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SPRING COLLEGE ON AMORPHOUS SOLIDS
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ELECTRONIC TRANSPORT IN NON-CRYSTALLINE SEMICONDUCTORS

(Part IV)

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What are Non-Crystalline Semiconductors

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1. Introduction

We are presently participating in the development of a fascinating new field of solid-state physics. Although glasses have been known for over 10,000 years and during the course of a day you are likely to encounter more non-crystalline than crystalline solids, there is hardly a solid-state textbook which mentions glassy or amorphous materials. The beginning of our field is difficult to pin down. In the 1950's KOLOMIETS [1] showed that chalcogenide glasses behaved like intrinsic semiconductors and that their electrical conductivity could not be increased by adding dopants. In 1957 SPEAR [2] reported the first drift mobility measurements in vitreous Se and TAUC [3] reported the first studies on amorphous Ge in the early 1960's. Many more scientists were drawn to our field through the work of OVSHINSKY [4]: the discovery of switching and memory effects in chalcogenide glasses. These as well as optical memory effects, imaging, photodoping, and the reversible photostructural changes suggested possibilities for new applications of non-crystalline semiconductors. These phenomena demonstrated that there was a large field of material science which was virtually unexplored.

The scope of our field was further widened by the discovery of SPEAR and LeCOMBER a few years ago [5] that glow-discharge-deposited amorphous Si can be doped both n-type and p-type. This material contains a sufficiently low concentration of defects that it is now the most interesting prototype amorphous semiconductor. Furthermore, it promises application for cheap and large area photovoltaic and photothermal devices.

In this paper I shall first discuss some important concepts which clarify the fundamental difference between the two main classes of noncrystalline semiconductors, the glasses and the amorphous films. In this discussion I shall call a glass only those materials which can be quenched from the super-cooled melt and usually exhibit a glass transition. The term amorphous will be restricted to noncrystalline materials which can normally be prepared only in form of thin films by deposition on substrates which are kept sufficiently cool to prevent crystallization. In the remainder of the paper I shall employ these ideas in a survey of some of the major problems confronting us in the study of noncrystalline semiconductors.

2. The Homogeneous Random Covalent Network

The atoms are completely disordered in a gas but not in noncrystalline semiconductors. Here the chemical nature of the atoms dictates the directed covalent bonding arrangements to their nearest neighbors. The first model of an ideal glass, shown in Fig. 1a, was proposed by ZACHARIESEN [6] in 1932; the figure is a two-dimensional representation of an A_2B_3 glass such as As_2S_3.

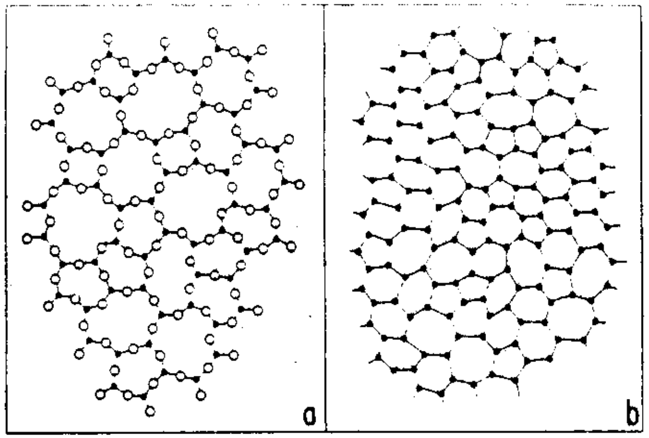


Fig.1a,b Two-dimensional continuous random network. (a) ZACHARIASEN's diagram for an A_2B_3 glass, (b) threefold-coordinated elemental random network

A definite short range order is imposed as each atom fulfills its chemical valency requirement according to the 8-N rule. Stronger heteropolar bonds (As-S) are favored over homopolar bonds (S-S,As-As) and the bond lengths are within 1% the same as those found in crystals. The figure illustrates that there are even and odd membered rings of different sizes. This type of disorder affects the electronic states near the band edges as explained by YONOZAWA later [7]. Another major element of randomness is the variation in bond angles. There we come to a very important point which leads to a differentiation between glasses and amorphous materials: the flexibility of covalent bond angles is largest for the two-fold coordinated group VI elements and least for the tetrahedrally coordinated group IV elements. The reason for this is the greater variety of admixture from other atomic orbitals to the covalent bond when the coordination number is less than the number of valence electrons. In SiO_2 glasses the oxygen atoms bridging the Si tetrahedra provide the essential flexibility which is needed to form a random covalent network without much strain. If one attempts to form a covalent random network without the flexing bridges of group VI elements one obtains amorphous Si which is highly overconstrained and no longer a glass. In Fig. 1b this step is illustrated by showing amorphous As because the structure of glassy SiO_2 and of amorphous Si are not easily sketched in two dimensions.

