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Effect of Cu alloying on metastable photoinduced absorption in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ and $Cu_x(As_{0.4}S_{0.6})_{1-x}$ glasses

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We have investigated the metastable photoinduced absorption (midgap absorption and photodarkening) in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ and $Cu_x(As_{0.4}S_{0.6})_{1-x}$ glasses. The addition of copper reduces the fraction of the chalcogen atoms which are twofold coordinated. Essentially no photodarkening effect has been observed in the sulfur system for $x \geq 0.01$ or in the selenium system for $x \geq 0.05$. Two possible interpretations are suggested for this observation. (1) The photodarkening effect may occur but be masked by some electronic states created by the copper alloying. (2) The photodarkening effect may be due to correlated changes of the lone-pair *p*-electron wave functions on a scale greater than that of a nearest-neighbor distance. The observed coexistence in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ with large x (around 0.02%) of a dark and a photoinduced electron-spin-resonance signal suggests the coexistence of defects with positive and negative effective electron-electron correlation energies. Midgap absorption can be induced optically at low temperatures in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ with $x \geq 0.05$ and can be annealed away at room temperature.

I. INTRODUCTION

Metastable photoinduced absorption in chalcogenide glasses has been an important experimental probe of the electronic processes in these materials. This absorption is metastable in that it stays after the termination of the irradiation if the sample is kept at the inducing temperature. It is also reversible in that it can be annealed away by heating the sample to temperatures above the inducing temperature but below the glass-transition temperature. In general, the photoinduced absorption $\Delta\bar{\alpha}$ (where $\Delta\bar{\alpha}$ represents the change in the average absorption coefficient) mainly consists of two parts:[1] photoinduced midgap absorption and photodarkening (PD). These photoinduced effects have been most often studied in binary chalcogenide glasses such as As_2Se_3 and As_2S_3. The contribution to $\Delta\bar{\alpha}$ from the photoinduced midgap absorption rises at about half the band-gap energy, is constant in the energy region below the optical band edge,[2] and decreases with energy in the Urbach-tail region. The contribution to $\Delta\bar{\alpha}$ from the PD effect increases exponentially with energy in the Urbach-tail region.[3,4] In addition, the photoinduced midgap absorption is annealed away completely at temperatures around 200 K.[5] The PD effect is annealed gradually and only disappears completely as the annealing temperature approaches the glass-transition temperature.[6]

The photoinduced midgap absorption has been ascribed to photoinduced paramagnetic defects which create electronic states near the middle of the energy gap.[2,5] The microscopic origin of the photodarkening effect is not yet well understood. Photodarkening is not observed in crystalline chalcogenides[7] or in other types of amorphous semiconductors such as amorphous arsenic[8] and hydrogenated amorphous silicon. Thus it is natural to relate the PD effect to the unique features of the chalcogenide glasses, such as the lack of long-range order coupled with the particular topological structure of the twofold-coordinated chalcogen atoms.[9] The twofold-coordinated chalcogen atoms provide lone-pair (or nonbonding) *p* electrons, which are responsible for the states at the top of the valence band.[10] Under irradiation there may be several types of changes in the topological structure which are called photoinduced structural changes. Different types of structural defects may be induced optically and there are corresponding changes in the electronic states. However, exactly how these changes are related to the photodarkening process is still unknown.

In this paper we investigate the role of twofold-coordinated chalcogen atoms in the photodarkening process. We monitor the influence on the photodarkening effect of changing the fraction of chalcogen atoms which are twofold coordinated. Changes in this fraction are achieved by alloying arsenic chalcogenides with copper. We also report the inducing and annealing behaviors of the photoinduced absorption and dark and photoinduced electron-spin resonance in Cu-As-Se and Cu-As-S glasses.

It has been known for some time[11] that copper is incorporated with fourfold coordination into As_2Se_3 and As_2S_3 glasses and that the average coordination number of the glassy alloys $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ and $Cu_x(As_{0.4}S_{0.6})_{1-x}$ increases with copper concentration x, approaching 4 as x appoaches about 0.35. Since the coordination number of As remains 3 for $x \leq 25$ at. %,[12] the increase of the average coordination number of $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ and $Cu_x(As_{0.4}S_{0.6})_{1-x}$ with increasing x implies an increase of the average coordination number of the chalcogen atoms and a decrease of the fraction of chalcogen atoms which are twofold coordinated. Based on these observations, other experimental results, and a few simple assumptions, we have recently developed a structural model (the formal-valence-shell model) which applies to the Cu-As-Se and Cu-As-S systems.[13,4] The formal-valence-shell (FVS) model assumes that the covalent component of the interatomic bonding governs the nearest-neighbor coordination numbers in amorphous semiconducting systems. The model is not concerned with the actual charge distributions of the interatomic bonds, which will, of course, be strongly influenced by ionic effects. We also ignore d and f electrons, so that the Periodic Table can be considered to consist of only eight columns. Second, all valence electrons are assumed to exist in pairs either as nonbonding electrons on a single atom or as bonding electrons which are *formally* shared between two nearest-neighbor atoms.

We now define a formal valence for each individual atom, N_f, which is the number of nonbonding electrons on the atom plus the number of single bonds to the atom. The quantity N_f is a formal valence because the real bonds may contain substantial ionic character and the actual charge distribution on the atom may be very different from that calculated using N_f. The quantity N_f provides a convenient way of counting valence electrons in order to ensure that all of the bonding requirements are satisfied for every atom in the amorphous solid. Each atom in the amorphous solid is assumed to obtain a value of N_f such that there are eight electrons formally surrounding that atom either as nonbonding electrons or as pairs of electrons shared between nearest-neighbor atoms in bonds.

With these definitions and assumptions, the nearest-neighbor coordination number of any given atom, Z, is given by[13,4]

$$Z=8-N_f \ . \tag{1}$$

In general, N_f will differ from the elemental valence N, and this difference is the result of a formal transfer of electrons between atoms in order to satisfy the two major assumptions of the FVS model.

The third assumption of the FVS model is that electrons are formally transferred only from nonbonding states on an atom to bonding states on another atom.[13,4] When one electronic charge is formally transferred to an atom, the formal valence of that atom is increased by 1, and the formal valence of the donating atom is decreased by 1. As a conseqauence of Eq. (1), the nearest-neighbor coordination number of the donating atom is increased by 1.

