

## Thermally induced effects in chalcogenide films.

### III. Diffusion and the kinetics of annealing in GeSe<sub>2</sub>

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(Received 27 April 1981)

The kinetics of annealing evaporated GeSe<sub>2</sub> films is investigated through measurements on the optical-absorption edge. The data are found to follow a second-order rate equation. This is understood in terms of Se-atom diffusion through a process involving the excitation and diffusion of close valence-alternation pairs. The explanation is proposed to apply also to pnictide- and oxide-containing glasses and justifies the miniscule diffusion rate found in all of them.

#### I. INTRODUCTION

In two earlier papers (called I and II), the movement of the optical-absorption edge upon annealing evaporated As<sub>2</sub>S<sub>3</sub>, As<sub>2</sub>Se<sub>3</sub>, and GeSe<sub>2</sub> films below the glass transition temperature was shown to be caused by the elimination of homopolar bonds.<sup>1,2</sup> In fact, a quantitative relationship between the absorption-edge shift and the concentration of homopolar bonds was discovered. There was, however, a qualitative difference between the distributions of homopolar bonds in the arsenic and germanium chalcogenides. In the former, numerous workers independently<sup>1,3-6</sup> showed that the deposition process results in a film consisting largely of As<sub>4</sub>S<sub>4</sub> (As<sub>4</sub>Se<sub>4</sub>) molecules and S (Se) chains or rings that with heat polymerize into an As<sub>2</sub>S<sub>3</sub> (As<sub>2</sub>Se<sub>3</sub>) network. Thus the atomic structure of the as-deposited film bears no direct topological relation to the glass. Furthermore, the homopolar bonds themselves are associated with particular molecular species and tend to be clustered as a consequence. In contrast, the homopolar bonds in as-deposited films of the latter were shown<sup>1</sup> to occur randomly in a continuous network. It is likely, therefore, that the process and kinetics of removal of homopolar bonds is much more complicated in the case of the arsenic chalcogenides than in that of GeSe<sub>2</sub> at least at a quantitative level. Work by Asahara and Izumitani<sup>7</sup> lends support to this conjecture, and for this reason the present study is concentrated on GeSe<sub>2</sub>.

The ingredients and scope of the problem are best seen by examining the atomic structure of GeSe<sub>2</sub>. When prepared as a glass, it consists of a chemically ordered network in which the Ge and Se atoms are four- and twofold coordinated, respec-

tively, and homopolar bonds are highly suppressed. The as-deposited evaporated film differs from this mainly in that homopolar bonds frequently occur. The annealing process in these films is determined, therefore, by the mechanism of diffusion of these bonds in the glassy network and the annealing rate may be related directly to their diffusion rate. These are the phenomena addressed in the three remaining parts of this paper. In Sec. II the experimental method, which takes advantage of the relation between the homopolar bond concentration and the absorption-edge shift mentioned earlier, and the experimental results are described. The results are analyzed in Sec. III to give a value for the diffusion rate of Se atoms in GeSe<sub>2</sub>, and the probable role of defects in diffusion is discussed. Finally, the work is summarized in Sec. IV.

#### II. EXPERIMENTAL METHOD AND RESULTS

##### A. Sample preparation and chemical composition

The films were evaporated from a tantalum boat onto Corning 7059 glass substrates held near room temperature after a base pressure of  $1 \times 10^{-6}$  Torr had been achieved in the deposition system. The boat temperature was chosen to give a deposition rate of approximately  $1 \mu\text{m min}^{-1}$  when a source-to-substrate distance of about 20 cm was used. The samples, with thicknesses ranging from 0.2 to  $1 \mu\text{m}$ , are expected from Raman measurements on identically deposited thicker films,<sup>1</sup> to be almost stoichiometric and have a chemical composition Ge<sub>33.6</sub>Se<sub>66.4</sub>.

### B. Optical experiments

Transmission measurements were made in the region of the optical-absorption edge in a highly stable, custom-designed, dual-beam spectrophotometer. The samples were mounted on a heater within the radiation shield of an evacuated chamber and a thermocouple, located next to the sample, registered that temperatures of up to 250°C could be controlled indefinitely to 0.1°C.

