Photoinduced anisotropy in vitreous As$_2$S$_3$:   A reflectance-difference study

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Results of the study of photoinduced anisotropy in a model chalcogenide glass As$_2$S$_3$ using reflectance-difference spectroscopy are presented. We find that anisotropy can be induced in the energy range much exceeding the energy of the photons of the exciting light and that not only defects but also main covalent bonds of the glass are reoriented by linearly polarized light. We further demonstrate that the sign of the photoinduced anisotropy, especially at higher energies, strongly depends on the photon energy of the exciting light. The observed difference is explained by photoinduced change in the bonds topology involving a conversion between bonding and nonbonding electrons. Strong differences are observed between bulk glass and thin films which are shown to be caused by interference effects. [S0163-1829(97)00914-4]

INTRODUCTION

Chalcogenide glasses are materials possessing a unique feature to change reversibly their properties under photoexcitation. See Refs. 1–3 for reviews. The most studied phenomenon is the photostructural change when scalar optical absorption is changed (photodarkening). Recently much attention was given to the investigation of the light-induced vectorial effect, namely photoinduced anisotropy, which includes photoinduced birefringence and photoinduced dichroism.[4–14] In an earlier paper, it was suggested that photoinduced scalar and vectorial changes reflect two sides of the same phenomenon.[4] Later, it was argued that photoinduced anisotropy and photodarkening are independent phenomena.[5] A phenomenological explanation of the effect was suggested recently in Ref. 6 following the idea of Ref. 4 that a macroscopically isotropic glass is made of microscopically anisotropic domains. Light interacts predominantly with the domains oriented in the direction parallel to the electric vector **E** of the exciting light. Subsequent recombination of excited carriers results in a photostructural change accompanied by a loss of the initial orientation and thus leading to macroanisotropy. Then, it was argued that anisotropy was caused by preferential orientation of dipoles within valence alteration pairs (VAP's)[7] which are the lowest-energy structural defects in amorphous chalcogenides, the concentration of which in chalcogenide glasses can reach the

value of 10^{19}–10^{20} cm^{-3}. The conclusion on the importance of VAP's followed from the fact that the photoinduced anisotropy was most effectively induced by the subband-gap light which interacts with the defects. Previous measurements were done in a transmission mode which means that interaction with the photons having the energy substantially exceeding the optical gap of the glasses could not be studied because of strong absorption.

In the present paper we report the results of the reflectance study of photoinduced anisotropy using reflectance-difference spectroscopy (RDS). RDS was developed rather recently and so far has mostly been applied to the investigation of the intrinsic anisotropy of solid surfaces.[15] Application of the reflectance technique allowed us to investigate the photoinduced anisotropy in chalcogenides glasses in a broad spectral range. The obtained results evidence that not only the defects but also the main covalent bonds of the glassy matrix are involved in inducing the anisotropy. A brief summary of the first results have been given elsewhere.[16]

EXPERIMENTAL

The samples were polished bulk glasses and thin films of As$_2$S$_3$. Bulk samples were prepared by polishing melt-quenched glasses and had a typical thickness of several millimeters. Thin film was produced by thermal evaporation of a starting bulk glass in a vacuum (10^{-6} Torr) onto silica glass
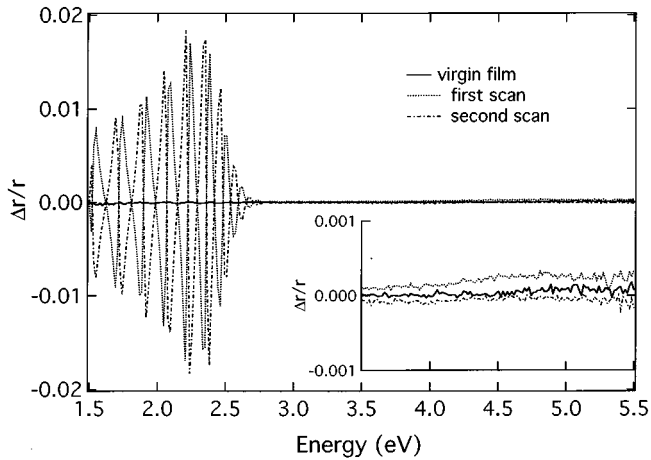
FIG. 1. RD spectra for a 3-μm-thick As$_2$S$_3$ film (solid line: annealed film, dotted line: film irradiated for 1 h by full linearly polarized light of a 1000-W Xe lamp, dashed-dotted line: similar to 2 but the light polarization is rotated by 90°. An insert shows the photoinduced change at higher energies. Notice the difference in scale of the vertical axis of the main plot and insert.

