

Photodarkening in amorphous As_2S_3 and Se under hydrostatic pressure

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Shifts in the optical-absorption edges induced by band-gap illumination and annealing under pressure have been studied for As_2S_3 and Se. Both materials, if annealed at 1 atm beforehand, undergo a decrease in the band-gap energy with illumination under pressure. This decrease is accompanied by a similar degree of densification as that induced by annealing. The As_2S_3 specimen annealed under pressure at the glass-transition temperature exhibits reversible photodarkening, the magnitude of which increases with pressure. These observations are accounted for quantitatively as resulting from an enhancement of the intermolecular interactions.

I. INTRODUCTION

Amorphous chalcogenide semiconductors exhibit a photodarkening phenomenon,¹ i.e., a shift of the optical-absorption edge to lower energies induced by photons with a greater energy than the band-gap. The photodarkening is reversible in the sense that the shift induced by the band-gap illumination can be removed by heat treatment at just below the glass-transition temperature. The absorption edge is substantially modified by the photodarkening, and, furthermore, the magnitude is a function of the glass-transition temperature.² Thus, the development of an understanding of the mechanism of the photodarkening will provide valuable information on the origin of the optical-absorption edge, as well as, some insight into the nature of the glass transition.

Recently, I demonstrated that the photodarkening mechanism can be understood through the use of a bond-twisting model.² This model is based on the argument that the chemical bonding structure of chalcogenide glasses is composed of covalent molecules (clusters) held together by intermolecular forces. In terms of the model, the photodarkening is considered as resulting from the distortion of the intermolecular distance between the chalcogen atoms, one of which has been transferred from a stable to a quasistable position by a photon having the band-gap energy. The covalent bonds are twisted by the movement of the atom, and the intramolecular bending force prevents the atom from relaxing to its stable position. Therefore, both intramolecular and intermolecular bonding have a significant role in the "bond-twisting model."

The intermolecular bond is of the van der Waals type and it is sufficiently weak that the distance is readily modified by stress.³ Consequently, it is expected that the photodarkening will be considerably affected by the application of hydrostatic pressure to illuminated samples.

Thus, the investigation of the photodarkening in samples under pressure serves as a test of the bond-twisting model.

The purpose of this paper is to describe the first observations of an increase in the photodarkening measured for glassy samples subjected to hydrostatic pressure. Section II of this paper deals with the experimental techniques and Sec. III presents the results. Section IV shows that the results can be accounted for by the use of the bond-twisting model. Section V presents a summary of the important points.

II. EXPERIMENTAL

Specimens examined in this study are bulk glasses and amorphous films of As_2S_3 and Se. The bulk specimens of thickness between 20 and 100 μm were prepared by polishing ingots quenched from the melt. Self-supporting films of thickness between 3 and 30 μm were obtained by peeling the deposited films off a substrate of silicate glasses or Al foil. These deposited films were prepared by conventional evaporation techniques.

Optical measurements as functions of hydrostatic pressure and temperature were performed using an optical-pressure cell, wound with an electric heater. A mixture of equal volumes of silicone oil and kerosene was used as the pressurizing fluid, except for the annealing experiments of As_2S_3 . For the annealing experiments silicone oil was employed, since kerosene rapidly deteriorates above 100°C. However, because of a decrease in the transparency of silicone oil upon intense illumination, the annealing experiments were limited below 3 kbar. The pressure was generated by a pump and intensified by a ram, and the magnitude was monitored by means of a Bourdon gauge connected to the pump. The scale of the gauge was calibrated using the phase-transition point at 3.63 kbar of a NH_4F pellet contained in the pressure cell. The optical transmission was measured by a photomultiplier and a lock-in am-

plier. The absorption coefficient α was calculated from the transmission T by a relation

$$\alpha = (1/d) \ln[(1-R)^2/T],$$

where d and R are the film thickness and the reflectivity evaluated from the index of refraction.^{3,4}