The formal number of nonbonding electrons is given by N_f-Z, which must be greater than or equal to zero. Together with Eq. (1), this condition means that tetrahedral coordination is the maximum obtainable within the model. Whenever a metal atom (groups I, II, or III) is present in an amorphous solid, the coordination number and the formal valence of the metal atoms will always be 4.

Because Eq. (1) is satisfied by every atom in the amorphous solid, the equation is also satisfied on the average. One can therefore write the average coordination number as

$$Z_{\mathrm{av}}=8-N_{\mathrm{av}} \ . \tag{2}$$

The great advantage of Eq. (2) is that N_{av} can be easily calculated for any composition because it is simply the average of the elemental valences (column numbers) of the constituent atoms. The value of Z_{av} is independent of any details concerning which atoms bond to which atoms or of the individual coordination numbers of specific atoms.

For compositions $\mathrm{Cu}_x(\mathrm{As}_{0.4}\mathrm{Se}_{0.6})_{1-x}$ and $\mathrm{Cu}_x(\mathrm{As}_{0.4}\mathrm{S}_{0.6})_{1-x}$, one immediately obtains from Eq. (2)

$$Z_{\mathrm{av}}=2.4+4.6x \ . \tag{3}$$

From Eqs. (2) and (3) and the fact that Cu and As are fourfold and threefold coordinated,[13,4] respectively, one obtains the average coordination number for the chalcogen atoms

$$Z_{\mathrm{av}}^{\mathrm{VI}}=2+5x/(1-x) \ . \tag{4}$$

$Z_{\mathrm{av}}^{\mathrm{VI}}$ is related to the numbers of twofold-, threefold-, and fourfold-coordinated chalcogen atoms. Because these three components are not determined independently with the assumptions we have made, there exists a range of twofold-coordinated chalcogen atoms which is given by

$$\max\{0,\ 1-5x/(1-x)\}\le v_2/v\le[1-2.5x/(1-x)] \quad \text{for } 0\le x\le \tfrac{2}{7} \ , \tag{5}$$

where v_2 is the number of the twofold-coordinated chalcogen atoms, and v is the total number of chalcogen atoms. The upper and lower limits correspond, respectively, to the exclusive production of fourfold- and threefold-coordinated chalcogen atoms by the addition of copper. Therefore the effect of twofold coordination of chalcogen atoms on the PD effect can be investigated by monitoring the change of the PD effect with x in $\mathrm{Cu}_x(\mathrm{As}_{0.4}\mathrm{Se}_{0.6})_{1-x}$ and $\mathrm{Cu}_x(\mathrm{As}_{0.4}\mathrm{S}_{0.6})_{1-x}$ glasses.

An inherent feature of the PD effect is the fact that one measures an average absorption coefficient $\bar{\alpha}$ because α varies throughout the sample after irradiation.[1] Values of α are the highest nearest the irradiated surface of the sample. One can define

$$\bar{\alpha}(t)=\frac{1}{d}\int_0^d \alpha(x,t)dx \ , \tag{6}$$

where $\alpha(x,t)$ is the absorption coefficient at a depth x in the sample and at a time t, and d is the sample thickness. Although $\alpha(x,t)$ is the important property, all that can be measured easily is $\bar{\alpha}(t)$.

II. EXPERIMENTAL DETAILS

Bulk samples were made by mixing 99.9999%-pure elements and loading them into clean, baked quartz ampoules (an o.d. of 25 mm, and i.d. of 22 mm for the sulfide samples; o.d. of 8 mm and an i.d. of 6 mm for the selenide samples). Ampoules were then sealed under a vacuum of 10^{-6} Torr. The $\mathrm{As}_2\mathrm{Se}_3$ and $\mathrm{Cu}_x(\mathrm{As}_{0.4}\mathrm{Se}_{0.6})_{1-x}$ samples were kept at 950 °C for about 100 h in a rocking furnace, and then cooled down to 850 °C, followed by quenching in ice water (for samples of $x=0.25$) or cooling in air to room temperature (for samples of $x=0$–0.231). The $\mathrm{As}_2\mathrm{S}_3$ and $\mathrm{Cu}_{0.01}(\mathrm{A}_{0.4}\mathrm{S}_{0.6})_{0.99}$ samples were kept at 950 °C for about 100 h in a rocking furnace and then cooled down to 500 °C at a rate of 40 °C/h, followed by air quenching to room temperature. Except for $\mathrm{As}_2\mathrm{Se}_3$ and $\mathrm{As}_2\mathrm{S}_3$, which are known to be hard to crystallize, powder x-ray-diffraction spectra were taken to ensure that there were no crystalline components in the samples. A film sample of nominal composition $Cu_{0.05}(As_{0.4}Se_{0.6})_{0.95}$ was prepared on a glass microscope slide using conventional evaporation techniques (growth rates of ~10 Å/s) with the bulk sample as a source. This sample was annealed for 22 h at about 164 °C before performing any experiments. In what follows, we will refer to bulk samples unless otherwise specified.

Absorption coefficients were measured with the conventional transmission method.[4] The irradiation sources were lasers or a xenon lamp filtered with deionized water and a long-pass glass filter with a cutoff wavelength of about 550 nm.

III. PHOTOINDUCED ABSORPTION

If the PD effect is tied to a nonbonding valence band and hence to twofold-coordinated chalcogen atoms, then it is expected that when v_2/v approaches zero the PD effect should vanish. Thus, we first discuss those samples with the largest possible copper concentration x because they have the smallest v_2/v. The largest possible x is determined by the glass-forming limits[14] and the constraint that the samples have to be bulk and large enough for optical experiments. The largest possible x in the $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ system turns out to be in the range 0.23–0.25 for the quenching conditions discussed in Sec. II.

Typical average absorption coefficients $\bar{\alpha}$ before and after irradiation, and the photoinduced contribution to the absorption $\Delta\bar{\alpha}$ for $Cu_{0.23}(As_{0.4}Se_{0.6})_{0.77}$, are shown in Figs. 1 and 2. In these figures, $\Delta\bar{\alpha}$ is constant at low photon energy and decreases as the energy approaches the band gap. Moreover, the annealing experiments (shown as diamonds in Fig. 2) indicate that $\Delta\bar{\alpha}$ is completely annealed away after cycling to room temperature.

