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Photoinduced effect in glassy crystalline As_4Se_3: Negative photoinduced anisotropy

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In studying the optical-transmission properties of the glassy crystalline chalcogenide composition As_4Se_3 with polarized light, we have observed a photoinduced phenomenon, called here *negative* vectoral photoinduced anisotropy. The negative anisotropy is ascribed to As_4Se_3 molecular units embedded in an amorphous network. During the course of illumination, the negative anisotropy gradually decreases in amplitude and is replaced by the well-known, previously observed *positive* vectoral anisotropy. A microscopic mechanism for the occurrence of negative anisotropy is suggested.

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I. INTRODUCTION

The phenomenon in which a previously optically isotropic chalcogenide glass becomes birefringent or dichroic upon illumination with linearly polarized light has stimulated considerable interest since its discovery by Zhdanov *et al.*[1] Often referred to as photoinduced vectoral anisotropy, the effect is not only of fundamental interest, where a microscopic understanding of the phenomenon is still being sought, but could also be of considerable interest for potential commercial applications due to the high degree of reversibility, wherein the photoinduced birefringence can be repeatedly erased by light having an orthogonal polarization to that of the inducing linearly polarized light beam.

Three basic structural models have been considered in the interpretation of vectoral anisotropy on a microscopic level: the reorientation of inherent or induced defects in the glass—a defect model;[2] the reorientation of covalent bonds during illumination;[3] and a reorientation or alignment of crystal-like structures—a crystal model.[4] Our results show that the photoinduced anisotropy (PA) in (at least some) chalcogenide glasses is not a single phenomenon, but can be composed, in certain circumstances, of at least two independent effects. These are the now well-recognized photoinduced vectoral anisotropy (PA), referred to here as *positive* PA, and a second phenomenon, seemingly associated with crystalline-like structures embedded in certain amorphous networks, called here *negative* PA.

II. EXPERIMENT

Thin films of composition As_4Se_3, of thicknesses 1 and 5 μm, were prepared by thermal evaporation from bulk glass samples onto silica substrates. The evaporation rate was between 1 and 3 nm/sec. Transmission anisotropy measurements were made using a monochromatic He-Ne laser source ($\lambda = 632.8$ nm). An inducing linearly polarized He-Ne laser (pump) beam was used to induce the anisotropy, and the resulting change in optical absorption coefficient α was probed at discrete time intervals (1 min) for a short time interval of typically 350 msec with the help of a modulated (probe) beam having the direction of linearly polarized light alternating between two orthogonal directions with a frequency of 600 Hz. The ratio

$$\chi = 2(I_\parallel - I_\perp)/(I_\parallel + I_\perp) \tag{2.1}$$

was employed to characterize the transmission photoinduced anisotropy. Here $I_\parallel$ and $I_\perp$ are the transmitted light intensities of two mutually orthogonal, linearly polarized probe beams incident on the sample; $I_\parallel$ refers to the intensity measured with a polarization parallel to that of the inducing beam, and $I_\perp$ to that with orthogonal polarization. The difference between transmitted light intensities of the probe beam, $(I_\parallel - I_\perp)$, was measured using a lock-in amplifier, and the average light intensity, $(I_\parallel + I_\perp)/2$, with a voltmeter, in both cases monitoring the output of a Si photodiode. The typical light intensity on the samples was 50–100 mW/cm^2 and the polarization ratio of the inducing laser light was better than 300:1. The measurements were performed in vacuum or an Ar atmosphere. X-ray-diffraction measurements of the films were performed using Cu$K\alpha_1$ and Cu$K\alpha_2$ radiation in an intensity ratio of 1:1 (Phillips PW1710 diffractometer). Raman spectra of the films were measured using an Equinox IFS55 infrared spectrometer fitted with a Fourier Raman accessory FRA106 in backscattering geometry (180° scattering angle), using a linearly polarized inducing Nd:YAG laser beam with a photon energy h$\nu \sim 1.17$ eV ($\lambda = 1.064$ μm), well below the typical energy of the optical band gap of the As_4Se_3 films [E_g (virgin)~ 2.06 eV].

