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Preparation of Nanocrystalline CdS Thin Films by a New Chemical Bath Deposition Route for Application in Solar Cells as Antireflection Coatings

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ABSTRACT

Nanocrystalline cadmium sulfide thin films as antireflection materials for solar cells have been prepared by a new chemical solution deposition route in an aqueous medium at 50 °C. as-deposited thin films were studied using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and optical absorption spectra. X-ray diffraction data indicated the formation of hexagonal nanocrystalline CdS thin films as the predominant phase. High film deposition rates, film uniformity and low percentage of reflection are achieved by proper optimization of CdS chemical bath. The as-deposited CdS films had more than 85% transmittance in the visible region. The direct band gap energy (E_g) of as-deposited films ranged from 3.85 to 3.90 eV depending on deposition time. This increase in E_g of deposited thin films can be assigned to the quantum size effect as expected from the nanocrystalline nature of the CdS thin films. Prog. Color Colorants Coat. 3(2010), 82-90. © Institute for Color Science and Technology.

1. Introduction

Antireflection coatings have been one of the key issues for mass production of solar cells. Antireflection coating is of interest for boosting the performance of the device of solar cells and hence increasing their efficiency [1]. Cadmium sulfide (CdS) is a wide band gap (2.42 eV) and direct transition semiconductor [2]. Consequently, it is potentially an important material to be used as an antireflection coating for heterojunction solar cells [3]. It has been widely used as a window material in high efficiency thin film solar cells based on CdTe or CIGS [4].

Methods of the thin films growth can be divided into two major groups: those carried out in gas phases (dry process) and in liquid phases (wet process). The dry vacuum physical process includes techniques such as sputtering, physical vapor deposition, chemical vapor deposition, and molecular beam epitaxy [5-8]. These methods require high vacuum and temperature to produce gaseous precursors. The gas-phase techniques have the advantages of high controllability of the film growth and the feasibility to obtain a pure material. The main disadvantages of these techniques are high energy needed for the deposition processing and the emission of

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gaseous waste materials in environment [9, 10]. The wet process includes techniques such as electrodeposition, spray pyrolysis, successive ionic layer adsorption and reaction, and chemical bath deposition [11-14]. Among the wet processes, the chemical bath deposition (CBD) technique has been actively studied for the deposition of various kinds of compound semiconductor thin films in the recent years [15-18]. The CBD method is the analogous in solution to the well known chemical vapor deposition (CVD) method in the gas phase, in which the deposition takes place between precursors in a single solution bath [19].

The CBD method is found to be an inexpensive, simple, and convenient method to depositing large area semiconductor thin films at relatively low temperatures [20]. In recent years, many researchers have studied the deposition of CdS thin films by CBD method [21-23]. Thin films of CdS have been mostly prepared by CBD in alkaline solution (pH=10-12) containing Cd^{2+} ions and thiourea, where species such as $Cd(OH)_2$ and/or CdO are present in their films [24-26]. In most of these works, an ammoniacal solution and one complementary complexing agent for the cation have been used. That is why the formation of hydrolyzed species in the solution and the formation of Cd–O bonds in the structure of CdS layer are inevitable in these basic media [27]. One alternative way to avoid such problem is to carry out the process in a weak acidic bath. In this work a pH of 6.0 in the solution is chosen to avoid the formation of such undesired species in the films.

This paper reports the preparation of nanocrystalline CdS thin films by a new chemical Bath deposition route at 50 ºC and pH of 6.0. These thin films have been studied as an antireflection coating which is an important part of the solar cell. The parameters studied include the absorbance/transmittance/reflectance spectra, energy gap, absorption coefficient, refractive index, extinction coefficient, and thickness. In addition, we have investigated the structural and morphological properties of CdS thin films.

2. Experimental

Glass slides were used as the substrates. The deposition solution was prepared by mixing 10 ml of $Cd(OAc)_2$, 0.02 M, 25 ml ammonium acetate, 2 M, 50 ml thioasetamide (TAA), 0.1 M, and the mixture was diluted to 100 ml by distilled water. Finally, the pH of deposition solution was adjusted to 6.0 by addition of 1 M NaOH solution.

