OPTICAL AND STRUCTURAL PROPERTIES OF CdSe THIN FILM PRODUCED BY CHEMICAL BATH DEPOSITION

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CdSe thin film was produced via chemical bath deposition at 50°C. Transmittance, absorption, optical band gap and refractive index have been investigated via UV/VIS. Spectrum. The hexagonal form has been observed as one of the structural properties in XRD. The structural and optical properties of CdSe thin films, which have been produced at different pH, were analyzed. SEM analyses have been performed; surface analyses of the films were made accordingly. Some properties of the films have been changed with pH and these properties have been investigated. Tested pH values were at range 7-10. The optical band gap has been changed with the pH of the bath, taking values between 1.76 and 2.09eV. Also, film thickness was measured as 74.65, 106.39, 107.95 and 138.15 nm for the films produces at pH: 7, 8, 9 and 10, respectively.

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1. Introduction

The production of selenides thin films is very cheap and easy. Some properties of selenides thin films, such as CdSe, ZnSe, are quite interesting. CdSe thin film is a very important material in the optoelectronic and electronic world, as the other selenides [1-4]. CdSe thin films is produced by various vacuum and non-vacuum film deposition methods [5], including vacuum evaporation and co-evoparation [6], molecular beam deposition [7], laser ablation [8], electrochemical deposition [9], spray pyrolysis [10] and chemical bath deposition [11]. Chemical bath deposition is more commonly used than the others, because it is cost effective.

Researchers attempted to produce CdSe thin film via chemical bath deposition many times, by trying different selenium sources each time. N,N-dimethylseleno urea and sodium selenosulphite were most commonly used selenium sources [12-13]. CdSe thin films are still produced using them, especially sodium selenosulphite.

$$Na_2SeSO_3 + 2OH^- \leftrightarrow Na_2SO_4 + H_2O + Se^{-2} \quad (1)$$

$$Cd^{+2} + Se^{-2} \leftrightarrow CdSe \quad (2)$$

$$Se^{-2} + H_2O \leftrightarrow HSe^- + H^+ \quad (3)$$

The equal (1) and (2) show the formation of CdSe and selenium source [14]. The Na_2SO_4 is not collapsed in the water media. They are equilibrium reactions and they occur at high pH environments. Consequently, many researchers worked on CdSe thin films via this method at high pH values [12-16]. Thus, the researchers could not focus on neutral pH area.In this study, we attempted to correct many improper data given in the literature. In the literature, it has been argued that CdSe thin films, produced in the bath with pH over 7, have usually crystalline structure. However, we found that CdSe thin films with crystalline structure can only be produced at pH: 9.

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2. Method

The selenium source was prepared with reflux. 1:1 (2.5×10^{-2} mol) mol ratio of solid selenium and sodium sulphide were put into the reflux with 100 mL distillated water. The reaction temperature was 80^{o}C and the reaction time was 4.5 hours. At the end of the reaction, the residual was filtered and cooled.

The components of the baths were NH_3 2 %, 10 mL 2.5×10^{-3} M cadmium nitrate and 10 mL of prepared Se source solution. First, 10 ml 2.5×10^{-3} M cadmium nitrate and 10 ml Se source solution were put into a baker, which was containing 30 ml deionized water. NH_3 2 % was used to adjust the pH of bath. In order to adjust the pH value of the solution to 10, 9 and 8;0.5, 1.0 and 2.5 mL of NH_3 2 %, was added to the solutions. The pH of the original solution was 7. pH values of the chemical baths were measured using a pH meter (Lenko mark 6230N). Then, substrates were dipped into these baths. Chemical baths have waited for 12 hours at room temperature (21 ^{o}C, and this is deposition temperature).

X-ray diffractogram (XRD) were recorded using a Rikagu Rad B model diffractometer with CuKα_1 (λ=1.5406 Å) radiation in the different range 2θ angle 10-90°. Surface morphology was studied by EVO40-LEO scanning electron microscopy (SEM) operating at an accelerating voltage of 20 kV. The optical absorption measurement was carried out in the wavelength range of 300 - 1100 nm, by using a Hach Lange 500 Spectrophotometer. Film-coated glass substrate was placed across the sample radiation pathway, while the uncoated glass substrate was put across the reference path. Absorption data were used to determine band gap energy. The thicknesses of the films were measured by an atomic force microscopy (AFM) with tapping mode.