The concept of a homogeneous random network has been extensively used in theoretical studies for both amorphous and glassy semiconductors [8-10], but it fails to encompass the fundamental difference between the two classes of materials. This difference, which is essentially due to the mismatch between bonding constraints and the number of degrees of freedom in three dimensions, and to the flexibility required to accomodate the mismatch, has been treated quantitatively the PHILLIPS [11] as follows.

Consider a binary alloy A_xB_{1-x} with only the short-range bonding interactions. Further let us introduce the average coordination number m defined by

$$m = xN_{cn}(A) + (1-x)\,N_{cn}(B) \qquad (1)$$

An empirical justification for this procedure will be presented later. The number of constraints N_{co} per atom is then given by

$$N_{co}\ (m) = m/2 + m\ (m-1)\ /2 \tag{2}$$

$$= m^2/2 \tag{3}$$

The first term on the right hand side of (2) is given by the bond stretching interaction and the second term by the bond-bending interactions which are assumed for simplicity to be equal for the A and B atoms. Equating the number of constraints to the three spatial degrees of freedom, $N_{co} = 3$, PHILLIPS obtains an average coordination corresponding to an optimal connectivity [11],

$$m_c = \sqrt{6} = 2.45 \tag{4}$$

Hence the glass-forming tendency is greatest when the short-range order imposed by bond stretching and bending forces is just sufficient to exhaust the local degrees of freedom. In Fig.2 we sketch a classification of non-crystalline solids based on these concepts. The average coordination m is shown decreasing from left to right because of the familiar arrangements of atoms in the periodic table. On the left-hand side of m_c the internal strain increases with m; toward the right, the entropy increases with decreasing m because the materials become insufficiently crosslinked. Glasses are normally restricted to $3>m\geqslant 2$. Materials with higher connectivity $4\geqslant m\geqslant 3$ are overconstrained amorphous. Those having lower connectivity $m<2$ are undercrosslinked amorphous. Examples of this latter group are amorphous films of I_2 and Br_2, presently being studied by LANNIN [12], and amorphous films of inert gasses. The mean coordination m = 4 separates noncrystalline metals from semiconductors or insulators.

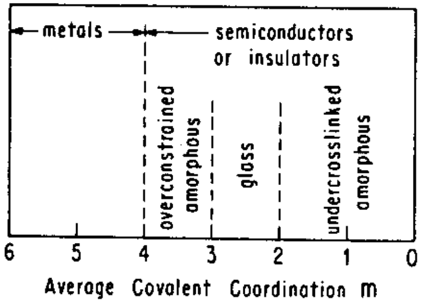


Fig.2 Classification of non-crystalline solids

This classification suffers as any other from uncertainties around the borderlines, near m = 3 and m = 2 for instance, since long range interactions, ionicity and size effects are neglected in this simple picture. Moreover, an interesting exception to the rule set forth by PHILLIPS is the class of materials known as tetrahedral glasses [13], which are obtained by quenching the melt of compounds such as $CdAs_2$, $CdGeAs_2$, and $CdGeP_2$. These have average coordinations m = 4. It appears that $A^{II}C_2^{V}$ is the essential building unit of these glasses since the concentration of group IV elements can be varied over wide limits.

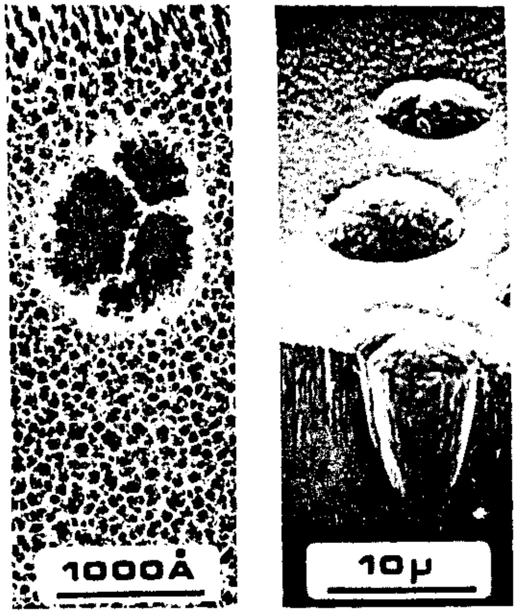
I discussed the homogeneous random covalent network to emphasize the prevalence of short-range order and the distinction between amorphous and glassy materials. Strong doubts are presently being raised regarding the homogeneity of non-crystalline materials.

