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Morphology, Analysis and Properties Studies of CdS Nanostructures under Thiourea Concentration Effect for Photovoltaic Applications

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CdS nanostructures are prepared by sol-gel spin coating method using different thiourea concentrations. The thiourea concentration effect for CdS nanostructures deposited on quartz substrate is studied. The CdS nanostructures give important analysis of X-ray diffraction (XRD), optical transmittance using (UV-vis) and photoluminescence (PL) spectroscopy, in addition to characterization of atomic force microscopy (AFM). The calculated refractive index and optical dielectric constant have proved a good agreement with experimental and theoretical results.

Keywords: CdS Nanostructure; Characterization; Optical Properties; Sol-Gel Method.

1. INTRODUCTION

Due to transparency in the visible and high infrared reflectivity, acoustic characteristics, high electrochemical stability and excellently electronic properties, CdS has been attracted for research and application. It has been widely used in chemical sensor [1], surface acoustic wave device [2] and photoanode films of solar cell [3,4]. Different techniques are to including sputtering [5], chemical vapor deposition (CVD) [6] and spray pyrolysis [7,8]. However, among these techniques, the sol-gel process is particularly attractive due to different reasons; good homogeneity, ease of composition control, low processing temperature, large area coatings, low cost efficient in producing thin, transparent, multi-component oxide layers of many compositions on various substrates. CdS nanostructures are regularly n-type due to sulfur vacancies. The variation of the Cd/S concentrations will presumably modify the physical properties of CdS nanostructures, such as morphology, analysis and optical properties. These concentrations will also have an effect on the structural and optical properties of the CdS nanostructures.

Kim et al. [9] have examined the enhancement of surface–plasmon-coupled photoluminescence from CdS nanoparticles for various thicknesses of sputtered Au films. They have found the improved luminescence with thickness control of Au correlated well with the increased density of surface–plasmon states, which was modified by plasmon-dispersion relation at the planar Au/PMMA interface. By annealing the Au films to form a rough surface morphology, the emission in the CdS nanoparticles was further enhanced by the improved excitation and coupling of the surface–plasmon modes. Otherside, Oliva et al. [10] have deposited polycrystalline cadmium sulfide (CdS) thin films on glass substrates by chemical bath deposition (CBD) and close-spaced sublimation (CSS) techniques. The typical deposition temperatures between these techniques are quite different. The CdS thin films deposited by CBD were prepared using two methods of bath agitation: magnetic and ultrasonic agitation. They have found that films deposited with ultrasonic agitation presented a cleaner surface with minor presence of contaminants as demonstrated by Auger analysis. Properties of CdS films such as morphology, optical transmission, crystallinity and band gap energy were discussed in order to compare them in both techniques. Thay have obtained that crystallinity of CdS films depends strongly on the temperature used for deposition. In agreement with several works, films prepared by CBD technique have presented a cubic structure, while films grown by CSS technique have exhibited a hexagonal one. While, Lahewil et al. [11] have presented the structural and optical investigations of cadmium sulfide nanostructures deposited on glass substrates by sol-gel technique for optoelectronic applications. They have investigated the lattice constants and analyzed the thickness and optical properties where proved distinguished results compared with other ones.

In the present work, we have used the sol-gel spin coating technique to prepare CdS nanostructures include Polythylene glycol (PEG 200) with different thiourea concentrations 0.01, 0.05, 0.07 and 0.1 mol/L deposited on quartz substrate for photovoltaic applications. Structural, morphological and optical properties of CdS nanostructures were investigated.

