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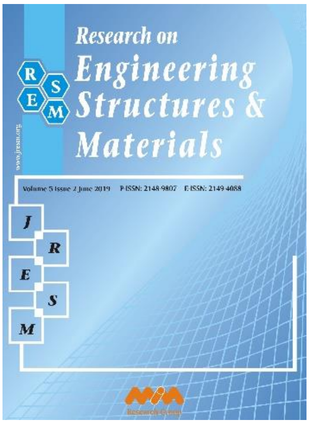

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Online Publication Date: 17 October 2019
URL: http://www.jresm.org/archive/resm2019.104ma0130.html
DOI: http://dx.doi.org/10.17515/resm2019.104ma0130

Journal Abbreviation: *Res. Eng. Struct. Mater.*

To cite this article
Yesilkaya SS, Ulutas U. Band gap modification of spray pyrolysed ZnS films by doping and thermal annealing. *Res. Eng. Struct. Mater.*, 2020; 6(2): 119-126.

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ResearchArticle

Band gap modification of spray pyrolysed ZnS films by doping and thermal annealing

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Article Info

Article history:
Received 30 Jan 2019
Revised 29 July 2019
Accepted 2 Sep 2019

Keywords:

ZnS;
Spray pyrolysis;
Band gap energy;
Doping

Abstract

ZnS thin films are widely used in solar cells as window material. Optical and electrical properties of the films such as band gap energy and resistivity directly affect device performance. In this work it was shown that properties of ZnS films can be changed by doping and thermal annealing. Therefore, films with convenient parameters can be chosen for the fabrication of any device. ZnS films were fabricated by spray pyrolysis technique. Zinc chloride and thiourea used as sources of Zn and S respectively. Films were grown on 350°C hot substrates. Furthermore 1, 5, 10, 15 % doped films prepared by addition of boric acid into the solution. Structural, optical and electrical properties of the films were examined by SEM, XRD, optical transmission and resistivity measurements. Later on all films annealed in air at 350°C for 30 min. All measurements were done also for annealed films. Effects of doping and thermal annealing on the band gap energy and resistivity of the films were shown. Band gap energies of the films were between 3.37-3.82 eV and surface resistivities were between 257.2-12.5 M*Ω*.

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1. Introduction

ZnS thin films are often used as window material in solar cells. The optical and electrical properties of the films, such as the band gap energy range and resistance, directly affect device performance. In this study, it has been shown that the properties of ZnS film can be changed by adding and annealing. This allows the selection of films with suitable parameters for the device to be planned.

ZnS is one of the most important wide band gap semiconductor materials for electronic device applications. It is commercially used in photovoltaic, phosphorescence and thin film electroluminescence devices [1–2]. Luminescent properties of impurity doped ZnS nano crystals are significantly different from the properties of undoped ZnS[6]. Optimization of film parameters directly affects the device performance. Caiying Mao et al. were grown boron doped ZnO (BZO) films with 0 to 6 % doping concentrations by RF magnetron sputtering technique on quartz substrates. They stated that crystalline quality of the films gets worse over 4% doping concentrations. They found that band gap energy of BZO films increases to 3.57 eV from 3.28 eV with increase of Boron concentration from 0 to 6% and minimum resistivity was obtained for 2% B doping as $1.58.10^{-3}$ (Ω cm) [4]. The resistivity of the film is particularly important in application of transparent conductive oxide in photovoltaics. Low resistivity promotes energy-conversion efficiency owing to improved

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DOI: http://dx.doi.org/10.17515/resm2019.104ma0130

photo current [10]. Karakaya et.al. [5] fabricated ZnO:B films by ultrasonic spray pyrolysis method due to low cost and simplicity. They showed that films were polycrystalline structured and oriented in [002] direction. They also found that increasing B concentration was lead to a decrease in crystalline quality of the ZnO films. Optical transmission of the films was higher than 80% for visible region. Resistivity of the films were decreased from 1.87×10^{-2} Ωcm to 2.40×10^{-3} Ωcm. Band gap energies were increased to 3.30 eV from 3.25 eV while boron concentration was increasing to 5% from 1%. According to these results B-doped ZnO is a promising material for photovoltaic solar cells [5]. Some research showed that doped nano crystalline semiconductors are a new class of materials which can be used in imaging, lighting, sensors and lasers [7-8]. Rajendra S. Gaikwad et al. found in their study that sprayed ZnO thin films revealed >95% transmittance in the visible wavelength range, 1.956 10^{-4} Ω cm electrical resistivity, 46 cm^2/V.s Hall mobility and 9.21 x10^{21} cm^{-3} charge carrier concentration. The X-ray photoelectron spectroscopy study has confirmed 0.15 eV binding energy change for Zn 2p3/2 when 2 at% boron content is mixed without altering electro-optical properties substantially. Finally, using soft modeling importance of these textured ZnO over non-textured films for enhancing the solar cells performance is explored. Due to decrease in grain size after boron doping hydrophilicity was decreased. One can use these highly conducting, transparent, high surface roughness and self-textured $Zn_{1-x}B_xO$ films, as a transparent conducting working electrode, in solar cells by assuming most of the incident solar radiation will be scattered and thereby, the solar cell efficiency will be improved [9].

