

Photodarkening in amorphous $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ films

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Photodarkening experiments have been performed on evaporated films of $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ in the composition range $0 \leq x \leq 0.60$ at 78 K. Thermal cycling between room temperature and 78 K was observed to reduce the optical absorption of the films. The photodarkening response is slightly enhanced at $x=0.1$ but is suppressed for higher Sn concentrations.

Chalcogenide glasses such as amorphous GeSe_2 , As_2S_3 , and similar compounds display an intriguing property known as "photodarkening." When exposed to light of energy near or above the band gap, they undergo a structural change resulting in a shift of the optical-absorption edge toward lower energies, thereby appearing darker in the visible range. This shift is typically stable at room temperature but can be reversed by thermal annealing below the glass transition temperature.¹

Although this phenomenon has attracted attention both for its intrinsic physical interest and for its possible applications in optical memory elements, the details of the mechanism by which the change in the optical band gap occurs remain obscure.

In an attempt to gain an understanding of this mechanism, this study of the photodarkening characteristics of amorphous $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ films was undertaken. It is to be expected that the substitution of Sn for Ge at alloy concentrations would result in alterations of the glassy structure, as the crystalline end-point compounds do not share the same structure.^{2,3} It was hoped that examination of the effects of the substitution of Sn for Ge would give some insight into the role of the bonding of the tathogen in the photodarkening process.

EXPERIMENT

Bulk amorphous $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ was produced by melt quenching from appropriate mixtures of 99.7% pure selenium powder, 99.999% pure germanium powder, and 99.7% pure tin granules in 4-mm-o.d. quartz tubes evacuated to 5×10^{-5} torr. Each tube was held at 1000°C for one day, then the temperature was lowered to 800°C and held for two more days, after which the tube was dropped from the vertical furnace into quenching oil.

Thin films were produced by evaporation of bulk, melt-quenched $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ in a 14-in. bell jar evacuated to 5×10^{-6} torr. The films were deposited at a rate of 5–10 Å/s onto 3×1 in.² crown glass slides held 12 in. above the boat. Interferometry was used to measure the thicknesses of the films, which were found to be between 40 nm and 160 ± 8 nm.

Before illumination the $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ films were annealed at 290°C in a flowing He gas atmosphere for 1 h.

The 442-nm line of a HeCd laser was used to illuminate the films while a nitrogen gas Joule-Thompson refrigerator was used to maintain the film temperature at 78 K. The films were illuminated at an intensity of 0.10 ± 0.04 W/cm² in a vacuum of better than 1 mtorr until the films' transmission of 442-nm light, measured continuously, reached a minimum (usually after about 20 min). Similar low power illumination conditions have been observed to cause photodarkening in GeSe_2 and GeSe_3 films.^{4,5}

The optical density of each $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ film was measured using a Cary 14 double beam spectrophotometer before annealing, before illumination, and after illumination. The thickness measurements were used to convert optical density to optical-absorption coefficient. There was no detectable change in thickness after illumination.

RESULTS

The choice of 290°C as the annealing temperature was experimentally determined by isochronally annealing identical films of GeSe_2 and $\text{Ge}_{0.4}\text{Sn}_{0.6}\text{Se}_2$ at different temperatures and observing changes in their optical densities. Annealing for 1 h at or above the crystallization temperature resulted in a sharpening of the absorption edge (Fig. 1). It was found that for 1 h of exposure, GeSe_2 crystallizes at $350 \pm 5^\circ\text{C}$ and anneals fully at or above 290°C, while $\text{Ge}_{0.4}\text{Sn}_{0.6}\text{Se}_2$ crystallizes at $300 \pm 5^\circ\text{C}$ and anneals at or above 260°C. It had been previously determined that bulk samples of glassy $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ with higher Sn concentrations crystallized more easily than those with lower Sn concentrations.⁶ It was therefore concluded that a safe annealing temperature for all Sn concentrations would be 290°C, which fully anneals GeSe_2 but does not crystallize $\text{Ge}_{0.4}\text{Sn}_{0.6}\text{Se}_2$.

The flat region of the α versus E curves at low energies that can be seen in Fig. 1 reflects the very low optical densities of these thin films at below-gap energies and the limited sensitivity of the measurement apparatus under these conditions. It is unlikely to have any physical significance. All conclusions regarding photodarkening and other changes in the optical band gap in these films were drawn from their behavior in the more strongly absorbing region at higher energies.

