Laser-induced polarization-dependent photocrystallization of amorphous chalcogenide films

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Abstract

Irradiation of amorphous a-Se$_{20}$Ag$_{15}$I$_{15}$ and a-Se films by linearly polarized He–Ne- and Ar$^+$ ion-laser light was shown to produce polycrystalline films with linear dichroism, the sign of which is determined by the polarization of the light. Photocrystallization of the films was confirmed by direct structural investigations. Thus, a new phenomenon, the effect of light polarization on the photocrystallization process and on the properties of resultant crystallized films was revealed. Photoinduced anisotropy in a-Se–Ag–I films was shown to have many peculiarities in comparison with that in the formerly studied films, for example, in AsSe films. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

A phenomenon of photoinduced anisotropy (PA) in thin films of different amorphous and glassy semiconductors was studied by many researchers in recent years [1–6]. In this study, we reveal that the PA in amorphous Se–Ag–I films has many peculiarities in comparison with the PA in the formerly studied films, for example, in AsSe films. Analysing the data obtained, we come to the conclusion that there is polarization-dependent photocrystallization, and this hypothesis was confirmed by direct structural investigations. Analogous results were obtained at the linearly polarized light irradiation of thermally treated a-Se films.

2. Experimental

Amorphous films from the Se–Ag–I system were prepared by the method of vacuum evaporation described in Ref. [7]. The a-Se films were fabricated by standard thermal evaporation in high vacuum. The thickness of all films was in the range of 300 to 1000 nm. Study of PA and photodarkening was carried out using a set up with two linearly polarized laser beams (inducing and probing beams) Illuminating the same area of the film [4]. A He–Ne laser beam (≈ 0.4 mW/cm$^2$ at $\lambda = 633$ nm) was applied always as a probing beam, while as an inducing beam we used either a He–Ne laser beam (≈ 2.75 W/cm$^2$, $\lambda = 633$ nm) or an Ar$^+$ ion laser beam (≈ 0.3 W/cm$^2$, $\lambda = 488$ nm). The dichroism was determined as the quantity $2 (I_1 - I_0)/(I_1 + I_0)$, where $I_1$ and $I_0$ are the intensities of the probing beam transmitted through the film and polarized parallel or perpendicular to the propagating direction of the probing beam.
perpendicular to the electric vector of the inducing beam.

3. Results

As-prepared Se–Ag–I films did not photodarken under the action of either He–Ne or Ar\(^+\) ion laser light but displayed the PA with properties analogous to that in the films of As–Se, As–S and others studied previously [1,4,5]. Such behaviour is demonstrated in Fig. 1 and Fig. 2a. At the same time, storage or the films at temperature of \(\sim 35^\circ\)C during 2 weeks of their artificial aging (annealing at 70°C for 2 h) resulted in a detectable change of photoinduced processes in them. Strong and prolonged photodarkening appeared during irradiation at room temperature (Fig. 1). In the treated film, a photoinduced dichroism (PD) was observed and a change of the polarization vector to orthogonal one resulted in the reorientation of the PD that was characterized by the constant change of reorientation kinetics and by following alteration of the dichroism sign (Fig. 2b). If at the beginning of the experiment the vertical polarization vector stimulated increase of positive dichroism while the horizontal polarization vector diminished positive dichroism and led to negative dichroism, in the following stages the reverse processes were observed.

![Fig. 1. Kinetics of transmission changes in as-prepared and thermally treated Se\(_{30}\)Ag\(_{15}\)I\(_{15}\) film stimulated by linearly polarized He–Ne and Ar\(^+\) laser light. The lines are drawn as guide for the eyes.](image)

![Fig. 2. Kinetics of dichroism generation and reorientation in as-prepared (a) and thermally treated (b) Se\(_{30}\)Ag\(_{15}\)I\(_{15}\) film stimulated by linearly polarized He–Ne laser light with horizontal (x) and vertical (y) directions of the electrical vector. The lines are drawn as guide for the eyes.](image)

The PD excited by the He–Ne laser light at constant direction of polarization vector changed the sign very soon and grew slowly, achieving \(\sim 18\%\) as shown in Fig. 3a. The light induced dichroism obtained by irradiation with an Ar\(^+\) ion laser followed similar dependence but the saturated dichroism was less and was achieved in less time (Fig. 3b). The sign of the final dichroism was determined by the direction of the exciting light polarization vector. Some relaxation of PD with time was observed for the early periods and was not observed in final stages as can be seen from Fig. 3a. Annealing of irradiated (photodarkened) films at glass transition

Fig. 3. Kinetics of dichroism generation in a thermally treated Se$_{30}$Ag$_{15}$I$_{15}$ film stimulated by linearly polarized He–Ne (a) and Ar$^+$ (b) laser light with vertical direction of the electrical vector. The inset shows the initial stage of dichroism kinetics. Dichroism relaxation is also shown. The lines are drawn as guide for the eyes.

Fig. 4. Scanning electron microscope photographs of a nonirradiated (a) and a laser light-irradiated (b) areas of Se$_{30}$Ag$_{15}$I$_{15}$ film.

results (photodarkening at room temperature, opposite sign and larger PD, absence of relaxation and thermal erasing) permitted us to assume that there is one photoinduced photocrystallization (PC) process [8,9].

This assumption was confirmed by the direct structural investigations including optical microscopy, electron microscopy and X-ray diffraction study. In Fig. 4, the results of scanning electron microscope investigation of Se$_{30}$Ag$_{15}$I$_{15}$ films are demonstrated. Initially, homogeneous films with an uniform morphology indicate distinct crystallization after irradiation. X-ray analysis of irradiated films showed the presence of Se, Ag$_2$Se and AgI microcrystals. Difference in the kinetics and the saturated magnitudes of PD excited by He–Ne and Ar laser beams is explained by different light penetration depths connected with different absorption coefficients of red and green light. Thus, we observed for temperature (55°C) and at ~85°C for several hours did not erase darkened areas and did not destroy the PD which is opposite to the situation in the AsSe films [4]. Optical anisotropy did not appear when irradiation was accomplished by the nonpolarized laser light. Analogous results were obtained also for other films of the Se–Ag–I system.

4. Discussion

All properties of PA in treated Se–Ag–I films differed from those in films studied previously. These
the first time the polarization-dependent laser-induced anisotropic PC of Se–Ag–I films.

To check if this phenomenon is only observed in amorphous Se–Ag–I films or for other amorphous chalcogenide films, we investigated the 'classical' amorphous material displaying the PC phenomena—amorphous selenium [8,9]. The whole complex of properties shown above for the Se$_{70}$Ag$_{15}$I$_{15}$ films was observed in these a-Se films. Initially, the a-Se films did not display the photodarkening at room temperature, but after thermal treating (annealing at 70°C for 30 min) they could be photodarkened by the He–Ne laser beam and displayed a large PD generation (~10%), the gradual change in the reorientation kinetics and the PD sign, absence of relaxation phenomena. Thus, we demonstrated that the effect of polarization-dependent PC is typical for different chalcogenide amorphous films and not only for Se–Ag–I films.

Our results are consistent with a mechanism of photoinduced crystallization considering PC as photodestruction of some interatomic bonds resulting in the growth of crystallites [9].

5. Conclusion

We have observed for the first time a dependence of laser-induced PC of amorphous Se–Ag–I and Se films on the polarization state of the inducing light beam. Polycrystalline films prepared as a result of linearly polarized light beam irradiation displayed larger linear dichroism with a sign that depends on the direction of light electric vector. Photoinduced dichroism of this magnitude in the photocrystallized films can be important for different applications of photoinduced anisotropy.

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References