Structural and optical properties of cadmium selenide thin film growth with different substrate temperatures by spray pyrolysis deposition

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In this work, cadmium selenide (CdSe) thin films were deposited successfully by spray pyrolysis at different substrate temperatures. The influence of the preparation technique on the optical, morphological, and structural properties of the different substrate temperature CdSe films were investigated by using X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-Visible optical transmission. The XRD analysis reveals that CdSe thin film has hexagonal (wurtzite) and (cubic) crystal structures with different particle sizes depending on the substrate temperature. The SEM image shows uniform and adherent crystals. The optical energy gap was found to be in the range of 1. 70 – 2.59 eV with different temperatures.

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1. Introduction

Cadmium Selenide CdSe is one of the most important chalcogenide semiconductor materials and belongs to the II-VI group, which has a cubic or hexagonal structure, high sensitivity of light at the visible region, and can be prepared as an n-type semiconductor [1-4], it has also an electrical resistivity 105-106Ω.cm. Due to the high absorption coefficient and photoconductivity with direct band gap and 1.74eV and the electron mobility of 450-900 cm2 /V ·s and indirect band gap of 1.23-1.25eV [5-9], which exhibits a powerful photoelectric effect when activated by visible light, falls within the solar spectrum's visible light range. Because of CdSe has a highly photosensitive nature, it is widely preferred in the fabrication of different optoelectronic devices such as PEC cells [10-12], field effect transistors [13], thin film transistors [14], and photodetectors [15-17]. Physical and chemical deposition techniques have been used in the preparation of CdSe thin films such as thermal evaporation [18-19], Pulsed laser deposition (PLD) [20-21], Rf-sputtering [22], electron beam evaporation [23], chemical vapor evaporation (CVD) [24], chemical bath deposition (CBD) [25-26], potentiostatic electrodeposition method [27], Silar [28] and Spray pyrolysis [29-30], etc. The spray pyrolysis system has many advantages such as non-vacuum equipment, non-toxic gas, quality thin film formation, and cheap manufacturing compared to other deposition systems. In this article, we present the spray pyrolysis deposition technique for the preparation of pure CdSe thin films at different substrate temperatures. The effect of temperature on optical, and structural properties of CdSe thin film were examined by using (UV – spectrometer), x-ray spectra, and Scanning electron microscope respectively.

2. Material and methods

Thin films of cadmium selenide CdSe have been deposited on soda lime glass (SLG) substrates by the Spray pyrolysis method at different substrate temperatures (60, 100, 150, 200, 250, and 300°C). The cleaning process of glass substrates includes several steps using deionized water, ethanol, and acetone ultrasonically to remove any contamination from the substrate's

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surfaces. All substrates were dried in the nitrogen atmosphere. Sodium Selenosulphate Na_2SeSO_3 solution was used as a precursor of Se^{2+} source (1 M), it was prepared from the dissolving of 1.2 gm of sodium sulfite (Na_2SO_3) and 0.8 gm of selenium powder in 20 ml of deionized water. The later solution stirring for 2hr at 70°C, Then the solution was filtered to remove the sediments. Cadmium chloride ($CdCl_2$) was used as a precursor of the Cd^+ source, it was prepared from the dissolving of 1gm of $CdCl_2$ in 20 ml of deionized water and 1 ml of ammonia NH_3 as a complex agent was added to reach PH=11. Finally, both solutions have been mixed and stirred at 70ºC for 15 min. Finally, the precursor was sprayed with pressurized atmospheric air into substrates with a spray pyrolysis system. On the other hand, the distance between the nozzle and substrate is fixed at 25 cm, and the flow rate is 4 ml/m. The following chemical equation illustrates the reactions:

$$Na_2\ SO_3 + Se \rightarrow N_2Se\ SO_3 \quad (1)$$

$$CdCl_2 + 4NH_3 \rightarrow Cd\ (NH_3)_4)^{+2} + CdCl_4^{-2} \quad (2)$$

$$(Cd\ (NH3)_4)^{+2} \rightarrow Cd^{+2} + 4NH_3 \quad (3)$$

$$Cd^{+2} + Se^{-2} \rightarrow CdSe \quad (4)$$

3. Results and discussion

3.1. Thickness measurements

In contrast to bulk material, thickness has a significant impact on the properties of films. Only when the deposition parameter and film thickness were kept constant were reproducible characteristics obtained. The gravimetric method as shown in relation (5) was used to determine the thickness of deposited films [31].

