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Observation of light polarization-dependent structural changes in chalcogenide glasses

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(Received 6 September 2002; accepted 5 December 2002)

The atomistic origin of photoinduced vector (polarization-dependent) phenomena in As–Se films is determined by extended x-ray absorption fine structure with *in situ* exposure to polarized laser light. A vector structural change is observed *directly* for any material: there is an expansion of the nearest-neighbor distance around the Se atoms, the magnitude of which depends on the direction of light polarization; the effect around As atoms is relatively smaller. The results point to the origin of scalar as well as vector changes in properties, which either persist after the light is removed, or exist only when light is incident on the sample. © 2003 American Institute of Physics.
[DOI: 10.1063/1.1541942]

In general, light interacts with a solid or molecule through its electronic states, which in turn depend on the constituent atoms and the structure of the material. In disordered materials, such interactions have led to a startling variety of photoinduced effects.^{1–5} In the last few years, fascinating new “vector” effects (meaning that the photoresponse depends upon the *polarization* of the incident light) have been observed,^{2–4} particularly in chalcogenide glasses. Salimnia, Galstian, and Villeneuve² reported the creation of an anisotropic crater induced by a linearly polarized laser beam of circular cross section in a chalcogenide glass film. A variety of technological applications for these surprising effects have been proposed, yet there is little specific data about the atomistic processes of photostructural rearrangement in any glassy system.

In the present work, we use extended x-ray absorption fine structure (EXAFS) analysis with polarized x rays to probe separately the changes in structure around As and Se atoms, and track the polarization dependence of these changes in an As₄₀Se₆₀ glass. We are able to provide direct evidence about the detailed vector changes around the As and Se atoms. It is hoped that such experiments will eventually prove to be useful in studies of more complex light-induced effects such as photosynthesis and photopolymerization.

Amorphous thick films (about 20 μm) of As₄₀Se₆₀ were prepared by first melting appropriate amounts of high purity As (99.9999%) and Se (99.999%) pieces in quartz ampoules,

avoiding oxygen contamination.⁶ Approximately 20-μm-thick films of this alloy were prepared by thermal evaporation onto glass (microscope slide) substrates in vacuum (10^{−5}–10^{−6} Torr), using deposition rates of 1–2 nm/s. For observing a vector (or anisotropic) property, the probe should also be anisotropic. This condition is readily fulfilled by the EXAFS analysis on the beamline X18B at the National Synchrotron Light Source, where the x rays are polarized in the plane of the ring (i.e., the electric field of the x rays, **E**, is parallel to the ground plane). Since the photoinduced changes can be temporary and/or permanent, it was important to investigate the structure under *in situ* conditions.^{7,8} Detuning and glitching shift devices with piezo-driven picomotors in the monochromator significantly improved the wavelength stability of the incident x rays. For EXAFS experiments, the As₄₀Se₆₀ glass film was peeled off the substrate, cut into four pieces and then divided into two groups of two pieces each. The samples from one group were exposed to the laser light of one of the two orthogonal polarizations [i.e., either horizontal polarization (HP): **E** (laser)∥**E** (x rays) or vertical polarization (VP): **E** (laser)⊥**E** (x rays)]. One piece of each group was used for *in situ* illumination by laser, and the other piece was used as a reference sample to calibrate the absorption edge for specific atoms. The sample was irradiated with a 17 mW He–Ne laser (λ = 632.8 nm) light of approximately the band gap energy ($E_g^{\text{optical}} = 1.8$ eV). The ensuing stability of the sample during irradiation provided an extremely high relative accuracy and reproducibility of the K-edge EXAFS data obtained in transmission mode. The effective intensity of the beam (~0.3 W/cm²) was insufficient to cause any signifi-

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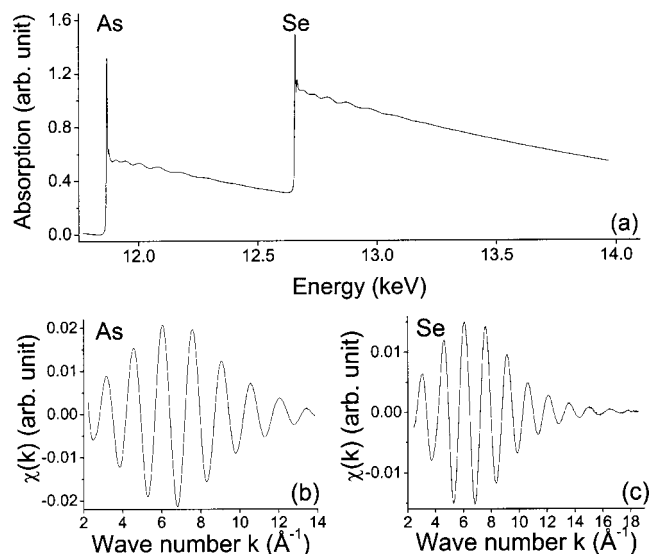


FIG. 1. (a) A typical EXAFS raw spectrum for an $a\text{-As}_{40}\text{Se}_{60}$ film. Absorption beyond the As and the Se K edges can be obtained during one scan. The EXAFS oscillations beyond the As K edge (b), and the Se K edge (c) are extracted from the raw spectrum in (a).

cant increase in sample temperature.⁹ A zero-order half-wave plate (reflectivity $< 0.5\%$) was used to vary the polarization of the laser light. The experimental error was significantly reduced by the use of a stable, high-brilliance, synchrotron x-ray source, high-performance ion chambers, and samples of uniform thickness measured under *in situ* conditions. The stability of the experimental conditions was confirmed by continuously recording the EXAFS spectra.

