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Characterization of Nanocrystalline CdS Thin Films Prepared by Thermal Evaporation

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Abstract Nanocrystalline CdS thin films were prepared by thermal evaporation on glass substrates at ambient temperature. The films were characterized by recording and analyzing their transmittance, X-ray diffraction (XRD) patterns, scanning electron microscope (SEM) images and Energy dispersive X-ray (EDAX) spectra. X-ray diffractograms revealed that the material is nanocrystalline with predominant cubic crystal structure and preferential orientation along (111) plane. SEM micrographs confirmed the nanostructure of the material and showed uniform and well covered surfaces. EDAX reports revealed that the films are cadmium rich and contain oxygen. The first derivative of the absorbance was used to estimate the effective bandgap energies of the nanocrystallites and the hyperbolic band model was used to estimate their radii. The results were compared with those obtained by XRD and SEM measurements.

Keywords II-VI Semiconductors, CdS/CdTe Solar Cells, Heterojunctions, Nanocrystallites, Thin Films

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1. Introduction

CdS thin films are of considerable interest as they can be used in fabrication of solar cells and other opto-electronic devices. In particular, heterojunction solar cells with a narrow band gap base and wide band gap window have been investigated in an attempt to develop efficient, stable and low-cost solar cells[1]. The CdS quantum dot embedded in a glass matrix is one of the well-known quantum dot systems and its electronic and luminescent properties have been studied extensively[2].Three-dimensional confinement of carriers within the quantum dots leads to the blue shift of the optical band-gap and to modification of many properties of semiconductor material[3]. It has been argued that in these semiconductor nanoparticles the hyperbolic band model gives a better fit to the observed quantum size effect as compared to the effective mass approximation[4].

There are different ways to synthesize CdS nanoparticles such as colloidal particulates[5], chemical deposition[6], sol-gel[7], spray pyrolysis[8], chemical bath deposition[3], thermal evaporation[9], etc. In the present work, thermal evaporation technique has been chosen for the deposition of nanocrystalline CdS thin films as it is simple compared with other new and sophisticated techniques[10].

Most studied nanocrystalline semiconductors belong to the II-VI group as they are relatively easy to synthesize and generally prepared as particulates or in thin film form. Among II-VI compounds, CdS is one of the most studied materials. For example, Němec et al.[3] reported on the control of nanocrystal sizes in CdS nanocrystalline films prepared by ammonia-free chemical bath deposition technique. Datta et al.[11] achieved size tunability of thiophenol capped CdS nanoparticles (NPs) by controlling the temperatures at the time of synthesis. In this work CdS nanocrystallites were produced by thermal evaporation on glass substrates at ambient temperature. A narrow range of nancrystallites' size was obtained as seen from the results deduced from the XRD diffractograms, SEM micrographs and first derivative with the hyperbolic model. It was found that narrower range of crystalline size could be obtained at lower values of film thickness.

2. Experimental Part

Undoped CdS thin films were deposited by thermal evaporation at ambient temperature on glass substrates of dimensions ($6\times2.6\times0.1 cm^3$) in a high vacuum system ($\sim10^{-5}$ mbar) provided with a Turboe pump. The evaporation rate was about 10 Å/s and it was measured by a cooled quartz crystal monitor. The distance between the source and the substrate was about 30 cm. Films of thickness 50-495 nm were produced through different individual evaporations.

The transmittance of the films was measured by using a double beam Shimadzu UV 1601 (PC) spectrophotometer with respect to a piece of glass similar to the substrates in the wavelength range 300-1100 nm. The thickness of the films was estimated from the interference maxima and minima in the transmittance by using the method of Alvin[12]. X-ray measurements were recorded by a Philips PW1840 Compact

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X-ray diffractometer system with Cu K_α (λ = 1.5405 Å). The SEM micrographs were taken by a FEI scanning electron microscope (Inspect F 50), which was supplied by energy dispersive analysis by X-rays (EDAX), so the compositional analysis of the films was performed by the same system.

3. Results and Discussion

Fig.1 displays the X-ray diffractograms of two CdS films with different thickness. As the figure shows, the structure is mainly identified as zinc blende, where the characteristic lines of the cubic phase C(1 1 1), C(2 2 0), C(3 1 1) and C(2 2 2) are evident in the diffractogram. The C(1 1 1) peak at 2θ about 26.2° is overlapped by a broad band produced by the amorphous glass substrate. Němec et. al.[3] says that cadmium sulfide nanocrystallites tend to crystallize in cubic (zinc-blende) structure unlike the bulk CdS which is usually hexagonal (wurtzite). But the diffractogram also shows some lines of the hexagonal phase, which are the H(1 0 0), H(1 0 1) and the H(0 0 2) lines. On the other hand it is known that the peak produced by the C(1 1 1) crystalline planes of the cubic CdS and that of the H(0 0 2) crystalline planes of the hexagonal structure coincide within 1 per cent. As the figure shows, the C(1 1 1) is the preferential orientation for crystal growth, but it is stronger and narrower in the case of the 300 nm film, indicating that the grain size in this film is larger.

