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Investigation of the effect of boric acid on the characterization of CdSe films grown by spray pyrolysis method

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Boron doped Cadmiuim Selenide (CdSe) films were prepared by spray pyrolysis technique at 275 °C substrate temperature using boric acid (H_3BO_3) as dopant source, and their properties were investigated as a function of doping concentration. In addition, CdSe(B) films were obtained by adding 0.0025M, 0.01M, 0.015M and 0.05M H_3BO_3 to the initial solution. The effects of boric acid concentration on the structural, morphological and optical properties of CdSe films were discussed in detail.

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1. Introduction

Binary semiconducting materials belonging to group II and group VI such as CdTe CdS, CdSe have been studied widely because they could be used in solar cells and optical devices [1-4]. Cadmium selenide chalcogenide coatings have been developed because they could have high absorption coefficient and their band gap energy is nearly ideal (around 1.73 eV). They could use in various applications including laser, solar cells, electro photography, light emitting diodes and photodetectors because they could be easily fabricated in low cost and simple methods [1,4-6]. These semiconducting materials have been grown on a glass substrate by using some different techniques including chemical precipitation [1,5], evaporation from vacuum atmosphere [6], electrochemical deposition [7], spray pyrolysis [8], physical vapour deposition [9] and SILAR [10]. When these techniques are compared, it could be seen that spray pyrolysis technique is a simple and inexpensive method to produce high quality thin films with the growth repeatability [11]. No research has been reported on analyzing the characteristic (structure, composition and optical properties) of boron doped CdSe films prepared by using the spray pyrolysis method. Therefore, the aim of this study is to examine the suitability of the spray pyrolysis method for the production of boron-doped CdSe films. Then, the effect of boric acid concentration on the structural, morphological and optical behaviour of CdSe:B films grown by using the spray pyrolysis method was investigated.

2. Experimental details

The spray pyrolysis method is a reaction involving the formation of a film on the glass substrate as a result of spraying the prepared solution onto the glass substrate heated to a certain temperature. Using this method, the aqueous solution prepared for the formation of CdSe:B films is created by spraying on the glass substrate (Objekttrager,1cmx1cm) that is brought to a constant temperature in an air atmosphere. In deionized water, $CdCl_2$ (Merck, ≥ 99%) and SeO_2 (Merck, ≥ 99%) were used as spray solutions, while boric acid (H_3BO_3) was used as a dopant source. The films were formed at a substrate temperature of 275° and controlled with a chromium-alumel thermocouple. The prepared solution was sprayed on the glass substrate for a settling time of 0.5 to 2.5 hours (5ml/min). Boron additive was obtained by adding H_3BO_3 at different molarities (0.0025, 0.010, 0.015 and 0.050 M respectively) together with the initial solution containing $CdCl_2$ and SeO_2 at a concentration of 1 M in 100 ml deionized water for the preparation of undoped and boron-doped CdSe films. Formation of CdSe films with no additives and boron additives as a result of chemical reaction:

$$CdCl_2 + SeO_2 + H_2O \rightarrow CdSe + 2HCl + 3/2O_{2(gas)}$$

$$CdCl_2 + SeO_2 + H_3BO_3 + H_2O \\ \rightarrow CdSe + 2HCl + 3OH + 3/2O_{2(gas)}$$

Structural characterization of films enlarged by spraying method was carried out by X-ray diffraction technique (XRD) with monochromatic CuK$_\alpha$ radiation when $\lambda = 1.54056$ A by using Braker AXS D5005 diffractometer [12]. Scanning electro-microscopy (SEM) micrographs of all films were obtained from JEOL JSM 6390 LV model scanning electro-microscopy. Optical studies of CdSe:B films prepared by changing boron concentrations at 275 °C substrate temperatures were studied by using UV-VIS spectrophotometer (Jasco 7800). A graph between $(\alpha h\nu)^{1/2}$ against photon energy (hν) was plotted. In this graph, α is the absorbance calculated from UV and hν can be calculated form wavelength. A straight line portion of the curves to 0 absorption coefficient value by extrapolating can give the optical energy band gap value [13].

