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Photoinduced changes of the optical parameters of thin films from $Ge_{30.8}As_{5.7}S_{63.5}$ glass

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Extremely high irreversible changes of the optical parameters have been found after long time illumination of thin films thermally evaporated from $Ge_{30.8}As_{5.7}S_{63.5}$ glass, which belongs to the Ge_2As_3-AsS_3 line. Illumination of virgin films leads to a blue shift of the absorption edge, photo-bleaching (PB). Changes of the optical band gap, E_g up to about 600 meV (~27%), of the refractive index, n up to 0.2 (~9.5%), as well as the thickness increase ~70 nm (11%) have been obtained. The dependences of the parameters of the irreversible PB on the film thickness (between 0.4 - 1.4 μm) and the time of illumination (up to 3h) have been investigated. The magnitude of the irreversible PB is compared with that of the irreversible thermo-bleaching after annealing near to the glass transition temperature, as well as with that of the reversible photo-darkening of the annealed films. The reasons for the appearance of such high photo-induced changes, which are interesting for practical uses, are discussed.

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1. Introduction

The photo-induced changes (PIC) in chalcogenides have been studied for more than 3 decades. In spite of some useful models given for explanation of the reversible PIC [1,2] there is no general consensus for predicting how to reach maximal PIC [3], reversible or irreversible ones. It is well known that they depend on the type of material and the conditions of illumination. It is accepted that the sulfide based multinary amorphous chalcogenides are more sensitive to reversible PIC (photo-darkening, PD) than the selenides, as well as than the binary chalcogenides. Usually the irreversible changes are higher than the reversible ones, which makes them very important for practical applications. Nevertheless, the irreversible PIC are not so widely studied because of their more complex nature [1,2]. Really, our studies on the Ge-As-S selective solubility have shown that materials with mean coordination numbers Z around 2.65 have a high sensitivity as non-silver inorganic photo-resists. In films from the $Ge_xAs_{40-x}S_{60}$ system, the highest irreversible PIC in Photo-bleaching (PB) and in refractive index n [4,5], and in photo-expansion [6] have been obtained around this Z value. These high changes have been related not only to the structural connectivity but also to the fact that this system is composed from two components one of which is non-stoichiometric (Ge_2S_3-As_2S_3). In a system with two non-stoichiometric components, Ge_2S_3-AsS_3, we have obtained a larger PIC, especially in the reversible PD [7]. The changes in the optical gap ΔE_g are up to 220 meV, accepted as "giant" in accordance with Ref. [3].

In this work, we present results from the films, evaporated from the $Ge_{30.8}As_{5.7}S_{63.5}$ glass, which belongs to the Ge_2S_3-AsS_3 system. Using suitable conditions of illumination and film thicknesses we obtain irreversible PIC of n and E_g much higher than those known up to now for chalcogenides.

2. Experimental

Films with thickness 0.4–1.4 μm were prepared by vacuum thermal evaporation with a rate of 6-8 nm/sec from the previously synthesized $Ge_{30.8}As_{5.7}S_{63.5}$ glass. The film composition was checked by electron microprobe X-ray analysis (Joel JSM 35 CF). In the thicker films, a decrease ~2.8 ± 1.5 at.% Ge at the expense of an increase mainly of As content was obtained. The Z value decreases by about 1.2% compared to the glass for which $Z = 2.673$.

The films were exposed in an ambient atmosphere using a high pressure Hg lamp (500 W) with an IR cut off filter. The power density was ~160 mW/cm^2. The annealing was performed in an Ar atmosphere for 45 min at 320-325°C.

The optical parameters (n, α, as well as E_g and the thickness, d) were determined by the well-known method of Swanepoel from the transmission spectra of thefilms. The parameters of the thinner films were calculated by a supplementary optical method [8], using the transmission and reflectance spectra measured using a Shimadzu 1240 UV-VIS spectrophotometer.

