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Photoinduced generation and reorientation of linear dichroism in AsSe glassy films

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The kinetics of linear dichroism generation and reorientation in glassy AsSe films induced by linearly polarized He-Ne laser light of different intensities is studied by means of a polarization-modulation technique. Two distinct processes are identified: creation of photoinduced defects and their photostimulated orientation and reorientation. The first process can be carried out by both unpolarized and polarized light and has a much larger time constant than the second one. The annealing temperatures of the two effects are also shown to be different. Comparison of restoration of the initial dichroism-generation kinetics after annealing with the photodarkened AsSe film thermobleaching leads to a conclusion about certain identity of the defects responsible for the photodarkening and photoinduced anisotropy phenomena. Tikhomirov and Elliott's model of photoinduced anisotropy in chalcogenide glasses is further developed. [S0163-1829(96)51918-1]

The phenomenon of photoinduced anisotropy (PA), manifested as linear dichroism and birefringence in chalcogenide glasses both bulk and thin films, has attracted the attention of many researchers in recent years.[1–8] Together with new observations of the anisotropy induced by both above-band-gap and sub-band-gap linearly polarized light in glasses of different composition, the possibility of PA generation by nonpolarized light was predicted[3] and then observed experimentally.[4] Recently, linear birefringence in bulk glasses was induced by circularly polarized light.[6] PA is of potential interest for optical data recording and holography[8,9] and for manufacture of binary phase gratings (Damman gratings),[10] opening new ways in electro-optics, light wave communications, and digital optical computing systems.

In the first papers, where the discovery of PA in chalcogenide glasses was reported,[11] this phenomenon was associated with the existence of highly dispersed, optically anisotropic structural fragments in the isotropic (on the average) glassy film. Different approaches to explain PA were developed later that are based on consideration of the interaction of inducing light with native quasiatomic defects,[1] with quasimolecular defects (three-center bonds)[12] or with bistable centers having a wide distribution of relaxation times.[13] Fritzsche discussed the photoinduced redistribution of anisotropic microvolumes as a base of PA (Ref. 3) and Tikhomirov and Elliott recently developed a model[5] in which the PA is connected with photostimulated reorientation of valence-alteration pairs (VAP's) that are characteristic defects in chalcogenide glasses.[14] Tikhomirov and Elliott meant the VAP's existing in the nonilluminated glass (natural defects) with concentration $\sim 5\times 10^{17}$ cm^{-3}, and in order to explain appearance of the large anisotropy at the expense of such a small concentration of defects, they suggested a very strong interaction of VAP's with their environment.[5] It is worth mentioning that after[1] the PA was considered to be a phenonenon that has nothing in common with the photodarkening effect.

In this paper, the data are presented which permit further development of Tikhomirov and Elliott's model.[5] It is shown that the whole process of linear dichroism generation in glassy films in the case of above-band-gap excitation can be divided into two subprocesses. The first of these is connected with the creation of some centers that can be oriented and the second one with photostimulated orientation of such centers. The attempt to find a correlation between PA and the photodarkening phenomenon is also made.

The samples studied were AsSe amorphous films of 0.5–4.0 μm thickness prepared by the vacuum evaporation technique in which the PA is exhibited very distinctly.[1,5] Investigation of photoinduced dichroism and photodarkening was carried out using an installation with two linearly polarized He-Ne laser beams (inducing and probing beams) illuminating the same area of the fim.[13,15] When the dichroism reorientation was studied, the state of the inducing light polarization was changed to the orthogonal one.

Figure 1 shows the kinetics of dichroism generation and reorientation in the typical AsSe film at two different intensities of exciting linearly polarized light. The dichroism D is determined as a quantity $(I_\parallel - I_\perp)/2(I_\parallel + I_\perp)$, where $I_\parallel$ and $I_\perp$ are the intensities of the probing beam transmitted through the

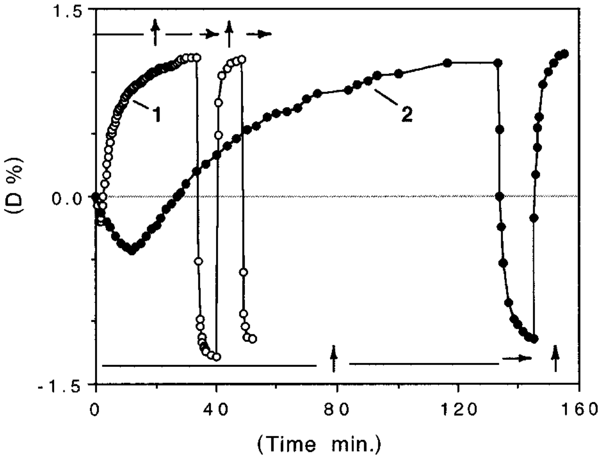

FIG. 1. Kinetics of dichroism generation and reorientation in AsSe film of 1.2 μm thickness stimulated by linearly polarized He-Ne laser light ($\lambda = 633$ nm) of intensity 2.75 W/cm^2 (1) and 0.24 W/cm^2 (2) with two orthogonal directions of the electrical vector (↑ and →).

