EFFECT OF THE SUBSTRATE TEMPERATURE ON THE CHARACTERİZATİON OF SPRAY-DEPOSİTED ZnS:B FİLMS DEVELOPED IN SCIENCE PARKS

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Science park has been widely recognized for its importance to the development of high-tech industries. Boron doped ZnS films which were developed in Science parks were prepared by spray pyrolysis technique within the glass substrate temperature range (450 ^{0}C to 550 ^{0}C), which is a low cost and large area technique to be well-suited for the manufacture of solar cells, using boric acid (H_3BO_3) as dopant source. The structural properties of boron doped ZnS films have been investigated by (XRD) X-ray diffraction techniques. The X-ray diffraction spectra showed that boron doped ZnS films are polycrystalline and have a hexagonal (wurtzite) structure. The grain size, microstrain and dislocation densities were calculated and correlated with the substrate temperature (T_S). The changes observed in the characterization of the films related to the substrate temperature are discussed in detail.

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1. Introduction

ZnS is a semiconductor compound suitable for a number of optoelectronic devices, such as solar cells[1], antireflective coatings [2], electroluminescent displays [3], optical sensors [4], etc. ZnS can be obtained as polycrystalline thin film by several deposition techniques**:** reactive sputtering [1], chemical vapour deposition [5], atomic layer epitaxy [6], chemical bath deposition [2, 7] and spray pyrolysis [8–12].

Spray pyrolysis is considered as a cheap technique to produce large area thin films [3, 13]. To deposit ZnS thin films by spray pyrolysis usually $ZnCl_2$ and $SC(NH_2)_2$ are used as initial chemicals [3, 8, 9,12]. Most experiments have been performed at $ZnCl_2$ and the molar ratio of 1:1 [3, 8, 9, 14]. It has been found that the films are amorphous at growth temperatures below 300 ºC [8, 9, 14]. Crystalline films with sphalerite structure or the mixture of sphalerite and wurtzite phases have been prepared at temperatures close to 450 ºC [8, 9]. ZnS films deposited at optimal conditions have been found to contain C, O and Cl beside Zn and S, whereas the films were slightly sulphur deficient[8]. In this work, In this work, the sprayed ZnS:B films were developed in Science park and investigation of the influence of substrate temperature on the structural properties of sprayed ZnS:B films are reported.

Science parks are sources of entrepreneurship, talent and economic competitiveness for our nation and are key elements of the infrastructure supporting the growth of todays global knowledge economy. They enhance the development, transfer and commercialization of technology. As science parks harness the combined power of education, research and private

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investment. The result is new jobs, new industries and solutions to age-old problems of mankind [15]. The science parks' role is to enable academics at the local university to commercialize their research ideas, and to provide well established businesses and small businesses, who are using and developing sophisticated technologies and prestigious accommodation [16].

2. Experimental studies

Boron doped ZnS films were deposited on highly clean glass substrates (about 0.5 cm^2 of geometric area) at different temperatures within the substrate temperature range (450 °C to 550 °C) by using spray pyrolysis technique. The starting materials used were $ZnCl_2$ as a Zn^{++} ion source, thiourea as an S^{--} ion source and H_3BO_3 as a boron source. Boron doped ZnS films were spray deposited from an aqueous solution containing 0.05 moles/lt $ZnCl_2$, 0.05 moles/lt $SC(NH_2)_2$ and as dopent source 0.05 moles/lt H_3BO_3. 100 mlt spraying solution was prepared at the same ratio, the spray flow rate was adjusted to about 0.3 mlt per minute and the distance between the nozzle (head of the sprayed source) and the substrate was kept at 20 cm in all cases. The films were characterized by using a PanAlytical (X'Pert PRO) model X-ray diffractometer with CuKα radiation (with 40 kV, 30 mA CuKα radiation, λ = 0.15406 nm).