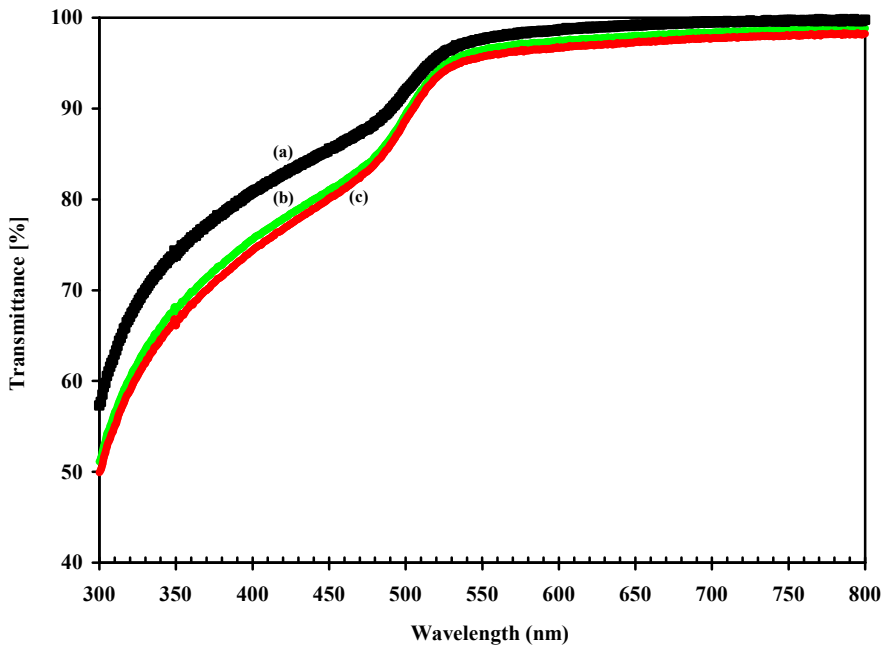

Figure 1: Optical transmittance spectra of CdS thin films at different deposition times: (a) 30, (b) 90, and (c) 120 min. The thickness of the films is 60, 104, and 135 nm, respectively.

This solution was poured into a glass tank as a reaction vessel for the film deposition. Glass substrates were immersed vertically in the reaction vessel, and the glass tank was placed in a thermostat bath set to the desired temperature. The deposition was carried out at 50 °C for 30 to 120 min. The deposited films were then washed with distilled water and dried in air at room temperature. Transmission, absorption and reflection spectra were obtained by means of a Varian Cary 300Bio UV-Visible Spectrophotometer. The film thickness was measured by a Dektak^3 profilometer. The crystallinity, phase, and orientation of the CdS films were determined by X-ray diffraction (XRD) using an automated X' pert Philips X-ray diffractometer with a Cu Kα radiation source (λ = 0.15406 nm) at 40 kV and 30 mA. The films were scanned in the range of 2θ=20-60°. The surface morphology of the CdS thin films were observed by field emission scanning electron microscopy (FE-SEM; Hitachi S-4160) under an acceleration voltage of 15 kV. The composition of the thin films were studied by an Oxford 7538 EDX analyzer equipped with a Cam Scan MV 2300 scanning electron microscope (SEM).

3. Results and discussion

Considering the fact that the chemical bath deposition method is usually carried out at near ambient temperatures (~25-80 °C), and controlling the deposition of nanocrystalline thin films is easier at lower temperatures, so the temperature of 50 °C is chosen for deposition of nanocrystalline CdS thin films. Figures 1 and 2 show the transmittance and reflectance spectra of nanocrystalline CdS thin films deposited on the glass substrates. The average transmittance of (a), (b), and (c) CdS thin films is calculated to be 93, 88, and 74%, respectively, in the visible wavelength region. Optical transmission spectra of the thin films are observed to be shifted towards the longer wavelengths with increasing deposition time. This suggests the decrease in the band gap energy (E_g) with increasing the deposition time. It is strongly observed that the CdS thin films exhibit the least reflectance for almost all wavelengths. From the above studies, it is believed that the CdS thin films may be used as an antireflection coating material for thin film solar cells.