3. Results and discussions

The appearance of many peaks in the X-ray analysis of boron-doped and undoped CdSe films, grown at 275 ^{o}C by spray pyrolysis method, results is an indication that the CdSe films are polycrystalline, as shown in Fig. 1. Generally, CdSe has two different crystaline structures, these are called cubic wurtzite and hexagonal zinc blende. It was shown that CdSe films prepared by spraying method depending on the conditions of the deposited films could be formed in their cubic, hexagonal or both cubic and hexagonal crystalline structures [14]. However, we can say that the undesired cadmium oxide (CdO) phase (200) is present in the line in films as seen in X-ray analysis [15]. The formation of CdO during growth of films using the spray pyrolysis method can be attributed to the oxidation of Cd. Cadmium ions are unstable and rapid equilibrium formation in solutions can be explained as causing CdO formation before CdSe formation. Thus, the aqueous solution with CdO was saturated when CdO was added in water and CdO was deposited in the first step of the experiment [16], indicating that the oxidized atoms that selenium are replaced by a non-crystalline region at the grain boundary. XRD patterns provide the most positive evidence of the expected the formation of CdSe phase. The diffraction lines that appear in the XRD model shown by CdSe films show several peaks at 2θ values about of 25^o, 27^o,30^o, 38^o, $46^{o,}$ 55^o, 68^o and 76^o, in which (100), (002), (101), $(200)_{CdO}$, (103), (202), (210) and (300) shows the hexagonal (wurtzite) structure in planes, respectively [17]. XRD pattern shows that (002), (103), (101) and (202) dominant plane peaks indicate that the CdSe films are a hexagonal (wurtzite) structure [18, 19]. Increasing the boron concentration during the formation of the CdSe films does not significantly change the location of the measured diffraction peaks, but the density of the peak of the (101) plane has been observed to increase significantly, indicating that crystallization has improved. According to the results in Fig. 1, it can be attributed to the change in the amount of boron concentration in the improvement of the crystallization of the CdSe:B films.

The increase in XRD peaks seen in Fig. 1 may indicate the formation of new nucleation centers due to boron dopants atoms in cases where there is a boron additive less than 0.01 M. At doping levels higher than 0.01 M, the reason for the reduction of XRD peaks can be based on two reasons; the first is the saturation of the new core centers, and the second is the change in energy absorption by physical and chemical interaction that occurs in the event of a collision between the ad-atoms and the film. In addition, an increase in grain size was observed with an increase in boron concentration up to 0.01 M, and a decrease in grain size was observed at higher boron concentrations. This indicates that the density of XRD is strongly dependent on the concentration of boron. As a result, the properties of CdSe: B films deposited with the spray pyrolysis method are strongly dependent on the boron concentrations, as similar behavior was observed by Pawar et al. [20]. In cases where boron concentration is more than 0.01 M, it was observed that the crystal structure deteriorates and the grain size decreases, thus increasing the full width of the half-width (FWHM). This reduction in grain size can be caused by a large difference in the ion radius of the boron. The resulting decrease in crystal size was caused by recrystallization by providing the thermal energy generated by the increase in boric acid concentrations. With the decrease of the crystal size, high grain boundaries are formed in the crystal and this situation prevents carrier transport and acts as a trap for free carriers. This trend suggests that the boron contributes to the creation of new nucleation centers that will heterogeneous the nucleation type and disrupt the crystalline structure at a high level of additive bor concentration.

