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THE CHARGED DEFECT EXISTS?

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The origin of gap states in chalcogenide glasses has been studied on the basis of optical spectra obtained for As_2S_3 using photoluminescence, photothermal deflection, and (resonant) Raman scattering. These results combined with other observations suggest that the weak-absorption tail arises from gap states below the conduction band, which are produced by As-As wrong bonds. The bond density is estimated at ~ 1 at.%, which is much greater than that of the charged defect proposed by Mott et al. These insights imply that, not the charged defect, but the wrong bond governs electronic properties in covalent chalcogenide glasses.

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Keywords: Chalcogenide glass, As_2S_3 , Optical absorption edge, Urbach edge, Weak-absorption tail

1. Introduction

Pioneering work upon chalcogenide glasses started in the middle of 20 century, and now at the beginning of 21 century, we have obtained a fair amount of experimental data, several hypotheses, and a few basic ideas [1-3]. Among the hypotheses, one of the most frequently employed for covalent chalcogenide glasses such as As_2S_3 is the charged-defect and valence-alternation pair models proposed by Street and Mott [4] and Kastner et al. [5]. Using these charged-defect concepts, they and successive researchers have asserted that unique electronic properties can be understood in coherent ways [1,3]. For instance, the photoluminescence (PL) with large Stokes shifts has been interpreted as creation of D^0 from D^+ and/or D^- (in Mott's notation). However, since D^+ and D^- are inherently ESR-inactive and the density is estimated to be ppm levels [1,3-5], direct evidence of the existence has not been obtained. On the other hand, other possibilities for gap states have been suggested by several researchers [6-10].

I have studied the origin of optical absorption spectra in covalent chalcogenide glasses with two motives. One is to understand the mechanism of subgap photoinduced phenomena, which are in some cases more prominent than those induced by bandgap light [11]. Since the subgap phenomena are induced by light with photon energies in Urbach-edge regions, which are expressed as $\alpha \propto \exp(\hbar\omega/E_U)$, where $E_U \approx 50$ meV in As_2S_3 [1,3], structural origins of the Urbach edge should be understood. The other is to grasp the origin of weak-absorption tails (WATs), which extend below the Urbach edge as $\alpha \propto \exp(\hbar\omega/E_W)$, where $E_W \approx 300$ meV in As_2S_3 [1,3]. Tauc et al. have demonstrated that Fe impurities enhance the WAT [12]. However, even in highly-purified ingots the tails still remain, which becomes to be a serious problem in applications to IR-transmitting optical fibers [13]. Therefore, the origin should be examined in more details.

To understand optical absorption mechanisms, it is necessary to resolve the spectra into densities-of-states. That is, the optical absorption spectrum $\alpha(\hbar\omega)$ in amorphous semiconductors is governed by the densities of occupied and unoccupied states, $D_V(E)$ and $D_C(E)$, as [1,3]

$$\alpha(\hbar\omega) \propto \int D_C(E + \hbar\omega) D_V(E) dE, \quad (1)$$

and accordingly, $D_V(E)$ and $D_C(E)$ must be known. We may expect that these densities can directly be obtained through photoemission studies, while nevertheless, the sensitivity of photoemission measurements seems to be insufficient at present for evaluation of gap states [1,3]. Then, another way to know the gap states responsible for $D_V(E)$ and $D_C(E)$ is to employ a variety of experiments, and to construct a model from the results. If several observations can be understood coherently by a simple model, we can assume it to be plausible.

Previously, it has been suggested that the Urbach edge arises from tail states above the valence band [7,14,15]. Circumstantial evidence for this suggestion is that the so-called Urbach

energy E_U is similar to the characteristic energy of the valence-band tail [15], which is obtained from pulsed photoconduction measurements through some assumptions.

In the present work, I will show that the WAT in As_2S_3 arises from unoccupied gap states below the conduction band and that the states are produced by As-As wrong bonds. Its density is estimated at percent levels, which are much greater than that of the charged defects. Actually, the existence of many homopolar bonds seems to be inherent to covalent glasses, and accordingly, I believe that the charged defects cannot govern electronic properties in chalcogenide glasses.

