RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 49, NUMBER 24 15 JUNE 1994-II

Metastable optical anisotropy in chalcogenide glasses induced by unpolarized light

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(Received 1 March 1994)

Semiconducting chalcogenide glasses become optically anisotropic solids with the optical axis parallel to the direction of the inducing light beam after exposure to unpolarized light. This photoinduced anisotropy (PA) can be detected in bulk samples by means of a probing beam directed perpendicularly to an unpolarized inducing beam. In chalcogenide films, PA induced by an unpolarized glancing-angle beam can be detected by means of a probing beam that is incident normal to the films.

INTRODUCTION

Semiconducting chalcogenide glasses (bulk and films), e.g., Ge(Sb,As)-S(Se) and other systems, on being exposed to linearly polarized light become metastable optically anisotropic solids with the optical axis parallel to the electric vector of the inducing light.[1,2] Such photoinduced anisotropy (PA) is also observed in oxide glass fibers and polymeric films (see, for example, Ref. 3); i.e., this phenomenon seems to be general for a wide class of amorphous solids, which may therefore be called light-polarization-sensitive solids.

Recently, it was predicted[4] that PA could be induced by irradiation of samples with *unpolarized* inducing light, the optical axis being parallel to the direction of the inducing light beam. This was suggested to be the result of a photoinduced change of the dielectric tensor. Should a sample be irradiated by linearly polarized or by unpolarized light, its dielectric tensor becomes an ellipsoid of revolution with the axis parallel to the electric vector of the light in the former case, but in contrast to that, with the optical axis parallel to the light wave vector in the latter case. In the latter case, optical anisotropy can be revealed only with a probe beam propagating perpendicularly to the inducing beam, thus complicating the geometry of the experiments. In principle, this could mean that a light-polarization-sensitive amorphous solid, exposed to ambient light, may always be optically anisotropic, in contrast to the generally accepted notion that amorphous solids are always isotropic.

The aim of this study was to verify experimentally the prediction[4] that PA can be induced by unpolarized light under certain conditions.

EXPERIMENT

Most experiments were done on bulk glassy $As_2S_3I_{0.8}$ which shows a high value of PA induced by linearly polarized light and strong photoinduced light scattering,[2] and on an a-AsSe film for which the PA quickly becomes saturated under the action of low-intensity linearly polarized light.[1] A schematic illustration of the experimental optical setup is shown in Fig. 1.

The sample of bulk glassy $As_2S_3I_{0.8}$ used was a thin plane-parallel plate of thickness $h = 0.2$ mm [Figs. 1(a) and 1(b)]. Both faces and one edge were carefully polished, as shown in Fig. 1(a). An unpolarized inducing He-Ne ($\lambda = 633$ nm) laser beam (hereafter called 1) was incident perpendicular to the polished edge. It was focused to a spot with a diameter 0.2 mm. A modulated, polarized probe He-Ne ($\lambda = 633$ nm) laser beam (hereafter called 2) was normally incident on one of the faces, i.e., perpendicular to the unpolarized beam, in accordance with the geometry suggested in Ref. 4. This beam was focused to a spot of diameter 0.2 mm so as to maximize as much as possible the overlap volume with the unpolarized beam inside the sample. (The beams were focused to give a high power density ~ 10 W/cm^2.) The point of incidence of the modulated beam was chosen to be as near as possible to the edge, where the intensity of the unpolarized beam was a maximum. (The optical absorption coefficient of $As_2S_3I_{0.8}$ for $\lambda = 633$ nm is $\alpha = 10$ cm^{-1} and so the photon energy is appreciably less than that of the band gap.)

A 5-μm-thick film of a-AsSe was deposited on a silica glass substrate [Fig. 1(c)]. The unpolarized laser beam [same as in Fig. 1(a)] was incident at a glancing angle ($\phi = 89°$) to the film, thereby exposing a long track on the surface on the film. The modulated laser beam [same as in Fig. 1(a)] was incident normal to the film surface at a point in the middle of the track of beam 1. Both laser beams had an intensity of ~ 3 mW and were not focused. (The optical absorption coefficient for a-AsSe films for $\lambda = 633$ nm is $\alpha \sim 10^3$ cm^{-1} and hence the inducing light causes interband transitions.)

The experimental setup described in Ref. 2 was used to measure the PA. In this technique, the polarization of the modulated beam 2 used for measurements is changed between mutually orthogonal states $\mathbf{E}_y$ and $\mathbf{E}_x$ with a frequency of 1 kHz. We measured the quantity $2(I_y - I_x)/(I_y + I_x)$, where I_y and I_x are the intensities of the light, transmitted through the sample and incident onto the entrance window of a photodetector, with polarizations $\mathbf{E}_y$ and $\mathbf{E}_x$, respectively.