Upon doping a semiconductor, impurity states are created which could appear either within its gap or outside of it. If the impurity states are formed within the energy range of the energy gap, this will cause its reduction and most probably will shift the Fermi energy, E_f, into the impurity bands. On the other hand, if the impurity states are created outside the gap, it is expected that they will not affect the gap value in an appreciable way. The gap problem, thus, turns to be the problem of finding the appropriate dopant(s) which can reduce the energy gap of the wide band gap materials [12].

Abdelhak Jrad and friends have deposited indium-doped zinc sulfide (ZnS:In) thin films by chemical bath deposition technique (CBD). The structural properties studied by X-ray diffraction indicate that ZnS:In has a cubic structure with an average crystallite size 4.7–11.0 nm. Transmission and reflection spectra reveal the presence of interference fringes indicating thickness uniformity and surface homogeneity of deposited material. All the films were transparent in the visible and infrared regions (P60%), which allows us to use this material as an optical window or a buffer layer in solar cells. The obtained band gap energy Eg is in the range of 3.70–3.76 eV [13].

II-VI semiconductor nano structures are of great interest due to their morphology and possible variety of applications. Band gap energy is an important parameter for these applications. Among all II-VI compounds ZnS one which has very large band gap. ZnS can be in two different crystalline structure, zinc blend with E_g=3.72 eV and wurtzite with Eg=3.77 eV. Because of these properties ZnS becomes a similar material to ZnO in UV based devices [1].

In this work we fabricated boron doped ZnS films for the first time using easy and cost-effective spray pyrolysis technique. Since all parameters are kept constant and only boron is added to ZnS solution, we think that films are doping with boron.

2.Experimental

0.05M ZnS solution was prepared by adding 1.74 g $ZnCl_2$ and 0.953 g thiourea (CH_4N_2S) into 500 ml distilled water at room temperature. ZnS films were grown on 26 mm×15 mm×2 mm glass substrates. Substrates cleaned by detergent, distilled water, alcohol and again distilled water respectively. ZnS films were grown by spray pyrolysis on the 400°C hot substrates with a spraying rate of 1/3 spray/s. 1, 5, 10 and 15% boron doped ZnS films obtained. Boric acid used as boron source. Films were annealed at 350°C in oven. Transmission spectra of films were measured by Lambda 2 Perkin Elmer UV spectrophotometer in 320-1100 nm wavelength range. Direct band gap energy of the films were calculated by equation 1 [3] according to absorption spectra obtained from transmission spectra of the films.

$$\alpha^2 = \frac{B(h\nu - Eg)}{(h\nu)^2} \tag{1}$$

In the eq.1 α is absorption coefficient, E_g band gap energy, hν photon energy and B is constant. The extrapolation of the straight line to hυ axis at $(\alpha h\upsilon)^2=0$ on the plot of $(\alpha h\upsilon)^2$ versus hυ gives the value of energy band gap (E_g).

In this study; the thickness of ZnS thin films formed on glass substrates was calculated by weighing method. In this method, after the necessary cleaning of the glass mats, a group of glass mats to be filmed were weighed with an electronic balance of 10^{-4} grams. After the film was formed on the glass mats, weighing was performed again. The difference between these two weighing results gave us the mass of the films. Subsequently, the dimensions of all film coated glasses were determined and their surface areas were calculated. Since we are not sure the homogeneity of the films, the average film thickness was calculated on 5 or more samples instead of a single sample. Thus, the average thickness of ZnS thin films;

$$d = \frac{\Delta m}{S.\rho_{fim}} \tag{2}$$

calculated with the formula (2). In this equation, Δm is the mass of the film, S is the total surface area of the films, ρ is the density of the film, and d is the average film thickness. The average thickness of the obtained ZnS thin films was calculated as 5.05 µm.