In order to investigate the photodarkening, As_2S_3 specimens were annealed for 1 h in an Ar atmosphere at 170°C, just below the glass-transition temperature. No annealing treatment for Se was required,⁵ since the glass-transition temperature is just above room temperature, approximately 35°C. Some specimens were annealed *in situ* in the pressure cell immersed in the pressurizing fluid. These materials exhibited the same behaviors as samples annealed in an Ar atmosphere. Band-gap illumination was supplied from ultrahigh pressure mercury lamps, and the photodarkening of the specimen was induced by two light beams irradiating simultaneously both surfaces of the specimen. To complete the photodarkening of a thick specimen in a short time, it is more efficient to illuminate in this way than to illuminate only one surface, since the region darkened by the illumination is limited by the penetration depth of the band-gap light.⁶

The thickness of the specimens was measured with a micrometer having an accuracy of $\pm 1 \mu\text{m}$, or calculated from the wavelengths of the interference fringes appearing in the transparent region of the transmission spectrum. On the other hand, changes in the thickness of specimens illuminated under pressure were measured using a multiple-beam interferometer. For this measurement, both surfaces of the illuminated specimen were coated with thin Al films and the changes in the thickness (not the product of the refractive index and the thickness) were measured at 1 atm. The experimental error by using the technique was about $\pm 100 \text{ \AA}$.

III. RESULTS

Figure 1 shows some characteristics of the optical-absorption edges of (a) As_2S_3 and (b) Se. For As_2S_3 , the absorption edges measured for the annealed film and the annealed bulk specimen do not match each other,⁷ as has already been reported by Hamanaka *et al.*⁸ However, the changes in the edges induced by pressure and illumination are similar for both film and bulk (see Table I). Thus, we shall consider only the changes, neglecting the difference of the location of the absorption edges. Furthermore, for As_2S_3 and Se specimens the changes in the absorption edges appear as lateral shifts, and consequently shape is modified little. Therefore, we evaluate hereafter this lateral shift, which represents the change in the optical band-gap energy.

The results of the pressure-induced shift dE/dP of the absorption edge are summarized in Table I. It is accepted³ that amorphous chalcogenides are constructed with molecules (clusters) held together by the van der Waals force, and that the increased interaction among the molecules induced by hydrostatic pressure causes negative coefficients of the shift. The results in Table I are in accord with this view. The fact that as-deposited As_2S_3 films manifest a smaller coefficient is regarded as a result

