Layer-by-layer production of CdS thin films by chemical bath deposition

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In this study, the effect of the number of layers on the optical, morphological and structural features of the CdS films grown on the glass substrates using chemical bath deposition method was investigated. In the experiments, the CdS thin films with one layer, two layers and three layers were produced. According to XRD analysis, all the films exhibited a cubic structure. However, the preferred orientation of the films was affected by the number of the layers.The crystallite size decreased from 15 nm to 6 nm as the number of layers was increased. From the optical analysis of the films, it was found that the optical bandgap increased from the 2.42 eV to the 2.74 eV with increasing the number of layers. The CdS thin films with one and two layers exhibited high transmittance. From the morphological analysis of the samples, it was also revealed that the cracks and pinholes observed on the sample surfaces can be eliminated by applying the process developed in this work.

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1. Introduction

Cadmium sulphide (CdS) is a II–VI compound semiconductor material important for scientific and technological applications due to its band gap of about 2.42 eV at room temperature [1]. CdS exhibits high refractive index, n–type conductivity, high absorption coefficient, and wide and direct band gap[2]. CdS is used in photocells and other photoconductive devices, light amplifiers image intensifiers, phosphors and electroluminescent devices, radiation detectors, thin film transistors and diodes, piezoelectric ultrasonic transducers and amplifiers, piezoelectric acoustic resonators and electron beam-pumped lasers [3]. CdS films have been deposited by various methods such as chemical bath deposition (CBD), vacuum evaporation[4,5], spray pyrolysis [6,7], sputter in process[8,9], successive ionic layer adsorption and reaction[10]etc. Techniques, other than chemical bath deposition are costly because complex equipments are needed and preparation steps require strict conditions. CBD is simple and inexpensive [11,12]. The CBD process is preferred due to the advantages of the CBD method [13]. For example, the thickness of the films can be controlled by changing precipitation parameters. Other advantages include coating of various (like plastics) and wide surfaces, usage of different substrates, and very low equipment cost [11].

The chemical reaction for chemical bath deposition of CdS thin films are given in following formulas:[14]

$$CdCl_2 + 2KOH \rightarrow Cd(OH)_2 + KCl \quad (1)$$

$$Cd(OH)_2 + 3NH_4NO_3 \rightarrow [Cd(NH_3)_4](NO_3)_2 + 2O_2 + H_2O \quad (2)$$

$$[Cd(NH_3)_4](NO_3)_2 \rightarrow Cd(NH_3)_4^{2+} + 2NO_3^- \quad (3)$$

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

$$CS(NH_2)_2 + 2H_2O \rightarrow 2NH_3 + CO_2 + H_2S \quad (5)$$

$$H_2S \rightarrow S^{2-} + 2H^+ \quad (6)$$

$$Cd^{2+} + S^{2-} \rightarrow CdS \quad (7)$$

Currently, there is no study for layer-by-layer production of CdS. In this study, CdS films were deposited on glass substrate layer-by-layer using chemical bath deposition method for the first time according to the literature. Coating up to three layers were made on the glass substrate with CBD method. The effects of layer-by-layer production were investigated in terms of the structure, composition, morphology, optical and electrical properties of the thin films. As stated in this study, it is understood that the film obtained in two layers are more beneficial for solar cells because of the fact that the problem of cracks and pinholes observed in one layer productions[14] were eliminated.

2. Experimental procedure

CdS thin films were deposited using chemical bath deposition method. CdS thin films were first prepared on soda-lime glass (SLG) substrates. Prior to the depositing, the substrates were cleaned successively with deionized water in order to remove any impurities and residuals.

The chemical deposition method was employed to deposit CdS thin films onto glass substrates. The precursor solutions for thin films consisted of cadmium chloride, potassium hydroxide (KOH), thiourea (TU), and ammonia. The cadmium chloride was used as the cadmium ion source and thiourea as the sulphide ion source for ammonia bath. The molar solutions of $CdCl_2$ (0.02M) and thiourea $SC(NH_2)_2$ (0.2M), KOH (0,5 M), were prepared using doubly distilled water. NH_4NO_3 (1,5M) solution was then added to the $CdCl_2$, and the pH of solutions was adjusted to 11 with the help of ammonia. All final solutions were stirred 800 rpm during the deposition.