3. Results and Discussion

CdSe thin films may have either sphalerite cubic or hexagonal structure. In our experiment, it has been observed that pH of the bath affected the structure of the film. Figure 1 show XRD patterns of CdSe thin films deposited at different pH levels, namely 7, 8, 9, and 10. Peak broadening has been observed in the recorded diffraction patterns, which implies the formation of crystalline structure.

Researchers have observed the most prominent peaks at 21.62^{o}, 24.02^{o}, 26.64^{o}, 31.84^{o} and 39.88^{o} in XRD pattern of CdSe thin film [13]. The observed structure was either hexagonal or cubic. The films produced by this method have polycrystalline structure The most important difference between our method and the ones previously used by other researchers, was that they were usually annealing the films after the production, which increases production cost considerably. In addition, we observed a Cd peak (31.94^{o}) at pH: 7 according to ASTM data files, many researchers didn’t mention it in their studies. We indexed hexagonal and cubic CdSe peaks according to the following data and ASTM standards: 45.06^{o} (pH: 7, ASTM Data file: 02-0330), 22.75^{o}, 26.81^{o} (pH: 8, ASTM Data file: 02-0330), 25.50^{o} (pH: 9, ASTM Data file: 019-0191). The best feature of this method was a cubic structure was observed at pH: 9 with a sharp CdSe peak. We also observed a Se peak at 29.011°, in the film produced at pH: 10, which were not mentioned before by the researchers. In fact, this peak was previously observed at 29.40°, however they could not demonstrate the existence of this peak because they were not able to reduce Selenium at this pH [14]. Even though the identification of the peaks in the amorphous structure was quite difficult due to the reflection of the base, they were indexed using XRD EVA program.