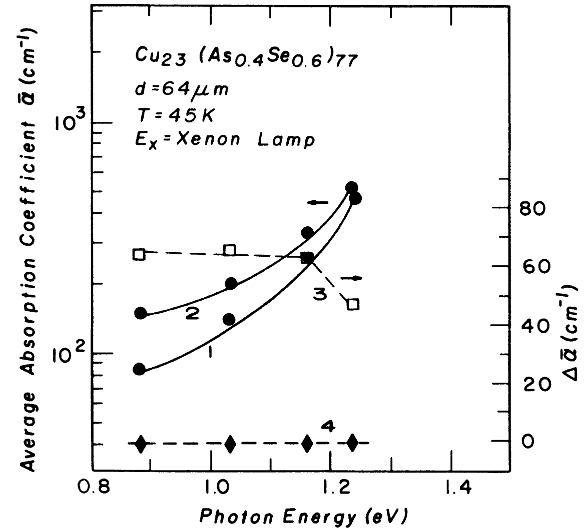

FIG. 2. Absorption spectra before (numbered 1) and after (numbered 2) irradiation with a xenon lamp (left scale), and photoinduced absorption (right scale, curve numbered 3) in $Cu_{0.23}(As_{0.4}Se_{0.6})_{0.77}$. The irradiation intensity is 250 mW/cm^2 and the irradiation time is 7200 s. The solid diamonds (right scale) represent the photoinduced absorption measured at 45 K after annealing up to 290 K following irradiation. The annealing was done by heating the sample to 290 K at a rate of 10 K/min, keeping the sample at 290 K for 5 min, and then cooling the sample back to 45 K at a rate of 15 K/min. This figure shows that the photoinduced absorption consists only of midgap absorption with no PD effect.

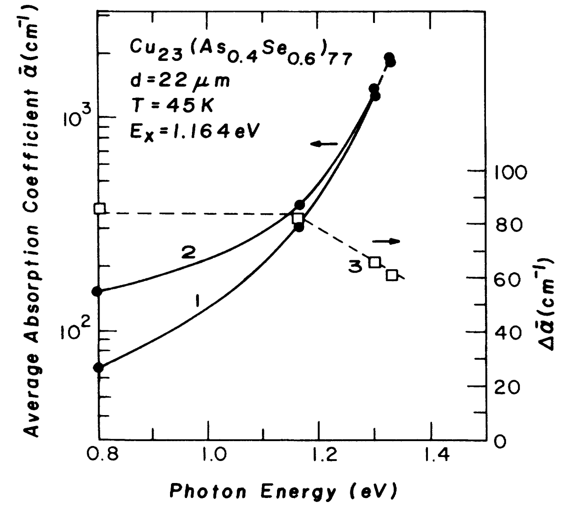

FIG. 1. Absorption spectra before (numbered 1) and after (numbered 2) irradiation with the 1.06-μm line from an yttrium-aluminum-garnet (YAG) laser (left scale) and the photoinduced component of the absorption (right scale, curve numbered 3) in $Cu_{0.23}(As_{0.4}Se_{0.6})_{0.77}$. d is the sample thickness. The irradiation intensity is 221 mW/cm^2 and the irradiation time is 14 000 s. This figure shows that the photoinduced aborption consists only of the midgap absorption with no PD effect.

As pointed out in the Introduction, the photoinduced absorption can be classified into two parts according to the energy dependence and the annealing behavior. These two parts are the midgap absorption and the PD effect. The energy dependence and annealing behavior show that the photoinduced absorption in Figs. 1 and 2 is midgap absorption and not PD. Therefore, no measurable PD effect is observed in these materials. In samples of $Cu_{0.25}(As_{0.4}Se_{0.6})_{0.75}$, the same results are obtained.

According to inequality (5), $0 \leq v_2/v \leq 17\%$ in $Cu_{0.25}(As_{0.4}Se_{0.6})_{0.75}$ and $0 \leq v_2/v \leq 25\%$ in $Cu_{0.23}(As_{0.4}Se_{0.6})_{0.77}$. These inequalities indicate that most of the twofold-coordinated chalcogen atoms have disappeared in these copper-rich glasses. The absence of the PD effect in these materials therefore clearly demonstrates that the mere presence of the chalcogen atoms in a glass is not sufficient to produce the PD effect. These data, with our model calculations [inequality (5)], provide strong evidence that a nonbonding chalcogen valence band, which is provided by twofold-coordinated chalcogen atoms, is necessary (though perhaps insufficient, as will be shown below) for the presence of the PD effect in the chalcogenide glasses.

Questions can be raised concerning the experimental resolution of a small PD effect. It is known that the PD effect tends to scale with the band gap of the material. The dependence of the optical-absorption edge on x in the $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ system is shown in Fig. 3. As can be seen from Fig. 3, the band gap decreases with increasing x. As the band gap decreases, the PD effect generally becomes smaller. It is therefore necessary to demonstrate that the PD effect in these copper-rich materials is much smaller than that in conventional chalcogenide glasses of the same band gap in which $v_2/v=1$. Glassy $As_2Se_{1.5}Te_{1.5}$ was chosen for this purpose. The PD effect in $As_2Se_{1.5}Te_{1.5}$, which is known to exist,[8] was measured under the same experimental conditions as those for the copper-rich samples. The results, which are shown in Figs. 4 and 5, show that the PD effect is present in $As_2Se_{1.5}Te_{1.5}$. In particular, Fig. 5 indicates that the xenon lamp is effective as an irradiation source. The results in Figs. 4 and 5 confirm that the PD effect is absent in $Cu_x(As_{0.4}Se_{0.5})_{1-x}$ for x equal to 0.23 and 0.25.

We have also investigated the photoinduced absorption in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ and $Cu_x(As_{0.4}S_{0.6})_{1-x}$ with low copper concentrations. Figure 6 shows the absorption spectra before and after the irradiation and the photoinduced absorptionn $\Delta\bar{\alpha}$ for a $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ sample. Again , the only component of the photoinduced absorption is the midgap absorption, and it is evident that the PD effect is absent. With this copper concentration, inequality (1) yields $12\% \le v_2/v \le 56\%$. Since v_2/v is not necessarily small in this material, the absence of the PD effect cannot easily be explained in terms of the disappearance of the lone-pair p electrons.