2. EXPERIMENTAL PROCESS

All chemicals of analytical grade were received from Sigma-Aldrich Company and prepared at Institute of Nano Electronic Engineering (INEE) in University Malaysia Perlis (UniMAP). CdS nanostructures were grown by sol-gel spin coating method at room temperature. Polyethylene glycol

(PEG 200) sol was prepared by mixing 0.6 ml of PEG, 8.5 ml of ethanol and 0.5 ml of acetic acid under stirring for 1 h. On different molarity thiourea 0.01, 0.05, 0.07 and 0.1 mol/L as a source of S, 1.2 mol/L cadmium nitrate as a source of Cd and 15 ml of ethanol accompanying 60 ^{o}C. Prepared solution was slowly added to the PEG sol with vigorous stirring for 5 h. As the reaction was started, the reaction system gradually changed from transparent to light yellow. The precipitate collected from centrifugation was dried on hot plate at 120 ^{o}C for 1 h and annealed in muffle furnace at 800 ^{o}C for 1 h. This dried and annealing temperature for CdS nanostructures is ready to deposit it on quartz substrates for characterizing and analyzing by atomic force microscopy (AFM), (SII Sciko Instrument INC SPI 3800N Probe station), X-ray diffraction (XRD) (Philips PW 1710 X-ray diffractometer), photoluminescence (PL) spectroscopy, (Jobin Yvon Horiba HR800UV system), were obtained at room temperature with 325 nm line of the HeCd laser at power 20 mW and UV-vis spectroscopy, (Perkin Elmer Lambda 950).

3. RESULT AND DISCUSSION

3.1 Analysis and characterization of CdS nanostructures

The crystalline properties have been investigated by X-ray diffraction (XRD) technique using CuKα radiation. Figure 1 shows XRD patterns of CdS nanostructures deposited on quartz substrates at different thiourea concentrations Cd:S 1.2: 0.01, 0.05, 0.07 and 0.1 mol/L. The CdS nanostructures deposited on quartz substrate at 0.01 mol/L, shows single peaks at 2 theta equals 26.56° and 29.44° corresponds to (200) and (210) planes, respectively. At 0.05 mol/L, the peaks are observed at 28.00° and 33.04^{o} correspond to (200) and (002) planes, respectively. While at 0.07 mol/L, the peaks are observed at 26.8^{o} and 29.72^{o} correspond to (200) and (210) planes, respectively. And at 0.1 mol/L, the peak is observed at 27.84^{o} corresponds to (002) plane orientation in the case of the hexagonal structure. These results confirm that the deposition has proved more favorable as the intensities of peaks. The measured peaks are in good agreement with others.

Crystallite size was calculated by Scherrer's formula [11,12].

$$D = k\,\lambda\,/\,\beta\,\cos\theta. \tag{1}$$

where K is a constant equals 0.91, λ is the x-ray wavelength of Cu-kα (λ = 1.54 Å), θ is the angle between the incident beam and the reflection lattice planes, and β is the full width at half maxima (FWHM) of the diffraction peak in radian. The lattice parameters a and c were calculated by [11]:

$$a = \sqrt{\frac{1}{3}}\,\lambda\,/\,\sin\theta. \tag{2}$$

$$c = \lambda\,/\,\sin\theta. \tag{3}$$

The estimated grains size and lattice constant a and c values are given in Table 1. These values are well agreed with other experimental and theoretical data [1,11,13,14].

Atomic Force Microscopy (AFM) is a useful for surface topography of CdS nanostructures. Figure 2 shows the 2-D and 3-D images of CdS nanostructures at different thiourea concentrations. The scanning area is 2x2 μm while the grains show complete coverage over the quartz substrates surface. The thickness of CdS nanostructures was measured using AFM technique. It can be found to be 10, 15, 30 and 40 nm for 0.01, 0.05, 0.07 and 0.1 mol/L respectively. The thickness increases as the thiourea concentration increases.