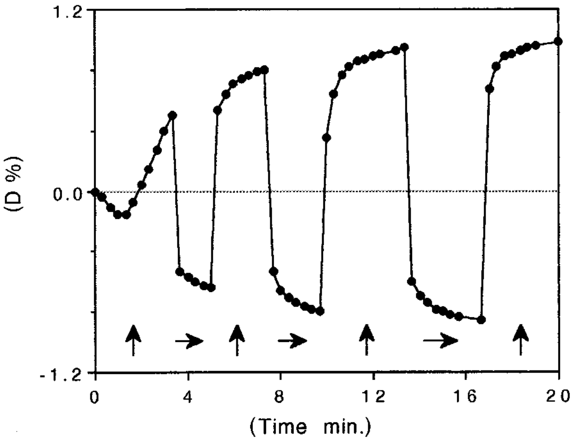

FIG. 2. Kinetics of dichroism generation and reorientation in AsSe film of 1.2 μm thickness stimulated by linearly polarized He-Ne laser light ($\lambda=633$ nm) of intensity 2.75 W/cm^2 when reorientation cycles are carried out in the process of dichroism generation.

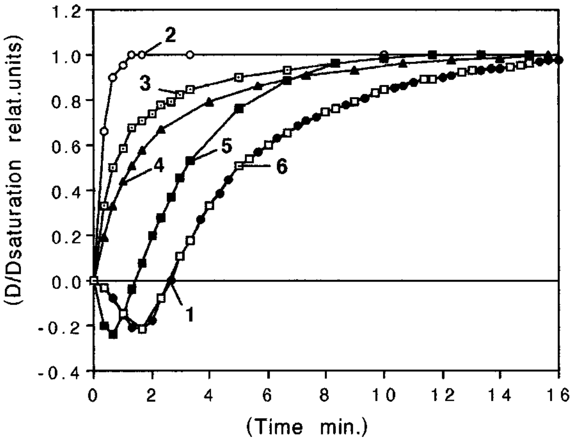

FIG. 3. Kinetics of room temperature dichroism generation in virgin AsSe film of 1.2 μm thickness (1), repeated dichroism generation after annealing at 75 °C (3), 95 °C (4), 140 °C (5), 180 °C (6), and kinetics of one of the cycles of room temperature dichroism reorientation in such film (2). Intensity of linearly polarized He-Ne laser light is 2.75 W/cm^2.

film and polarized parallel or perpendicular to the electric vector of the inducing beam. It is seen that at both light intensities dichroism reorientation occurs much quicker than the initial dichroism growth, although at smaller light intensity both initial dichroism generation and its reorientation are more prolonged than at higher light intensity. It is necessary to stress that in both cases the dichroism achieves approximately the same value but for substantially different time periods. Quick reorientation occurs not only after dichroism saturation but also in the initial moments of dichroism generation (Fig. 2), but in this case the quick process is always accompanied by a prolonged increase of the anisotropy at constant state of light polarization. The initial negative parts in the dichroism generation curves of Figs. 1 and 2 were shown to be due to dynamical light interference phenomena caused by the photoinduced change of refractive index[16] in the process of the initial film irradiation. When the film was initially irradiated for a long time by nonpolarized light, the following irradiation by linearly polarized light leads to the quick growth of a dichroism without any prolonged processes and initial negative parts did not appear in this case.

The results reported show that both polarized and nonpolarized light leads to creation of some centers in the nonirradiated film that can be oriented quickly under the action of linearly polarized radiation (in the case of polarized light these centers are oriented immediately). The constant value of the dichroism saturation at different light intensities testifies to the limited number of centers that can be oriented.

The influence of heating of preliminary irradiated anisotropic films on the dichroism value and on the kinetics of repeated dichroism growth was studied next. Disappearance of the dichroism was shown to take place at 80–100 °C in agreement with Ref. 1. Figure 3 demonstrates the room-temperature kinetics of repeated photoinduced dichroism generation after heating the film to a certain temperature, keeping it at this temperature for ten minutes (annealing) and then cooling to room temperature. The kinetics of room-temperature dichroism reorientation in the nonannealed film is also shown. A gradual increase of annealing temperature was shown to bring the form of the dichroism growing curve nearer to that in the virgin film. Perfect coincidence of the form of these curves was observed on annealing at temperature 170–180 °C, close to the softening temperature. We note here that the bleaching of photodarkened AsSe film in the process of heating also starts at a certain temperature (the threshold of thermobleaching), while the total bleaching occurs at a temperature close to the softening temperature.[17]

The results of the heating experiments imply that the same centers which cause photodarkening of the film (possibly some part of these centers, capable to be oriented) are also responsible for the photoinduced anisotropy. Such centers (defects) are created from the regular atoms in the form of VAP's in the reactions[14]

$$2C_2^0+h\nu\rightarrow C_1^-+C_3^+ \quad \text{and} \quad C_2^0+P_3^0+h\nu\rightarrow C_1^-+P_4^+\,, \tag{1}$$

where C and P mean the chalcogen and pnictogen atoms respectively, and the superscript and subscript refer to the charge state and the coordination number.

