multi-atomic statistical fluctuation in
the density, composition, or short-range order of the
amorphous structure, detailed microscopic calculations of

wave functions do not seem at all promising. Here, one has been forced to use such simplifications as the effective-mass approximation, deformation potentials, etc. For various simple assumptions about the probability distribution of the relevant fluctuations, it is possible to estimate the density of states and perhaps the optical properties, using methods similar to those developed to investigate the effects of fluctuations in the impurity distribution in crystalline semiconductors (Li 63,Bon 62, Ka 63,Mor 65,Ha 66,Zit 66). Using this kind of approach, Stern has been able to fit observations of the optical absorption in poorly annealed samples of amorphous Si, in the region below and just above the fundamental edge (Ster 71a). Stern assumes a fluctuating deformation potential, obeying a Gaussian distribution with a short correlation length (~6A), and with a root-mean-square potential that depends on the annealing history of the sample. Using his wave functions and density of states, in conjunction with Mott's theory of hopping conductivity (described below), Stern has also been able to explain the observed d.c. conductivity in amorphous Si (Ster 71b). Unfortunately, Stern's assumptions do not have a simple physical interpretation. Moreover, it is very difficult to test the assumptions underlying this kind of description, since it is entirely possible that similar transport and optical properties could result from very different models for the fluctuation statistics.

Various pieces of experimental evidence have

been cited recently to support the idea that the most important fluctuations responsible for states in the quasi-gap result from long-wavelength (~100A) electric fields in the sample (Fr 71b,Mo 67a,b,Ow 67,Boe 70a,Bag 70,Ta 70d). The effect of the resulting electrostatic potential would be to shift the position of the valence and conduction band edges locally, relative to the Fermi level. If the fluctuations in the potential are large enough, the Fermi level may sometimes be above the bottom of the conduction band and sometimes below the top of the valence band. This would lead to a finite density of states at the Fermi level, even in the absence of deep trap states bound to point defects (see Fig.5). A model with long-wavelength potential fluctuations might account for the relatively large density of states inferred from susceptibility measurements (Wo 71) and from various electrical measurements in the chalcogenide glasses (Fr 71b), while at the same time explaining the very low-optical absorptions inside the quasigap, and the long recombination times for trapped carriers seen in these materials. The long recombination times result from the large spatial separation between the regions where electrons and holes will respectively accumulate. The absence of substantial optical absorption well below the fundamental edge is accounted for in that a potential fluctuation causing a depression of the conduction band edge also causes a depression of the valence band edge, and vice versa. The large spatial extent of the fluctuations here serves to prevent absorption via photon-induced tunneling between a

Density of States g(E)
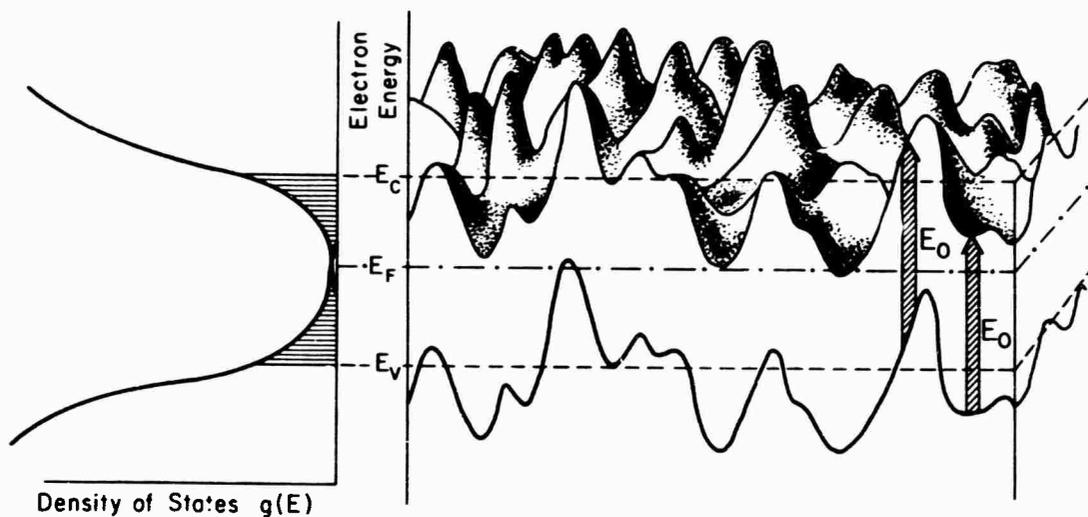
Fig. 5. The heterogeneous model. [Reproduced by permission
from (Fr 71).] The right-hand side shows the edges
of the valence and conduction bands modified by long wavelength
electrostatic potential fluctuation. Optical transitions take
place with an energy gap E_o as shown. The left-hand side shows
the density of states. The region of localized states lies
between the mobility edges E_c and E_v. Short-range potential
fluctuations which may give rise to additional localized states
are not shown here. Any non-electrostatic long wavelength
fluctuations that cause a variation of E_o are omitted from
this figure.

valence band state and a conduction band state, localized in regions of negative and positive electrostatic potential respectively. A model of this type, in which the spatial range of fluctuations is sufficiently large to prevent overlap between bound states for electrons and holes, will be referred to as a heterogeneous model.

A possible source of the hypothesized electrostatic potential fluctuations is a random distribution of charged defects, such as atoms which do not locally satisfy their valence requirements. Long wavelength statistical fluctuations in the position of the valence and conduction band edges could also arise from composition fluctuations in systems that are close to a phase separation, or as a result of fluctuations in the conditions of deposition of the sample. Such composition fluctuations would not normally preserve the relatively sharp threshold for optical absorption, however. It remains to be demonstrated whether the above-mentioned fluctuations do in fact occur with the required statistical distribution and spatial variation to explain the observations in the chalcogenides. (There is some evidence to support a heterogeneous model for amorphous Ge and Si, as well as in the chalcogenides, but the experimental case is weaker in the former case [Fr 71b] .)

As already pointed out in connection with optical properties, the exponential tail of the optical absorption below the fundamental edge of well-annealed amorphous semiconductors bears a strong resemblance to the Urbach tails observed in crystalline materials, from partially ionic

semiconductors to alkali halides. Optical absorption tails
can be produced, for example, by interaction with phonons,
from the Franz-Keldysh effect in the electric fields of
random impurities and defects, and by frozen-in strains.
There have been many attempts to calculate the frequency-
and temperature-dependence of the absorption tail based on
these mechanisms (To 59,Ho 61,Kei 66,Ha 65,Re 63). There
are difficulties with all of these attempts, however
(Hop 68). Recently, Dow and Redfield (Dow 70) have obtained
an exponential dependence of the optical absorption from
numerical solution of a model of an interacting electron-
hole pair in the presence of random electric fields caused
by charged impurities in semiconductors, or by optical
phonons in ionic insulators. Davis and Mott (Da 70)
attribute the temperature-dependence of the steepness of
the exponential edge, commonly observed in amorphous
semiconductors, to a temperature-dependence of the dielectric
constant entering the Dow-Redfield calculation. Final
resolution of the Urbach-tail problem is still awaited.

Phillips has emphasized the importance of a self-
consistent consideration of the displacements of atomic
positions in understanding the binding energy of impurity
states in crystalline semiconductors (Ph 70a). In view of
the relative ease with which atoms in an amorphous structure
can rearrange themselves, these effects may be even more
important in determining the nature of localized states in
the amorphous semiconductors, and may therefore be an
essential ingredient of a correct theory of these states
(Ph 70b).

Transport Properties

Two kinds of mechanisms have been proposed for
the d.c. electrical conductivity of an amorphous semi-
conductor: a "free-carrier" contribution resulting from
electrons or holes thermally excited into the high mobility
extended states, and a "hopping" contribution resulting
from phonon-assisted tunneling between localized states of
random energy, not too far from the Fermi level. The free-
carrier contribution has an activation energy which is the
separation between the Fermi level and the nearest mobility
edge. As noted earlier, this activation energy need not be
equal to one-half the optical gap, as in the crystalline
case, since the width of the mobility gap need not coincide
precisely with the width of the optical gap, and since the
Fermi level need not lie precisely in the middle of the
quasigap if there is a finite density of states there.
For the hopping conductivity, Mott has proposed a form
(Mo 69a):

$$\ln \sigma \propto -(\alpha^3/\rho_o kT)^{\frac{1}{4}}, \qquad (2)$$

where ρ_o is the density of localized states at the Fermi
level, α^{-1} is the length for exponential decay of the
states, and the variation of these quantities with energy
is neglected. The unusual temperature dependence arises
from the existence of a continuum of possible activation
energies for hopping between two localized states of
random distance from the Fermi energy. At low temperatures,
pairs with low-activation energy become important. The
activation energy cannot be made too small, however,

because the average spatial separation between sites
acceptably close to the Fermi energy would then be large,
and this would make the tunneling matrix element small.
The hopping conductivity can have forms other than (2),
including a simple activation-energy form, when the assump-
tion of constant density of states is not valid (Da 70).
It is not clear why amorphous Ge, Si, and C show the form
(2), while other amorphous materials show activation-
energy forms for their conductivities. It is also possible
that some unknown mechanism, quite different from the ones
considered, is responsible for one or both of the observed
conductivity behaviors. Other functional fits to the
experimental data must also be considered (Ch 70).

The mobility of carriers in the extended states
of the valence or conduction band is difficult to measure
directly, since observed drift mobilities are probably
strongly trap-limited. Theoretical estimates of the lower
limit to the mobility of an electron in an extended state
have generally ranged from 5 to 100 cm^2/v sec at room
temperature (Io 60). (These estimates are obtained by
equating the mean-free-path to the interatomic spacing, or
to the thermal de Broglie wavelength, respectively.) In
c-NiO, however, an observed Hall mobility of 1 cm^2/v sec
has been attributed to extended-state conduction (Bosm 66).
Davis and Mott (Da 70) interpret transport measurements in
the chalcogenide materials using a band mobility of the
order of 10-50 cm^2/v sec.

A. C. Conductivity

When the d.c. conductivity of a material is small, it is often the case that the a.c. conductivity is large compared to the d.c., even at relatively low frequencies. Austin and Mott (Au 69) obtained the following result for the a.c. conductivity arising from phonon-assisted hopping between localized states:

$$o\,(\omega) \;=\; \frac{\pi}{3}\,\rho_o{}^2 kTe^2 \alpha^{-5}\omega[\,\ln(\nu_p/\omega)\,]^4, \qquad (3)$$

where ν_p is a typical phonon frequency, and the remaining symbols are the same as in the d.c. expression (2). This result has already been mentioned in connection with the discussion of electrical properties. As noted there, Equation (3), which is based on the results of Lax, Pollak, and Geballe (Po 61) for impurity bands in crystalline semi-conductors, is indistinguishable from a frequency-dependence of the form ω^s, where s is about 0.8. The a.c. conductivities of a number of materials have been fit to this expression.

In addition to the mechanism included in (3), there will be a contribution to $\sigma\,(\omega)$ from simple photon-assisted tunneling between localized states (no phonon necessary) which will be present even at $0°K$. The associated frequency-dependence has been predicted to be of the form $\omega^2(\ln\omega)^4$ (Mo 69a). Such a contribution may have been observed in several materials (Ar 68, Cha 69).