3. Topological and Compositional Heterogeneities

Even glasses with average coordination $m \simeq m_c$ contain a considerable strain energy. A measure of this energy is the difference in heats of solution between the glass and the corresponding crystal or the enthalpy of crystallization. 2.16 Kcal/mol are found for example for the enthalpy difference between vitreous silica (m = 2.67) and α-quartz, and 1.52 Kcal/mol when compared with α-cristobalite [14]. The origin of this energy is to be found not only in the variations in bond angles and to a smaller degree in bond lengths, but in accumulation of strain of longer range forces and van der Waals interactions associated with lone-pair electrons of Group V and VI elements in the bond-free directions. This strain energy can be uniformly distributed, but a lower energy state can also be established by forming low-strain grains or islands or strain relieving voids. Thus a network of voids is found in the highly overconstrained amorphous films of evaporated Si and Ge, as evidenced by the large density deficit (10-15%) of these materials with respect to their crystals and by small angle X-ray scattering [15], electron microscopy [16], and by porosity studies [17].

Another example of heterogeneity is the hydrogen-rich interconnecting tissue in the granular structure of glow-discharge deposited a-Si:H alloys [18]; both columnar and pebble-like morphologies are easily seen on electronmicrographs for certain growth conditions [19], as shown in Fig.3. NMR studies reveal compositional heterogeneities even in a-Si:H films which appear homogeneous under the electronmicroscope [18]. A further example of large-size domain formation in a 600 Å thick evaporated film of As_2Se_3 is shown in Fig.4. This transmission electronmicrograph [20] shows hexagonal domains which have diameters of 1000 ± 100 Å and are separated by about 30 Å wide troughs which nearly penetrate through the film. Even though evaporated films do not have the fully polymerized and crosslinked structure of relaxed bulk glasses, those domains may possibly demonstrate the accumulation of strain energies from long range interactions and a subsequent strain-relief mechanism in such thin films [21]. Once such a domain network is formed during film growth, the different surface mobilities of the gas phase constituents will likely lead to a connecting tissue with a composition which is different from that in the island or grains. Heterogeneities of this kind are then difficult to eliminate by annealing.

We now turn our attention to structural units in $GeSe_2$ and As_2Se_3 type glasses of the scale 15-30Å, i.e. the medium-range order. The presence of a very sharp first peak in the diffraction spectra of these semiconducting glasses has been associated with polyatomic, cagelike clusters containing 8-20 atoms or more [11,22]. UEMURA et al. [23] reported that the first peak of neutron diffraction spectra of some materials even sharpens as they are heated above T_g and that it is still observed above the crystalline melting temperature. This as well as the presence in vitreous GeS_2 of an extra A_1 Raman line which is absent from the Raman spectra of the crystals rule out a microcrystallite theory [22]. One difficulty in modeling the structure of these glasses is the great flexibility in the choice of the molecular units. This greater freedom of choice may actually be the basis for the glass-forming tendency. The similarity of the radial distribution or intensity functions [illegible] problem [24,25]. One [illegible] the random network model for As and insert a [illegible] As [illegible]. However, such a model would not [illegible] the layer like molecular units which make up the crystals.



(A) (B)

Fig.3 (a) Transmission electron micrograph of nodular feature in a-Si:H film prepared at 250°C with 25W power; (b) scanning electron micrograph of columnar growth features in a-Si:H film prepared at 230°C with 25W power. Courtesy of KNIGHTS [19]

Correlating the present data not only from diffraction but from infrared and Raman experiments, PHILLIPS suggests the presence of large molecular units shaped like outrigger rafts of various conformations [11,22]. At this point I can only draw attention to this ongoing work which attempts to describe the medium-range order that appears to exist not only in the glass but also above the glass transition temperature.