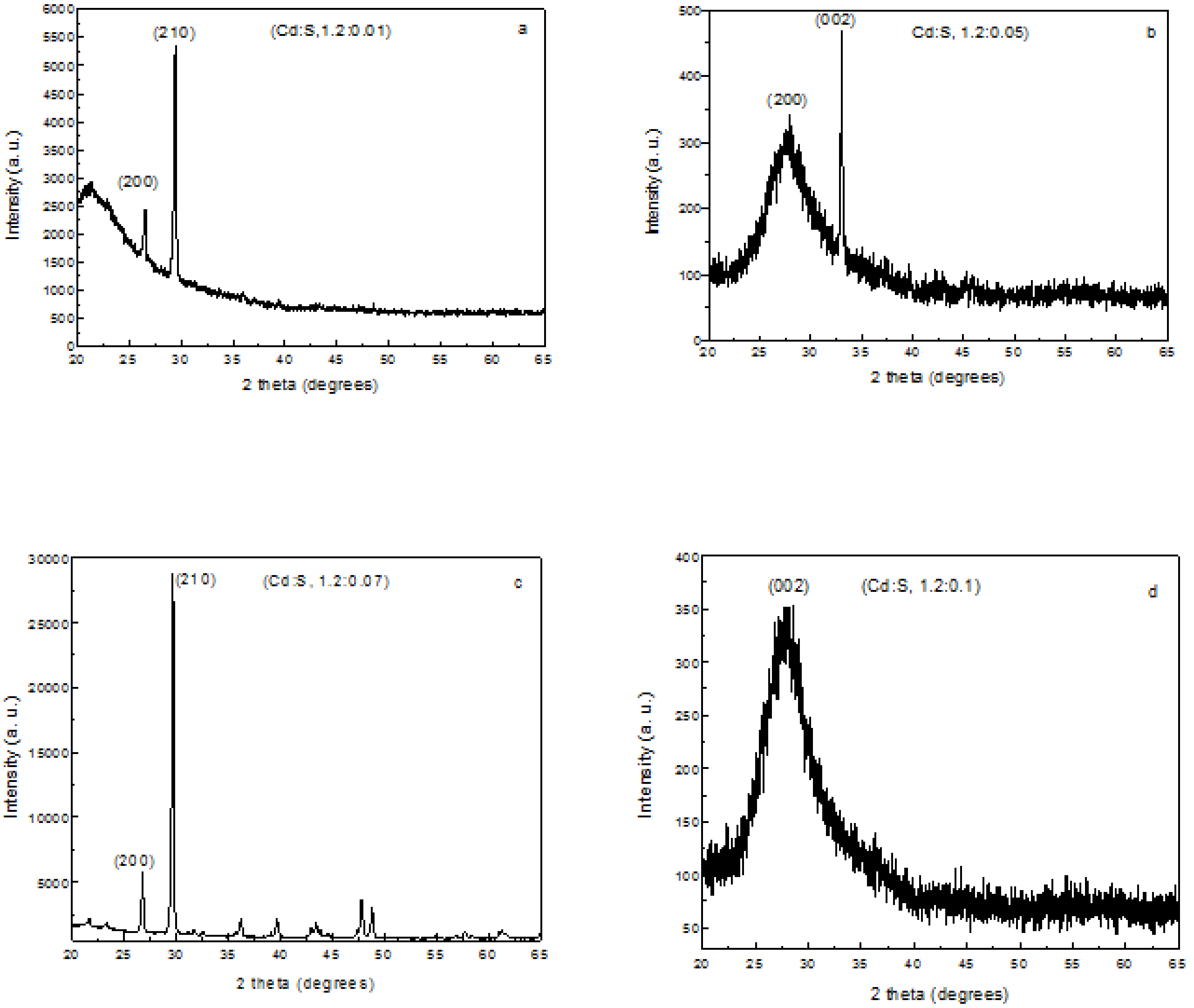

Figure 1. X-ray diffraction (XRD) of CdS nanostructures at different thiourea concentrations 0.01 (a), 0.05 (b), 0.07 (c) and 0.1 (d) mol/L.

3.2 Optical properties of CdS nanostructures

The optical photoluminescence (PL) spectra are performed at room temperature in the range of 300-900 nm. Figure 3 displays the emission spectra. One band in the range of 360 nm to 550 nm is centered at 404.35 nm (3.0662 eV) and shown in Fig. 4a. Two bands in the range 361 to 438.39 nm and 450.66 to 570 nm are centered at 402.45 and 509.09 nm (3.08 and 2.43 eV), respectively (Fig. 4b). While one band in the range of 354 to 456.85 nm is centered at 402.35 nm (3.08 eV) as shown in Fig. 4c.