The grain size was calculated by using Scherrer formula and the line C(1 1 1) in the XRD pattern of the film with thickness 300 nm, where it has the largest intensity.

$$d = \frac{\lambda}{D\cos\theta} \tag{1}$$

where d is the grain size (diameter of the nanocrystallites), λ is the X-ray wavelength used, D is the angular line width of the half-maximum intensity and θ is Bragg angle. The grain size was found to be about 15 nm for the crystallites grown in this direction, or the average radius of the nanocrystallites is about 7.5 nm. It is necessary to remind by the fact that, lines of smaller intensity give smaller values of d in both films.

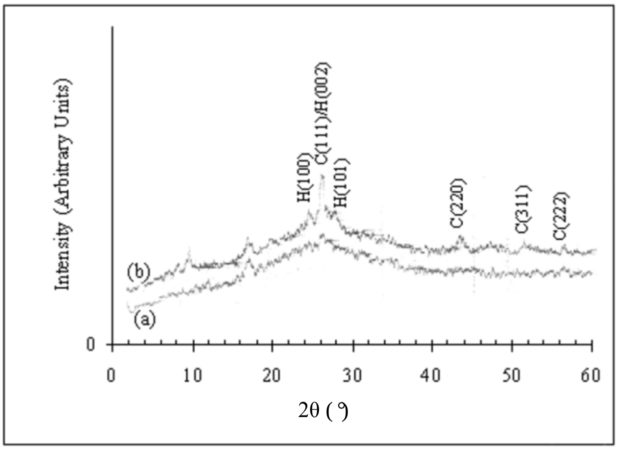
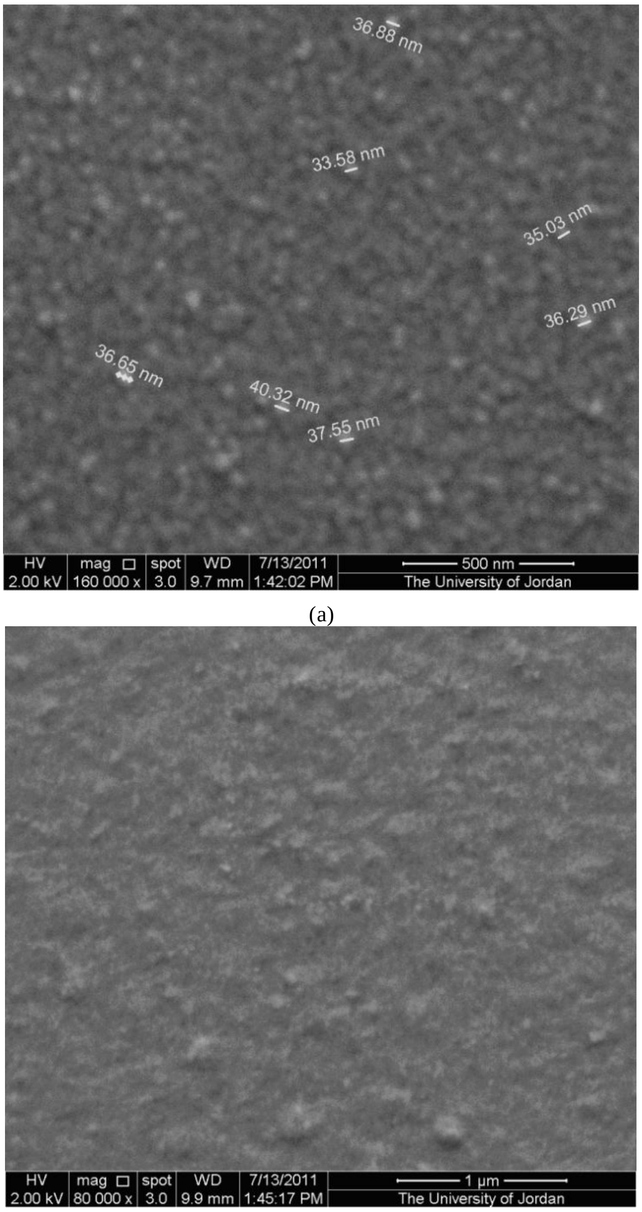


Figure 1. X-ray diffractogram of thermally evaporated CdS thin films of thickness a) 100 nm. b) 300 nm

Fig.2 depicts the SEM micrographs for two films of thickness 100 and 400 nm. The images show uniform and close-packed films with complete coverage of the substrates. The micrograph of the thicker film shows larger grain size than the thinner one. The grain size was estimated for seven nanocrystallites randomly in the image of the 400 nm film, and the average grain size obtained by this method is about 36.57±2.10 nm, which gives an average radius of about 18.0 nm.



