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Effect of Zn:Se ratio and of the heat-treatment on the optical properties of multi-stacked Zn/Se nanolayered thin films

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Zn/Se multilayered thin films (*d* = 230 – 450 nm) have been evaporated in the vacuum onto unheated glass substrates by multi-stacked technique. The Se source temperature varied in the 850 K – 900 K range whereas that for Zn evaporation source was of 723 K. The effect of Zn:Se ratio on the optical and structural properties of the as grown and heat-treated samples was investigated. The structural characteristics have been analyzed by XRD and AFM techniques. Both as-deposited and heated samples are amorphous. The film heating up to temperature of 540 K determines the formation of yellowish-like highly transparent ZnSe films. The optical measurements in the wavelength range 380 – 1100 nm revealed that such ZnSe films are characterized by an optical band gap of about 2.8 eV.

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1. Introduction

Zinc selenide (ZnSe) have attracted considerable interest due to their important properties (it has a wide direct band gap, E_g, of 2.7 eV, a remarkable photosensitivity, it is transparent over a large range of visible spectrum, it can be prepared in both n- and p-type conduction, etc) that make them a promising material for fabrication of thin film devices such as the blue-green light emitting diodes, photodetectors, multi-layer tandem solar cells, etc.

The quality of respective devices is strongly influenced by the physical properties of the component films, which in their turn are dependent on the deposition technology used for the film preparation. Also, the film stoichiometry can play an important role in the determining of the electrical and optical properties of ZnSe thin films [1]. Usually, ZnSe films have been grown by molecular beam epitaxy [2], electro-deposition [3, 4], thermal evaporation in vacuum [5 – 7], spray pyrolisis [8], laser assisted evaporation [9], atomic layer deposition [10], photochemical deposition [11], etc. In this paper, the Zn/Se nanolayered films evaporated under vacuum by multi-stacked method are studied. The effect of Zn:Se ratio and the heat treatment on the optical properties of such samples was investigated.

2. Experimental

The studied films (*d* = 230 – 450 nm) were deposited under vacuum onto glass substrates at room temperature using multi-stacked method [12]. The film substrates have been fixed to a rotating holder which passed successively over the Zn and Se evaporation sources. These are separated between them by two vertical glass cylinders which close the space between each source and substrates holder. In order to prepare the sample with different Zn:Se ratio, the Se source temperature, T_{Se}, was varied between 850 K and 900 K, whereas, those for Zn source was maintained constant at 723 K.

Using a special mask and an appropriate arrangement of the glass slides on the holder, some Zn/Se samples with variable Se content along the sample were deposited. Also, both Zn/Zn and Se/Se multilayered reference samples were deposited simultaneously with different Zn/Se samples.

The thickness of the individual sub-layers deposited in each step were of about of 0.3 nm for Zn and of 1.2 – 2.5 nm for Se sub-layers, respectively, and have been estimated by taking into account the rotation speed of the substrates holder, the deposition times and the thicknesses of the corresponding reference samples.

In order to investigate the effect of the heat-treatment on the optical and structural properties of as-grown Zn/Se films, some of them were heated in ambient atmosphere, from room temperature to final 540 K, with a temperature rate of 5 K/min. During this heat treatment, the color of Zn/Se films changes from reddish (at room temperature) to yellowish-like transparent aspect.

The structural characteristics of the as-grown and heat-treated samples were investigated by atomic force microscopy (AFM) and X-ray diffraction (XRD) technique, in the 2θ range 20° – 90°, with CuK_α radiation.

The transmission and absorption spectra for investigated samples were studied in the wavelength range 380 – 1100 nm.

3. Results and discussion

3.1. Optical properties

In Fig. 1, the transmission spectra for three typical Zn/Se samples deposited at different Se source temperatures, T_{Se}, are shown. It can be observed that the increase of T_{Se} determines the increase of film transmittance. This behavior can be correlate with the decrease of Zn:Se ratio due to the increase of Se content in the films.

It is known that the optical properties of the thin films can be influenced by their evaporation conditions, particularly by the evaporation source temperature [13].