2. Experiments

Samples employed were As_2S_3 glasses of two purity levels. One was those prepared previously [16]. Here, an ingot was synthesized from As and S chunks with 6-nine purity through the conventional melt-quenching procedure. Then, splinters obtained from the ingot were sealed again into quartz ampoules, heated to 1000 °C, and then rapidly-quenched (10^2 K/s) or slowly-cooled (10^{-1} K/s) to room temperature. The other was a high-purity ingot, which was prepared for optical fibers, the details of purification and synthesis procedures being unknown [17]. Sliced samples were polished to small disks, and then annealed at 180 °C before optical measurements. In addition, $\text{As}_x\text{S}_{100-x}$ glasses with $x = 17 - 43$, which were prepared through the conventional melt-quenching procedure, were also investigated.

Sample compositions were inspected using an X-ray fluorescence system (MESA-500, HORIBA). Comparison of As_2S_3 glasses with crystalline As_2S_3 (orpiment) demonstrated that the compositional ratio between As and S was held at 40/60 within ± 1 at. % accuracy. For impurities, the conventional ingot might contain Fe by ~ 10 ppm, which was a detection limit of the X-ray system, while the high-purity ingot did not show any traces except As and S. The 10 ppm impurity level is similar to those of Taucs' samples [12].

Three kinds of optical measurements were performed. These were PL, photothermal deflection spectroscopy, and (resonant) Raman-scattering spectroscopy.

PL was excited at 5 - 300 K using several lasers and a Xe lamp filtered by a monochromator. PL spectra were monitored by a polychromator attached with a linear InGaAs detector. For PL-excitation spectra, i.e. dependence of PL intensities on excitation photon-energies, PL total intensities at a photon-energy region of 0.7 - 1.3 eV were measured using an InGaAs detector fitted with wavelength filters.

Small absorption in thin As_2S_3 samples was evaluated using the photothermal deflection spectroscopy [18]. The spectra were obtained at room temperature using a system described by Nonomura et al. [19]. In brief, the absorption of monochromatic light, the wavelength being varied, in a sample was monitored as a deflecting signal (mirage effect) of probe light which propagated nearby the sample surface. The deflecting signals were converted to absorption coefficients by following the conventional procedure [18,19]. Then, the absolute values were determined by fitting the spectra at $\alpha \approx 10^2 \text{ cm}^{-1}$ to absorption spectra obtained from subsidiary optical transmission measurements. Among several kinds of photothermal methods, the deflection spectroscopy appears to possess the highest sensitivity at room temperature [18,19].

Raman-scattering spectra were obtained at room temperature using a triple dispersing system fitted with a cooled charge-coupled-device (T64000, Jobin Yvon). Several laser sources were employed to monitor resonant Raman-scattering spectra. The laser light could provide photoinduced changes in some cases [11], and accordingly, samples were moved during spectral measurements. Polarization of scattered light was unanalyzed.

3. Results and discussion

A. Electronic state

Fig. 1 shows a PL-excitation spectrum for a high-purity sample with a thickness of ~ 1 mm. For comparison, two spectra are also plotted; one being a spectrum obtained by the constant-photocurrent method for a sample obtained from the same ingot [15] and the other being an optical absorption curve, in which small absorption is evaluated using high-purity As_2S_3 optical fibers [13]. These photocurrent and absorption spectra are obtained at room temperature, and the PL-excitation

spectrum has been measured at 5 K. Accordingly, the PL-excitation spectrum is redshifted, taking the temperature dependence [20] of the absorption edge into account. The vertical position of the PL-excitation spectrum is tentatively fixed by fitting it to the absorption spectrum at $\alpha \approx 10 \text{ cm}^{-1}$.

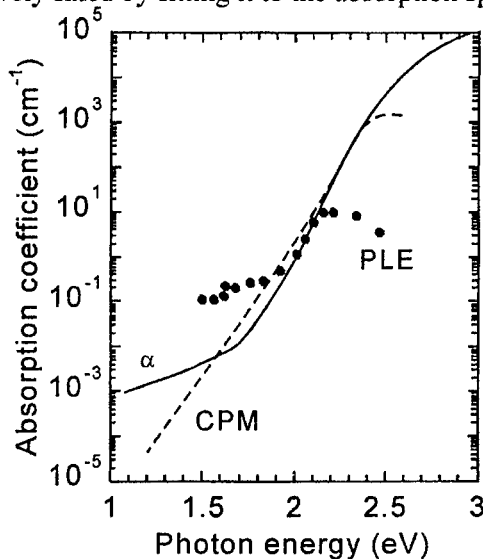


Fig. 1. Dependence of PL intensities on the excitation photon energy (PLE) in high-purity As_2S_3 . Also shown are a photoconductive spectrum (CPM) [15] and an absorption spectrum α [13] at room temperature.

