Polarization-dependent, laser-induced anisotropic photocrystallization of some amorphous chalcogenide films

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(Received 31 March 1997; accepted for publication 29 July 1997)

We report the observation of the influence of light polarization on the photocrystallization process and on the properties of crystallized films. Irradiation with linearly polarized He–Ne laser light results in the preparation of polycrystalline films with strong optical anisotropy (dichroism), the sign of which is determined by the direction of the electrical vector of light. The results obtained allow one to select from previously proposed mechanisms of photocrystallization. Large values of photoinduced dichroism in the films studied can be interesting for different applications of photoinduced anisotropy. © 1997 American Institute of Physics.

We observed polarization-dependent photocrystallization (PC) during the study of the photoinduced anisotropy in amorphous films of the Se–Ag–I system. The phenomenon of photoinduced anisotropy displayed as a photoinduced dichroism (PD) in films of As–Se, As–S, Ge–Se, and Ge–Pb–S systems was investigated by many authors. In spite of some difference in the results obtained by various investigators and for different materials, the main characteristics of the phenomenon were shown to be common for all materials studied. They can be summarized as follows: (1) Linearly polarized light induces dichroism of a certain sign that is usually saturated during tens of seconds or several minutes of irradiation depending on the light intensity. Slow relaxation of dichroism to a certain stable value after cessation of irradiation was shown. (2) The anisotropy can be destroyed after heating the anisotropic sample to a temperature somewhat lower than the glass transition temperature and can be created repeatedly by subsequent irradiation of the cooled sample by linearly polarized light. (3) The anisotropy can be destroyed (optically erased) when the anisotropic sample is irradiated by nonpolarized light. The anisotropy can be restored many times by means of irradiation by linearly polarized light with an orthogonally oriented electrical vector without any fatigue effect.

In this research, we investigated the PD and the photodarkening in amorphous films of the Se–Ag–I system and, in particular, in Se$_{20}$Ag$_{15}$I$_{15}$ films in which polarization holographic recording was accomplished but the characteristics of the photoinduced anisotropy have not been studied. The investigation of the PD and photodarkening was carried out using an installation with two linearly polarized He–Ne laser beams (inducing and probing beams with an intensity of $\sim 2.75$ W/cm$^2$ and $\sim 0.4$ mW/cm$^2$, respectively, and $\lambda = 633$ nm) illuminating the same area of the film. The dichroism is determined as $2(I_0 - I_\perp)/(I_0 + I_\perp)$, where $I_0$ and $I_\perp$ are intensities of the probing beam transmitted through the film and polarized parallel or perpendicular to the electric vector of the inducing beam. Thin films studied were prepared by the method described in Ref. 8 and had a thickness of $\sim 800$ nm.

As-prepared films did not display any photodarkening but did display PD with properties analogous to that in As–Se, As–S and other films studied previously. At the same time, storage of the films at a temperature of 30–35 °C during 2–3 weeks or their artificial aging (annealing at 70 °C during 2 h) resulted in a noticeable change of the photoinduced processes in them. Strong and prolonged photodarkening appeared upon irradiation at room temperature (the inset of Fig. 1). Then, at a constant direction of the polarization vector, PD was observed that changed the sign soon and grew slowly, achieving very large values of about 15%–20%, as is shown in Fig. 1. The sign of the resulting dichroism was determined by the direction of the polarization vector of the exciting light. Relaxation of PD in time was not observed. Optical anisotropy did not appear when irradiation was accomplished by the nonpolarized laser light or by the linearly polarized light with a periodically changing direction of the electrical vector.

Reorientation of PD was characterized by a constant change of reorientation kinetics and by following the alter-

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![Diagram](image-url)
The dichroism sign (Fig. 2). If, at the beginning of the experiment, the vertical polarization vector stimulated an increase in positive dichroism while the horizontal polarization vector diminished the positive dichroism and excited the negative dichroism, in the following stages the reverse processes were observed. Annealing of the irradiated (photodarkened) film at the glass transition temperature \[55 \, ^\circ C\] (Ref. 9) during 1 h did not lead to the erasing of the darkened areas and/or to the destruction of PD. Annealing at 80–90 °C during several hours also did not erase the darkened spots. Similar results were also obtained for other films of the Se–Ag–I system.