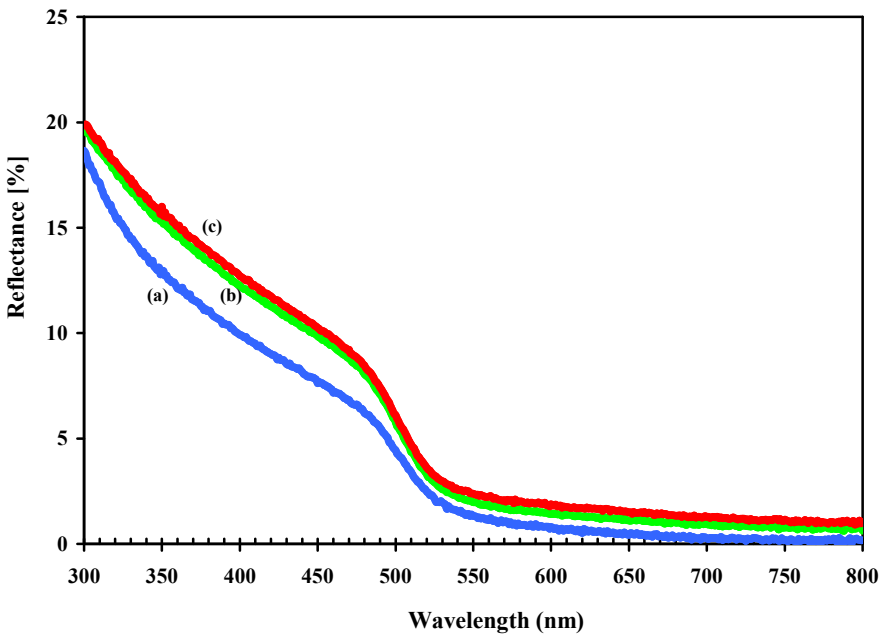

Figure 2: Optical reflectance spectra of CdS thin films prepared at different deposition times: (a) 30, (b) 90, and (c) 120 min. The thickness of the films is 60, 104, and 135 nm, respectively.

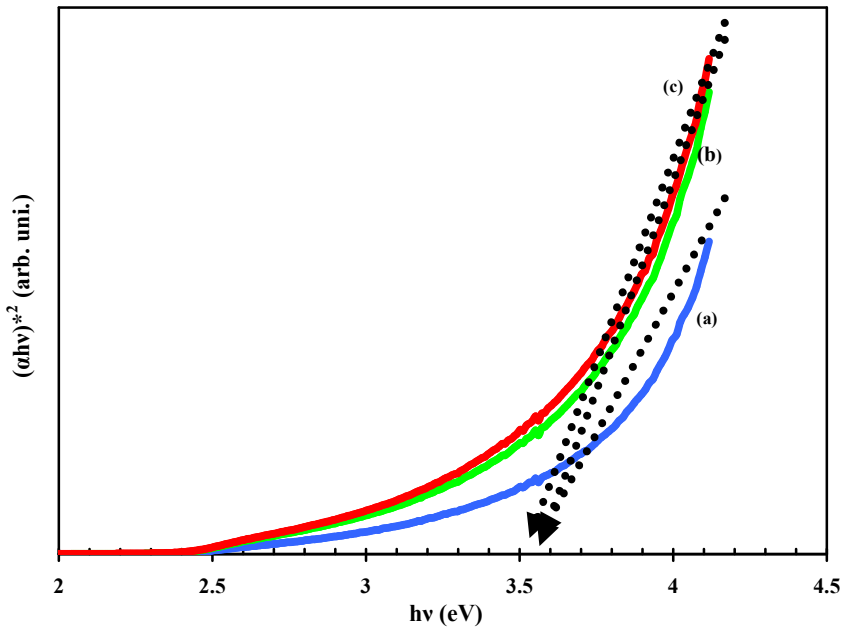

Figure 3: Plot of $(\alpha h\nu)^2$ for CdS thin films at different deposition times: (a) 30, (b) 90, and (c) 120 min. The thickness of the films is 60, 104, and 135 nm, respectively.

