PHOTOINDUCED OPTICAL CHANGES IN VACUUM DEPOSITED NANOCRYSTALLINE As$_2$S$_3$ FILMS

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The optical properties of as-deposited and illuminated till saturation As$_2$S$_3$ films with amorphous and nanocrystalline structure are followed. It is established that within the spectral range $\lambda = 400 \div 1000$ nm the crystalline samples are characterized by lower refractive index n and higher absorption coefficient k than the n, k values of the amorphous films. Besides, the optical band gap energy E_g for indirect allowed transitions in nanocrystalline samples is considerably smaller than this for amorphous ones. It is found that the photoinduced changes in the optical parameters and band gap energy are more pronounced in c-As$_2$S$_3$ films. On the basis of the results obtained the effect of granular microstructure on the optical behaviour of nanocrystalline As$_2$S$_3$ films is discussed

1. Introduction

The photoinduced changes in the physical and chemical properties of vacuum deposited a-As$_2$S$_3$ thin films have been extensively investigated for more than 30 years. Although numerous experimental studies performed the nature of these so-called "photostructural" changes remains still not quite clear [1]. Literature offers a variety of models for the mechanism of the phenomena, most of them being speculative [2]. Generally, it is believed that the photoinstability is a privilege of the amorphous state only and is due to a re-arrangement in the local order of the glassy network [3]. This assumption could be verified by following the photoinduced transformations in As$_2$S$_3$ films with crystalline structure. However, the performance of such investigations is complicated by the fact that As$_2$S$_3$ is an excellent glass former and the thin films obtained by thermal evaporation on various substrates are always amorphous [4].

Recently, we studied the possibilities for preparing of crystalline As$_2$S$_3$ films by applying some basic experimental conditions for epitaxial growth [5]. It is established that the vacuum condensation of As$_2$S$_3$ on air cleaved NaCl single crystals at extremely low deposition rate leads to the obtaining of thin films with nearly stoichiometric composition and nanocrystalline structure [6]. Thus, an opportunity for further investigations on the influence of structural disorder on the photoinduced transformations in thin As$_2$S$_3$ films has been revealed. As a first step in this direction the present paper aims to study the photoinduced changes in the optical properties of vacuum deposited amorphous and nanocrystalline As$_2$S$_3$ thin films.

2. Experimental details

The experiments were performed with thin films obtained by thermal evaporation of high

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purity As_2S_3 in a standard high-vacuum unit maintaining 5×10^{-4} Pa residual pressure. A resistively heated Ta crucible with a special design [7] was used as an evaporation source. It allowed the sublimation and evaporation of As_2S_3 without local overheating, thus preventing undesirable effects of thermal decomposition. The crystalline samples - c-As_2S_3, were grown on air-cleaved NaCl single crystals at deposition rate 0.005 nm/s. The amorphous films - a-As_2S_3, were prepared at conventional deposition rate of about 0.5 nm/s on BK-7 optical glass plates. The both kinds of substrates are transparent in visible and near IR spectral regions which is very important for accurate determination of optical constants. Besides, opaque Si substrates were additionally used in every evaporation cycle. The substrate temperature was always kept 25 °C. The thickness of crystalline and amorphous As_2S_3 films was usually 70 nm. The surface morphology of the films was inspected under a Jeol Superprobe 733 scanning electron microscope. The structure and the composition of the samples were controlled by XRD and EDS analysis in SEM (HNU – USA).

The exposure was done by a 200 W mercury lamp having light intensity on the film surface 25 mW/cm^2. The samples studied were illuminated by the lamp till saturation, i.e. to the moment when further exposure does not lead to a new shift of the absorption edge. The time of irradiation of amorphous and crystalline As_2S_3 films was determined experimentally and was 10 and 15 min, respectively.