Thus, all characteristics of PD in treated Se–Ag–I films were different from those in films studied previously. These results permitted us to assume that we deal with a photoinduced PC process,\(^{10,11}\) and this assumption was confirmed by direct structural investigations such as optical microscopy, electron microscopy, and x-ray diffraction study. Figure 3 shows two optical images observed in a microscope. It is seen that, initially, more or less homogeneous Se\(_{70}\)Ag\(_{15}\)I\(_{15}\) films with a uniform morphology, after irradiation distinctly indicate crystallization. X-ray analysis of irradiated films showed the presence of Se, Ag2Se, and AgI microcrystals. A small area of the spot irradiated with the laser beam was the reason for using the Debye–Sherer–Hull method for three ranges of the irradiation angle with x-rays; 5°–30°, 30°–70°, and 70°–90°. Investigating the structure of the films with all the above-mentioned methods, we did not observe any preferential orientation of the crystallites in the photocristallized films.

Thus, we observed a laser-induced PC of the Se\(_{70}\)Ag\(_{15}\)I\(_{15}\) films that is polarization dependent. To our knowledge, this is the first such observation.

To check if this phenomenon is characteristic only of amorphous Se–Ag–I films or also of other amorphous chalcogenide films, we decided to investigate the "classical" amorphous material displaying the PC phenomenon, amorphous selenium.\(^{10,11}\) The \(a\)-Se films of 0.5–2.0 \(\mu m\) in thickness were prepared by vacuum evaporation at \(p = 2 \cdot 10^{-6}\) Torr. The whole complex of characteristics shown above for the Se\(_{70}\)Ag\(_{15}\)I\(_{15}\) films was also observed in \(a\)-Se films. Initially, the \(a\)-Se films did not display the photodarkening at room temperature, in agreement with the results obtained in Ref. 12, but after some thermal treatment (annealing at 70 °C during 30 min) they could be photodarkened by the He–Ne laser beam (\(\lambda = 633\) nm). The treated films displayed a large PD generation (up to 8%–10%), and the reorientation of the dichroism in them was characterized by a change of reorientation kinetics and the dichroism sign (Fig. 4). The appearance of PC in \(a\)-Se films was shown by all structural methods used for the Se\(_{70}\)Ag\(_{15}\)I\(_{15}\) films. Thus, we demonstrated that the phenomenon of polarization-dependent PC is typical for different chalcogenide amorphous films and not only for Se–Ag–I films.

A possibility of obtaining strongly anisotropic crystalline films is interesting both for people studying photo- and thermocrystallization of different materials and also for various applications. This result allows one to select between ideas...
explaining PC by the movement of photogenerated charge carriers to the boundaries of growing crystallites and with recombination there\textsuperscript{10} and proposals considering PC as photodestruction of some interatomic bonds resulting in a growth of crystallites.\textsuperscript{11} Our data support the second point of view, since it is difficult to think that the behavior of photoexcited charge carriers is dependent on the polarization of the exciting light, especially in the case of $\alpha$-Se where the light of $\lambda=630$ nm produces excitons but not free charge carriers.\textsuperscript{12} Opposite to that, photoinduced weakening and even destruction of interatomic bonds (either directly or through the exchange interaction with lone-pair electrons)\textsuperscript{16} is a very probable process in chalcogenide glasses. We want to stress that in many cases of light-induced crystallization of different films, the polarization dependence makes it possible to distinguish whether the crystallization is caused by pure thermal action of the light or photoaction is also essential.

Photoinduced anisotropy is of potential interest for optical data recording and holography,\textsuperscript{13} for the manufacture of binary phase gratings (Damman gratings),\textsuperscript{14} for optical Fourier processing,\textsuperscript{15} and incoherent–coherent conversion.\textsuperscript{16} Therefore, large value of PD accompanying the polarization-dependent anisotropic PC can be used in modern optoelectronics and photonics.

In conclusion, we have observed the dependence of laser-induced PC of Se–Ag–I and Se amorphous films on the polarization state of the inducing light beam. Polycrystalline films prepared as a result of irradiation by a linearly polarized light beam displayed a large linear dichroism with the sign that depended on the direction of the electrical vector of light. At the same time, irradiation by nonpolarized light or by light with a periodically changing direction of the electrical vector led to obtaining optically isotropic polycrystalline films. The obtained results support the model of PC based on the photoinduced rupture of interatomic covalent bonds and allow recommending polycrystalline anisotropic films for practical application.

This work was supported by a grant from the Israel Science Foundation as well as by a grant from the Bulgarian Science Foundation and EC Grant No. ERBCIPACT.