It was found that the process of cooling the films to 78

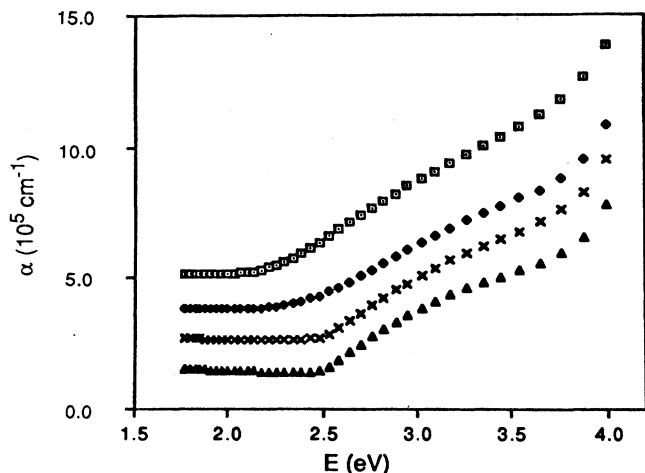


FIG. 1. Optical-absorption coefficient vs photon energy of $\text{Ge}_{0.4}\text{Sn}_{0.6}\text{Se}_2$ films annealed at various temperatures. \blacktriangle , 320°C; \times , 300°C; \blacklozenge , 280°C; \square , unannealed. Each successive curve is displaced upward by $1 \times 10^5 \text{ cm}^{-1}$ for clarity.

K with the Joule-Thompson refrigerator and reheating them caused an increase in the optical band gap as evidenced by a decrease in the optical absorption at fixed energy (Fig. 2). Furthermore, this effect was found to be smaller for portions of the sample located 2 cm away from the cold pad than for those portions located 1 cm away. As only relative shifts as a function of Sn concentration were desired, the band-gap shift ΔE_g was (somewhat arbitrarily) defined in this study as the energy shift observed at the optical-absorption coefficient $\alpha = 2.8 \times 10^5 \text{ cm}^{-1}$. To obtain the portion of the band-gap shift due only to illumination, it was necessary to determine the energy shift at $\alpha = 2.8 \times 10^5 \text{ cm}^{-1}$ due to the

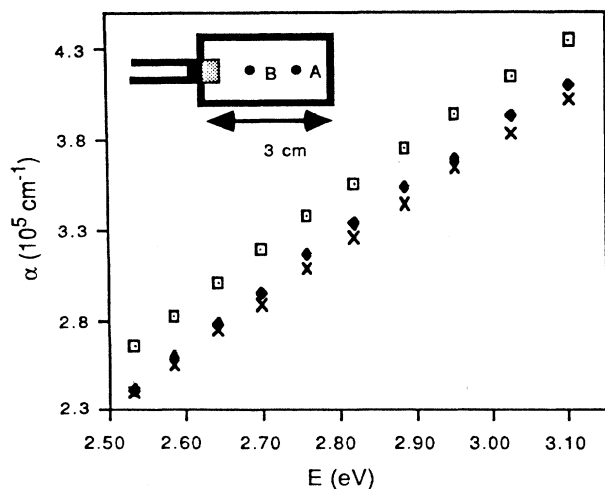


FIG. 2. Optical-absorption coefficient of $\text{Ge}_{0.5}\text{Sn}_{0.5}\text{Se}_2$ film at room temperature before and after cycling once between room temperature and 78 K. \square , before cycling; \blacklozenge , after cycling, point A (see inset); \times , after cycling, point B. Inset: schematic of glass slide mounted on cold pad.

thermal cycling. This shift was estimated from either the measured shifts in cooled but not illuminated portions (where possible) or from the difference in the total optical-absorption shift between two illuminated portions of the film at different distances from the cold pad. Using this definition for ΔE_g and correcting for the thermal cycling effect, the photoinduced band-gap changes as a function of Sn content are given in Fig. 3. The data suggest that the inclusion of Sn at a concentration of $x=0.10$ slightly enhances the photodarkening capacity of the films, while Sn concentrations of $x=0.20$ or greater suppress it.