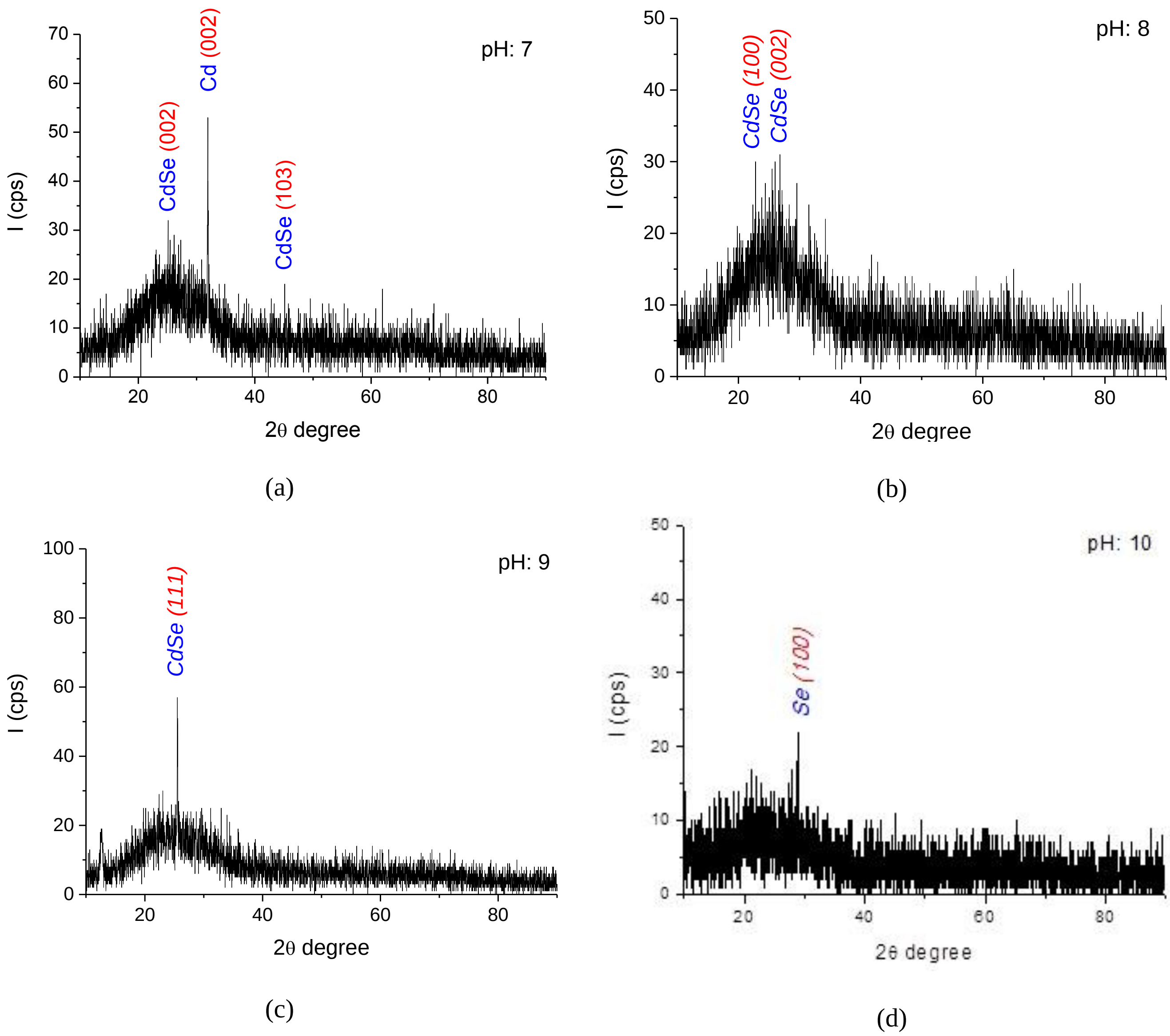


Fig. 1. X-ray patterns of CdSe films deposited in bath solution with various pH (a) pH : 10, (b) pH : 9, (c) pH : 8 and (d) pH : 7

The structural parameters, such as grain size (D) and dislocation density (δ) of the films were evaluated by XRD patterns and the results are presented in Table 1. The grain size of the thin films was calculated from XRD patterns using Debye Scherrer's formula [13],

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (4)$$

where D is the grain size, λ is the X-ray wavelength used, β is the angular line width at half-maximum intensity in radians and θ is Bragg's angle. The grain size and dislocation density of the films were calculated through the Scherrer's method, using the FWHM of (100) peak obtained. The dislocation density (δ), which gives more information about the amount of defects in the films, is given by the formula [18)],

$$\delta = \frac{1}{D^2} \quad (5)$$

Higher δ value means lower crystallinity and indicates high amount defects in the structure. Larger D and smaller δ values indicate better crystallization [18].

$$N = \frac{t}{D^3} (6)$$

where N is the number of crystallites per unit area. The higher N value indicates the abundance of crystallization. Grain size (D), dislocation density (δ) and the number of crystallites per unit area (N) could only be calculated for CdSe thin films produced at pH: 8 and 9 and the results are shown in table 1, the films produced at other pH levels were ignored. This is because distinctive characteristics CdSe peaks were observed only for these pH levels, namely (002) at pH: 8 and (111) at pH: 9. The average grain size (D) and dislocation density (δ)have higher values at pH: 8 whereas they were lower at pH: 9. Similarly, number of crystal per unit area (N) was found to be higher for pH: 8 compared to pH: 9.

Table1. Grain size (D), dislocation density (δ), number of crystallites per unit area (N) of CdSe thin films at pH: 8 and 9

pH	D (nm)	$\delta \times 10^{-3}$ (lines/nm^2)	$N \times 10^{-2}$ (1/nm^2)
8	13.40	5.55	4.40
9	10.92	8.38	8.20