As cadmium chloride, TU, and ammonia solution were completely mixed, three cleaned SLG substrates were immersed in the final solutions. The precursor solutions were heated at 80°C and the reaction duration was 40 minutes. The color of solutions changed gradually to yellow after nearly four minutes. This refers to the start of the chemical reaction.

After the reactions, the precipitated CdS films were rinsed with deionized water. This operation was prepared three times.

The crystal properties of the CdS thin films were investigated using X-ray diffraction (XRD) measurements obtained with a PANALYTICAL –EMPYREAN X-ray diffractometer, for 2θ in range of 20°-35°. This device uses Cu-Kα radiation with a 1.54Å.

The optical transmission spectra of the deposited thin films of CdS were determined with A JASCO V–530 double-beam UV–Vis Spectro photometer in order to determine the band gap energy, within the range of 300-900 nm. The surface images of the CdS films were obtained by a NANO SEM 650 (scanning electron microscope).

3. Results

3.1. Structural analysis

The thicknesses of the films were calculated by using the well-known gravimetric method. According to these results, the thicknesses of the films were calculated 310 nm, 560 nm and 780 nm depending on one layer, two layers and three layers, respectively.

XRD analysis was carried out for investigating the structure of CdS films. Typical diffraction patterns of CdS thin films prepared by chemical bath deposition technique on glass substrates were analyzed with different thicknesses. The XRD patterns are presented in Fig. 1.

The preferred orientation of the one-layer film and three-layer film were (111) and the preferred orientation of two layers was (002). According to the XRD pattern, all films were formed as to be cubic structures.

The crystallite sizes of the films were calculated by using Scherrer equation which is presented below:

$$\text{cs} = \frac{0.089 * 180 * \lambda}{314 * \beta * \cos\theta_c}\,\text{nm} \quad (8)$$

where β is full width half maximum (FWHM), λ is the wavelength of X-ray radiation (1.54056 Å) and $2\theta_C$ is the peak center [15]. Highly remarkable results were observed in crystallite sizes. Crystallite sizes of the films are given Table 1.

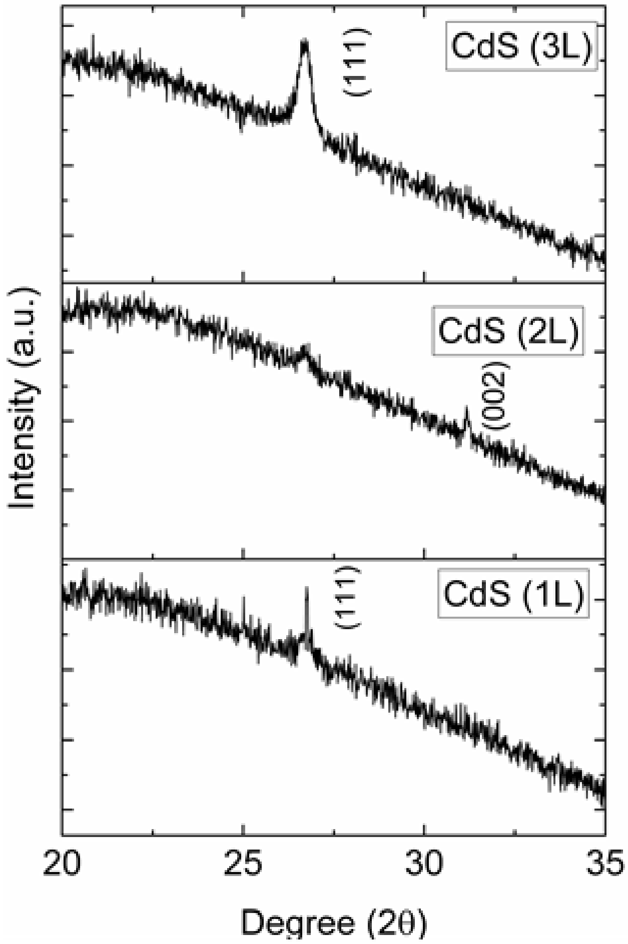

Fig. 1. XRD analysis of one, two and three layers of CdS thin films

Table 1. The thickness, crystallite size and band gap

Number of layer	Thickness	Crystallite sizes (nm)	Band gap (eV)
1 layer	310	15	2.42
2 layers	560	8	2.63
3 layers	780	6	2.74

When the numbers of layers were two and three, the crystallite size was down almost two times. This situation had great effects on optical properties of the films.