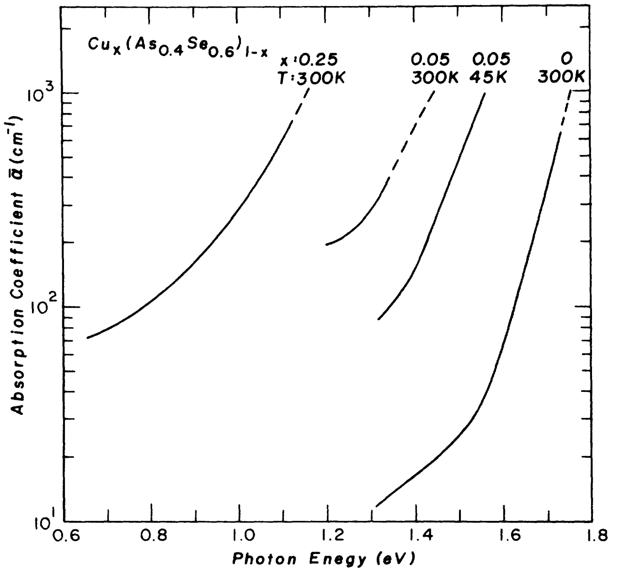

FIG. 3. Absorption spectra for bulk, glassy samples of $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ for various values of x. The measurement temperatures T are indicated. The solid curves represent data and the dashed lines are extrapolations. The energy at which the absorption coefficient is 10^{-3} cm^{-1} may be taken as a measure of the band gap. At 300 K these values are 1.75, 1.44, and 1.17 eV for $x=0$, 0.05, and 0.25, respectively.

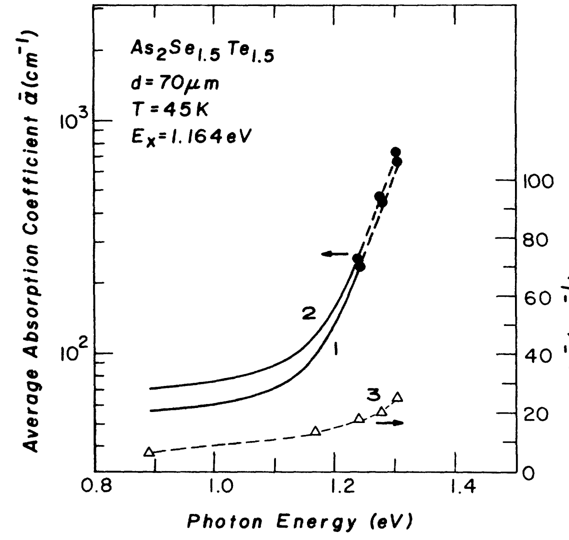

FIG. 4. Absorption spectra before (numbered 1) and after (numbered 2) irradiation with the 1.06-μm line from a YAG laser (left scale), and the photoinduced absorption (right scale, curve numbered 3) in $As_2Se_{1.5}Te_{1.5}$. The irradiation intensity is 221 mW/cm^2 and the irradiation time is 7800 s. This figure shows that the PD effect occurs in this material under conditions similar to those of Fig. 1.

Figure 7 shows the optical-absorption spectra before and after irradiation for samples of $Cu_{0.05}(As_{0.4}Se_{0.6})_{0.95}$ with different thicknesses, and Fig. 8 shows the spectra of the photoinduced component of the absorption $\Delta\bar{\alpha}$ for the same samples in the same experiments. The film sample (labeled D) shown in Fig. 7 will be discussed later. From the criteria stated above, it can be seen that the

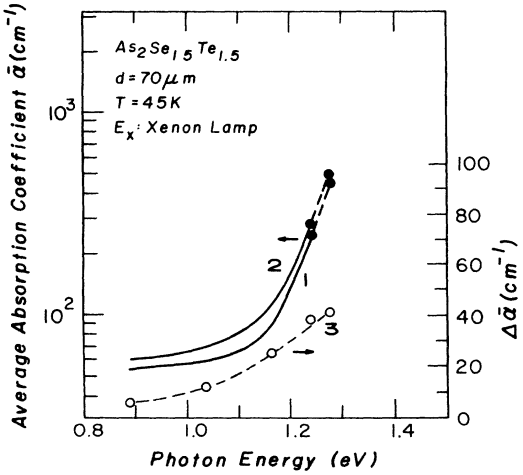

FIG. 5. Absorption spectra before (numbered 1) and after (numbered 2) irradiation with a xenon lamp (left scale), and the photoinduced absorption (right scale, curve numbered 3) in $As_2Se_{1.5}Te_{1.5}$. The irradiation intensity is 250 mW/cm^2 and the irradiation time is 7200 s. This figure shows that the PD effect occurs in this glass under conditions identical to those of Fig. 2.

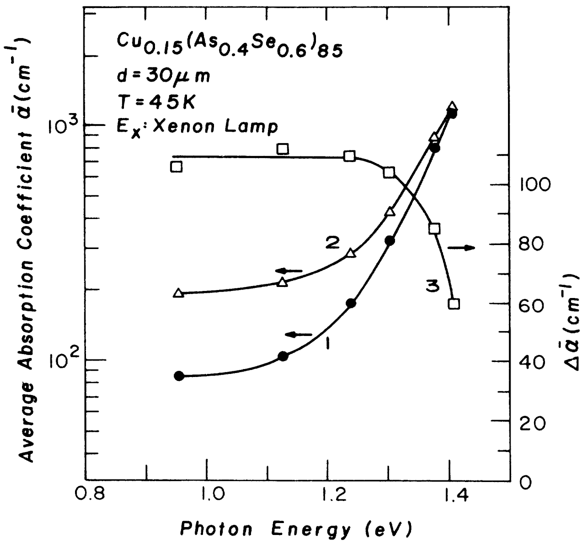

FIG. 6. Absorption spectra before (numbered 1) and after (numbered 2) irradiation with a xenon lamp (left scale), and the photoinduced absorption (right scale, curve numbered 3) in $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$. The irradiation intensity is 250 mW/cm^2 and the irradiation time is 2700 s. This figure shows that the photoinduced absorption consists only of midgap absorption with no PD effect.