The optical constants (refractive index n and absorption coefficient k) and physical thickness d of as-deposited and irradiated amorphous and nanocrystalline As_2S_3 films were determined by a combination of methods based on three spectrophotometric measurements - transmittance T and reflectance R_f of samples deposited on transparent substrates (BK-7 glass plates and NaCl crystals) and reflectance R_m of the corresponding films deposited on opaque Si-substartes. The transmittance and reflectance spectra were recorded by a high precision Cary 5E spectrophotometer at normal light incidence in the wavelength region $\lambda = 400 – 1000$ nm with an accuracy of 0.1 and 0.5 %, respectively. The values of n, k and d were derived from previously developed three step algorithm that ensures reliable isolation of physically correct solutions and high accuracy determination, for instance $\Delta n = \pm 0.03$, $\Delta k = \pm 0.003$ and $\Delta d = \pm 1$ nm [8]. The algorithm includes application of the so-called (TR_fR_m) algebraic inversion method [9], followed by (TR_f) and (TR_m) methods and finally a selection of the most accurate solution of each of the above methods. The first application of (TR_fR_m) method allows simultaneously determination of n, k and d. Then, the value of the film thickness obtained is used for recalculating of n and k by the more accurate (TR_f) and (TR_m) methods using Newton-Raphson iterative algorithm [10]. The combination of the most accurate solutions from each of the applied methods is accepted as final dispersion curves for n and k.

3. Results and discussion

Fig. 1 shows SEM micrographs of the surface of 70 nm As_2S_3 films deposited on NaCl single crystal (a) and BK 7 glass plate (b) at deposition rate 0.005 nm/s and 0.5 nm/s, respectively.
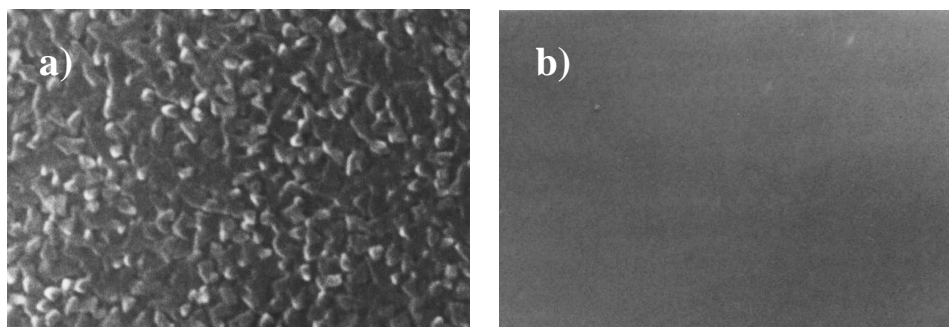

Fig. 1. SEM micrographs of the surface of 70 nm As_2S_3 films deposited on NaCl single crystal (a) and BK 7 optical glass plate (b) at deposition rates 0.005 nm/s and 0.5 nm/s, respectively.

As seen from the figure there is a great difference between the surface morphology of samples prepared at different evaporation conditions. The film grown on NaCl at extremely low deposition rate consists of randomly oriented nanocrystallities while the sample obtained at conventional deposition conditions is completely smooth. Simultaneously, the results from the EDS analysis performed showed that both samples have similar composition, very closed to the stoichiometric As/S ratio – 39.63 %at. As and 60.17 %at. S for crystalline film and 40.17 %at. As and 59.83 %at. S for the amorphous one. Besides, the XRD analysis confirmed the polycrystalline and amorphous structure of samples, presented in Fig. 1, as it has been already shown in our previous investigation [6]. Therefore, the evaporation conditions chosen really ensure the preparation of As$_2$S$_3$ thin films with similar composition and currently different structure – crystalline and amorphous. This is an important prerequisite to perform further experiments according to the aim of the paper.
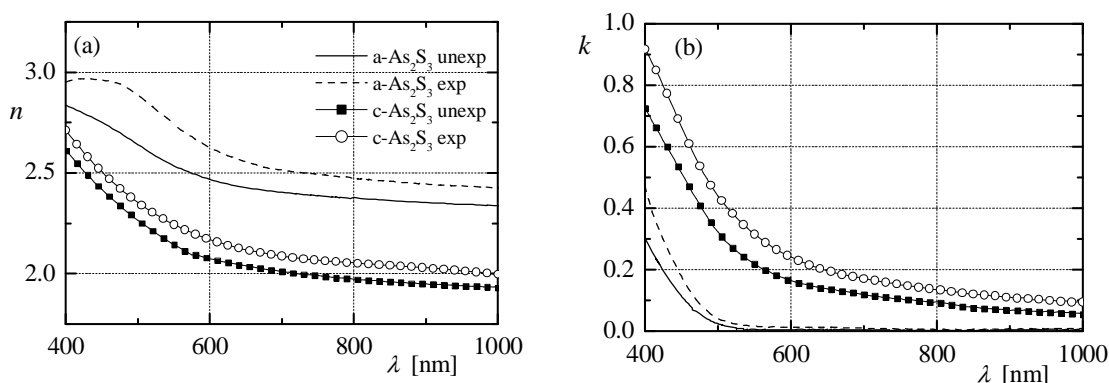

