Chemical and medium-range orders in As$_2$S$_3$ glass

Keiji Tanaka

Department of Applied Physics, Faculty of Engineering, Hokkaido University, 060 Sapporo, Japan

(Received 18 June 1987)

Structures and optical-absorption edges of As$_2$S$_3$ glasses prepared by quenching at various temperatures have been studied. Raman scattering spectra show that the medium-range order decreases in the specimens rapidly quenched from temperatures higher than the glass-transition temperature, and that in the samples quenched from the vapor phase the homopolar-bond density is substantially increased. The medium-range order is recovered with annealing at the glass-transition temperature, and in contrast, for lessening the homopolar bonds and improving the chemical order, annealing at temperatures higher than the melting temperature is required. Increases in the structural disorders accompany red shifts of the optical-absorption edge and decreases in the slope of the Urbach tail.

I. INTRODUCTION

Amorphous materials are characterized by disorder or structural randomness, and atomic configurations of a material having a fixed chemical composition are different from sample to sample, depending on the preparation method and so forth. The existence of a variety of amorphous structures is then tightly connected with another nature, i.e., the metastability. The material is in one of quasiequilibrium states having different internal energies. In a liquid, however, numerous disordered configurations can be regarded as a manifestation of thermal fluctuation. For a crystalline material, in contrast, we can in principle prepare a single crystal having a periodic structure, and its properties are uniquely determined under a combination of temperature and pressure.

The structural variations in amorphous semiconductors substantially modify the electronic properties. For instance, it is known that as-evaporated As$_2$S$_3$ films have wider optical energy gaps than those of annealed As$_2$S$_3$ films. DeNeufville has demonstrated that the as-evaporated films are composed of molecular units interconnected in network structures, and that the annealed films are cross linked. Thus the electron wave functions in the as-evaporated films are assumed to be localized, and the interaction among electron orbitals belonging to different molecules is reduced. Bandwidths may, therefore, be smaller in as-deposited films, contributing to the blue-shifted absorption edges. In contrast, for amorphous GeS$_2$, it has been shown that the optical-absorption edges of evaporated films are shifted to lower energies than those of melt-quenched glasses. A number of dangling and homopolar bonds in the film appear to be responsible for the red-shifted absorption edges.

For glassy materials, the diversity of properties may be reduced when the preparation method is restricted to melt quenching; however, the properties are still influenced by several parameters characterizing the quenching process. A well-known example is the fact that the glass-transition temperature becomes higher with increasing quenching rate. The relations between various properties and structures depending on preparation procedures, however, have not been fully studied so far.

In order to elucidate the correlation between structures and properties of amorphous semiconductors, we examine systematically the preparation dependence for As$_2$S$_3$ glass. The main reasons why this material was selected are that the energy gap of about 2.4 eV is pertinent to optical measurements and that the material hardly crystallizes thus permitting a wide range of preparation conditions.

In contrast to crystalline structures, atomic configurations of amorphous materials are not known explicitly, and therefore arguments on the properties may necessarily be weak, being constructed on speculative ideas. For obtaining insight as clear as possible, we will try to interpret the electronic and structural results in a coherent fashion, at least in a qualitative sense. In Sec. II experimental details are described. Section III provides results and discussion for properties of As$_2$S$_3$ glasses. Finally, we summarize arguments in Sec. IV. A preliminary result of the present work was published previously.

II. EXPERIMENTS

As$_2$S$_3$ glasses were prepared as follows. A bulk ingot was synthesized in an evacuated ampoule by having elements of 99.9999% purity react at 800°C in a rocking furnace with subsequent quenching. The ingot was crushed, and chunks of 1 g were again vacuum sealed in quartz ampoules. The materials were heated in the furnace, stored for 10 h at various temperatures denoted as $T_q$, and then quenched into water or cooled down to room temperature in the furnace. Cooling rates of these two processes were estimated to be 10 and 10$^{-2}$ K/sec. On the basis of previous results for quenching experiments, it could be assumed that the fast and slow cool-
ing rates are appropriate, respectively, to freeze high-
temperature states and to produce stabilized glasses. It
could also be assumed that the composition variation
among the samples was small because of the above-
mentioned procedure, and x-ray microprobe analyses
indeed revealed that the variation was smaller than ±1
at.-%, the resolution being limited by the analyzing
procedure.