DISCUSSION

The most surprising result of this study is the decrease in optical absorption induced by thermal cycling of the films between room temperature and 78 K. The salient features of this decrease appear to be that it occurs for all Sn concentrations and that it is more marked for portions of the sample which are closer to the cold pad (and therefore presumably brought to a lower temperature). All the samples were returned to room temperature before the optical-absorption measurements were made, so these observations do not discriminate between bleaching during cooling and during rewarming. Although the mechanism that produces this bleaching is as yet undetermined, several possibilities can be eliminated. One of these is the stress induced by differential thermal contraction. The films are evaporated on glass slides, so the difference in thermal expansion coefficient between crown glass and $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ would cause the films to undergo strain as they are cooled. Although the thermal expansion coefficients for these chalcogenide compounds have not been measured, this strain can be estimated using the value⁷ for the thermal expansion of As_2S_3 , which is $26 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. This value, combined with the coefficient of $8.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for crown glass,⁸ implies a biaxial strain in the film of -0.4% at 78 K. The stress corresponding to this strain can be estimated using the mea-

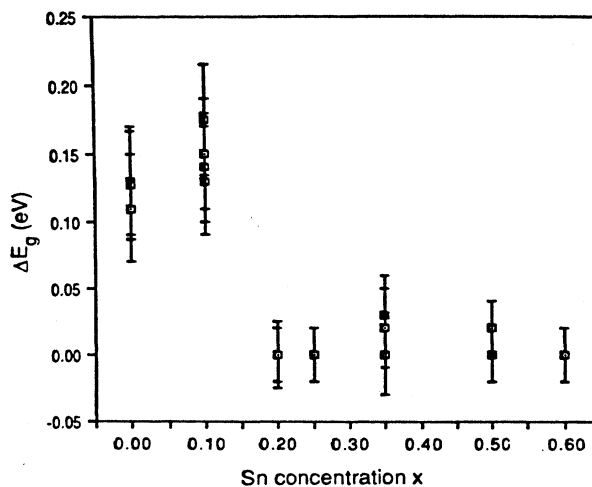


FIG. 3. Photoinduced change in optical band gap vs Sn concentration x for $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ films.

sured elastic constants⁹ of $\text{Ge}_{1.5}\text{As}_{0.5}\text{Se}_3$, and it is compressive with a magnitude of approximately 1 kbar. While stresses of this magnitude have been observed to shift the band gap of chalcogenide glasses by approximately the amount seen here,^{10,11} the shifts observed under pressure are always *negative*, i.e., of opposite sign to those seen here. This is attributed to the broadening of the electronic bands produced by the increased molecular overlap.

Another possible source of apparent bleaching of the films could be the formation of cracks and pinholes during the thermal cycling, which would lead to an increase in the transmission of light through the film. However, to account for the observed change in optical-absorption coefficient such cracks would have to cover approximately 20% of the film area. No such defects were seen in the films when they were examined with back lighting in an optical microscope at a magnification of $500\times$.

Without more detailed information on the changes which can be induced in the structure of annealed $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ films by thermal cycling and the relationship between such structural changes and the optical band gap, it is difficult to identify the mechanism of the observed bleaching. Such information could possibly be obtained using x-ray techniques such as extended x-ray-absorption fine-structure spectroscopy (EXAFS), but such studies appear not to have been performed on films of this composition.

The suppression of the photodarkening in the films with larger Sn concentrations is not related to changes in

the optical band gap. For all the films with Sn concentration $x \leq 0.35$, the band gap (defined here as the energy for which $\alpha = 2.8 \times 10^5 \text{ cm}^{-1}$) has the value $E_g = 3.44 \pm 0.20 \text{ eV}$. Films of higher Sn concentration ($x \geq 0.50$) have a lower band gap, $E_g = 2.52 \pm 0.20 \text{ eV}$. The observed photodarkening behavior is therefore not correlated with the value of the band gap.

The suppression of the photodarkening response probably results from changes in the structure caused by the substitution of Sn—Se bonds for Ge—Se bonds. Mössbauer and Raman measurements^{12,13} have demonstrated that Sn substitutes for Ge in GeSe_2 , and recent experiments⁶ suggest that large concentrations of Sn induce alterations in the cluster size in bulk glasses. The Sn atom is 15% larger than the Ge atom, so it is likely to occupy predominantly sites at the edges of the clusters in the glass. The suppression of the photodarkening response under these conditions suggests that the cluster edges play an important role in the photodarkening process.

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