A typical set of experiments was as follows. The absorption edge at room temperature was first measured. The temperature was next ramped to 100°C, and the evolution of the transmission at a fixed photon energy was followed for 250 min. This process was then repeated at increasing temperatures up to 250°C. Finally an anneal at 250°C was carried out for 400 min. Since the glass transition temperature of GeSe<sub>2</sub> is 265°C,<sup>8</sup> this final annealing stage brings the material very close to a fully annealed state that typically could not be attained in the time allotted at the lower annealing temperatures used. However, by measuring the absorption edge at these intermediate annealing temperatures during the return to room temperature, the necessary end-point information is obtained.

There are two points to note about the experiment. First, it is clear that photometric and temperature stability are crucial in order to perform the experiment at all. That these are sufficient is readily checked by repeating the experiments with a well-annealed bulk glass sample.<sup>9</sup> Second, it is apparent that a single sample can be used at a number of annealing temperatures, as long as each sample is fully annealed at the highest temperature to allow the required end points to be established. The advantage of this approach, as opposed to that of using a different sample at each stage, is that any error associated with thickness measurement is not transmitted to the analysis. The disadvantage is that the measured changes during annealing are not maximized. The optimum situation, therefore, is a judicious use of both approaches.

### C. Results

In Fig. 1 the absorption edge, measured at room temperature, is shown at various stages of anneal: curve 1 several weeks after deposition, curve 2 after storing at room temperature for an additional ten months, and curve 3 after annealing at 250°C for 400 min. For comparison, the absorption edge of a bulk glass, annealed at 330°C for 250 min, is

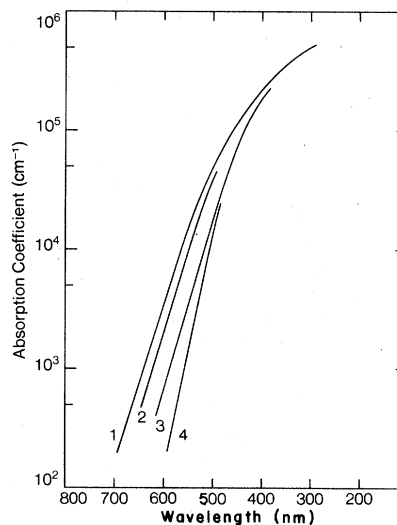


FIG. 1. Absorption edges of amorphous GeSe<sub>2</sub>: (1) an evaporated film several weeks after deposition, (2) an evaporated film after storing at room temperature for an additional ten months, (3) an evaporated film after annealing at 250°C for 400 min, and (4) a well-annealed bulk glass.

shown as curve 4. Several points can be noted. First the annealing process, albeit slow at room temperature, is enormously accelerated upon heating. Second, although the edges of the fully annealed film and bulk glass essentially coalesce above 10<sup>4</sup> cm<sup>-1</sup>, they differ below—more specifically, the edge of the glass is steeper in this range. It is unlikely that this difference represents incomplete annealing of homopolar bonds in the annealed film, since their earlier removal is apparently accomplished with little change in slope of the absorption edge. More likely, annealing above the glass transition temperature allows structural relaxations to occur that cannot occur during annealing below the glass transition temperature. In this case, the difference between the edges of the fully annealed film and glass represents the attainment of a lower free-energy state in the glass, but in both cases like bonds are absent. This is an important point both for data analysis and for choosing the temperature range for the annealing experiment. It also would indicate that the annealing process below the glass transition temperature does not involve large structural changes and is qualitatively different from that above. This supposition would appear to agree with Oheda's recent speculations on the structural contributions to the slope of the edge in bulk Ge<sub>x</sub>Se<sub>1-x</sub> glasses.<sup>10</sup>