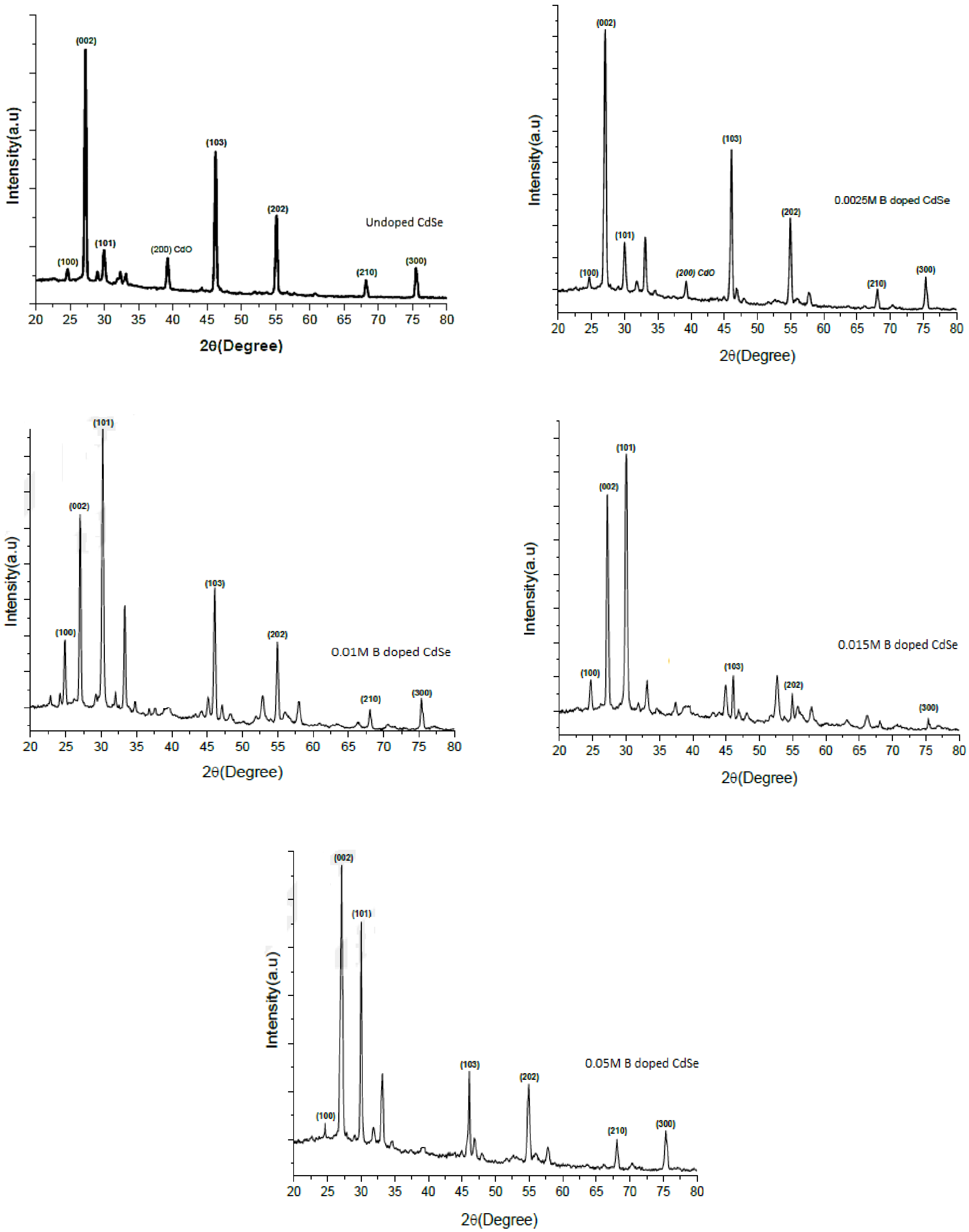

Fig. 1. A typical XRD pattern of spray deposited undoped and boron doped CdSe films at substrate temperature of 275 ^{0}C