thicker 69- and 30-μm $Cu_{0.05}(As_{0.4}Se_{0.6})_{0.95}$ samples (labeled *A* and *B* in these figures) show the photoinduced midgap absorption only, and no evidence for the PD effect. In the thinner 4.07-μm sample (labeled *C*) the PD effect can be seen in Fig. 8. Note that the $\Delta\bar{\alpha}$ spectra for samples of different thickness should not be continuous because the thinner sample exhibits a larger $\Delta\bar{\alpha}$ due to the influence of the finite penetration depth of the irradiation. Note also that the PD effect in the 4.07-μm sample is very small compared with the PD effect in its copper-free counterpart As_2Se_3. In the former, the band-edge shift $\Delta E = 0.005$ eV, as shown in Fig. 7, while in the latter, typically $\Delta E \approx 0.1$ eV under similar experimental conditions (sample thickness, inducing temperature, etc.). At 77 K Tanaka[15] finds that $\Delta E \approx 0.07$ eV in glassy As_2Se_3. Therefore it is concluded that the PD effect in $Cu_{0.05}(As_{0.4}Se_{0.6})_{0.95}$ is essentially eliminated. Note that the model calculation [inequality (5)] predicts that $74\% \le v_2/v \le 87\%$ in $Cu_{0.05}(As_{0.4}Se_{0.6})_{0.95}$. That is, most of the chalcogen atoms are still twofold coordinated in this glass.

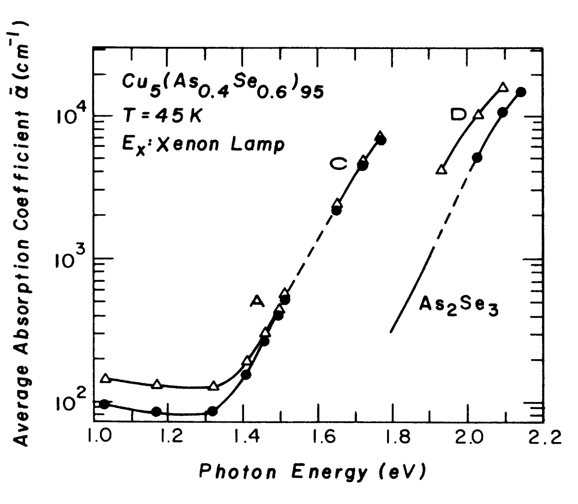

FIG. 7. Absorption spectra before and after irradiation with a xenon lamp in $Cu_{0.05}(As_{0.4}Se_{0.6})_{0.95}$. The samples are *A*, 69 μm bulk; *C*, 4.07 μm bulk; and *D*, 1.85 μm film—for nominally the same composition (see text for details). The solid circles represent the absorption before irradiation and the open triangles the absorption after irradiation. The irradiation intensity is 250 mW/cm^2 and the irradiation time is about 3000 s. The absorption spectrum of a well-annealed sample of As_2Se_3 is also shown for comparison.

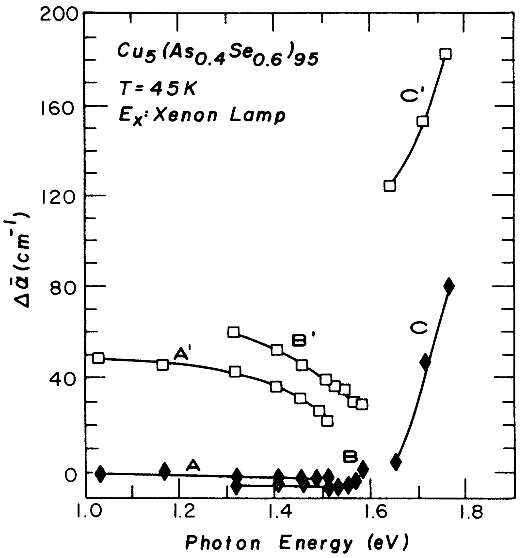

FIG. 8. Spectra of the photoinduced component of the absorption in $Cu_{0.05}(As_{0.4}Se_{0.6})_{0.95}$ in the same experiments as those shown in Fig. 7. The samples are *A*, 69 μm bulk; *B*, 30 μm bulk; and *C*, 4.07 μm bulk. The open squares represent the photoinduced absorption after irradiation but before annealing. The solid diamonds represent the photoinduced absorption at 45 K after annealing at 270 K following the irradition. The annealing was done by heating the sample to 270 K at a rate of 10 K/min and then immediately cooling the sample back to 45 K at a rate of 15 K/min. This figure shows that the PD effect is detectable in this glass, but that the magnitude is greatly reduced from that for pure As_2Se_3.

The PD effect can be observed in $Cu_{0.01}(As_{0.4}Se_{0.6})_{0.99}$. This fact is shown in Fig. 9, but note that the magnitude of the PD is already 25% less than that in its copper-free counterpart As_2Se_3, as shown in Fig. 10, even though the band gaps are essentially identical in these two materials. In the Cu-As-S system, the PD effect is essentially destroyed, even in $Cu_{0.01}(As_{0.4}S_{0.6})_{0.99}$. This fact is shown in Fig. 11. In $Cu_{0.01}(As_{0.4}Se_{0.6})_{0.99}$ and $Cu_{0.01}(As_{0.4}S_{0.6})_{0.99}$, inequality (5) yields $95\% \le v_2/v \le 98\%$.

A measurable PD effect in film samples of $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ with $x > 0.05$ has been reported in

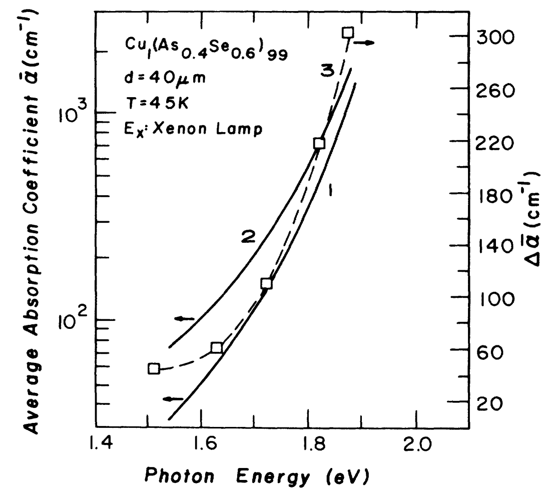

FIG. 9. Absorption spectra before (numbered 1) and after (numbered 2) irradiation with a xenon lamp (left scale), and the photoinduced absorption (right scale, curve numbered 3) in $Cu_{0.01}(As_{0.4}Se_{0.6})_{0.99}$. The irradiation intensity is 250 mW/cm^2 and the irradiation time is 3360 s. This figure shows that the PD effect occurs in this glass, but is 25% less than that shown in Fig. 10 for pure As_2Se_3.