3.2. Optical properties of the CdS films

The transmittances of the films were recorded by using a UV-vis spectrophotometer. The transmittance plots are given in Fig. 2.

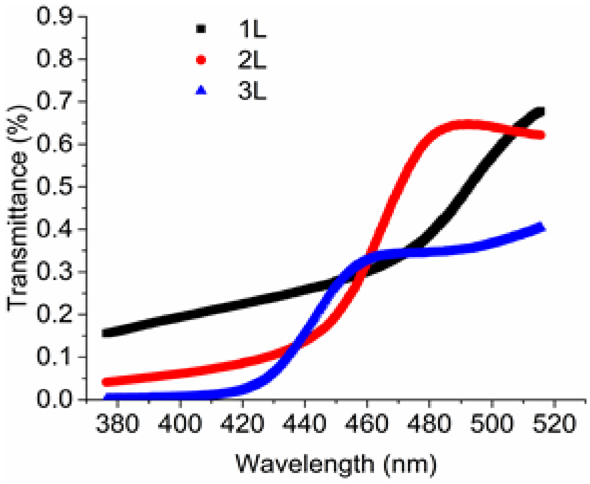

Fig. 2. Transmittance values versus wavelength (color online)

The films obtained as one and two layers exhibited 70% transmittance above 480 nm. In this case, it can be said that the film obtained in two layers are suitable as much as one layer of CdS for solar cell. But, three layers of the CdS film showed 40% transmittance which is not suitable for solar cells.

For calculating band gaps of the films, the Tauc plot was used and it is given in Equation 9 below:

$$\alpha = \frac{A(hv - Eg)^{1/2}}{hv} \qquad (9)$$

where hv is the energy of photon, Eg the optical gap of the samples and A is a constant.

The linear portion of the plot $(\alpha hv)^2$ versus hv extrapolated for $(\alpha hv)^2 = 0$ gives a band gap value of the films [16,17].The Tauc plots are given in Fig. 3.

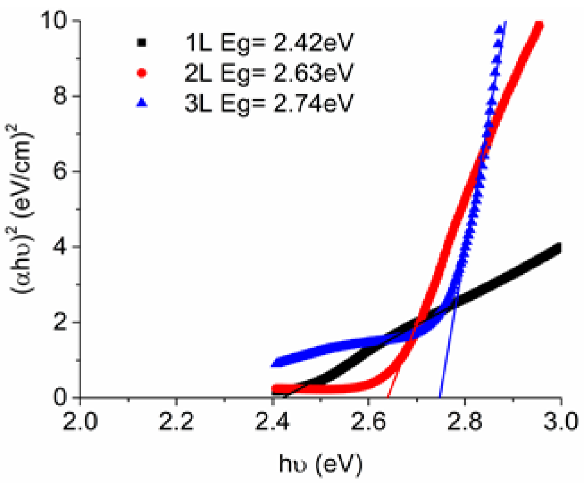

Fig. 3. Tauc plots of the CdS thin films (color online)

According to the Fig. 3, as the numbers of layers were increased, the band gap of the films were also increased from 2.42 to 2.74 eV since the crystallite size was decreased.

3.3. SEM images of the CdS films

The surface morphology was taken at both 5000 and 90000 magnification values due to the fact that cracks and pinholes may be not seen relatively at a high magnification such as 90000x.

The 5000x magnified surface images are given Fig. 4.