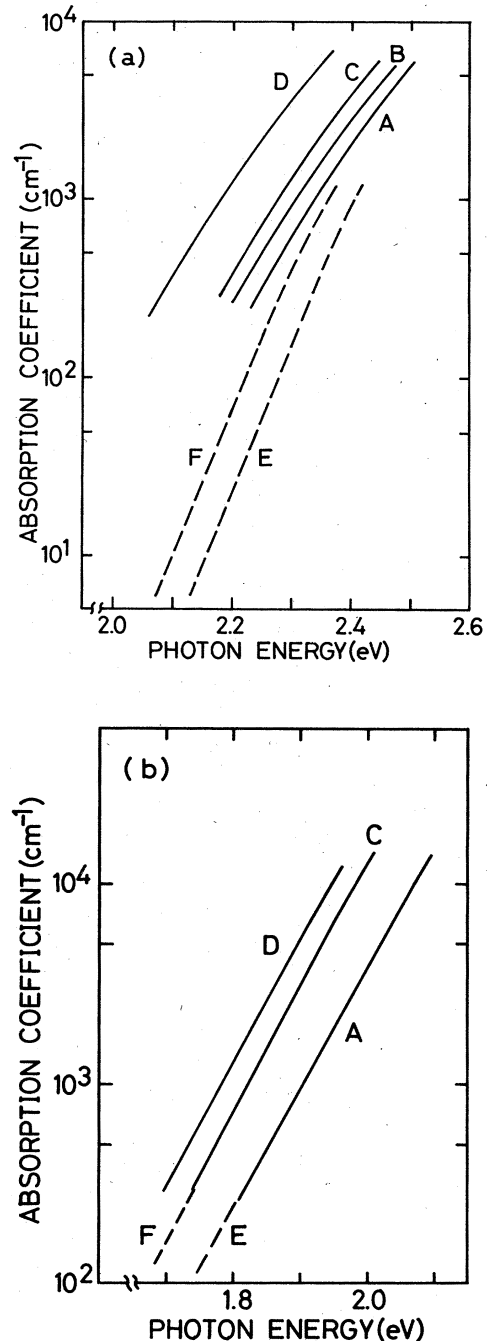


FIG. 1. Optical-absorption edges of (a) As_2S_3 and (b) Se measured at 1 atm (A, B, E) and 5 kbar (C, D, F). A and C represent the films annealed at 1 atm; B and D represent the films illuminated at 1 atm and at 5 kbar; E and F represent the bulk specimens annealed at 1 atm.

of its peculiar bonding structure.¹

Figure 2(a) displays the dependence of the absorption edge on the applied pressure for As_2S_3 . In this figure, the absorption edge of the annealed specimen at 0 kbar is denoted by X. Under pressure, the optical band gap decreases along a line LA, and the specimen once pressed to 5 kbar returns to X upon removal of the pressure; no hys-

TABLE I. Shifts of the absorption edge induced by hydrostatic pressure up to 5 kbar. The experimental error is about ± 1 meV/kbar. The shifts are evaluated at (a) $\alpha=1 \times 10^3 \text{ cm}^{-1}$, (b) $2 \times 10^2 < \alpha < 1 \times 10^3 \text{ cm}^{-1}$, (c) $\alpha=2 \times 10^2 \text{ cm}^{-1}$, and (d) $\alpha=5 \times 10^3 \text{ cm}^{-1}$, where α denotes the absorption coefficient.

| Material | Treatment | dE/dP (meV/kbar) | |
|-------------------------|-------------------|--------------------|-----|
| As_2S_3 | As-deposited film | -18 | (a) |
| | Annealed film | -13 | (a) |
| | Illuminated film | -13 | (a) |
| | Annealed bulk | -12 | (b) |
| Se | Film, bulk | -13 | (c) |
| | Film | -19 | (d) |

teris effects are encountered. If we illuminate the specimen at 0 kbar until the photodarkening is completely saturated, then the edge shifts to Y. By an annealing at 170°C , Y is restored to X. It is known¹ that this reversible behavior is characteristic of photodarkening. In contrast, if we illuminate the specimen to saturation under, e.g., 3 kbar at A, then its absorption edge decreases to C. When the illuminated specimen is depressurized the edge shifts to Z. At room temperature, the state at Z is stable at least several hours in the dark, while Z immediately changes to Y with band-gap illumination. Upon annealing both states Z and Y relax to X. We note here that illuminated states such as Y and C are determined uniquely by the pressure and irrespective to previous history.

The result for Se is shown in Fig. 2(b), and is qualitatively similar to that of As_2S_3 . However, the Se specimen does not exhibit the photodarkening at 1 atm and room temperature,⁵ and Y is identical to X. In addition, the relaxation from Z to X is completed within 1 h. (The specimen relaxes even when depressed slowly from C to Z.) These differences in the behavior of Se compared to that of As_2S_3 may be ascribed to the low glass-transition temperature of Se.

In Fig. 2, it is evident that the edge shift induced by band-gap illumination, the difference between the lines LA and LC, becomes greater with an increase in the hydrostatic pressure. This observation, however, contrasts with the result for As_2Se_3 reported by Kolobov *et al.*,⁹ which indicates the decrease in the photoinduced shift with compression. However, it is not possible to compare their result with that of the current study, since details of the compression geometry and the evaluation method of the photodarkening used by Kolobov *et al.* are not clear.