The grain size of the materials were calculated for the (101) plane by using the Scherrer equation [22]:

$$d = \frac{\lambda}{D\cos\theta} \tag{1}$$

In which λ is the X-ray wavelength, d is the grain size of material, θ is the Bragg diffraction angle and D is the angular line width of the half maximum intensity. As can be seen from Table 1, when the boron concentration is increased to 0.01 M, the grain size increases, which indicates an improvement in crystallization. A decrease in grain size when the boron concentration is more than 0.01 M indicates that crystallization is disturbed, which has also been shown in analyses to be associated with the XRD patterns. The carrier is prevented from moving, as well as the concentration of grain boundaries that act as traps with the decrease of the crystal size. As a result, grain boundary scattering increased [23] which could be observed from XRD patterns. As a result, the characteristics of all films prepared by spray pyrolysis are largely dependent on the combination of boron in the films. It was concluded that the crystallization of the films improved with an increase in boric acid concentration up to 0.01 M due to a decrease in lattice defects and also an increase in grain size of film. These results proved that high quality CdSe:B films with different amount of boron on well-cleaned glass substrate were formed by using spray pyrolysis method.

The microstrain (ε) in the sprayed CdSe:B films were calculated for the (101) plane from equation [25]:

$$\varepsilon = \frac{D\cos\theta}{4} \tag{2}$$

Table 1 shows the change of the microstrain (ε) with different boron concentration in CdSe:B films. It was observed that a decrease in microstrain upto 0.01 M donor concentrations, as well as an increase in grain size, in the process of polycrystalline recrystallization, Cd atoms move through the crystallites to the grain boundaries, as a result, it has led to a decrease in the concentration of lattice defects and an improvement in crystallinity because of the regularity of the atoms in the crystal lattice [26].

Dislocations indicate defects in which atoms are out of position in the crystal structure. In this research, the density of dislocation was calculated from Williamson's and Smallman's method using Equation 3 for undoped and boron-doped CdSe films [27] and the dislocation values are shown in Table 1:

$$\rho = \frac{15\varepsilon}{aD} \tag{3}$$

The length of the dislocation lines per unit of the crystal is defined as the dislocation density (ρ). As seen from Table 1, the dislocation density (ρ) decreases with the increasing the boron concentration up to 0.01 M, hence, a number of imperfections in the film are reduced and the grain size of the film increases which could be because of a decrease in the formation of grain boundaries and is deposited upon the formation of high quality CdSe:B films on the glass substrate by spray pyrolysis method. At boron concentrations higher than 0.01 M, the increase in dislocation density and microstrain defects indicates the formation of lower quality films [28]. This has shown that the doping of the boron element in films is effective in the crystallization and the formation of their microstructure of all films.

Table 1. XRD pattern results of the undoped and boron doped CdSe films for the (101) plane

Sample	Grain Size d(A^0)	Dislocation density ε($x10^{-3}$)	Microstrain ρ($x10^9$)/cm^3
Undoped CdSe	2.501	1.6364	6.8119
0.0025M	2.563	1.5812	6.7829
0.010M	2.864	1.4769	6.7365
0.015 M	2.598	1.6012	6.7824
0.050M	2,492	1.6917	6.8861

The absorption coefficient was calculated for allowed direct transitions as a function of photon energy by using the expression [29]

$$\propto = \frac{A}{hv}(hv - E_g)^{1/2} \tag{4}$$

where E_g is the optical band gap of the film, A is a characteristic parameter and hv is the photon energy of the light. Photon energy "hv" is shown in Fig. 2(a-e) as a function of $(\alpha hv)^2$. These figures show that all CdSe films have direct band-band transitions and optical band gap energy (E_g) and their absorption coefficient (α) are interrelated [29]. The values of E_g were found by extrapolation of linear sections $(\alpha hv)^2 \rightarrow 0$ of curves shown in Fig. 2(a-e). It is seen from Fig. 2(a-e) that the band gap energy of all CdSe films are found between 1.74 and 2.17eV at the substrate temperature of 275 ^{0}C [30,31].

