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Thermally induced effects in evaporated chalcogenide films. II. Optical absorption

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The shift of the optical-absorption edge when evaporated films are annealed at the glass-transition temperature is investigated in amorphous $GeSe_2$, As_2S_3, and As_2Se_3, and is related to structural studies described in the previous paper. A higher density of homopolar bonds in as-evaporated films, compared to annealed films, is responsible for the difference in absorption. A model is described that evaluates the effect of homopolar bonds in terms of the absorption in off-stoichiometric bulk glasses, and a good agreement with experiment is obtained.

INTRODUCTION

Many techniques are available for preparing amorphous chalcogenide semiconductors.[1] However, there is no *a priori* reason to suppose that the local structure is necessarily identical in specimens of the same average composition. Indeed, the preceding paper (Paper I) demonstrates differences in the local bonding between evaporated and bulk-glass samples of $GeSe_2$, As_2S_3, and As_2Se_3. Bulk-glass samples are chemically ordered, and comprise well-defined structural units, for example, $GeSe_4$ tetrahedra in $GeSe_2$, and the bonding is between unlike atoms (Ge-Se, As-S, As-Se).[2] In contrast, Paper I shows that the evaporated films are partially chemically disordered and contain a fairly large fraction of homopolar bonds. Chemical disorder could occur because during deposition the surface mobility of the adatoms is insufficiently high to prevent random, as opposed to ordered, bonding. Alternatively, the bonding in the film may reflect the molecular structure of the vapor species, as discussed in Paper I. When the evaporated films are annealed at the glass-transition temperature, the density of homopolar bonds decreases and the films approach the structure of the bulk glass.

It is reasonable to suppose that a change in the chemical bonding would affect the electronic properties of the material. In this paper, we describe the changes that occur in the optical-absorption edge when evaporated films of $GeSe_2$, As_2S_3, and As_2Se_3 are annealed at their glass-transition temperatures. In order to understand the influence of homopolar bonds, the composition dependence of the absorption in the bulk-glass alloys, Ge_xSe_{1-x}, As_xS_{1-x}, and As_xSe_{1-x} is also investigated since, in these glasses, departure from the stoichiometric compound necessarily introduces homopolar bonds. A brief discussion of the relation between these annealing effects and the photostructural transformation observed in chalcogenides is also given.

II. EXPERIMENTAL

The samples of both the evaporated films and the bulk-glass alloys used in this investigation are identical to those described in Paper I. The absorption measurements were performed at room temperature on a Cary 17 Spectrophotometer. The optical-absorption edges of the films before and after annealing are displayed in Fig. 1. In each case, the edge is exponential for absorption coefficients between 30 and 3000 cm^{-1}, as is generally found in chalcogenides, and the observed shifts seem to correspond to a parallel movement of the edge, rather than a broadening. It is interesting that the effect of annealing in each film is very different. The largest shift occurs in $GeSe_2$ where the edge moves 0.3 eV to higher energy. In contrast, there is a shift of 0.055 eV to low energy in As_2S_3, and only a very small effect is observed in As_2Se_3.

Figure 2 shows the dependence of the optical band gap $E_0(x)$ on composition x in the three alloy systems. E_0 is arbitarily defined as the energy at which the absorption coefficient $\alpha = 10^3$ cm^{-1}. Since the slope of the exponential edge is almost independent of composition, the trends shown in Fig. 2 are insensitive to the precise definition of E_0. However, the slope of the absorption edge of the evaporated films is smaller by approximately 10%, compared to the bulk glasses in all three materials. In bulk-glass As_2S_3, the various reported values of the slope differ by up to 25%, and the reason is presumed to be changes in the quench rate.[3] However, in that material all the measured absorption edges intersect at $\alpha \sim 10^3$ cm^{-1}. Thus by defining E_0 at this absorption, the effect of changes in slope should be minimized. In Ge-Se alloys, $E_0(x)$ has a pronounced maximum at $GeSe_2$, and decreases particularly strongly in Ge-rich samples. In contrast, E_0 in both As-S and As-Se glasses is less sensitive to composition, and minima occur near the stoichiometric compounds. In As_xS_{1-x}, the minimum seems to