$$\tau = \Delta m / (A \times \rho) \quad (5)$$

where Δm is the weight difference between before and after deposition of soda lime glass substrate (SLGs), while A is the area of deposited (SLGs); finally, the intensity of the CdSe material is defined by the symbol ρ. The thickness of the film decreased with increasing the substrate temperature as shown in the Figure 1 Due to reduce adhesion of precursor at high temperatures, the thickness of the film decreases with increasing substrate temperature.

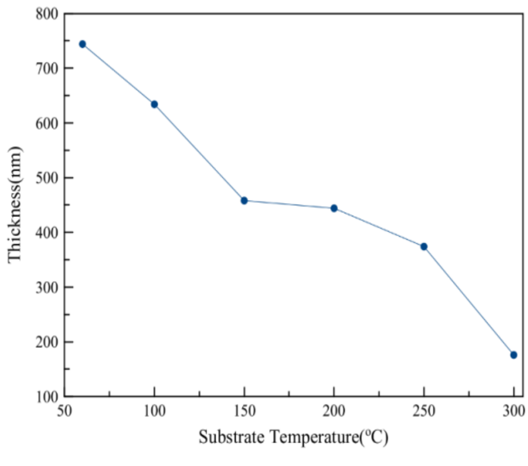

Fig. 1. Thickness of film vs substrate temperature.

3.2. X-ray diffraction

To determine the crystallographic structure, determine the crystal size of the deposited CdSe thin film, X-ray diffraction patterns were taken. XRD pattern of spray pyrolysis deposited CdSe thin films with 60ºC, 100ºC, 150ºC, 200ºC, 250ºC, and 300ºC substrate temperatures are given in Figure 2, respectively. The XRD patterns clearly showed the influence of the substrate temperature on the crystallinity of the films. In general, CdSe exists in two crystalline forms, zinc blende (cubic) and wurtzite (hexagonal). Because of this, the CdSe films may exhibit mixed, cubic, or hexagonal phases. CdSe typically exhibits mixed phases in XRD patterns, as shown in [32]. The spectrums show that the films were crystalline with a small presence of the mixed phase at (100-250ºC), while at temperatures 60ºC and 300ºC the phases were amorphous. On the hand, the average grain diameter varied with substrate temperatures, at 60ºC the average grain diameter is (53.53nm) then it increases with temperature to (83.2) at 200ºC it decreases to (61.6569 nm) at 300ºC, may be explained by the decrease of the crystalline quality due to the increase of disorder during film growth. These results were calculated by Debye-Scherrer formula (6) [32].

$$D = (0.94\,\lambda) / (\beta\cos\theta) \qquad (6)$$

where D is the crystallite size, λ is the wavelength of the X-ray source, β is the full width at half maximum value and θ is the Bragg's angle.