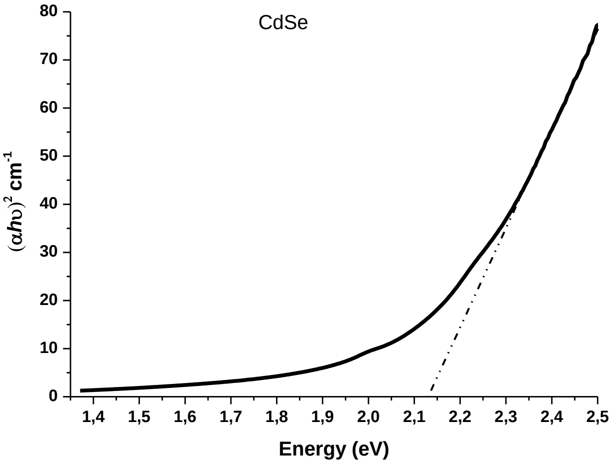

Fig. 2(a). The band gap energy graph of undoped CdSe film prepared at 275 ^{o}C on glass substrate

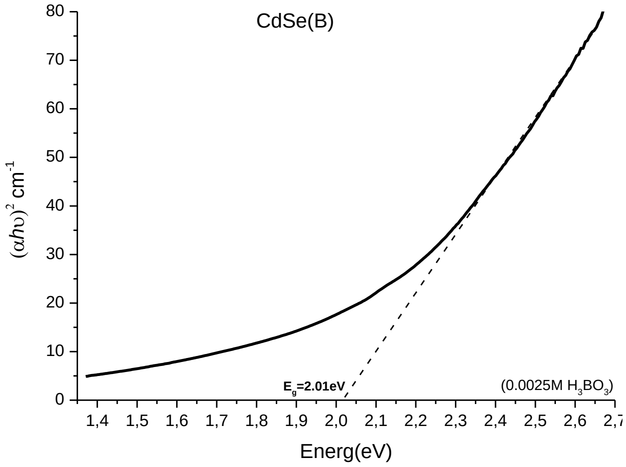

Fig. 2(b). The band gap energy graph of CdSe:B film prepared at 275 ^{o}C on glass substrate

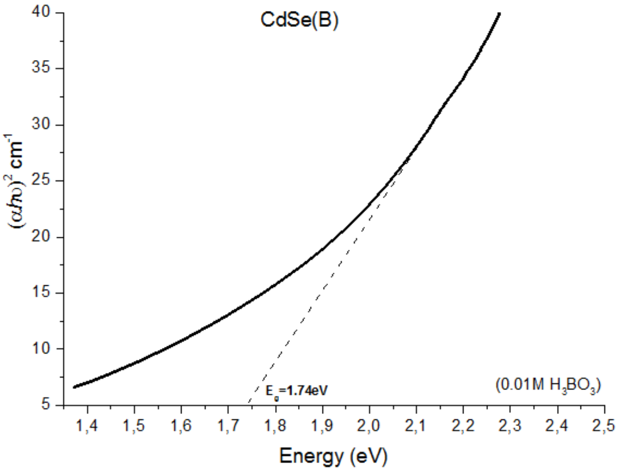

Fig. 2(c). The band gap energy graph of CdSe:B film prepared at 275 ^{o}C on glass substrate

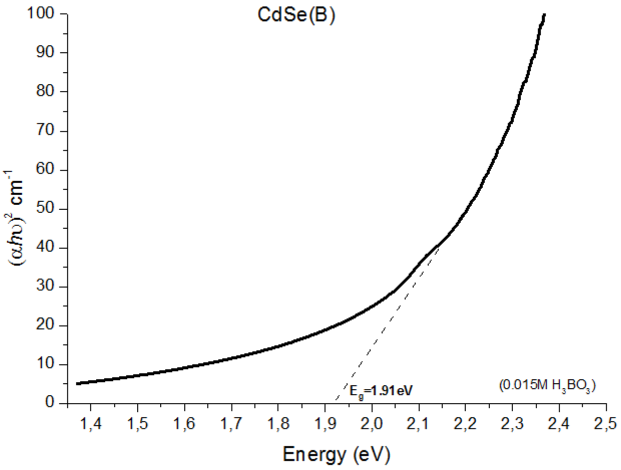

Fig. 2(d). The band gap energy graph of CdSe:B film prepared at 275 ^{o}C on glass substrate