III. RESULTS

Before we discuss our results on glassy As_4Se_3, for purposes of comparison it is important to show the typical kinetics of the well-recognized (positive) photoinduced anisotropy in an annealed and photodarkened 2-μm-thick a-$As_{50}Se_{50}$ film at room temperature (Fig. 1). In Fig. 1(a), the polarization plane of the inducing light was changed after certain time intervals (210 min—the polarization direction

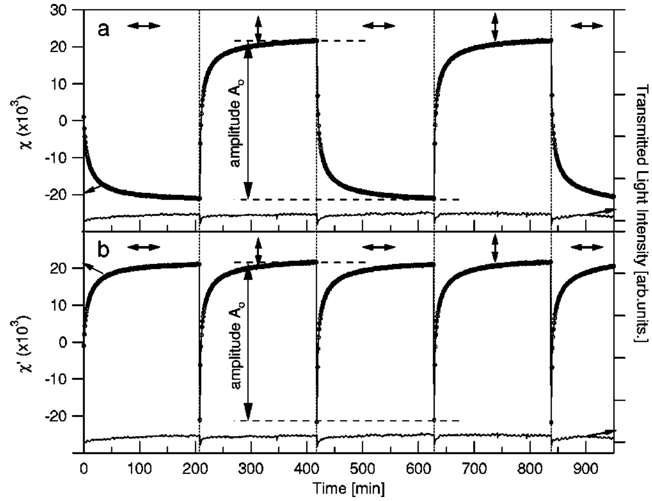

FIG. 1. (a) Typical kinetics of the PA signal χ in an annealed and photodarkened a-$As_{50}Se_{50}$ 2-μm-thick film caused by the alternation of the plane of polarization of linearly polarized light between orthogonal directions, the plane of the polarization being denoted by the arrows at the top of the figure. Also shown is the optical transmission curve of the beam used to induce the PA kinetics [bottom of (a)] and the saturation PA amplitude A_0 which is defined as the difference between the two saturated values of PA induced by two orthogonal polarizations. (b) The same data as in (a), but redrawn by taking into account Eq. (2.1) and the fact that by the definition the polarization of the *inducing* light $I_{\parallel}$ can be both in the vertical ↕ or horizontal ↔ orientation. To differentiate between the different representations of the same PA kinetics, we choose to use the symbols χ and χ' for the PA kinetics in (a) and (b), respectively.

being denoted by arrows between the grid lines) and the induced PA, defined by the ratio χ described in Eq. (2.1), is plotted against time. It has been conventional to present the PA kinetics as shown in Fig. 1(a), where the direction of the electric vector of light with intensity $I_{\parallel}$ is thought of as being always coincident with, say, the vertical axis (↕) and, vice versa, the direction of the electric vector of the light with intensity $I_{\perp}$ as being coincident with, say, the horizontal axis (↔) with respect to the measurement setup. Note that, in this representation, the PA can be induced, from an initially optically isotropic sample ($\chi = 0$), to both negative and positive χ values, following the orientation of the electric vector of the inducing light. It is true, however, that in this representation, the sign of χ is arbitrary, as it refers to a certain direction of polarization axis which was chosen at the beginning of the experiment as a reference. At the bottom of Fig. 1(a) is shown the intensity of transmitted light (for a given polarization denoted by the arrows at the top of the figure) which, in this example, always increases after a change of the polarization plane; that is, the absorption coefficient $\alpha_{\parallel}$ always decreases during illumination with polarized light (here $\alpha_{\parallel}$ is the absorption coefficient measured with light having an electric vector parallel to that of the inducing light). If we choose, however, the PA-inducing beam as the reference beam with respect to Eq. (2.1), then the PA signal, here called χ', after the change of polarization would be always increasing, in this case to positive values. This representation is shown in Fig. 1(b). Although Fig. 1(b) shows a rather different picture to the results previously published [i.e., Fig. 1(a)], we believe that it is more correct to represent PA in this way, as it removes the ambiguity associated with the sign of PA. It should be noted that both polarizations induce the same photostructural change with respect to the photoinduced anisotropy, i.e., a reorientation of structural units in a given direction related to the polarization direction of the inducing beam, and thus should have the same average kinetics with respect to polarization.