Basic Theory of Disordered Systems

Many of the properties of amorphous semiconductors should be characteristic of disordered systems in general, and indeed many of the important ideas in this field have originated from the study of simpler disordered systems. Conversely, efforts spent in understanding amorphous systems may turn out to be useful in the study of other disordered systems. Among the systems whose electronic properties have attracted attention in recent years, are systems with <u>compositional disorder</u>, such as metallic substitutional alloys and impurity bands in crystalline semiconductors, as well as systems showing <u>structural disorder</u>, such as liquids and gases. The need to consider effects of strong multiple scattering arises not only for electronic states in disordered structures, but also for phonon propagation and for the propagation of electromagnetic waves through sufficiently irregular media. Furthermore, many aspects of disordered systems seem to be related to unsolved problems in the theory of turbulence in fluids, the theory of second-order phase transitions, and the quantum mechanical many-body problem in general.

Conceptually, the amorphous semiconductor is one of the most difficult cases to treat. For a substitutional alloy, it is usually possible to understand the electronic states in terms of a periodic model potential, which is in some sense intermediate between the potentials or pseudo-potentials of the individual constituents. Ideally, the scattering due to the difference between the actual and

model potentials is small.

For liquid metals, it is often possible to treat
the electrons as nearly free, the scattering of the
electrons from the ions now being treated as a weak pertur-
bation. In this case, scattering contributions from the
different Fourier components of the ionic pseudopotential
are additive, and only the structure factor, or pair
distribution function of the liquid need be specified. In
amorphous or liquid semiconductors, however, particularly
for states near the band edges, it is clear that multiple
scattering of the electrons is very important, and the
short-range order, involving correlations of three or more
atoms, plays an essential role.

Many approximate techniques, of varying degrees
of sophistication based on one form or another of pertur-
bation theory, have been developed to study extended states
in disordered systems, when the scattering is not too
strong. These techniques - which include the multiple
scattering theory of Lax (Lax 51); the Green's function
approach of Klauder (Kla 61); the various Green's function
theories for liquid metals developed by Edwards (Edw 67),
Ziman (Zi 66), Anderson and McMillan (An 67), and Schwartz
and Ehrenreich (Schw 71); the "virtual crystal approxima-
tion" (Nor 31), "average t-matrix approximation" (So 66),
and the "coherent potential approximation" (So 67) for
binary alloys; the cluster expansions used in alloys
(Yo 68, Ai 69)and in liquid metals (Cy 66) - are valid
when the mean-free-path is greater than the characteristic

wavelength of the electrons. Transport properties in
this regime may be handled by means of a Boltzmann equation
or by Green's function approximations based on the Kubo
formulas, such as in the calculation of Velicky (Ve 69).
The situation where the mean-free-path is comparable to
the characteristic wavelength of the electrons is much
more difficult to handle, however, even for the case of a
purely random distribution of scatterers, and quantitatively
accurate methods are not known. Nonetheless, various of
the Green's function methods have been applied to simple
models in this regime in order to estimate such properties
as the density of states, the mobilities, and the position
of the mobility edge (Ki 70, Ec 70a). These methods may
someday find extensions to the case of amorphous semi-
conductors.

The original suggestion of a sharp transition
between localized and extended states in a disordered
system was made by Anderson, using a model appropriate to
spin-diffusion in disordered structures, or for electron
transport in a tight-binding impurity band (An 58). Much
of the subsequent discussion of this transition has been
based on this kind of tight-binding model with random site
energies (Zi 69, Ec 70b, Tho 70). Nonetheless, the crucial
conclusion is believed applicable to many systems including
amorphous semiconductors (Mo 67b, Coh 69). This is the
conclusion that the one-electron levels of an infinite,
macroscopically homogeneous, disordered system fall into
two distinct classes - extended and localized. Further-
more, at any given energy, all of the states belong to

the same class, except at a few isolated energies (mobility
edges) where there is a boundary between a region of
localized and a region of extended states. If the Fermi
level falls in a region of localized states, then the d.c.
conductivity will be zero at $0°K$; otherwise, the conductivity
remains finite at low temperatures. The inclusion of
electron-electron and electron-phonon interactions should
not change this situation for the ground state at $0°K$
(An 70), although the interactions must blur the distinc-
tion between localized and non-localized states at finite
temperatures, or for high-energy states even at absolute
zero.

The energy-dependence of the mobility of an
electron just above the mobility edge is likely also to be
independent of the details of the disordered system.
Several authors have attempted to investigate this behavior
theoretically using simple models (Da 70,Eg 70). The
close relationship between the localized-delocalized
transition and the transition in percolation problems has
been emphasized. The concepts of percolation theory may
prove useful in understanding a number of aspects of the
transport process (An 58,Eg 70,Amb 71).

Some insight into the properties of random
systems, and checks on the validity of various approxima-
tion methods, can be obtained from the study of various
exactly soluble models. For example, for a large class of
one-dimensional random systems, one can calculate with
arbitrary accuracy the density of states and the average

one-particle Green's functions (i.e., the spectral density as a fur_tion of wavevector, $\vec{k}$, as well as of energy, E) [Ha 68,Hor 68]. Similar exact results can be obtained for a three-dimensional, tight-binding model with a special distribution (Lorentzian) for the random site energies (Li 69). Rigorous theorems have been proved concerning the existence of energy gaps in various simple models of disordered systems in both one and three dimensions (Hor 68, Ki 70), including a model with some resemblance to a tetrahedrally coordinated, amorphous semiconductor (Wea 71, Hei -). Theorems that exactly give the low-order moments of the density of states for various tight-binding models have also been exploited (Mon 42,Ka 62,Brin 70).

An interesting feature of the exact results for the "Lorentzian" model (Li 69), which was rigorously extended to a wide class of models by Edwards and Thouless (Edw 71), is the fact that the density of states and the averaged one-particle Green's functions are analytic functions of the energy on the real axis, even in the regions where the localized-delocalized transition is supposed to occur. Thus the mobility edge is not reflected in these properties of the system. In one-dimensional random systems, all the one-electron states are believed to be localized, and the d.c. conductivity always is zero, if the model has no electron-phonon or electron-electron interactions (Бог 63,Mo 61,Ha 68,Lan 70).

Let us remark in conclusion, that although the theoretical studies described above have been useful in

clarifying concepts invoked in the description of amorphous semiconductors, they are still rather far from providing the basis for a quantitative understanding of amorphous semiconductors. For instance, the question of whether there is a mathematically precise transition between localized states and non-localized states at $0^{\circ}K$, which has attracted so much theoretical interest, is of less practical interest than, say, the question of the <u>location</u> of the mobility edge in a real amorphous material. (Of course, experimentally observable quantities would be little affected if, in fact, the transition between localized and non-localized states were somewhat ill-defined, and there were simply a rapid change in the magnitude of the mobility over some narrow range of energy.) It would seem that only limited progress can come from the study of abstract models, and that most of the effort will have to be spent in relating the electronic properties to the structure of real amorphous materials. The construction and analysis of realistic models is a difficult task, but is a challenge that must be faced if real progress is to be made. The continued evolution of computer technology and computational techniques is a factor that greatly enhances the eventual prospects for analysis of realistic models.

VI.   DEVICE PHYSICS

Scope of Applications

Amorphous semiconductors lend themselves to a wide array of possible uses. A few of these, which have particularly stimulated fundamental work in recent years, will be singled out for detailed discussions. These will include:

(a) The use of inorganic amorphous semiconductors in electrophotography, i.e., document copying through the use of an electrostatic image of the material to be copied. This image is produced, after corona charging, through a selective discharge by photoconductivity, and the electrostatic image is used in turn to control the deposition of charged pigment particles.

(b) The use of selective crystallization (or phase separation) in amorphous films, through incident light, in image handling methods, such as photography and electrophotography.

(c) The use of the same sort of selective crystallization (or phase separation) induced by a laser beam to write digital information. The laser beam can also produce local melting and quenching and thus can restore the amorphous material to its original form. The information thus written and/or erased, can be read out through the significant change in optical properties between the amorphous and crystalline state.

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(d) The use of amorphous chalcogenides in a negative
resistance device. Any nonlinear resistance in which
current and voltage are not monotonically increasing func-
tions of each other is a negative resistance device. If
the current-voltage characteristic gives voltage as a
single-valued function of current, we speak of a current-
controlled device. If, in the I vs. V plot, V is the
abcissa, this characteristic will typically be "S" shaped,
and is therefore called an "S" type negative resistance.
If current is a single valued function of voltage, a
voltage controlled device, sometimes called an "N" type
negative resistance, is involved. The devices of principal
concern here are current-controlled devices of the type
illustrated in Figure 6a.

(e) The use of somewhat similar devices (particularly
compositions containing 81 percent Te, 15 percent Ge, and
2 percent each of two minor constituents) in which the
resistance at zero voltage is history sensitive. These
can be left in a high- or low-resistance state (Dew 62) as
illustrated in Figure 6b and used in random access computer
memories.

There are other applications which make less use
of the properties emphasized in the preceding sections of
this report and where the device work has been less inti-
mately coupled to the attempt to understand the kinetics
of the materials.

Even though they fall outside the scope of this
report, it may, nevertheless, be of help to list some of
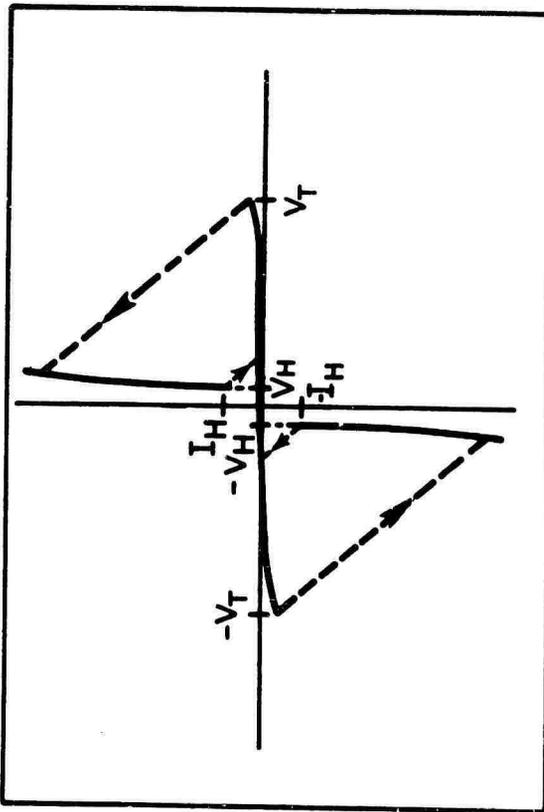
Fig. 6a. Current-voltage characteristic of a typical current controlled negative resistance chalcogenide device. The dotted lines are primarily signifi- cant for their end points, showing the transitions made with a particular value of series resistance, as the total voltage applied to the series combination is varied. See, for example, (Ov 68a).
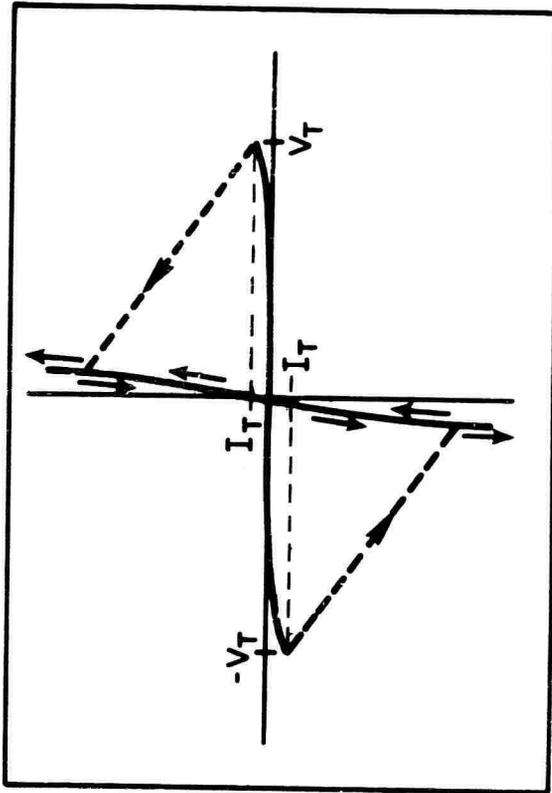
Fig. 6b. Current-voltage character- istic of a memory device, showing bistability at $V = I = 0$.