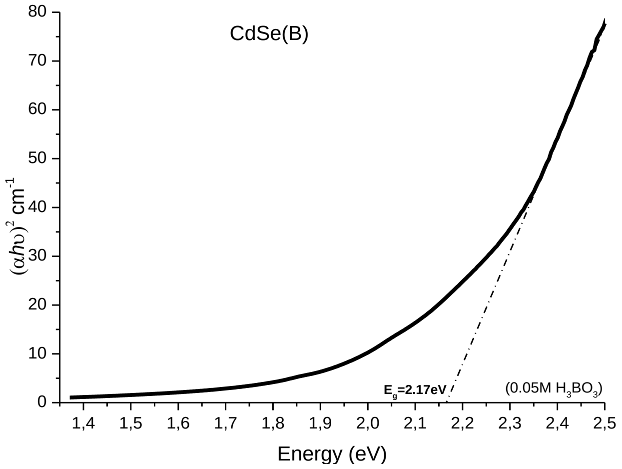

Fig. 2(e). The band gap energy graph of CdSe:B film prepared at 275 ^{o}C on glass substrate

Table 2 shows that the optical band values decrease until the boron concentration of 0.01 M was reached probably because of an increase in grain size (101) plane of the film. Another reason may be improved crystallization with increased grain size. It means that boron concentration could also affect the film's band gap. For doping concentrations higher than 0.01 M, it is observed that the band gap increases and the grain size of CdSe: B films decreases. A similar result was observed for ZnO:Cu films deposited by the same spray pyrolysis technique [21]. Therefore, the effect of boric acid content on the band gap of the sample can be attributed with the change of the film structure.

Table 2. The band gap energy values of the undoped and boron doped CdSe films

Sample	Substrate temperature (^{o}C)	Molarity of Boric Concentration (M)	Energy gap (eV)
CdSe	275	0	2.14
		0.0025	2.01
		0.010	1.74
		0.015	1.91
		0.050	2.17

Using the SEM technique, the effect of boric acid concentrations on the surface morphology, the grain shape and the grain size of CdSe films and the proportion in which quality CdSe film is formed, were studied as shown in Fig. 3(a-e). The SEM image of undoped and boron doped CdSe films additives, which are prepared at 275◦ substrate temperature and a stack of rectangular shaped grains appeared as shown in Fig. 3(a-e). According to the observed changes, it shows that boron atoms act as nucleation centers. During the magnification of the films, small droplets form on the glass substrate into micro-crystallites of various sizes. As a result of this, it was observed that grain size increased by increasing boron concentration to 0.01 M. In the formation of the crystallinity of the film, it is clear that large crystallites are formed by the concentration of boron on the glass substrate. For higher boric acid concentrations, increased roughness can be explained as a result of a decrease in grain size with a homogeneous and more compact surface morphology, as seen from SEM images. As a result that the amount of the boric acid concentration was effective in changing the morphology of CdSe films, which is associated with the change in grain size.

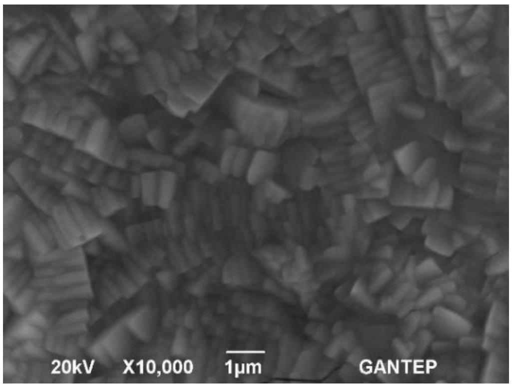

Fig. 3(a). SEM photography of undoped CdSe film at T=275^{0}C substrate temperature

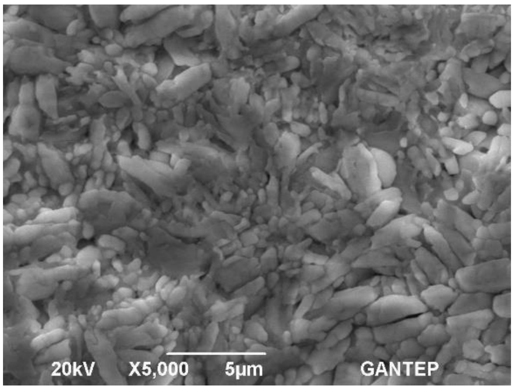

Fig. 3(b). SEM photography of Boron (0.0025M H_3BO_3) doped CdSe film at T=275^{0}C substrate temperature