We see in the figure that the PL-excitation spectrum also shows a WAT-like exponential response at $\hbar\omega \leq 2 \text{ eV}$. This feature is the same as those previously reported for conventional-purity samples [21]. A characteristic energy of the exponential tail is $\sim 300 \text{ meV}$, which is similar to E_W of the WAT [1,3]. It is mentioned here that, although the WAT level of the PL-excitation spectrum appears to be higher than the real WAT, the PL level depends on the PL spectral region detected (described later) and also on other experimental conditions such as sample thickness [21]. In addition, the difference may partly be due to different ingots. Accordingly, we neglect the quantitative difference of the WAT levels between the PL-excitation spectrum and the optical absorption spectrum.

What should be underlined here is that only the photocurrent spectrum does not manifest the WAT. The non-existence of the photoconductive WAT suggests that the WAT arises from optical absorption processes which cannot produce mobile carriers, i.e. holes in As_2S_3 . (Also in Se and As_2Se_3 , WATs are not detected by the constant-photocurrent method [15].) Then, what electronic density causes the WAT?

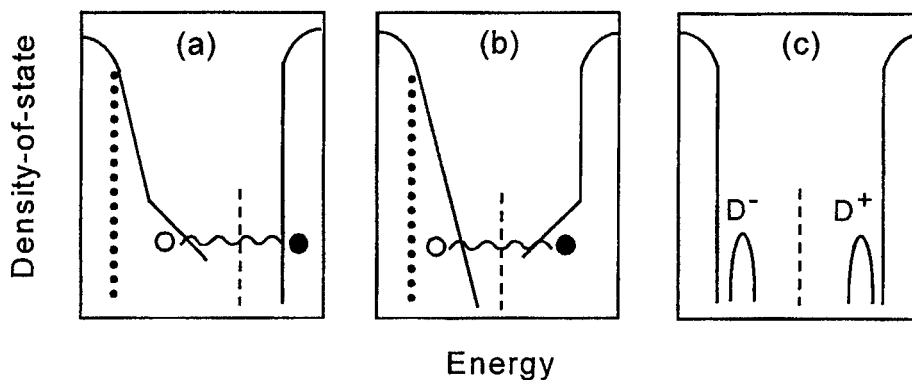


Fig. 2. Proposed densities-of-states and related sub-gap electron-hole generation processes (a,b) and the charged-defect model (c). In (a), both the Urbach edge and the WAT belong to the valence band. In (b), the Urbach edge and the WAT arise from the valence and the conduction band, respectively. Dotted and dashed lines show the mobility edge in the valence band and the Fermi level.

Here, since the WAT shows a broad exponential curve, as the simplest cases, we can assume two possibilities for the energy location of the density-of-states responsible for the WAT. That is, as illustrated in Fig. 2, the WAT may arise from the valence-band (occupied) tail (a) or from the conduction-band (unoccupied) tail (b) [15]. In these illustrations, following the previous idea [7,10,14,15], we have located the density-of-states giving rise to the Urbach edge at the valence-band edge. The mobility edge is indicated there [22].

The following three reasons support the model in which the WAT states exist below the conduction band, Fig. 2(b). First, it is demonstrated that the chalcogenide glass behaves as an intrinsic semiconductor [1,3], i.e. the Fermi energy being pinned near the center of the bandgap. This feature is inconsistent with the model (a), in which the Fermi level tends to approach the conduction band, and as a result, n-type behaviors may emerge. Second, it is also demonstrated that holes are more mobile than electrons in conventional chalcogenide glasses [1,3,15], which suggests the existence of deep trapping states for electrons. The tail states below the conduction band in (b) can work as such traps. Third, a simple calculation shows that if tail states existed at above the valence band, as in (a), these could give photocurrent signals [23]. But, no such signals can be detected as shown in Fig. 1. This disagreement is negative for the model (a). For the case of (b), electron-hole pairs in the conduction-band tail (WAT) and the valence-band tail (Urbach edge) may geminately recombine, and accordingly photocurrents cannot appear, in consistent with the observations. With these three reasons, we can assume that the gap states, which govern the WAT, are located at the conduction-band tail, as illustrated in Fig. 2(b). It is mentioned here that in amorphous hydrogenated Si the density-of-states has the (a) form, which is consistent with n-type conduction behaviors [1,3].