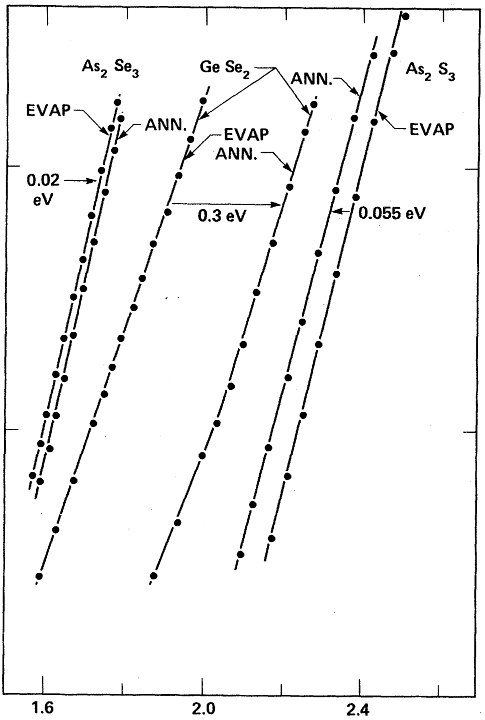

FIG. 1. Room-temperature absorption-edge data for evaporated films of $GeSe_2$, As_2S_3, and As_2Se_3, before and after annealing at their respective glass-transition temperatures. The magnitudes and directions of the shifts of the edge are indicated.

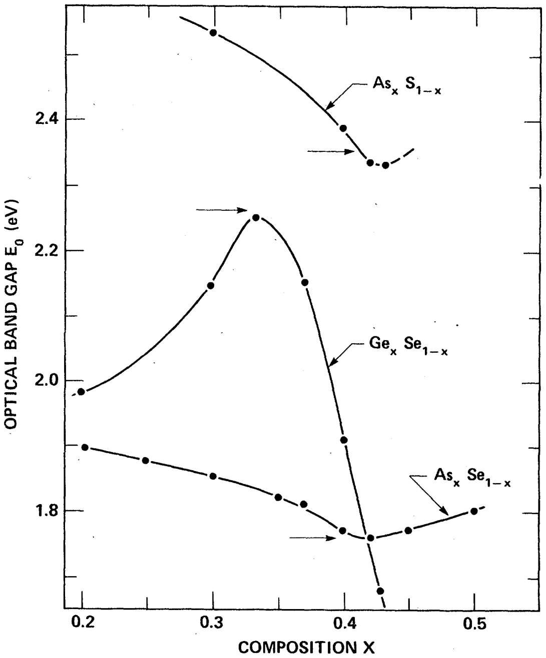

FIG. 2. Room-temperature optical band gap E_0, defined as the energy at which $\alpha = 10^3$ cm^{-1}, for bulk glasses in the alloy systems Ge_xSe_{1-x}, As_xS_{1-x}, and As_xSe_{1-x}. The As_xSe_{1-x} system includes data for the relative position of E_0 taken from Ref. 8. The arrows indicate values of E_0 for the three evaporated and annealed films of Fig. 1.

be near $x = 0.42$, but since $x = 0.43$ represents the limit of glass formation by quenching, the As-rich regime cannot be fully investigated.

III. DISCUSSION

The structural investigations in Paper I conclude that as-deposited chalcogenide films are partially chemically disordered. This result is shown by the observation of features in the Raman spectra that are known to originate from structural units containing homopolar bonds. In As_2S_3, the As-As bonds are also observed directly by extended x-ray-absorption fine-structure (EXAFS) measurements. Upon annealing these materials, the fraction of homopolar bonds is decreased. At the same time the absorption edge is shifted. It is well known that the chemical bonding of a semiconductor determines the optical gap, and therefore we propose that the observed edge shifts originate in large part from the annealing away of homopolar bonds. However, there are other possible structural effects that could contribute to the shift of the absorption edge, but we argue that it is unlikely that any of these could provide either a universal explanation or even account for the observed magnitude in the majority of cases. (As we discuss later, As_2Se_3 is the one possible exception, and our explanation is not unique here because of the small effect involved.) For example, dangling bonds, voids, or increased quantitative disorder might introduce extra localized states between the mobility edges of as-deposited evaporated films. Optical absorption from these states would then shift the absorption edge of the as-deposited material below that of the glass. However, this effect could not explain the As_2S_3 data. Furthermore, there is no clear evidence from transport and structural properties that room-termperature-evaporated chalcogenide films contain a sufficient defect density to account for the magnitude of the shift in $GeSe_2$. Another example is the effect of internal strain fluctuations, not associated with voids, in as-deposited films. The magnitude of their effect can be obtained through the Grüneisen constant from the broadening, relative to that in the glass, of the Raman lines. Thus, using the reported values of the bulk modulus and the pressure dependence of E_0,[4] we find for $GeSe_2$ that the local strain would account for a shift of E_0 of only 0.04 eV, a value that is insignificant compared with the observed shift of 0.3 eV. In the As-chalcogen systems, no broadening of the Raman lines is observed and this effect might be neglected entirely.