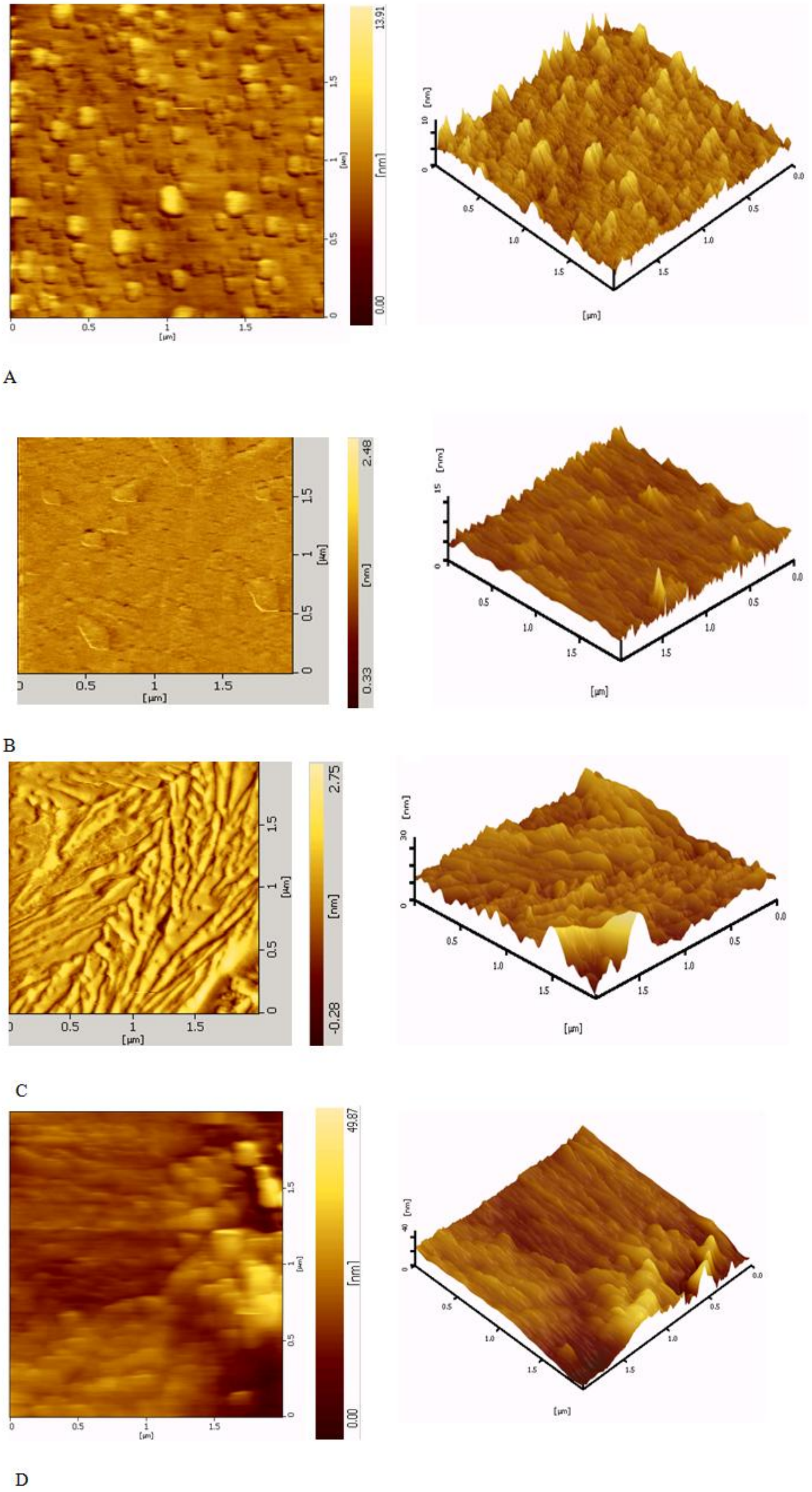

Figure 2. Atomic force microscopy (AFM) of 2-D and 3-D for CdS nanostructures at different thiourea concentrations 0.01 (a), 0.05 (b), 0.07 (c) and 0.1 (d) mol/L.

