Structural characteristics and optical properties of zinc selenide thin films

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Zinc selenide (ZnSe) thin films (d = 0.10 – 1.20 μm) were deposited onto glass substrates by the quasi-closed volume technique under vacuum. The film structure was studied by X-ray diffraction technique, transmission electron microscopy and atomic force microscopy. The investigations shown thin films are polycrystalline and have a cubic structure. It was experimentally found that the films with stable structure and reproducible properties can be obtained if they were subjected to a heat treatment. The spectral dependences of transmission and absorption were studied. Optical energy gap, calculated from the absorption spectra for the studied samples was in the range E_g = 2.42 – 2.72eV. These values are in a good agreement with the values of E_g obtained for bulk ZnSe crystals.

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1. Introduction

Zinc selenide (ZnSe) is an important II – VI semiconductor material with many interesting characteristics (large energy bandgap, low electrical rezistivity, high optical transparency, photosensibility, etc.). Consequently, this compound offers a large variety of applications such as photodetectors, thin-film solar cells, blue light-emitting devices, etc. For the past few years many studies have been focused on the electronic transport and optical properties of ZnSe crystals. But the information on the properties of ZnSe thin films one rather few [1-3]. In a series of previous papers [4-6], we have investigated some electrical properties of ZnSe thin films deposited by quasi-closed volume technique under vacuum.

In this paper we extended these investigations by studying some structural and optical properties on the deposition conditions and post-deposition heat treatment.

2. Experiment

ZnSe thin films were prepared onto glass substrates by physical vapour deposition under vacuum ($p < 10^{-5}$ Torr) of high-purity ZnSe single crystals. The quasi-closed volume technique was used [4,7].

The samples were prepared using the following deposition parameters: sourse (evaporator) – substrate distance was 8 cm; sourse temperature, T_{ev}, ranged between 1000 K and 1300 K; deposited rate, r_d, ranged from 1.2 nm to 1.7nm; substrate temperature, T_s, was varied between 300 K and 600 K.

The experimental arrangement and deposition technique used for preparation of ZnSe films are in detail described in [5-7].

Film thickness was determined by an interferometric method and for studied samples ranged between 0.12 μm and 1.23 μm.

The film structure was examined by X – ray diffraction technique (using DRON-2 diffractometer CoK_α and CuK_α radiations) and transmission electron microscopy (using a PHILIPS CM 120 ST microscope).

The temperature dependences of the electrical conductivity and Seebeck coefficient were studied using surface – type cells [4].

The reflection and transmission spectra (in the range from 300 nm to 1400 nm) were recorded using a PMQ – II (Carl Zeiss, Jena) spectrophotometer.

The absorption coefficient, α, was determined from the following expression [3, 4, 8]

$$\alpha = \frac{1}{d} ln\left[\frac{(1-R_\lambda)^2}{T_\lambda}\right] \quad (1)$$

were d denotes film thickness, and R_λ and T_λ are reflection and transmission coefficient, respectively, at wavelength λ.

3. Results and discussion

The XRD (Fig. 1) and TEM (Figs. 2 and 3) patterns indicate that the samples are polycrystalline and have a cubic (zinc blende) structure. These patterns also reveal that as-deposited samples are characterised by a preferential orientation of the crystallites with the (111) planes parallel to the substrate surface

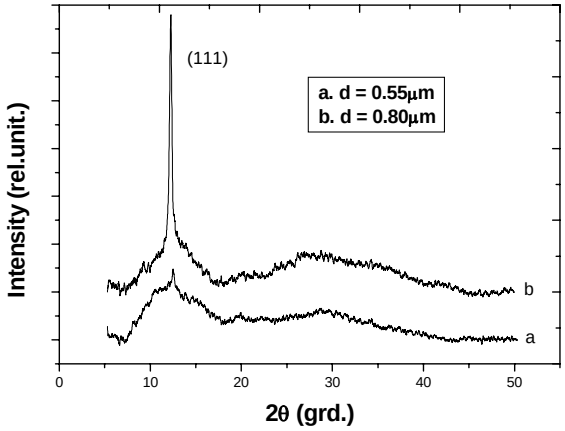

Fig. 1. X – ray diffraction patterns for ZnSe thin films.