The samples were annealed at a temperature denoted
as $T_a$ for 1 h. When $T_a < T_g$ (the glass-transition
temperature), the annealing treatment was performed in
a flowing Ar ambient. In contrast, when $T_a > T_g$ the
glassy samples were annealed in vacuum-sealed quartz
ampoules. For both treatments, specimens were slowly
cooled to room temperature after being stored at $T_a$.

The bulk glasses were polished into parallel-sided
wafer thickness of 10–300 μm for optical transmittance
measurements. The optical absorption coefficient $\alpha$
around the absorption edges was evaluated from the
transmittance $T$ by using an equation

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

where $d$ is the sample thickness and $R$ is the reflectivity
at sample surfaces. $R$ was calculated using the Fresnel
formula from the refractive index $n$ given by Rodney
et al.\(^5\) for glassy As$_2$S$_3$. It is known that the magnitude
of the refractive index depends on preparation pro-
cedures, e.g., at $\lambda = 6328$ Å, $n = 2.45$ for as-evaporated
As$_2$S$_3$ films\(^7\) and $n = 2.61$ for Rodneys’ bulk glasses.\(^8\)
The difference is 0.16, and the influence on $\alpha$ is less than
100 cm$^{-1}$. Taking gross structural differences between
as-deposited films and bulk glasses into account,\(^2\) it can
be assumed that the variation of refractive indices
among melt-quenched As$_2$S$_3$ samples is substantially
smaller.\(^9\) Accordingly, errors introduced from neglecting
slight modification of $n$ may not be essential in the
present discussion.

Raman scattering spectra were excited by an un-
foocussed beam from a 15-mW He-Ne laser, and scattered
light at a right angle was dispersed by a double monochromator and detected by a photon-counting apparatus.
No polarization analyses were performed. Photoinduced
changes\(^2\) were not detected in the counting intervals of 1 h.
\(^9\) Differential-scanning-calorimetry (DSC) thermograms
were measured with a heating rate of 10 K/min
($= 0.2$ K/sec) for samples of 5 mg contained in Al sam-
ple pans. X-ray diffraction experiments showed that all
specimens exhibit no crystalline peaks. In addition, no
discernible differences were observed among the x-ray
patterns of As$_2$S$_3$ glasses having different $T_g$ and the
quenching rate.

III. RESULTS AND DISCUSSION

Figure 1 shows the DSC thermograms typical to slow-
ly cooled and rapidly quenched samples from
$T_q > 250$°C. The inflection points in the thermograms,
the temperatures of which correspond to $T_g$, are located
at about 190°C, seemingly similar to each other. It is
pointed out, however, that a hump is accompanied only
with the glass-transition signal of the slowly cooled sam-
ple. According to Owen’s argument\(^1\) based on relaxa-
tional kinematics, existence of the hump indicates that
$T_g$ is lower than the inflection point of the DSC trace.
The argument predicts that if the DSC heating rate were
slower than the cooling rate of the sample preparation,
the heat capacity would change at a lower temperature.
(In the present experiment, the heating rate could not be
arranged slower because of the small glass-transition sig-
nals.) Thus the hump is considered to be a signature indi-
cating that the slowly cooled sample is more stabilized
or nearer to the equilibrium state. A difference in DSC
thermograms similar to Fig. 1 has been detected between
as-evaporated and annealed As$_2$S$_3$ films.\(^10\)

A. Optical-absorption edge

Figure 2 shows the optical-absorption edges of slowly
cooled and rapidly quenched glasses from 650°C. We see
that when $\alpha \approx 10^2$ cm$^{-1}$ both samples exhibit the
characteristics represented by

$$\alpha = \exp(\Gamma \hbar \omega),$$

where $\Gamma$ may be called the Urbach parameter\(^11\) and $\hbar \omega$
is the photon energy. There are, however, distinct dif-
fences between the two samples. The quenched glass shows a less steeper absorption tail located at a
lower-energy side than that for the stabilized sample.
The location and the steepness parameter may be good
measures of the optical absorption edges, and hence we
will evaluate the optical energy gap $E_g$ defined as the
photon energy where $\alpha = 1 \times 10^1$ cm$^{-1}$. We also examine
$\Gamma$ calculated at $\alpha = 1 \times 10^2$ cm$^{-1}$.