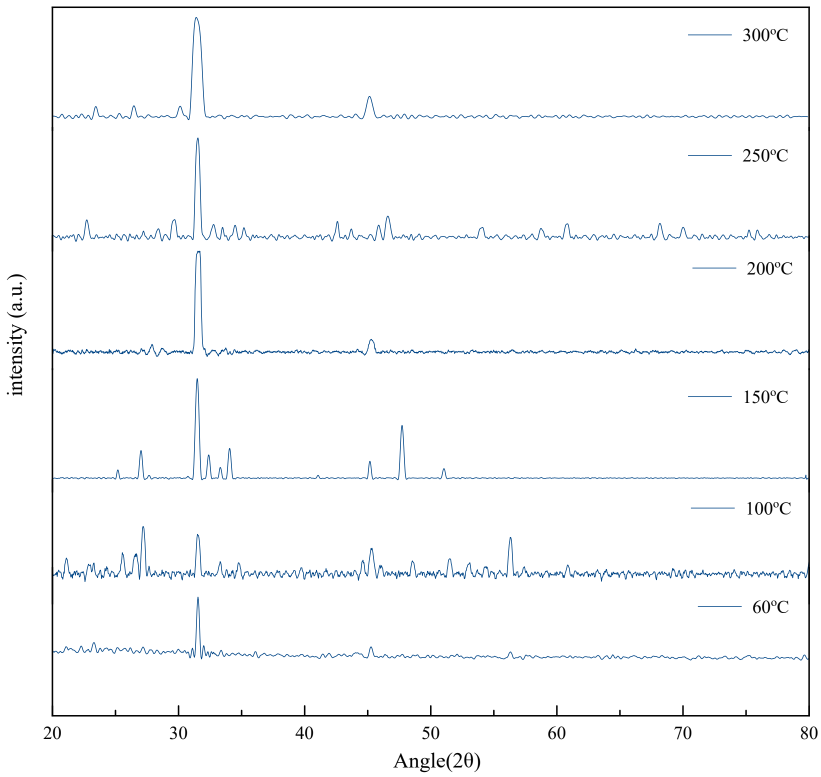

Fig. 2. XRD pattern of deposition films vs substrate temperature.

The peaks that belong to the CdSe films summarized in Table (1) and peak intensity comparisons show strong agreement with baseline JCPDS data [33].

Table 1. CdSe thin film structural parameters at various substrate temperatures.

Substrate Temp ºC	(Angle) 2θ	*hkl*	FWHM	Grain Size (nm)
60	23.219 27.1935 36.064 45.2839 56.3228	(1 0 0) H (1 0 1) H (2 0 0) H (1 0 3) (2 0 2)	0.2362 0.1181 0.1574 0.1181 0.2362	34.34338 69.21317 53.0825 72.88729 38.14925
100	23.4598 27.2033 45.3173 49.5316 56.3045	(1 0 0) H (1 0 0) H (1 0 3) (1 1 2) H (2 0 2) H	0.0590 0.1181 0.4723 0.2362 0.6298	137.534 69.11183 17.99119 37.0022 14.29957
150	23.3054 27.5388 45.4054 49.2868	(1 0 0) H (1 0 1) H (1 0 3) (1 1 2) H	0.1181 0.9446 0.0590 0.0720	68.68966 8.678568 145.8999 122.6504
200	37.002 42.6556 50.0743 66.7268	(2 0 0) C (1 1 0) H (1 1 2) H (2 1 1)	0.7872 3.7786 0.0720 0.0480	10.64249 2.257113 121.7824 198.1483
250	23.4989 24.9981 34.3398 42.4151 49.0978 57.8979	(1 0 0) H (0 0 2) H (1 0 2) C (1 1 0) H (1 1 2) H (2 0 2)	0.7872 0.7872 0.9446 0.0984 0.0787 0.0720	10.30879 10.33778 8.803133 86.60337 110.9774 125.6581
300	25.7169 36.3231 42.1178 45.1493	(0 0 2) H (1 0 2) C (1 1 0) H (1 0 3)	0.1574 0.0787 3.7786 0.1574	138.1251 106.2434 2.253014 54.66191

3.3. Morphological study

The SEM analysis method is the one-of-a-kind, best, practical, and flexible approach to examine the morphological characteristics of film and provide information on grain size. The morphological characteristics of spray-deposited CdSe films were examined using the SEM technique, and it was determined which substrate temperature allowed for the formation of good CdSe film quality. The SEM images show that the CdSe film was coated homogeneously and smoothly on the SLGs surface. It's seen at (100-250ºC) substrate temperature the crystal grains are regularly arrayed granules to form a regular crystal. Moreover, the average size of the SEM image is strongly in agreement with the XRD results, as shown in Figure 3.