The values of the energy gap, E_g, were calculated from the transmittance spectra by plotting $(\alpha h\upsilon)^2$ versus $h\upsilon$ (Figure 3). α, h, and υ are absorption coefficient, Planck constant, and frequency, respectively. As can be seen $(\alpha h\upsilon)^2$ varies linearly with $h\upsilon$ above the energy gap. Accordingly, the energy gap is obtained by extrapolating the straight portion of the curve to zero absorption coefficients. CdS thin films grown here have the energy gap in the range of 3.85 to 3.90 eV.

These values are somewhat larger than the typical value of the bulk CdS (ca. 2.42 eV), probably due to the quantum size effect as expected from the nanocrystalline nature of the CdS thin films [5]. The refractive index is an important parameter for optical materials and applications. Thus, it is important to determine optical constants of the films. the complex optical refractive index of the films is described by the following relation (equation 1) [28].

$$\hat{n} = n(\omega) + ik(\omega) \qquad (1)$$

where n is the real part and k is the imaginary part (extinction coefficient) of complex refractive index. The refractive index of the films were determined from the following relation (equation 2).

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \qquad (2)$$

where k ($k = \alpha\lambda/4\pi$) is the extinction coefficient. The k and n values dependence on wavelength are shown in Figure 4. The value of extinction coefficient increases with the energy of the incident beam. The refractive index found to increase by increasing the deposition time. This may be due to the change in nanocrystallite size, stoichiometry and internal strain of CdS films. In order to obtain the maximum transmittance, a film should have the refractive index closer to the square root of the refractive index of the substrate [29]. It is clearly observed from the variation of refractive index (n) that the refractive index of CdS thin films in visible wavelengths is very close to the square root of therefractive index of the glass substrate ($n^{0.5}$=1.2).

X-ray diffraction (XRD) data obtained by scanning 2θ in the range of 20-60º, with a grazing angle equal to 1.5º for the deposited CdS thin films on the glass substrate. The X-ray diffraction patterns in Figure 5 show the crystallinity of the thin films deposited at various deposition times of 30, and 120 min, respectively.

