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Photoinduced anisotropic conversion of bonding and lone-pair electrons in As_2S_3 glass

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We present the results of a study of photoinduced anisotropy in a model chalcogenide glass As_2S_3 in a wide spectral range using reflectance-difference spectroscopy. We have found that the anisotropy is induced at energies much exceeding the energy of the inducing photons and that the sign of the photoinduced anisotropy is opposite at smaller and higher energies. To explain the results, we suggest a model considering redistribution between bonding and lone-pair electrons. [S0163-1829(97)04602-X]

INTRODUCTION

Reversible photoinduced anisotropy in originally isotropic materials, such as chalcogenide glasses, is an issue of basic interest.[1–9] The mechanism of this phenomenon has remained unclear. Following the idea of an earlier paper,[10] it was recently suggested that macroscopically isotropic glasses are composed of anisotropic microdomains.[2,6] Light is predominantly absorbed by the domains with an electric dipole oriented parallel to the **E** vector of light, and subsequent recombination and bond rearrangement result in the loss of random distribution of domain axes, and hence, in macroanisotropy.

Recently, it was argued[5] that photoanisotropy results from the spatial rearrangement of charged defects, or valence-alternation pairs, which are the lowest-energy defects in amorphous chalcogenides. This model was in good agreement with the experimental findings[7,8] that photoanisotropy is most efficiently induced by the sub-band-gap light which is absorbed by the defect states. Previous studies mostly used the transmission measurements, and for this reason only the effect of sub-band-gap and near-band-gap light was studied.

We have used the reflectance-difference spectroscopy[11] which has allowed us to investigate the photoinduced anisotropy in a wide spectral range. We have found that photoanisotropy can be detected at energies much higher than the photon energy of the inducing light. Results of the experiment are reported in this paper. Further details of this work will be published elsewhere.[12]

EXPERIMENT

The samples were polished plates of As_2S_3 glass and had a typical thickness of several millimeters. Anisotropy was induced using the linearly polarized light of an Ar-ion laser ($\lambda = 488$ nm). The light intensity on the surface of the sample was around 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. The experimental setup is shown in Fig. 1. For a more detailed description of the reflection difference spectroscopy see Ref. 11.

RESULTS

Figure 2 shows the spectrum (after subtraction of built-in anisotropy) of photoinduced anisotropy and its reorientation induced by an Ar-ion laser light. 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

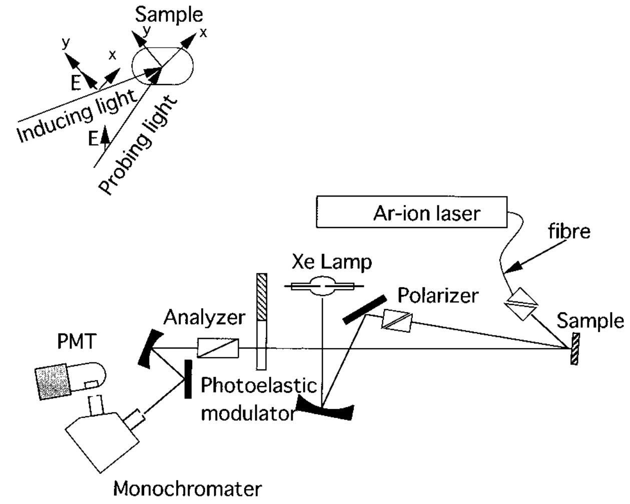

FIG. 1. Experimental setup for reflectance difference measurements.

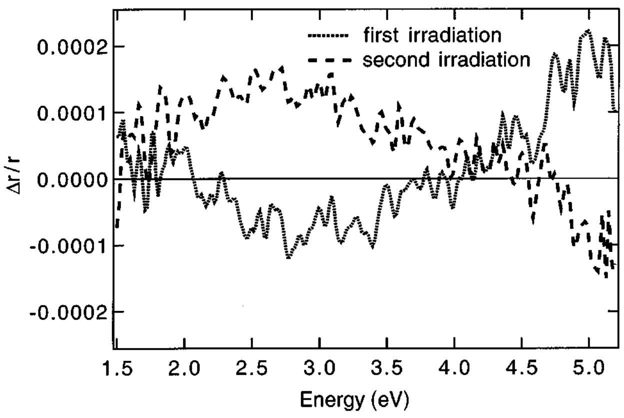

FIG. 2. Spectra of photoinduced anisotropy and its reorientation in bulk As_2S_3 glass, the irradiation source being the light of an Ar-ion laser.

axis shown in Fig. 1, the polarization of the inducing beam being parallel to the x axis. One can see that the change in $\Delta r/r$ (relative change in reflection amplitude) is observed in a spectral range going to much higher energies than that of the exciting light. Another unusual feature is that, while positive $\Delta r/r$ is observed for higher photon energies (above 4.5 eV), for lower photon energies, an opposite change (negative $\Delta r/r$) is detected. A change in the light polarization results in a reversal of the photoinduced anisotropy.

