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Some physical investigations on $ZnS_{1-x}Se_x$ films obtained by selenization of ZnS sprayed films using the Boubaker polynomials expansion scheme

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ABSTRACT

$ZnS_{1-x}Se_x$ thin films have been grown by selenization process, applied to ZnS sprayed thin films deposited on Pyrex glass substrates at 550 °C. The crystal structure and surface morphology were investigated by the XRD technique and by the atomic force microscopy. This structural study shows that selenium-free (x=0) ZnS thin films, prepared at substrate temperature T_S=450 °C, were well crystallized in cubic structure and oriented preferentially along (1 1 1) direction. The thermal and mechanical properties were also investigated using a photothermal protocol along with Vickers hardness measurements. On the other hand, the analyze of the transmittance $T(\lambda)$ and the reflectance $R(\lambda)$, optical measurements of these films depicts a decrease in the band gap energy value E_g with an increase in Se content (x). Indeed, E_g values vary from 3.6 to 3.1 eV.

1. Introduction

The II–VI semiconductors are important compounds, which have been investigated for their numerous applications especially in light-emitting and laser diodes and as Cd-free buffer layer in solar cells [1–3]. ZnSe/$ZnS_{1-x}Se_x$ heterostructure has received a great deal of interest in optoelectronic devices such as a blue semiconductor laser with high optical power output and differential quantum efficiency at room temperature [4]. In the same way, thin films of $ZnS_{1-x}Se_x$ ternary materials by altering the energy band gap and the lattice constant and electron affinity by changing the mole ratio of S to Se, could be better than ZnSe for application as a buffer layer for CIS and p-CdTe solar cells (e.g., n-ZnSe/p-CdTe solar cell has an efficiency greater than 11% [1]). Films of $ZnS_{1-x}Se_x$ material have been prepared by different methods such as: spray pyrolysis [5], epitaxy [6], atomic layer epitaxy [7], high pressure sputtering [8] and metalorgano vapour phase epitaxy [9].

In this study, the spray pyrolysis system of aqueous solution has been selected to prepare ZnS thin films. Second, an annealing treatment in selenide atmosphere has been performed in order to change S–Se ratio. $ZnS_{1-x}Se_x$-obtained thin films were characterized by the X-ray diffraction (XRD) and the atomic force microscopy (AFM).

2. Experiment

2.1. Films preparation

First, ZnS thin films, having 1 μm as thickness, were obtained on $20 \times 10 \times 3\ mm^3$ Pyrex glass substrates by spraying an aqueous solution containing zinc chloride ($ZnCl_2$, 0.1 M) and thiourea ($SC(NH_2)_2$, 0.1 M) as precursors. The solution and gas flow rates were kept constant at $2\ cm^3\ min^{-1}$ and $4\ l.min^{-1}$, respectively, corresponding to a mini-spray pyrolysis. Nitrogen was used as the carrier gas to avoid chemisorptions of oxygen. The substrate temperature T_s, of the order 450 °C was used to prepare these films because in our laboratory successful deposition of

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such films by the spray pyrolysis process was achieved; thanks to a careful control of the spray conditions [10].

Second, ZnS thin films were introduced with Se grain (99.98% of purity) into a Pyrex tube, then this tube is sealed under vacuum (10^{-3}–10^{-4} Pa) and annealed during various time (0.5–48 h) at 550 °C using a programmed tubular oven. The selenide pressure is assumed to be less than 5.10^2 Pa. This temperature is selected as a suitable annealing temperature for chalcogenide element [10,11].

The films are named A, B, C, D and E corresponding to pure ZnS film (A) and annealed films at 0, 0.5, 1, 12 and 48 h, respectively.

2.2. Characterization techniques

The X-ray diffraction spectra were obtained by means of a diffractometer (SIEMENS D5000) using monochromatic CoK_α radiation (λ=1.78901 Å). The surface topography and cross-sections of the films were examined by the atomic force microscopy (AFM) using a VEECO digital instrument 3 A microscope in contact mode.

On the other hand, optical measurements of transmittance and reflectance spectra at near normal incidence were performed, over a large spectral range (350–1800 nm), on all prepared films, using a Shimadzu 3100S spectrophotometer. The apparatus was equipped with an integrating sphere, which was used for the measurement of specular reflection attachment.

Finally, ZnSSe thin films have been characterized by electron microscope analysis (EPMA). A software program (PGI-IMIX PTS) performed the background correction and gave the percentage of each element.

3. Results and discussion

3.1. X-ray analysis

The X-ray diffraction spectra shown in Fig. 1 concern ZnS unannealed and annealed thin films under Se atmosphere. The diffractogram of unannealed film shows in addition to (1 1 1) principal orientation the presence of others peaks such as (2 2 0) and (3 1 1) corresponding to cubic structure (JCPDS no 5-0566). In Table 1, we summarized the reticular distance of (1 1 1) principal orientation and lattice constant as a function of the selenization time. These results depict that the formation reaction of Zn–S–Se material goes on slowly and may require a thermodynamic activation with the annealing time. Thus, for annealed films at 12 and 48 h, we remark the appearance of novel diffraction peaks having other reticular distances, (d_1=1.9357 Å, d_2=1.6480 Å) which are not belonged to ZnS or ZnSe materials.