3. Results

The detailed studies of the dependence of the PIC on time of illumination have shown that the previously used illumination time (45 min) [7] does not lead to saturation of the magnitude of the PI effects, independent on the high photon flux in the blue and UV spectral region. In Fig. 1*a* one can see the blue shift of the absorption edge (PB) after 180 min illumination of a sample with thickness d ≈ 1.3 μm (curves 1 and 2). The evaluated increase of E_g using the Tauc plot is ~ 400 meV. Taking into account that the penetration depth of the active photons with energy higher than E_g will be nearer to the *d* value of the thinner samples, a sample with $d \approx 0.63$ μm is displayed in Fig. 1*b*. The PB effect increases and $\Delta E_g \approx 600$ meV. As known [4,5] the PB is accompanied by a decrease in the refractive index *n*. In Fig. 2 the dispersion of *n* according to the Wemple-DiDomenico (W-D) model is shown for the latter sample. The decrease in the saturated value of *n* after illumination reaches $\Delta n_o \approx 0.21$, while in the thicker sample Δn_o is about -0.14. It can be seen that the slope of the curves in the Tauc plot increases in the illuminated films (Fig.1*a*) as expected by ordering of the structure. The evaluated values of the accompanying thickness increase (photo-expansion [6]) are about 70 nm, which is 5.5% for the thick film and 11% for the thinner ones.

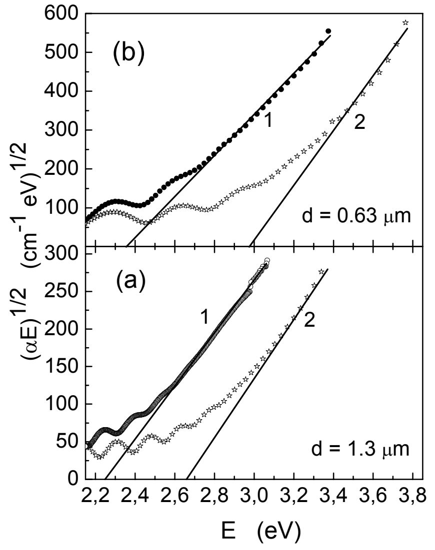

Fig. 1. Tauc plot of optical absorption,$(\alpha E)^{1/2}$ vs. photon energy E, for fresh (1) and illuminated 180 min (2) films with different thicknesses.

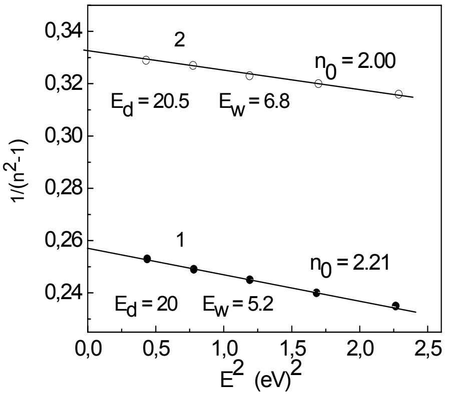

Fig. 2. Dispersion of the refractive index **n** *for fresh (1) and illuminated (2) films (d = 0.63 μm). The lines correspond to the W - D model and the energetic parameters are also given.*

In Fig. 3*a* one can see the PB leading to $\Delta E_g \approx 610$ meV for another thin sample. The influence of the subsequent annealing is also illustrated in this figure. In spite of the increase in the slope of the Tauc plot, the ordering of the structure does not lead to the expected further increase of E_g (a small decrease ~30 meV can be evaluated). This fact is confirmed for the samples with d ≈ 0.97 nm (Fig. 3*b*). Here the decrease is ~50 meV. In Fig. 3*b* one can also see the reversible photo-darkening (PD) leading to $\Delta E_g \approx 210$ meV. This result is near to the "giant" PD reached before in other compositions from the Ge_2S_3-AsS_3 system [7].

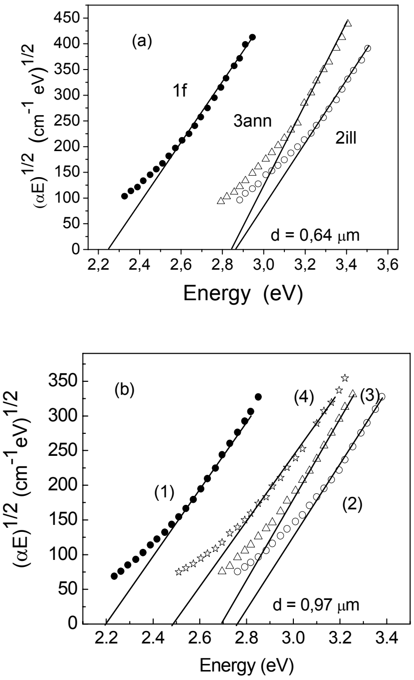

Fig. 3. Tauc plot of optical absorption, $(\alpha E)^{1/2}$ vs. E for fresh (1), illuminated 180 min (2), annealed (3) and post illuminated (4) films. (2) – (1) irreversible PB, (3) – (1) irreversible TB (4) – (3) reversible PD.