The dependence of $E_g$ on $T_q$ is shown in Fig. 3(a). Ir-
respective of $T_q$ values, all slowly cooled samples exhibit
a fixed $E_g$ of 2.43±0.01 eV, implying a unique electronic
property. In contrast, quenched samples reveal a pecu-
liar variation. When $T_q < T_g$, $E_g$ is the same as that of
the stabilized sample, the result being reasonable since
these samples are cooled slowly through $T_g$. When
$T_q > T_g$, $E_g$ becomes smaller to 2.40 eV, retaining the
constant value in a region of $T_g < T_q < T_b$ (the boiling
temperature\(^5\)). It decreases further with $T_q$ if $T_q > T_b$.

The dependence of $\Gamma$ on $T_q$ is shown in Fig. 3(b). Al-

![FIG. 1. DCS thermograms of slowly cooled (upper) and rap-
 idly quenched (lower) samples from 950°C. Endo- and exo-
 thermic directions are indicated on the vertical axis.](image-url)
though sample-to-sample variations of about ±4 meV appear to be relatively large, it demonstrates that the quenched samples exhibit an abrupt change at $T_g$ and an inflection at $T_b$.

Figure 3 includes the characteristics for the samples annealed at 180°C ($\approx T_g$). For the slowly cooled glasses and the samples quenched from temperatures of $T_q < T_g$, the annealing induces no appreciable changes. In contrast, upon the annealing all the samples quenched from temperatures higher than $T_g$ exhibit an increase in $E_g$ of 30 meV, or a reduction of $\alpha$ by two factors, and a decrease in $\Gamma^{-1}$ of $\sim 5$ meV. These changes may manifest approach to the stabilized state. It should be mentioned, however, that the glasses of $T_q \geq T_g$ are, even after the annealing, different from the stabilized glass in respects of $E_g$ and $\Gamma^{-1}$.

Figure 4 shows the correlation between $E_g$ and $\Gamma^{-1}$, which is obtained by reploting the dependences on $T_q$ depicted in Fig. 3. Also included in the figure are the results summarized by Street et al. The results spreading at around $E_g = 2.4$ eV and $\Gamma^{-1} = 65$ meV are compatible with the present data, which indicate a negative correlation:

$$E_g \propto -\Gamma^{-1}.$$ (3)

It is worth mentioning in Fig. 4 that the results for as-prepared and annealed samples seem to be plotted on a common line. Cody et al. have discovered a similar proportionality for amorphous Si:H films having various H contents. Therefore, the relationship between $E_g$ and $\Gamma^{-1}$ appears to be universal to amorphous semiconductors. The correlation is predicted theoretically for generalized random structures. According to the argument given by Abe and Toyozawa, the relation is resulted from uncorrelated increases in interband potential fluctuations.

### B. Raman scattering

In order to investigate the origin of the changes in the electronic properties, Raman scattering spectra of the samples denoted as A, B, C, and D in Fig. 3(a) were inspected. The results are shown in Fig. 5. Here, A represents the characteristics of the slowly cooled sample as well as the sample quenched from 350°C and then annealed at 180°C. Both of these may be regarded as reference materials in the following discussion.