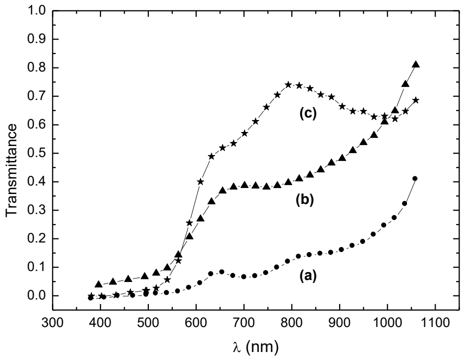


Fig. 1. Transmission spectra for three typical as-grow Zn/Se films deposited at different Se source temperatures: (a) – 850 K; (b) – 875 K; (c) – 900 K.

From this reason, for confirmation of the above conclusion regarding the effect of Zn:Se ratio on the transmission spectra, the optical measurements were recorded on different points of one and the same Zn/Se films with Se content varying along the sample.

In Fig. 2, the optical transmittance recorded at different point of such as-grown film, deposited at temperature T_{Se} = 900 K are ilustrated. In the same figure, the transmittance spectra both of Se and Zn reference samples, deposited simultaneously with respective Zn/Se film are presented. It can be observed that the film transmittance increase with decrease of Zn:Se ratio. Similar results were obtained for Zn/Se sample deposited at temperature T_{Se} of 875 K and 850 K respectively. A such decrease of transmittance with the increase of Zn:Se ratio, in the range of 0.2 - 0.4, for ZnSe films prepared by spray pyrolisis were also observed by Oztas et al. [8].

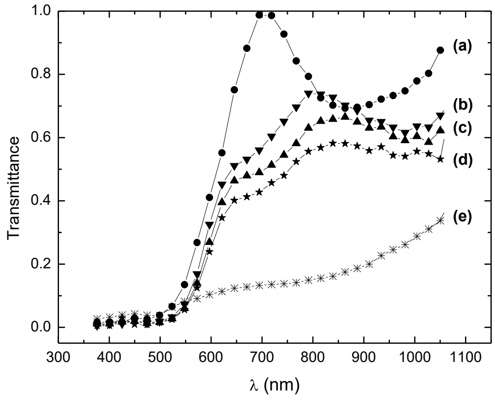


Fig. 2. Transmission spectra recorded in different points on the as-deposited Zn/Se sample with variable Se content (T_{Se} = 900 K) (a) Se reference sample; (b) Zn:Se – 0.12; (c) Zn:Se – 0.13; (d) Zn:Se – 0.14; (e) Zn reference sample.

The effect of heat-treatment on the transmission spectra for different Zn/Se samples was investigated. In Fig. 3 the transmittance before and after heat-treatment, for a sample with varying Se content, deposited at T_{Se} = 850K are presented. An increase of film transmittance as consequence of the heat-treatment can be observed. This fact can be attributed to the increase of the content of ZnSe compound in respective sample. Indeed, the increase of film heating temperature determines on the one side the evaporation of the highly volatile selenium and on the other side the increase of ZnSe content as consequence of the interaction between remaining free Zn and Se atoms in the sample. The color change of the as-deposited films from reddish (at room temperature) to yellowish-like transparent aspect, specific for ZnSe thin films [6], confirm the above assumption.

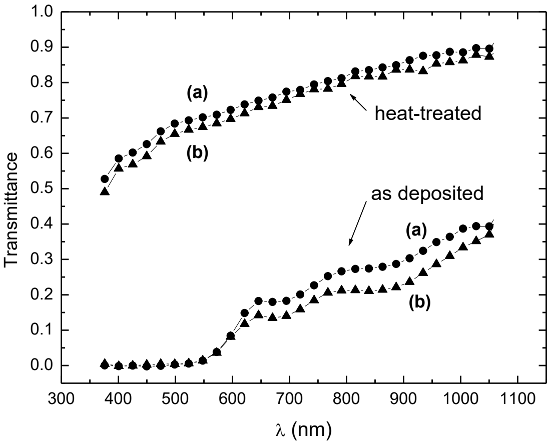


Fig. 3. Transmission spectra for Zn/Se film with variable Se content before (bottom) and after (top) heat-treatment (T_{Se} = 850 K), Zn:Se ratio: (a) — 0.21; (b) – 0.23.