The remainder of the paper will be devoted sole-

ly to the dependence of the absorption edge on annealing at photon energies  $h\nu$  for which the absorption coefficient in state  $j$  is given by

$$\alpha_j = \exp \left[ \frac{h\nu - E_j}{\Delta_j} \right], \quad (1)$$

where  $E_j$  and  $\Delta_j$  are constants at a given temperature. The evolution of the annealing process with time can, therefore, be followed in detail through  $\alpha_j$  as shown in Fig. 2. The data are plotted according to the theory developed later, but the qualitative aspects should be noted here. As suggested earlier, the progress toward the situation in which homopolar bonds are absent is rapidly accelerated with increasing temperature, this represented by the approach of the absorption coefficient during annealing to its value in the fully annealed film. Furthermore, from the data at 249°C, it is readily deduced that after 400 min an approach to within 10% of a fully annealed state is attained, confirming earlier speculations.

### III. DISCUSSION

#### A. The annealing process

Following I and II, I define a parameter  $P_j$  which is the probability that in state  $j$  a Ge atom

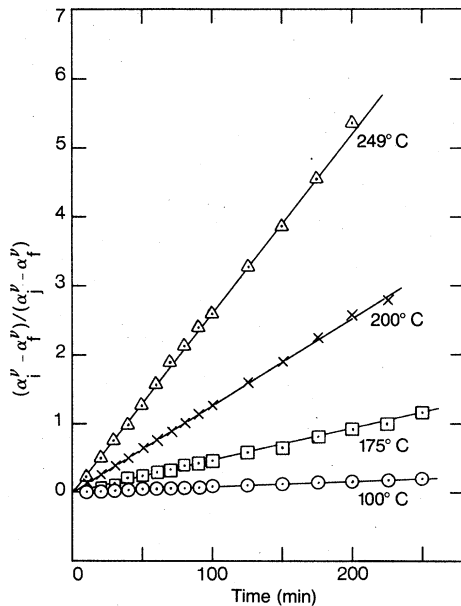


FIG. 2. Variation of the absorption coefficient with time during annealing at specified temperatures. The linear dependence of  $(\alpha_i^v - \alpha_f^v)/(\alpha_j^v - \alpha_f^v)$  on time at each temperature indicates that a second-order rate process is involved.

is bonded to a Se atom. It then follows that  $C_j = (1 - P_j)/2$  is the concentration of homopolar bonds of each type in  $\text{GeSe}_2$ . If the removal of homopolar bonds is now considered as a process in which two heteropolar bonds are created by the simultaneous annihilation of two opposite homopolar bonds, the rate of diluting homopolar bonds of a given type in a single event is

$$\frac{dC_j}{dt} = -2fC_j^2, \quad (2)$$

where  $f$ , the event frequency, is exponentially activated according to

$$f = f_0 \exp \left[ -\frac{E_0}{kT} \right]. \quad (3)$$

The annealing process, therefore, follows a second-order rate equation.

Equation (2) can be put in a form that makes contact with optical data using the results of II. To a reasonable approximation, the concentration of homopolar bonds can be written as

$$C_j = A^v \left[ \alpha_j^v - \alpha_f^v \right], \quad (4)$$

where  $A^v$  is a constant and the absorption coefficients at photon energy  $h\nu$  in state  $j$  and final state  $f$  are in the exponential absorption region described by Eq. (1). After integration Eq. (2), therefore, becomes

$$\left[ \frac{\alpha_i^v - \alpha_f^v}{\alpha_j^v - \alpha_f^v} \right] = 1 + 2f_0 A^v (\alpha_i^v - \alpha_f^v) \exp \left[ -\frac{E_0}{kT} \right] t, \quad (5)$$

where  $i$  now refers to the initial state.