If the sample only exhibits dichroism, the relation $2(I_y - I_x)/(I_y + I_x) = (\alpha_x - \alpha_y)h$ holds, where α_x and α_y are the optical extinction coefficients for beams with polarizations $\mathbf{E}_x$ and $\mathbf{E}_y$; $(\alpha_x - \alpha_y)$ is the linear dichroism and h is the thickness of the sample.[2] Amorphous solids may scatter light effectively and thus the extinction coefficient is the sum of absorption and scattering coefficients, that is the dichroism is composed of absorption and scattering dichroisms. (For the low absorption spectral range, i.e., for the bulk samples in our experiments, scattering is therefore dominant.)

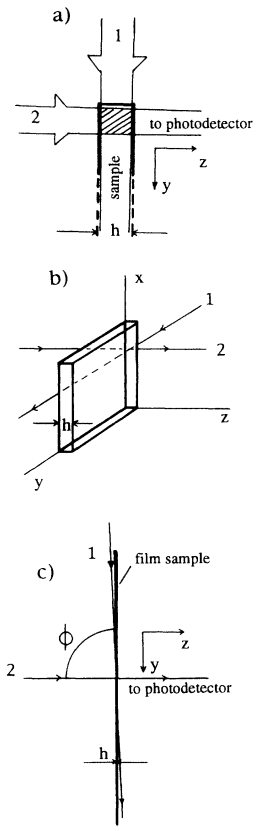

FIG. 1. Schematic optical arrangement of the experiments: for a bulk glass (a) viewed from above; (b) relative orientations of bulk sample and beams; (c) for a film, viewed from above.

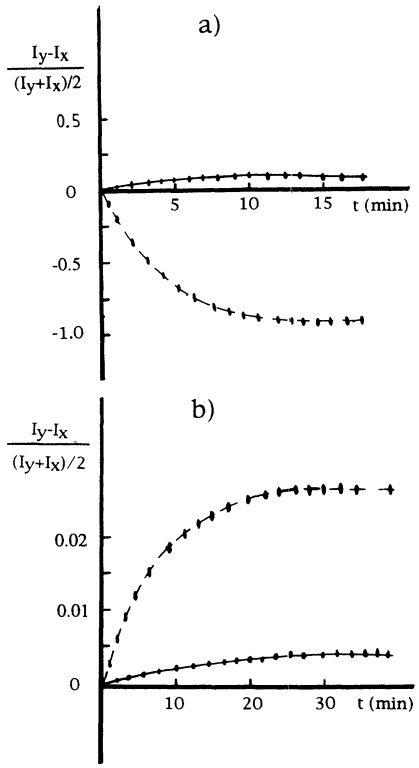

FIG. 2. Kinetics of the quantity $2(I_y - I_x)/(I_y + I_x)$ measured for (a) bulk glassy $As_2S_3I_{0.8}$: the dashed curve corresponds to the PA induced by the linearly polarized beam 2 with electric vector $\mathbf{E}_y$ and measured with the same linearly polarized (modulated) beam; the solid curve corresponds to the PA induced by an unpolarized beam 1 and measured using the modulated, linearly polarized beam 2 [see Fig. 1(a)]; (b) a-AsSe film; the dashed and solid curves correspond to the same situation as in (a) [see Fig. 1(c) for the geometry]. All curves are drawn to connect data symbols.

RESULTS

Figure 2(a) shows the kinetics of the quantity $2(I_y - I_x)/(I_y + I_x)$ measured according to the geometry shown in Fig. 1(a) for the $As_2S_3I_{0.8}$ bulk glass sample. The dashed curve corresponds to the case when the PA was induced by a linearly polarized laser beam 2 with fixed electric vector $\mathbf{E}_y$. Note that, in this case, the same laser 2 was used first as an inducing beam with fixed electric vector and then as a probe beam with modulated electric vector, thereby ensuring complete coincidence of the volume inside the sample in which PA was induced and measured. [Measurements were done only in a discrete manner. The periods of measurement were short ($\sim$ 1 sec) in order to avoid the destruction of PA during the periods of measurement.] These kinetics are in agreement with previously published data.[2]

The solid curve in Fig. 2(a) corresponds to the case when the PA was induced by the unpolarized laser beam 1. It can be seen that the solid curve approaches a limiting value which is much less in absolute value, and is of opposite sign, compared to the dashed curve.