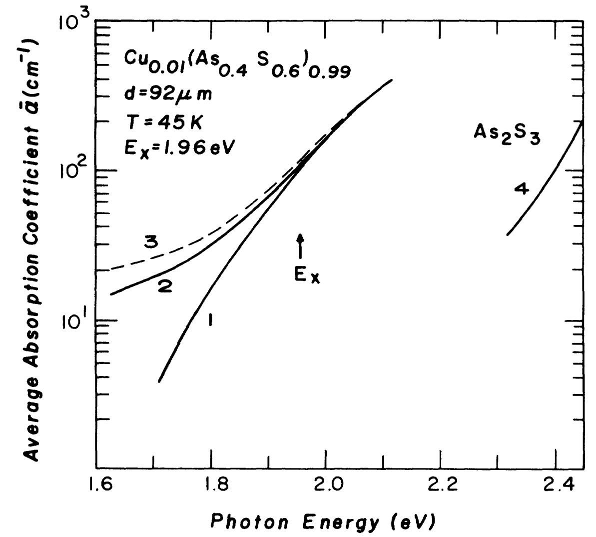

FIG. 11. Absorption spectra before (numbered 1) and after (numbered 2 and 3) irradiation with He-Ne laser, and the absorption spectrum of a well-annealed sample of As_2S_3 (numbered 4). For curve 2, the irradiation intensity is 109 mW/cm^2 and the irradiation time is 5100 s. Curve 3 was obtained by additional irradiation with intensity 436 mW/cm^2 and irradiation time 2280 s. This figure shows that the PD effect does not occur in $Cu_{0.01}(As_{0.4}S_{0.6})_{0.99}$.

the literature.[16] Experiments on a film sample of nominal composition $Cu_{0.05}(As_{0.4}Se_{0.6})_{0.95}$ have been carried out in this research. Before the irradiation, the sample was annealed for 22 h at 160–170 °C (the glass-transition temperature of this material is about 175 °C).[11] The result is shown as sample *D* in Fig. 7, which confirms the existence of the PD effect in the film sample and shows that $\Delta E \approx 0.075$ eV, much larger than that in the 4.07-μm bulk sample ($\Delta E \approx 0.005$ eV). After the sample is annealed for 11 h at 170 °C, 5 ° C below the glass-transition temperature, the absorption spectrum returns to the spectrum before irradiation. Thus the observed PD effect in this film sample is reversible. However, atomic analysis (microprobe) on this film sample indicates that the sample does not contain copper ($x < 0.0003$), while the result of the same analysis on the corresponding bulk material is consistent with the nominal composition. This result means that the copper in the bulk source was not incorporated into the film during the preparation of the sample. The actual composition of this film sample is very close to As_2Se_3. This analysis is consistent with the fact that the optical band gap of this film is essentially the same as that of the copper-free bulk sample (Fig. 7). Therefore, we conclude that the preservation of the PD effect in this film sample is due to the absence of copper. The same conclusion may be applicable to the reported PD effect in the literature[16] in films with nominal nonzero copper concentration. For example, in Ref. 16 the film whose nominal composition is $Cu_{0.1}As_{0.3}Se_{0.6}$ has an optical-absorption spectrum which is very close to that for $As_{0.4}Se_{0.6}$.

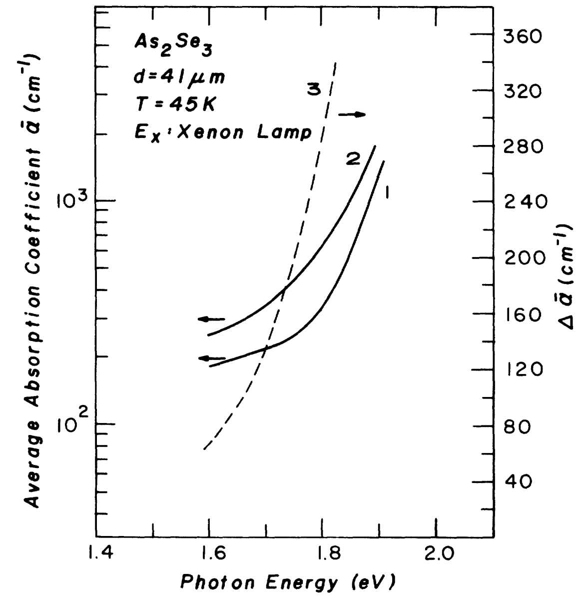

FIG. 10. Absorption spectra before (numbered 1) and after (numbered 2) irradiation with a xenon lamp (left scale), and the photoinduced absorption (right scale, curve numbered 3) in As_2Se_3. The irradiation intensity is 250 mW/cm^2 and the irradiation time is 3000 s. This figure shows that the PD effect occurs in this glass.