The crystalline structures of ZnS thin films which were annealed at different temperatures were analyzed using X-ray diffraction (XRD, Panalytical Diffractometer Philips) with Cu $K_\alpha$radiation (λ=1.54056 Å) in the range of 5°–80°. The lattice constants of the ZnS thin films with wurtzite phase structure were calculated from Eq. (3). Debye-Scherrer's Formula given in Eq. (4) was used for estimating the average crystallites of the thin films. The dislocation density (δ) given in Eq. (5) Williamson and Smallman's formula, which is related to the dislocation lines per unit area in the film, was estimated using the average of the grain size (D) [11].

$$\frac{1}{d^2} = \frac{4}{3}\frac{(h^2+hk+k^2)}{a^2} + \frac{l^2}{c^2} \tag{3}$$

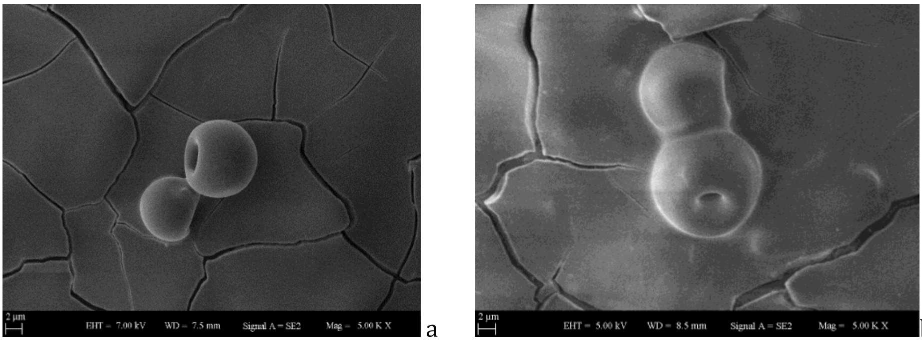
$$D = \frac{K\lambda}{\beta cos\theta} \tag{4}$$

$$\delta = \frac{lines}{D^2 m^2} \tag{5}$$

Where in the Eq. (3), a and c are the lattice constants, d is the distance between adjacent lattice planes and (hkl) is Miller indices. Where in the Eq. (4), D is the crystal size, K is the constant shape factor (0.9), λ is the wavelength of X-ray radiation source, θ is the diffraction angle and β is the full width at half maximum of the prominent peak in radian.

3. Results

FEI-Quanta FEG 250 scanning electron microscopy was used to observe the surface morphologies of the ZnS films. SEM analysis was applied to the films. Small particle size differences were seen in particle sizes of doped and undoped films. It can be seen from Figure 1 that doped films has a little bit larger particle size comparing to the undoped one.



a b

Fig. 1 SEM images of a)non-doped and b) 15% boron doped ZnS films.

X-ray diffractograms of the films prepared with different boron doping are shown in Figure (2 and 3). According to XRD results intensities of [111], [220] and [311] Zn peaks at 29°,48° and 57° for 2θ were increased with boron doping and thermal annealing. Samples are amorphous at the lowest doping rate. The intensity of the reflection increased as the doping rate increased before any new reflection appeared. Thus, no other phase was formed, but only the crystallization of the formed phase was improved.

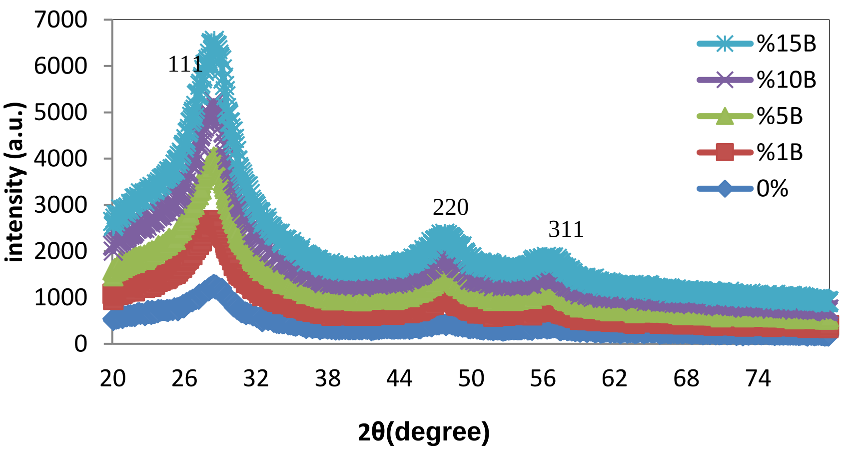


Fig. 2 XRD patterns of boron doped non-annealed ZnS films

A well-crystallized film was obtained with 15% boron doping. The phase identification revealed that only cubic ZnS was formed. Therefore, the preparation conditions of a given technique greatly affect not only the number of phases formed but also its microstructural properties such as crystallinity. These results are in agreement with Muraliet al.[14]. The crystallite size was measured using Debye Scherrer's formula [11].