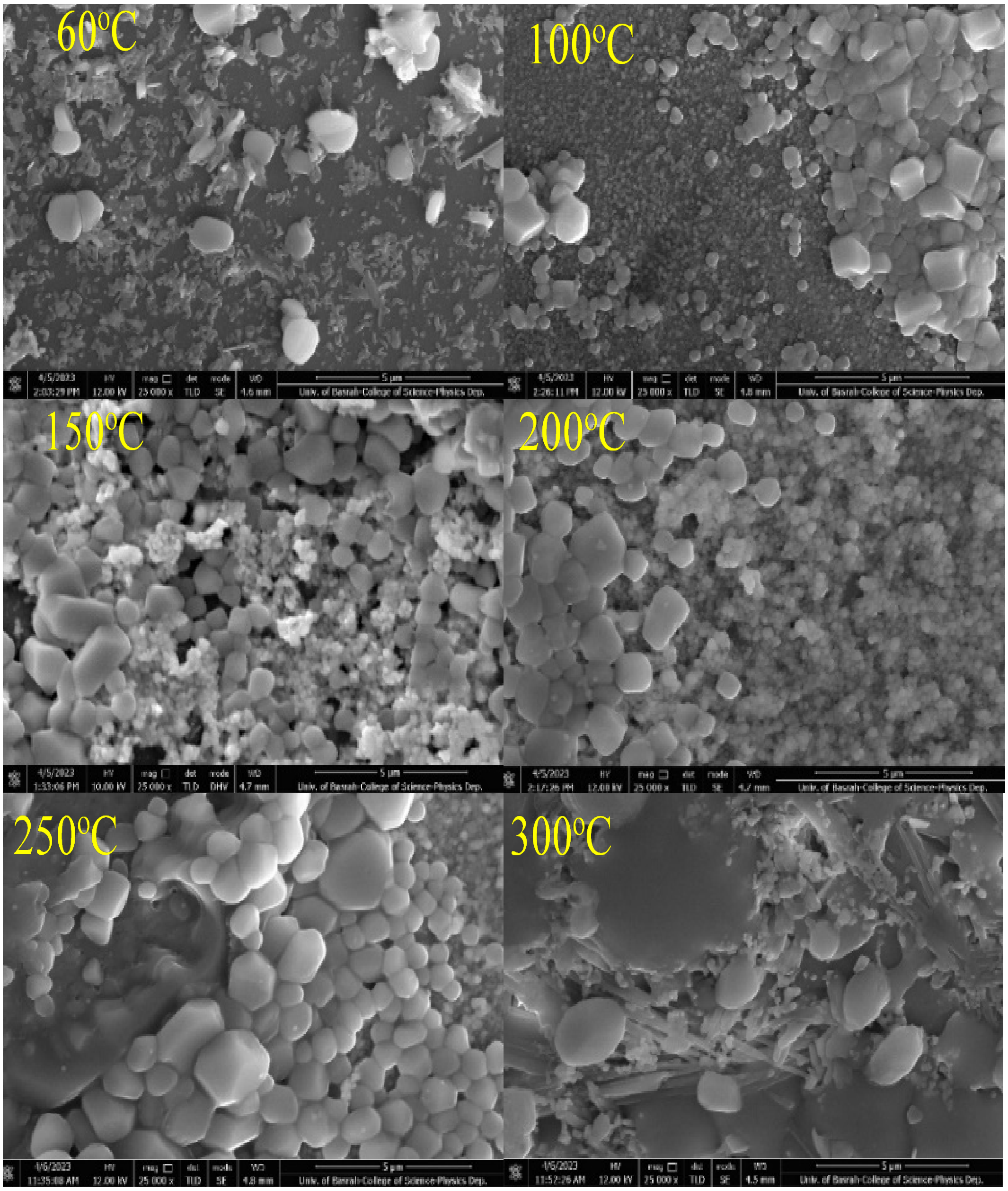

Fig. 3. SEM images of deposition films vs substrate temperature.

The surface morphologies of the sprayed films are depicted in Figure 4 as a function of the substrate temperature. all grain properties grain size and grain boundaries change considerably with the substrate temperature of the films.