An important feature of this kind of PA is its repeatibility. The experiment in Fig. 1 was run for several days with the polarization alternating every 30 min, amounting to more than 500 PA cycles,[5] without any observed change of the kinetics or amplitude of the PA signal. Here, we call the above-described, previously recognized behavior, *positive* PA.

In constrast to the optical anisotropy observed in annealed a-$As_{50}Se_{50}$ films (Fig. 1), illumination of an As_4Se_3 film with linearly polarized light at first causes a considerable *decrease* of the transmitted light intensity during the course of illumination, hence, in effect, changing the relative sign of the parameter χ, i.e., causing χ' to decrease with time, rather than increase as in the *positive*-PA effect (Fig. 2). Figure 2(a) shows an example of the result of illumination of a virgin 1-μm-thick As_4Se_3 film, where the polarization was changed at 30-min intervals (denoted by markers and arrows at the top of the figure). Also shown in Fig. 2(a) is the transmission of the inducing, linearly polarized light which is a superposition of the effect of a scalar photodarkening of a virgin, previously unilluminated sample and a change of transmission due to the alternation of the electric vector of the inducing linearly polarized light during the course of illumination (every 30 min). A sudden increase of transmission after the change of polarization (cf. the grid lines at the top of the figure) is clearly visible [compare with the bottom curve in Fig. 1(a), where a sudden decrease of the transmitted light after a change of polarization and a slow increase of transmission during the course of illumination with a given polarization can be observed]. We suggest the name *negative*-photoinduced anisotropy for this behavior.[6] Note the increasing overshoot in the kinetics of χ' in Fig. 2(a) after changes in polarization, which progressively grows and changes the appearance of the measured PA virtually into that of *positive* PA after several hours of illumination. For comparison, Fig. 2(b) shows PA characteristics in a virgin 2-μm-thick $As_{50}Se_{50}$ film under similar conditions. The PA in this case is always positive, even in a virgin sample (the same applies to As_2Se_3 films). Note that the characteristic increase of transmission [i.e., in Fig. 1(a)] after the change of polarization is not directly visible due to the scaling factor.

It should be noted that as the composition As_4Se_3 is on the edge of the glass-forming region,[7] the properties of the samples can vary substantially with a negligible change of the composition. Figure 3 shows typical x-ray-diffraction results of two seemingly equivalent virgin 1-μm-thick As_4Se_3 films; the first (a) is considerably more ''amorphous'' than the second film (d). The amount of crystallinity appears to be the determining condition for the observation of *negative*-PA