The TEM patterns for films with different thickness (Figs. 2 and 3) show that the films with greater thickness are characterized by a higher orientation degree of crystallites.

The lattice parameter of ZnSe cubic structure, calculated from the XRD – patterns, is a = 5.667Å and do not vary semnificantly after heat treatment.

The separation of the planes with inces Miller (111) is d_{111} = 2.212 Å (for CuK_α radiation, λ = 1.5418 Å) and d_{111} = 3.196Å for CoK_α (λ = 1.790 Å).

These values are in good agreement with the values obtained for bulk ZnSe samples [1-3].

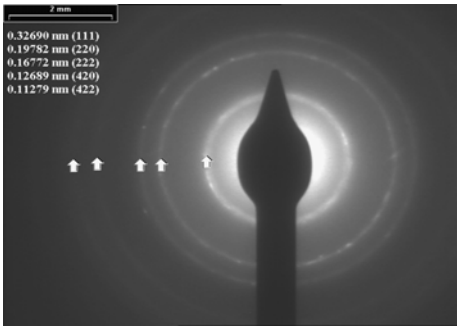

Fig. 2. TEM pattern for ZnSe thin film (sample 224, d = 0.83μm, T_s = 400K, r_d = 1.54nm/s).

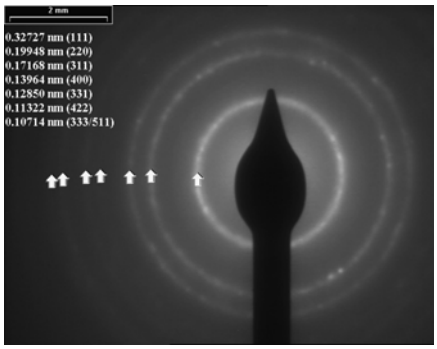

Fig. 3. TEM pattern for ZnSe thin film (sample 332, d = 1.50μm, T_s = 500K, r_d = 1.95nm/s).

In Fig. 4 and 5 are presented typical AFM images for two investigated samples. We observe that the grains have similar size and shape. The presense of pin holes in the studied films is not observed. The crystallite size are strongly influenced from the deposition conditions

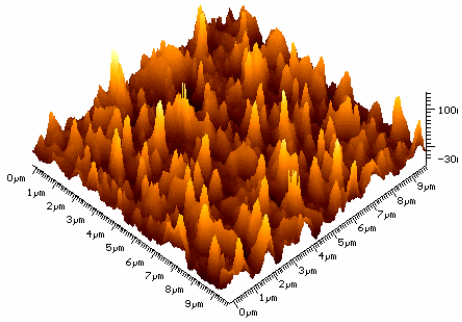

Fig. 4. AFM images for ZnSe thin film (sample 135, d = 0.98μm, T_s = 300K, r_d = 1.62nm/s).

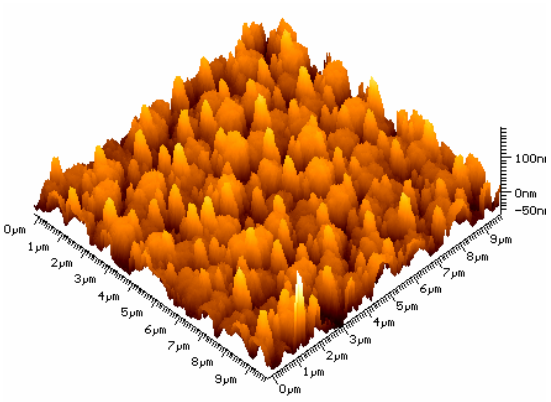

Fig. 5. AFM images for ZnSe thin film (sample 224, d = 0.83μm, T_s = 400K, r_d = 1.54nm/s).