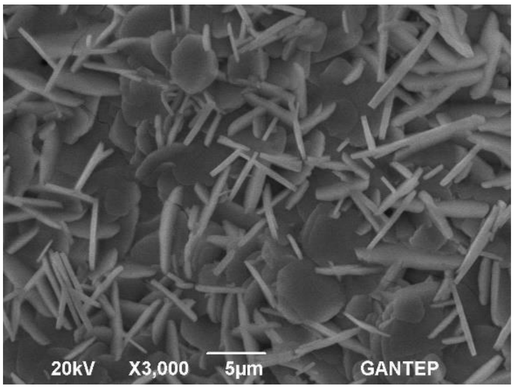

Fig. 3(c). SEM photography of Boron (0.015M H_3BO_3) doped CdSe film at T=275^{0}C substrate temperature

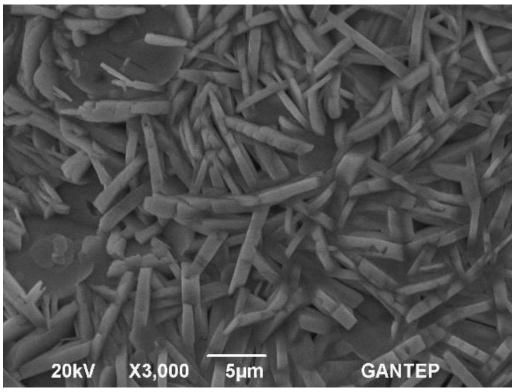

Fig. 3(d). SEM photography of Boron (0.01M H_3BO_3) doped CdSe film at T=275^{0}C substrate temperature

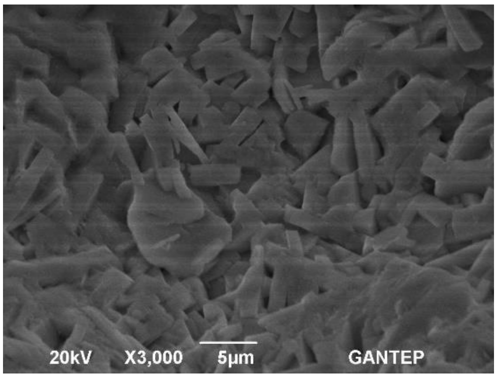

Fig. 3(e). SEM photography of Boron (0.05M H_3BO_3) doped CdSe film at T=275^{0}C substrate temperature

4. Conclusions

The study of the structural, morphological and optical properties of CdSe films prepared at the substrate temperature of 275 oC with different boron concentrations, has been shown to be strongly dependent to boron concentration. In particular, the best crystallization of CdSe films was achieved at a boron concentration of 0.010 M. Therefore, it can be said that the observed decrease in dislocation density, microstrain and band gap energy with increased grain size can be attributed to the improvement of the crystallinity. The films have polycrystalline structures and are preferred orientation along well-defined microstructures to the planes (002), (103), (101) and (202). The undoped and doped CdSe films obtained at doping levels higher than 0.01 M were found to have lower crystallization levels due to increased grain boundaries acting as a defect affecting their structural properties. As a result of the effect of boron concentrations on the morphological, optical and structural properties of CdSe films, it can be said that the contribution of the boron material to the semiconductor films can be used as a more suitable material than other doping materials used in optoelectronic device technology.

References

[1] P. P. Hankare, V. M. Bhuse, K. M. Garadkar, S. D. Delekar, I. S. Mulla, Semicond. Sci. Technol. **19**, 70 (2004).

[2] K. R. Murali, V. Swaminathan, D. C. Trivedi, Sol. Energy Mater. Sol. Cells **81**, 113 (2004).