A strong medium-range order of a different kind is found in As_2S_3 and As_2Se_3 films deposited by evaporation [26-28]. This is illustrated in Fig.5 which compares Raman spectra of the bulk glass with those of an evaporated film before and after annealing [29]. Here the molecular units in the freshly deposited film derive from those present in the gas phase. Subsequent annealing produced polymerization toward the structure of the bulk glass and a decrease in the intensity and sharpness of the first diffraction peak.

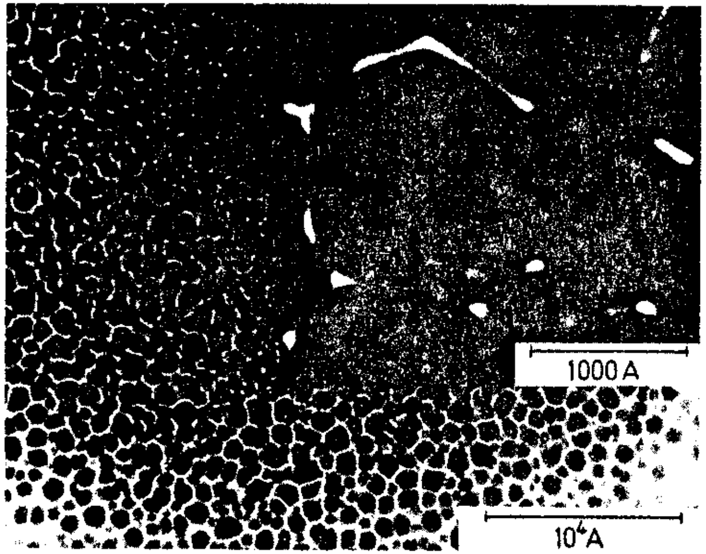


Fig.4 Transmission electron micrograph of domain wall network in a 600Å thick evaporated film of glassy As_2Se_3. The bright lines are deep troughs which are nearly normal to the plane of the film. Courtesy of CHEN et al. [20]

In this section I gave a few examples of the growing evidence for medium-range structure and heterogeneities in both amorphous and glassy noncrystalline materials. In the following I mention some basic differences between glasses and amorphous materials.

4. Glass Formation and Amorphous States

The melts of most crystalline solids have viscosities of less than 1 poise near the melting temperature T_m. The viscosity of water, in comparison, is about 0.1 poise. Some of these melts can be supercooled by perhaps 10-20 degrees below Tm but the presence of impurities or a slight disturbance will lead to rapid crystallization. A low viscosity facilitates the diffusion of atoms or molecules which is needed to transform the liquid into a crystalline solid. The melts of glass-forming materials behave entirely differently. Their viscosity increases rapidly with decreasing temperature [30] according to

$$\eta = \eta_0 \exp\left[-A/(T-T_0)\right] \tag{5}$$

and reaches a value of order 10^7 poise near T_m. Nucleation and growth of crystals becomes difficult and the supercooled liquid remains stable over several hundred degrees. Its viscosity continues to increase with decreasing T. Near $\eta = 10^{14}$ poise the supercooled liquid becomes a solid glass. The large increase in viscosity indicates that the structural units, mentioned in the previous section, are already formed during supercooling.