IV. PHOTOINDUCED ELECTRON-SPIN RESONANCE

The copper-rich chalcogenide glasses exhibit other properties which are more similar to the tetrahedrally bonded amorphous semiconductors than to the conventional chalcogenide glasses. For example, there exists a dark electron-spin-resonance (ESR) signal in

$Cu_{0.23}(As_{0.4}Se_{0.6})_{0.77}$, which corresponds to about 10^{18} spins/cm^3. This result provides evidence for the presence of defects whose effective electron-electron correlation energies $U_{\rm eff}$ are positive, similar to those in amorphous silicon, glassy $CdGeAs_2$, and other tetrahedrally coordinated amorphous semiconductors.[17] Irradiation for about 5200 s at 20 K with a Kr^+ laser at $\lambda = 752.5$ nm ($h\nu = 1.647$ eV) and an intensity of 51 mW/cm^2 induced a metastable increase in the ESR. This photoinduced ESR signal is annealed away at about 180 K. This annealing behavior of photoinduced ESR has been reported in binary chalcogenide glasses with low-intensity irradiation and interpreted as the evidence[2,5,17] for the presence of defects with negative $U_{\rm eff}$. The existence of dark and photoinduced ESR in the copper-rich samples suggests the coexistence of defects with both positive and negative $U_{\rm eff}$, probably due to the existence of both a three-dimensional local structural arrangement with fourfold-coordinated copper and threefold- or fourfold-coordinated chalcogen atoms and a two-dimensional local structural arrangement with twofold-coordinated chalocogen atoms ($0 \le v_2/v \le 25\%$ for $x = 0.23$).

V. DISCUSSION

Several models have been proposed to explain the photodarkening effect in the chalcogenide glasses. These models can be classified into two types. One involves subtle changes of nonbonding p electrons on the chalcogen atoms[8,18] and the other involves local rearrangements of As-chalcogen bonds.[19]

Based on their results that there is no observable photoinduced change in the ^{75}As nuclear quadrupole resonance (NQR), the two-phonon infrared (ir) absorption, and one-phonon Raman spectrum in bulk glassy As_2Se_3, Treacy *et al.*[18] proposed that the PD effect is due to subtle changes in the wave functions of the lone-pair p electrons and not due to major bonding changes. However, the lack of observation of any photoinduced changes using NQR, ir, and Raman techniques could be due to insufficient sensitivity of these techniques.

Other models relate the PD effect to local-bonding changes.[19–22] Elliot has recently reviewed and further developed these models.[19] Most of the models invoke photoinduced changes of the strength of the intermolecular bonding (the interaction between layers or chains) or of the strength of the intermolecular bonding (the covalent bonding within the layers or chains). The former mechanism relates the PD to metastable changes of the positions of the chalcogen atoms which involve twisting of the As-chalcogen bonds, but not breaking of bonds within the layers. The latter mechanism relates the PD to the formation of overcoordinated or undercoordinated defects or to the formation of homopolar bonds. The photoinduced modifications or rearrangements introduce states in the tails of the valence and conduction bands which shift the absorption edge to lower energy. According to Dow and Redfield,[23] the presence of internal electric fields may be responsible for the Urbach absorption tail which is observed in all amorphous semiconductors. It is therefore also possible that, if the metastable defects are charged, they may change the internal electric fields, which may, in turn, be responsible for the PD effect in the Urbach-tail region.

The reduction or elimination of the PD effect in bulk, glassy $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ and $Cu_x(As_{0.4}S_{0.6})_{1-x}$ with low copper concentrations is surprising. These results cannot be easily explained by the disappearance of the lone-pair p electrons since most of the twofold-coordinated chalcogen atoms, which provide these electrons, remain after alloying with the small amount of copper ($x \le 0.01$ in the sulfur system and $x \le 0.05$ in the selenium system). The increase of the average coordination number Z upon copper alloying also cannot satisfactorily explain the absence of the PD effect. Tanaka[24] recently found that the PD effect is maximum at $Z = 2.65$ among the Ge-As-S, Ge-S, and Ge-Se glass systems. This result does not agree with our data in the $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ and $Cu_x(As_{0.4}S_{0.6})_{1-x}$ glasses. In these systems, the average coordination number is given by Eq. (3). For $x = 0.01$ and 0.05, $Z_{\rm av} = 2.45$ and 2.63, respectively. The PD effect decreases monotonically with x as x increases from zero, and essentially disappears at $x = 0.05$ ($Z_{\rm av} = 2.63$) for the $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ system and at $x = 0.01$ ($Z_{\rm av} = 2.45$) for the $Cu_x(As_{0.4}S_{0.6})_{1-x}$ system. The disagreement between the Ge-As-Se(S) systems and the Cu-As-Se(S) systems may arise from the fact that in the former the chalcogen atoms remain twofold coordinated, while in the latter some of the chalcogen atoms become threefold coordinated or fourfold coordinated upon alloying with copper.

We propose two possible interpretations for our results. Further investigations are needed to test these interpretations. First, the PD effect may have occurred in these materials but may have been masked by other optical transitions. The PD effect is a nearly parallel shift of the absorption spectrum at the high-energy end of the Urbach-tail region[3] ($100 \le \alpha \le 10^4$ cm^{-1}). Such a shift may correspond to a parallel shift of the energy spectrum of the valence-band-tail states toward the middle of the band gap. It is assumed in this interpretation that the states related to the lone-pair p electrons will be shifted upon irradiation. If such states are at the top of the valence band, the shift will manifest itself as the PD effect. However, if other states, which do not shift upon irradiation, are dominant at the top of the valence band, then the shift of the lone-pair p-electron states may be masked and therefore may not be observed in the absorption spectrum. The photoinduced midgap absorption is commonly believed to result from the photoinduced defect states near the middle of the gap. Such midgap states will not be masked by these additional states, which by assumption occur near the edge of the valence band, and the photoinduced midgap absorption will still be observed.

This interpretation is further supported by the fact that while different copper concentrations are needed to eliminate the PD effect in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ and $Cu_x(As_{0.4}S_{0.6})_{1-x}$ (where $x = 0.05$ and 0.01, respectively), the decreases of the band gaps of these materials relative to those of their copper-free counterparts As_2Se_3 and As_2S_3, respectively, are almost the same: 0.3 eV for $Cu_{0.05}(As_{0.4}Se_{0.6})_{0.95}$ and 0.4 eV for $Cu_{0.01}(As_{0.4}S_{0.6})_{0.99}$.

In both cases, the band-gap decrease is larger than that of the maximum shift of the band gap due to the PD effect in the copper-free materials, which is ~ 0.07 eV for As_2Se_3 (at 77 K) and ~ 0.16 eV for As_2S_3 (at 20 K).[15]

The problem with this interpretation is the lack of direct experimental evidence for the existence of such additional masking states at the top of the valence band. For $x \leq 0.1$, photoemission studies on glasses in the $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ system are not conclusive with regard to the character of the electronic states at the top of the valence band.[25,26] For high copper concentration ($x > 0.2$) the states at the top of the valence band are probably[25] bonding states involving Se. For values of x less than 0.1, the additional states are not apparent in the photoemission data. Thus, the fact that the band gap decreases with increasing x does not prove the existence of states which are prevalent enough to mask the photodarkening.