When considering the result shown in Fig. 2, we regard the state represented by A as being thermally metastable at 3 kbar. To obtain a stable specimen at 3 kbar, we must anneal the specimen at just below the glass-transition temperature under the constant pressure. However, the glass-transition temperature is dependent on pressure and as the reported data¹⁰⁻¹² are scattered, we studied the effects of variation in the annealing temperature upon the photodarkening behavior. The annealing temperature was defined as the lowest temperature at which no photoeffect was induced by band-gap illumination.² The results are

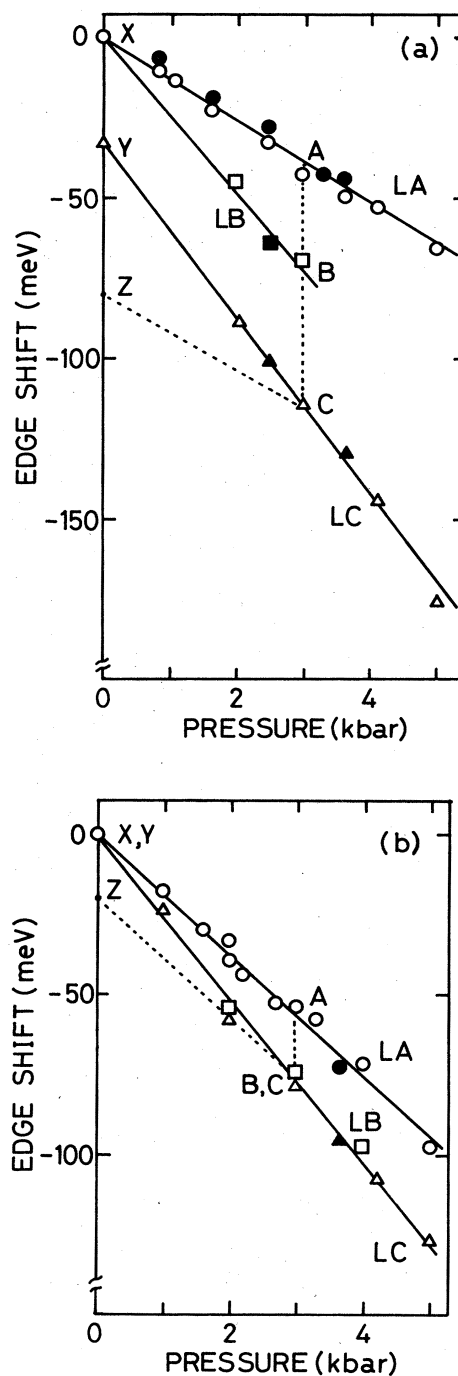


FIG. 2. Shifts of the optical-absorption edges for (a) As_2S_3 evaluated at $\alpha=1 \times 10^3 \text{ cm}^{-1}$ and (b) Se at $\alpha=5 \times 10^3 \text{ cm}^{-1}$, where α denotes the absorption coefficient. The results obtained with the film and bulk specimens are plotted with open and solid symbols. A line LA (data are indicated by circles) represents the shift of the specimens annealed at 1 atm, and LB (squares) and LC (triangles) denote, respectively, the annealed and illuminated states under pressure. In (b), the lines LB and LC overlap each other. Point X and A indicate the absorption edges at 1 atm and 3 kbar of the specimen annealed at 1 atm. Y and C indicate the edges of the illuminated specimens at 1 atm and 3 kbar. Z denotes the state depressed from C, and B the state annealed under 3 kbar.

shown in Fig. 3. There is a reasonable correlation between the temperature obtained in this way and the glass-transition temperature and pressure data reported in Refs. 10–12.

The absorption edges for As_2S_3 and Se were measured after annealing under pressure, and the results are indicated by lines *LB* in Fig. 2.¹³ Furthermore, it was confirmed that for As_2S_3 the change between *LB* and *LC* in Fig. 2(a) could be induced reversibly by illumination and annealing under a constant pressure. Thus, in order to understand the intrinsic role of pressure to photodarkening, we must investigate the difference between the lines *LB* and *LC*, which increases monotonically with the pressure. It is noted here that the annealed state under the pressure, e.g., the state represented by *B*, is determined irrespective of the previous history of the sample.