the more diversified applications. An extended discussion
of proposed applications for amorphous <u>oxide</u> films has
been given by Dearnaley, et al (Dea 71). This review
discusses cold cathode electron emitters, display panels,
electroluminescent devices, oxide coated cathodes, triodes,
microphones, and others. The use of glasses, including
chalcogenide glasses as infrared windows was the subject
of an earlier Materials Advisory Board Report (MAB-68).
Applications to acoustic delay lines and to infrared
acousto-optic devices have already been mentioned in the
earlier section on optical properties. Other optical
applications include the bonding of germanium prisms to
gallium arsenide film. The use of amorphous semiconductors
in Vidicons, i.e., as photoconductors in television camera
tubes has been investigated. The May 1951 issue of the
RCA Review, in a series of articles (Ros 51), discusses
this role of photoconductors, including Sb_2S_3, and Se in
particular. Sb_2S_3 is used in commercial cameras for
studio transmission from motion pictures. Electrolytic
capacitors utilize Al_2O_3 in low-cost applications, and
Ta_2O_5 in more demanding high-capacitance devices. Bell
Laboratories has, in fact, developed a complete tantalum-
based technology for integrated passive circuits (McL 64,66),
and this technology is widely used and manufactured within
the Bell System. Tantalum nitride and tantalum with, and
without, interstitial oxygen content are used as the
resistive materials, Ta_2O_5 as a dielectric. The use of
SiO_2 as an insulator and passivator in the silicon tech-
nology is well established. Particularly demanding

requirements are imposed on SiO_2 in the Insulated Gate
Field Effect Transistor. In a recent modification of this
transistor, the MNOS (Metal-Nitride-Oxide-Silicon) device,
the insulator consists instead of a thin layer of SiO_2 in
contact with the silicon, and a much thicker layer of
Si_3N_4 on top of that. In this device (which will be
further discussed in the section on technological compar-
isons), tunneling through the SiO_2 layer is an intentional
part of the device's operation. Another application of
As-S glasses relates to the passivation and encapsulation
of devices, where there is a need to keep the previously
manufactured device at low temperatures (Fla 60).

The rich variety of phenomena available in the
oxide glasses (Dea 71,Si 70) includes switching devices.
Oxide glasses exhibit both current controlled and voltage
controlled negative resistance. The larger gap materials
tend to be accompanied by voltage controlled negative
resistance. Sometimes both types of switching can be
found in one material (e.g., Nb_2O_5). One oxide device
particularly worth noting is an Nb_2O_5 memory device, which
will be briefly discussed in the next chapter on techno-
logical setting. Other oxide devices, e.g., copper
bearing glasses can also be switched repetitively at useful
rates (1 MHz) and 10^8 times before failure (Dra 69).
Oxide devices do not seem to depend on phase changes and
phase separation in the manner characteristic of the
chalcogenide memory devices, and we will return to this
point in the section on technological comparisons. The

oxides have been studied less intensively in recent years
than the chalcogenides and offer an even less coordinated
array of phenomena and models than is found in the chal-
cogenides. The proposals for oxide applications are also
at an earlier stage of development, typified by the charac-
terization of oxide switches (Dea 71):

> "The chief objection lies in the fact that the
> characteristics are not reproducible, from one
> operation to the next, or over a useful life.
> Most structures cannot be used in atmospheric
> conditions, and require encapsulation which adds
> substantially to the cost, but even when so
> protected the switching threshold is variable
> and there is a lack of stability below the thres-
> hold voltage. Over successive operations the
> devices frequently deteriorate and show evidence
> of local overheating: they may eventually persist
> in either the high or low impedance state. The
> switches are also rather noisy."

Chalcogenide glasses, which have benefited from more
development activity, are not as much beset by these
difficulties. For example, the variability in switching
voltage for a given delay time is small, well above thres-
hold (Lee 71).

In reading the following discussion of the key
device areas, it is well to remember that there is proprie-
tary information in this field, not available to this
committee. We may be posing some questions that are in
fact already answered. Furthermore, some of the available
knowledge stems from private communications rather than
published data.

Image Handling and Optical Memories

a) Electrophotography

Electrophotography, as currently used in document copying machines, is undoubtedly the major existing application for amorphous chalcogenides. The particular form of electrophotography historically associated with the Xerox Corporation utilizes Se and As-Se compositions as the photoconductive element of the system. These materials have high resistivities in the dark, combined with reasonable photoconductive properties. The basic process steps are (Des 65,Scha 71):

(1) sensitization of the photoreceptor by corona charging to fields greater than 10^5 V/cm

(2) exposure and latent image formation

(3) image development by triboelectrically charged toner consisting of pigmented polymer particles typically 10μ in diameter

(4) image transfer, usually by electrostatic means with the paper in contact with image and photo-conductor surface

(5) image fixing by thermal fusing of the polymer based toner to the paper

(6) removal of the remaining toner from the photo-receptor by mechanical means, and

(7) erasing the residual electrostatic image by uniform light exposure.

From an electrical standpoint, the following factors describe an idealized electrophotographic photoreceptor (Wart 69):

(1) The surface charge density required to reach a given voltage is proportional to the voltage, with the geometric capacitance per unit area as the constant of proportionality.

(2) Each photon absorbed results in the transport of one electronic charge unit completely through the photoreceptor.

(3) There are no mobile carriers that are not photo-generated. Thus there is no dark decay and no surface conductivity to neutralize the electrostatic image.

(4) The interface to the back conducting electrode is a perfect blocking contact and does not allow charge injection into the photoreceptor or the accumulation of an interfacial potential drop.

(5) The top surface also is blocking and does not permit charge placed on the top surface to be injected into the bulk or to move on the surface.

(6) There is no change in the photoreceptor characteristics with cycling.

(7) The properties of the photoreceptor are the same everywhere on the photoreceptor surface.

No real photoreceptor meets this ideal and extensive

discussion of each point, illustrated by Se, As_2Se_3 and As_2S_3, can be found in the literature (Tab 71). Non-electrical requirements for a photoreceptor in this process are also demanding, and include uniformity and freedom from defects over large (5,000 cm^2) areas, low cost and long operating life in a hostile environment.

Se, while not outstanding in meeting these requirements, represents a reasonable compromise. Inorganic amorphous semiconductors are not unique for this application. Crystalline photoconductors dispersed in a glass or polymer are widely studied. For example, ZnO, in paper, forms the basis of Electrofax process (Ami 65). Organic photoconductors have also received much recent attention: a poly-N-vinylcarbazole-2,4,7-trinitro-9-fluorenone charge transfer complex has been developed by IBM (Scha 71).

b) Optically Induced Phase Transitions

Aside from electrophotography, light can also be used to induce phase transitions in thin films of amorphous semiconductors, as has already been discussed in Section II on Structure and Bonding. This effect has potential utility in both the handling of images and in computer memories. The applications to image handling arise from the many ways in which the crystallized material differs from the amorphous, and awareness of these possibilities, which are mentioned in the Introduction, seems to stem largely from recent talks and discussions by S. R. Ovshinsky at ECD (Energy Conversion Devices, Inc.).

At this time only preliminary aspects of that work have
been publicly discussed. The modified properties include
electrical conductivity and, therefore the adherence of
electrostatically charged toner. The modifiable properties,
however, also include wettability, etch rates, the adherence
of the illuminated material to adhesive tape, and optical
properties. Thus the optically induced modification of
reflectivity and absorption permits a form of photography.
Other possibilitie inherent in these properties relate to
printing, photolithography, photoresists, and the direct
generation of conductive paths under illumination. The
material, which has been crystallized under exposure to
light, can, if desired, be returned to the amorphous state
through a heating and quenching cycle. This thermal
erasure process can, in fact, also be accomplished through
the use of light, in the form of a laser beam (Fei 71a).
In the proposed application to digital memory, this
erasure process is crucial. In the memory application it
is also the same laser beam, at lower intensities, which
would be used to probe the difference in optical properties.

As mentioned in Section II, it has been shown
that incident light accelerates the growth of surface
crystallites in amorphous selenium. Through the use of
simultaneous electric fields, as well as through analyses
plotting, the growth rates both as a function of absorbed
light intensity and as a function of hole-electron pairs,
Dresner and Stringfellow (Dr 68) make a convincing case
for the fact that it is the hole-electron pairs that
account for the accelerated growth rate. They suggest

that the hole, viewed as a broken bond, gives the structure
the freedom required for crystal growth. It is not entirely
clear whether the hole is only needed catalytically to
reduce the activation energy for local reconfigurations or
whether it is "used up" in the process. If it were, in
fact, possible to use the same hole repeatedly in a catalytic
fashion, we would have a more sensitive process with its
own built-in gain mechanism. It would seem important to
acquire an understanding of the mechanism as a guide in the
search for more sensitive systems.

As a directly usable mechanism, the effect
observed by Dresner and Stringfellow suffers from the fact
that the enhancement in growth rate is proportional to the
flux at low-light intensities and becomes less sensitive
at higher intensities. This simultaneous absence of a
development step and a "threshold" means that the sample
continues to be sensitive to stray light, after its
intentional exposure. One could, of course, use this
mechanism in connection with a gating action, which elevates
the sample to a higher temperature during the intentional
exposure. Another way of obtaining a more sensitive
mechanism with built-in gain would be to control the
nucleation process, rather than the growth process, via
light. Ovshinsky and Klose (Ov 71b) have, in fact, shown
that the number of nuclei can be greatly increased by light,
especially in films sensitized by the incorporation of
certain catalysts. The nuclei can then be developed through
subsequent grain growth induced either purely thermally, or
through a combination of elevated temperature and light.

The grain growth can, if desired, be enhanced by the same
light that has controlled the nucleus formation. Ovshinsky
(Ov 71b)   reports materials sensitive to exposures as low
as 10^{-5} joules/cm^2. These films are self-fixing, i.e.,
grain growth at room temperature is negligible.

Another recent study (Bra 70) demonstrates an
effect probably related to light-induced crystallization,
accompanied by phase separation, in As-S and related
glasses. These authors show that phase holograms can be
recorded in such glasses. Exposure times with 10 milli-
watts/cm^2 were of the order of minutes and the effect is
probably too insensitive to be of immediate practical
appeal. Refractive index changes continue for minutes
after the light is turned off. This system also dispenses
with a separate development process. As pointed out above,
this is not an unmitigated advantage, since the system
remains sensitive to light after its intentional exposure.

