Transient photorefraction in Ge-Pb-S glassy films

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In glassy $Ge_{28.5}Pb_{15}S_{56.5}$ films, we observed and studied the phenomenon of transient photorefraction—a change in refractive index during light irradiation, which is not accompanied by metastable photodarkening. Some possibilities for the explanation of this phenomenon are pointed out, and this phenomenon is claimed to be typical of films of many chalcogenide glassy semiconductors.

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I. INTRODUCTION

Photoinduced phenomena in films of chalcogenide glassy semiconductors, especially photoinduced structural transformations[1] and photoinduced optical anisotropy,[2] continue to attract the attention of scientists and engineers.[1–9] Photoinduced structural transformations are manifested in reversible effects of photodarkening (or photobleaching), a change in optical band gap and also in film transparency, and in photorefraction, a change in the refractive index of a glassy material.[1] "Reversible" means that the initial values of transparency and refractive index can be restored after heating the film up to the softening temperature. Several models of photodarkening effect have been considered. Some of them are phenomenological, some are purely electronic, and others involve bond switching and atom movement or increased interaction between lone-pair electrons of the chalcogen atoms.[1]

Photoinduced anisotropy is the emergence of dichroism or birefringence in an initially optically isotropic film under the action of linearly polarized light. This effect is explained by the orientation of interatomic bonds or specific defects of the glass, leading to the appearance of some optical axis with a direction determined by the electrical vector of exciting light.[2]

In most cases, glassy As-Se and As-S films were used for both investigations and application of photoinduced processes. Binary glassy Ge-Se and Ge-S films or multicomponent As-S-Se-Te and As-Ge-S-Se films are occasionally utilized. In all these samples, the photodarkening and photorefraction are accompanied by photoinduced anisotropy. Incorporation of metals, for example, of Cu or Pb in chalcogenide glassy films and bulks, resulted in diminishing and then in a complete disappearance of photosensitivity.[10,11]

An unusual situation was reported for glassy three-component Ge-Pb-S films, in which large photoinduced anisotropy was observed but photodarkening was not recorded.[12] In the present paper, we attempted to understand this contradiction, taking into consideration the recent results of Ganjoo *et al.*[13,14] and Ganjoo and Shimakawa,[15] who demonstrated the existence of two components of photodarkening: the well-known metastable one and the transient one, occurring only during irradiation of the film. In the course of the investigation of transient photodarkening in the Ge-Pb-S films, we discovered a phenomenon—*transient photorefraction*.

II. EXPERIMENT

Ge-Pb-S films were prepared by thermal evaporation of crushed bulk $Ge_{28.5}Pb_{15}S_{56.5}$ glass in vacuum of the order of 10^{-6} Torr. This composition was selected as the most stable glassy material in the Ge-Pb-S system,[16] having high optical band gap (1.75–1.8 eV) and bipolar photoconductivity.[17] This bulk glass was synthesized using Ge, Pb, and S all of which had a purity of 99.999%. Sample films were prepared by evaporation from quartz crucible onto oxide glass substrates and had thickness within the 0.1–1.0 μm range.

First, we attempted to search for photodarkening in the studied films, using the traditional method, when the transparence of the sample was studied after switching the irradiation off. Later, we applied the two-beam method used in the experiments of Ganjoo *et al.*[14] and also in our earlier study of photorefraction and photoinduced birefringence in As-S glassy films.[18,19] We used the apparatus shown schematically in Fig. 1. Two He-Ne laser beams (633 nm) were used to irradiate the same area of the sample. The less powerful (attenuated by the attenuator) *probe* beam (0.4 mW/cm^2) passed through an electro-optical modulator and polarizer, which together permitted the modulation of light intensity discontinuously between zero and a maximum value at the frequency of 2 kHz. Then, this laser beam was passed through the sample and was incident on the Si photodiode, permitting a measurement of photoinduced transmission changes.