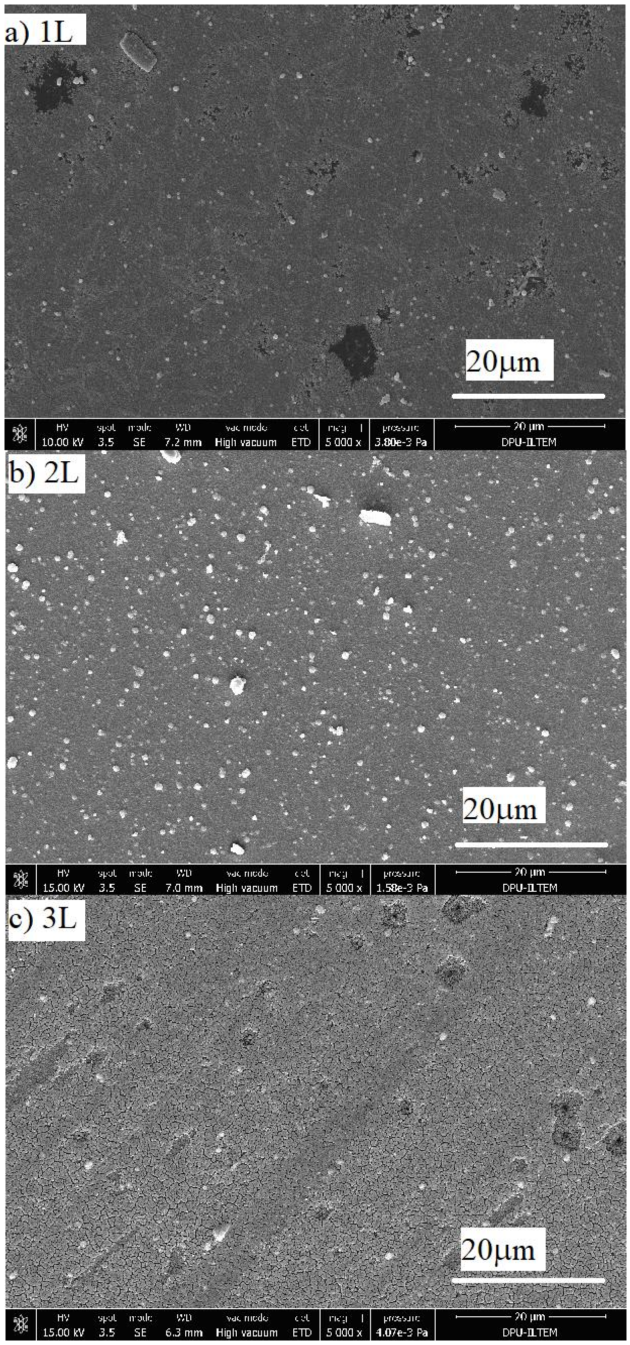

Fig. 4. 5000x magnified SEM images

As seen in Fig. 4, there are plenty of cracks and holes on the surface of the film obtained as one layer. On the other hand, when the film obtained was consisted of three layers, cracks and surface defects were seen. However, there were no cracks and pinholes seen on the surface of the film obtained as two layers. Pinholes and cracks might be caused by an electrical leakage. It was revealed in this study that when the film was consisted of two layers, the surface was compact and no pinholes or cracks were observed.