It is known that during the thermal evaporation process, the II – VI semiconducting compound dissociated into the components (Zn atoms and Se_2 molecules) [3] which recombine and form the respective compound at the substrate. An incomplete recombination of the components on the substrate may lead to non-stoichiometric films [3]. The used arrangement for deposition and postdeposition heat treatment permit to obtain homogenous and stoichiometric films.

The presence of excess atoms in the films can be evidenced by measuring the optical transmission of the respective films [5]. The pure compound has a sharp transmission (absorbtion) edge at that wavelength which corresponds to the forbidden gap of semiconductor [4, 5].

For two studied samples the destribution curves of crystallite size are illustrated in Figs. 6 and 7. The curves were fitted with lognormal functions (fitting parameters are indicated in respective figures).

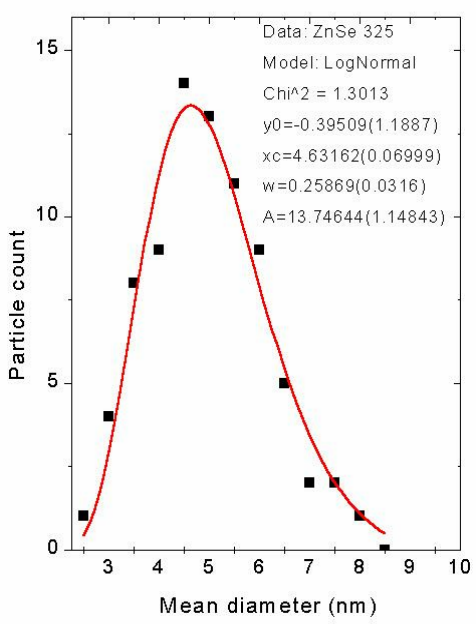

Fig. 6. Distribution curve of crystallite size for ZnSe thin film: (Sample 325, d = 1.14μm, T_s = 500K, r_d = 1.73nm/s).

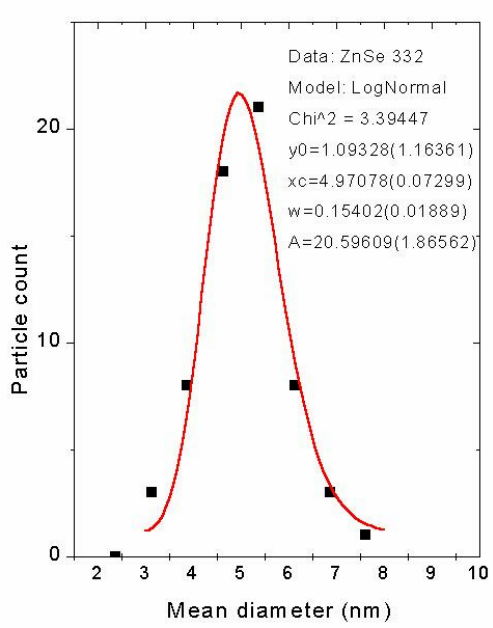

Fig. 7. Distribution curve of crystallite size for ZnSe thin film: (Sample 332, d = 1.54μm, T_s = 500K, r_d = 1.95nm/s).

In previous papers [4-6] we studied the temperature dependence of the electrical conductivity and Seebeck coefficient. The mechanism of electrical conduction has been discussed in terms of Seto-s model for polycrystalline semiconducting films, with several modifications proposed by Baccarani et. al. [9-12].

In the temperature range 350 – 450K, the Seebeck coefficient is negative and decreases with increasing temperature.

Transmission and absorption spectra are strongly influenced from the deposition conditions, especially from substrate temperature.

The influence of heat treatment on the shape of the transmission spectra is presented for two samples in Figs. 8 and 9. For other samples under study the similar behaviors were found.

For heat-treated samples with small thicknesses (d < 0.4 μm) the transmission coefficient is greater than those for untreated samples (Fig. 8) [5] This fact has been explained by assuming that the heat treatment has as result an increase of the crystallite size and a decrease of the concentrations of impurities (excess atoms) and structural defects. In the case of the films with greater thickness the heat treatment little influences transmission spectra (Fig. 9).