The more powerful (2.75 W/cm^2) *pump* beam was used to produce photodarkening. The kinetics of photodarkening was studied by exposing the Ge-Pb-S film to the pumping beam for intervals of ~200 s separated by ~300 s periods of rest. Alternating periods of pumping and rest were produced using a shutter. The intensity of the transmitted probe beam was measured continuously.

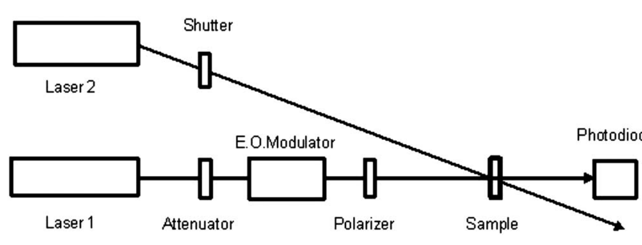

FIG. 1. Experimental installation.

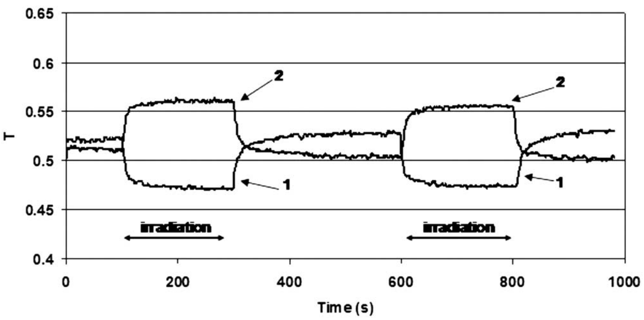

FIG. 2. Transparency of the films.

The study of the refractive index spectra was carried out using ellipsometer VASE series of J. A. Wollam Co. Measurements were performed with an angle of incidence of 70° (near the pseudo-Brewster angle of the sample, where the relative phase between reflections of the *s* and *p* polarizations is close to 90°), and, for the study of photoinduced change of refractive index, the He-Ne laser beam falling orthogonally to the film was used.

III. RESULTS

Applying the traditional method (investigation of the optical properties of a film after the exciting irradiation is turned off), we replicated previous findings that the photodarkening effect does not exist in the studied $Ge_{28.5}Pb_{15}S_{56.5}$ films, but using the two-beam installation (Fig. 1) we recorded photosensitivity of the samples. The transparency of the films sufficiently quickly (with relaxation time of several seconds) decreased after the start of irradiation by the pump beam and achieved saturation, as shown in Fig. 2 (curve 1). When the pump beam was switched off, transparency sufficiently quickly increased until the initial value. Such a situation was observed for several of the studied films, and we decided that we observed the transient component of photodarkening, similar to that reported in Refs. 13–15. However, in other films, we observed the opposite picture: The transparency of the film increased at irradiation and decreased after irradiation stopped (Fig. 2, curve 2). We noticed that these opposite pictures were obtained in films of different thicknesses.

Then, we fabricated wedge-type samples (the thickness was changed from 500 to 700 nm), in which we observed,

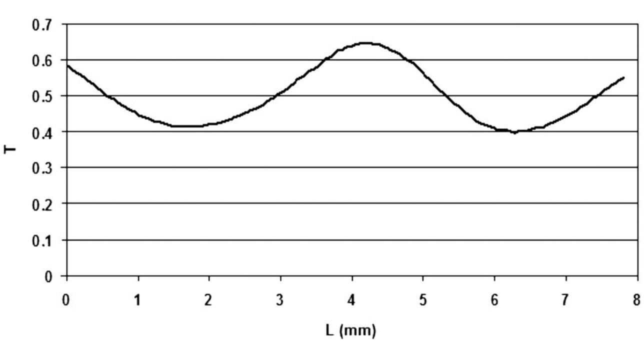

FIG. 3. Change of transparency in the wedge-type sample.