3. Results and discussions

3.1 Structural properties

The XRD patterns of sprayed boron doped ZnS thin films prepared at different substrate temperatures are shown in Figure 1 which were carried out at room temperature. Spray pyrolysis is a chemical deposition technique where the endothermic thermal decomposition takes place at the hot surface of the substrate to give the final product. The substrate temperature plays an important role in the film formation. When the substrate temperature is below 450 °C, the spray falling on the substrate undergoes incomplete thermal decomposition (oxidation) giving rise to a foggy film whose transparency is very poor. If the substrate temperature is too high (>500 °C), the spray gets vaporized before reaching the substrate and the film becomes almost powdery. Whereas at optimum substrate temperature in the range of 450-500 °C, the spray reaches the substrate surface in the semi-vapor state and complete oxidation will take place to give clear ZnS:B films as a final product.As seen from the Figure 1, the intensity of ZnS $(002)_\alpha$ or $(111)_\beta$ peaks increase with increasing the substrate temperature and the peak becomes narrower indicating an improvement of the crystallinity up to the substrate temperature 500 °C. This means that the grain size of the thin films increases with increasing substrate temperature. The diffraction peak is indicating that the films are polycrystalline with a preferred orientation along the $(002)_\alpha$ or $(111)_\beta$ directions which could be assigned to both, the (002) peak of wurtzite or the (111) peak of sphalerite. These temperatures are significantly lower than reported for sphalerite-wurtzite polymorphic transition [17]. The presence of these peaks also indicates a mixture of hexagonal and cubic phases with a predominance of the hexagonal phase. Depending on the preparation method, boron doped zinc sulfide exists in both cubic and/or hexagonal structures. No peaks corresponding to either boron, cadmium or any of its sulphides were observed in the XRD patterns, which indicate that there is no additional phase present in B-doped ZnS films. Films grown at 500 °C shows strong preferred orientation with c-axis perpendicular to the substrate. Also, the XRD result suggests that the addition of boron atoms leads to an inhibition of the crystal growth along the *c*-axis. The peak intensity is found to be high for the samples prepared at 500 °C indicating a better crystallinity and indicating the formation of more crystallites with well-defined orientation (002) plane of hexagonal phase. So, 500 °C is the optimum temperature to obtain uniform well adherent boron doped ZnS films. For the films deposited at 450 °C, the XRD peak intensity is low because of the low crystalline growth of the films on substrate surface due to insufficient thermal energy. The intensity of the peak shows a significant decrease as the substrate temperature increases from 500 to 550 °C. This indicates the deterioration of crystallinity and strain is induced at high substrate temperatures.