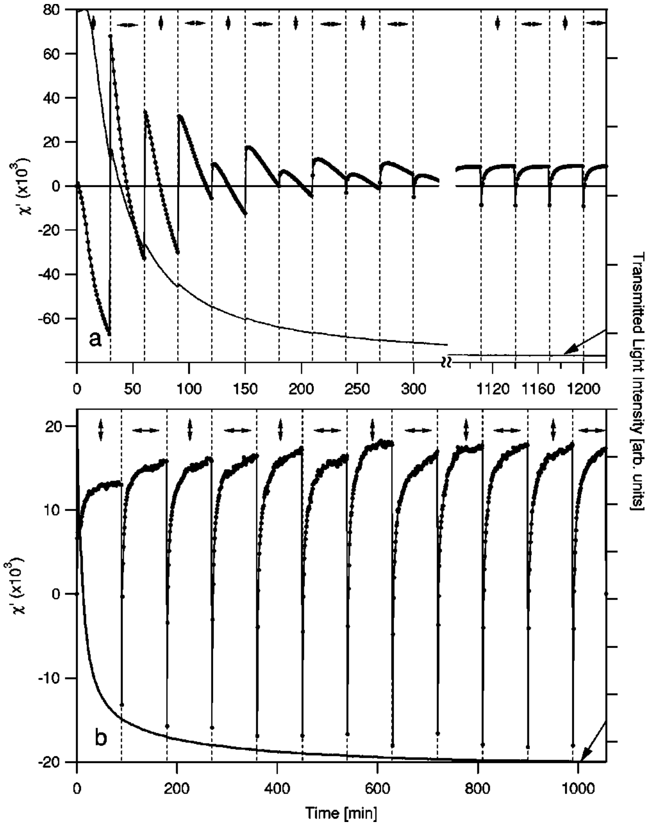

FIG. 2. (a) Typical behavior of a virgin 1-μm-thick As_4Se_3 film upon illumination with linearly polarized light at room temperature. The change of the polarization state (shown by the grid lines) during the first few hours causes a *negative*-PA effect, which has the opposite sign (i.e., a decrease of χ' with time) to that found in As_2Se_3 or $As_{50}Se_{50}$ films. (b) A virgin 2-μm-thick $As_{50}Se_{50}$ film under similar experimental conditions to those in (a). The positive nature of PA from the very beginning of its appearance is apparent. Similar behavior to this was measured in As_2Se_3 films (not shown).

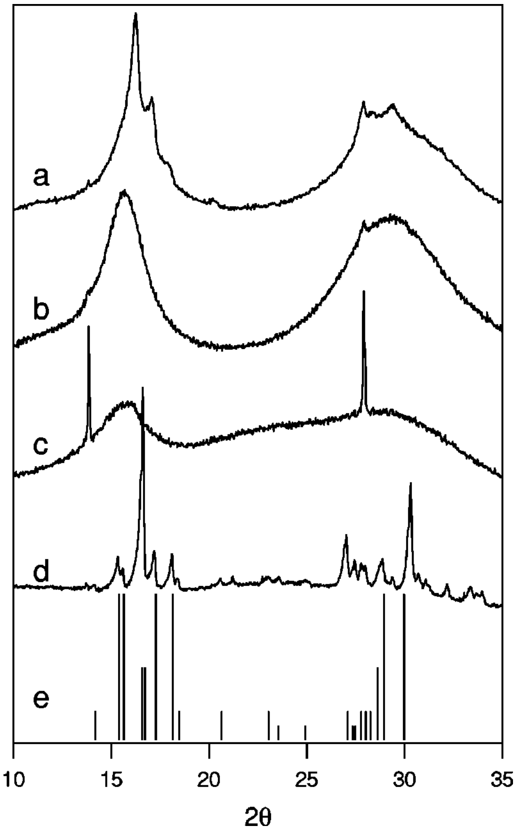

FIG. 3. X-ray-diffraction patterns [$CuK_{\alpha1}$:$CuK_{\alpha2}$ (1:1)] of two 1-μm-thick As_4Se_3 films with marginally different compositions (a)–(d). An as-evaporated (virgin) As_4Se_3 film (a); the same film annealed for 6 h at 115 °C (b) and illuminated with a Xe lamp (50 mW/cm^2) for 24 h (c). A second as-evaporated (virgin) As_4Se_3 film (d) and crystalline product (e) prepared by vacuum sublimation of As_4Se_3 and extraction in CS_2, and assigned in Ref. 10 as monoclinic α-As_4Se_3 (the peak intensities were estimated from x-ray photographs).

behavior. The more amorphous sample [Figs. 3(a) and 2(a)] exhibits a substantially faster decay with time of the *negative* PA; typically a period of several hours of continuous illumination (with a He-Ne laser of intensity 100 mW/cm^2) leads to the complete visual disappearance of negative PA. Thermal annealing of the sample (a) also caused the disappearance of the *negative* PA in unilluminated films. Figure 3(b) shows the x-ray-diffraction pattern of the virgin As_4Se_3 film [cf. Fig. 3(a)] annealed for 6 h at 115 °C and Fig. 3(c) shows the x-ray-diffraction pattern of the As_4Se_3 film [also corresponding to Fig. 3(a)] illuminated with a Xe lamp (50 mW/cm^2) for 24 h. Both treatments, annealing and illumination of the virgin sample, clearly cause the disappearance of the two groups of molecular (crystalline) peaks at scattering angles $2\Theta=16.3-17.1°$ and $2\Theta=27.9-29.4°$ characteristic of virgin As_4Se_3. The appearance of two new peaks in light-exposed As_4Se_3 at $2\Theta=13.9$, 27.9° [Fig. 3(c)] is caused by surface oxidation of excess arsenic to form the cubic form of As_2O_3 due to the illumination of the sample in air.[8] On the other hand, the more crystalline sample [Fig. 3(d)] does not photoamorphise even after prolonged illumination (24 h, 50 mW/cm^2) with a Xe lamp (not shown),[9] and also the *negative* PA in this sample is still pronounced even after long illumination times. Also shown for comparison in Fig. 3(e) is the diffraction pattern of the crystalline product prepared by vacuum sublimation and extraction in CS_2, which was assigned as a monoclinic α modification of As_4Se_3 molecular crystals.[10,11]

