JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 1, January 2007, p. 170 - 173

Grain-size effect on the optical properties of vacuum deposited nanocrystalline As_2S_3 thin films

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The microstructure and optical properties of nanocrystalline and amorphous As_2S_3 films with thicknesses in the range 15-70 nm are followed. It is found that within the spectral interval 200-600 nm, the thickness dependencies of the refractive indices n and extinction coefficients k have different trends for both kinds of sample. It is established that the optical band gap energy, E_g, for indirect transitions is almost independent of the thickness of the amorphous films, while a strong reduction of this parameter is observed for the thickest nanocrystalline samples. Also, a fairly strong grain-size effect on the values of E_g for direct optical transitions in crystalline films is found. On the basis of the results obtained, the impact of a nanocrystalline structure on the optical behaviour of vacuum deposited As_2S_3 films is discussed.

(Received November 1, 2006; accepted December 21, 2006)

Keywords: Chalcogenide glasses, Thin films, Nanocrystalline structure, Optical properties

1. Introduction

During the past four decades, chalcogenide semiconducting materials have been intensively investigated from a scientific point of view and also for potential applications [1]. Research has mainly been focused on As_2S_3 samples, which continue to be the preferred model system for studying the problems of order-disorder, glass forming ability, intrinsic defects, photo-structural changes, etc [2]. Studies of the crystalline form of the compound has been limited to the naturally occurring material, called orpiment, since As_2S_3 is an excellent glass-former, so the synthesis of bulk samples by melt quenching or the preparation of thin films by thermal evaporation always results in a glass [3].

Recently, we succeeded in preparing crystalline As_2S_3 films by applying experimental conditions, which should lead to epitaxial growth [4]. It was established that vacuum condensation of As_2S_3 on air-cleaved NaCl single crystals at extremely low deposition rates leads to the creation of thin films with nearly stoichiometric compositions and nanocrystalline structures [5]. The first investigations of the optical properties of 70 nm thick samples showed that their optical constants are quite different from the refractive index value and extinction coefficient of orpiment [6]. Also, a surprisingly enhanced photoresponse for crystalline As_2S_3 films as compared to their amorphous counterparts was established. This unusual optical behaviour was attributed to the nanocrystalline structure of the films studied. On this basis, it could be expected that the optical properties of crystalline As_2S_3 films with different thickness would be governed mainly by the size of the nanocrystallities. The present work verifies this statement, considering the importance of such data for the nanoscience of chalcogenide semiconducting materials.

2. Experimental details

The experiments were performed with thin films obtained by thermal evaporation of high purity As_2S_3 in a standard high-vacuum unit at a residual pressure of $5x10^{-4}$ Pa. A resistively heated Ta crucible was used as an evaporation source. The crystalline - c-As_2S_3 films were grown on air-cleaved NaCl single crystals at a deposition rate of 0.005 nm/s and a substrate temperature of 25°C. The amorphous - a-As_2S_3 films, used for comparison, were prepared at a conventional deposition rate of about 0.5 nm/s on fused silica optical plates. Additionally, opaque Si substrates were used in every evaporation cycle. The thicknesses of the both kinds of sample were varied between 15 and 70 nm. The surface morphology of the films was inspected using a Philips 515 scanning electron microscope. The structures and compositions of the samples were controlled by XRD and EDS analysis in a SEM (HNU-USA).

The refractive index, n, extinction coefficient, k and physical thickness, d, of the As_2S_3 films were determined by a combination of methods based on three spectrophotometric measurements – the transmittance T and reflectance R_f of samples deposited on transparent substrates (NaCl crystals and fused silica plates) and the reflectance R_m of the corresponding films deposited on opaque Si substrates [7-9]. The T and R spectra were recorded by a high precision Cary 5E spectrophotometer at normal light incidence in the wavelength region $\lambda = 200 – 600$ nm, with an accuracy of 0.1 and 0.5 %, respectively. The values of n, k and d were derived from a previously developed three-step algorithm [9] that ensures reliable isolation of physically correct solutions and a high accuracy determination, for instance, $\Delta n=\pm0.03$, $\Delta k=\pm0.003$ and $\Delta d=\pm1$nm.

3. Results and discussion

Fig. 1 presents SEM micrographs of the surface of nanocrystalline As_2S_3 films with thicknesses of 15 (a), 35 (b), 55 (c) and 70 (d) nm, deposited on NaCl single crystals at a deposition rate of 0.005 nm/s. As seen, there is a great difference in the surface morphology of the c-As_2S_3 films with different thicknesses. The thinner samples (15 and 35 nm thick) consist of almost uniformly distributed spherical grains, with a mean diameter of 106 and 150 nm, respectively. On the contrary, films with thicknesses of 55 and 70 nm are built up of randomly oriented well-defined nano-crystallities, with mean diameters of 230 and 297 nm, respectively. Obviously, the grains sizes increase with the films' growth, and are much greater than the thickness of the corresponding samples. This can be attributed to the two-dimensional crystal growth mechanism, typical for layered crystals like natural orpiment [10]. Simultaneously, the size histograms showed that the standard deviation, from the mean size value, also increases with the film thickness, which shows a transformation of the granular structure from almost a mono-dispersed to a poly-dispersed one in the thicker c-As_2S_3 samples.