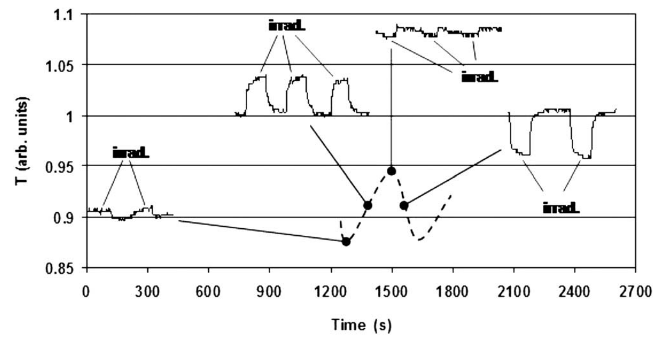

FIG. 4. Transparency changes for different areas of the wedge-type sample.

using scanning of the weak probe beam along the sample, a periodical change in transparency, demonstrated in Fig. 3. After that, we investigated, using the two-beam installation, the photoinduced processes in the areas of the wedge-type sample showing maximum, minimum, and intermediate transparencies. The results of these experiments, shown schematically in Fig. 4, demonstrate diametrically different transparency changes for different areas; moreover, the changes in the areas with extreme transparency are much smaller than those in the areas with intermediate transparency. Figure 5 shows that relative transparency changes ($\Delta T/T_0$) depend linearly on the pump beam intensity P, where T_0 is the initial transparency.

The obtained results lead to the following conclusions. The periodical change of transparency (Fig. 3) shows that the He-Ne laser beams are in the spectral range of interference for the studied films and that the observed changes of transparency indicate a photoinduced change in the optical range of the light, $H=nd$, where n and d are the film's refractive index and thickness, respectively. Comparing the observed transparency changes with the data in Fig. 3, we estimated the relative H change as 1.5%–2.5%. Previous studies of metastable photoinduced changes in glassy As- and Ge-chalcogenide films showed that changes in the refractive index are always larger than those in film thickness.[1] This fact permits us to assume that in the current study of transient photoinduced changes, the main role is played by the photorefractive effect and that just the relative change of the refractive index is 1.5%–2.5%.

In order to confirm our conclusions, we performed an ellipsometric study of very thin (~0.1 μm) $Ge_{28.5}Pb_{15}S_{56.5}$

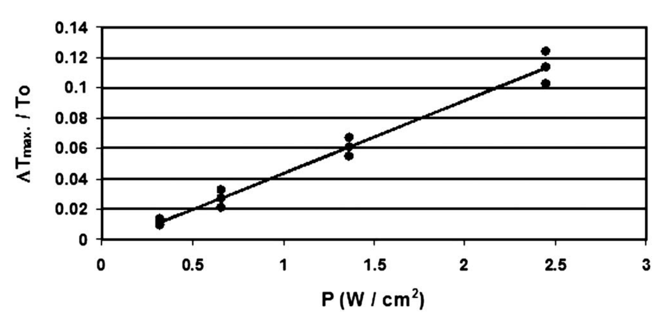

FIG. 5. Relative transparency changes vs pump beam intensity.

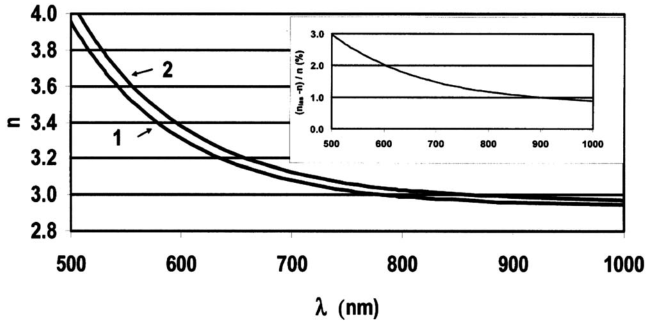

FIG. 6. Refractive index spectra for nonirradiated film and film under irradiation. Inset: relative change of refractive index under irradiation.

films evaporated onto substrates from a BK-7 oxide glass. On the basis of this study, the refractive index spectra for both the nonirradiated film and the film when it was irradiated by the He-Ne light beam were built. These spectra are shown in Fig. 6, together with the spectrum of the relative change of refractive index ($\Delta n/n$). The figure shows that at the wavelength of the He-Ne laser (632 nm), the $\Delta n/n$ value is ~1.58%. This value roughly coincides with the data obtained from the evaluation of the photoinduced transparency changes.