Figure 4 shows Raman spectra of a virgin As_4Se_3 thin film (a), a virgin As_4Se_3 film illuminated with a Xe lamp (~50 mW/cm^2) for 30 h (b) and a film annealed for 24 h at 374 K in an Ar atmosphere (c). For comparison, a Raman spectrum of a virgin film of stoichiometric composition As_2Se_3 is also shown in Fig. 4(d). An increase in intensity of the peak at 227 cm^{-1} corresponding to symmetric vibrations of $AsSe_3$ pyramidal units[12] characteristic of the stoichiometric glass composition during the illumination (b) or annealing (c) of a virgin As_4Se_3 film, together with a relative decrease of intensity of the narrow ‘‘crystalline’’ peaks, is clearly visible as a result of decomposition of the As_4Se_3 molecular units. An increase in intensity of the Raman peak at 205 cm^{-1} during the decomposition during light exposure or annealing is likely to be caused by the formation of either As_4Se_4 (Ref. 10) or As_4 (Ref. 13) molecular clusters.

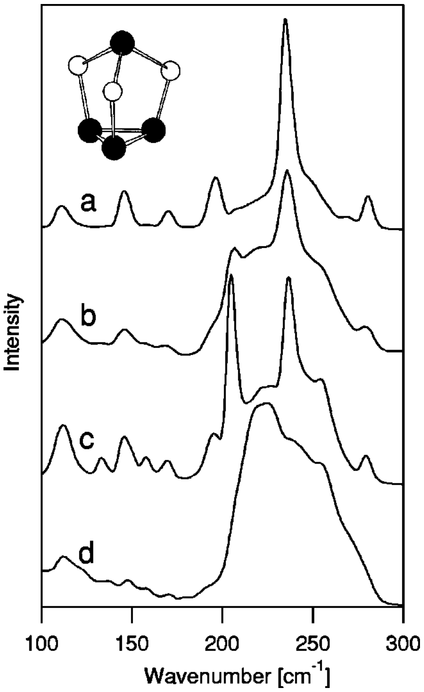

FIG. 4. Raman spectra of a virgin As_4Se_3 thin film (a), a virgin film illuminated with a Xe lamp (50 mW/cm^2) for 30 h (b) and a film annealed for 24 h at 374 K in an Ar atmosphere (c). For comparison, the Raman spectrum of a virgin amorphous film of stoichiometric composition As_2Se_3 is shown in (d). Also shown in the inset is the As_4Se_3 molecular unit, after Ref. 17.

It is worth mentioning that, in order to try to avoid photodarkening in the early stages of the development of *negative* PA, we tried several experiments on samples prepared by thermal evaporation of As_4Se_3 with 1, 2, 5, and 10 mol % of copper.[14] Unfortunately, these samples did not show any significant decrease of photodarkening, and also a certain amount of copper in the evaporated films[15] did not have any significant influence on the observation of *negative* PA.

IV. DISCUSSION

By examining the available data, we can see that negative anisotropy is directly related in our observations with an increased concentration of molecular units and crystallites thereof present in the sample, as determined by x-ray diffraction (Fig. 3) and Raman spectroscopy (Fig. 4). As the characteristic crystallite peaks disappear as a result of photo or thermal treatment, the amplitude of the negative anisotropy decreases accordingly. The strong resemblance of the x-ray-diffraction pattern of a virgin As_4Se_3 sample [Figs. 3(a) and (d)] with the diffraction pattern of the monoclinic modification of α-As_4Se_3 molecular crystals[16] [Fig. 3(e)] suggests that the major constituent of as-evaporated As_4Se_3 films is the molecular unit As_4Se_3 shown in the inset in Fig. 4. We also propose that it is these molecular units which are mainly responsible for the observation of *negative* PA in As-Se materials.