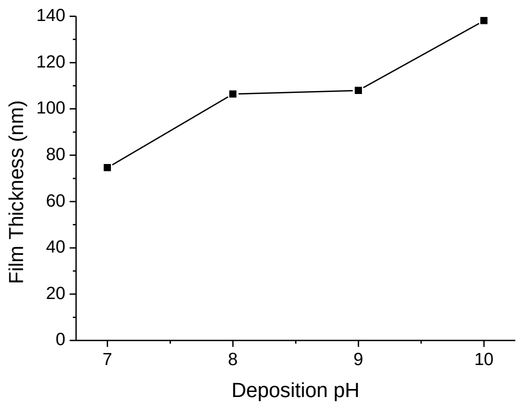


Fig. 2. Film thickness of CdSe thin films at different deposition pH

Film thicknesses, which were changed with deposition pH, are shown in figure 2. Film thickness was measured as 74.65, 106.39, 107.95 and 138.15 nm for the films produces at pH: 7, 8, 9 and 10, respectively. It was expected that film thickness would increase with the increase of pH, since the formation of CdSe is related to the presence of OH ions in the media. The thickness of the films produced by this method was in nanometer scale, as computed by Nawfal Y. Jamil et al. [15] and D.D.O. Eya [16] focused on the molar ratio of chemicals that they have used in the bath composition, whereas Nawfal Y. Jamil et al. examined the films according to different annealing temperatures, namely 373, 473, 573 and 673 K. They observed a strong red shift in the optical spectra. Even though the method used were similar to the one that we have used, their film thicknesses were higher than ours.

Transmittance (T) of CdSe thin film can be calculated using reflectivity (R) and absorbance (A) spectra from the expression [19]:

$$T = (1 - R)^2 e^{-A} \quad (7)$$

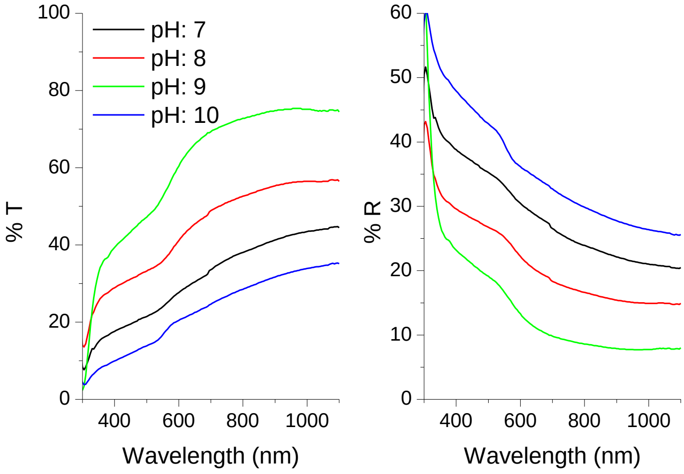


Fig. 3. Transmittance and reflectance of CdSe thin films obtained from baths with different pH

Transmission measurements are performed at room temperature in the range of 300-1100 nm. The transmission and reflectance of the films deposited at different pH was shown in Figure 3. The transmittance and reflectivity were inversely proportional; (T %) 23.98, 35.81, 52.48 and 16.71 whereas (R %): 33.22, 25.21, 16.66 and 39.71; moreover they were not correlated with film thickness which was 74.65, 106.39, 107.95 and 138.15 nm (550 nm wavelength). This may be due to the production of a different film at each pH level. It has been observed that, in some films Se structure was dominant to CdSe structure, whereas in some of them Cd structure was dominant; therefore transmittance and reflectance curves did not varied according to film thickness. Some results were in accordance with the literature. Asogwa and Nawfal Y. Jamil et al. have also measured the transmission below 20 % [13-14]. Film thickness affects transmission and reflectivity very much. Asogwa observed very low transmittance for both visible and infrared area. A slight red shift has been observed in annealed films. The peaks occurred at 625 nm (not annealed), at 655 nm (annealed at 100^{o}C) and both at 290 nm and 655 nm (annealed at 150^{o}C)
The refractive index and extinction coefficient of the films are obtained by the formulas [19]:

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (8)$$

$$k = \frac{\alpha\lambda}{4\pi} \quad (9)$$

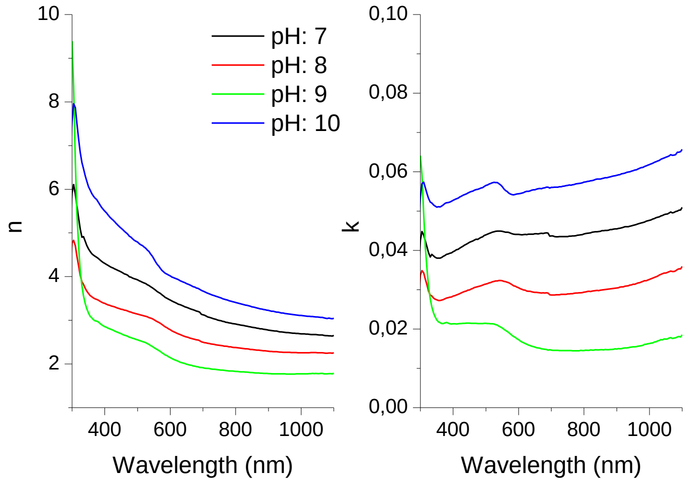


Fig. 4. Refractive index and extinction coefficient of CdSe thin films obtained from baths with different pH

As mentioned before, different structures have been produced for different pH levels, thus refractive index was not proportional to film thickness. Refractive indexes, were found to be 3.72, 3.01, 2.37 and 2.40 for film thicknesses 74.65, 106.39, 107.95 and 138.15 nm, respectively(see figure 4).In addition, extinction coefficient has behaved similar to refractive index, taking values0.04; 0.03, 0.02 and 0.02 for film thickness 93.27 nm, 60.97 nm, 61.09 nm and 60.18 nm respectively (in 550 nm wavelength). The structure was metallic Cd and amorphous CdSe at pH: 7 and 8, so the refractive index was different than the others. D.D.O. Eya has also calculated refractive index of CdSe films around 2-2.5. He did not cite the effect of film thickness on refractive index. He argued that, if the refractive index was 2.64 then electromagnetic radiation would be 2.64 times slower in CdSe films compared to the space. Therefore, they pretended that they have observed these peaks within the visible region of the electromagnetic spectrum [16]. In our study, we observed characteristic peaks of a typical CdSe film.

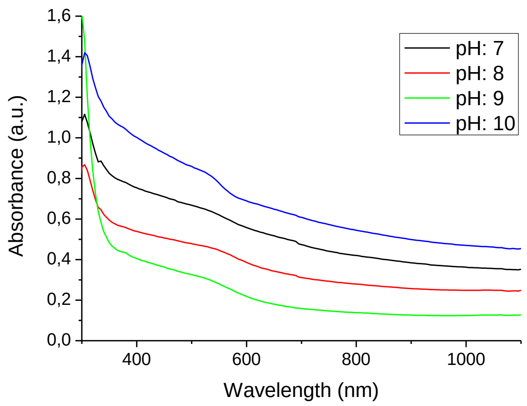


Fig. 5.Absorbance Plot of CdSe films produced at different pH

The absorbance of CdSe thin film can also be calculated with equal (7), shown in figure 5. The absorbance did not behave as extinction coefficient and refractive index, measured as 0.62, 0.44, 0.28 and 0.77for pH: 7, 8, 9 and10, respectively (in 550 nm wavelength). We observed the lowest absorbance for the film produced at pH: 9. Similar to transmittance and reflectance (and as mentioned there), the change of absorbance was not proportional to film thickness. Some researchers investigated absorbance whereas some others investigated absorbance constant [13, 15, 17]. Asogwa has calculated the absorbance of CdSe thin films and found to be between 0.70-0.95 at different annealing temperatures. They obtained the highest absorbance within the visible region of the solar spectrum for the film without annealing. The results were different than the literature. The optic band gap energy (Eg) was calculated from the absorption spectra of the films using the following relation [13]:

$$(\alpha h\nu) = A(h\nu - Eg)^n \tag{11}$$

Where A is a constant, α is absorption coefficient, hν is the photon energy and n is a constant, equal to ½ for direct band gap semiconductor. The plot of $(\alpha h\nu)^2$ versus hν was drawn in figure 5 (a: pH 7, b: pH 8, c: pH 9, d: pH 10).