The sample A shows two prominent peaks at $\sim 350$ cm$^{-1}$ and $\sim 30$ cm$^{-1}$. The high-frequency peak is attributed to vibrational modes of pyramidal AsS$_3$ units. For the low-frequency Raman peak, interpretation of the origin has still been controversial. According to the argument given by Abe and Toyozawa, the relation is resulted from uncorrelated increases in interband potential fluctuations.
According to a recent study by Ahmad et al.,\textsuperscript{18} the Raman peak is ascribed to a non-Debye-type phonon density of states $g(\omega)$. They have demonstrated that $g(\omega)$ at around $\omega = 0.5$ THz of quenched As$_2$S$_3$ samples is reduced by a heat treatment at 150°C, a stabilization process. This reduction accompanies a shift of the Raman peak to a higher wave number and a decrease in its intensity. The phonon mode of interest has a wavelength of $\sim 40$ Å, and therefore the reduction in the phonon density may imply decreases in structural fluctuations having similar spatial dimensions. In contrast, Strom and Freitas\textsuperscript{19} have argued on the basis of the distorted layer model\textsuperscript{20} for the structure of glassy As$_2$S$_3$ that a higher-wave-number part in the low-frequency Raman peak can be attributed to the rigid-layer modes, which are observed in the layered As$_2$S$_3$ crystal. In light of their model, an increase in the medium-range order may provide an increase in the optic mode intensity, so that the low-frequency peak is seemingly shifted to higher frequencies. Thus both interpretations predict that when the medium-range structural correlation is enhanced, the peak frequency increases. We will, therefore, evaluate the degree of the medium-range structural order by $k_{\text{max}}$, the wave number of the low-frequency peak.

The difference between sample $A$ and $B$ lies in the low-frequency Raman peak, or in the medium-range correlations. The peak $k_{\text{max}}$ of $B$ is located in a lower wave number than that of $A$. This observation is understandable if the medium-range structure in $B$ is more disordered than that in $A$. That is, the difference indicates that the annealing at $T_q$ improves the medium-range order.

With regard to the Raman scattering spectra in Fig. 5, sample $C$, which is quenched from the higher temperature than $T_b$, shows two distinct features from the sample $A$. One is the position of the low-frequency peak, the consequence of which has been discussed in the above. In addition to this characteristic, we see small humps at around $230$ cm$^{-1}$ and $500$ cm$^{-1}$ in the spectrum for $C$. These peaks can be ascribed, respectively, to As—As and S—S homopolar bonds, on the basis of a compositional study for As-S glassy systems.\textsuperscript{21} It is known that in glassy As-S systems heteropolar As—S bonds are energetically favored,\textsuperscript{11} and accordingly the humps indicate inclusion of a small number of the homopolar bonds in the stoichiometric glass, i.e., a broken chemical order.

If we may assume that the intensity $I_{230}$ of the Raman peak at $230$ cm$^{-1}$ is linearly dependent on the content of the As—As bond, the composition dependence of $I_{230}/I_{350}$, where $I_{350}$ denotes the intensity of the As-S peak, implies that approximately 1% bonds are homopolar in sample $C$.\textsuperscript{4} This magnitude is comparable to the compositional uncertainty of the investigated samples, and whether the stoichiometry is retained in the sample or not might be doubtful. Nonetheless, we may speculate that the quenched sample contains appreciable numbers of the homopolar bonds with the reasons that the homopolar peaks were more conspicuous in all samples of $T_q > T_b$ than in the stabilized sample [see Fig. 6(b)]. Moreover, the compositional uncertainty of 1% in x-ray microprobe analyses is attributable to the measuring process, and a real compositional variation is estimated to be smaller. We can, therefore, assert that sample $C$ is stoichiometric, but it is degraded in respect of both medium-range and chemical orders.

Sample $D$, which is obtained through annealing $C$, exhibits the low-frequency peak similar to that in $A$. This means that the medium-range order is recovered by the

![FIG. 5. Raman scattering spectra for samples A, B, C, and D defined in Fig. 3(a). $k$ denotes the wave number.](image)

![FIG. 6. The dependence of $E_g$ on $k_{\text{max}}$ (a) and on $I_{230}/I_{350}$ (b) for samples having various $T_q$ values. Results for as-quenched (circles) and annealed (triangles) glasses are shown, and changes induced by annealing at 180°C are depicted by arrows.](image)
annealing. In contrast, however, no appreciable changes are induced in the homopolar bond peaks, suggesting that the annealing at 180 °C is ineffective to convert the defective bonds to the heteropolar bonds.