Fig. 2. Spectral dependences of refractive indices n (a) and absorption coefficients k (b) of 70 nm nanocrystalline and amorphous As$_2$S$_3$ films before and after irradiation.

Fig. 2a presents the dispersions of refractive indices n of as-deposited and illuminated 70 nm polycrystalline and amorphous As$_2$S$_3$ films. As seen from the figure in the whole spectral range studied the crystalline sample is characterised by a lower refractive index than the value for the amorphous film. Besides, the refractive indices of both kinds of samples increase after the exposure, the change being slightly higher for the amorphous film at $\lambda = 633$ nm. Therefore, a photorefraction effect, which invariably occurs in amorphous As$_2$S$_3$ films under illumination [3], is also observed in the films with nanocrystalline structure, although to a less extent.

Fig. 2b shows spectral dependences of absorption coefficients k of 70 nm amorphous and crystalline As$_2$S$_3$ films, before and after irradiation. It is seen that in the wavelength range studied the value of k is remarkably higher than this for the amorphous film. Simultaneously, the photoinduced change in this parameter is greater for c-As$_2$S$_3$ film in comparison with that for the a-As$_2$S$_3$ film. Hence, under the illumination a photodarkening effect that is well known in arsenic chalcogenides [3], not only proceeds in crystalline As$_2$S$_3$ films, but it is even stronger than the observed in the amorphous samples.

The results presented in Fig. 2 show that the optical constants of as-deposited amorphous and nanocrystalline samples differ substantially which is a demonstration of the very strong influence of microstructure on the basic physical properties of vacuum deposited As$_2$S$_3$ thin films. It should be stressed here that the difference between the optical constants of the thin films studied is just the opposite in sign than the observed between natural As$_2$S$_3$ crystal (orpiment) and bulk As$_2$S$_3$ glass, obtained by melt quenching [11]. It can be supposed that this is mainly due to the existence of some granularity effect on the optical properties of nanocrystalline As$_2$S$_3$ film. Obviously, the microstructure of this sample would involve larger free volume and more internal voids in comparison with the amorphous one, which is smooth. This would lead to increasing of the porosity and to lowering of the refractive index due to decreased density. To check the validity of this suggestion the packing density P, which is defined as the ratio of the film density ρ_f to the

bulk density ρ_b of the material, was calculated. For the purpose the Glausius-Mossotti expression [12] was used in the form

$$P = \frac{\rho_f}{\rho_b} = \frac{\left(n^2 - 1\right)}{\left(n^2 + 2\right)} \frac{\left(n_b^2 + 2\right)}{\left(n_b^2 - 1\right)}, \tag{1}$$

where n and n_b are the refractive indices at $\lambda = 633$ nm of the film and bulk material, respectively. It is established that the parameter P is really quite different for the samples studied and has values of 0.71 for c-As_2S_3 and 0.95 for a-As_2S_3 film. Thus, the results obtained demonstrate the role of granular microstructure on the optical behaviour of nanocrystalline As_2S_3 films. Simultaneously, it can be supposed that the internal voids would cause a considerable internal light scattering, which would lead to a higher effective absorption. This higher absorption would presuppose the stronger photodarkening effect in As_2S_3 film with nanocrystalline structure.