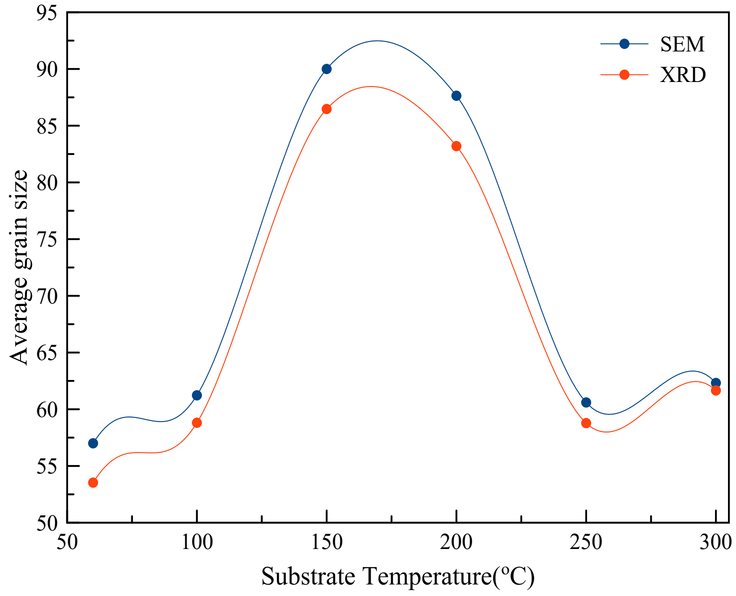

Fig. 4. Variation of average crystallite size as a function of temperatures.

3.4. Optical properties

The following relation can be used to calculate the optical band gap from experimental results of the absorption coefficient (ν) as a function of photon energy (hν), [34]:

$$\alpha hv = A(hv\text{-}Eg)^n \tag{6}$$

where A is the constant, and Eg is the band gap of the film. hv is the photon energy, n= 2 or 1/2 for indirect or direct transition. The energy gap (Eg) of spray-deposited CdSe film was determined (1.74 eV) from the experimental investigation at 100oC. The energy gap (Eg) increases with increasing temperatures as shown in Figure 5.

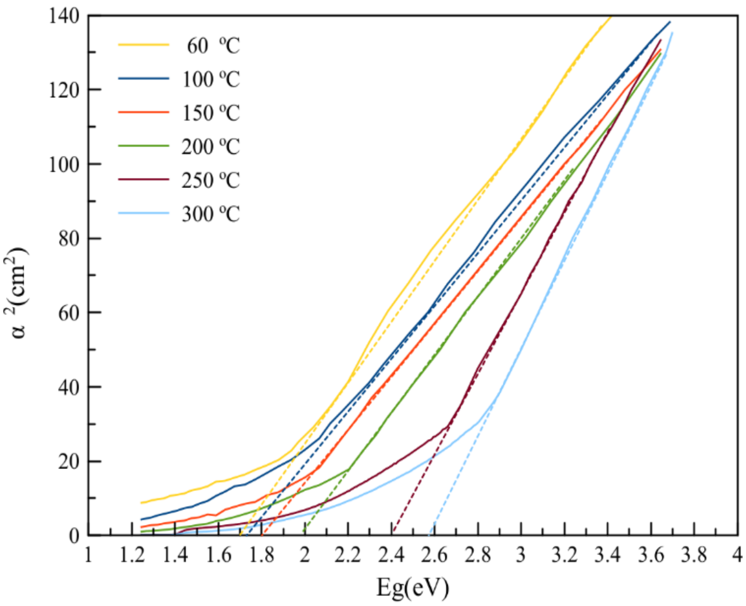

Fig. 5. The optical band gap of deposition films vs. substrate temperature.

The energy gap values of films at different substrates temperature are shown in Table (2). these results agree with [26].

Table 2. CdSe thin-film band gap for various deposition temperatures.

Deposition Temperature	Energy Band Gap (eV)
60ºC	1.70
100ºC	1.74
150ºC	1.80
200ºC	2.00
250ºC	2.40
300ºC	2.59

4. Conclusions

CdSe thin film was deposited on (SLGs) at different substrate temperatures by chemical spray pyrolysis deposition method. The XRD analysis reveals that CdSe thin film has a mixed crystal structure with different particle sizes depending on the substrate temperature. While SEM image shows the development of wurtzite and cubic nanoparticles over the entire substrate between (100-250oC). According to the results of the SEM image and XRD data, the average grain size is strongly in agreement with each other. The optical energy gap was in the range of (1.70–2.59 eV) with the direct allowed transition depending on the substrate temperature.

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