Next we demonstrate that chemical ordering of the films upon annealing is able to explain both the magnitude and the sign of the edge shifts. If the shift is due to the presence of homopolar bonds in the as-evaporated films, then there should be a correlation between the effect of annealing, and the composition dependence of the band gap of bulk glasses. Figure 2 shows that in Ge-Se glasses, E_0 is sharply peaked at the $GeSe_2$ composition, from which it is clear that homopolar bonds have a strong tendency to lower the band gap. Thus the much smaller gap in the as-evaporated film is explained. In contrast, As-S glasses exhibit a minimum band gap near As_2S_3. Thus homopolar bonds increase the band gap, which explains the larger gap in as-evaporated films compared to annealed films. In As-Se glasses, the composition dependence of the band gap is very weak, which is consistent with the observation of a very small annealing effect.

A quantitative estimate of the edge shift in each material can be found by modeling the evaporated film as an average over an appropriate range of bulk-glass compositions. The actual composition range used will be determined by the degree of chemical disorder, which is taken from the results of Paper I. We also have to find an appropriate method of averaging the composition dependence of the band gap. One possibility is to evaluate the absorption coefficient α from a sum of bond susceptibilities. In $GeSe_2$ films, α can then be expressed as

$$\alpha = P_1\alpha_{\mathrm{GeGe}} + P_2\alpha_{\mathrm{GeSe}} + P_3\alpha_{\mathrm{SeSe}} , \tag{1}$$

where α_{GeGe}, etc., are the partial absorption coefficients from Ge-Ge bonds, etc., and the P_i are the relative probabilities of each bond type. However, when applied to the Ge-Se glass system, this model does not give consistent values of α_{GeGe}, etc., when evaluated for all the data points in Fig. 2. The reason is that the bond susceptibilities themselves are sensitive to changes in the chemical bonding, even when small ranges of chemical composition are involved.

To circumvent this problem, we use an empirical model that calculates the effect directly from the observed compositional dependence of the gap in the glasses. In effect, instead of attempting to calculate a single-valued composition-independent bond susceptibility for each bond type, this method takes an average value for the bulk glass over an appropriate composition range. Thus the composition dependence of bond susceptibility is allowed for in an empirical way. The justification for this approach is that in the evaporated film there will also be a range of local chemical compositions. Provided similar chemical bonding units occur in both the evaporated film and the off-stoichiometric glass, this model should give a reasonable representation of the absorption of the film. The absorption coefficient $\alpha^G(\hbar\omega)$ of the bulk glasses is exponentially dependent on energy,

$$\alpha^G(\hbar\omega) = \alpha_0 \exp[-\gamma(E_0 - \hbar\omega)] , \tag{2}$$

where, if α_0 is taken to be 10^3 cm^{-1}, E_0 is the value of the gap given in Fig. 2. Within any alloy system, γ is approximately constant. We therefore calculate the absorption of the evaporated film $\alpha^F(x_0,\hbar\omega)$ for the composition x_0 by averaging Eq. (2) using the band gap of the glass $E_0^G(x)$ as a variable,

$$\alpha^F(x_0,\hbar\omega) = \alpha_0 \int F(x) \exp[-\gamma(E_0^G(x) - \hbar\omega)]\, dx , \tag{3}$$