In marked contrast to As_2S_3 , Se specimens annealed under the pressure exhibit no detectable photodarkening. As shown in Fig. 2(b), the states annealed (*LB*) and illuminated (*LC*) under the pressure are the same with respect to the location of the absorption edges.

We have examined the density change induced by the annealing under the pressure. It is known¹⁴ that chalcogenide glasses are densified by annealing under hydrostatic pressure. Thus, it is possible that the edge shift from *LA* to *LB* in Fig. 2 may accompany an appreciable decrease in the thickness of the specimen. However, it is rather difficult to detect slight thermally-induced changes in the thickness of thin specimens. It is more convenient to measure the change induced by illumination, since the changed area can be limited by an aperture and the resultant relief step at the boundary can be inspected. The fact that the relaxation of As_2S_3 specimens illuminated under the pressure is slow at room temperature and 1 atm enables the thickness change accompanying the edge shifts from *LA* and *LB* to *LC* to be measured at 1 atm. The re-

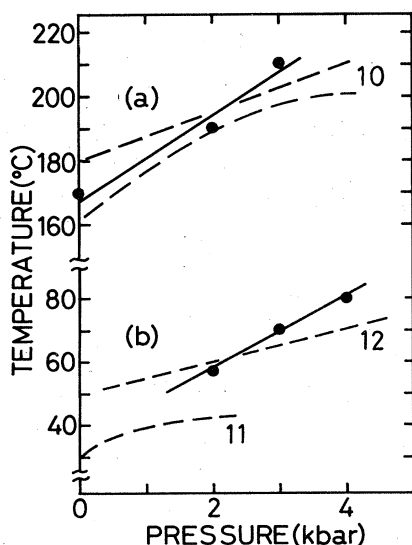


FIG. 3. Annealing temperatures for investigating the photodarkening under the pressure for (a) As_2S_3 and (b) Se. Also shown by dotted lines are the glass-transition temperatures reported in Refs. 10–12.

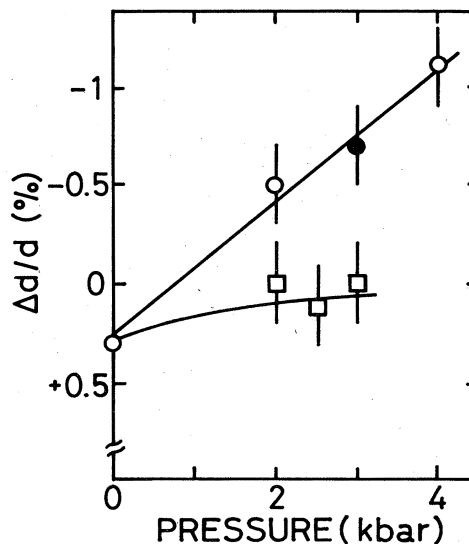


FIG. 4. Fractional changes in the thickness $\Delta d/d$ by band-gap illumination of As_2S_3 accompanying the edge shifts from *LA* to *LC* (circles) and from *LB* to *LC* (squares) in Fig. 2(a). The results obtained with the film and bulk specimens are plotted with open and solid symbols.

sults of the measurement are shown in Fig. 4. It is seen in the figure that the shift from *A* to *C* in Fig. 2(a) accompanies a thickness decrease of 0.7%, while there is little change following the shift from *B* to *C*. As described previously, Se rapidly relaxes after being released to 1 atm, thus we cannot measure similar thickness changes.

