# Absence of Photodarkening in Bulk, Glassy $As_2S_3$ and $As_2Se_3$ Alloyed with Copper

J. Z. Liu and P. C. Taylor
*Department of Physics, University of Utah, Salt Lake City, Utah 84112*

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We report the first observation of the absence of the photodarkening (PD) effect in bulk chalcogenide glasses. In the prototype systems $Cu_x(As_{0.4}S_{0.6})_{1-x}$ and $Cu_x(As_{0.4}Se_{0.6})_{1-x}$, the PD effect is essentially destroyed for $x \geq 0.01$ and 0.05 for the S and Se systems, respectively. A structural model for Cu-As-Se and Cu-As-S systems is proposed, which is based upon the assumptions of covalent bonding and the absence of doping. According to this model, the absence of the PD effect indicates that medium-range interactions among the lone-pair $p$ electrons may be important for the effect to occur. This structural model can be generalized to many other amorphous semiconducting systems.

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Other than the thermally activated electrical conductivity from which the name "semiconducting glass" originated, perhaps the most universal feature of this class of amorphous solids is the so-called photodarkening (PD) effect or shift of the optical absorption edge to lower energies after irradiation with band-gap light.[1,2] The PD effect is a subtle effect which does not involve gross bonding rearrangements and, with the possible exception of amorphous Te,[3] occurs in all chalcogenide glasses studied to date. Because group-IV and group-V amorphous semiconductors do not exhibit this effect,[4] it has long been assumed that PD requires the presence of twofold coordinated group-VI (chalcogen) elements, which leads to a valence band whose highest lying levels are comprised of nonbonding (lone pair) electronic states with charge density only on the chalcogen atoms. Because of its universal nature, an understanding of the PD effect in the semiconducting chalcogenide glasses should contribute greatly to our understanding of the glass-forming tendencies of these important amorphous solids.

In this Letter we report the first evidence for the destruction of the PD effect in two prototype chalcogenide glasses, $As_2S_3$ and $As_2Se_3$. With the addition of 1 and 5 at.% copper to glassy $As_2S_3$ and $As_2Se_3$, respectively, the PD effect is essentially destroyed. These results imply either that the PD effect involves intermediate-range interactions between the chalcogen atoms which the addition of Cu destroys or that the PD effect is produced by a specific native defect which the addition of Cu somehow compensates.

It has been known for some years that Cu goes into $As_2S_3$ and $As_2Se_3$ in a fashion which does not generate any deep defects as measured by photoluminescence and optically induced ESR.[5] In spite of earlier suggestions[6,7] that Cu might "chemically modify" the structure of $As_2S_3$ and $As_2Se_3$ and produce defects deep in the gap, the arguments which we shall present below show that Cu goes into these glasses so as to satisfy all of its normal bonding requirements and there is essentially no doping or chemical modification of the structure.

The $Cu_x(As_{0.4}S_{0.6})_{1-x}$ and $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ systems are most appropriate for this study because most of the details of the local structural order can be determined for these systems. It is well known that in $As_2S_3$ and $As_2Se_3$ the arsenic atoms are threefold coordinated, the chalcogen atoms are twofold coordinated, and there are only arsenic-chalcogen bonds (no like-atom bonds or homobonds). When copper is added to these glasses, extended x-ray absorption fine-structure results show that the copper is always tetrahedrally coordinated.[8] From analogies with bonding in minerals of the Cu-As-S system, one can model the bonding in the glasses and predict such measurable quantities as the average coordination number. In the minerals[9] Cu is fourfold coordinated, As is threefold coordinated for low enough Cu concentrations ($x \leq \frac{6}{19} = 31.6\%$), and S is either twofold or fourfold coordinated. In these minerals[9] only Cu—S and As—S bonds are present. We assume that the same rules hold for the Cu-As-S and Cu-As-Se glasses. (Nuclear-quadrupole-resonance and nuclear-magnetic-resonance measurements have confirmed the threefold coordination for As in these glasses and the symmetric tetrahedral environment of the Cu.[10])

These restrictions determine the allowed stoichiometries in the Cu-As-S and Cu-As-Se systems for which all bonds are satisfied and there is no doping. For this situation to be the case, the average number of bonding electrons per atom must be equal to the average coordination number. If we ignore $d$ electrons, it can be shown that, with these assumptions, the only allowed compositions are[11]

$$(Cu_{2/3}\chi_{1/3})_z(As_{2/5}\chi_{3/5})_{1-z}, \qquad (1)$$

where $\chi$ represents the chalcogen atom, either S or Se.