B. Structural origin

Fig. 3 shows optical absorption spectra obtained using the photothermal deflection spectroscopy for rapidly-quenched and slowly-cooled. As mentioned in 2, these samples were made from one original ingot, and accordingly, the purity levels of these samples are assumed to be comparable. Hence, we may neglect impurity effects upon the WATs [12]. For each samples, two specimens with thicknesses of 0.2 - 0.4 mm have been examined, and the two data show satisfactory agreements. The dips at 1.4 eV are artificial noises arising from filter exchange. Note that, since quenched glasses are necessarily cracked into small pieces with mm scales, it is difficult to evaluate low optical absorption without using such sensitive methods as the photothermal deflection spectroscopy [18,19].

In this result, the most remarkable difference between the two kinds of samples is the level of the WATs. The quenched samples exhibit the WAT which is higher by one order than that in the slowly-cooled samples.

With regard to structural differences between the rapidly-quenched and slowly-cooled samples, the most noticeable one appears to be the density of wrong bonds. The previous [16] and the present (Fig. 4) Raman-scattering spectra indicate that the concentration of As-As bonds, which can be estimated from the intensity of 230 cm^{-1} peak [24], in the quenched samples is greater than that in the slowly-cooled samples. Although the S-S peak at 490 cm^{-1} [24] is weak, the present Raman spectra in Fig. 4 show that it is stronger also in the quenched samples. That is, these observations demonstrate that the wrong-bond density is higher in the quenched samples. Here, although quantitative evaluation of the concentration difference is not straightforward, a plausible difference is typically 5 times [25].

These optical and structural correspondences imply that the wrong bonds (As-As and/or S-S) are responsible for the WAT. The higher concentration of the wrong bonds in the quenched samples appears to cause the greater WAT. Then, does the WAT arise from As-As or from S-S?

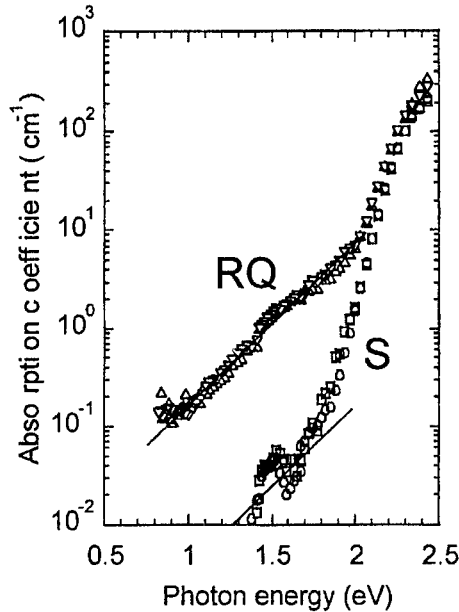


Fig. 3. (left) Optical absorption spectra obtained using the photothermal deflection spectroscopy for As_2S_3 glasses prepared through rapidly-quenching (triangles) and slowly-cooling (circles and squares) processes. The lines represent WATs.

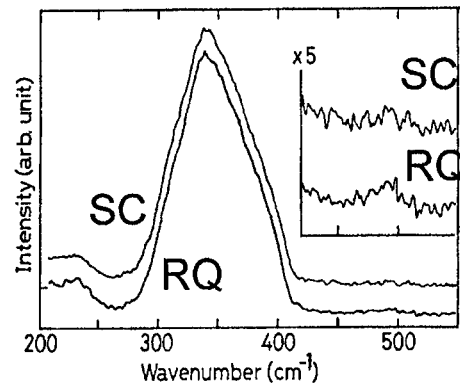


Fig. 4. (right) Raman spectra of slowly-cooled (upper) and rapidly-quenched (lower) samples obtained using probe light of $\hbar\omega = 2.0$ eV. The inset shows magnified views for the 490 cm^{-1} peak.