IV. DISCUSSION

The results of this study show that in chalcogenide glassy Ge-Pb-S films, the transient (reversible) photorefraction can exist without photodarkening. In order to understand this result, it is necessary to remember the difference between Ge-Pb-S glassy films and As-Se and As-S glassy films. In the As-chalcogenide films, the top of the valence band is known to be formed by the chalcogenide lone-pair electrons. This peculiarity explains the monopolar (hole) photoconductivity of such films. The excitation of these valence band electrons results in specific structural changes and in the narrowing of the forbidden gap, that is, in metastable photodarkening and metastable photorefraction.[1] In the Ge-Pb-S films, the *p* electrons of Pb play an essential role at the top of the valence band. This fact leads to the better symmetry of permitted bands and, as a consequence, to the appearance of bipolar photoconductivity.[17] The excitation of these *p* electrons is not accompanied by the narrowing of the forbidden gap, hence the absence of metastable photodarkening and metastable photorefraction.

The transient photorefraction observed in our experiments must have some other reason, for example, it can be connected with strong photoconductivity, which is typical of the $Ge_{28.5}Pb_{15}S_{56.5}$ films. Electron transitions and distortion of electron clouds that occurred in the studied glassy films can be the reason for both the photoconductivity and photorefraction. In our previous work,[20] we already considered the refractive index change due to photoexcited electrons for the explanation of the observed structural transformations induced by short laser pulses in the glassy $As_{50}Se_{50}$ films. The photoconductivity was also assumed to be the reason for a nonlinear optical response in some chalcohalide glasses[21]

Another explanation of transient photorefraction may be found in the effect of trapping of photocarriers and the creation of strong electrical fields, leading to a change in refractive index; these effects are thought to give rise to photorefraction in the photoconductive crystals of the sillenite family ($Bi_{12}MO_{20}$, where M=Si, Ge, Ti).[22]

Photoinduced anisotropy, which was observed in the $Ge_{28.5}Pb_{15}S_{56.5}$ films,[12] can also be due to photoconductivity. As shown in Ref. 23, in chalcogenide films under the action of linearly polarized light, anisotropic photoconductivity was observed, which in turn can induce anisotropy of refractive index, that is, birefringence, which was probably observed in Ref. 12.

In conclusion, we can say that the phenomenon of transient photorefraction is typical not only for Ge-Pb-S, but also for many other glassy chalcogenide films. Using wedge-type samples, we observed thickness-dependent variable-sign photoinduced transient effects in thin Sb_2S_3 and *a*-Se films, in which metastable photodarkening either was not observed or had a very small value.[12] We observed weak metastable photorefraction in wedge-type As_2S_3 and As_2Se_3 films as well, where it coexisted with metastable photodarkening. It is possible that the change of refractive index in such films plays a certain role in the observations of transient photodarkening.[13–15] The phenomenon of transient photorefraction can be interesting for some applications in optical information recording, holography, and adaptive optics due to its comparatively short relaxation time.

V. SUMMARY

Earlier, in the works of Ganjoo *et al.*[13,14] and Ganjoo and Shimakawa,[15] two components of photodarkening effect, a metastable and a transient one, were demonstrated in the glassy films of As chalcogenides. In the glassy $Ge_{28.5}Pb_{15}S_{56.5}$ films, in which the metastable photodarkening was not observed, we discovered and studied transient photoinduced changes of transparency. Experiments with wedge-type samples and direct ellipsometric measurements showed that, in the studied films, the observed transient photoinduced change of transparency is due to the phenomenon of transient photorefraction. In this phenomenon, a change in the refractive index occurs only under irradiation of the samples and relaxes quickly after the stopping of irradiation.

Some possibilities for the explanation of the transient photorefraction are considered. A similar photorefraction phenomenon was also observed in several other chalcogenide glassy films (Sb_2S_3 and *a*-Se films). We concluded that transient photorefraction is typical for films of many chalcogenide glassy semiconductors.