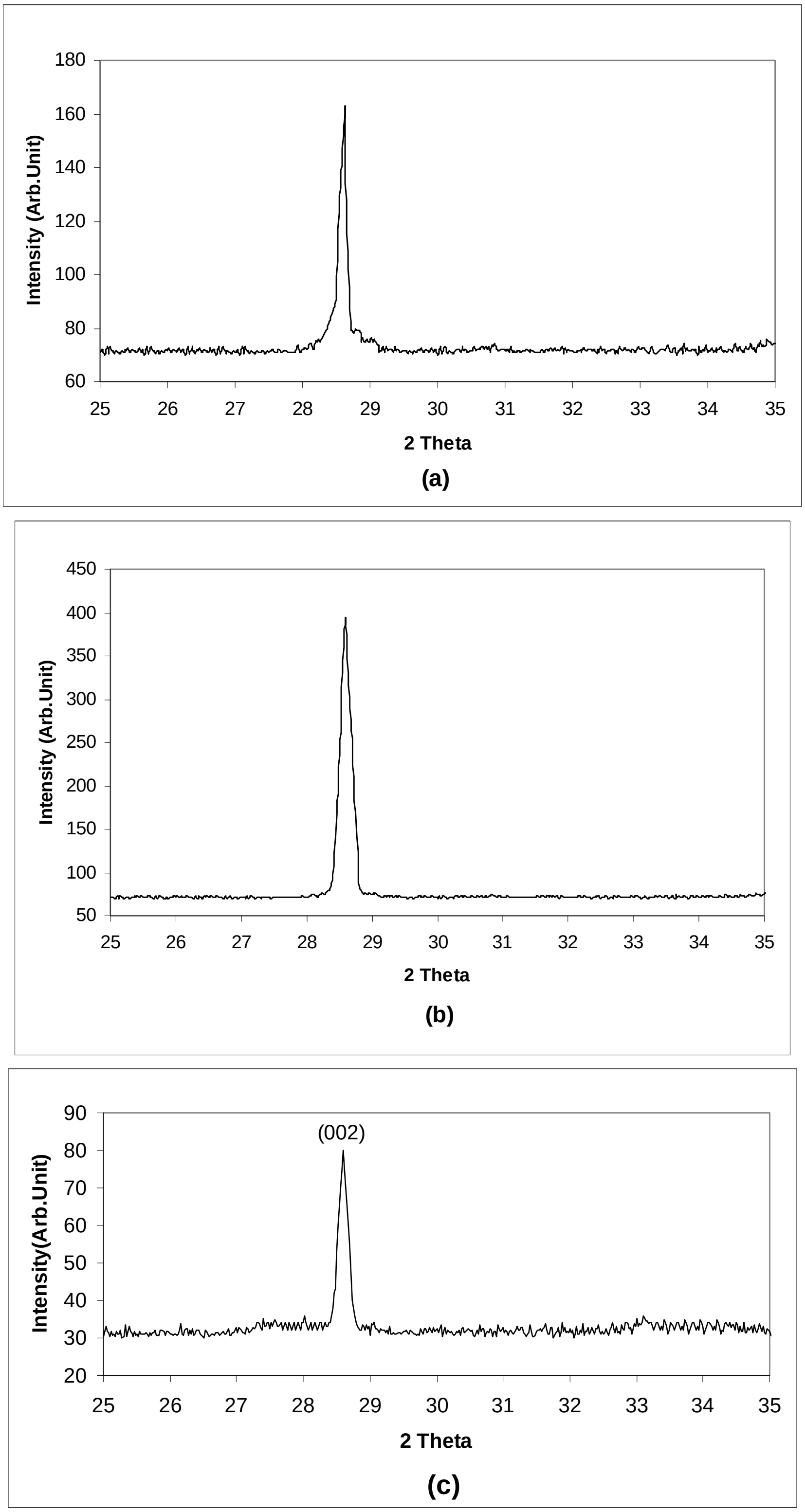

Fig. 1. XRD patterns of boron doped ZnS films with different substrate temperatures (a) 450 ^{o}C, (b) 500 ^{o}C, (c) 550 ^{o}C .

Table 1. Various grain parameters of the boron doped ZnS films with different substrate temperatures.

Substrate temperature T_s (^{0}C)	Grain Size (nm)	Microstrain ε(x10^{-4}) (line^{-2}m^{-4})	Dislocation, Density ρ(x10^{14}) (line m^{-2})
450	165	9.539	15.612
500	252	11.639	14.559
450	172	9.726	16.843

To obtain information about the crystal structure in detail, the grain size of the boron doped ZnS films were estimated for the (002) plane by using the Scherrer Formula, dislocation density (ρ) and microstrain (ε) for preferential orientations are listed in Table 1 which are calculated using the formulas given references [18,19], As seen in Table 1, the structural properties changed depending on the substrate temperature. The grain size, microstrain, first increases, reaches a maximum value around 500 ^{0}C and then appears to decrease with substrate temperature as shown in Table 1. The increase of the grain size represents the decrease of the grain boundaries and so the amount of defects in the structure. The ρ values decrease with substrate temperature for films. The dislocation density (ρ) is defined as the length of dislocation lines per unit of the crystal, and the small ρ means that the crystallization of the films is good. So, the films are deposited at 500 ^{o}C substrate temperature which have the best structural properties due to their smaller ρ values. The temperature dependence of crystallinity may be interpreted as follows. When substrate temperature increases, the sulphide deficiency leads to the growth of less homogeneous films with more crystallographic faults. It suggests that the non-stoichiometric films show poor crystallinity due to the increasing grain boundaries which behave as defects in the structure affecting both the structural properties of the films [20]. The poor crystallinity of films indicates that the films are consisted of few atomic layers of disordered atoms. Since the atoms in the poor crystallized area were disordered, there were a large number of defects due to incomplete atomic bonding [21]. It is observed from Table 1 that the microstrain (ε) exhibits a slow increasing trend up to about 500 ^{o}C and afterwards ε decreases with higher substrate temperatures. This type of change in microstrain may be due to the predominant recrystallization process in the polycrystalline films and due to the movement of interstitial Zn atoms from inside the crystallites to its grain boundary which dissipate and lead to a reduction in the concentration of lattice imperfections. Dislocations are an imperfection in a crystal associated with the misregistry of the lattice in one part of the crystal with respect another part. Unlike vacancies and interstitial atoms, dislocations are not equilibrium imperfections, i.e. thermodynamic considerations are insufficient to account for their existence in the observed densities. In fact, the growth mechanism involving dislocation is a matter of importance. It is observed that dislocation density (ρ) exhibits a slow decreasing trend up to about 500 ^{0}C and afterwards increases with higher values of T_S. These parameters indicate the formation of high quality boron doped ZnS films deposited on the well cleaned glass substrate by spraying pyrolysis method at 500 ^{o}C substrate temperature. This may be attributed to enhance the reduction mechanism of imperfections originating from lattice misfit in the films.

4. Conclusions

The study of the structural of boron doped ZnS films obtained by the spray pyrolysis technique shows that they are strongly dependent on the substrate temperatures Particularly, it is observed that the best crystallinity of ZnS:B films is obtained at the 500 ^{o}C substrate temperature. The films have polycrystalline structures and show a preferential orientation along (002) with well-defined microstructures. The crystallization level is low at higher or lower substrate temperature from the substrate temperature 500 ^{o}C due to the increasing grain boundaries which behave as defects in the structure affecting the structural properties of the films. Therefore it is observed that there are two possibilities to improve the crystallinity of the films; the increase of the grain size to decrease the number of grain boundaries; the decrease of the barrier height at the grain boudaries. The results of these analyses provide some policy implications and government of the local university for Yalova. Thus, a science park is learning site, combining in a pre-established territorial area productive, scientific, technical, educational and institutional agents, based on the assumption that the co-location of these agents is expected to enhance the technological and innovation capability of the host region.

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