Further, the spectral dependences of linear absorption coefficients α, obtained from $\alpha = 4\pi k/\lambda$, were used for estimation of optical band gap energy E_g for illuminated and non-illuminated As_2S_3 films with amorphous and crystalline structure. As known [3], for incident photon energies above the band gap the optical absorption in semiconducting materials follows a power law:

$$\alpha = \frac{G(h\nu - E_g)^m}{h\nu} \tag{2}$$

where G is a constant, E_g is the optical energy gap and m is an exponent. The latter determines the type of electronic transitions causing the absorption and has different values for direct and indirect allowed or forbidden transitions. It has been established [13] that in amorphous chalcogenides mainly indirect allowed band transitions occur. In this case m has the value of 2 and E_g is determined according to the so-called Tauc's law [14] by plotting $(\alpha h\nu)^{1/2}$ vs. $(h\nu)$ and extrapolating the linear fit of the experimental points to $(\alpha h\nu) = 0$. In crystalline semiconductors mainly direct allowed band transitions are expected to proceed [13]. In this case $m = 1/2$ and the E_g values are estimated from the dependence of $(\alpha h\nu)^2$ vs. $(h\nu)$ in the way already described. In a nanocrystalline material, however the nature of optical transitions may be different from the bulk. This is confirmed by the curves shown in Fig. 3, which represents the dependences of $log\,(\alpha)$ on $log\,(h\nu)$ for the samples studied.
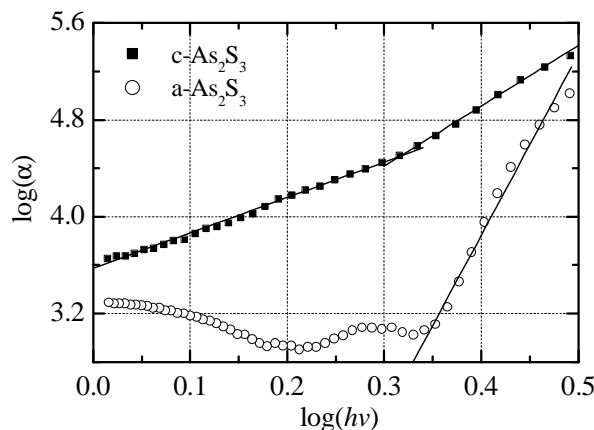

Fig. 3. *Log* (α) plotted against *log* $(h\nu)$ for 70 nm as-deposited nanocrystalline and amorphous As_2S_3 films.

As seen from the figure there is one linear part in the curve for a-As_2S_3 film while the dependence for c-As_2S_3 film has two linear parts with different slopes. This means that most probably in nanocrystalline As_2S_3 films the both types of allowed optical transitions – direct as

well as indirect, proceed. The values of E_g for as-deposited and illuminated samples studied were determined from data, presented in Figs. 4 and 5.

Fig. 4 shows the dependence of $(\alpha h\nu)^2$ on $(h\nu)$ for 70 nm c-As₂S₃ film before and after irradiation. The good fitting of the experimental points to the straight lines is clearly seen. The estimated band gap energy for direct allowed transitions in unexposed crystalline sample is 2.65 eV, which is very closed to the value, determined for natural orpiment [11]. This result is another confirmation for the crystalline nature of our As₂S₃ films. As could be expected E_g for direct optical transitions reduces after irradiation due to the occurrence of the photodarkening effect.
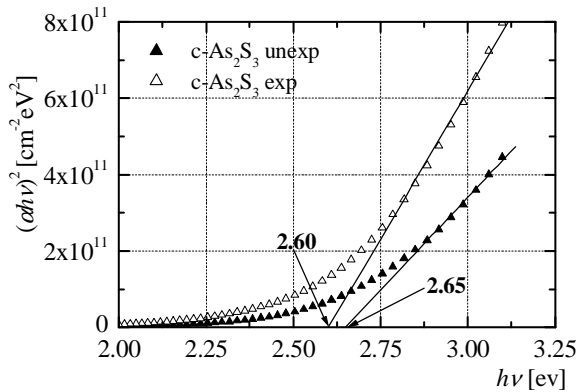

Fig. 4. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for 70 nm vacuum deposited c-As₂S₃ films before and after irradiation.
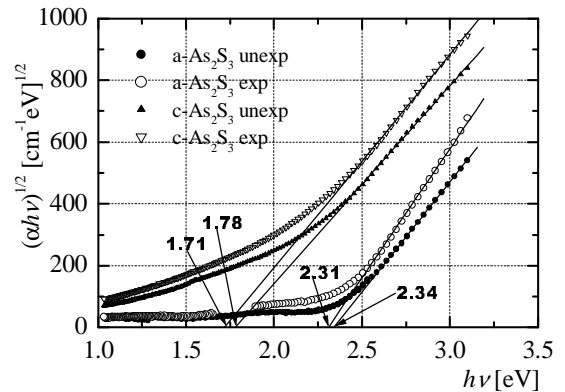

Fig. 5. Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for 70 nm vacuum deposited a-As₂S₃ and c-As₂S₃ films before and after irradiation.