Fig. 5 displays a series of Raman-scattering spectra with the photon energy of probe light. Here, the intensity is normalized with a peak at 340 cm^{-1} , which is identified to As-S vibrations [24]. We see that the As-As peak (230 cm^{-1}) increases with an increase in the photon energy, while the S-S peak (490 cm^{-1}) does not show appreciable changes. The details are shown in the inset, in which the As-As peak exponentially increases with the photon energy in the spectral range of $1.5 - 2.4$ eV, which covers the WAT. In contrast, the S-S peak remains at a small level. It should be underlined that the results obtained for the conventional and the high-purity samples, which are plotted by different symbols, show no meaningful difference.

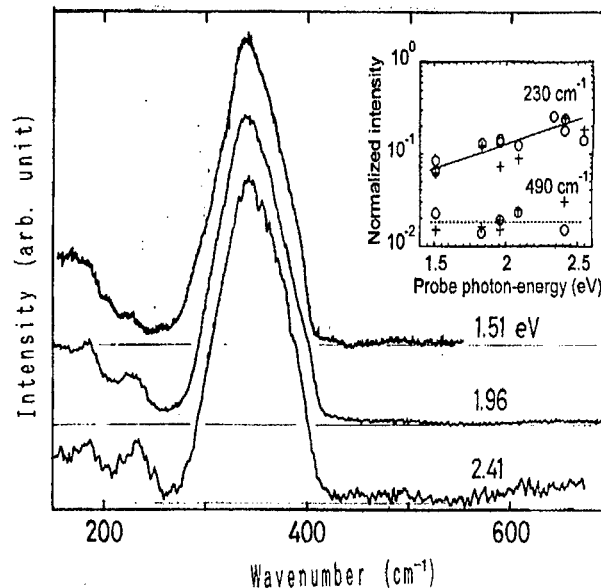


Fig. 5. A series of Raman scattering spectra obtained for a high-purity As_2S_3 as a function of the photon energy of probe light. The inset shows the intensities of 230 and 490 cm^{-1} Raman peaks as a function of the photon energy of probe light. The intensity is normalized with that of the main peak at 340 cm^{-1} . The two symbols show the two kinds of samples; high-purity samples (+) and conventional-purity samples (O).

That is, these photon-energy dependences are intrinsic to As_2S_3 glass. The present result may be consistent with that reported for 1.96 - 2.61 eV probe light by Kawazoe et al. [26].

The exponential dependence of the As-As peak intensity on the photon energy implies a resonant Raman-scattering process [27]. Conventional analyses of resonant Raman scattering show that, when the photon energy of probe light coincides with an electronic excitation energy E_i , Raman scattering processes associated with the electronic transition enhance dramatically, resulting in the strengthening of related Raman peaks [27]. The resonance curve may be written as $R(\hbar\omega - E_i)$, which has a prominent peak at $\hbar\omega = E_i$. Here, in a disordered system, E_i is probably distributed, and we may intuitively assume that the resonant Raman scattering measures $\sum_i R(\hbar\omega - E_i)$. This represents the electronic density-of-states of the resonant sites, provided that R is replaced by the δ -function, which we take here as a rough approximation.

Then, we can assume that As-As bonds cause the WAT. Actually, the characteristic energy representing the exponential increase in the As-As Raman peak (the inset in Fig. 5) is ~ 700 meV, which is comparable to E_w (≈ 300 meV) in the WAT [28].

On the other hand, the photon-energy independence of the S-S peak implies that its resonance feature is similar to that of As-S bonds. Since the bandgap in As_2S_3 is constructed between lone-pair electron states of S and anti-bonding states of As-S [1,3], these similar resonance behaviors are plausible. In other words, it is inferred that S-S wrong bonds are not responsible for the WAT.