The (2 2 0) and (3 1 1) peaks are indeed related to the formation of ternary compounds when the selenization occurs for ZnS sprayed films, which are exposed to a long selenization time. On the contrary, for B and C samples the percentage of Se content is less than 10%; that is why these peaks do not appear in the XRD spectra.

Moreover, the (1 1 1) direction remains very strong and the full-width at half-maximum (FWHM),which is very small (less than 0.3°) shows a good crystalline state of all films, Table 2. This phenomenon concerning the shift in the reticular distance can be explained by the formation of the ternary compound and the incorporating of Se that comes via this annealing process in the place of sulphur and not to the presence of very small zinc selenide domains randomly distributed in the polycrystalline matrix. In the same line, the result regarding the calculation of the

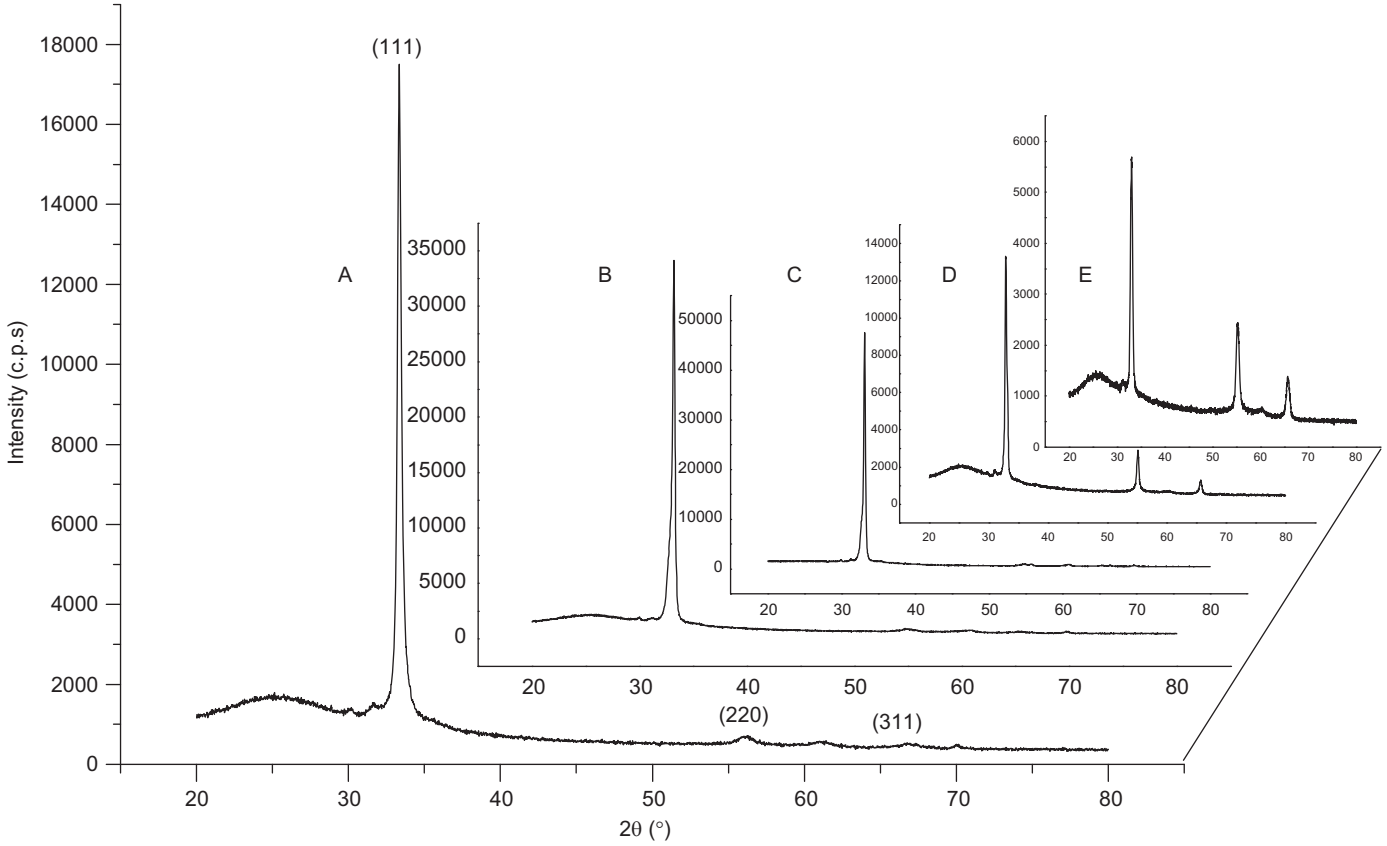

Fig. 1. The X-ray diffraction of $ZnS_{1-x}Se_x$ prepared at various annealed time under Se atmosphere. "A (ZnS film), B, C, D and E correspond to annealed films at 0.5, 1, 12, 48 h, respectively".