substrates and had thicknesses of 1000 Å to 5 μm. The measurements were done at room temperature using the setup schematically shown in Ref. 16. For a detailed description of the reflection-difference spectroscopy see Ref. 15. Anisotropy was induced using the light of either (a) a 1000 W Xenon lamp equipped with an IR-cutoff filter which generated radiation in a wide energy range including subband-gap, near-band-gap, and superband-gap light or (b) the same light passed through a few-micron-thick As$_2$S$_3$ film in order to filter out the near-band-gap and superband-gap light or (c) an Ar-ion laser (λ=488 nm) generating near-band-gap light. The light passed through a Glan-prism polarizer and the light intensity on the surface of the sample was from 25 to 100 mW/cm^2. The intensity of the measuring light on the surface was much smaller (about 5 mW/cm^2) and did not induce any noticeable change in the anisotropy during the measurements.

RESULTS

Figure 1 shows the reflectance-difference (RD) spectra of an as-evaporated As$_2$S$_3$ film before light irradiation and after irradiation by linearly polarized full light of the Xe lamp with two different (orthogonal) polarizations. Changes in the amplitude of the reflected light are shown. The measured value is defined as

$$\Delta r/r = (r_x - r_y)/[(r_x + r_y)/2],$$

where r_x and r_y are field reflectances for the polarization of the probing beam in the direction parallel to the x axis and y axis shown in Ref. 16, the polarization of inducing beam being parallel to the x axis. One can see that the starting film is very isotropic (solid line) while after one cycle of irradiation the film becomes strongly anisotropic (dotted line). On changing the light polarization to orthogonal, the reflectance curve was reversed with respect to the x axis (dashed-dotted line) indicating a change in the anisotropy sign. It can be seen that the change is mainly observed at energies close to
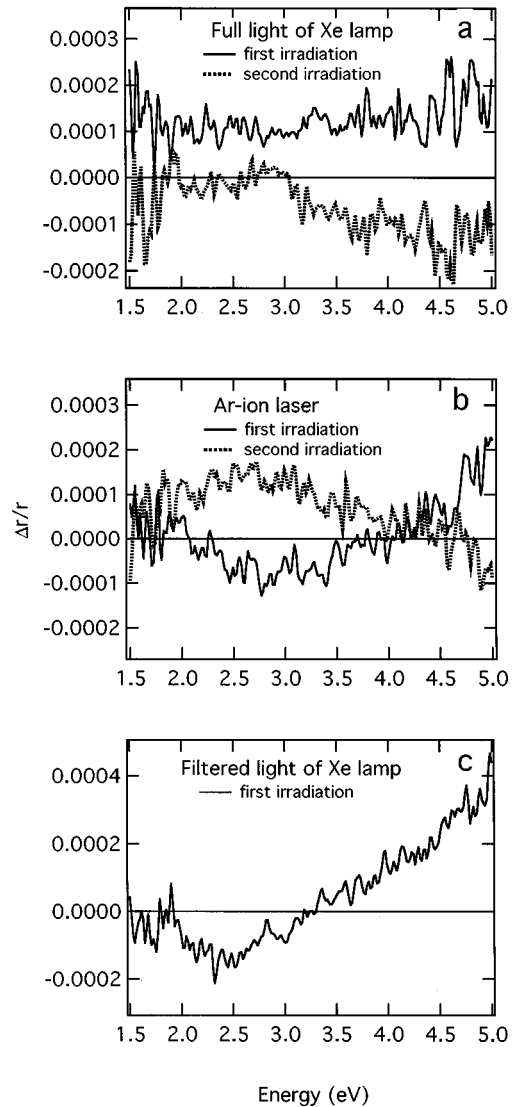