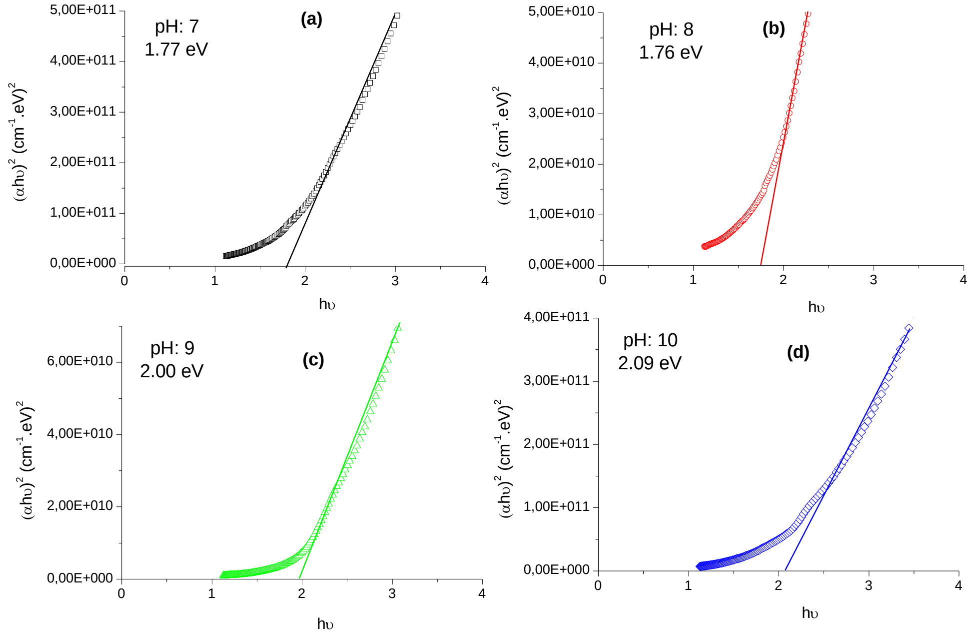
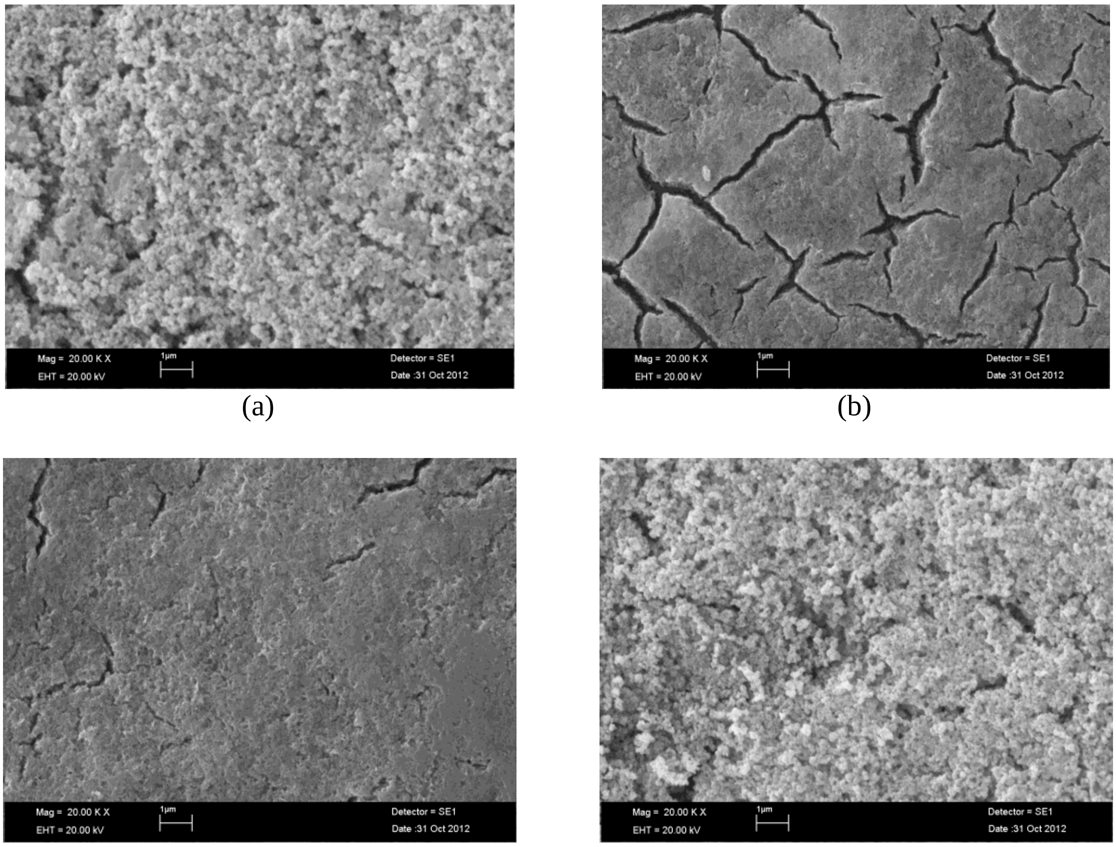