Fig. 5 shows the dependences of $(\alpha h\nu)^{1/2}$ on $(h\nu)$ for 70 nm as-deposited and illuminated As₂S₃ films with amorphous and crystalline structure. As seen the experimental points for the both kinds of samples are fitted very well to straight lines. The estimated value of E_g for indirect optical transitions in a-As₂S₃ film is 2.34 eV, which is in a good coincidence with numerous previous data [2]. The value of E_g for c-As₂S₃ is 1.78 eV and is considerably smaller in comparison with that for amorphous sample. Obviously, some kind of defect states in the forbidden band exists not only in the As₂S₃ film with amorphous structure but also in the crystalline one. It should be noted that similar results have been obtained for amorphous and polycrystalline thin films of other materials, for example V₂O₅ [15], Sb₂Se₃ [16] etc. The reduced values of E_g for the crystalline counterparts of these samples were attributed to the structural disorder introduced by the intergrain boundaries. Having in mind the SEM micrographs presented in Fig. 1, this explanation seems reasonable for thin As₂S₃ films studied in the present work. Simultaneously, as seen from the figure E_g for both samples reduce after the exposure, the change being greater for crystalline film. Therefore, the photoinduced transformations associated with the photodarkening effect proceed with a higher efficiency in c-As₂S₃ film. Most probably the microstructure of these samples provides a lot of free space where light induced bond distributions and atom movements are facilitated.

Around the fundamental absorption edge the optical absorption α depends exponentially on the incident photon energy and obeys the empirical Urbach rule [13]

$$\alpha = \alpha_0 e^{h\nu/E_e} \qquad (3)$$

where α_0 is a constant and E_e is the Urbach energy, which is often interpreted as the width of the localized defect states in the band gap of the material. The values of E_e for as-deposited and illuminated samples studied were easily determined from the slopes of $ln(\alpha)$ vs. $(h\nu)$. It is found that the localized states width for a-As₂S₃ film is 0.34 eV and increases after the illumination to 0.43 eV. Having in mind that in amorphous chalcogenides the disorder is mainly due to the existence of "wrong" homopolar bonds and coordinated defects in the form of VAP's [3], it can be

suppose that the exposure increases their number. Simultaneously, the value of E_e for nanocrystalline sample is very high – 1.34 eV and does not change under irradiation. Obviously, the disorder introduced by the intergrain boundaries in c-As_2S_3 films is so strong that masks the changes associated with the formation of new bonds and/or VAP's under the action of light.

Finally, it is evident that due to the established strong influence of the microstructure on the optical behaviour of nanocrystalline films further investigations on the role of structural disorder of the amorphous state on the basic physical properties of As_2S_3 thin films and their photoinduced changes are complicated. To overcome these frustrations it is worth to find out experimental conditions for vacuum deposition of As_2S_3 films with single crystalline structure, where the effect of intergrain boundaries will be excluded. Our studies in this direction are in progress.

4. Conclusion

The present work is a first attempt to study the role of structural disorder on the photoinduced transformations in As_2S_3 thin films by comparing the optical behaviour of samples with amorphous and nanocrystalline structure. It is established that the optical constants of c-As_2S_3 thin films are quite different from that of a-As_2S_3 films with similar composition and thickness. Most probably, the existence of larger free volume and more internal voids in nanocrystalline samples leads to lowering of the refractive index and increasing of the absorption coefficient as compared to amorphous As_2S_3 films. Besides, it is found that the changes in the optical absorption and band gap energy under the illumination are more pronounced in nanocrystalline samples. Therefore, the photoinduced transformations in nanocrystalline As_2S_3 films proceed with a higher efficiency than in their amorphous counterparts. However, the existence of intergrain boundaries in the structure of polycrystalline As_2S_3 films introduces structural disorder, which is much stronger than that associated with the amorphous state. Evidently, for further investigations experimental conditions must be found for preparing of As_2S_3 thin films with single crystalline structure where the effect of granularity on their optical behaviour will be eliminated.

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