Figure 2(b) shows the kinetics of PA in an a-AsSe film measured according to the geometry of Fig. 1(c). As for Fig. 2(a), the dashed and solid curves correspond to PA induced by a linearly polarized laser beam 2 and an unpolarized laser beam 1, respectively. The measurements were also done in a similar manner. It can be seen that the solid curve approaches a limiting value which is considerably less in absolute value and is of the same sign compared to the dashed curve. The kinetics described by the dashed line are in agreement with the data given in Ref. 1.

DISCUSSION

In order to understand the data of Fig. 2, we start from the phenomenological model proposed by Fritzsche.[4] This model considers chalcogenide glasses as being comprised of an ensemble of strongly anisotropic microvolumes. The structural origin of this microanisotropy will be the aim of further investigations, although a hypothesis has been suggested[5] based on specific structural elements of glassy chalcogenides composed of neighboring (and obviously correlated) units (AsS_3 pyramids for g-As_2S_3, for example). Spin pairing of electrons and the corresponding appearance of fragments with substantial dipole moments (D^+D^- or $C_3^+C_1^-$ pairs[6,7]) may also play a role. Fritzsche[4] concluded that PA is produced by nonradiative geminate recombination events that occur in the microvolumes and which cause local changes in atomic bond configurations. This conclusion is in agreement with experimental data[1,2] which show that PA is increased when passing from interband to subband induc-

ing light, i.e., when geminate recombination is dominant.

Before irradiation, samples are assumed to be optically isotropic, i.e., they have equal diagonal components of the dielectric tensor $\varepsilon_x = \varepsilon_y = \varepsilon_z$. This implies isotropy also for the absorption coefficients $\alpha_x = \alpha_y = \alpha_z$, refractive indices $n_x = n_y = n_z$, and scattering coefficients $\alpha_x^s = \alpha_y^s = \alpha_z^s$, in the coordinates of Fig. 1. Irradiation with light can cause the samples to become optically anisotropic, i.e., the components of their dielectric tensor become nonequal.

As argued in Ref. 4, irradiation by linearly polarized light with an electric vector $\mathbf{E}_y$ produces a dielectric tensor having an ellipsoid of revolution with the optical axis in the y direction and optical absorption coefficients having the relationship

$$\alpha_y < \alpha_x = \alpha_z \ . \tag{1}$$

Note that this relation must lead to a positive sign of the measured quantity $2(I_y - I_x)/(I_y + I_x)$, which is observed only in films [dashed curve of Fig. 2(b)] in the spectral region corresponding to high absorption coefficients (in agreement with all previous data[1,2]). Hence, we infer that the negative value of $2(I_y - I_x)/(I_y + I_x)$ measured for bulk $As_2S_3I_{0.8}$ [in the spectral range corresponding to low absorption—dashed curve of Fig. 2(a)] is not determined by dichroism of absorption, but rather by dichroism of scattering.

In order to account for the experimental observations for the bulk glass, we require that $\alpha_y^s > \alpha_x^s = \alpha_z^s$. This is a nontrivial fact and we suggest that its origin lies in the appearance of the "fanning effect," which has been observed in photorefractive crystals, e.g., $BaTiO_3$ (see, for example, Ref. 8 and references therein). This is a common phenomenon in which a primary incident beam is scattered into a broad fan as it propagates through a photorefractive material. Although the microscopic origin of fanning is currently under investigation, some kind of imperfections (scattering centers) are essential for its appearance.[8] Beam fanning has been associated with self-induced scattering,[9] which obviously leads to more effective scattering for the inducing light with polarization $\mathbf{E}_y$. Further confirmation of this suggestion comes from the observation of a resonant dependence on the exciting wavelength of the photoinduced light scattering in $As_2S_3I_{0.8}$,[10] since a resonant dependence is a characteristic of beam fanning.[11] We add that one should also take into account the appearance of photoinduced birefringence which complicates the phenomena studied due to the resulting path differences inside bulk samples for beams with different polarizations. Further studies of fanning and birefringence are in progress.

Irradiation by unpolarized light in the y direction of the geometry of Fig. 1 causes the dielectric tensor to become an ellipsoid of revolution with the optical axis in the direction of the beam propagation,[4] that is

$$\alpha_y > \alpha_x = \alpha_z \ . \tag{2}$$

The observation of the appearance of the signal $2(I_y - I_x)/(I_y + I_x)$ in Fig. 2(a) (solid curve) confirms that PA really is induced by unpolarized light. If we make the natural assumption that the microscopic mechanism of PA induced by polarized and unpolarized light is the same,[4] then we infer that $\alpha_y^s < \alpha_x^s = \alpha_z^s$ when unpolarized light is used to induce the effect.