The results from the EDS analysis showed that all nanocrystalline samples have similar compositions, very close to the stoichiometric As/S ratio. Additionally, the XRD analysis confirmed the polycrystalline structure of the c-As_2S_3 films presented in Fig. 1, as has been demonstrated in our previous investigations [5].

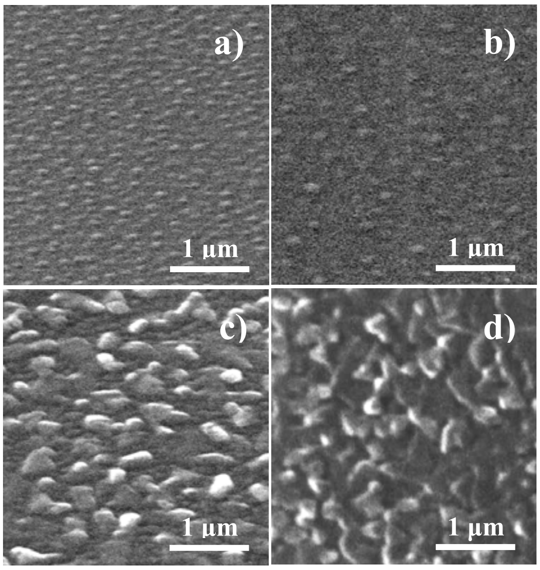

Fig. 1. SEM micrographs of nanocrystalline As_2S_3 films with thicknesses of 15 (a), 35 (b), 55 (c) and 70 (d) nm.

Consequently, the evaporation conditions used ensure the preparation of nanocrystalline samples with similar compositions and different granular surface morphologies, which are strongly influenced by the film thickness. This is an important prerequisite for revealing the grain-size effect on the optical properties of nanocrystalline As_2S_3 films.

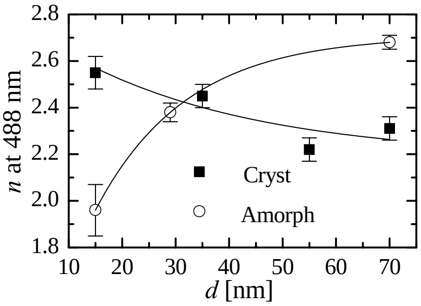

Fig. 2. Thickness dependences of the refractive index, n, at a wavelength of 488 nm for crystalline and amorphous As_2S_3 thin films.

Fig. 2 presents the thickness dependence of the refractive index, *n*, for c-As_2S_3 films at a wavelength of 488 nm, as well as the corresponding errors of *n* as vertical lines. For comparison, the *n* values of amorphous a-As_2S_3 films with the same thickness intervals are also shown in the figure. It is seen that the thickness dependences of *n* have different trends for the two types of sample i.e. increasing thickness leads to a reduction of *n* for crystalline films and to an increase for amorphous ones. Considering that the refractive index is proportional to the effective electronic polarizability and inversely proportional to the interatomic spacing, in the case of similar stoichiometry the changes of *n* can be directly related to changes in the film density [11]. This was confirmed by the values of the packing density, *P*, defined as the ratio of film density to material bulk density, calculated using the Clausius-Mossotti expression [11]. The thickness dependences of the parameter *P* for nanocrystalline and amorphous As_2S_3 films are presented in Fig. 3. As seen, the values of *P* increase with the thickness of the a-As_2S_3 films while the opposite relationship is established for c-As_2S_3 samples. Obviously, during the c-As_2S_3 films' growth, the free volume and internal voids increase, thus reducing the density and therefore the refractive index. Thus, the results obtained demonstrate the impact of the granular microstructure on the optical behaviour of crystalline As_2S_3 films.

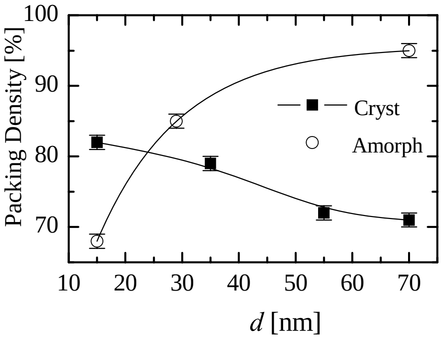

Fig. 3. Thickness dependences of the packing density for crystalline and amorphous As_2S_3 thin films.

Simultaneously, our calculations showed that the extinction coefficients, *k*, of nanocrystalline samples are greater than the values of *k* for the corresponding amorphous films. Also, the observed difference is more pronounced for the thickest c-As_2S_3 films. Most probably, the higher porosity of these samples pre-supposes the existence of a larger free volume and more internal voids, which cause considerable internal light scattering and consequently a higher effective absorption.