A reversible laser-induced crystallization in
$Te_{.81}Ge_{.15}Sb_{.2}S_{.2}$ was observed by Feinleib, et al (Fei 71a).
In this experiment, 3μ spots were crystallized in times
varying from 1 to 16 μsec., and with peak laser powers of
100 to 10 mw into the 3μ spot. Two micron spots have also
been observed in Se-Te films (Ov 71a). This work is at an
early stage and considerable improvement may be expected.

The return to the amorphous state accomplished
with the same laser (but at different power levels)
(Ad 71a) is presumably a straightforward melt and quench
process. Feinleib, et al (Fei 71a, Ad 71a), however, argue

that the crystallization process is not a simple thermal
process, since it is much faster than any other observed
thermal crystallization process in these materials and
occurs in a time comparable to that which the molten
material spends in the same temperature range, while being
quenched. In fact, Feinleib, et al, go on to propose
that even the electrically induced crystallization process
is not purely thermal and is assisted by the excess
electron-hole population. The area crystallized by the
laser beam darkens visibly. Changes in optical properties
can arise from the fact that the reflectance of the
crystalline state below 4 eV in this material is approxi-
mately 50 percent larger than in the amorphous state (Ad 71a).
The light scattering can also be changed by textural alter-
ations in the film which can include bubble formation
(Fei 71b, Ov 71b).

The numbers discussed by Feinleib, et al, appear
to involve several photons per bond and thus no built-in
gain mechanism. There is, however, appreciably more sensitivity
than in the process discussed above in connection with hologram
recording (Bra 70). The Se-Te films presently require 0.2
joules/cm^2 exposure (Ad 71a). This is somewhat higher
than the range of sensitivity for Diazo materials (10 to
100 millijoules/cm^2), which represent close to unit quantum
efficiency. Diazo materials are probably at the lower
edge of useful sensitivity for contact exposure systems,
which, in turn, is a relatively undemanding application.
The films described by Ovshinsky and Klose, which require
a development step, require 10 μjoule/cm^2. The electro-
photographic process requires about 1 μjoule/cm^2. The

small size of the recorded spots observed by Feinleib, et
al, combined with the microsecond time required for illumi-
nation, make this a contender for a beam addressed memory.
This will be further discussed in Section VII on Techno-
logical Setting.

The various investigations reported above seem
to have barely started to explore a rich variety of cordi-
tions for photocrystallization.   These can involve
variation of temperature during exposure, chemical sensiti-
zation, thermal pre-treatment and development, the applica-
tion of electric fields during illumination, and the role
of the substrate.

Many properties of many materials are strongly
affected by phase changes. The relatively small energy
gap of the amorphous semiconductors, which on the one hand
permits photo-excitation of carriers, and on the other
hand lowers the temperature required for reasonable crystal-
lization rates, provides them with a unique range of
possibilities in this image handling area.

Electrical Devices

The amorphous chalcogenide current controlled
negative resistance is sometimes called "Ovonic Threshold
Switch" (OTS), the name used by ECD. The threshold switch
and the bistable memory device are closely related and
both represent phenomena, which, with some variations, are
in fact very widespread, although their physical mechanisms
may be diverse. A review article oriented toward memory

devices (Mat 71) gives a table with 23 different systems
showing switchable resistances. Some of these entries are
whole groups of chemically related systems. Not all of
the settable resistances (memory devices) in this table
are guaranteed to be reversible. In fact, it is possible
in these systems to find a misleading first appearance of
reversibility, which comes from a process in which highly
conducting filaments are formed and then irreversibly
burned out, leading to a quick consumption of the device
material as new conducting filaments are formed.

The systems in Matick's table offer great
diversity and include GaAs films, single crystal yttrium
iron-garnet, as well as semiconductor heterojunctions.
It is not hard to find many additional possible entries,
e.g., magnetite (Fre 69), Schottky barriers in GaAs (Es 70),
and liquid Se and Te (Bus 70).

As already pointed out, all these systems do not
necessarily utilize the same switching mechanisms. The
behavior with respect to time constants, voltage and current
levels, and polarity effects is sufficiently diverse to
suggest that there are several mechanisms involved. Nor
are these systems all equally likely candidates for the
same set of applications. The diversity of system does
exist, however, and is noteworthy in itself. Recent
history has provided a heavy emphasis on the chalcogenides.
Such a concentration on one aspect of a field is undoubt-
edly worthwhile because it extends and deepens physical
insight. It would be unfortunate, however, to equate

resistive memory devices and amorphous chalcogenides extensively and to let a judgment on one become a judgment on the other. Switchable resistances need not necessarily be chalcogenides, and chalcogenides have application potential that transcends electrically activated devices.

Threshold Switch Behavior

The typical behavior of this device, as shown in Figure 6a, is best summarized by a slightly condensed quotation (Sha 70b):

"a.   The I-V curve is symmetrical with respect to the reversal of the applied voltage and current.

"b.   The same switching characteristic is observed when the active material is sputtered, evaporated, or hot pressed between the [metallic] electrodes. It remains symmetrical even when the electrodes are of different contacting areas or of different materials.

"c.   In the highly resistive state, the conduction is ohmic at fields below 10^4 V/cm. At higher fields, the dynamic resistance, R_{dyn} decreases monotonically with increasing voltage: Typical values are 50 MΩ at 0.1 volt and 1 MΩ just prior to switching.

"d.   When the applied voltage exceeds a threshold voltage, V_t, the OTS switches along the load line to the conducting state. The transition time, t_t, of this switching process has been measured to be about 150 picoseconds. The shunt capacitance of a few picofarads and a lead inductance of about 10 nanohenries make it likely that measurements of t_t are limited by the package time constant. ... The threshold voltage, V_t, is nearly proportional to the film thickness and can be adjusted by utilizing different materials to lie between two volts and 300 volts.

"e. In the conducting state, the current can be
increas d or decreased without significantly
affecting the voltage drop, termed the conducting
voltage, V_c, across the device. Here the dynamic
resistance is of the order of 10 ohms, an appre-
ciable fraction of which is due to the lead
resistance of the electrodes. V_c is nearly
independent of thickness. By altering the elec-
trode material, conducting voltage values
between 0.5 and 1.5 volts can be obtained.

"f. As the current is reduced below holding current,
I_h, the OTS switches back to the original highly
resistive state along the load line. The value
of the holding current is typically between
0.1 mA and 0.5 mA, depending upon the composition
of the active material."

"... The OTS does not switch to the conducting state
immediately as the threshold voltage is exceeded, but
remains in the high resistance state for a period of
time, t_d, called the delay time. The magnitude of
this delay is strongly dependent on the amount by
which the threshold voltage has been exceeded. t_d
can be several micro-seconds for an applied voltage
pulse of amplitude slightly greater than V_t or tens
of nanoseconds for a voltage twice V_t."

"... If current is rapidly removed from an OTS in the
conducting state, a finite time is required for a
device to recover its normal high resistance state
characteristics. During this recovery time, t_r, V_t
increases approximately exponentially. The character-
istic time constant, τ, for the device to recover
approximately 63 percent of its nominal threshold....
is 3 microseconds for 30 volt units, 0.3 of a micro-
second for 10 volt units, and should be considerably
less for lower threshold voltage devices."

Fifteen volts are typical threshold voltages.

Current controlled negative resistance (CCNR)
has been seen in many systems, going beyond our previous
list of internally relatively unstructured devices, and
includes avalanche processes in gas discharges, e.g., neon
bulbs. CCNR also occurs in many semiconductor structures
including p-i-n diodes (We 64), four-layer diodes, trigger
diodes (Ti 69), and Reeves-Cooke diodes (Ree 55), uni-
junction transistors, and in two terminal devices synthe-
sized out of transistors (Ti 69). It is therefore not
surprising to have a wealth of possible models, including
the whole variety of mechanisms which have been invoked to
explain nondestructive breakdown in insulators (Fra 56,
Od 64). The situation in connection with the threshold
switches is well characterized by Adler (Ad 71b): "... a
large controversy still remains as to the mechanism for
threshold switching in thin films of chalcogenide glasses."
New mechanisms are being added as fast as old ones get
demolished. A typical recent addition (Hom 71) invokes a
filamentary plasma with high conductivity that travels
from one electrode to the other. The present situation is
too fluid to warrant the display of a complete set of
rejected explanations. Many of the arguments and counter-
arguments involved can be contested by invoking
geometrical nonuniformities. A plausible overview of
some of the mechanisms is given by Adler (Ad 70,Ad 71b)
and we shall here concentrate on the two most widely
accepted sorts of explanation.

One of these, the "purely thermal" theory,
pictures the rapid increase of conductivity with current

that is implied by CCNR as a consequence of the strong
temperature dependence of the conductivity found in these
materials. The temperature changes in turn are a result of
the heat dissipation resulting from the current flow. In
this sort of explanation, one then invokes only macroscopic
quantities: thermal conductivities, heat capacities, and
the temperature dependence of the electrical conductivities.

The other kind of theory invokes microscopic
concepts including the injection of charges, the redistri-
bution of charges in traps, the modulation of barriers at
the surface of the amorphous semiconductor, and the
modulation of the effective mobility and of the internal
field distribution through trap filling. Plausible recent
versions of such theories stem from Fritzsche and Ovshinsky
(Fr 70a), and from Henisch, Fagen, and Ovshinsky (Heni 70).
Earlier versions stem from Mott (Mo 68,Mo 69b, Mo 69c).
These are qualitative pictures. The detailed elements,
which enter into such a theory, e.g., the existence or
nonexistence of barriers at the electrodes, are not avail-
able with any confidence from other investigations. Van
Roosbroeck (VanR 71) has pointed out that injection effects
in a material with a dielectric relaxation time larger than
the recombination time are very different from those typi-
cally seen in crystalline semiconductors and has provided a
theory for both switching and storage devices on this basis.

It is becoming relatively widely accepted that
for thicker samples and higher temperatures the purely
thermal picture applies, while for the thinner samples

and lower temperatures an electronic injection mechanism
must also be involved. At room temperature, films thicker
than 10μ are generally believed to exhibit purely thermal
breakdown. Unfortunately, it is not clear that the thermal
theories that are most often invoked really apply.

Lueder and Spenke (Lue 35, Spe 36) have given
a theory of thermal breakdown. Their paper contains
information that does not appear to have been fully
appreciated by all subsequent authors. In particular,
Lueder and Spenke show:

(1) For the typical capacitor geometry with thermal
gradients and current flow parallel, and with the electrodes
held at constant temperature, there is no CCNR but only a
limiting voltage which is approached asymptotically at high
currents.

(2) For this same geometry, a CCNR results if the
electrodes are not kept at constant temperature but
connected to the heat sink through a thermal resistance.
One would thus expect to see expressions for threshold
field which depend on this additional thermal impedance.

(3) If the capacitor geometry device, assumed to be
conducting uniformly over its area, shows a CCNR, then
there is a spatial instability leading to filamentary
current flow, and this can drastically sharpen the drop in
voltage with increasing current seen in the negative
resistance region. The point of onset of the spatial
instability depends on the relative ease with which heat
is transported from one part of the device to another, as

compared to the transport of heat out of the device altogether.

These features are supported, in part, by the work of others (Böe 70b, 71, Key 71, Od 64).

