On dual action of light and light annealing effect in chalcogenide films

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The new light annealing effect (LAE) in photodarkened Ge-As-S films found by us was explained on the basis of dual action of light (DAL). Light not only increases the network disorder at photodarkening (PD) but could also provoke its decrease leading to photobleaching (PB), competing with PD. To show that the PB is not related with photooxidation on the film surface we perform the illumination through the substrate with highly absorbed monochromatic light with penetration depth lower than the film thickness. Direct evidence has been found that the DAL governs the peculiarities of the photoinduced phenomena in chalcogenides.

(Received August 12, 2012; accepted October 30, 2012)

Keywords: Chalcogenide thin films, Optical properties, Photoinduced changes

1. Introduction

The highly photosensitive chalcogenides are perspective materials for photonic and optoelectronic applications. Especially attractive are the unique photoinduced (PI) phenomena based on photostructural changes in thin films. The reversible red optical absorption shift, i.e. the photodarkening, where not only the respective optical band gap E_g decreases, but also the film thickness d changes, accompanied by refractive index n changes, are applicable for optical recording. Difficulties arise to explain the microscopic nature of the PD, accepted as the only one reversible PI change of E_g in well-annealed films [1] and different approaches are suggested [1,2] for the mechanism of PD. Independent that PD is usually explained on the base of bond changes in chalcogenide atoms (changing interactions of their lone-pair electrons) which leads to decrease of network disorder, many peculiarities of the phenomena can not been understood, especially in films with decreased d: (i) In well-annealed Ge-As-S films when d decreases to and below ~100 nm the obtained PI change is a reversible PB [3] instead of the expected PD; (ii) On prolonged illumination of thinner than 1μm films light annealing of the saturated PD state appears. The PD begins to decrease and after prolonged enough time it disappears completely. The disappearance of the PD starts after shorter illumination time in films with more decreased d; so that the surface/volume thickness ratio increases [4,5]. The light annealing effect can be related to a PB process on the film surface, competing with the PD [5,6]. In many papers the PB process is connected with photooxidation (PO) of the film [7,8]. In this paper we show that the PB cannot be related with PO on the film surface. Our previous study of the parameters of the disorder [6] has shown that the LAE is accompanied with an ordering process when PB overcomes the PD, i.e. it is based on the dual action of light. To show that LAE could appear without any PB due to surface PO we use suitable irradiation through the substrate with penetration depth lower than the film thickness. In this way we exclude any surface photooxidation process and demonstrate that only the ordering of light in a disordered state, i.e. the DAL, can lead to LAE.

2. Experimental

The studied films with thickness ~990 nm were thermally evaporated in vacuum (10^{-3} Pa) onto quartz substrates from the previously synthesized $Ge_{32}As_5S_{63}$ glass. The irradiation was performed through interference filter with λ = 375 nm. Due to the low intensity (~10 mW/cm^2) long term irradiation in an evacuated cell (10^{-1} Pa) was used; detailed information about the experimental set up, measurement equipment and methods of optical parameter evaluation can be found elsewhere [5]. The penetration depth d_p estimated from $d_p(h\nu) \approx 1/\alpha(h\nu)$, with absorption coefficient $\alpha = 5.10^4$ cm^{-1}, was ~200 nm. It is low enough in comparison with the film thickness and when the sample was irradiated through the substrate any photooxidation of the chalcogenide film can be excluded.

3. Results and discussion

The transmission curves of the illuminated through the substrate sample in the evacuated cell with the low intense monochromatic light show a low PD. It reaches saturation after total illumination time ~500 min. The decrease of E_g, (Fig. 1), evaluated by the Tauc plot of the optical absorption [9], reaches 150 meV. At a continuing illumination this value decreases and at about twice prolonged illumination, the change of E_g reaches the value of 120 meV. To establish that the E_g changes result respectively from competing disordering and ordering

processes the changes in the parameters of disorder are evaluated.

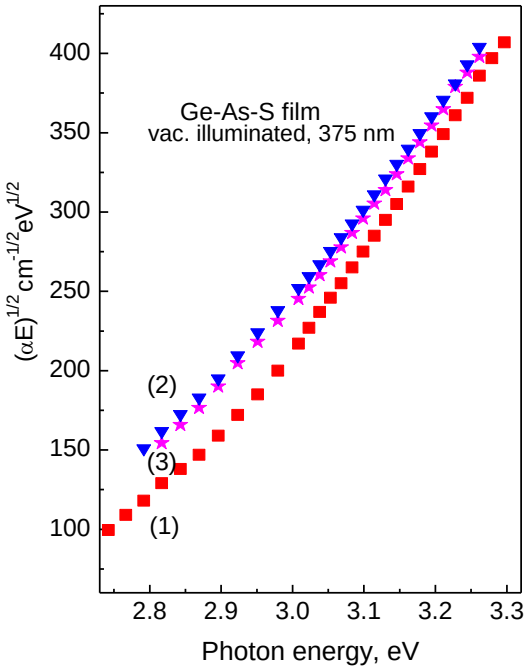

Fig.1. Spectral dependence of the optical absorption plotted according to Tauc law $(\alpha E)^{1/2} \sim B^{1/2}(E-E_g)$ for Ge-As-S film: annealed (1), illuminated through the substrate 525 min (2) and 965 min (3).

As is known [9,6] the slope $B^{1/2}$ in the Tauc plot (at photon energies where it is not influenced by tail states) decreases when the degree of disorder of the regular bonds in the network structure increases (at PD) and increases when the order increases. As can be seen (Table 1) an increase of the order is found, because the Tauc coefficient $B^{1/2}$ increases with prolonging the illumination after saturation of the PD.

Table 1. Optical band gap E_g and Tauc slope $B^{1/2}$ of Ge-As-S film in the different states.

States	E_g, eV	$B^{1/2}$, $(eV.cm)^{-1/2}$
Annealed film	2.68	653
Illuminated 525 min	2.53	540
Illuminated 965 min	2.56	551

4. Conclusion

It can be concluded that the found increase in $B^{1/2}$ after prolonged illumination of annealed Ge-As-S films manifests the dual action of light – light not only causes a disorder in the network but it also can bring about its ordering and this competing process at some stage of illumination leads to the light annealing effect. This is an evidence that dual action of light governs the photodarkening and photobleaching processes. In experiments with Ge-chalcogenides one must accept that photobleaching could not only result from photooxidation, but also only from the ordering process of the dual action of light. Many peculiarities of the photoinduced phenomena can be clarified taking into account the dual action of light, which is out of the scope of this short communication.

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