where $F(x)$ is a normalized distribution function. For simplicity, we shall take $F(x)$ as a flat distribution covering the composition range $x_0 - A$, $x_0 + A$. Expanding $E_0^G(x)$ about x_0 to second order and substituting $y = x - x_0$ gives, from Eq. (3),

$$\frac{\alpha^F(x_0,\hbar\omega)}{\alpha^G(x_0,\hbar\omega)} = \frac{1}{2A} \int_{-A}^{A} \exp[-\gamma(\beta y + \delta y^2)]\, dy , \tag{4}$$

where

$$\beta = (dE_0^G/dx)_{x_0}$$

and

$$\delta = \tfrac{1}{2}(d^2E_0^G/dx^2)_{x_0} .$$

Paper I shows that the annealed film is chemically ordered and therefore we assume that it is identical to the bulk glass of the same composition. Thus, Eq. (4) evaluates the change in absorption with annealing. Since the right-hand side of Eq. (4) is independent of energy, a parallel shift of the absorption edge is expected, in agreement with the observations of Fig. 1. Furthermore, it can be seen that the magnitude of the effect is strongly dependent on the sign of β and δ, with negative values giving a much larger effect than positive values because of the exponential term. Since the curvature of $E_0^G(x)$ is negative in Ge-Se glasses and positive in As-S glasses, the largest effect is expected in $GeSe_2$, in agreement with observation. In materials with negative curvature, the dominant contribution to the integral in Eq. (4)

comes from $y \sim \pm A$, whereas in material with positive curvatures, the largest contribution is from $y \sim 0$. Thus, we would expect that the absorption of evaporated $GeSe_2$ is more sensitive to the details of preparation than that of As_2S_3.

Table I gives the experimental values of β, γ, and δ for the different films, obtained by fitting the absorption edge data of Fig. 2 to a parabola. Also shown in Table I are the values of A obtained from Eq. (4) which yield the observed edge shifts. These values of A will be compared to estimates derived from Paper I.

Consider first $GeSe_2$. The above model is expected to be of greatest applicability in this material for various reasons. First, the effect is large so that the other contributions to the edge shift should be of minor importance. Secondly, $E_0^G(x)$ peaks at the $GeSe_2$ composition, so that β is zero and there is only one term in the exponent of Eq. (4). Finally, the absorption edge of the annealed film is very close to that in glassy $GeSe_2$ (see Fig. 2), which confirms our assertion that the two materials have identical structures.

We now calculate the proportion of Ge-Ge bonds in the evaporated film from the average Ge-Ge coordination in off-stoichiometric glasses and the value of A in Table I. In the composition range between 33- and 40-at. % Ge, the chemically ordered glasses can be separated into two components.[2] One component has only Ge-Se bonds and corresponds to the composition $Ge_{33}Se_{67}$. The other component comprises Ge_2Se_6 units in which each Ge atom is bonded to one other Ge and to three Se atoms, which corresponds to the composition $G_{40}Se_{60}$. Thus

$$Ge_{33+y}Se_{67-y} \equiv (1-\tfrac{1}{7}y)Ge_{33}Se_{67} + \tfrac{1}{7}y\,Ge_{40}Se_{60}\,. \tag{5}$$

Therefore, for this compound, the Ge-Ge coordination per Ge atom is $\frac{1}{7}y$, while the Ge-Se coordination is $4-\frac{1}{7}y$. When x takes values between 40- and 43-at. %, Ge_2Se_6 and Ge_3Se_8 units coexist.[5] The Ge-Ge coordination for this range can be calculated in a similar way. It then follows that for the range of composition determined by A the average Ge-Ge coordination is

$$C_{GeGe} = \left(\frac{1}{2A}\right)\int_0^A (\tfrac{1}{7}y)\,dy + \ldots\,, \tag{6}$$

where other terms are included as necessary if A is greater than 7. The calculation of the Ge-Ge coordination for the value of A in Table 1 gives the result that $C_{GeGe}=0.31$.

In Paper I, a bonding probability P_C in a chemically disordered material was introduced, where P_C is the probability that a particular Ge bond is to a Se atom. Thus the Ge-Ge coordination is $4(1-P_C)$. Equating this expression to the value from Eq. (6) yields $P_C \sim 0.92$. This result is within the range of values found from the Raman work, and demonstrates that the model is able to give quantitative as well as qualitative agreement with experiment.