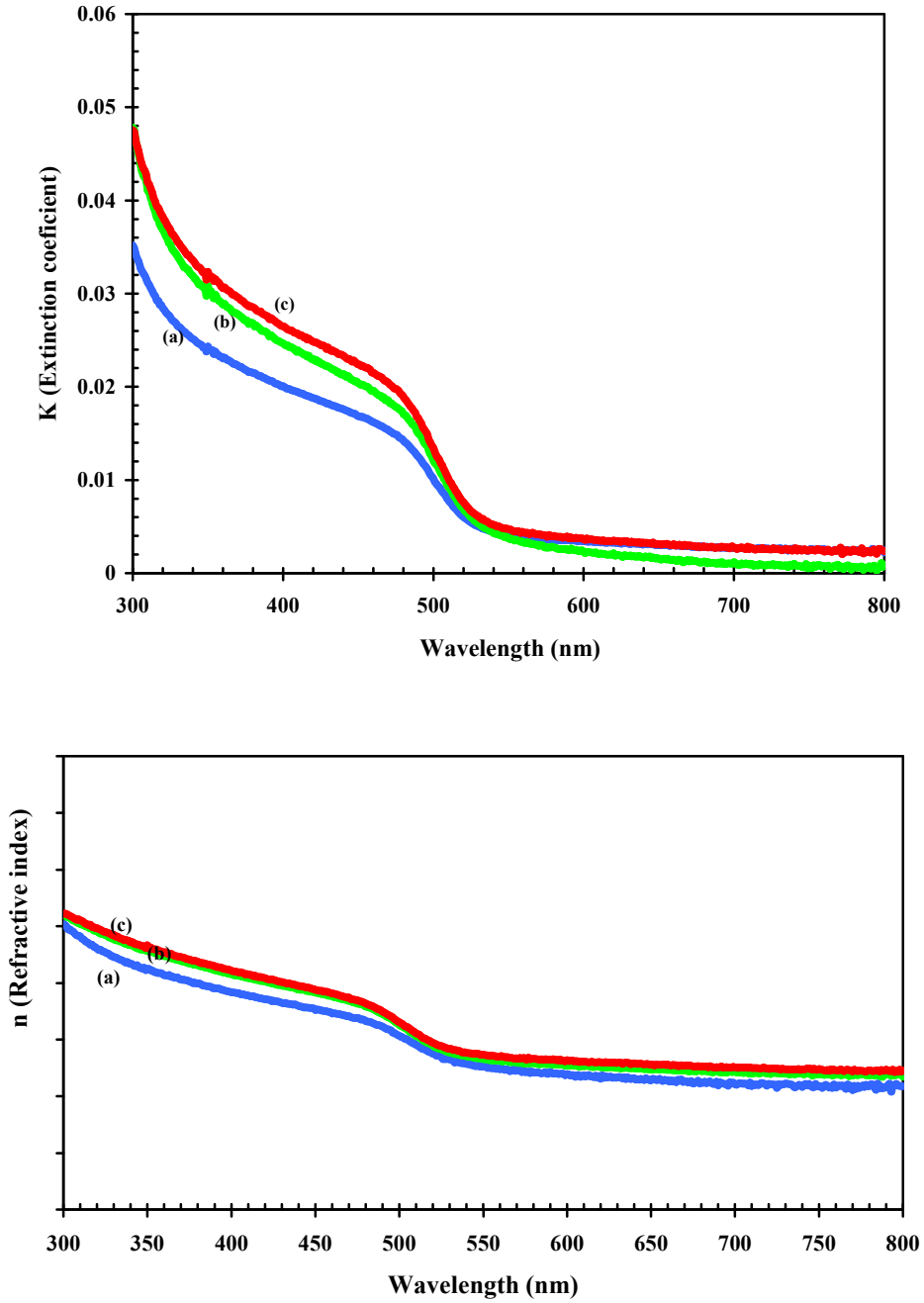

Figure 4: The variation of the extinction coefficient and the refractive index of CdS thin films at different deposition times: (a) 30, (b) 90, and (c) 120 min. The thickness of the films is 60, 104, and 135 nm, respectively.

The standard XRD pattern for CdS (Joint Committee for Powder Diffraction Standards, JCPDS card No. 02-0454) is given at the bottom of Figure 5. As the deposition time increases from 30 to 120 min, the degree of crystallinity of the nanocrystalline CdS thin films increases and this is due to the growth of the size of nanocrystallites involved in the diffraction process. The films are polycrystalline with random crystal orientation and show no signs of texturing. The three broad peaks observed in the diffractogram at around 26.52°, 43.93° and 51.90° reveal a cubic lattice structure of CdS (zincblende). These peaks could be readily assigned to the (111), (200), and (311) planesof the cubic phase, respectively [30].