The raw EXAFS spectrum for $a\text{-As}_{40}\text{Se}_{60}$ is shown in Fig. 1(a). After background subtraction the EXAFS oscillations beyond the As and Se K edges were obtained [Figs. 1(b) and 1(c), respectively] and analyzed using standard programs.¹⁰ The main results of the experiments are summarized in Fig. 2. The results were highly reproducible when we repeated the experiment on different sets of samples of the same composition, and under four different synchrotron beam conditions over a 1 year period. Exposure to x rays

alone did not lead to any detectable change in the structure, as demonstrated also for $a\text{-As}_2\text{S}_3$.¹¹ Therefore, the observed changes in the structure are a consequence of laser irradiation only.

The data were recorded for three sample conditions: Stage AP: as-prepared, unirradiated sample; Stage ON: sample exposed to polarized laser light for 1 h before starting the EXAFS experiment (one more hour was needed to collect the data); Stage OFF: sample after exposure to laser light for 1 h. Thus, any difference in the parameters between stages AP and ON represents light-induced changes, both transient and permanent. The difference between stages ON and OFF indicates recovery of any transient effect that occurs only when the light is incident on the sample. Finally, a difference between stages AP and OFF indicates a permanent change in the structure of the sample. Disorder around a given atom can arise from the variation in the position of neighboring atoms (i.e., the mean-square relative displacement, MSRD) and/or in the coordination number. In the EXAFS analysis, these two quantities are strongly correlated and their separate evaluation would increase the uncertainty. Therefore, we have determined only the combined disorder in Figs. 2(b) and 2(d), where, for simplicity, the coordination number was kept constant at an average value (As: 3.1, Se: 2.1) for all the three stages.

We wish to emphasize the error bars in Fig. 2. Typically, there are two kinds of error bars: one is from the difference between the true value and the measured value, or the so-called accuracy; the other is from the difference between the average measured value and the measured value, the so-called precision. In EXAFS, the accuracy is determined by many factors including theoretical modeling, sample conditions, etc.; the error bar from such sources is relatively large (e.g., for bond distance, it is typically from ± 0.005 to ± 0.01 Å). Since we are interested in the relative changes induced by laser light during the *in situ* experiment, precision is of primary interest to us. It is much smaller in our experiments than the accuracy. When we use x rays to probe the same spot of the sample for several continuous scans, the precision in R is obtained as $\pm 2 \times 10^{-4}$ Å. The results obtained even for different spots of a given sample agree with each other within this precision, which was confirmed on several different samples.

Figure 2(a) shows that the average bond length, R , for the arsenic atoms slightly increases as the sample is illuminated. This expansion of local structure is permanent in the sense that the value of R does not revert to its original value when the light is turned off (stage OFF). Within the experimental uncertainty, it is difficult to discern if this bond-length change is significantly different for the two polarizations. If we normalize the R of AP stage to the same initial value for two polarizations, there is an indication that perhaps the HP laser beam creates a little more expansion than the VP laser beam. The change in R for Se [Fig. 2(c)] parallels the expansion around As. The increase of R for both the elements provides an atomistic explanation for at least part of the photoexpansion observed in these materials.¹²

The difference between the data for the Se edge for the two polarizations is a striking feature in Fig. 2(c). The local structure expands significantly more when the \mathbf{E} vectors of

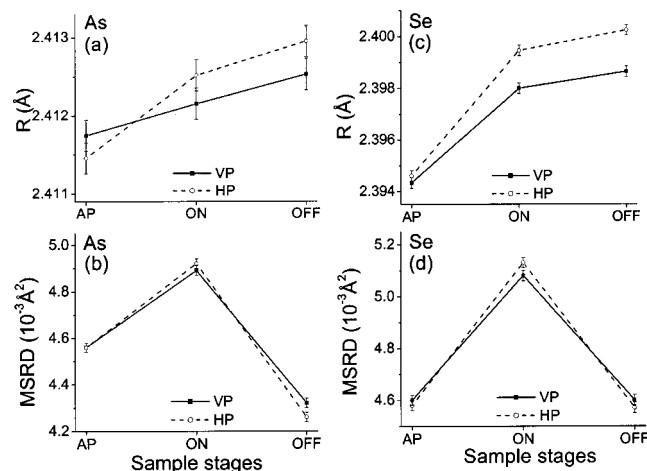


FIG. 2. (a) and (c) The average nearest-neighbor bond distance (R) for As and Se atoms, respectively. (b) and (d) The mean square relative displacement (MSRD), i.e., the disorder around As and Se atoms, respectively. HP, horizontal polarization, means $\mathbf{E}(\text{laser}) \parallel \mathbf{E}(\text{x rays})$; VP, vertical polarization, means $\mathbf{E}(\text{laser}) \perp \mathbf{E}(\text{x rays})$. The sample stages are denoted, AP: as-prepared; ON: laser was on; OFF: laser was turned off.