In As-S glasses, $E_0^G(x)$ has a minimum at about 42-at. % As. Microprobe analysis of the evaporated films also shows them to be about 2% As rich, in agreement with other investigations,[6] and the result is deduced from Raman studies described in Paper I. Furthermore, the absorption of the annealed films near 10^3 cm^{-1} is close to that in bulk glass $As_{42}S_{58}$ (see Fig. 2). Thus we consider the film to have an average composition $As_{42}S_{58}$ in deriving the values in Table I. There is limited absorption data for As-rich bulk glasses, because glass formation only extends to $As_{43}S_{57}$. Therefore, we arbitrarily assume that $E_0^G(x)$ is symmetrical about the $As_{42}S_{58}$ composition, and this uncertainty introduces a potential error in the result. Another complication is the possibility discussed in Paper I that the as-deposited film contains As_4S_4 molecules. It is not known what effect a molecular, as opposed to a cross-linked, topology would have on the absorption. Nevertheless, an analysis of the edge shift according to Eq. (5)

TABLE I. Values of parameters used to evaluate the absorption-edge shift of annealed films; γ is the slope of the absorption-edge data in Fig. 1; β and 2δ are the first and second derivatives of $E_0(x)$ from Fig. 2; A is the composition range evaluated by fitting Eq. (4) to the data of Fig. 1.

	γ (eV^{-1})	β [eV(at %)$^{-1}$]	δ [eV(at %)$^{-2}$]	A (at %)
$GeSe_2$	10.5	0	-7×10^{-3}	8.9
As_2S_3	14	0	$+2.5 \times 10^{-3}$	11.6
As_2Se_3	16.5	-7×10^{-3}	$+5 \times 10^{-4}$	[a]

[a] The shift of the absorption edge is too small to give a reliable value.

gives $A \sim 12\%$, corresponding to an average As-As coordination of ~0.4, which is in reasonable agreement with the value of 0.6 obtained in Paper I.

In As_2Se_3 the small annealing effect makes it difficult to obtain a reliable estimate of A. We observe that the shift is to higher energy despite a positive value of δ (see Table I). This result might be explained by a contribution from the nonzero value of β, which tends to shift the edge in the opposite direction. However, it is recognized that a fairly low density of defects, or a change in quantitative disorder, could also dominate the observed effect. Indeed, some confirmation of this possibility follows from the observations that evaporated and sputtered films of As_2Se_3 can shift in opposite directions upon annealing, even though the absorption edges of the final annealed states are identical.[7] Thus we merely remark that the small edge shift is consistent with our expectation that the effect of chemical disorder will be small in As_2Se_3 because of the weak composition dependence of $E_0^G(x)$.

Finally we mention the possible connection between the annealing effects and the photostructural transformation observed in chalcogenides.[9] The shift of the absorption edge after optical excitation has been studied in a number of chalcogenide glasses. It is found that the shift can be reversible or irreversible by thermal annealing, depending on the initial condition of the sample. In general, As-deposited films have an irreversible shift that is similar in magnitude and sign to the annealing effects discussed here. This result indicates that optical excitation causes a rearrangement of the bonding in such a way that homopolar bonds are suppressed. The mechanism is presumably a transient bond-breaking process caused by above band gap excitation.

The reversible photostructural change is observed as a shift of the absorption edge to low energy, but in this case the shift can be reversed by annealing.[10] It does not seem possible to explain this effect simply by the creation of homopolar bonds, because in As_2S_3, for example, the edge shift has the opposite sign to that expected from our model. One suggestion for the mechanism is the optical creation of defect pairs in which the atoms change their coordination.[11] A bond-breaking process is also required to form this defect. To this extent, both types of photostructural transformation can be explained by a similar physical process.

IV. CONCLUSIONS

A shift in the optical-absorption edge is observed when evaporated films of $GeSe_2$, As_2S_3, and As_2Se_3 are annealed. The major contribution to the shift is the reduction in the density of homopolar bonds. The influence of homopolar bonds can be calculated from absorption data in bulk-glass alloys, and good agreement with experiment is obtained. The largest edge shift occurs when the composition dependence of the band gap in bulk-glass alloys is sharply peaked.

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