Finally, we consider PA induced in films by an unpolarized glancing-angle beam. (The "normal" geometry of inducing and probing beams [Fig. 1(a)] is impossible for very thin films.) It is known that the polarization of a beam refracted at a surface strongly changes at glancing-angle incidence (in accordance with the Fresnel formulas). This is illustrated schematically in Fig. 3. The refractive index of a-AsSe films is very high ($n \sim 3$) and the refracted beam is inclined to the normal to the film surface at the angle $\gamma = 19°$ for $\phi = 89°$ [Fig. 3(a)]. The reflectance coefficients for the components of the unpolarized beam which are polarized parallel and perpendicular to the plane of incidence are different [Fig. 3(b)] and the refracted beam is partially polarized with the dominant component polarized in the plane of incidence [indicated by double-headed arrows in Fig. 3(a)]. In this case, after irradiation by unpolarized light, the dielectric tensor is such that $\alpha_y < \alpha_x < \alpha_z$ [in the coordinates of Fig. 1(c)]. If we probe this anisotropic tensor with beam 2, then we get the kinetics represented by the solid curve in Fig. 2(b) with the same sign as the dashed curve in the same figure, but with a smaller absolute value. [We were not able to achieve saturation for the solid curve in Fig. 2(b) because the reflectance coefficients at $\phi = 89°$ are very high and the area covered by beam 1 is also very large, together leading to a very small power density of beam 1.]

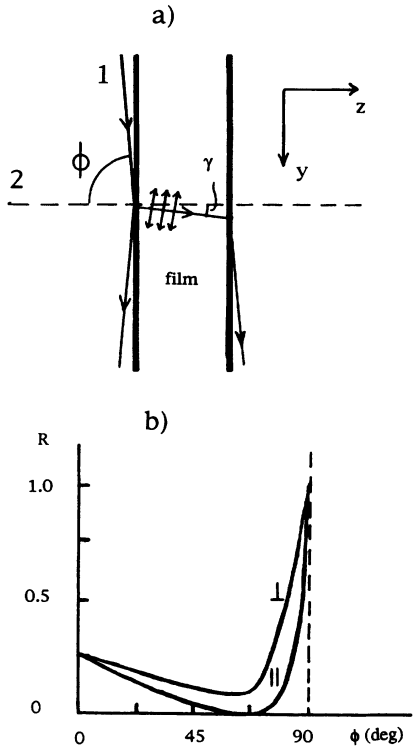

FIG. 3. (a) Optical path of beam 1 in the geometry of Fig. 1(c). (b) Schematic representation of the reflectance coefficients for an unpolarized beam with polarizations parallel (||) and perpendicular (⊥) to the plane of incidence.

The measurements of PA induced by unpolarized light are complicated for several reasons: (i) to measure the effect in films, one has to use a glancing angle of incidence of the inducing unpolarized beam, and this necessitates taking into account the change of polarization state of the refracted beam at the surface; (ii) for bulk samples, one should use inducing and measuring beams with wavelengths corresponding to low absorption in order to achieve the requisite perpendicular geometry. No photoinduced dichroism of absorption takes place under such conditions, but rather dichroism of scattering takes place. This effect decreases the value of PA which can be measured with a probe beam normal to the inducing beam because of at least two factors: the inducing beam takes the form of a cone inside the sample,[2] resulting in a small overlap volume for the inducing and probe beams, and the electric vector of the inducing beam scattered inside the sample is not strictly in the plane perpendicular to the wave vector of the incident unpolarized beam (due to fanning of the beam).

CONCLUSIONS

Photoinduced anisotropy detected in a direction normal to an inducing beam of unpolarized subgap light has been observed in a bulk chalcogenide glass ($As_2S_3I_{0.8}$). The sign of this anisotropy and the effect itself are not due to dichroism of absorption, but rather to dichroism of scattering. In films, where the requisite perpendicular geometry cannot easily be achieved, anisotropy induced by an unpolarized glancing-angle beam can be detected by means of a probing beam that is incident normal to the films, taking into account the partial polarization of the inducing light when refracted at the film surface.

ACKNOWLEDGMENT

V.K.T. would like to acknowledge the Royal Society for financial support.

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* On leave from the Ioffe Physical-Technical Institute, St. Petersburg, Russia.

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