For compositions of the form $Cu_x(As_{0.4}\chi_{0.6})_{1-x}$, the requirement for no doping is achieved, at least formally, by separation into compositions of the form of Eq. (1) which contain Cu and compositions of the form $As_w\chi_{1-w}$, which are necessarily As rich and must contain As—As bonds. The only compositions allowed are of the form[11]

$$(\mathrm{Cu}_{2/3}\chi_{1/3})_{3x/2}(\mathrm{As}_{2/5}\chi_{3/5})_{1-u-3x/2}(\mathrm{As}_w\chi_{1-w})_u, \qquad (2)$$

where $u=x/(5w-2)$ and where $0 \le x \le \frac{2}{7}$ and $\frac{2}{5} \le w \le 1$. Expression (2) yields the following average coordination number for glasses in the systems $\mathrm{Cu}_x(\mathrm{As}_{0.4}\chi_{0.6})_{1-x}$:

$$n_{\mathrm{av}}=2.4+4.6x, \qquad (3)$$

independent of the value of $w$.

Figure 1 shows the average coordination number as determined from the available x-ray radial distribution data[12,13] for the $\mathrm{Cu}_x(\mathrm{As}_{0.4}\mathrm{Se}_{0.6})_{1-x}$ system compared to the predictions of Eq. (3). The excellent agreement confirms that we understand the local bonding configurations very well in these glasses. With this understanding of the structure, we are encouraged to try to understand the photodarkening behavior in these glasses.

Another major result of the model just described is that the addition of each (four coordinated) copper atom to the glass produces $1\frac{1}{2}$ chalcogen atoms which are also tetrahedrally coordinated. The fraction of chalcogen atoms which are tetrahedrally coordinated, $\chi_4$, is given by

$$\chi_4=\tfrac{5}{2}x/(1-x), \qquad (4)$$

and this model prediction is also plotted in Fig. 1. As the copper concentration approaches ≃28%, one would expect the PD process to be destroyed because at this point essentially all of the chalcogen atoms are tetrahedrally coordinated and there are no remaining nonbonding electrons in the valence band. The surprising result of the present work is that the PD process is destroyed long before this copper concentration is reached ($\chi_4 \ge 3\%$ in the S system and $\ge 13\%$ in the Se system).

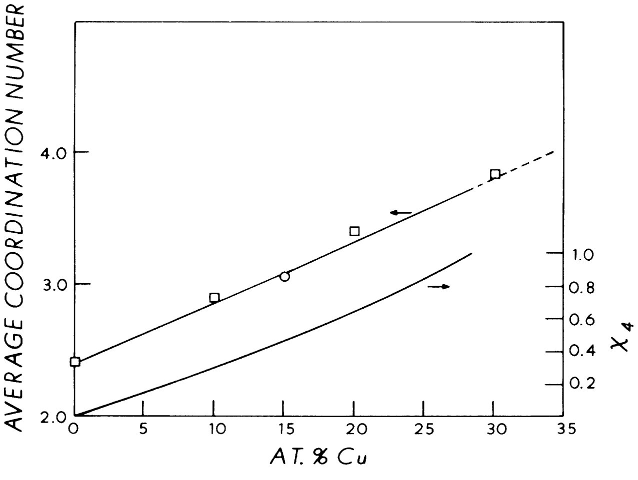

FIG. 1. Average coordination number in $\mathrm{Cu}_x(\mathrm{As}_{0.4}\mathrm{Se}_{0.6})_{1-x}$ glasses (left-hand scale). Circle and squares are data from Refs. 12 and 13, respectively. Solid line is the prediction of Eq. (3) from the model described in the text. Also shown (right-hand scale) is the fraction of chalcogen atoms which are tetrahedrally coordinated, $\chi_4$, as predicted by the model.

Mixtures of 99.9999% pure elements were loaded into clean quartz ampoules (outer diameter, 8 mm; inner diameter, 6 mm) which were then sealed under $10^{-6}$-Torr vacuum. The samples were kept at 950 °C for about 100 h in a rocking furnace and then cooled down to about 850 °C and quenched into ice water [for $\mathrm{Cu}_{25}(\mathrm{As}_{0.4}\mathrm{Se}_{0.6})_{75}$] or air (for other samples). X-ray diffraction spectra were taken to make sure that there was no crystalline component. The average absorption coefficient $\bar{\alpha}$ is calculated from the standard transmittance equation.