Combining the ideas proposed in Refs. 3 and 5, it is possible to assume that polarized light initiates the one-photon reactions

$$C_1^++C_3^++h\nu\rightarrow C_1^0+C_3^0 \quad \text{and} \quad C_1^-+P_4^++h\nu\rightarrow C_1^0+P_4^0 \tag{2}$$

and that these reactions occur much more preferably in the VAP's with dipole moment oriented parallel to the electrical vector of the exciting light, decreasing their number. All singly, threefold-, and fourfold-coordinated neutral defects are unstable[14] and therefore afterwards, the energetically advantageous reactions

$$C_1^0+C_3^0\rightarrow C_1^-+C_3^+ \quad \text{and} \quad C_1^0+P_4^0\rightarrow C_1^-+P_4^+ \tag{3}$$

proceed but now the restored $C_1^-+C_3^+$ and $C_1^-+P_4^+$ defects are oriented randomly. The whole process is accompanied by a decrease of the number of defects having dipole moments codirected with the electrical vector of the inducing light and by diminishing the absorption of the probing light with electrical vector parallel to that of the inducing light, i.e., by appearance of an anisotropy which we recorded in our experiments. The positive sign of the observed dichroism just corresponds to smaller absorption of the probing light with electrical vector parallel to that of the polarizing light.

The same consideration allows us to understand the reorientation of the anisotropy as the number of lone-pair defects with dipole moments parallel to the new direction of the electrical vector of the reorientating light will decrease quickly.

The concentration of the photocreated defects responsible for photodarkening is very large, about $10^{20}\ \mathrm{cm}^{-3}$ (Ref. 18) and if some substantial part of these defects provides the dichroism, it is not necessary to assume a strong interaction with the environment to explain the large anisotropy generation as was made in Ref. 5.

In conclusion, we want to stress that the model considered can be applied only in the case of above-band-gap light dichroism excitation in the thin chalcogenide films. We believe that PA in bulk chalcogenide glasses excited by the sub-band-gap light[2,6,7] has another nature, as it is difficult to suppose effective creation and recharging of defects by light quanta having so small an energy. Generation and reorientation of anisotropic scattering centers[7] is a substantially more appropriate mechanism of PA in this case.

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[1] V. M. Lyubin and V. K. Tikhomirov, J. Non-Cryst. Solids **114**, 133 (1989).

[2] V. M. Lyubin and V. K. Tikhomirov, J. Non-Cryst. Solids **135**, 37 (1991).

[3] H. Fritzsche, J. Non-Cryst. Solids **164-166**, 1169 (1993).

[4] V. K. Tikhomirov and S. R. Elliott, Phys. Rev. B **49**, 17 476 (1994).

[5] V. K. Tikhomirov and S. R. Elliott, Phys. Rev. B **51**, 5538 (1995).

[6] K. Tanaka, M. Notani, and H. Hisakuni, Solid State Commun. **95**, 461 (1995).

[7] V. Lyubin, M. Klebanov, S. Rosenwaks, and V. Volterra, J. Non-Cryst. Solids **164-166**, 1165 (1993).

[8] V. K. Tikhomirov and S. R. Elliott, J. Phys. Condens. Matter **7**, 1737 (1995).

[9] Sh. D. Kakichashvily, Opt. Spek. **33**, 171 (1972) [Opt. Spectrosc. **33**, 324 (1972)].

[10] C. H. Kwak, S. Y. Park, H. M. Kim, and E. H. Lee, Opt. Commun. **88**, 249 (1992).

[11] V. G. Zhdanov, B. T. Kolomiets, V. M. Lyubin, and V. K. Malinovskii, Phys. Status Solidi A **52**, 621 (1979).

[12] S. A. Dembovsky, Solid State Commun. **83**, 761 (1992).

[13] T. Kosa and I. Janossy, Philos. Mag. B **64**, 355 (1991).

[14] M. Kastner and H. Fritzsche, Philos. Mag. **37**, 199 (1978).

[15] V. M. Lyubin and V. K. Tikhomirov, Fiz. Tverd. Tela **33**, 2063 (1991) [Sov. Phys. Solid State **33**, 1161 (1991)].

[16] B. T. Kolomiets and V. M. Lyubin, Mater. Res. Bull. **13**, 1343 (1978).

[17] V. L. Averyanov, A. V. Kolobov, B. T. Kolomiets, and V. M. Lyubin, Phys. Status Solidi A **57**, 81 (1980).

[18] D. G. Biegelsen and R. A. Street, Phys. Rev. Lett. **44**, 803 (1980).