Fig. 6.Plot of $(\alpha h\upsilon)^2$ vs. hυfor CdSe films: (a) pH 7, (b) pH 8, (c) pH 9, (d) pH 10

The band gaps (Eg) of the films varied as1.77, 1.76, 2.00 and 2.09 eV, depending on the structure. Lowest values of the optic band gap were observed for pH: 7 and 8, because Cd peak was the dominant structure at pH: 7 and amorphous CdSe was the dominant structure at pH: 8.The main reason of obtaining the lowest optic band gaps at pH:7 and 8, was the formation of ubrach tail, since the films produced at these pH levels had amorphous structure. Many researchers investigated optic band gap. They found different values, due to different processes after the deposition. H. Metinet. al. produced nearly amorphous thin films and they calculated optic band gap around 1.8 eV [20]. Asogwa, D.K. Dwıvedı, H. M. Pathanet. al., Nawfal Y. Jamil et al.and D.D.O. Eya also calculated optic band gaps as 1.50-1.90, 2.60-3.00, 1.80, 1.60-2.00, 2.60 eV, respectively [13-15, 16, 20].



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

Fig. 7. SEM images of CdSe thin films produced at different pH,
(a) pH: 7, (b) pH: 8, (c) pH: 9, (d) pH: 10

SEM images of CdSe thin film are given in figure 7. SEM images of the films deposited at pH: 7 and 10 were quite different than the ones produced at pH: 8 and 9, because they were containing Cd and Se. The crystalline peaks of CdSe were observed at pH: 8 and 9. Even though crystalline peaks were observed for the film produced at pH: 8, there were many cracks at the surface. Regarding SEM images, the film produced at pH: 9 had a very tight structure and a few cracks. Therefore, the refraction index of the film produced at pH:9 is lower than the others. The results of SEM images were in agreement with the XRD patterns.

4. Conclusion

The reduction of selenium with sodium selenium sulfite is awell-known method in the literature. However, nobody produced CdSe thin films at neutral pH. The cadmium peak was more dominant than the CdSe peaks on amorphous structure. We found that the best pH values for producing CdSe thin films were pH: 8 and 9. If this study had achieved a success at pH: 7, the rest of the study would be performed at acidic area. The other parameters of the films produced at pH: 8 and 9 were also good. This paper shows that, for this method there is a lack of information in the literature or the existing ones were misinterpreted by the researchers. The production of CdSe thin film using sodium seleno sulphite as the source of selenium provided best results at pH:9 and to some extent at pH: 8. In this study, we attempted to correct many improper data given in the literature. In the literature, it has been argued that CdSe thin films, produced in the bath with pH over 7, have usually crystalline structure. However, we found that CdSe thin films with crystalline structure can only be produced at pH: 9. In addition, the existence of Cd peak at pH: 7 and Se peak at pH: 10 was shown in this study for the first time. As a result, it has been concluded that researchers can produce CdSe thin films only at pH: 8 and 9. We discovered that CdSe cannot be formed at lower pH levels whereas at higher pH levels $CdSeO_4$ was formed instead of CdSe (These result were not shown in this paper because they are not relevant to CdSe production).

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