4. Discussion

The obtained irreversible PIC after a long time of illumination (180 min) of the parameters of the studied films are much higher than those known for chalcogenide films up to now. The values of E_g obtained from Fig. 1 increase by about 400 and 600 nm (which are 18 and 27% for the thick and thin films, respectively), exceeding the highest values known by us for PB by other authors.Stabl and Tichy [11] obtained in Ge-As-S thin films a saturated value of $\Delta E_g \approx 270$ meV after 750 min illumination. This result is comparable only with that obtained by us [7] for thick samples from the same Ge_2S_3-AsS_3 system, where maximal values ~15% are reached after a shorter illumination time (45 min). The Δn values of about 0.2 seem also to be the highest decrease of n at PB known by us.

The irreversible photo-bleaching in the fresh Ge-chalcogenide films, which contain quickly condensed fragments of the network constituents, is related to the increase in structural order. It can be accepted that upon band gap illumination the excitation of electrons from p-LP states changes the p-LP interactions and the network relaxes from the as-deposited state into a more energetically stable one [2,9]. The network polymerizes with a decreasing distribution of valence angles, bond lengths and with the creation of heteropolar bonds. In the studied films from the system composed of two non-stoichiometric components, the density of "wrong" bonds (homopolar and broken bonds) and voids is expected to be higher than in films from the systems used before [7], especially taking into account the chosen rate of evaporation. This could be one of the reasons for the established higher PB.

Our results on irreversible thermo-bleaching (not displayed here) have shown an increase of optical gap $\Delta E_g \approx 350$ meV in 1.3 μm thick films, $\Delta E_g \approx 420$ meV in films of intermediate thickness ~ 0.97 μm, and $\Delta E_g \approx 500$ meV in 0.67 μm thin films. The last two values are higher than those obtained ~350 and 370 meV in Ge-As-S and Ge-S films in Ref. [9] and [10], respectively. The irreversible thermo-bleaching leads also to ordering of the short and medium range order (SRO and MRO) of the structure of the films. It has been shown that in Ge-As-S films the annealing mainly increases the number of Ge-S heteropolar bonds at the expense of a decreasing number of As-S bonds [10]. This is reflected in the high degree of ordering of the MRO, connected with the increased degree of polymerization of the edge-shared Ge- tetrahedra and/or outrigger raft clusters.

The substantial difference between both irreversible PB and TB is explained by the fact that during the TB the whole matrix is excited (all atoms are more mobile [9]). One expects that the ΔE_g value has to be higher in TB than in PB, especially when the dual effect of the light is taken into account, i. e. the reversible darkening in the well-annealed films can proceed simultaneously with the irreversible photo-bleaching. Up to now, TB has been always higher than PB. However, in Fig. 3 we show that in films of intermediate and low thickness the magnitude of the TB is not higher than that of the PB. The obtained PD (curve 4, Fig. 3*b*) in well annealed films leads to $\Delta E_g \approx 210$ meV. The higher changes during PB than those during TB can be explained if one proposes that the active photons with energy higher than the band gap induce two-photon processes. This has been proposed before for the process of PD [9] but can also proceed during PB. The two-photon process leads to a greater probability for PIC than for thermo-induced ones [3], so that the PB will exceed the TB. The role of the penetration depth of the light leads to the higher effects in the thinner films. This, as well as the role of the surface oxidation, which cannot be neglected in some cases, and will be discussed in more detail in a forthcoming paper.

5. Conclusion

Significantly greater values of the optical bandgap increase, refractive index decrease and photo-expansion have been observed in thin films from $Ge_{30.8}As_{5.7}S_{63.5}$ glass. These results are obtained not only with a long time of illumination, but with sufficientlylow film thicknesses, at which the photons with greater energy suitable for two-photon processes can penetrate and induce large photo-structural changes interesting for optoelectronic applications.

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