Figure 2 shows the disappearance of the PD effect when essentially all (≃75%) of the Se is tetrahedrally coordinated. There still appears an optically induced midgap absorption, but the parallel shift of the absorption edge which is the signature of the PD effect is not present. Measurements were also made under identical conditions in $\mathrm{As}_2\mathrm{Se}_{1.5}\mathrm{Te}_{1.5}$ glass which has a band gap very close to that of $\mathrm{Cu}_{23.1}(\mathrm{As}_{0.4}\mathrm{Se}_{0.6})_{76.9}$ but where the chalcogen atoms are all twofold coordinated. In this glass the PD effect is observed and the change in the average absorption coefficient $\Delta\bar{\alpha}$ increases exponentially at the band edge.

The absence of PD in the copper-rich glass shown in

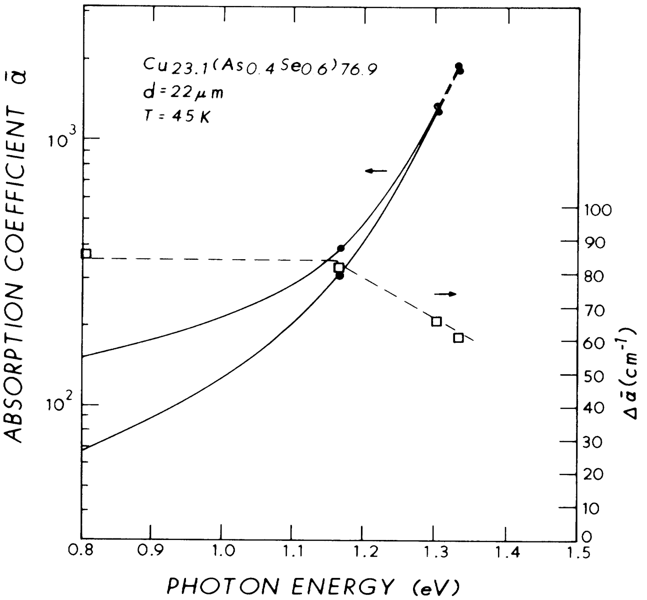

FIG. 2. Absorption coefficient, $\bar{\alpha}$, in inverse centimeters (left-hand scale), in a Cu-rich chalcogenide glass where approximately 75% of the chalcogen atoms are tetrahedrally coordinated. The lower and upper curves are before and after irradiation with band-gap light (1.164 eV), respectively. Also shown (right-hand scale) is the change in $\bar{\alpha}$ after irradiation, which indicates that photodarkening is absent in this glass.

Fig. 2 clearly demonstrates that the mere presence of chalcogen atoms in the glass is not sufficient to produce PD. Our structural model predicts that the fraction of chalcogen atoms which are twofold coordinated, $1-\chi_4$, is $\simeq 23\%$ for this composition. Therefore, these data provide strong evidence that a nonbonding chalcogen valence band, which is provided by twofold coordinated chalcogen atoms, is necessary for the presence of PD in the chalcogenide glasses. This result, although not necessarily surprising, is a strong indication that twofold coordinated chalcogen atoms are indeed a necessary condition for the presence of the PD effect.

The glass shown in Fig. 2 exhibits other behavior which is more similar to the tetrahedral amorphous semiconductors than to the traditional chalcogenide glasses. For example, there exists a dark ESR signal in this glass which corresponds to $\simeq 10^{18}$ spins/cm$^3$. There is thus evidence for the existence of defects with positive electron-electron correlation energies similar to those which exist in amorphous silicon, glassy $CdGeAs_2$, and other tetrahedrally coordinated amorphous semiconductors. Optical excitation at low temperatures ($T < 80$ K) with band-gap light causes a metastable increase in the ESR which is also on the order of $10^{18}$ spins/cm$^3$.

Figure 3 illustrates the more surprising result that even a small concentration of tetrahedrally coordinated chalcogen atoms can begin to reduce the PD effect. Although the band gap for the glass shown in Fig. 3 $[Cu_1(As_{0.4}Se_{0.6})_{99}]$ is essentially the same as that of pure $As_2Se_3$, the PD effect is only about 75% of the magnitude which is observed in $As_2Se_3$ for identical measuring conditions and similar sample thicknesses. In addition, the PD effect is unobservable with 5 at.% Cu in $As_2Se_3$, and in the $As_2S_3$ system the PD effect is unobservable with 1 at.% Cu. This disappearance of the PD occurs even though the band gap changes by only about 0.3 eV.