From the transmission spectra, the absorption coefficients were calculated for different samples. Assuming allowed direct transitions, the dependence $(\alpha h\nu)^2$ *vs.* $h\nu$ for two typical films before and after their heat-treatment is plotted in Fig. 4. By extrapolating the linear portion of respective plots to $(\alpha h\nu)^2 = 0$, the values of the optical band gap energy, E_g, were calculated.

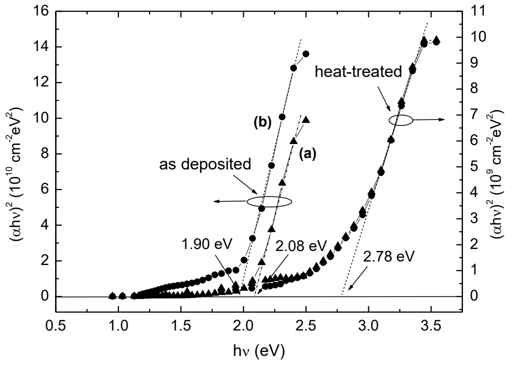


Fig. 4. The dependences $(\alpha h\nu)^2$ vs. $h\nu$ before and after heat-treartment for two typical as-grow Zn/Se films deposited at different Se source temperatures: (a) – 850 K; (b) – 900 K.

On can be observe that the as-deposited Zn/Se samples are characterized by different values for E_g. The samples deposited at higher value for T_{Se} (900 K) present a relative higher value for E_g (2.08 eV) in comparison with that of 1.90 eV obtained for as-deposited samples evaporated at lower T_{Se} temperature (850 K). After heat-treatment, both typical samples are characterized by the almost the same value of 2.78 eV for E_g, characteristic for bulk ZnSe sample [14]. This indicates that in the both case, the heat-treatment determines the evaporation of Se excess and the formation of ZnSe compound. The measurements of the film thicknesses after their heat-treatment revealed a decrease with about 1/3 of the film thickness and confirm the above assumption. A looses in weight by heating in air of the ZnSe was revealed by other researchers [15] and was also attributed to the evaporation of highly volatile selenide.

The E_g value of 2.78 eV obtained for heat-treated samples is quite close to the accepted room temperature value of 2.7 eV for ZnSe and is in concordance with similar results reported by other researchers for ZnSe films deposited by different techniques [6, 8].

3.2. Structural properties

The structural characteristics of the both as-deposited and heat-treated samples, were analyzed by the XRD and AFM techniques.

In Fig. 5 the typical XRD patterns obtained for reference Se films and for the as-grown and heat-treated Zn/Se films are shown, respectively.

It may be observe that the Se reference sample present a nanocrystalline structure while the Zn/Se films are amorphous. The heat treatment does not influences significantly this structure. These results can be explained both by the quasi-amorphous structure of Se films deposited onto unheated glass substrates [16] and by the nanolayered structure of the Zn/Se as-deposited samples. The presence of Zn sublayers between Se layers in such structures limits the grown of larger Se or ZnSe crystallites and determines many structural defects.