Finally, two bands in the range 365.64 to 439.12 nm and 451.35 to 582.04 nm are centered at 402.35 nm and 511.47 nm (3.08 and 2.42 eV), respectively (Fig. 4d). These are attributed to emissions near the absorption edge that involves surface states or traps associated to interfacial crystalline defects. This emission is associated to sulphur and cadmium atoms vacancies. Comparing the exciton bands in both species, no significant relative shift is observed. However, in the band near 511.47 nm, slight blue shift is detected. The estimated E_g values are given in Table 2. These values are well agreed with experimental data [1,11,12].

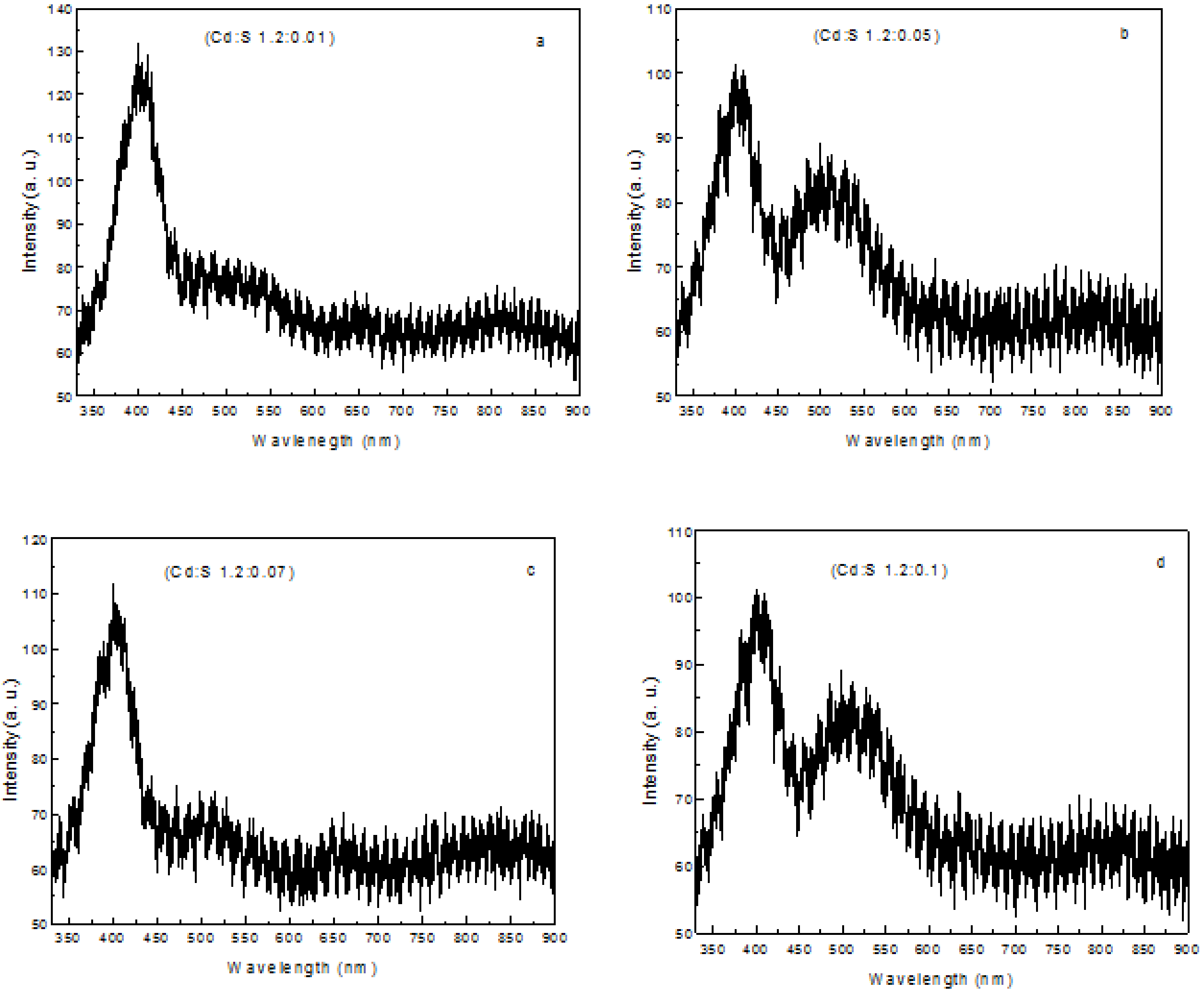

Figure 3. Photoluminescence spectra (PL) of CdS nanostructures at different thiourea concentrations 0.01 (a), 0.05 (b), 0.07 (c) and 0.1 (d) mol/L.

The optical transmission spectra (T) are performed at room temperature using UV-vis spectroscopy in the range of 400-2000 nm as displayed in Fig. 4. High optical transmission is an indication of improvement for solar cells applications. The highest average optical transmission is observed at Fig. 4b, while all the studied CdS nanostructures have high optical transmittance (> 80%) in the visible range. The thickness and optical transmission are given in Table 2.