the x rays and laser light are parallel to each other than when they are perpendicular. Similar results were also obtained for α -As₅₀Se₅₀ film, which will be presented elsewhere. By combining the expansion around As and Se atoms, we observe an anisotropic local photoexpansion inside the material created by the polarization of the laser light. It implies a polarization-dependent driving force for mass transport from the illuminated region to the unirradiated region, giving an atomistic picture of the recently reported light-induced, vector mass transport.² It also provides an important clue to the anisotropic density change induced by polarized light in silica.⁵

Results in Fig. 2(d) emphasize the temporary or transient aspect of the light-induced structural changes. We find that the disorder around Se increases during exposure to light [Fig. 2(d)], but almost all of this increase disappears when the light is turned off. These results demonstrate the relative ease with which readily reversible changes occur in the structure around the chalcogen atoms. The magnitude of the reversible increase in disorder around Se [the height of the peak in Fig. 2(d) with respect to the base line] is slightly higher for the horizontal than for the vertical polarization of the laser beam, which means that, during laser illumination, the structural disorder around Se atoms is higher along the direction of the polarization of the laser light than to its perpendicular direction. The disorder around As [Fig. 2(b)] also *increases* with exposure to light, but after the light is turned off, it decreases to a level lower than the AP stages. Thus, the laser irradiation causes an increase in *transient* disorder and a decrease in the disorder around As. Two different origins of the permanent light-induced changes have been established from other experiments as well.^{9,13} Put together, the reversible change in the disorder around Se and As should provide a key to the understanding of the transient changes recently reported in photodarkening.^{9,14,15}

The microscopic mechanism of the above reported changes is incompletely understood. Absorbed light promotes electrons to low-lying unoccupied conduction-band (antibonding) states, which can cause bond breaking.^{16–19} Theoretical calculations¹⁶ and x-ray photoelectron spectroscopy (XPS) experiments²⁰ suggest that even in stoichiometric α -As₄₀Se₆₀ glasses, there are quite a few wrong bonds (e.g., As–As and Se–Se bonds). If such homopolar As bonds are confined to clusters, such as As₄Se₃ and/or As₄Se₄, embedded in a glassy matrix, the absorbed light could preferentially break such very strained As–As bonds (present in a triangular configuration in the As₄Se₃ molecule), resulting in the formation of heteropolar As–Se bonds with excess Se atoms in the glassy matrix. As a consequence, it is expected that the structural disorder around As atoms should permanently decrease, as observed [Fig. 2(b)]. Since the three-coordinated As atoms are difficult to move or reorient along a given direction, there is little light-polarization dependence of the photoinduced change in the disorder around As atoms. However, the low coordination, and consequent structural flexibility, of the Se atoms allows a bond reorientation relatively easily, and so the photoinduced structural changes become sensitive to the polarization of the laser light. Alternatively, the so-called “wrong coordination” may also be an

important reason for the vector effects around Se atoms. Theoretical calculations²¹ and XPS experiments²⁰ show that in α -As₄₀Se₆₀ 19.4% and 20.3% of Se atoms are in threefold and onefold coordination, respectively. However, only 1.2% and 2.3% of As atoms are in twofold and fourfold coordination, respectively. Therefore, the homopolar wrong bonds (e.g., As–As and Se–Se bonds), as well as structural flexibility and highly concentrated wrong coordination of Se atoms, should be responsible for the light-induced vector effects around Se atoms. The present results provide important tests for a successful theory of photostructural processes in glassy materials.

In conclusion, we have directly observed a polarization-dependent, light-induced, permanent expansion of the nearest-neighbor bond length and an increase in the transient disorder of local atomic structure around Se in amorphous As₄₀Se₆₀ films. Such vector changes around As are not as obvious as those around Se atoms, which is consistent with the flexible, twofold coordination of Se compared to the threefold coordination of As in the structure. These observations provide an atomistic view of several light-induced vector and scalar effects in chalcogenide glasses, and possibly oxide glasses.

The authors thank the U.S. National Science Foundation under Grant Nos. DMR 00-74624 and DMR 00-81006 for supporting this work, and the U.S. Department of energy for the experiments at Brookhaven National Laboratory (DE-AC02-98 CH10886). M.V. thanks MSM T Czech Republic for support under Grant No. ME471.

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