To obtain some more insight into the atomic structure responsible for the WAT, I have also investigated the dependence of PL spectra upon excitation photon-energy, which is varied at 1.5 - 2.6 eV. Then, a similar result to that reported by Tada et al. [29] has been obtained; i.e. when the excitation photon-energy is higher (Urbach edge) and lower (WAT region) than ~ 2 eV, a broad PL peak appears at around $\hbar\omega \approx 1.1$ eV and 0.9 eV. Tada et al. interpret on the basis of their compositional study that the 0.9 eV PL originates from As-As bonds. This interpretation is consistent with the present idea, which assumes the correspondence between the WAT and As-As bonds. However, Tadas' interpretation may be inconsistent with a result obtained using optically induced electron-spin resonance [30]. In addition, I have also observed that other samples such as crystalline As_2S_3 (orpiment), which nominally has no As-As bonds, give rise to broad peaks at $\hbar\omega \approx 0.9$ eV. Therefore, it is fair to conclude that, although Tadas' assertion is consistent with the present idea, the 0.9 eV PL peak cannot be a firm evidence indicating the existence of As-As bonds.

C. Energy level and atomic structure

We have obtained two ideas, and the connection of the two is the next subject. That is, in A, it has been inferred that the WAT arises from tail states below the conduction band. In B, some observations suggest that the WAT is produced by As-As wrong bonds. Then, can the tail states below the conduction band be produced by As-As bonds? Fig. 6 shows several levels of interest in As_2S_3 . In this illustration, the energy difference between the outermost p levels of As and S atoms is estimated at ~ 2.5 eV [31]. The lone-pair p -electron level of S broadens to form the top of the valence band (LP), the width of which is demonstrated to be 2 - 3 eV [1,3]. On the other hand, the conduction band is produced by the anti-bonding state σ^* of As-S bonds, and the gap giving rise to the so-called Tauc optical gap of ~ 2.4 eV appears [1,3].

We now consider the energy levels of wrong bonds. As-As bonds existing in As_2S_3 glass must also produce the bonding and anti-bonding states, and the energy split can be estimated at 3 - 4 eV from experimental studies on solid As [32]. Then, we can predict that the As-As σ^* states are located at just below (or at around the bottom of) the conduction band [33]. Since As-As bonds are weaker than As-S bonds [6,34], which form disordered environments, the As-As bond distance (R' in Fig. 7) probably fluctuates at around a typical value 2.5 Å [32]. Related dihedral angles may also fluctuate. Then, it is plausible that such fluctuation causes a broad energy distribution of As-As σ^* states, which appears as the WAT. (However, why the distribution has the exponential form remains to be studied.) On the other hand, it is known that S dimers possess excitation energy of ~ 10 eV [35], and accordingly the antibonding states are probably included in the conduction band, i.e. these cannot provide any contribution to gap states. (In As_2Se_3 , Se-Se σ^* bonds may contribute to the WAT, since the energy difference between the p -electron levels of As and Se is ~ 2.0 eV [31], and the excitation

energy of Se dimers seems to be comparable to that of As dimers.)

Fig. 7 gives an image of atomic structures in As_2S_3 glass. As suggested previously [7,14,15], we here assume that the Urbach edge arises from an exponential density-of-states at the top of the valence band. Such an exponential edge may appear, since the valence band is formed by lone-pair electron states of S atoms [1,3] and the interaction between the lone-pair electrons is governed by disordered interlayer distances (R in the figure). In addition, the covalent atomic structures are in favor of production of homopolar bonds, As-As and S-S, and the exponential edge may also be influenced by intralayer S-S interaction. On the other hand, As-As bonds are assumed to be responsible for the WAT as described above.

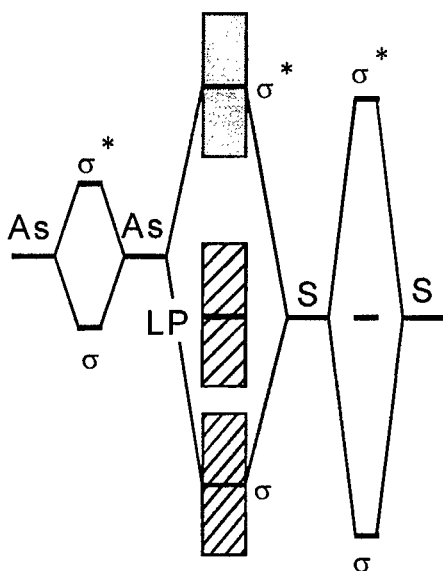


Fig. 6. (left) Electronic structures in As_2S_3 containing As-As and S-S wrong bonds. LP denotes the lone-pair electron state.