C. Relations between electronic properties and structures

It is seen in Fig. 6(a) that in all samples investigated the annealing induces the increase in the structural order of $\Delta E_g^{\text{max}} = \sim 5 \sim 10$ cm$^{-1}$ accompanying the increase in $E_g$ of $\sim 30$ meV. Therefore, we speculate a proportionality:

$$\Delta E_g^{\text{M}} \propto k_{\text{max}},$$

where $\Delta E_g^{\text{M}}$ expresses the change in $E_g$ influenced from modifications in the medium-range order. Kawamura et al. have studied the dependence of energy gaps and Raman scattering spectra of As$_2$S$_3$ glasses on $T_g$, where $170 ^\circ C \leq T_g \leq 400 ^\circ C$ in their work. Their results exhibit a tendency similar to that shown in Fig. 6(a).

Taking the Raman scattering results into account, we can connect the further decrease in $E_g$ of the quenched sample C from that in B to the broken chemical order. A possibility that the homopolar bonds in a stoichiometric glass, or “wrong” bonds, produce electronic defect states at band edges which lessen the energy gap has been theoretically predicted by Vanderbilt and Joannopoulos. It is also demonstrated experimentally that deposited GeS$_2$ films containing a large number of homopolar bonds exhibit the optical-absorption edges located at lower energies than that of bulk GeS$_2$ glasses.

Figure 6(b) shows the relation between $E_g$ and the normalized intensity of the Raman peak attributable to As—As bonds. Within the experimental errors of $\pm 0.01$ eV for $E_g$ and $\pm 0.01$ for the intensity, each results for as-quenched and annealed states seem to be plotted on straight lines representing negative proportionalities,

$$\Delta E_g^C \approx -I_{330},$$

where $\Delta E_g^C$ denotes the change in $E_g$ induced with the chemical disorder. In this figure the effect of the annealing is represented approximately as shifts along the vertical direction. That is, no changes in the homopolar density are induced with the annealing. The fact that only the medium-range order is recovered with annealing at $T_g$ [Fig. 6(a)] while the covalent bonds are intact is compatible with a model proposed for structural relaxation at $T_g$.

The dependence of $E_g$ on the homopolar-bond density gives insight to electronic states at the band edges. As was mentioned in the previous section, the homopolar-bond density of the quenched sample of $T_q = 1100$ °C is estimated to be 1 at.%. This means, under an assumption of a homogeneous distribution of the defective bonds, that the separation between them is $\sim 10$ Å, since the atomic volume of As$_2$S$_3$ glass is $\sim 15$ Å$^3$/atom. In contrast, Fig. 6(b) suggests that the defect density in the stabilized sample is approximately one third of the quenched glass, which can be converted to the separation of $\sim 20$ Å. Accordingly, we may assume that the reduction in the distance between the defects from $\sim 20$ Å to $\sim 10$ Å is responsible for the shrinkage in $E_g$ of $\sim 30$ meV.

As shown in Fig. 6, two kinds of disorders affect additively on $E_g$, and thus we can summarize the above argument as

$$E_g = 2.43 \text{ (eV)} - \Delta E_g^M - \Delta E_g^C,$$

where 2.43 eV is the energy gap of the stabilized glass. The second term expresses the effect of potential fluctuations relating to the medium-range structure, and the third term is ascribed to fluctuations arising from the wrong bonds.

The change in the Urbach parameter shown in Fig. 4 is consistent with the present model assuming the structural modifications. It is accepted that the parameter $\Gamma$ reflects the degree of structural randomness, although a theoretical understanding on the origin of the Urbach tail is still in infancy. It becomes smaller with increasing disorder. Thus the observations that the quenched samples have smaller $\Gamma$ can be attributed to the increase in the structural randomness, which reduces $E_g$ as was discussed in the above. By recalling Eq. (3), we may obtain an expression for $\Gamma^{-1}$ similar to that for $E_g$ in Eq. (6).

In order to examine further the annealing effects on $E_g$, the quenched samples from 1000 °C were heat treated at various temperatures. As shown in Fig. 7, the sample annealed at $T_a \approx T_g$ shows an increase in $E_g$, which has been ascribed to the recovering of the medium-range order. In a higher $T_a$ region, the scattering of data becomes greater with presently unknown reasons. Nonetheless, it seems that a further increase in $E_g$ occurs when $T_a \approx 600$ K $\approx T_m$ (the melting temperature), and upon the annealing the quenched glasses show a similar $E_g$ to that of the stabilized glass.