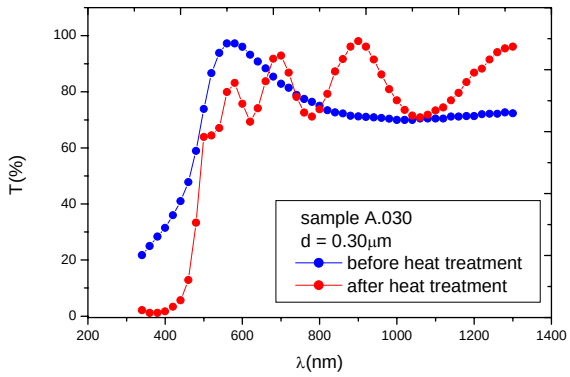

Fig. 8. Influence of heat treatment on the transmission spectra (sample A.030).

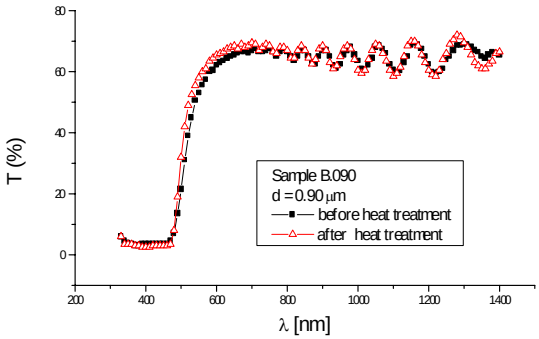

Fig. 9. Influence of heat treatment on the transmission spectra (sample B.090).

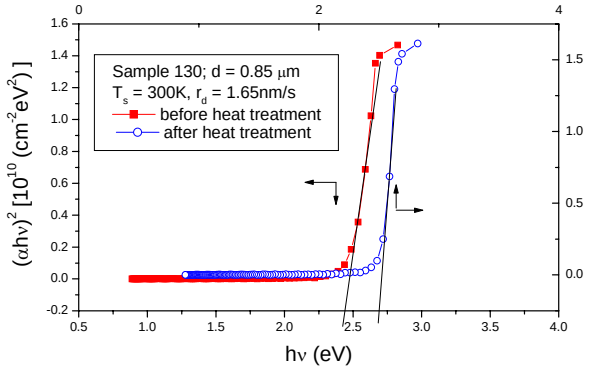

Fig. 10. Absorbtion spectra for ZnSe thin film.

For one films absorption spectra are presented in Fig. 10. From transmission spectra, the absorption coefficient as a function of photon energy was calculated and has been plotted for allowed direct transitions (neglecting exciton effects) by using the expression [4, 8, 12]

$$\alpha = \frac{A_a}{(h\nu)}\left(h\nu - E_{go}\right)^{1/2} \qquad (2)$$

where hν is photon energy, E_{go} denotes the optical energy bandgap and A_a is a characteristic parameter (independent of photon energy) for respective transitions.

Consequently, according to Eq. 2, the $(\alpha h\nu)^2 = f(h\nu)$ dependences are linear. Fig. 9 shows that for studied samples the depedences of $(\alpha h\nu)^2$ as a function of photon energy hν, indicates the direct nature of band-to-band transitions.

The values of optical band gap, E_{go}, have been determined by extrapolating the linear portions of respective curves to $(\alpha h\nu)^2 \rightarrow 0$. For the studied samples these values (E_g = 2.42 – 2.72 eV) are in a good agreement with the values of E_g obtained for bulk ZnSe crystals [1, 2]. These values have been used for estimation of activation energy of electrical conduction according to Seto's model.

4. Conclusions

Structural investigations shown that ZnSe films deposited by the quasi-closed volume technique under vacuum are polycrystalline and have a zinc blende structure. A preferential orientation of film crystallites with (111) planes parallel to the substrate was observed. In order to obtain samples with stable structure and reproducible properties all films were subjected to a heat treatment.

The results show a marked influence of heat treatment on the transmission and absorption spectra. The optical energy bandgap (supposing optical allowed transitions) is ranged 2.42 eV – 2.72 eV, which is in good agrement with the values of bandgap obtained for bulk ZnSe.

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