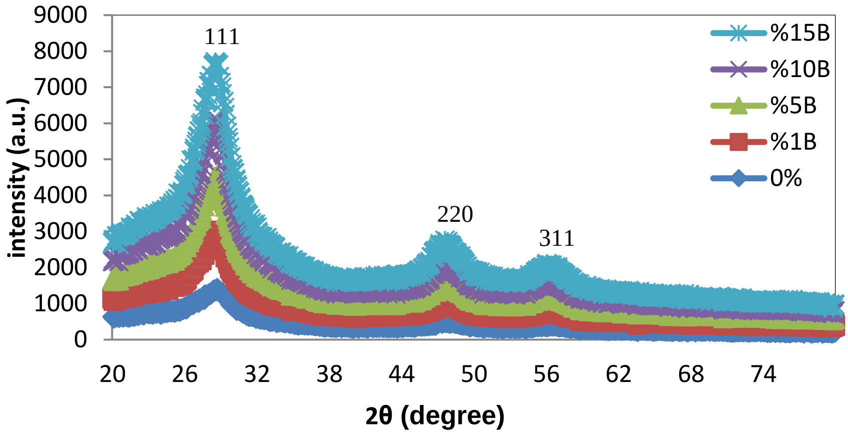


Fig. 3 XRD patterns of boron doped annealed ZnS films

Some differences observed in optical transmission spectra of ZnS films due to boron doping (Fig. 4 and 5). Band gap energies of the films were in the range of 3.37-3.82 eV (Fig. 6 and 7). This wide range is very important for different working requirements and design of optoelectronic devices. Band gap energy values of the films were given in table 1 according to boron doping and thermal annealing. An ohmmeter was used to measure the surface resistances of boron doped ZnS films and the measurements were made 10 times from 10 different locations of the films and the average resistance values were calculated. It was also seen that surface resistivity of annealed films were changed from 257.2MΩ to 86.3MΩ with boron doping while this change was from 189.5MΩ to 12.5MΩ for non-annealed films.

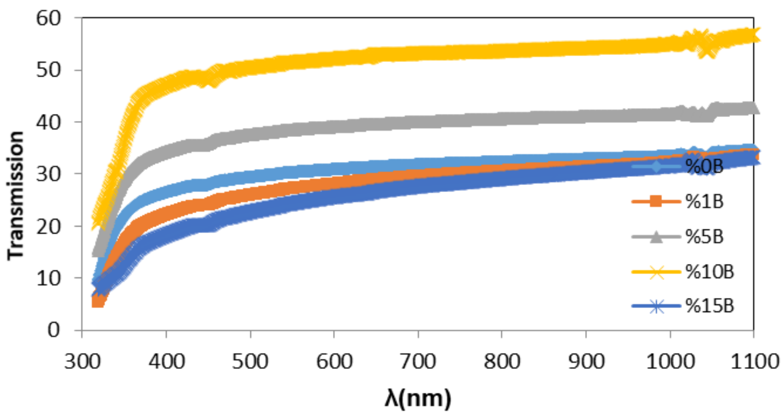


Fig. 4 Optical transmission spectra of boron doped non-annealed ZnS films.

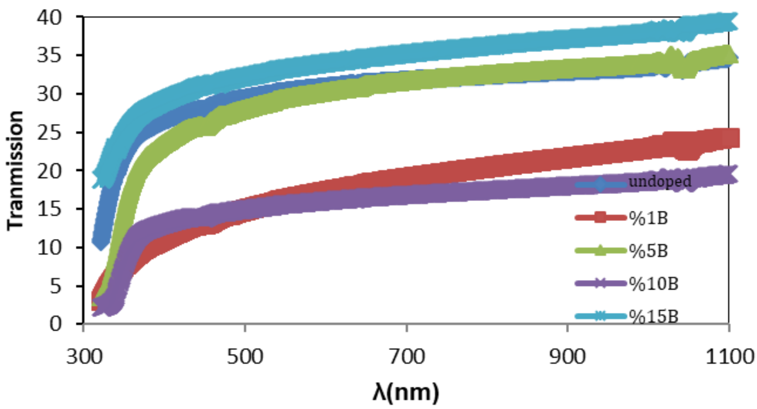


Fig. 5 Optical transmission spectra of boron doped annealed ZnS films.