This result appears to be irrational, since in a glassy material the melting temperature has no physical consequences. The change between liquid and super-cooled states is continuous and smooth for good glass formers, and indeed DSC studies could detect no specific signals at around 600 K. It is also worthwhile to mention that $T_g$ of As-S glassy systems is lower than 470 K, which deviates significantly from the temperature of interest.

![FIG. 7. The dependence of the energy gap $E_g$ of samples quenched from 1000°C on the annealing temperature $T_a$.](image-url)
The mechanism for which the annealing at \( T_g \geq T_m \) is effective to stabilize the quenched glasses is not understood at present.

Correlation between the magnitude of the optical bandgap and structures in evaporated \( \text{As}_2\text{S}_3 \) is discussed here. It is known that as-evaporated \( \text{As}_2\text{S}_3 \) films have comparable energy gaps with that of the stabilized glass. In addition, Nemanich and Street et al. have demonstrated through Raman scattering and EXAFS studies that the as-evaporated films are constructed with many small molecules containing homopolar bonds. The existence of the wrong bonds contributes to a decrease in that the as-evaporated films are constructed with many small molecules containing homopolar bonds. The existence of the wrong bonds contributes to a decrease in comparable energy gaps with that of the stabilized glass. However, electron wave functions may be strongly localized in the molecules, and lessen bandwidths as demonstrated by ultraviolet photoemission spectroscopy (UPS) studies. This molecular effect may cancel the chemical influence, resulting in the similar optical-absorption edge.

There seems to exist some connections between the quenched \( \text{As}_2\text{S}_3 \) glass and annealed films in respect of amorphous structures. Historically, it had been assumed that there are no gross structural differences between the films which were annealed at \( T_g \) and bulk glasses. Hamanaka et al., however, have discovered that the optical-absorption edge of annealed films is located in a lower-energy side than that of annealed bulk samples. Furthermore, Nemanich et al. have shown that annealing cannot induce complete transformations from homopolar to heteropolar bonds. Kosek et al. have demonstrated the existence of the defective bonds in films by using a novel chemical technique. It is, therefore, envisaged that the structure of the annealed films resembles that of the bulk glasses which are quenched from \( T_q > T_b \) and then annealed at \( T_g \). Most of bulk glasses prepared in previous studies are quenched from temperatures of \( T_g < T_b \), so that these may contain a smaller number of homopolar bonds.

It may be worthwhile to mention that the structure of quenched glasses of \( T_q \geq T_b \) is distinct from that of as-deposited films mainly consisting of spherical molecules. This may suggest, although both materials are prepared through vapour phase, the quenching in bell jars is much milder than that in small ampoules.

IV. SUMMARY

Dependence of atomic and electronic structures of glassy \( \text{As}_2\text{S}_3 \) on preparation methods and annealing treatments has been studied. The amorphous structure is modified by changes in three parameters, i.e., the temperature from which the melt is quenched, the quenching rate, and the annealing temperature. The present result can be summarized as shown in Fig. 8. Slowly cooled samples are mostly stabilized. Samples quenched into water from temperatures between \( T_g \) and \( T_b \) are lacking mainly in medium-range orders. Samples quenched from higher temperatures are in addition chemically disordered. To improve the medium-range order, annealing at temperatures above \( T_g \) is required, whereas the chemical order is recovered with annealing above \( T_m \).

It has also been discovered that the optical-absorption edge is affected with the two kinds of structural disorders. Accompanying the increase in the disorders, the optical absorption edge is red shifted with decreasing its slope. The influence of the disorders on the position and the steepness parameters of the Urbach tail are represented by the additional formula. Characteristics of deposited \( \text{As}_2\text{S}_3 \) can be understood as influenced by the chemical disorder and molecularity.

ACKNOWLEDGMENTS

The author would like to thank Professor S. Minomura and Professor J. Nakahara for use of Raman scattering equipment, and to Mrs. M. Tazawa and R. Kawase for their experimental assistance. The present work is partially supported by The Asahi Glass Foundation for Industrial Technology.

---

9752 KEJI TANAKA

Am. 48, 633 (1958).