There seems to be a need for a more adequate thermal theory based on modern device geometries, which (Lue 35, Spe 36' takes into account the exact point at which spatial instabilities commence, as well as the strong dependence of conductivity on electric field observed in these materials. The work of Volkov and Kogan (Vo 67) concerns itself with the formation of lateral instabilities but does not seem to have been generally understood. There is room for a simpler theory closer in spirit to the existing thermal theories. Recent calculations by Warren and Male (Warr 70), and Böer (Böe 71) deal with a number of the above points adequately and report better agreement with experiment for threshold field and switching delay time respectively. Other thermal calculations are cur- rently reported to be in progress and it can be hoped that the existing gap in theory will soon be closed.

The experimental data that bear on the thermal model vs. the space charge modulation models are primarily of three kinds:

(a) Thickness depend nce of threshold field (Ko 69). The threshold field is independent of thickness for thin samples and decreases with thickness for thick samples. This thickness dependence is invoked (Ko 69, Fr 70b, Sto 70) to show agreement with thermal theories for thick samples

(> 10μ). Since a really good thermal theory is not used in these comparisons, they provide suggestive, but incomplete, evidence. The improved theory of Warren and Male (Warr 70) claims to explain the threshold field in films as thin as 2μ.

(b) An effect due to the polarity of the preceding pulse on the threshold field would be expected only for an injection model, not for a thermal model. Shanks (Sha 70a) and Balberg (Bal 70) find no such polarity effects, whereas Henisch and Pryor (Heni 71) find such effects, though modest at room temperature. These are nonexistent at an above-room temperature in some devices. At - 78°C, the polarity effects become appreciable (Pr 71). Although more evidence is needed, there seems to be at least some indication for the presence of charge injection effects.

(c) Measurement of total injected charge required for switching. Haberland (Hab 70) considers the delay in switching as a function of applied field and thus provides some evidence for the need of a minimum accumulated charge as a condition for switching. He discriminates against a mechanism requiring elevation to a critical temperature by showing that more energy input is required for switching at high temperatures than at low temperatures. As in (b) above, the evidence is not as clear as one would like but favors a model in which injection plays some role. In contrast to Haberland, Csillag and Jäger (Cs 70) report a switching process in which the accumulated energy seems to

be the critical parameter.

The Memory Device

Typical memory device characteristics are shown in Figure 6b. The basic action of the memory device is best described by a slightly condensed quotation from Helbers (Hel 71):

> "...The normal amorphous...phase is an insulator, having a room temperature resistivity of 5×10^4 ohm-cm. If, however, the material is heated above a critical temperature and cooled slowly, a second micro-crystalline phase will form. This material behaves as a degeneratively doped semiconductor having a resistivity of 0.3 ohm-cm. The material may be easily returned to the high resistance state by once again heating it beyond its glass transition temperature and cooling very rapidly, thus freezing the material in the disordered or amorphous phase. The threshold switching action provides a conducting path through the active material, which allows subsequent deposition of the required transformation energy in a confined region using reasonable currents and voltages..."

> "...The SET pulse is a high-voltage pulse (typically 25 volts) which is in excess of the memory device's breakdown or threshold voltage. This pulse will cause the memory switch to fire and conduct current. This current is limited to a few milliamperes by a high pulse source impedance. The SET pulse is fairly long (typically 10 milliseconds) so that not only the active region of the switch is heated but also the immediate surroundings. When the current is stopped, the active region cools slowly; the active material is thus left in the micro-crystalline low resistance state. In order to make this slow cooling process more reliable and predictable, a trailing edge is normally added to the SET pulse. This trailing edge provides a gradually decreasing current density in

the device and thus insures the slow cooling of the
active region. It should be noted that if the SET
pulse is terminated a few hundred microseconds after
the onset of conduction, the memory switch will
automatically revert to the OFF or blocking state.
This is due to the fact that insufficient time will
have elapsed for nucleation of the micro-crystalline
phase of the active material.

"To return the memory switch to the OFF or blocking
state, the active material must be converted back to
the amorphous or glassy phase. This is accomplished
by applying a short pulse of high current to the
device, typically 150 milliamperes for 5 microseconds.
This pulse will heat only the active region of the
device causing a very steep temperature gradient.
Thus, after the current pulse ends, this steep
temperature gradient will cause a rapid cooling or
quenching of the active region; freezing the material
in the OFF state. The memory switch then, actually
turns OFF _after_ the RESET pulse; not during it..."

There is, in fact, much more widespread agree-
ment on the above picture than there is on the mechanism
for the threshold switching action which precedes the
crystallization process. It has, however, not been clearly
proven that the crystallization process is entirely thermal.
As already indicated in the earlier section on optical
effects, it may be supplemented by the effects of non-
equilibrium hole-electron populations. There have also
been observations (Ver 57) of direct electrical effects on
crystallization in anodic tantalum oxide.

The above description may be supplemented by
additional characteristics. The crystallization process
is accompanied by phase separation, as discussed in the
section on structure and bonding, and the filament consists

of Te rich needle-shaped crystallites (200-400Å) (Si 71).
The glasses that yield memory devices rather than threshold
switches are materials which have lower glass temperature,
i.e., they crystallize more readily. As in almost any
memory device, there is likely to be some compromise
between ease of switching and the stability of the terminal
states. The crystallized filament has a diameter of 2 to
3 microns (Si 71). The current density in this thin filament
during the reset operation far exceeds that which can cause
electromigration (Ame 70) in room temperature metals.
As pointed out by Pearson (Pea 70), the crystallization
(as well as the quenching) is not necessarily homogeneous
throughout the filament, but could be dependent upon
making and destroying bridges between regions that remain
highly conducting. Even if the filament is a uniformly
crystallized region, its diameter can vary, depending upon
the exact previous electrical history (Hel 71). We thus
do not necessarily have a memory device with two well-
defined, self-stabilizing states between which one can
cycle back and forth. (In reliability tests of these
devices, it is important therefore to have a diversity of
test patterns, and not to depend on just one very simple
highly periodic sequence.) The range of excitation per-
mitting stable operation has been investigated (Heni 71,
Nea 70). In the reset process, a region about twice as
wide as in the set process becomes liquid and is cooled
too quickly to permit crystallization in the surrounding
region (Sie 71).

For the further development of the memory device,
the microscopic nature of the filament, its changes during
switching, and the effect of the filament structure on the
electrical characteristics need to be studied in more
detail. The presence or absence of electromigration and
its effect on characteristics must also be determined.
The role of electromigration as a failure mechanism is
currently under study at ECD, together with some of the
other kinetics and geometry of phase transformations in
the filament.

Radiation Hardness

It is clear from the literature and from
comments made to the committee that amorphous chalcogenide
negative resistance devices can have a very high tolerance
to radiation exposure. The question of radiation hardness
in systems is an exceedingly complex one. It involves
classified material specifying a meaningful degree of
exposure to various kinds of radiation. The radiation
immunity question, furthermore, cannot sensibly be addressed
at the component level but stresses systems questions. We
shall, therefore, content ourselves by pointing out that
there are some positive data. We must also stress the
distinction between memory devices (on which less data
have so far been published) and threshold devices. Thres-
hold devices, combined with passive devices, can perform
all digital logic functions and perhaps most other required
electrical circuit functions. Such circuitry, based
entirely on two terminal devices is, however, often

awkward and is delicate in terms of its sensitivity to
device parameters. Radiation hardness questions can be
separated into questions concerning permanent structural
change in the device involved, and questions concerning
the reliability of operation during radiation exposure due,
for example, to radiation induced hole-electron pairs.

The available literature is cited in the refer-
ence list as (Ov 68b,Eva 68,Henc 70,Fl 70,Sha 70b,70c,
Smi 71, and Ni 71). The last three of these discussions
are the only ones with bearing on memory devices.
Nicolades (Ni 71) asserts that 40 percent of the memory
samples initially in the "on" state converted to the "off"
state during irradiation at an integrated neutron flux of
10^{15} neutrons/cm^2. Smith (Smi 71), however, finds that
ECD's memory devices are relatively insensitive to an
exposure in excess of 10^{16} neutrons/cm^2. This reference
list does not do justice to the level of insight into the
radiation hardening question that exists at Picatinny
Arsenal and the Naval Ordnance Laboratory, but which at
this time, at least, has not reached a convenient publicly
available form.

The above section should not be construed as an
indication that amorphous chalcogenide devices are, in a
very general sort of way, insensitive to other aspects of
their environment. For example, the threshold voltage of
memory devices can change from 25 volts at $20^{\circ}C$ to 4 volts
at $70^{\circ}C$.

VII.   TECHNOLOGICAL SETTING

Scope

The preceding section covered device physics.
In this section we shall compare the resulting devices to
some of their competitors. Our purpose here is not that
of providing guidance to the technologist, much less to the
device user, but rather to sketch the setting in which this
new field finds itself. While new technologies can create
their own special opportunities, it is instructive to view
them in the context of competing technologies. It is in
this spirit that we will provide some comparisons with
other technologies.

The electrophotographic applications are, on the
one hand, so well established, and, on the other hand,
their future potential so intimately coupled to systems
questions and to proprietary information that further
discussion here would be difficult. The image handling
potential through selective photocrystallization is at
such an early stage that again very little can be said.
We shall, therefore, restrict this discussion to the
threshold switch, the electrical memory device, and the
optically accessed memory device.

Threshold Switch

As indicated before, the threshold switch is one
of many negative resistance two-terminal devices. Three-
terminal devices are generally preferred to two-terminal

devices, with the same general capabilities for control
and switching applications, because they provide a more
natural isolation between control signal path and the
controlled signal, and seem to be less demanding in terms
of the required device parameter tolerances. Special
performance capabilities or ease of fabrication may, never-
theless, make two-terminal devices preferable in some
applications.

The most widely discussed application for the
threshold switch (Ad 70,Heni 69) is in a display panel.
In this case, the threshold switch is used to control the
excitation supplied to an a.c. electroluminescent light
emitting element. The electroluminescent element, acting
largely as a capacitance in series with the threshold
switch, becomes a bistable circuit in its mode of response
to an impressed a.c. voltage. It can be set in an "on" or
"off" mode and left there until reset. The display, there-
fore, has a built-in memory and need not be continually
regenerated from an external buffer memory as long as the
image content is left unchanged. The use of a.c. electro-
luminescence in displays is, of course, not new (Gre 64)
and has been tried with a variety of control mechanisms.
It is the use of the threshold switch for this purpose
that is novel.

This display scheme is in competition with many
other old and new proposals, some oriented principally at
the large area display, i.e., at replacing the cathode ray
tube (CRT) and others oriented more at the display of a

relatively modest number of alphabetic and numerical
characters. The large area display proposals frequently
still involve an electron beam but go beyond the cathode
ray tube to provide some kind of storage mechanism built
into the display itself. These proposals include the
photochromic storage CRT (Me 70), the cathodochromic
storage tube, secondary emission charge storage tubes, and
others, many of which are reviewed by Kazan and Knoll
(Kaz 68). Other recent display proposals include tne use
of liquid crystals, semiconductor light emitting devices,
ceramic ferroelectrics, and cylindrical magnetic domains
(Al 71). Uniformity of light output over the area of a
display is easily achieved in an undeteriorated CRT, where
the phosphor on the CRT face has come from one uniform
batch. Uniformity is not always equally easily achievable
in proposals involving a discrete device for each picture
element and where light output can be a very highly non-
linear function of electrical excitation.