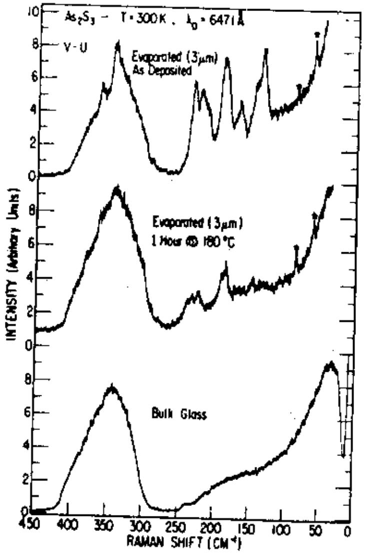


Fig.5

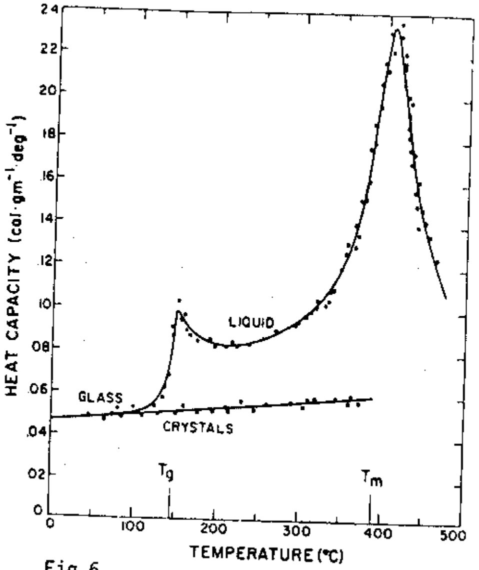


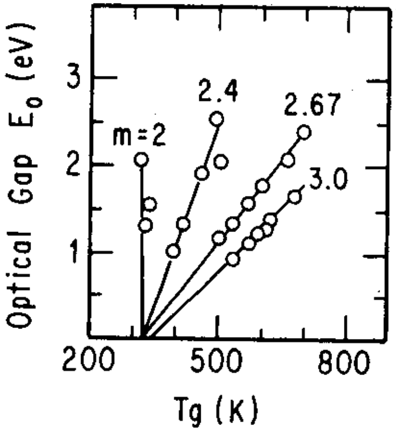
Fig.6

Fig.5 Raman spectra of (a) an evoporated vitreous As_2S_3 film, (b) after annealing at 180°C for 1 hour, (c) bulk glass. Asterics indicate instrumental artifacts. Courtesy of SOLIN et al. [29]

Fig.6 Heat capacity of glassy, liquid, and crystalline $Ge_{17}Te_{83}$ as a function of temperature. Courtesy of DeNEUFVILLE [33]

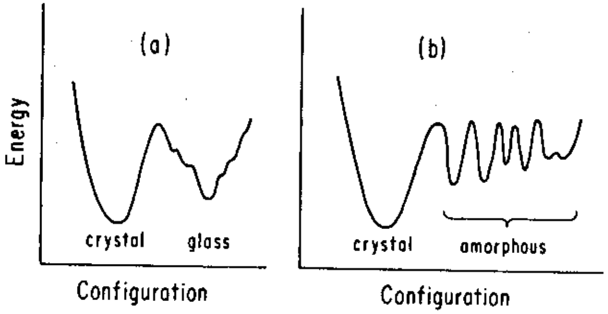
The process of glass transition which leads to the freezing of a supercooled liquid at $T=T_g$ into a noncrystalline solid (glass) is still an actively pursued theoretical problem [31,32]. Empirically the glass transition temperature can be measured with an accuracy of about one percent or a few degrees. As a glass is heated, abrupt changes in thermal expansion, compressibility, specific heat and other properties occur at the glass transition temperature T_g. This is illustrated in Fig. 6 for $Ge_{17}Te_{83}$, which is the eutectic composition of the GeTe-Te system [33]. At low T the heat capacity c_V of the glass and of the polycrystalline eutectic are equal to that of a harmonic oscillator solid. At T_g the glass becomes liquid. The additional motional degrees of freedom available in the liquid cause the sudden increase in c_V at T_g. Above T_g the structure of the supercooled liquid resembles that of the glass. As the temperature is further raised the structure of the liquid may change in a complicated manner. In the example shown in Fig.6 one observes a kind of order-disorder transition between 300 and 500K. The area under c_V peak centered at the melting temperature T_m of the eutectic is smaller than the heat of the fusion of pure Te. This suggests that vestiges of short range order still remain above T_m which may disappear when T is raised further [33]. I might remark here that metallic glasses do not show the characteristic increase in viscosity. Their melts remain very fluid, very high quench rates are needed to produce the non-crystalline solid, and glass transitions are very seldom observed.

An experimental justification for using the average coordination number m in characterizing the connectivity of semiconducting glasses is demonstrated in Fig.7 which shows the relationship between the optical gap E_0 and the glass transition temperature T_g. Materials, including elements, binaries and ternaries, but having the same mean coordination m, lie essentially on the same line; the other important parameter which distinguishes them is the average strength of the covalent bonds, which increases with increasing E_0.