FIG. 2. Photoinduced anisotropy (solid line) and its reorientation (dotted line) in bulk As$_2$S$_3$ glass, the irradiation source being full light from a 1000-W Xe lamp (a), Ar-ion laser (b), and subband-gap light (c).

and below the band gap of As$_2$S$_3$ (E_g=2.4 eV). It should be noticed that the change is also induced at higher energies as shown in the insert to Fig. 1. Notice that the scaling of the insert is 20 times smaller than that of the main plot.

Figure 2(a) shows the photoinduced anisotropy and its reorientation for the bulk As$_2$S$_3$ induced by the same (full light of the Xe lamp) light. Different from a thin film, the largest change is observed for energies corresponding to the interaction of light with bonding electrons (4.5–5.5 eV). It should be noticed that absolute changes in the reflection anisotropy for energies higher than E_g are of a comparable magnitude for both bulk glass and thin film.

Figure 2(b) shows the photoinduced anisotropy induced in bulk As$_2$S$_3$ glass by an Ar-ion laser light. Again, the amplitude of the change is of the same magnitude but there appears a very important difference. While for the glass excited by Xe-lamp light the trend in the reflectance change was the same (increase or decrease depending on the polarization) throughout the studied spectral range, for the case of excita-
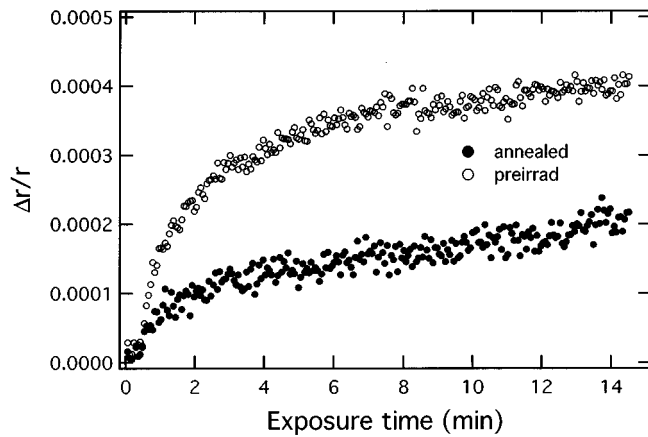
FIG. 3. Comparison of kinetics of photoinduced anisotropy in an annealed (closed circles) and preirradiated (open circles) As_2S_3 film induced by the subband-gap light.

FIG. 4. Schematic representation of the photostructural change induced by the near-band-gap light.

tion with the Ar laser, sign variation of the effect is clearly observed. While the increase in $\Delta r/r$ is observed for larger photon energies (above 4.0 eV) similar to the case of polychromatic light excitation, for smaller photon energies an opposite change (decrease) is detected. A change in the light polarization results in a reversal of the photoinduced anisotropy with the same crossover energy of 4.0 eV preserved.

Similar measurements with the subband-gap light (passed through an As_2S_3 filter) led to the same result, namely, an increase in larger energies accompanied by a decrease in smaller energies [Fig. 2(c)]. The crossover energy was shifted to smaller energies in this case.

Now we would like to concentrate on the effect of preliminary photoexcitation on the magnitude of the photoinduced anisotropy. Figure 3 shows photoinduced anisotropy created by subband-gap light in an annealed film and in a film which was preirradiated for 3 h by the nonpolarized full light of the same lamp. One can see that the anisotropy is induced faster and to a larger magnitude in the preirradiated film.