Numerical displays have long been commercially
available in the form of gas discharge tubes with shaped
electrodes. More recently miniaturized incandescent
filaments have been developed for numerical displays.
Multidigit gas discharge panels, in which the information
is fed in at one end and then shifted along (analogous to
the famous news display at Times Square), have also
appeared (Har 70). Progress in a number of display tech-
nologies has been reported at a recent conference (SID 71).
The technology that perhaps most closely resembles the
threshold switch combined with an a.c. electroluminescent

phosphor is the plasma display technique of Bitzer and
Slotow (Joh 70,SID 71), which also invokes an array of
bistable elements, excited by a.c., each consisting of a
CCNR (current controlled negative resistance) in series
with a capacitor. In the plasma display, however, the
CCNR is that of the light emitting gas discharge and the
capacitance is that of the passive walls of the element.
In the current version of the plasma display, where no
walls separate adjacent light emitting elements, uniformity
over the display area is readily achievable.

Many of the more recent display proposals
(including the one utilizing the threshold switch) are
characterized by (a) the many peripheral connections
characteristic of a rectangular matrix array, rather than
the few terminals of a scanning device such as the CRT
tube, and (b) built-in memory. The pros and cons of these
alternatives are complex and beset with over-all systems
considerations.

The plasma display panels require somewhat
higher voltages than the electroluminescent devices. On
the other hand, a.c. electroluminescent devices suffer
from a well-known deterioration of light output during
operation (Iv 63,Sy 68), which has thus far limited their
really widespread utilization. Energy Conversion Devices,
Inc., in a contract report (Van 70), reports progress
toward obtaining longer life phosphors. If this result is
obtained under reasonable operating conditions with good
light output, it is of significance quite aside from

questions regarding the utility of the threshold switch.

The Electrically Addressed Memory Device

Information can be held in continuous media (often called storage) or else in discrete devices (often called memory). Magnetic tapes, disks, and proposals for reading and writing with optical beams are all examples of continuous media. The discrete category is typified by magnetic cores and integrated circuit memories. It is this latter group into which the amorphous chalcogenide memory (hereafter called A.C.M.) device fits, and which we will consider first.

Attempts to make integrated random access memories out of magnetic elements has led to discouragement (Pet 70), and most current proposals for random access memory developments center on the utilization of a silicon chip. The devices that can go on the silicon chip, however, show continually increasing diversity, and now also include the chalcogenide devices. In our discussion here, we will by no means try to survey the full flexibility of the silicon technology but only allude to some typical schemes. Deposition on silicon permits the realization on the same chip of peripheral address decoding circuitry, which selects the particular memory lines being addressed, and thus reduces the number of interconnections to the chip. Deposition on top of silicon also permits auxiliary devices, required for an information holding cell, to be made on the chip. Thus, for example, A.C.M. devices require a series diode with each memory device. This is

needed so that a high-resistance device will not be unintentionally shorted out by a group of neighboring low-resistance devices. If there are series diodes present, then each potential "shorting" path will have to traverse at least one diode in its reverse direction.

The chalcogenide devices, as has already been stressed, presently require about 10 milliseconds for the transition to the low-resistance state. Since the device reacts somewhat unpredictably to switching pulses, a "verify" interrogation after each switching attempt is recommended (Hel 71); if switching has not taken place, then another switching attempt is made. These featur have led to a designation of A.C.M. as a "Read Mostly Memory," i.e., as one that has to have its information content reset only very intermittently. Such memories are certainly useful, particularly as control memories which help set a computer's internal information flow structure. They can also be used, for example, in encoding arrays. On the other hand, it must be remembered that a special technology is not needed for this purpose: an ordinary read-write memory does not necessarily have to be written very often. Thus we will, in our comparisons, compare amorphous chalcogenide devices to a number of ordinary memory candidates, as well as some more specialized proposals.

Amorphous chalcogenide devices do have two possible advantages over most of the comparison candidates. Their radiation immunity is one. The other is that A.C.M.

hold information in a more permanent and less volatile form than most of the other comparable devices. A.C.M. does not require power to maintain information; there is no indication that stored information degrades during storage, and it can be interrogated nondestructively, i.e., without an intentional switching process. This lack of volatility is certainly desirable, all other things being equal. On the other hand, lack of volatility is generally crucial only in the really large information arrays kept on disks, drums, and tapes. Computer memory proposals have, in recent years, pushed in the opposite direction: they have gone to _more_ volatile schemes for the sake of gains in cost and density. There are, however, applications, particularly in military systems, where a premium is put on nonvolatility and nondestructive readout.

As a first comparison candidate, we shall refer to plated wire memories that store information in the magnetization of a film (McC 70,Ms 70,En 70). These magnetic memories can be read in access times comparable to the amorphous chalcogenide memories (70 ns), are read nondestructively, and are nonvolatile. Write cycles for plated wire memories are also in this same nanosecond range rather than in the millisecond range, which is characteristic of the A.C.M. The question of relative costs is open, but the A.C.M. does have the advantage of higher density and potential integrability with peripheral circuits on the silicon chip, which would not be easy for the magnetic arrays. Furthermore, the A.C.M. requires somewhat less drive current in their switching process.

On the other hand, the plated wire memories with their
fast write capability have broader application potential
and this can have a strong effect on cost.

Our remaining comparison candidates are all
silicon chip technologies. Within these technologies,
density (bits/in^2) is the key to cost. Processing costs
for silicon wafers may vary by modest factors, depending
on device details. Densities, however, can change over
several powers of ten, and density is, therefore, the
most important single parameter. Currently, A.C.M.
memories (Nea 70a, Hel 71) can be made with 256 bits,
without peripheral circuitry on a chip 116 mils x 126 mils,
or 17,500 bits/in^2.

All of the densities to be cited, for both A.C.M.
and the other technologies, are subject to improvement.
For example, current A.C.M. as available from ECD, and
developed by ECD and Intel, have the chalcogenide device
and its series p-n junction side by side. A more refined
version places them on top of each other. Nevertheless,
there is a basic distinction between A.C.M. and the other
silicon technologies. For all the other approaches,
current flow and power dissipation in the device can be
reduced as the device cross-section is reduced. The A.C.M.
device, however, in its low-resistance state uses a fila-
ment cross-section independent of the device area, and
neither its heat dissipation nor its current demand can be
decreased by analogous techniques. It is, therefore,
important to discover ways of reducing A.C.M. current

requirements. Since the present chalcogenide device involves very high reset currents, high-device densities will probably require such a current reduction. Even at the present density (Nea 70a, Hel 71), steps had to be taken to prevent an excessive voltage drop within the diffused semiconducting regions, which are used to give access to the devices in one of two perpendicular directions leading into the array. These semiconducting "lines" could, of course, be replaced by much more highly conducting metallic lines, resulting in a chip with two layers of perpendicular transmission lines insulated at their cross-overs. This is a more complex and expensive technology but certainly one worth considering. But even with the metal lines, with densities of 10^6 bits/in^2 (potentially feasible in some of the other technologies to be discussed), there would be difficulties (Mat 71). This density would require the feeding of 200 mA through a line perhaps 0.2 mil by 1μ thick. The high current density of 4×10^6 amps/cm would then lead to electromigration problems in the metallic paths (Ame 70). Of course, electromigration need not be a problem if the memory is to have its content reset only very occasionally and thus is subject primarily to the much smaller read currents.

In comparing bit densities for the various silicon chip technologies, it must be borne in mind that most current memory developments work with chips in the same general size range (somewhat over .01 in^2). As a first approximation, it is therefore reasonable to compare

bits/chip instead of bits/in^2. A number of recent collections of papers on integrated circuit memories (SS 70, IE 71, Com 71, SSC 71) yield the following chip densities, to be compared to the current 256 bits/chip for A.C.M. (without decoding on the chip in the case of A.C.M.):

(a) 128 for a high performance bipolar transistor memory cell, with decoding on the chip. [One company (Cog 71) has announced a 512 bit chip, and a trade press publication refers to another company's plans for a 1,024 bit chip (El 71a).]

(b) 256 for a high performance bipolar transistor memory cell, without decoding on the chip.

(c) 256 for Insulated Gate Field Effect Transistor memory cells, with decoding on the chip, and using six devices in each cell.

(d) 1,024 for an Insulated Gate Field Effect Transistor circuit, using 3 devices per bit, and including peripheral circuitry on the chip. This circuit does not have steady state bistability and its content must be refreshed every few milliseconds. This is typical of the extent to which an extreme degree of "volatility" is accepted for the sake of density. [A trade press column (El 71b) refers to a 1 device/bit cell, leading to a 2,048 bit chip.]

(e) 8,192 bits for Insulated Gate Field Effect Transistors used in a Read Only Memory. Unlike the A.C.M., this device has its content permanently set in the factory.

[A trade press report (El 71c) refers to 8,192 bits also obtainable with bipolar transistors.]

All of the above densities (a)-(e) can be expected to increase as the state of the art of photolithography used in the manufacturing process improves.   Densities closely approaching that of (e) above can be reached in other ways without sacrificing the ability to change the information content of the memory. In several recent proposals (SSC 71,San 70,Eng 70), charges are moved across a silicon surface, under the control of electrodes applied to an oxide over the silicon, and without taking the current in and out of the silicon. These devices thus store information (presence or absence of a charge) in a delay line, without taking the charge in and out of the silicon surface. One to two square mils per stored bit are required. These charge transfer proposals do not permit random access since the bits are passed sequentially through the read apparatus. Thus very long delays are involved in the readout process. These devices also lack steady state bistability and information must be continually circulated and regenerated to prevent it from disappearing. Furthermore, the intrinsic device speed (transfer of one bit) is also somewhat lower than in the transistor arrays listed in (a) through (e) above. Very similar systems compromises are involved in the use of cylindrical magnetic domains or "bubbles" (Bon 70). These are also used in a delay line scheme, and also involve basic time constants long compared to those of the transistor memories. Bubble memories have been operated at data rates of 10^6 bits/sec. (Fisc 71),

and with bit densities in the $10^6/in^2$ range (Shi 71).
Bubble memories are volatile only if the d.c. bias field
they require is supplied through an electromagnet.

We shall now go on to describe three devices
probably utilizable on a silicon chip, which have the
potential of yielding very high densities without sacri-
ficing random access, and which require at most a very
limited sort of regeneration. All three devices are
relatively novel and are, perhaps, less clearly understood
and under control than the chalcogenide devices. All of
these devices have the potential of allowing bits to be
about a mil apart, i.e., giving densities $\sim 10^6/in^2$ with a
silicon technology whose smallest controllable surface
dimensions are 0.2 mils. As the manufacturing capability
in silicon progresses, all of these technologies can be
expected to advance in density.

1.   The Metal-Nitride-Oxide-Semiconductor device
(MNOS) (Fro 70). This is a field effect transistor in
which the gate insulator is a two-layer sandwich. A thin
SiO_2 layer next to the silicon has a thick Si_3N_4 layer
superimposed. The gate electrode can cause tunneling back
and forth between states at or near the interface of the
two insulators and the silicon surface, and thus can "set"
the device in one of two modes of operation. This device,
in the reading process can be about as fast as the other
high-speed silicon technologies we have discussed. It is
not equally clearly a fast "write" device, requiring a
fair fraction of a microsecond in a system with reasonable

parameters. Like A.C.M., it involves voltages (20 to 40 volts) that are higher than those required by transistor memories and is, therefore, more demanding on the peripheral circuitry. But, as in the case of the A.C.M., these voltages are certainly within the range of achievability. The charges at the interface can leak away slowly over a period of perhaps months. Thus the memory is not completely nonvolatile. Only one device per memory bit is required. The area per bit has not been clearly defined as a result of a detailed proven design, but would not be far from the optimum obtainable for a given silicon capability, e.g., 1.0 square mil for a 0.2 mil resolution capability (Mat 71, Te 70).