As discussed earlier, it is convenient to use samples with different  $C_i$ 's, and necessary to make measurements at different photon energies at each annealing stage. Both of these requirements are compensated for when determining  $E_0$  by noting for an exponential edge that

$$\left[ \frac{\alpha_i^v - \alpha_f^v}{\alpha_i^q - \alpha_f^q} \right] = \frac{\alpha_f^v}{\alpha_f^q}, \quad (6)$$

where  $hq$  is the photon energy at which  $A^q$  is related through Eq. (4) to the initial homopolar bond concentration obtained in I and II. An experimentally usable form of Eq. (4) is thus finally obtained as

$$\left[ \frac{\alpha_i^v - \alpha_f^v}{\alpha_i^q - \alpha_f^q} \right] = 1 + 2f_0 A^q (\alpha_i^v - \alpha_f^v) \left[ \frac{\alpha_f^q}{\alpha_f^v} \right] \exp \left[ -\frac{E_0}{kT} \right] t, \quad (7)$$

where  $h\nu$  is the photon energy at which the experiment is performed.

The data in Fig. 2 may now be examined in detail. They clearly fit Eq. (7) and, therefore, permit an evaluation of the parameters describing the activation process. These are found from Fig. 3 in which the logarithm of the slope of each line in Fig. 2, normalized by  $(\alpha_i^v - \alpha_f^v)(\alpha_f^q/\alpha_f^v)$ , is plotted against inverse temperature. Additional data has also been included. Then using  $C_i \approx 0.04$  from II,  $E_0 = 0.61$  eV and  $f_0 \approx 3 \times 10^4$  sec<sup>-1</sup> are obtained.

### B. Diffusion, photodiffusion, and the photostructural change in chalcogenide glasses

The annealing process presumably occurs by diffusion of either Se or Ge atoms in what is essentially a glassy GeSe<sub>2</sub> network. Then the measured activation energy  $E_0$  is the activation energy for diffusion and

$$D_0 = \frac{1}{6} f_0 a^2 \exp(-\beta/k) \quad (8)$$

is the diffusion constant of the species in question.<sup>11</sup> Here  $a$  is the average atomic motion during each event and  $\beta$  is the linear temperature dependence of the activation energy that represents the entropy of migration.<sup>12</sup> After substituting reasonable values for  $a$  ( $\approx 0.5$  nm) and  $\beta$  ( $\approx -5 \times 10^{-4}$  eV/K),  $D_0 \approx 5 \times 10^{-9}$  cm<sup>2</sup>/sec is obtained. While the magnitude of  $E_0 \approx 0.6$  eV is typical of many

diffusion processes, the magnitude of  $D_0$  would appear at first sight to be remarkably small. Nevertheless, it is comparable with the values for diffusion of Se (and also As) in Se-As-Ge glasses<sup>13</sup> and for the diffusion of oxygen in oxide glasses.<sup>14</sup> Moreover, Ge itself has not been observed to diffuse.<sup>13</sup>

A qualitative explanation for these results would appear to derive from the special characteristics of the defects, which Kastner *et al.*<sup>15</sup> describe in terms of valence alternation, that exist in chalcogenide and pnictide glasses.<sup>16,17</sup> Thus positively charged threefold-coordinated ( $C_3^+$ ) and negatively charged, singly-coordinated ( $C_1^-$ ) atoms occur in pairs in amorphous selenium, and  $P_4^+$  and  $P_2^-$  atoms occur in pairs in amorphous arsenic or other pnictides. The energy of their formation  $E_f$  even at large separations is small and, in fact, has been estimated to be only  $E_f \approx 1$  eV in selenium.<sup>15,18</sup> Moreover, for close pairs it is still less.<sup>19</sup> In contrast, no equivalent situation can exist with tetrahedrally coordinated atoms because  $T_5^+$  is not an allowed structure. It is therefore reasonable to assume that diffusion basically occurs by a process of thermal excitation and diffusion of close valence-alternation pairs at homopolar chalcogen or pnictide bonds where, as seen later, the effects of ionicity are optimized.<sup>20</sup>

The proposed mechanism of diffusion is illustrated microscopically in Fig. 4 and as a configurational coordinate diagram in Fig. 5 for the case of Se diffusion in GeSe<sub>2</sub>, although an analogous situation is easily developed for pnictide diffusion. The first part of the process is the formation of a  $C_3^+ - C_1^-$  defect in the neighborhood of a selenium homopolar bond where very little atomic movement is needed. At such selenium homopolar bond sites, the activation energy  $E_f$  is a minimum, and since the heteropolar bond density does not change  $E_f \approx 0.5$  eV seems reasonable from our earlier discussion. The  $C_3^+ - C_1^-$  pair may then diffuse through the system in a way that to some extent resembles interstitial diffusion in a crystalline material. The activation energy for this motion  $E_m$  should be small ( $\leq 0.5$  eV), and the measured activation energy for diffusion,  $E_0 = E_m + E_f$ , is reasonably of order 1 eV.