◄ Fig.7 Optical gap as a function of glass transition temperature for semiconducting glasses having different average coordination m. After DeNEUFVILLE and ROCKSTAD [30]

Fig.8 Sketch of energy-configuration diagram of (a) semiconducting glass and (b) amorphous semiconductor ▼



A major theoretical difficulty in describing the conditions for and the kinetics of the transition between a supercooled liquid and a glass is that the glass is not a thermodynamical equilibrium state. Nevertheless the macroscopic properties of a large number of glasses are very reproducible. Unstable glasses which require extreme quench rates are exceptions and are excluded from this bird-eye-view discussion. This empirical evidence suggests that the energy depends on a general configurational coordinate as sketched in Fig.8a. The energy minimum of the glass lies higher than the minimum which corresponds to the crystalline state because of the strain energies mentioned earlier. The barrier between the two main minima represent the kinetic hindrance which prevents crystallization of the glass below T_g. Substantial atomic rearrangements are necessary to accomplish this. The subsidiary minima on the glass side of the sketch indicate less stable higher energy configurations for instance of evaporated glass films which can be converted to the minimum energy glass configuration by annealing near T_g.

The somewhat wild sketch of Fig.8b is intended to illustrate the situation for amorphous films. These can exist in many different configurations depending on the preparation techniques and for each technique on a variety of preparation and substrate parameters. In contrast to glasses, the amorphous films can exist in many non-crystalline configurational states. Annealing can lower the energy of a given amorphous film. However, it cannot transform the configuration of an overconstrained amorphous film from one state to another. Major atomic rearrangements would be required to accomplish this which lead instead to crystallization. This figure is meant to reflect our experience that even annealed amorphous films prepared in various ways are different. An additional cause for the observed differences are of course impurities which are unintentionally incorporated during growth. As discussed above, the minimum energy of the homogeneous random covalent network might lie higher than those of strain-relieved heterogeneous structures. I hope Fig.8b does not convey a too pessimistic point of view regarding our ability to gain an understanding of the properties of amorphous films in general. In the case of plasma-deposited a-Si:H film we are after all dealing with very exciting energy minima in configuration space. However, the decomposition of these alloys by effusion of hydrogen at elevated temperatures is an additional problem that is not considered in the sketch of Fig.8b.

5. Defects in Non-Crystalline Materials

5.1 Chalcogenide Glasses

Thermodynamic arguments require that at finite temperatures all crystals contain defects [34]. This can be seen in a simple way. Let ΔG be the free energy for creating a point defect. The equilibrium density of such defects at T is then $N_A \exp(-\Delta G/kT)$ where the factor N_A (the number of lattice sites) arises from the entropy of mixing. The defect density in crystals normally does not continue to decrease to zero with decreasing temperature but freezes in near a temperature at which healing of such defects by diffusion and lattice reconstruction ceases.

By the same argument, all glasses have intrinsic defects defined as deviations from the lowest energy bonding arrangements [35,36]. At present we exclude from consideration defects arising from foreign atoms. The temperature at which a given equilibrium density of intrinsic defects freezes in is probably close to T_g. Of all possible deviations from the ideal bonding configuration, the one that requires the least amount of energy will naturally be present at the highest concentration. KASTNER et al. [35,36] proposed that the least-costly bonding deviations in chalcogenide materials can be achieved when two defects are always created at the same time: a positively charged overcoordinated atom and a negatively charged undercoordinated atom. These are called valence-alternation pairs (VAP), because the valence or coordination is altered for the defect atoms.

Since the total number of bonds in the glass has not changed by creating these defects two at a time, the energy needed for creation of a pair is relatively small. It is approximately the energy required to place the negative charge onto the under-coordinated atom (reduced by relaxation effects of the surrounding matrix). In typical chalcogenide glasses this results in a VAP defect density of about $10^{17}\,\mathrm{cm}^{-3}$ in agreement with defect densities measures by photo-induced spin resonance and absorption and by photoluminescence [37].

These VAP centers have all the features of the defects postulated earlier by STREET and MOTT [38] and MOTT et al. [39] for explaining a large number of electronic properties of chalcogenide glasses. In particular, these defects are associated with a negative effective correlation energy, which means that the reaction

$$2D^0 \rightarrow D^+ + D^- \qquad (6)$$

is exothermic and that the charged defect centers can interconvert by charge transfer into their oppositely charged counterpart:

$$e + D^+ \rightleftarrows D^0 \rightleftarrows D^- + h \qquad (7)$$

Here D^0, D^+ and D^- denote the different charge states of a defect center. In the VAP model the defects can be a group V, VI or VIII atom; group IV atoms are ruled out because their coordination cannot exceed four in a covalent matrix. Hence, bonding constraints may hinder the interconversion expressed by (7) for some defects in glasses containing appreciable amounts of group IV atoms [40]. Heterogeneities in the glass of the kind discussed in section 3 may introduce variations in the density of VAP centers as their creation energy depend on the local strain and composition. The VAP defect centers are normally diamagnetic. Since the concentration of unpaired spins in relaxed glasses is less than $10^{15}\,\mathrm{cm}^{-3}$ [41], it is not likely that defect centers of entirely different nature are present. Exposure of chalcogenides to light at low temperatures brings these centers, by capture of photo-excited charge carriers, into their neutral and paramagnetic state [37]. This allows a study of their atomic structure by electron spin-resonance [37,42]. BIEGELSEN and STREET [43] have shown that VAP centers can also be photo-created because the energy required is less than the optical gap energy. It is not yet certain whether this process accounts for the light-induced shift of the optical absorption edge known as photo-darkening, or only for part of it.

Above T_g the concentration of valence alternation defects increases exponentially with temperature. I expect that they play an important role in aiding the formation of the structural units in the supercooled melt which give rise to the increase and narrowing of the first sharp diffraction peak mentioned earlier.

5.2 Amorphous Films

Defects in amorphous semiconductors probably result from a strain-relief mechanism and from bonding misfits during the growth process. Here we restrict the discussion to overconstrained amorphous materials. Except for a-As, these materials contain group IV elements as major constituants which cannot undergo valence alternation. A variety of paramagnetic and diamagnetic defects have been proposed and discussed by ADLER [44] for a-Si and a-Si:H. The dominant paramagnetic center in these films has a g-value of 2.0055 and is attributed to a dangling bond. No evidence has been found for the presence of defects having a negative effect correlation energy, despite some early claims to the contrary. The overconstrained nature of amorphous films suggests that the defects might not be randomly distributed but could be predominantly located at internal voids and strain-relief interfaces between low-strain regions. The close correlation between the photoluminescence efficiency and the spin density in a-Si:H indicates, on the other hand, that the distribution of at least the paramagnetic defect centers is nearly random [45].

6. Conclusions

In the past we have learned much about the electronic properties of non-crystalline semiconductors without a full knowledge of their atomic structure. However, it appears that future progress depends first on improved preparation techniques which enable us to avoid structural and compositional heterogeneities in amorphous films as well as on theories which are applicable to non-crystalline materials which contain medium-range and larger heterogeneities. Substantial deviations from a homogeneous random covalent network will affect the electronic transport properties most strongly. Phenomena and properties which are particularly poorly understood both in films and glasses include the ac conductivity, the photoconductivity, the Meyer-Neldel relation between the preexponential factor and the activation energy of the conductivity [46], the different activation energies derived from thermopower and conductivity measurements [47,48], and the anomalous sign of the Hall coefficient [49,50].

I suppose that several of these phenomena are strongly influenced by heterogeneities. Consider for instance the extreme case of a semiconductor consisting of grains surrounded by thin interfacial material which is less conducting and which acts as potential barriers. Theoretical studies [51-55] as well as experiments on polycrystalline films [53,56-58] have shown that the Hall coefficient measures fairly accurately the carrier concentration in the grains. The activation energy of the conductivity on the other hand is roughly the sum of the carrier activation energy and the barrier height of the interfacial material. Hence the effective Hall mobility [50] contains the barrier height activation energy, which in turn may depend on temperature [58]. At low temperatures one expects that the carriers tunnel through the barrier.

In this model, the temperature dependence of the thermopower is governed essentially by the carrier activation energy in those grains which are in contact with the electrodes because one measures an open circuit voltage due to a temperature difference of the electrodes [59]. This activation energy is less than that of the conductivity. In many glassy and amorphous semiconductors one finds an energy difference between conductivity and thermopower measurements of about 0.15 eV [47,48] comparable to the activation energy of the Hall mobility [50]. Moreover, the common observation of the Meyer-Neldel relation [60] in heterogeneous semiconductors also suggests that one must be concerned about the possible presence of medium-range order and microstructure in non-crystalline semiconductors. Inhomogeneities will undoubtedly have a profound effect on the dielectric loss mechanisms and the ac conductivity [61,62]. I trust that some of these problems will be discussed in the following papers.

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