2. Heterojunctions. Memory effects have been observed in ZnSe-Ge heterojunctions, in which the resistance can be switched from low to high values (Hov 70,71). Similar, but less well-studied effects have been obser ed in GaP-Si heterojunctions. Of these, the GaP-Si system would, of course, be of greater technological appeal since the integrated silicon technology is much more highly developed than the corresponding germanium technology. Switching times into the low- and high-resistance states are respectively 100 ns and 10 ns. Switching voltages and cu rents are of the order of 1 volt and 1 ma. These dَ ces are, therefore, fast and low-powered compared to A.C.M. Unlike A.C.M., switching in the heterojunctions requires polarity reversals. This causes more demanding specifications on the diode in a memory, which will have

to be put in series with each device. Uninterrupted
switching of the heterojunction at frequencies above 500k
Hz causes problems. The information state of the hetero-
junction is not as unconditionally stable as in the A.C.M.
and it may require some very occasional regeneration. The
simultaneous appearance of strong polarity effects,
switching ease, and poorer information stability sug-
gests more purely electronic phenomena than in the chal-
cogenide device. The heterojunction technology, like the
MNOS device, could be expected to lead to a near minimum
cell area for a given state of silicon technology. The
device does seem to depend on some kind of filamentary
action and is, therefore, not completely "scalable." On
the other hand, the filament current is much smaller than
in A.C.M. and, therefore, should be less of a problem.
Some "forming" treatment is typically required by these
devices, more clearly than by the chalcogenide devices,
but not as clearly as for the next device to be discussed.

3. $\underline{Nb-Nb_2O_5-Bi\ Junctions.}$ Switchable resistances
have also been observed in anodized amorphous (i.e.,
crystallites < 20Å) Nb_2O_5 with a bismuth counterelectrode
(Herr 71,Bas 71). A real "forming" process is involved
resulting in a permanent filament of about $2\mu^2$ cross-
sectional area in which structural changes have occurred.
Just as in the heterojunction,device polarity reversal is
required. The switching time into the high-conductance
state is 10 ns or less. Switching time into the low-
conductance state is a complex function of forming

treatment and previous pulse history but probably can be
kept below 1μ second. Switching voltages are about 1 volt
as in the heterojunctions. The switching currents are
still smaller, of the order of 0.1 ma. The stability of
information in these devices has not yet been well charac-
terized but there are indications that the information can
deteriorate over a period of weeks. As in the case of the
heterojunctions, all of this is suggestive of a more
purely electronic mechanism than in A.C.M.

Optically Addressed Memories

Any consideration of optically addressed memories
must take into account the prevailing technology: magnetic
surface recording which is written and sensed through flux
changes. (Some of the optical memories also invoke magnet-
ization changes but we shall use "magnetic recording" to
signify this classical inductive form.) Magnetic recording
utilizes tapes, drums, and disks as well as a number of
other geometrical forms. As in the case of the wired
memories, bit density is a key index to the usefulness of
the technology. Optical technologies are limited by the
wavelength of light. The achievement of greater density
in magnetic recording has been a slow and painful process.
Development activity is directed toward obtaining smaller
dimensions for the thickness of the magnetic layer, for
the gap in the head, and for the spacing between head and
magnetic layer, all without risking too much wear between
head and surface. This involves ingenuity in signal
coding methods, which eliminates the need to record through

the whole thickness of the magnetic layer.

Where is this technology currently? An existing commercial disk system (PP 70) has about 4,000 bits per inch along the track, 200 adjacent tracks per inch, giving an areal density of $0.8 \times 10^6/in^2$. Data is read out from one head at about 6.4×10^6 bits/second. Advanced existing tape systems (Hu 70,Dam 68) have very similar areal densities and data rates.

It is widely accepted that progress in magnetic recording beyond this status is possible. One prediction (Hopn 69) anticipates densities of 5×10^7 bits/in^2. Densities along the track as high as 40,000 cycles/in were achieved in audio recording over a decade ago (Bro 60). In more modern digital applications, 16,000 bits per inch (Auf 70) have been achieved. The miniaturized heads required by greater track density may also lead toward new methods of head manufacture, more akin to semiconductor processing technology than to mechanical assembly (Rom 70). Such integrated head arrays could provide the capability of placing one head over each track, thereby eliminating the need for track-to-track motion. (This is routinely done today in low track density drums and disks.)

Optical storage proposals are either holographic or else direct digital. The holographic schemes handle large digital arrays in parallel and this gives them a great deal of system appeal (Ra 70). The parallelism, however, also leads to a more demanding set of requirements than when handling only one bit of information at a time.

At the current time, even the direct digital schemes have
shown feasibility in only a marginal way. With this in
mind, we shall, in the following discussion, orient our-
selves more toward the direct digital schemes.

Direct digital optical schemes are investigated
largely because they offer promise of a higher track density
and also perhaps permit quicker switching and servoing of
the transducer in its track-to-track motion. They may not
be, in the long run, competitive with magnetic recording
in density along the track. For a given area density, a
high density along the track is more desirable since it
gives higher data rates (for the same relative velocity
between transducer and recording medium), and fewer tracks
between which switching is required. Thus it is not enough
for optically accessed memories to provide higher track
densities at the expense of a lower density along the track.
The optical scheme must provide either a much faster track-
to-track switching time (e.g., by replacing mechanical
motion with electro-optic or acousto-optic deflection at
modest cost), or else must provide a _much_ _higher_ density
of bits.

The general resolution capability of optical
schemes is well illustrated by a storage system called
Unicon being developed by Precision Instruments (PI 70).
In this system, a laser is used to vaporize, or perhaps
melt, spots in a metal film. This is a scheme in which
information cannot be erased, once written. All other
things being equal, one would, of course, much prefer a

reversible storage medium. In this system, bits are about 3μ apart along the tracks and 8μ apart between tracks, giving about 25×10^6 bits/in^2. Three microns may well be the limit for a practical system in which a depth of focus has to be preserved in the presence of large moving surfaces. Furthermore, the 8μ is also likely to be characteristic of the fact that for reasonably easy track servoing, the tracks should be further apart than the bits along the track. The data rate is 4×10^6 bits/sec. It is therefore the track density, and only the track density, which is impressive compared to current magnetic schemes.

As another standard of comparison for optical technologies, we may also mention a kind of ultra-high density phonograph record developed for home display of previously recorded television programs (Gil 70). It is one of several technologies currently being developed for this purpose (Boy 71). This disk is stamped in a factory. It is not recorded in real time or erasable. It is thus representative of a much more limited technology than the others discussed in this section. This disk, however, has an information density of 3×10^8 bits/in^2 (using an FM scheme with more than one bit of information per hill and valley).

A great many proposals for reversible optical media have been made utilizing photochromic effects, photoconductor-thermoplastic combinations, color center alignment, and optical damage in LiNbO$_3$. We shall here consider only a typical subset of relatively active

contenders. These are Ferroelectric-Photoconducting (FE-PC)
combination sandwiches, thermomagnetic schemes, and the
amorphous chalcogenides.

The FE-PC schemes (Chapm 70, Ken 70a, Ken 70b) use
light to control a photoconducting current which, in turn,
controls the switching of a ferroelectric. The ferroelectric
can be read electrically (Chapm 70) or optically (Ken 70a,
Ken 70b). It should be noted that 1.26μ gratings have
been recorded in the ferroelectric, demonstrating the high
resolution capability of the scheme. This scheme can, in
principle, be very sensitive in the writing process since
it can utilize the gain of a photoconductor. It is, there-
fore, a particularly likely candidate for either holographic
schemes, or for schemes that dispense with the laser and
its accompanying complex optical deflection methods in
favor of the readily deflectable spot on a CRT. It is
also a system that may suffer from the long decay time of
the photoconductor. However, this need not be a crucial
problem, with a sensible over-all systems design. This
proposal involves two technologies (ferroelectrics and
photoconductors) that have both been beset by a long
history of difficulties in precision applications and it
is likely to require a major materials effort.

The thermomagnetic schemes (Esc 70, Mag 70, Hu 70)
use a laser beam simply to heat a material to or through a
Curie point or compensation temperature at which an applied
magnetic field can switch the material. Reading is done
magneto-optically. A particular sensitive magneto-optic

proposal has been developed utilizing doped EuO (Far 71,
Pat 71),but at the expense of having to keep the medium
at liquid nitrogen temperatures. The EuO memory has been
demonstrated under conditions resembling those of a
practical memory with densities along the track of 3,000
bits/inch, areal densities of 4×10^6 bits/in^2, and data
rates of 5 Mb/sec. It is probably the only one of the
optical schemes that has been shown to operate at rates
comparable to those already existing in commercially avail-
able magnetic recording. The EuO scheme can also be
utilized with a GaAs laser that exists in the form of
integrated arrays of many lasers. Thus the EuO scheme can
eliminate or minimize the need for light deflection schemes
or mechanical transducer motion.

The amorphous chalcogenide proposal (Fei 71,
Ad 71a) has already been discussed. The fact that the
laser written spots are very small (2 to 3μ) is attractive.
The time and energy requirements that have been demonstrated
are not yet very impressive but the technology is at such
an early and poorly understood stage that one can hope for
major improvements. Amorphous chalcogenide films can be
given much greater sensitivity (Ov 71b) if a subsequent
development step is allowed. While a development step is
not easily included in high-speed digital equipment, it is
not completely out of the question, especially if it can
be accomplished in milliseconds.

In addition the following points should be noted:

1.   The change in refractive index, which is available for detection in the readout process, is much larger for the amorphous chalcogenide films than for the magnetic or ferroelectric devices.

2.   In any complete or partial thermal scheme involving, for example, thermomagnetic or crystallization methods, in which thin films are continually and rapidly cycled over appreciable temperature excursions, there must be some concern about the effects of thermal strain on the adhesion and integrity of the thin film.

3.   The amorphous chalcogenide crystallization process has so far resulted in far cleaner demonstration experiments than any of the other optically addressed materials (Ov 71a).

Order of magnitude estimates for the sensitivities during the writing process are as follows:

a)   Crystallization of amorphous chalcogenides 10^{-1} joules/cm^2

b)   Europium oxide 10^{-1} joules/cm^2

c)   FE-PC observed (with a photoconductor
        gain well below unity) 10^{-3} joules/cm^2

d)   Amorphous chalcogenides with development 10^{-5} joules/cm^2

e)   FE-PC calculated (on the basis of observed
        photoconductor and ferroelectric
        properties, but not in actual sandwiches) 10^{-6} joules/cm^2

In connection with these figures, it must be remembered that a purely thermal scheme, such as that involved in EuO storage, is not susceptible to really dramatic further improvements in sensitivity. The erasure process in (Fei 71) may also fall into the same category.

Sensitivity is a critical parameter only if the available light is limited. In an arrangement having only one laser per system, writing on only one spot at a time, sensitivity may not be a critical problem.