[1] M. Frumar, B. Frumarova, T. Wagner, and P. Nêmec, in *Photo-induced Metastability in Amorphous Semiconductors*, edited by A. V. Kolobov (Wiley-VCH, Berlin, 2003), p. 23.
[2] V. M. Lyubin and M. L. Klebanov, in *Photoinduced Metastability in Amorphous Semiconductors*, edited by A. V. Kolobov (Wiley-VCH, Berlin, 2003), p. 91.
[3] S. I. Simdyankin, T. A. Niehaus, G. Natarajan, T. Frauenheim, and S. R. Elliott, Phys. Rev. Lett. **94**, 086401 (2005).
[4] K. E. Asatryan, T. Galstian, and R. Vallee, Phys. Rev. Lett. **94**, 087401 (2005).
[5] A. Feigel, M. Veinger, B. Sfez, A. Arsh, M. Klebanov, and V. Lyubin, Appl. Phys. Lett. **83**, 4480 (2003).
[6] N. Ponnampalam, R. G. Decorby, H. T. Nguyen, P. K. Dwivedi, C. J. Haugen, J. N. McMullin, and S. O. Kasap, Opt. Express **12**, 62270 (2004).
[7] S. Wong, M. Deubel, F. Perez-Willard, J. Sajeev, G. A. Ozin, M. Wegwner, and G. Von Freymann, Adv. Mater. (Weinheim, Ger.) **18**, 265 (2006).
[8] V. Lyubin, M. Klebanov, M. Veinger, I. Lyubina, and B. Sfez, Opt. Mater. (Amsterdam, Neth.) **28**, 115 (2006).
[9] M. W. Lee, Ch. Grillet, C. L. C. Smith, D. J. Moss, B. J. Eggleton, D. Freeman, B. Luther-Davies, S. Madden, A. Rode, Y. Ruan, and Y. Lee, Opt. Express **15**, 1277 (2007).
[10] J. Z. Liu and P. C. Taylor, Phys. Rev. Lett. **59**, 1938 (1987).
[11] A. Masuda, Y. Yonezawa, A. Morimoto, M. Kumeda, and T. Shimizu, J. Non-Cryst. Solids **217**, 121 (1997).
[12] V. M. Lyubin and V. K. Tikhomirov, Sov. Phys. Solid State **32**, 1069 (1990).
[13] A. Ganjoo, K. Shimakawa, H. Kamiya, E. A. Davis, and J. Singh, Phys. Rev. B **62**, R14601 (2000).
[14] A. Ganjoo, K. Shimakawa, H. Kamiya, and E. A. Davis, J. Non-Cryst. Solids **299-302**, 917 (2002).
[15] A. Ganjoo and K. Shimakawa, J. Optoelectron. Adv. Mater. **4**, 595 (2002).
[16] A. Feltz and B. Voigt, Z. Anorg. Allg. Chem. **403**, 61 (1974).
[17] G. A. Bordovsky, L. P. Kazakova, E. A. Lebedev, V. M. Lyubin, and N. A. Savinova, J. Non-Cryst. Solids **63**, 415 (1984).
[18] V. M. Lyubin and V. K. Tikhomirov, Sov. Tech. Phys. Lett. **15**, 804 (1989).
[19] V. M. Lyubin and V. K. Tikhomirov, Sov. Phys. Solid State **33**, 1161 (1991).
[20] G. Rosenblum, B. G. Sfez, Z. Kotler, V. Lyubin, and M. Klebanov, Appl. Phys. Lett. **75**, 3249 (1999).
[21] G. Dong, H. Tao, X. Xiao, C. Lin, Y. Gong, X. Zhao, S. Chu, S. Wang, and Q. Gong, Opt. Express **15**, 2398 (2007).
[22] M. P. Petrov, S. I. Stepanov, and A. V. Khomenko, *Photorefractive Crystals in Coherent Optical Systems* (Springer, New York, 1992).
[23] V. Lyubin, M. Klebanov, and V. K. Tikhomirov, Phys. Rev. Lett. **87**, 216806 (2001).