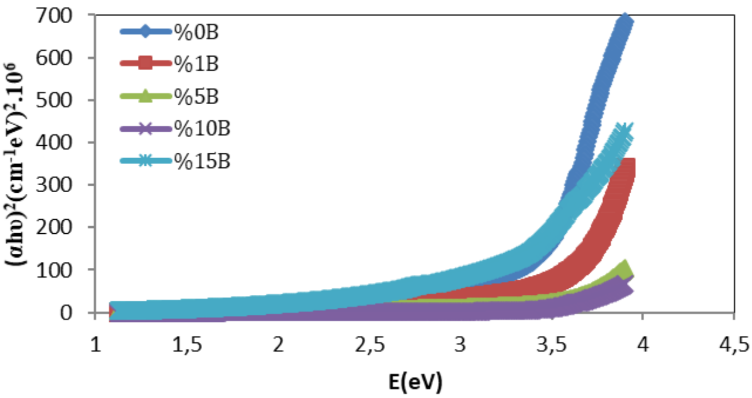


Fig. 6 Absorption spectra of boron doped non-annealed ZnS films.

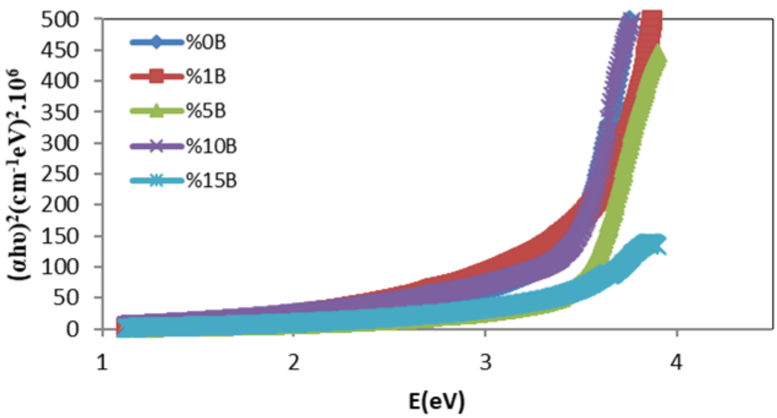


Fig. 7 Absorption spectra of boron doped annealed ZnS films.

Table 1Band gap energy values of ZnS films.

ZnS(E_g)	Undoped	1% Boron	5%Boron	10%Boron	15%Boron
Non-annealed	3.48eV	3.62eV	3.63eV	3.73eV	3.82eV
Annealed	3.69eV	3.68eV	3.52eV	3.48eV	3.37eV

4. Conclusions

XRD results of the spray pyrolysed ZnS thin films showed that the positions of [111], [220] and [311] Zn peaks did not change by boron doping or thermal annealing. Furthermore, no new peak was seen in the spectra. Therefore, it can be concluded that no new phase was formed in film and compound remained as ZnS. More beneficiary, intensities of these XRD peaks were increased by boron doping and more increase was observed after thermal annealing. Band gap energy values of spray pyrolysed ZnS thin films were changed by boron doping and thermal annealing. Band gap widening in doped ZnS thin films can be attributed to the Burstein–Moss effect. According to mentioned effect Fermi level moves upward with increasing donor concentration. This also causes the shift of unoccupied levels in the conduction band. Therefore, the energy gap between the valence band and the conduction band widens and higher energies are needed for electrons to reach from the valence band to the shifted conduction band. Surface resistivity of the ZnS thin films were decreased with boron doping and also with thermal annealing which was a preferred result for increasing the performance of fabricated devices. Surface resistivity of annealed ZnS films were changed from 257.2MΩ to 86.3MΩ with boron doping while the change in surface resistivity was from 189.5MΩ to 12.5MΩ for doped but non annealed ZnS films. All results and obtained data show that it is possible to tune the band gap energy of ZnS thin films by boron doping and thermal annealing which are easy and cheap processes. In our doping range band gap energies of the ZnS thin films had a wide range of 3.37-3.82 eV. This wide range makes doped ZnS thin films applicable for fabrication of different optoelectronic devices such as sensors, solar cells, photodiodes etc. with different band gap requirements.

Acknowledgement

This work was supported by Yıldız Technical University Scientific Project Coordination with project no:2015-01-01-DOP01

We would like to thank to Dr. ÖzlemYağcı for her help on structural analysis of the films.

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