VIII. GENERAL OBSERVATIONS AND RECOMMENDATIONS

General Scientific Interest

The field of amorphous semiconductors is sufficiently challenging and difficult to occupy experimentalists and theorists for some time to come. It is important both in connection with the general study of disordered systems as well as the established usefulness of glasses. Indeed, there has been considerable growth of the R&D effort and a marked increase in the scientific interest in the area of disordered materials during the last few years. This comes appropriately at a time when, after forty years of concentrated effort, a remarkably high level of scientific understanding and technical use of crystalline materials has been achieved.

1. In view of the absence of a fully developed conceptual framework for the science of amorphous semiconductors, the Committee believes that close collaboration between experimentalists and theorists is essential for further progress in the field. Experimentalists should be encouraged to choose investigations that might differentiate between various theoretical models. Similarly, theorists should concentrate their efforts in areas where results are subject to experimental verification.

2.   <u>Although the development of simplified models
has been extremely useful, it is desirable that more
attention be focused on calculations of electronic potentials,
energy levels, and transport properties directly applicable
to physically realized glass structures.</u> Initially, these
would require large-scale computer calculations. As pointed
out in this report, such programs are now in their beginning
stages. Hopefully, it will be possible to extract from
this body of experience some simpler approaches and models
that yield semiquantitative results which can be compared
with experimental data. It is particularly important to
inquire how the short-range order in an ideal glass
determines the band structure and whether there are features
of the density-of-states near the band edge that are general
for various classes of amorphous materials.

3.   <u>Experimentalists should realize that not all of
the highly rewarding measurements on crystalline materials
are necessarily fruitful when applied to amorphous semi-
conductors.</u> Efforts should be concentrated on the acqui-
sition of high-quality physical data (transport, optical,
magnetic, etc.) that challenge theoretical interpretation.

4.   <u>Coordinated experimental programs should be
encouraged where all aspects of preparation, characterization
and measurement are addressed, results correlated, and
cause and effect relationships pursued and understood.</u>

Preparation, Characterization, and Sample Reproducibility

1.   It is essential to develop a more widespread awareness of the methods of material preparation and characterization, since the structure and properties of an amorphous material may depend intrinsically on the method of preparation. It is commonly believed that simplicity of sample preparation is an advantage of these materials as compared to crystals. While certain aspects of sample preparation may be simpler, there are also many special problems peculiar to amorphous semiconductors. Presently available characterization tools should be applied more broadly and new tools should be developed which are useful, especially in the microscopic structure region where diffraction techniques are now inadequate.

2.   Publications should include details concerning preparation, characterization, and measurement sufficient that both samples and measurements on them can be reproduced at other laboratories. In particular, items known or suspected to affect property measurements directly and estimates of purity and impurity effects should be delineated.

3.   Efforts should always be made to distinguish between experimental properties that are characteristic of the actual materials and artifacts, perhaps resulting from poor material preparation. It is presently impossible to specify the actual structure of a given sample completely. The following suggestions may help to overcome these difficulties:

(a) One should try to distinguish between
properties that are largely structure
sensitive and structure insensitive. Useful
information will emerge from investigations
comparing bulk quenched and thin film samples
of the same material, and examining the
effects of various sample treatments such as
quenching and annealing.

(b) The reliability of experimental observations
should be ascertained by

    i) performing several kinds of
    experiments, for example, transport
    and optical, on the same sample

    ii) studying the same effect for a
    group of homologous materials in
    order to ascertain whether the
    observed trends are physically
    reasonable.

(c) Samples may be, and probably are, macro-
scopically inhomogeneous in many cases.
The possible existence of voids and phase
separated regions should be recognized and
examined experimentally. Inhomogeneities
may influence the experimental results and
their interpretation profoundly.

4.   It is important to encourage an exchange of
samples among different laboratories to permit identical
measurements using different apparatuses as another check
on reproducibility. Such "round robin" measurements and
subsequent discussions among the investigators involved
would serve to clarify questions concerning preparation
difficulties and to pinpoint the sources from which dis-
agreements on measurements might arise. For example,
ambiguities involving very small Hall voltages, to the
extent they exist, might well be clarified in this way.

5.   A better understanding of the dynamics of the
preparative process is needed. Areas receiving very little
attention to date, but of potentially great significance,
are the vaporization, vapor transport and condensation
processes so frequently used in sample preparation. Solid-
liquid-vapor equilibria data, deviations from equilibrium
introduced by various low- and high-energy evaporation and
sputtering methods, and energy losses during and after
condensation could yield significant information about the
glass structure and structural variations among samples.
Special attention should be given to simple monatomic and
binary systems representative of chain, layer and network
structures, and the comparison of bulk quenched with thin
film samples.

Atomic and Electronic Structure

1.   The Committee recommends that investigations
directed toward better understanding of how to control the
evolution of structure in amorphous semiconductors, e.g.,
by crystalli-ation or phase separation, be strongly
encouraged.   Two of the most promising categories of study
in this area are:

> (a)   catalysis of crystallization by photons,
>   trace impurities, or electric fields,
>
> (b)   thermodynamics, kinetics, and morphology of
>   phase separation in chalcogenides.

This recommendation is principally motivated by the judg-
ment that some of the most promising applications of
amorphous semiconductors result from the ease with which
changes in the spatial distribution of phases with
different properties can be produced.

2.   Studies of the generation, manually or by
computers, of random network models and their dynamic
evolution, should be extended, especially to 3-coordinated
systems and to systems of two or more components in which
the coordination is mixed.   Where possible the methods of
generating these structures ought to be designed to
simulate conditions that might obtain in actual deposition
processes.   Further, the annealing processes following the
generation of the structure should be followed by molecular
dynamic studies.   These studies can provide important
insights into the atomic and electronic properties of the

ideal structures as well as the occurrence and properties of defects in the actual amorphous structures.

3. _Studies of those aspects of the theory of solid state cohesion which are especially pertinent to the amorphous state should be extended._ Important aspects are the effects of distortions from ideal bond angles and of dispersion of bond lengths on the cohesive energy and on the electronic structure of the system.

4. _There is a need for good measurements of the temperature dependence of the specific enthalpy and volume of amorphous semiconductors, especially chalcogenides._ Such data, from which the entropy can be calculated, are often crucial for the testing of models for the amorphous state. While available for some molecular and oxide glass formers, they are quite sparse for chalcogenides.

5. _Careful diffraction and spectroscopic studies in conjunction with precise density measurements can greatly delimit the acceptable models for the structure of an amorphous system._ Research on structure determination, using the many excellent spectroscopic and diffraction techniques now available should be continued. However, the Committee recommends that more emphasis be placed on

> (a) techniques for minimizing Compton modified scattering in X-ray studies,
>
> (b) neutron scattering studies, and
>
> (c) application of scanning electron diffraction techniques to studies of t structure of thin amorphous films.

Radiation Hardness and Radiation Induced Defects

One of the unique properties of amorphous semi-conductor devices is their low sensitivity to high-energy radiation. There is relatively little in the published literature pointing to extensive investigations of this effect. In view of this, <u>further and more complete investigations to explore radiation hardness and the reasons for its existence will be of interest</u>. Tests should be made not only on different devices and geometries, but also on the amorphous materials themselves. From a more fundamental point of view, such investigations should also answer questions about the nature of radiation induced defects and the electronic states produced by them.

Device Oriented Physics

1. <u>The Committee underlines the importance of continuing and initiating research aimed at the technological exploitation of the unique properties of amorphous semiconductors</u>. While the semiconducting and photo-conducting properties of these materials will continue to be a source of application possibilities, the ease with which phase changes can be induced through a variety of influences should particularly motivate invention and exploration. Recent demonstrations of applications based on light induced phase changes (crystallization and phase separation) suggest that this is the beginning of a field rich in possibilities.

2.   In view of the continuing uncertainty about the
relative role of electronic and thermal switching mechanisms,
it is important to provide information that can distinguish
between them. Although there is still great uncertainty in
the formulation of an electronic switching theory, the
precise consequence of a purely thermal theory can be
worked out at the present time. Such a calculation must
take into account the specific device geometry and the
non-linear electrical conductivity of the device material.
More detailed experimental data on the dependence of device
behavior on thickness, temperature, deposition parameters,
composition, and time sequence of electric fields are also
needed.

Level, Scope, and Support

In recent years, the influence of N.F. Mott and
S.R. Ovshinsky and his collaborators has had a particularly
strong catalytic effect on the interest in and the develop-
ment of the area of amorphous semiconductors in this
country. Some indication of the present level of research
activity in this field and its growth is provided by an
examination of contributed papers presented at the Fourth
International Conference on Amorphous Semiconductors
(Ann Arbor, 1971) and a comparison with previous conferences.
Of 126 papers, roughly a third originated abroad. These
represent work performed at 40 laboratories in the United
States and 31 laboratories in 13 foreign countries. Of
the U.S. papers, 40 percent, 50 percent, and 10 percent

originated respectively in industrial, academic, and government laboratories. About half of the U.S. work was supported by government funds. In terms of numbers of submitted papers, the 1971 Conference exhibits a substantial increase over the size of the preceding Conference held in 1969, and thus reflects a marked increase in activity. The subject matter of these papers encompasses a broad range extending from the sort of fundamental work described in Sections II and V of this report, to technologically motivated research, such as that typified by Section VI. These international conferences have been most useful in bringing together active contributors and in summarizing the state of research.

Considering the broad range of present and future applications of amorphous materials (from windows and coatings, to electronic, optical, and ultrasonic devices), the Committee urges that a sizable effort or high-quality research regarding the physical, chemical, and engineering properties of amorphous materials be encouraged. The present level of financial support should be maintained and probably increased somewhat, in order to insure a continuing growth of the field. In connection with the more fundamentally oriented activities, it seems particularly important to encourage research dealing with reproducible experiments on well-characterized materials, and to discourage work concerned with uncritical and often ill-considered isolated measurements of one or two effects in poorly prepared materials. Such measurements are unlikely to be reproducible and their report in the

literature may well be counterproductive. While some
excellent and high-quality work is being carried on at
many laboratories, there is unfortunately still too much
information that is produced and accepted by the scientific
community without proper critical appraisal. The field of
amorphous materials is certainly far more complex than
the physics of crystalline materials but the standard of
excellence characte· izing research in the latter field
shculd be regarded as a hopefully attainable ideal.

While there have been substantial efforts in
some established areas, such as materials for photocon-
ductive applications, the total level of industrial support
for the remainder of the field is by itself too small to
ensure continuing development. Many companies are con-
ducting small monitoring operations which, to be sure, are
frequently of high quality. Except for ECD, few seem to
have a major commitment to this area at the present time.
Since the field of amorphous semiconductors has a techno-
logical potential whose impact cannot yet be accurately
predicted, support by governmental agencies should be
continued. This could be effectively spread over govern-
ment, industrial, and university laboratories. For
example, more fundamental research of the type that can
be profitably pursued at universities is needed. On the
other hand, the more technological aspects might well be
investigated more intensively in industrial or in-house
government laboratories.

Optimal support of research on amorphous materials will lead to both a better understanding of the disordered state as well as a clearer assessment of the technological potential of devices incorporating amorphous materials.

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IX   REFERENCES

The convention for references is the following:
Each paper is identified by giving the first two letters
of the author's name and the year of publication. When
necessary, as many additional letters are provided in order
to resolve remaining ambiguities (e.g. Mo = Mott, Mor =
Morgan). When several papers involving the same first author
have appeared in one year, they are distinguished by lower
case latin letters (e.g. 70a, 70b, etc.). Preprints for which
the year of publication is not yet known are labeled by a
dash following the author code (e.g., Hei -). Review or more
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