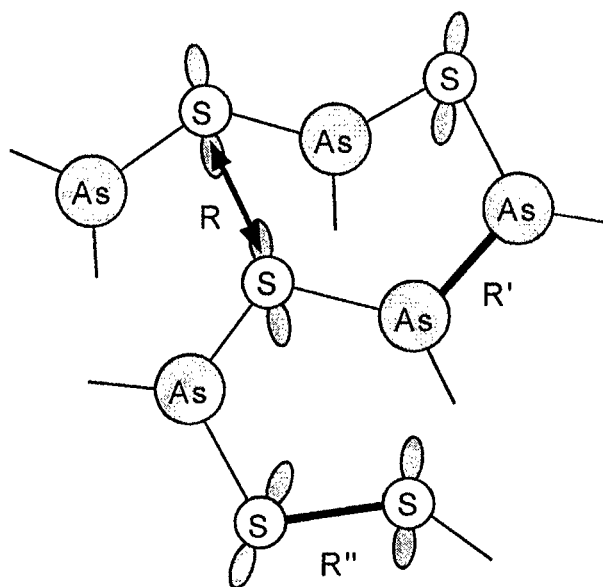


Fig. 7. (right) A schematic structure of As_2S_3 glass. R , R' , and R'' denote, respectively, the interlayer distance, intralayer As-As distance, and intralayer S-S distance.

D. Other related features

The present model seems to be consistent with temperature dependence of WATs. Tauc et al. have demonstrated for As_2S_3 that, with an increase in temperature from 100 to 600 K, the Urbach edge substantially redshifts while the WAT changes little [36]. This temperature independence of the WAT is consistent with the present model, since the wrong-bond density cannot change at temperatures below the melting temperature, 580 K [2,16]. On the other hand, thermal disordering may govern the Urbach-edge behavior [37].

The present model is also in harmony with the fact that, in crystalline $\text{As}_2\text{S}(\text{Se})_3$, electrons are more mobile than holes [38]. In these crystals, As-As wrong bonds do not exist under ideal situations, and accordingly, in the present view, no traps for electrons exist.

The present model predicts that elemental chalcogenide glasses, in which no wrong bonds exist, do not show WATs, while reported results appear to be inconclusive. Among many optical spectra reported for amorphous Se, the smallest attenuation may be 10^{-2} cm^{-1} at $\hbar\omega \approx 1 \text{ eV}$ with WAT-like spectral features [39]. The photo-acoustic spectroscopy [40] and the present photothermal deflection spectroscopy for Se layers (unpublished) also demonstrate absorption levels of 10^{-1} cm^{-1} at 1 eV with WAT-like features. These attenuation or absorption levels appear to be comparatively smaller than those in compound glasses such as As_2Se_3 ($\alpha \approx 10^{-1} \text{ cm}^{-1}$) [1], while WAT-like features still remain. However, we cannot identify the origin of these attenuations, which may be governed by surface and/or bulk scattering. Alternatively, it may be due to absorption caused by impurities and/or defects. Liquid S also shows absorption of $\sim 10^{-1} \text{ cm}^{-1}$ with WAT-like features [41].

The present model also predicts that, in the As-S glass system, the WAT becomes smaller

with an increase in the S content, since As-As bonds become fewer. Fig. 8 shows related absorption spectra for $\text{As}_x\text{S}_{100-x}$ ($x = 17 \sim 43$), which were obtained using the photothermal deflection spectroscopy. The inset shows composition dependence of the absorption coefficients evaluated at, tentatively, $\hbar\omega = 1.5$ eV. We see that, with an increase in S content, the level of WAT decreases, which is consistent with the prediction. We also see, however, that the level becomes smaller in $\text{As}_{43}\text{S}_{57}$. This result may indicate that many As-As bonds form extended states. It is mentioned here that subsidiary X-ray fluorescence measurements did not show marked impurity difference in these glasses.