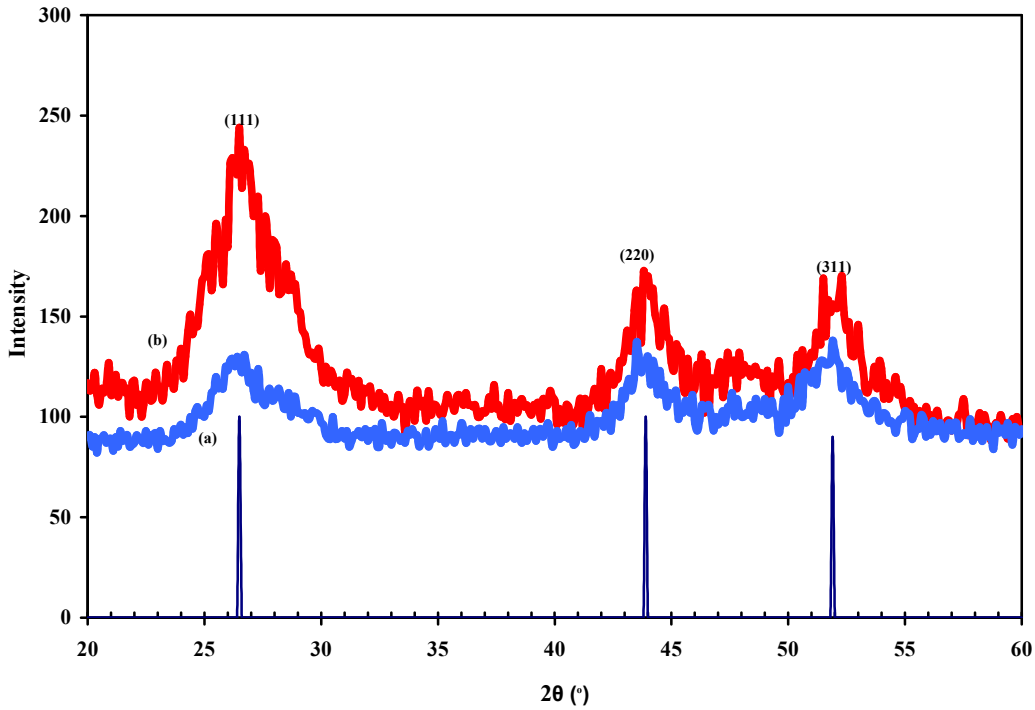

Figure 5: X-ray diffraction patterns of CdS thin films grown at different deposition times: (a) 30, and (b) 120 min. The thickness of the films is 60 and 135 nm, respectively.

Table 1: The film thickness, energy gap, and the nanocrystallites size values for CdS thin films deposited from a chemical bath at pH 6.0, 50 °C and different deposition times.

Deposition time (min)	Film thickness (nm)	Energy gap (eV)	Grain size (nm)
30	60	3.90	20
90	104	3.88	25
120	135	3.85	28

From the full-width at half-maximum of the (111) diffraction peaks, the average sizes of the nanocrystallites (Table 1) have been calculated using the Debye-Scherrer equation [15, 31]. These results show that the size of the ZnS nanocrystallites depends mainly on the deposition time and it increases with increasing the deposition time (the size of nanocrystallites change from 20 nm at 30 min to 28 nm at 120 min). This deposition time dependence of size may be explained according to that the larger crystallites being more stable than the smaller ones which are formed at the initial deposition time.

The surface of the film was examined by FE-SEM. The CdS thin films showed a surface structure consisting of small uniform grains free of pinholes. Figure 6 show FE-SEM images of the films deposited at 50 °C for 120 min with thickness of about 135 nm. The film compactness was high, the surface's uniformity was good, the particle size was quite fine, and the particle size distribution was also narrow. These characteristics are in good agreement with the film's high transparency, which was discussed in the previous section. The Fe-SEM Image shows that the size of the observable grains was approximately 30 nm, whereas the average nanocrystallite size estimated from the XRD peak was 28 nm.