However, it appears that *negative* PA may not be unique to the As-Se glass-crystal system containing As_4Se_3 units. The observation of a gradual change from *positive* PA to *negative* PA (i.e., opposite to our findings) during the process of photocrystallisation of $Se_{70}Ag_{15}I_{15}$ films was made by Lyubin *et al.*[19] According to Ref. 19, the photocrystallisation was accompanied by the creation of Se, Ag_2Se, and AgI microcrystals. Similar behavior in a-As_2S_3 being photodoped by silver was observed in Refs. 20 and 21. Also, according to our observations, negative anisotropy can be induced in a-Se films under certain conditions.[22] These observations show that As_4Se_3 units cannot be solely responsible for the observation of negative anisotropy, and a more general explanation of negative PA has to be sought.

Let us first consider the so-called *positive* PA. As mentioned earlier, several models have been suggested in order to explain a relative decrease of $\alpha_\parallel$ during the course of illumination with linearly polarized light. A microscopic model given by Fritzsche[23] proposes that randomly oriented anisotropic microvolumes can be grouped into three categories, having the largest projection of their dielectric tensor for light polarization in the x, y, and z directions. Upon illumination of an originally isotropic sample, for which $N_x = N_y = N_z$, where $N = N_x + N_y + N_z$ is the total number of anisotropic microvolumes, the absorption process will take place preferentially in those microvolumes having their dipole moment parallel to the electric vector of the polarized light. Such preferential absorption would leave a microvolume either intact or change its anisotropy, leading to redistribution: for example, $\Delta N_z = N_x + N_y$. The structural origin of such microvolumes has been the subject of an extended debate; however, an effective orientation of intrinsic dipole moments in directions orthogonal to the electric vector of the inducing linearly polarized light is commonly considered to explain the decrease of the absorption coefficient $\alpha_\parallel$.[23]

The structural origin of *negative* PA is, however, even less clear than that of *positive* PA. As shown above, during the course of illumination, the As_4Se_3 molecular units are vulnerable to bond breaking, leading to subsequent homogenisation of the sample (Figs. 3 and 4). Although the creation of some oriented medium-range pseudoamorphous structures based on breaking of As_4Se_3 units might be envisaged to explain the structural origin of *negative* PA, it would be difficult to explain the reversibility of the *negative* PA phenomenon based on this scenario.

On the other hand, a photoinduced rotation of the nearly spherical dipolar As_4Se_3 molecular units in an amorphous network (in our example) could lead to the repeatable orientation of the individual dipole moments associated with relatively free, van der Waals bonded, As_4Se_3 molecules parallel to the oscillating electric field of the inducing linearly polarized light, a process effectively opposite to that of the Fritzsche model. Such preferential orientation would have a considerable influence on the dielectric susceptibility of the medium. However, a detailed optical analysis is needed to resolve whether the observed negative transmission anisotropy χ is an absorption anisotropy (dichroism) or an anisotropy due to a significant increase of the refractive index of the medium with preferentially aligned molecular units (birefringence) (see also Ref. 4 for a discussion on optically induced birefringence in chalcogenide glassy crystalline systems). The mechanism of such a photoinduced rotation is, however, unclear. Photon-to-molecule angular-momentum transfer, change of electronic polarizability of the molecule, electronic transitions, or dipole-dipole interactions could all result in a lowering of the energy of the molecule by orienting it parallel to the direction of the electric vector of the inducing light. In a similar way, one could also argue that orientation of crystallization nuclei based, for example, on weakly bonded Se ring structures in *a*-Se or $Se_{70}Ag_{15}I_{15}$, could also lead to a similar effect to that observed for As_4Se_3 films.

V. CONCLUSION

We report an interesting phenomenon, called here *negative*-photoinduced anisotropy (PA), in the chalcogenide glassy crystalline system As_4Se_3. It has been shown that, in our example, the occurrence of *negative* PA is associated with quasispherical As_4Se_3 molecular units embedded in an amorphous network. Reorientation of the As_4Se_3 molecular units is suggested as a structural origin of the effect. As the concentration of the molecular units decreases due to their breakup as a function of temperature or illumination treatment, the negative anisotropy is gradually changed into the previously well-recognized *positive* PA. Further research on the spectral and temperature dependence of *negative* PA is planned to throw further light on the origin of this effect.

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