IV. DISCUSSION

The result shown in Fig. 4 indicates that the densities of the state thermally densified at 3 kbar, represented by *B* in Fig. 2(a), and the state illuminated at 3 kbar, *C*, are nearly the same, and both states are denser than the compressed state of the specimen annealed at 1 atm, *A*. This means that the densification of the same magnitude is induced not only by the annealing but also by the illumination under the pressure. Since the fractional volume and thickness changes, $\Delta V/V$ and $\Delta d/d$ are correlated as $\Delta V/V = P\Delta d/d$, where $1 < P < 3$, it is estimated from the data in Fig. 4 that the states of *B* and *C* are denser by 1–2% than that of *A*. This value agrees with the densification induced thermally in bulk specimens.^{10,14}

This measured level of densification is comparable with the value that may be calculated from the shift in the optical-absorption edge. Using the data that $dE/dP = -13$ meV/kbar as summarized in Table I and the compressibility $\beta = (-1/V)(dV/dP) = 8 \times 10^{-3}$ kbar⁻¹,^{3,14,15} we calculate that a densification of 2% accompanies the edge shift of -30 meV from *A* to *B* in Fig. 2(a). Therefore, the difference between the absorption edges represented by the lines *LA* and *LB* in Fig. 2(a) is attributable to the densification alone.

The densification for Se is evaluated in a similar way. Since the volume contracts inevitably with annealing under pressure, the shift of the absorption edge from *A* to

B in Fig. 2(b) can be ascribed to the densification. Therefore, we estimate the magnitude from the shift. This is calculated as $\Delta V/V = -1\%$ at 3 kbar with the results; $dE/dP = -19$ meV/kbar (Table I), $\beta = 1 \times 10^{-2}$ kbar $^{-1}$,³ and that the difference of the edges between A and B is 20 meV. In addition, it is not thought to be coincidental that the annealed (LB) and illuminated (LC) states under the pressure have the identical energy gap. We suggest that the illumination under pressure leads to a densification of the same magnitude as that induced by annealing in a similar manner to that for As_2S_3 .

It is of interest that in both As_2S_3 and Se, the densification under pressure is induced not only by annealing, but also by illumination. The detailed mechanism connected with this phenomenon is not known at present, but it probably has some relation with the observations¹⁶ of the release of the internal stress by illumination in Se films.

The fact that the photodarkening in As_2S_3 , that is the difference between the lines LB and LC in Fig. 2(a), increases with pressure can be quantitatively explained in terms of the bond-twisting model for photodarkening.² It is known that the hydrostatic pressure both reduces intermolecular distances,³ and also increases the force constant K associated with the intermolecular bonding with a rate $(1/K)(dK/dP) = 5 \times 10^{-2}$ kbar $^{-1}$.¹⁵ In contrast, the dependence of the photodarkening ΔE on the pressure in Fig. 2(a) gives a value

$$(1/\Delta E)(d\Delta E/dP) = 8 \times 10^{-2} \text{ kbar}^{-1}.$$

In the bond-twisting model,² it is assumed that the photodarkening results from the photoinduced distortion of the van der Waals distance. The distortion energy is proportional to K , and thus the magnitude ΔE of the photodarkening is thought to increase with K , because the excitation energy of electrons in strong electron-lattice coupling systems is modified by the distortion of the lattice. Therefore, the agreement¹⁷ of the pressure coefficients of K and ΔE implies that the photoinduced distortion of the van der Waals distance is essential to the photodarkening, and that the bond-twisting model is appropriate for the understanding of the photodarkening, although other possibilities¹ may still remain.

However, another explanation for the observations is possible. It is demonstrated in Fig. 1 of Ref. 2 that the photodarkening ΔE correlates with T_i/T_g ; ΔE becomes zero as T_i/T_g increases to unity, where T_i and T_g denote the temperature at which the specimen is illuminated and the glass-transition temperature. Applying this empirical relationship obtained at 1 atm to the present case, we calculate the photodarkening at 3 kbar to be 50 meV, since $T_i/T_g = 0.6$ [$T_i = 300$ K and $T_g = 480$ K as shown in Fig. 3(a)]. This magnitude also agrees with the experimental result shown in Fig. 2(a).