This model, therefore, immediately provides a basis for understanding the magnitude of  $E_0$  for diffusion of selenium and arsenic and also separates the diffusional behavior of germanium. In addition, it predicts that photoenhanced diffusion is possible since light could enlarge the population of

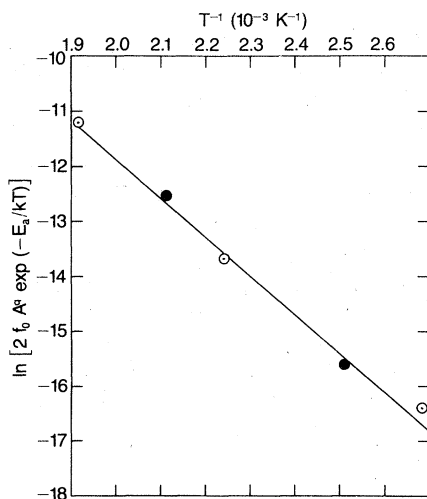


FIG. 3. Plot to demonstrate that the rate process is thermally activated. Data from two samples are used and an activation energy  $E_0 = 0.61$  eV and rate constant  $f_0 \approx 3 \times 10^4$  sec<sup>-1</sup> are obtained.

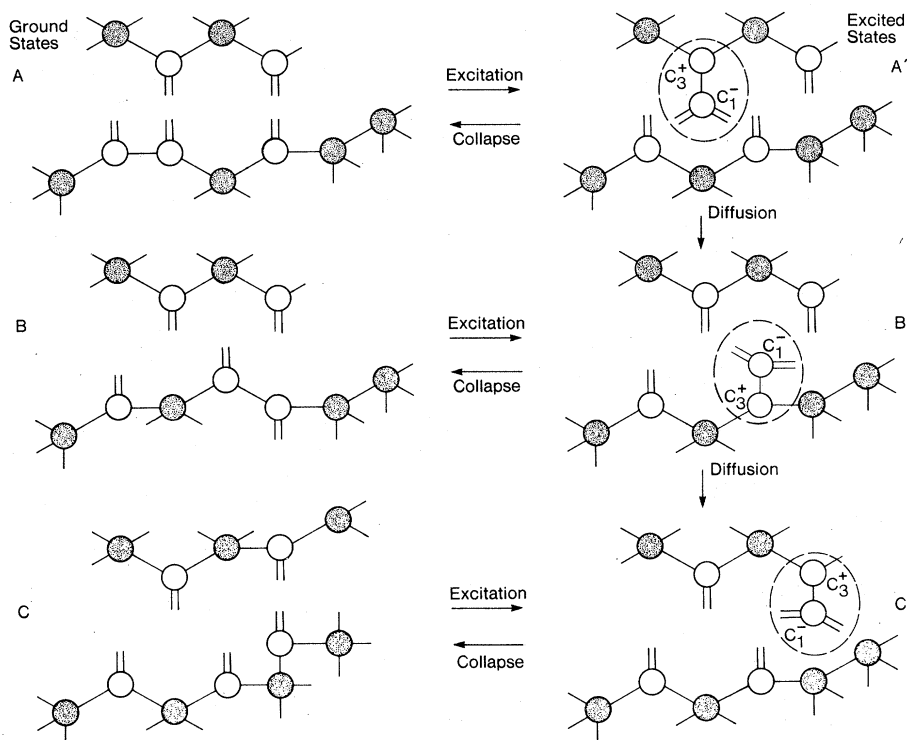


FIG. 4. Schematic representation of the diffusion of Se in  $\text{GeSe}_2$ . The ground states of the system are shown to the left and the excited states to the right. At each stage thermal excitation creates a  $C_3^+ - C_1^-$  pair which may either collapse back to the ground state with large probability or diffuse to a new position in the network with small probability. Eventually such diffusive motion allows a collapse to the final ground state in which no like bonds occur.