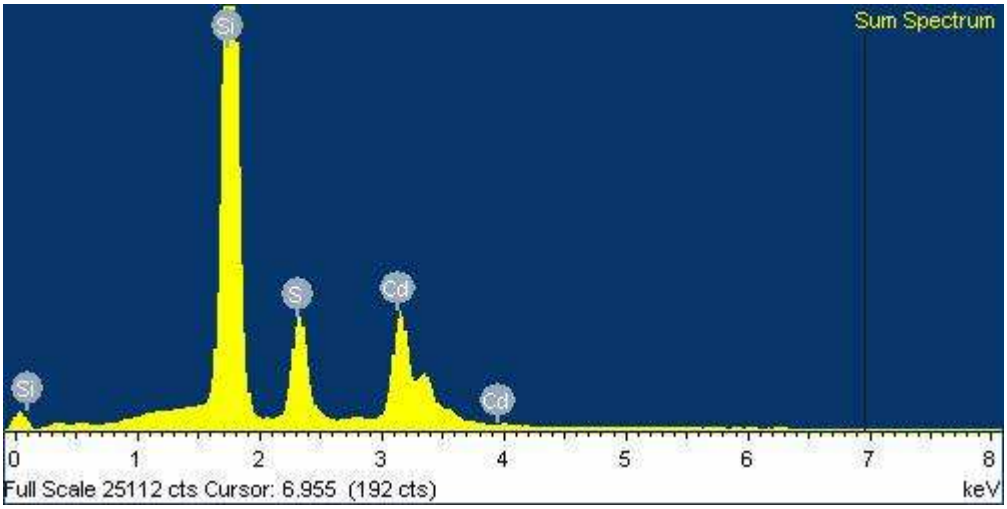

Figure 7: EDX spectrum of a typical cadmium sulfide thin film deposited on silicon substrate from a chemical bath at pH 6.0, 50 °C and deposition time of 120 min. The thickness of the film is 135 nm.

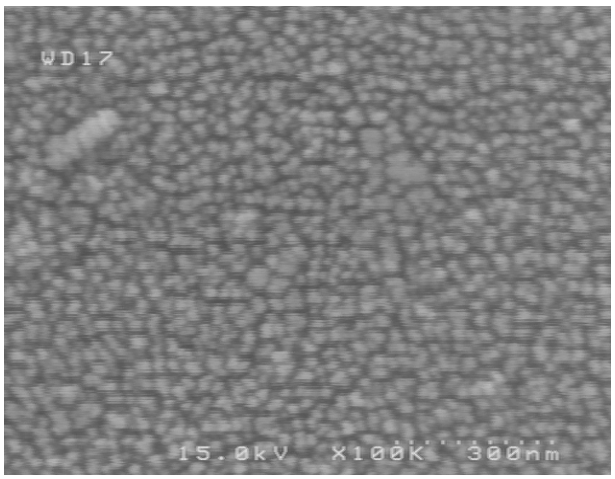

Figure 6: FE-SEM image of the CdS thin film on glass substrate deposited from a chemical bath at pH 6.0, 50 °C and deposition time of 120 min. The thickness of the film is 135 nm.

Chemical composition of CdS thin films on silicon substrate were analyzed by energy-dispersive X-ray analyzer (EDX) (Figure 7). The EDX analysis indicated the presence of cadmium and sulfur, (typically Cd = 50.3, S = 49.7 atomic percent) for all the deposited layers. Furthermore, two peaks corresponding to silicon were observed which are related to their presence in the silicon substrate.

4. Conclusions

Nanocrystalline cadmium sulfide (CdS) thin films with different thicknesses were deposited on glass substrate by a chemical solution deposition technique. Optical study was performed to calculate the refractive index (n), extinction coefficient (k), absorption coefficient (α) and optical band gap (E_g) using transmission and reflection spectra in the range of 300-800 nm. The measured band gap was found to be in the range of 3.85 - 3.90 eV. The band gap values were somewhat larger than the typical value of the bulk CdS (2.42 eV), which could be attributed to quantum confinement effects due to the nanometer crystallite size of the CdS thin films. The FE-SEM image demonstrated a dense and uniform surface that was free of pits or pinholes with a narrow grain size distribution. The composition of the film is much close to the CdS Stoichiometry due to a significantly lower concentration of $Cd(OH)_2$ and CdO species in the film.

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