[3] J. Y. Choi, K. J. Kim, J. B. Yoo, D. Kim, Sol. Energy **64**, 41 (1998).

[4] P. O'Brien, J. McAleese, J. Mater. Chem. **8**, 2309 (1998).

[5] S. Gorer, G. Hodes, J. Phys. Chem. **98**, 5338 (1994).

[6] S. Kodigala, Y. Su, S. J. Chang, F. S. Juang, K. Ohdaira, Y. Shiraki, H. P. Liu, I. G. Chen, A. K. Bhatnagar, J. Cryst. Growth **224**, 74 (2001).

[7] S. M. Rashwan, S. M. Abd El-Wahab, M. M. Mohamed, J. Mater. Sci. Mater. Electron. **18**, 575 (2007).

[8] Yu. V. Meteleva, N. A. Redychev, G. F. Novikov, Inorg. Mater. **43**, 455 (2007).

[9] K. N. Shreekanthan, B. V. Rajendra, V. B. Kasturi, G. K. Shivakumar, Cryst. Res. Technol. **38**, 31 (2003).

[10] O. Yamamoto, T. Sasamoto, and M. Inagaki, J. Mater. Res. **13**, 3394 (1998).

[11] M. R. Islam, J. Podder, Cryst. Res. Technol. **44**(3), 286 (2009).

[12] M. Öztaş, Z. Kaya, International Conference on Energy, Regional Integration and Socio-economic Development, September 5-6, 2013, **EcoMod2013**, Bakü.

[13] P. Srivastava, K. Singh, Advanced Materials Letters **3**(4), 340 (2012).

[14] I. A. Kariper, Journal of Non-Oxide Glasses **8**(1), 1 (2016).

[15] M. Kul, M. Zor, A. S. Aybek, S. Irmak, E. Turan, Thin Solid Films **515**(24), 8590 (2007).

[16] K. Tanaka, A. Kunioka, Y. Sakai, Japanese Journal of Applied Physics **8**(6), 681 (1969).

[17] G. Ramalingam, J. Madhavan, Archives of Applied Science Research **3**(3), 217 (2011).

[18] Z. Deng, L. Cao, F. Tang, B. Zou, Journal of Physical Chemistry B **109**(35), 16671 (2005).

[19] A. Van der Drift, Philips Res. Rep. **22**, 267 (1967).

[20] B. N. Pawar, S. R. Jadkar, M. G. Takwale, J. Phys. Chem. Solids **66**, 1779 (2005).

[21] M. Öztas, M. Bedir, Thin Solid Films **516**, 1703 (2008).

[22] K. J. Kim, Y. R. Park, J. Cryst. Growth **270**, 162 (2004).

[23] M. Bedir, M. Öztas, S. S. Çelik, Y. Özdemir, Acta Phys. Pol. A **126**, 840 (2014).

[24] I. A. Ovid'ko, Rev. Adv. Mater. Sci. **1**, 61 (2000).

[25] M. Bedir, M. Oztas, O. F. Bakkaloglu, R. Ormancı, Eur. Phys. J. B **45**, 465 (2005).

[26] F. A. Kroger, The Chemistry of Imperfect Crystals, North-Holland, Amsterdam 1964.

[27] I. M. Khan, in: Handbook of Thin Film Technology, Eds. L. I. Maissel, R. Gland, McGraw-Hill, New York, CH:10, (1970).

[28] N. Jabena Begum, K. Ravichandran, J. Phys. Chem. Solids **74**, 841 (2013).

[29] O. S. Heavens, Optical Properties of Thin Solid Films, Dover, New York 1965.

[30] R. I. Chowdhury, M. S. Islam, F. Sabeth, G. Mustafa, S. F. U. Farhad, D. K. Saha, F. A. Chowdhury, S. Hussain, A. B. M. O. Islam, Dhaka Univ. J. Sci. **60**(1), 137 (2012).

[31] M. M. Betkar, G. D. Bagde, Materials Physics and Mechanics **14**, 74 (2012).

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