On the one hand, the copper-chalcogen bonds may add states to the edges of the valence and conduction bands and thus decrease the band gap. These states may serve as the masking states. On the other hand, the increase of the average coordination number may crosslink the layer structures in As_2Se_3 and As_2S_3, and thus change the interactions between the lone-pair p electrons. Such changes may broaden the corresponding energy bands and decrease the band gap. In this case the dominant states at the top of the valence band may still be the lone-pair p-electronic states, and the observed absence of the PD effect would suggest that the lone-pair p-electronic states do not undergo a parallel shift toward the middle of the band gap upon irradiation. This interpretation suggests a second explanation for the absence of the PD effect, which we shall now describe.

The absence of the PD effect in the $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ ($x \geq 0.05$) and $Cu_x(As_{0.4}S_{0.6})_{1-x}$ ($x \geq 0.01$) systems may imply that the PD effect is due to photoinduced changes in medium-range (a scale greater than that of the nearest-neighbor distances) correlations between the lone-pair p electrons. The small number of copper atoms which are fourfold coordinated and the small number of chalcogen atoms which are not twofold coordinated in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ and $Cu_x(As_{0.4}S_{0.6})_{1-x}$ for low x are scattered within the networks of the copper-free As_2Se_3 and As_2S_3, respectively. Such dilutely scattered atoms should not affect any photoinduced local (on a scale of the nearest-neighbor distance) rearrangement of the structure. This statement is supported by the preservation of the photoinduced midgap absorption, which is more likely to be related to photoinduced local rearrangements of charge and/or atoms.[2,5] However, the dilutely scattered copper atoms and the threefold- and fourfold-coordinated chalcogen atoms may hinder correlated changes of the lone-pair p-electronic wave functions on a medium-range scale. The reduction or elimination of the PD effect in these materials therefore may indicate that the PD effect is related to changes of medium-range correlations between lone-pair p electrons.

This interpretation has an important impact on the possible mechanisms for the PD effect because many existing models relate the PD effect only to photoinduced local rearrangements. The problem with this interpretation is that it is hard to quantify the medium-range changes of the lone-pair p-electronic wave functions.

VI. SUMMARY

We have investigated the photoinduced absorption in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ and $Cu_x(As_{0.4}S_{0.6})_{1-x}$ to study the role of the twofold-coordinated chalcogen atoms in the photodarkening effect. The twofold-coordinated chalcogen atoms provide lone-pair p electrons which, in As_2Se_3 and As_2S_3 glasses, are responsible for the electronic states at the top of the valence band. The addition of copper increases the average coordination number of chalcogen atoms and therefore reduces the fraction of the chalcogen atoms that are twofold coordinated. We have monitored the influence on the PD effect of increasing the copper concentration. We have found that the magnitude of the PD effect decreases very rapidly with increasing copper concentration and that the PD effect is essentially eliminated in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ for $x \geq 5$ at. % and in $Cu_x(As_{0.4}S_{0.6})_{1-x}$ for $x \geq 1$ at. % The only photoinduced absorption in these materials is the photoinduced midgap absorption. Our model calculations give the fraction v_2/v of chalcogen atoms which are twofold coordinated. This fraction is $0.74 \leq v_2/v \leq 0.87$ in $Cu_{0.05}(As_{0.4}Se_{0.6})_{0.95}$ and $0.95 \leq v_2/v \leq 0.98$ in $Cu_{0.01}(As_{0.4}S_{0.6})_{0.99}$. Therefore, our results indicate that the mere appearance of twofold-coordinated chalcogen atoms is not sufficient for the PD effect to occur.

A unique interpretation of these results is not available at present. The addition of copper may introduce electronic states which dominate the density of states at the top on the valence band. These states may not be related to the lone-pair p electrons and may mask the photodarkening effect. Alternatively, the results may suggest that the PD effect is due to some photoinduced correlated changes of the lone-pair p-electronic wave functions on a scale greater than nearest-neighbor distances. Dilute concentrations of atoms with high coordination numbers (>2) in these alloys may impede such photoinduced correlated changes. This latter interpretation implies that the PD effect involves more than just local rearrangements at one atomic site or the breaking of a single covalent bond.

The observed coexistence of the dark and photoinduced electron-spin-resonance signal in $Cu_{0.23}(As_{0.4}Se_{0.6})_{0.77}$ indicates the coexistence of defects with positive and defects with negative effective electron-electron correlation energies in this material. This fact is probably due to the coexistence of a three-dimensional local structural arrangement along with twofold-coordinated chalcogen atoms.

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[1] Since the absorbing sample has a finite penetration depth for the irradiation, and the photoinduced absorption depends on the irradiation intensity, the sample after irradiation does not possess a uniform absorption coefficient. Therefore it is only meaningful to speak about an average absorption coefficient $\bar{\alpha}$ over the sample thickness [see Eq. (6) in text], which is what we obtain by the transmission method employed in this study. See J. Z. Liu and P. C. Taylor, J. Non-Cryst. Solids **77&78**, 1195 (1985).

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[3] Detailed study (Ref. 4) indicates that photoinduced absorption in the binary chalcogenide glass As_2S_3 can be classified as (1) the usual photoinduced midgap absorption, which is relatively independent of photon energy and occurs at low temperatures; (2) the photodarkening (PD) effect, which is defined conventionally as a parallel shift of $\bar{\alpha}$ and thus $\Delta\bar{\alpha}(\mathrm{PD}) \propto \exp(h\nu)$ in the Urbach-tail region ($h\nu$ is the photon energy); and (3) a new type of photoinduced below-band-gap-absorption, which at higher temperatures usually dominates in the region at the low-energy end of the Urbach tail and is characterized by $\Delta\bar{\alpha}$ increasing with $h\nu$ more slowly than exponentially. In this paper we only distinguish the photoinduced midgap absorption and ignore this new effect, because our main concern is whether or not the PD effect disappears and whether the observed photoinduced absorption is due to the photoinduced midgap absorption or PD.

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