DISCUSSION

We discuss possible microscopic mechanisms for the photoinduced anisotropy and its difference in the two spectral regions. 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 or lone-pair (LP) orbitals can be reoriented, but also the *main covalent network of the glass becomes anisotropic*. Within the framework of the above-mentioned model which considers reorientation of valence-alternation pairs[5,7,8] (VAP) this effect can be understood as a spatial reorientation of covalent bonds, forming the main covalent network, following the change in the defect rearrangement. There is an important fact not realized at the earlier stage of studies, namely, since positively and negatively charged defects have different valence, a change in the charge of the defects, *necessarily* involves breaking of covalent bonds around C_3^+, transforming C_3^+ (or its nearest neighbor) into C_1^- and formation of new covalent bonds around C_1^-, transforming this C_1^- (or its nearest neighbor) into C_3^+. Therefore, the swapping in the charged defects positions leads to a change in the *topology* of covalent bonds as shown in Fig. 3(a) for the simplest case of elemental amorphous selenium. In the initial state, atom 3 is threefold coordinated and atom 10 is onefold coordinated. Following the photoexcitation by the light whose polarization is shown in the figure, LP electrons oriented parallel to this orientation will predominantly be excited. As a result, atom 10 may form a covalent bond with a neighboring atom 8, making the latter threefold coordinated. To keep the defect concentration and charge balance, initial threefold coordinated atom 3 decays into a singly coordinated defect and a twofold coordinated ‘‘regular’’ atom. This process can proceed in two different ways marked in the figure. In the case of path I, a redistribution of LP and bonding orbitals is obvious. Before photoexcitation the bond between atoms 2 and 3 was covalent (parallel to the x axis) while atoms 8 and 10 had LP orbitals parallel to the z axis. After the photoexcitation, atoms 8 and 10 became bonded by a covalent bond in the z direction while the bond between atoms 2 and 3 broke and two LP orbitals parallel to the x axis were created. As a result, the total number of bonding electrons along the z axis decreases while the number of nonbonding electrons along the x axis increases, which explain the opposite change in the anisotropy probed at lower and higher energies.

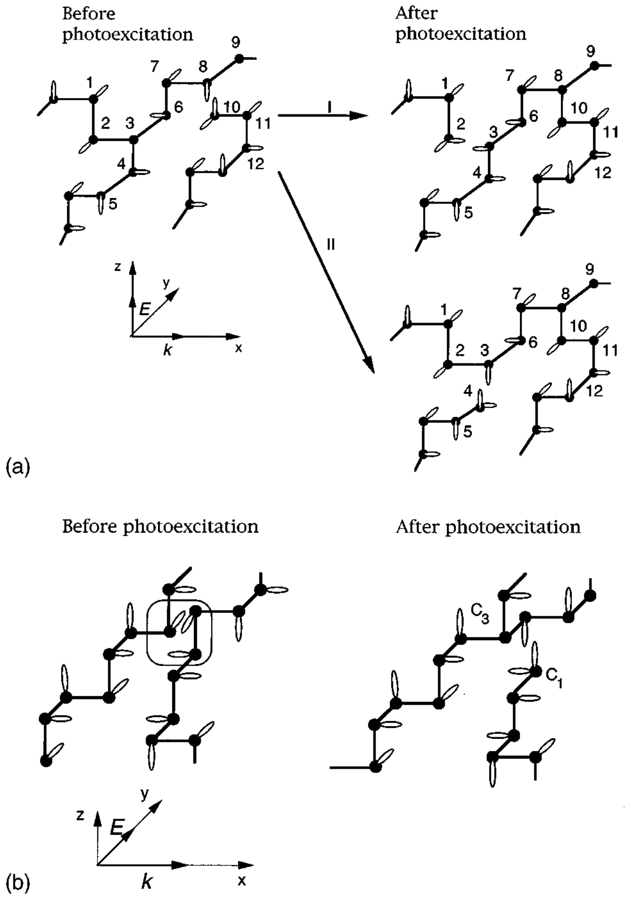

FIG. 3. Schematic representation of the photostructural change induced by the near-band-gap light for the case involving the charged defects (a) and proceeding without participation of charged defects (b). See text for details.

Note that in the case of path II, bond rearrangement does not lead to any anisotropy. The conversion between bonding and nonbonding electrons, involving atoms 3, 4, 8, and 10 takes place entirely in the direction parallel to the z axis.

We can also envisage an alternative model that does not require interaction of the exciting light with native or photoinduced charged defects [Fig. 3(b)]. 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 [y axis in Fig. 3(b)]. Two excited lone-pair electrons can be stabilized by forming a new covalent bond with breaking of existing bonds[13] leading to the formation of a valence-alternation pair as shown schematically in Fig. 3(b) again for a simplified case of elemental amorphous selenium. The described structural change takes place within an encircled area shown on the left in Fig. 3(b). As a result, a new covalent bond is created parallel to the y axis, while breaking of an existing bond leads to formation of two lone-pair orbitals oriented parallel to the z axis as seen from the same figure. This bond reconstruction lowers the electrons from the lone-pair state to the bonding state, decreasing the number of lone-pair electrons and increasing 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, anisotropic conversion between bonding and lone-pair electrons takes place under photoexcitation. This results in the opposite change in the anisotropy measured at lower and higher energies.

Both models seem to explain the observed results and further studies are needed in order to select one of them.

Although creation of VAP defects by recombination and bond rearrangement and changes in bond topology associated with recombination have been the subject of numerous discussions,[2,4,6,14] an important feature of our model is that following the recombination, covalent bonds are created in place and in the direction in which nonbonding electron orbitals were oriented prior to irradiation and, on the other hand, bond breaking leaves nonbonding electron orbitals oriented in the direction of previously existing covalent bonds. In other words, conversion between bonding and nonbonding electrons takes place.

CONCLUSION

Application of reflectance-difference spectroscopy allowed us to study the photoinduced anisotropy in As_2S_3 glass in a broad spectral range. We have demonstrated that irradiation with photons of a certain energy results in anisotropy at energies much higher than that of the exciting light and, what is especially important, at energies corresponding to the excitation of the bonding electrons. The near-band-gap light irradiation induces negative $\Delta r/r$ at smaller energies, simultaneously inducing positive $\Delta r/r$ at larger energies, resulting from photoinduced anisotropic conversion between bonding and lone-pair electrons.

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