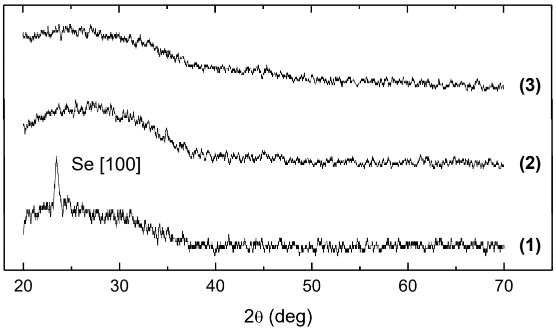
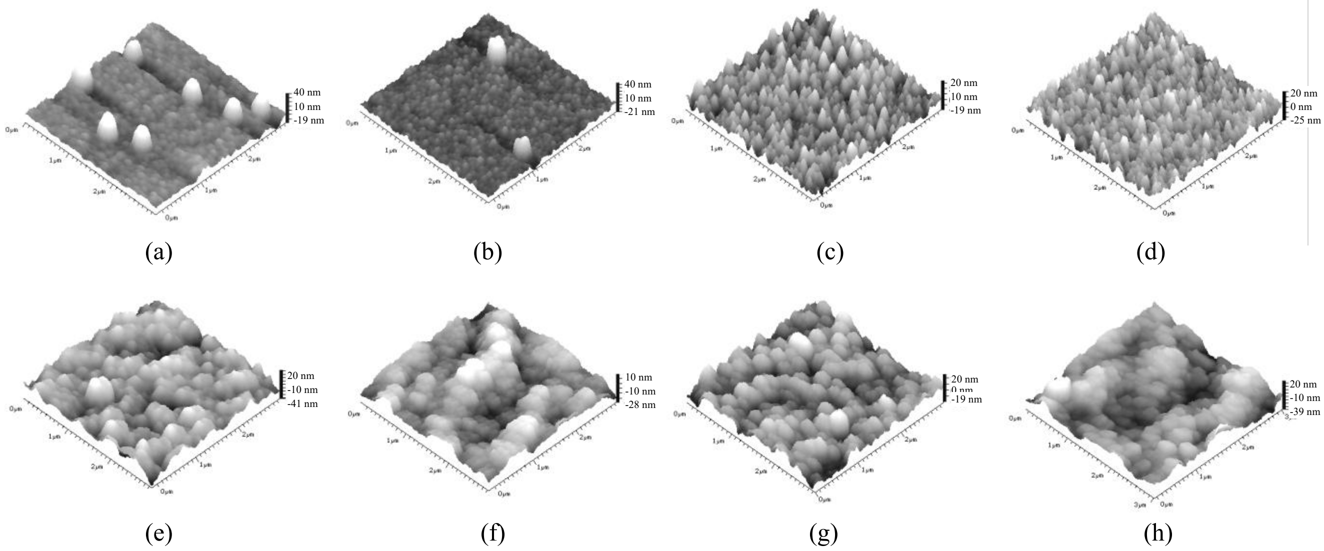


Fig. 5. Typical XRD patterns for studied films (T_{Se} = 850 K): (1) – Se reference sample; Zn/Se film before (2) and after (3) heat-treatment.

In order to study the effect of the Zn:Se ratio on the surface morphology of the studied films, some AFM micrographs obtained in different points of a Zn/Se sample with variable Se content were analyzed. In Fig. 6, the respective micrographs are presented for the Zn/Se sample before and after their heat treatment. The analysis of the micrographs from Fig. 6 indicates that the surface morphology of the as-deposited Zn/Se films is influenced by the value of the Zn:Se ratio from respective sample. On can observe that the surface morphology of the film after annealing is practically the same in all positions on the sample. This can be attributed to the evaporation of Se excess and formation of ZnSe structure. These results confirm the conclusion from § 3.1.



(a) (b) (c) (d)

(e) (f) (g) (h)

Fig. 6. AFM micrographs (3x3 μm) for different positions on the Zn/Se sample with variable Se content (T_{Se} = 850 K), Zn:Se ratio: (a, e) – 0.18 ; (b, f) – 0.19; (c, g) – 0.23; (d, h) – 0.24 (top – as deposited; bottom – heat treated).

4. Conclusions

In the paper, the optical and structural characteristics of the multi-stacked Zn/Se nanolayered films were investigated. The effects of Zn:Se ratio and of the heat treatment on these properties were studied.

The as-deposited samples present an amorphous structure which practically is not affected by the heat-treatment. The increase of the Se evaporation source temperature from 850 K to 900 K determines an increase of the film transmittance from about 10 % (for T_{Se} = 850 K) to about 70 % (for T_{Se} = 900 K). The heat treatment determines an increase of the film transmittance up to 85 % and a three times decrease of the optical absorption. An increase of the optical band gap from about 2 eV to 2.8 eV as consequence of the heat treatment was also observed.

The obtained results revealed that the multi-stacked method used for preparation of multilayered Zn/Se thin films and the post-deposition heat treatment of such structures can be a promising method to obtain amorphous and transparent ZnSe thin films for different technological applications.

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