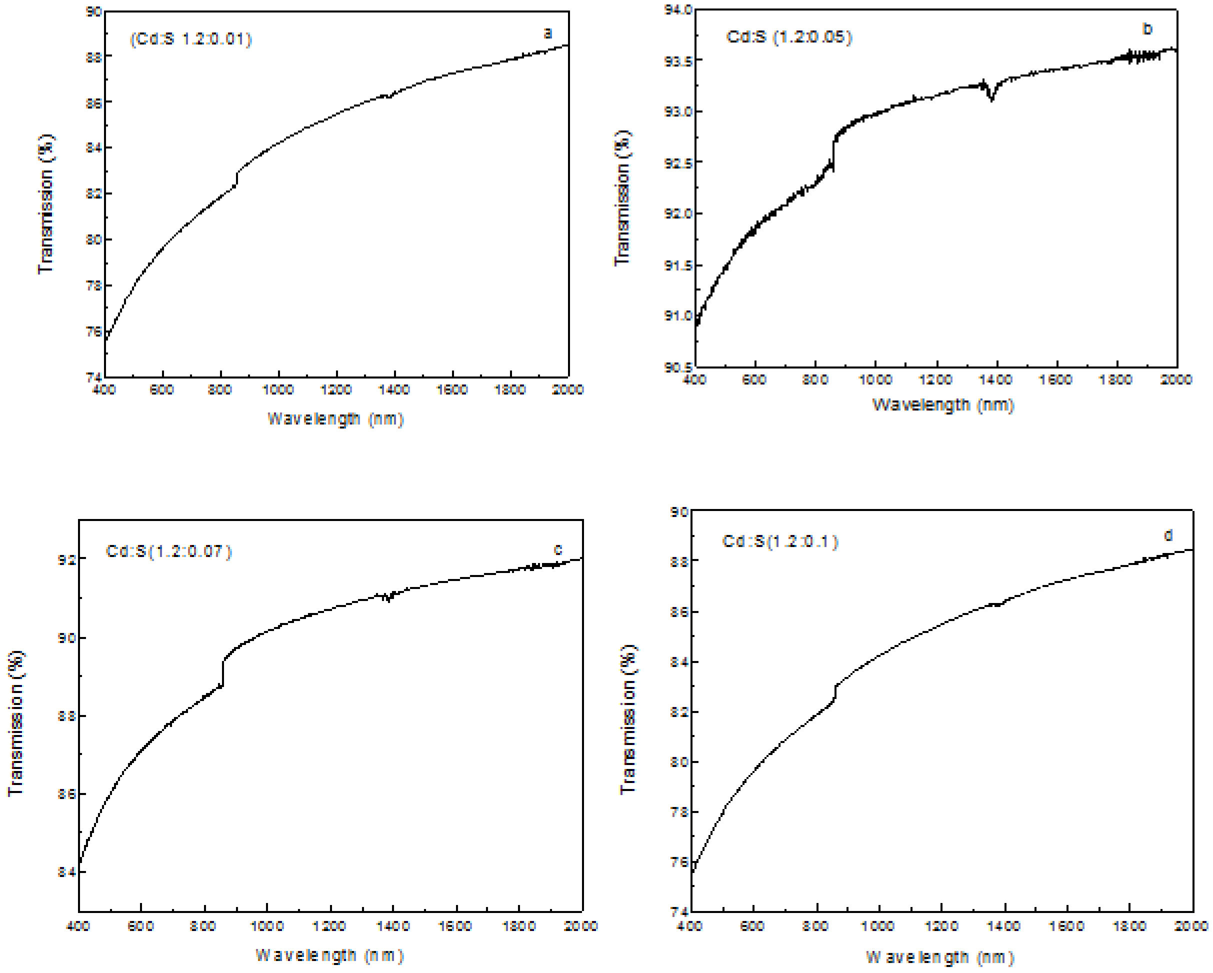

Figure 4. Transmission (%) of CdS nanostructures at different thiourea concentrations 0.01 (a), 0.05 (b), 0.07 (c) and 0.1 (d) mol/L

The refractive index *n* is an important physical parameter related to microscopic atomic interactions. Theoretically, the two different approaches in viewing this subject are the refractive index related to density, and the local polarizability of these entities [15]. On the other hand, the crystalline structure represented by a delocalized picture, "*n*" will be closely related to the energy band structure of the material, complicated quantum mechanical analysis requirements and the obtained results. Many attempts have been made to relate the refractive index and the energy gap E_g through simple relationships [16-21]. Here, the various relationships between "*n*" and E_g will be reviewed. Ravindra et al. [20] suggested different relationships between the band gap and the high frequency refractive index and presented a linear form of "*n*" as a function of E_g:

$$n = \alpha + \beta E_g, \quad (4)$$

where $\alpha = 4.048$ and $\beta = 0.62\ \text{eV}^{-1}$.

To be inspired by simple physics of light refraction and dispersion, Herve and Vandamme [21] proposed an empirical relation as:

$$n = \sqrt{1 + \left(\frac{A}{E_g + B} \right)^2}, \qquad (5)$$

where A = 13.6eV and B = 3.4eV. Ghosh et al. [22] took a different approach to the problem by considering the band structural and quantum-dielectric formulations of Penn [23] and Van Vechten [24]. Introducing A as the contribution from the valence electrons and B as a constant additive to the lowest band gap E_g, the expression for the high-frequency refractive index is written as:

$$n^2 - 1 = A / (E_g + B)^2, \qquad (6)$$

where A = $25E_g + 212$, B = $0.21E_g + 4.25$ and (E_g + B) refers to an appropriate average energy gap of the material. Thus, these three models of variation *n* with energy gap have been calculated. The calculated refractive indices of the end-point compounds are given in Table 2. It is proven that Ghosh et al. model is more appropriate for photovoltaic applications.

4. CONCLUSION

Sol-gel spin coating technique has been successfully used to prepare CdS nanostructures in different thiourea concentrations 0.01, 0.05, 0.07 and 0.1 mol/L. It is simple, economic, good structural and optical properties which are desirable for photovoltaic applications. Hence, the grain size increases as the concentration increases, followed by increasing of thickness, transition, refractive index and optical dielectric constant. It is proven that Ghosh et al. model is appropriated for photovoltaic applications.

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