Furthermore, the influence of a nanocrystalline structure on the optical band gap energy, E_g, of the As_2S_3 films was studied. As is known, in amorphous semiconductors mainly indirect allowed band transitions occur [12]. In this case E_g^{ind} is determined from spectral dependence of the linear absorption coefficient $\alpha=4\pi k/\lambda$ according to Tauc's law [12] 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 the E_g^{dir} 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 the optical transitions may be different from those for the bulk [13]. This was demonstrated in our previous paper for 70 nm thick As_2S_3 films with nanocrystalline and amorphous structures [6]. It was established that in c-As_2S_3 films, two types of allowed transition - direct as well as indirect - proceed, while in amorphous samples only indirect band transitions occur. The same results were obtained for nanocrystalline and amorphous As_2S_3 films with different thicknesses, as studied in the present work.

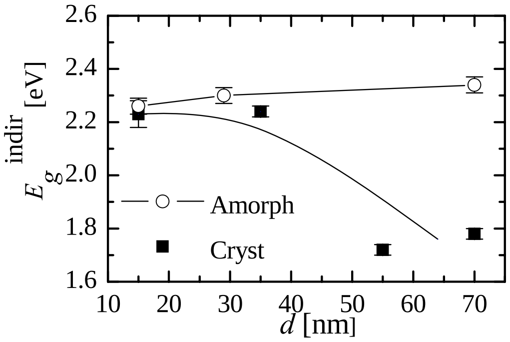

Fig. 4. Thickness dependences of the optical band gap for indirect allowed transitions for crystalline and amorphous As_2S_3 thin films.

Fig. 4 presents the dependencies of E_g^{ind} on the thickness of crystalline and amorphous As_2S_3 films. As seen, E_g^{ind} for amorphous films is almost independent of the thickness, while for crystalline films, a strong reduction of the E_g^{ind} values is observed for the thicker samples. It should be noted that similar results have been obtained for amorphous and crystalline thin films of other semiconducting materials, for example V_2O_5 [13], Sb_2Se_3 [14] etc. The reduced values of E_g for the crystalline counterparts of these samples were attributed to the structural disorder introduced by the inter-grain boundaries. Having in mind the SEM micrographs presented in Fig. 1, this explanation seems reasonable for the c-As_2S_3 films studied in the present work. Obviously, in the thickest c-As_2S_3 films where the polycrystalline structure is the most pronounced, the influence of the inter-crystalline boundaries on their optical behaviour is the strongest.

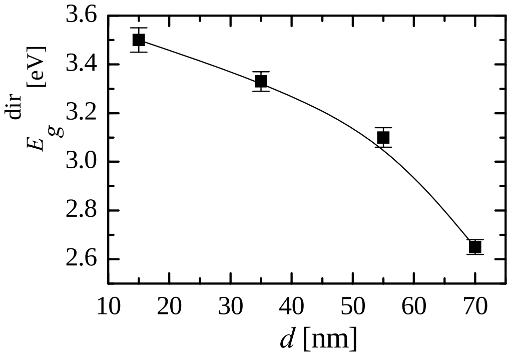

Fig. 5. Thickness dependence of the optical band gap for direct allowed transitions for crystalline As_2S_3 thin films.

Fig. 5 shows the thickness dependence of optical band gap, E_g^{dir}, for direct transitions in c-As_2S_3 films. The estimated value for a 70 nm thick film is 2.65 eV, which is very close to the value for natural orpiment [10]. However, with decreasing films thickness, respectively to the grains size, a strong increase of E_g^{dir} is observed. The obtained value of 3.50 eV for the thinnest c-As_2S_3 film is much higher than the value for the bulk crystal, manifesting a fairly strong size effect, observed in polycrystalline films of other semiconductors [15]. Thus, the results obtained demonstrate the common regularities in the optical behaviour of semiconducting films, with thickness laying on the nanoscale.

4. Conclusions

The results of the present study show that the optical properties of nanocrystalline As_2S_3 films, with thicknesses in the range 15 – 70 nm, are strongly influenced by their granular surface morphology, and differ substantially from those of amorphous samples with similar compositions and thicknesses. Obviously, the free volume and internal voids within the crystalline samples increase with increasing film thickness, leading to a lowering of their densities and refractive indices. Simultaneously, the granular microstructure affects notably the light absorption in the c-As_2S_3 films, especially in the thickest ones. This is confirmed by the established strong decrease in the optical band gap energy E_g for indirect transitions in these films, which can be attributed to an increase of the structural disorder introduced by the intergrain boundaries. Furthermore, a fairly strong grain-size effect on the values of E_g for direct transitions in c-As_2S_3 samples, observed in many other semiconducting films with nanocrystalline structures, has been found. Hence, the results obtained demonstrate the possibilities of controlling the optical behaviour of As_2S_3 thin films by varying their thickness in the nanoscale, and thus contribute to the nanoscience of chalcogenide semiconducting materials.

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