DISCUSSION

Below we discuss possible microscopic mechanisms for the photoinduced anisotropy. The fact that anisotropy can be observed at energies much larger than the photon energy of the inducing light, indicates that by irradiation of chalcogenide glasses with linearly polarized light not only the defects can be reoriented by light but also the main covalent network of the glass becomes anisotropic.

We believe, following Ref. 9, that in the subgap region defects play an important role. Since these defects, which are valence-alternation pairs, are charged and have a dipole they can interact with light the electric vector of which is oriented parallel to the dipole arm. After the excitation the defects are reoriented as suggested in Refs. 9, 11–13. Both intrinsic and light-induced defects can participate in this process and this is clearly evidenced if one compares the kinetics of the initial and subsequent photoinduced anisotropy shown in Fig. 3. When anisotropy is induced by the subband-gap light due to reorientation of defects, the geometry of the main network of the glass is also changed since "defective" atoms are
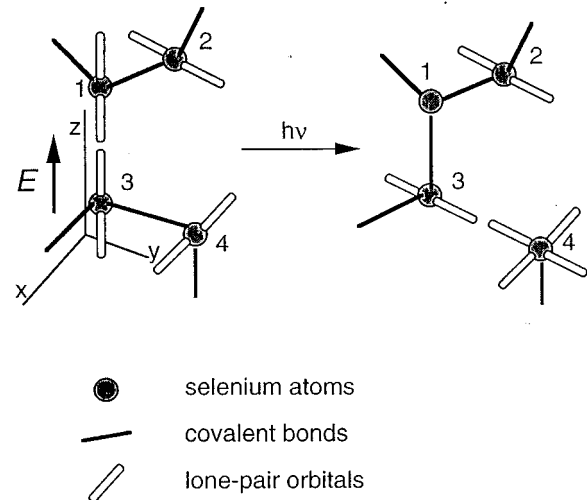
bonded to "regular" atoms. Such a change in the topology of covalent bonds results in photoanisotropy at higher photon energies.

We would like to stress that rearrangement of VAP defect positions necessarily involves bond switching. This process, details of which have been discussed in Ref. 16, results in a change of the covalent bond topology in such a way that, following the bond breaking, lone-pair orbitals are left in place of covalent bonds and *oriented in the direction of former covalent bonds*. On the other hand, in place of lone-pair orbitals *and in their direction* covalent bonds are formed. Such conversion between lone-pair and bonding electrons explains the opposite trend in $\Delta r/r$ in different energy ranges.

Assuming, as suggested in Ref. 17, that irradiation results in the creation of photoinduced VAP defects, a different microscopic mechanism can be suggested. When the semiconductor is excited by the light with the photon energies close to the band gap, lone-pair electrons which form the top of the valence band are excited, preferably in the direction parallel to the **E** vector of the exciting light (z axis in Fig. 4), and a dynamical interchain bond is formed[18] which breaks into a valence alternation pair. The initial and final configurations are shown schematically in Fig. 4 for a simplified case of elemental amorphous selenium. As a result, a new covalent bond is created parallel to the z axis between atoms 1 and 3 while breaking of an existing bond between atoms 3 and 4 leads to the formation of two lone-pair orbitals oriented parallel to the y axis as seen from the figure. This bond reconstruction decreases the number of lone-pair electrons and increases the number of bonding electrons in the direction parallel to the orientation of the **E** vector of the exciting light with an opposite change in the direction perpendicular to the **E** vector. In other words, we have a conversion between bonding and nonbonding electrons which results in the opposite change in the anisotropy measured at lower and higher energies. We believe that this component of photoanisotropy is closely related to scalar photodarkening.

In the case of broad-spectrum light, this process still exists but, in addition, direct excitation of bonding electrons becomes possible. In such a case, weak bonds, present in

amorphous materials, can be excited (and broken) directly leading to a decrease in the number of bonding electrons in the direction of the light polarization. Since the density of states is larger for bonding electrons than for lone-pair electrons, this process will (over)compensate a decrease in the number of covalent bonds caused by excitation with the subband-gap light resulting in the same change in the sign of anisotropy for both lower and higher energies.