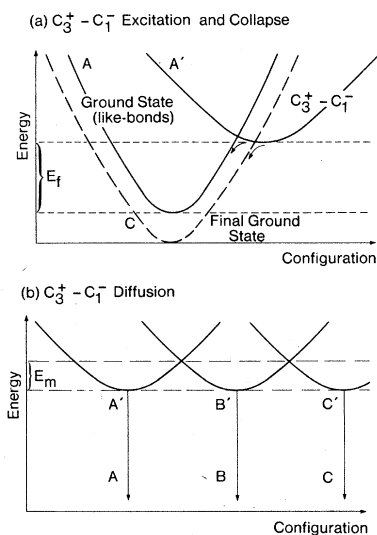


FIG. 5. Configurational coordinate diagrams representing (a) thermal excitation and collapse of  $C_3^+ - C_1^-$  pairs and (b) the diffusion of  $C_3^+ - C_1^-$  pairs. Note that the barrier for return to the ground state is much smaller at every stage than that for diffusion to a new excited state.

valence-alternation pairs over their thermal value, permitting diffusion with a smaller activation energy to occur. Of course, this reasoning is identical to Strom and Martin's explanation<sup>5</sup> of the irreversible photostructural change in  $\text{As}_2\text{S}_3$  and is also very much related to the explanation given for the reversible photostructural change in chalcogenide glasses.<sup>19</sup> In the latter case, the sample is irradiated at low temperatures to create a metastable population of close valence-alternation pairs. Although this situation is insufficient to cause photoenhanced diffusion to occur, since a pair is required to diffuse after formation, it nevertheless represents in a sense the intermediate state through which diffusion occurs.

There are several factors that could contribute to the smallness of  $D_0$  and it is difficult *a priori* to identify which if any is the major one. First, the fraction of selenium homopolar bond sites at which  $C_3^+ - C_1^-$  pairs may be excited is small since the proper location of a third selenium atom is required, as is clear from Fig. 4. (If the range of activation energies for  $C_3^+ - C_1^-$  pair creation is  $E_f$

to  $E_f + \Delta$  with  $\Delta \gg kT$ , it is easily shown that the number of effective homopolar bond sites is reduced by  $kT/\Delta$ .) Second, although the activation energy for motion of a  $C_3^+ - C_1^-$  pair is small, the probability of reforming a selenium homopolar bond at any stage is the predominant process since this can occur with minimal activation energy<sup>19</sup> as indicated in Fig. 5. (Of course, when a  $C_3^+ - C_1^-$  pair eventually progresses to the vicinity of a Ge homopolar bond, it is this process that leads to the simultaneous dilution of both the Se and Ge homopolar bond densities.) Third, the diffusion is different from the typical crystalline situation to the extent that the  $C_3^+ - C_1^-$  defect energy changes by a disorder energy at each site because the local environment changes. (This is ignored for simplicity in drawing Fig. 5.) Thus, if the disorder energy is large enough, diffusional motion may be restricted by the number of open percolation channels.<sup>21</sup> Obviously, each of these effects will reduce the effective attempt frequency for diffusion, and a net

value much less than the fundamental phonon frequency does not appear unreasonable. It remains a speculation, however, that a reduction of  $10^6 - 10^7$  can be accounted for.

#### IV. SUMMARY

The annealing process in evaporated GeSe<sub>2</sub> was shown to follow a second-order rate equation, a behavior that can be successfully explained by the diffusion of Se atoms through a process involving the excitation and diffusion of close alternation pairs. This mechanism is proposed to apply also to pnictide- and oxide-containing glasses and thus to go some way towards a universal explanation for their minuscule  $D_0$ 's.

#### ACKNOWLEDGMENT

I would like to thank R. A. Street for a number of stimulating conversations.

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