We shall now show that these two interpretations are equivalent. It is known^{2,18} that the glass-transition temperature of various chalcogenide glasses increases with N , the average coordination number of the covalent bond per atom. We may consider that the number N represents the rigidity of the covalent molecules (clusters) contained in the glass. In Se, each atom is connected to two adjacent atoms and forms a chain molecule, and this is regarded as

more flexible than the distorted layer molecule¹⁹ of As_2S_3 , in which the atom is bonded to 2.4 neighbors on the average. Since the glass transition is accompanied with the breakage of the intermolecular bonds and the consequent slipping of the molecules through each other,¹⁹ the glass-transition temperature is low, provided that the molecules can be deformed smoothly and the diffusive motion can be readily induced thermally. Therefore, the observations that the number N scales with the glass-transition temperature are reasonable. In this argument, however, the variable strength of the intermolecular interaction has been neglected.

In order to understand clearly the change induced by pressure, we introduce the concept of an effective coordination number N_e , which is the sum of the covalent coordination number N and a measure of the strength of the intermolecular bonding proportional to the force constant K . The application of the hydrostatic pressure causes even closer contact between the constituent molecules,^{3,15,20} which gives rise to an increase in N_e . As the number becomes larger, a greater amount of thermally-induced fluctuations is required to break the intermolecular bonds, and thus the glass-transition temperature of the material increases with N_e . Accordingly, the correlation between the glass-transition temperature and the force constant K can be understood in a coherent way. We see, therefore, that the two interpretations of the photodarkening in As_2S_3 under the hydrostatic pressure are compatible with each other. It is noted here that the consideration of the pressure-induced increase in the glass-transition temperature presented above is essentially the same as the model of Eisenberg,¹¹ in which the rise of the transition temperature is related to a reduction of the free volume with increasing pressure.

This approach also explains why the densified Se does not exhibit photodarkening at room temperature. Although the force constant for Se may be enhanced by pressure,²⁰ the value of N_e is approximately 2 and then the glass-transition temperature is not sufficiently high to prevent the distorted structure from relaxing. In fact, by using the result shown in Fig. 3(b) we calculate T_i/T_g to be 0.85 at 4 kbar, and this value leads to $\Delta E = 5$ meV,² a magnitude comparable with the experimental error of the results shown in Fig. 2. In addition, the structure of Se is sufficiently flexible that the intermolecular distance may be compressed efficiently by pressure and no space is available for bond twisting.² This contributes to the absence of photodarkening in Se under pressure.

V. SUMMARY

Application of pressure to solids, in which van der Waals bonding plays a dominant role, offers the possibility of a deeper insight into their physical properties. In this paper, the photodarkening phenomenon in amorphous As_2S_3 and Se was investigated under hydrostatic pressure up to 5 kbar. The magnitude was limited so that complicated nonlinear effects were not induced, however, it was still sufficient to bring about changes in the photoinduced phenomenon.

There are several common features to behaviors of

As₂S₃ and Se. Firstly, the illuminated or annealed states are determined uniquely by the applied pressure and do not depend upon previous treatment. Secondly, the specimens annealed at 1 atm exhibit a decrease in the band-gap energy upon illumination under pressure. Thirdly, in addition to densification effects due to annealing,^{10,14} densification is induced also by illumination under pressure.

In contrast, there is a significant difference between these two materials. Under pressure the photodarkening is observed for As₂S₃, while for Se it is not. The reason why the photodarkening is not detected in Se is attributable to its low glass-transition temperature resulting from the flexible microscopic structure. The photodarkening in As₂S₃ monotonically increases with the pressure, which can be interpreted quantitatively with the aid of the

bond-twisting model.² This offers new evidence that the model is appropriate to the understanding of the photodarkening behavior in chalcogenide glasses. This model also draws attention to the important role of intermolecular interactions in determining the glass-transition temperature.

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