We now turn to observed differences between bulk glass and thin films where changes in the subband-gap region corresponding to defects are much more strongly pronounced. There was a possibility that this difference resulted from the fact that as-evaporated films used in our experiments contain a large number of so-called ''wrong'' As-As and S-S bonds[19] and these local deviations from stoichiometry might have played a role. In order to check this, we have studied photoinduced anisotropy in as-prepared and annealed (for 2 h at 160 °C) films. Our Raman measurements (not shown) revealed that the concentration of As-As bonds decreased after annealing but the magnitude and character of photoinduced anisotropy remained unchanged which demonstrates that the role played by ''wrong'' bonds is not decisive for the different behavior of thin films and bulk glass.

Another possibility to explain an increased signal for the subband-gap region was a strong signal coming from reflection at the film/substrate interface. In order to check this, we have evaporated a film of As$_2$S$_3$ onto a bulk glass of the same composition. In such a sample the amplitude of the anisotropy was decreased which indicated that interference could be responsible for the different behavior. We have, apart from that, simulated a $\Delta r/r$ curve for a thin film using a three-phase model (ambient-film-substrate) and assuming for simplicity a uniform photoinduced change in ε. The ε values for amorphous As$_2$S$_3$ were taken from Ref. 20. The generated curves, one for a change in real part of ε only and the other one for a change in imaginary part of ε only (Fig. 5), although not identical to the experimental one, are quite similar to it and from this similarity we conclude that processes in thin films and bulk glass are essentially identical and the seeming difference is caused by an interference phenomenon.

CONCLUSION

The application of RDS allowed us to study the photoinduced anisotropy in amorphous chalcogenides in a broad spectral range. We have demonstrated that not only defects but also main covalent bonds of the glass are reoriented due to excitation with linearly polarized light. An important difference between excitation with subband-gap light and broad-spectrum light is observed. The subband-gap light and
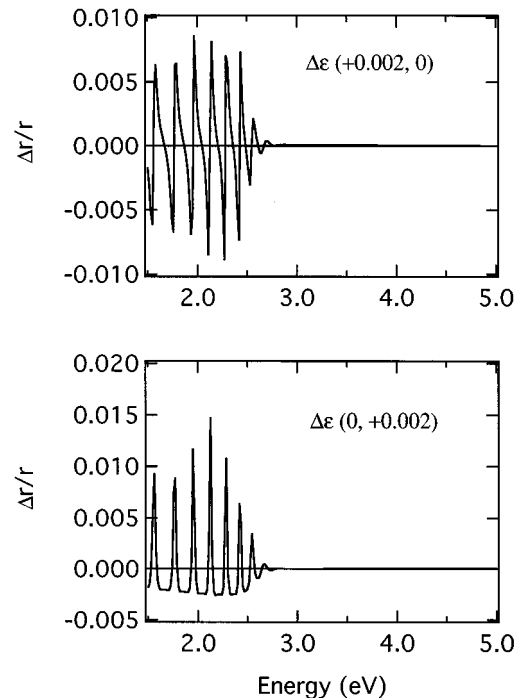

FIG. 5. Simulated photoinduced $\Delta r/r$ for an As$_2$S$_3$ film assuming a uniform change in ε (for a change in real part: top, and for a change in imaginary part: bottom). The assumed numerical change in ε is marked on the figure.

near-band-gap light decreases reflection at smaller energies while increasing it at larger energies. On the other hand, broad-spectrum light increases the reflection in all spectral range. This difference is explained on the basis of the proposed mechanisms of the photoinduced effect in the two cases. Preirradiation of the glass by nonpolarized light increases substantially the magnitude and creation rate of the photoinduced anisotropy indicating that both native and photoinduced defects play a role. The observed difference in photoinduced anisotropy of thin films and bulk glass is shown to be caused by an interference phenomenon.

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