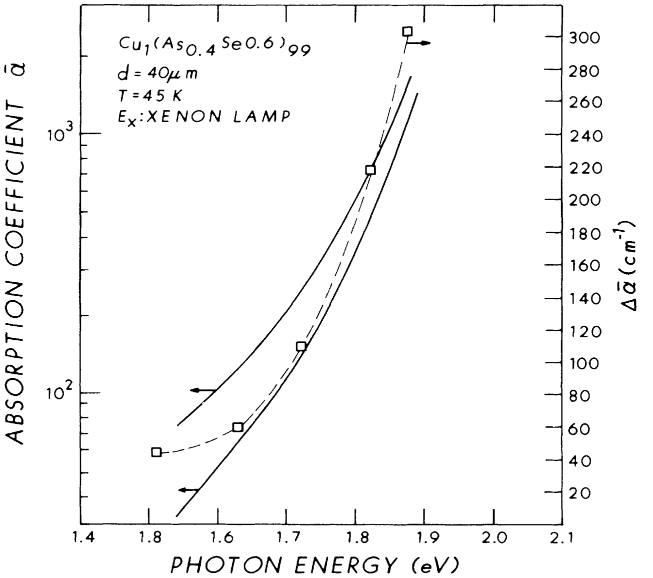

FIG. 3. Absorption coefficient, $\bar{\alpha}$, in inverse centimeters (left-hand scale), in $As_{0.4}Se_{0.6}$ glass alloyed with 1 at.% Cu. The lower and upper curves represent data taken before and after irradiation with above band-gap light, respectively. Also shown (right-hand scale) is the change in $\bar{\alpha}$ after irradiation, which indicates the presence of a photodarkening effect in the glass.

As one adds Cu to $As_2S_3$ or $As_2Se_3$ two things happen: metal-chalcogen bonding states are added near the top of the valence band,[13,14] and the band gap decreases. Even though the PD disappears at different Cu concentrations in $As_2S_3$ and $As_2Se_3$, the disappearance corresponds to essentially the same shift in the band gap from the pure $As_2\chi_3$ glasses ($\simeq 0.3$ eV). This shift is also very close to the "saturated" PD shift for the thicknesses of samples we have employed.[15] We therefore conclude that the introduction of Cu either masks the PD effect by producing some bonding electronic states at the top of the valence band or eliminates the PD effect by producing tetrahedrally coordinated chalcogen atoms. The fact that the PD effect appears to remain[16] at high values of $\alpha$ ($\alpha > 10^4$ cm$^{-1}$) in thin films of $As_2Se_3$ alloyed with as much as 10 at.% Cu supports the first possibility, although it is not obvious that the structure of these films is the same as that of the bulk glasses.

The microscopic mechanism for PD in the chalcogenide glasses has been the subject of much debate. Explanations range from the production of defects created by the optically induced breaking of bonds,[17] the tunneling of twofold coordinated chalcogen atoms in double-well potentials,[2,18] the reorientation of small anisotropic structural sites such as layer segments or "rafts,"[19] and changes in the overlap of neighboring nonbonding chalcogen electronic levels due to subtle rearrangement of the chalcogen atoms.[20] These various models fall into two general categories: Those which involve isolated chalcogen-related "defects" and those which involve correlated effects among more than one chalcogen atom.

The appearance of optical anisotropy after illumination with polarized light[21] suggests that motion of at least one chalcogen atom is important. The introduction of tetrahedrally coordinated S or Se into $As_2S_3$ and $As_2Se_3$ on levels of 3 to 13 at.% may inhibit this motion.

The tetrahedral coordination of the Cu is not primarily responsible for the disappearance of the PD effect in the Cu-As-S and Cu-As-Se glasses. Also, although atomic motion of some sort undeniably accompanies PD, the effect is not related to the average coordination number or the "rigidity percolation threshold"[22] which occurs at $n_{av}=2.4$. For example, PD is observed in $GeS_2$ and $GeSe_2$, where the Ge is also tetrahedrally coordinated and where $n_{av}=\frac{8}{3}$. The real difference between the Ge and Cu systems is the appearance in the Cu system of tetrahedrally coordinated chalcogen atoms. These tetrahedrally coordinated chalcogen atoms are probably responsible for the disappearance of the PD effect. The surprising fact is that tetrahedral coordination of only about (3–13)% of the chalcogen atoms (see Fig. 1) essentially eliminates the PD effect.

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