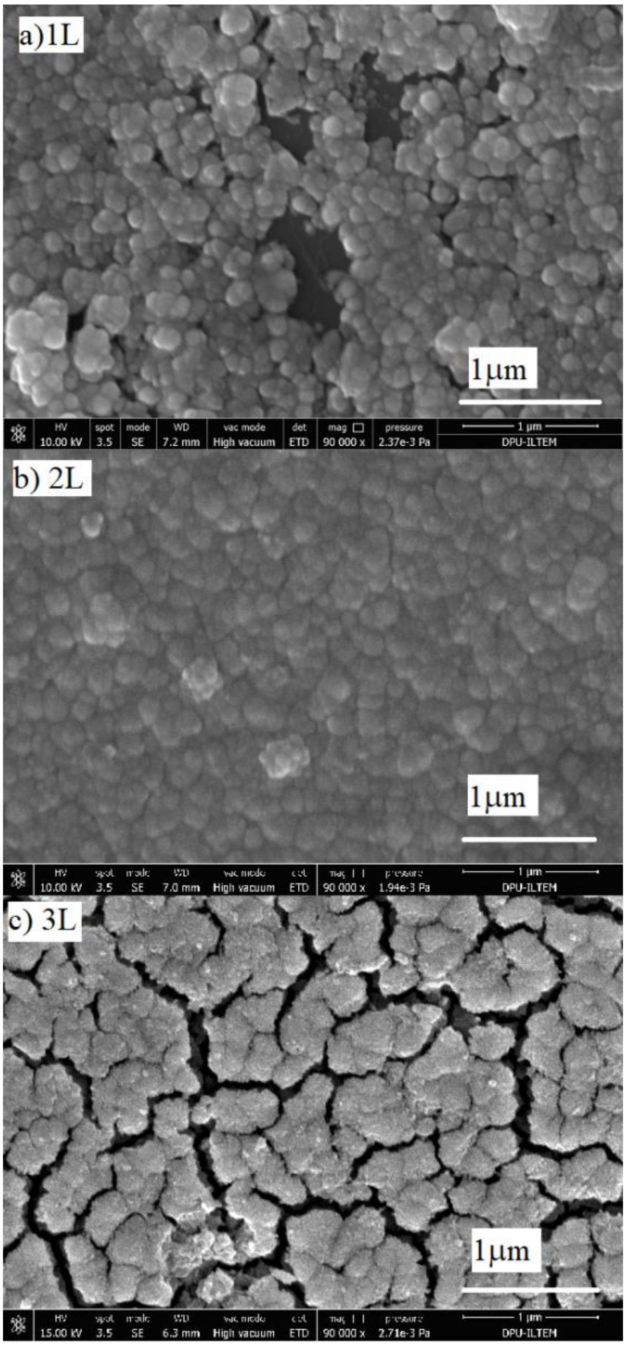

Fig. 5. 90000x magnified SEM images

The 90000x magnified surfaces are given in Fig. 5. When the Fig. 5 is analyzed, it can be seen that the surface of the films obtained as one and three layers have cracks and pinholes. This study demonstrates that the film obtained as two layers is more suitable for solar cells.

3.4. The visual properties of the CdS films

The photos of the films are given in Fig. 6. As the thickness was increased, the color of the surface changed gradually from light yellow to dark yellow.

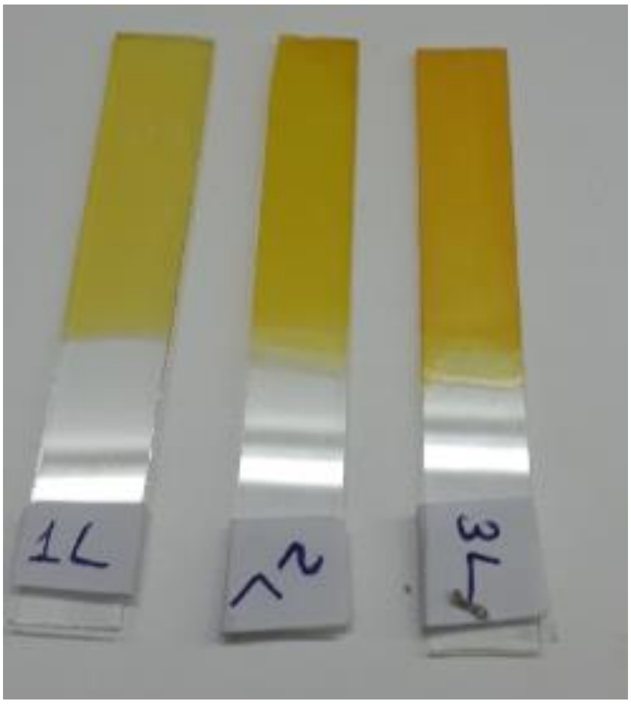

Fig. 6. The photos of the samples (color online)

It is also shown in the Fig. 6 that the CdS films were well adherent on the surface of the glass substrates.

4. Discussion

In this study, the CdS thin films with one layer, two layers and three layers were fabricated on the glass substrates by the chemical bath deposition method and the effect of the number of layers on the optical, structural and morphological features of the samples was studied for the first time. The XRD analysis showed that the films had the cubic crystal structure. The CdS thin films with one and three layers showed the [111] preferred orientation while the preferred orientation of the CdS thin film with two layers was in the [002] direction. The crystallite size significantly decreased from 15 nm to 6 nm as the number of layers was increased. This decrease in the crystallite size caused an increase in the energy bandgap of the films from 2.42 eV to 2.72 eV. The CdS thin films with one and two layers exhibited 70% transmittance above 480 nm. However, the CdS thin film with three layers showed 40% transmittance. The surface properties were analyzed using the SEM images. It was revealed from the SEM images that the CdS thin films with one and three layers had some pin holes and cracks. However, the CdS thin film with two layers exhibited the most compact morphology without pin holes and cracks. In conclusion, the CdS thin film with two layers is more suitable for solar cells compared to the CdS thin films with one and three layers. This study shows us that when the film was produced as two layers, it is more suitable for solar cells.

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