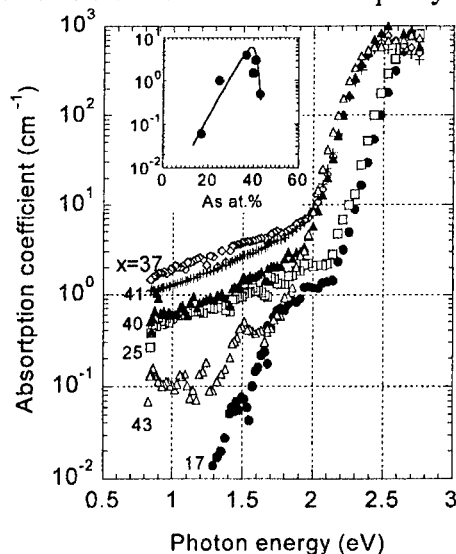


Fig. 8. Absorption spectra of $\text{As}_x\text{S}_{100-x}$ glasses. The inset shows the composition dependence of absorption coefficients evaluated at a photon energy of 1.5 eV.

In contrast to chalcogenide glasses, it has been repeatedly demonstrated that SiO_2 glass possesses no WAT [42]. Alternatively, optical attenuation below the Urbach edge is governed by light scattering arising from density fluctuation. This ultimate transparency can be understood coherently with the present model, since Si-O bonds are fairly ionic [31], and accordingly the wrong bonds (Si-Si and O-O) are few. Similar situations may be expected for ionic chalcogenide glasses such as Ga_2S_3 - Na_2S , while the glass is hygroscopic and residual absorption still remains [43].

E. Comment on the charged-defect model

It seems valuable to consider a consequence of the present model upon the charged-defect models proposed by Street and Mott [4] and Kastner et al. [5]. The charged-defect models assert [1,3] that, in chalcogenide glasses, D^- and D^+ (in Mott's notation) become to be intrinsic gap states, and their electronic states are located, respectively, at above the valence band and below the conduction band (see, Fig. 2c). The density is estimated at ppm levels, $\sim 10^{18} \text{ cm}^{-3}$.

These models should be re-considered, at least, in two respects. One is that the models presume that the chalcogenide glass is completely transparent [4,5], i.e. no midgap states. However, we have seen that there is residual absorption in highly-pure As_2S_3 glasses, in which no impurities are detected, i.e. less than 10 ppm. The other is that recent studies suggest that the PL with large Stokes shifts, which was interpreted as creation of D^0 from D^+ and/or D^- [1,3], has been demonstrated using optically-detected ESR to be caused by self-trapped excitons [44]. That is, no charged defects are needed.

The present model assumes the electronic density-of-states with the form of Fig. 2(b). Here, the conduction-band tail is composed with the As-As bonds of 0.1 - 1 at.% [25], which govern the WAT. On the other hand, it has been inferred that the valence-band tail is governed by the disordered interaction between lone-pair electrons of S atoms [7,10,14,15]. No unpaired electrons exist in the present model, which is consistent with observations [1,3].

The two models may be incompatible. Since the existence of a large number of As-As bonds has been firmly demonstrated by several experiments [25], and since the bonds appear to produce gap states as discussed in 3C, it is difficult to envisage that the charged defects govern macroscopic

electronic properties, at least, in real $\text{As}_2\text{S}(\text{Se})_3$ glasses. It seems that *most of electronic properties in covalent chalcogenide glasses can be understood with homopolar bonds and interlayer interaction*. For instance, the photoinduced ESR [1,3] can be understood by assuming creation of D^0 states through photoinduced bond scission of homo- and hetero-polar bonds, which is predicted theoretically [45].

4. Summary

The existence of WATs appears to be inherent to chalcogenide glasses, and understanding of its origin has been desired. The understanding has also been required from a viewpoint of applications to IR-transparent optical fibers.

We have studied the WAT using As_2S_3 glass as a sample, and have presented some observations, which give the following two ideas:

- i) The WAT originates from tail states below the conduction band.
- ii) As-As wrong bonds (0.1 - 1 at.%) are responsible for the WAT.

These two ideas have been understood coherently with an electronic-level diagram, in which the antibonding states of As-As are located below the conduction band. Finally, it has been asserted that the wrong bonds behave as more dominant gap states than the charged defects.

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