(a)

(b)

Figure 2. SEM micrographs of thermally evaporated CdS thin films with thickness a) t = 400 nm. b) t = 100 nm

Fig.3 shows a typical EDAX pattern for the film of thickness 100 nm. It is found that the ratios of Cd: S: O concentrations in the film are 45.33: 36.30: 18.37. This means that the CdS films are Cd rich and the ratio of Cd to S is 1.25. This result is consistent with the findings of Nanda et. al.[13] who showed that CdS nanoparticles have excess Cd, the amount of which increases on decreasing the size. It is known that excess Cd can produce acceptor states within the gap of CdS. These states together with those originating from quantum size effect will form a continuum of localized states near the valence band edge[13]. The presence of oxygen in the films is because of the long exposure to atmosphere.

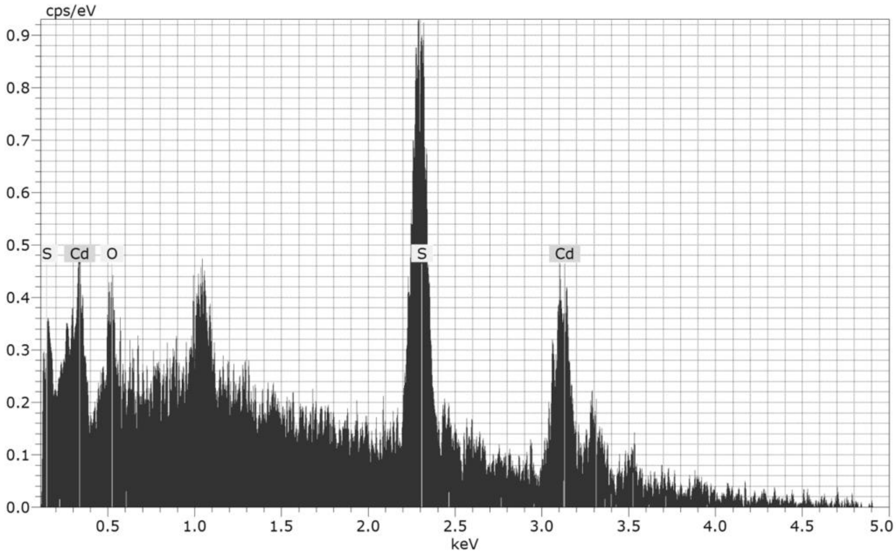
The transmittance curves which are recorded at room temperature for five values of film thickness are shown in Fig.4. The transmittance is as high as 100% for films thicker than 100 nm for values of wavelength larger than the cut-off value for CdS which is about 513 nm. Films of thickness more than 100 nm showed interference maxima and minima, while thinner films didn't show this, because the minima and maxima are more separated in this case. The sharpness of the absorption edge decreases with decreasing film thickness, which is evidence of the presence of nanocrystallites. These results are in excellent agreement with the results obtained by Sahay et al[9] that for sulfide films deposited on the glass substrate; nano-confined effects begin to play substantial role in the optical spectra near the band edge.

The absorbance curves for CdS films of different thickness are displayed in Fig.5 where the absorbance is high in the UV region and low for values of wavelength larger than the cut-off wavelength of CdS. These curves show that the absorption edge is not sharp, but it is graded. This phenomenon is evidence on the presence of nanocrystallites or quantum dots with different sizes and then the presence of different values of the bandgap energies[14]. To confirm this expectation, the first derivative of the absorbance curves was plotted in Fig.6.

The minima of the first derivative for the films of thickness 300 and 400 nm were displayed in tables.1 and 2 respectively and used to find the optical bandgap energies. As we see there is a wide range of bandgap energies that is; 2.594-3.930 eV and 2.594-4.113 nm for the films of thickness 300 and 400 nm respectively. The increase in the bandgap energy could be explained as follows; the nanoparticles have the crystalline structure of their bulk counter parts and hence are characterized by the fully occupied valence band and an empty conduction band separated by the energy gap (E_g). However, the charge carriers in these bands e.g., the electrons in the conduction band and holes in the valence band experience an overall confining potential due to the finite size of these particles. As a result there will be size-dependent discrete states in the conduction and valence bands resulting in the effective enhancement of the bandgap; the so-called quantum size effect[4, 10]. It has been argued that in these semiconductor nanoparticles the hyperbolic band model gives a better fit to the observed quantum size effect as compared to the effective mass approximation[4]. So it was used in this work to estimate the size of the nanocrystallites. The equation derived for the bandgap, E_{gn} of nanocrystallites according to[13] is:

$$E_{gn} = \left[E_{gb}^2 + 2\hbar^2 E_{gb} \left(\frac{\pi}{R} \right)^2 / m_e^* \right]^{1/2} \tag{2}$$

where E_{gb} is the bandgap for the bulk semiconductor which equals to 2.42 eV[15], R is the particle's radius, and m_e^* is the effective electron mass. Taking $m_e^* = 0.2 m_e$ [16] for CdS, where m_e is the mass of a free electron. The calculated values of particle's radii for the two aforementioned films are displayed in tables 1 and 2.



(b)

Figure 3. The EDAX pattern for the thermally evaporated CdS film of thickness 100 nm.

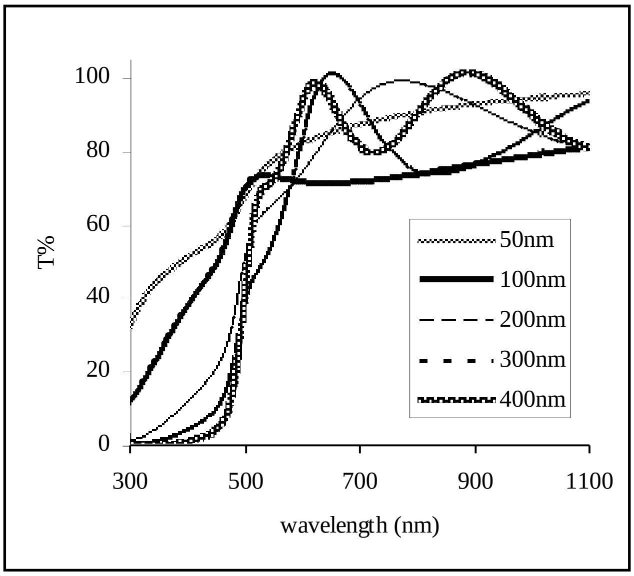


Figure 4. Transmittance curves of vacuum evaporated CdS thin films of different values of film thickness

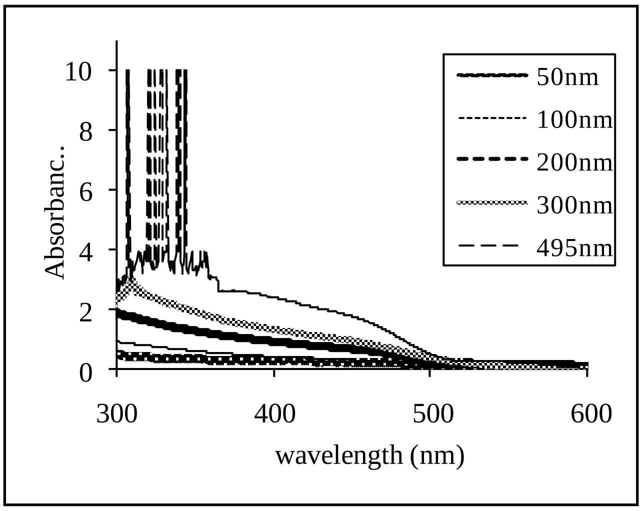


Figure 5. The absorbance curves of vacuum evaporated CdS thin films of different values of film thickness

From table 1 the average value of the radius is R±ΔR = 5.2±2.8 nm, and from table 2 it is R±ΔR = 5.7±2.7 nm. The large values of the standard deviation are due to the first value in each table which is 11.4 nm. If we look at Fig.6 we find that this minimum is very small and it could be neglected. In this case the average values with standard deviations will be 3.9±0.4 and 4.3±1.0 for the 300 and 400 nm values of film thickness respectively. So a narrow range of the nanoparticles radii is obtained by the thermal evaporation technique. It is noticed that the nanocrystallites are smaller and have narrower size distribution in the case of the thinner film. So, decreasing film thickness results in smaller size of the nanoparticles and narrower distribution of their radii.

By comparing the average value of R in table 1 with the value obtained from the X-ray diffractogram of the film of thickness 300 nm, it is found that there is a considerable difference. The reason of this discrepancy is that the C(1 1 1) line of the cubic phase that was used in the calculation is overlapped with the H(0 0 2) line of the hexagonal phase, which results in increasing its intensity and hence reducing its full width at half maximum. The result of this is a larger value of the estimated grain size. The comparison between the average value of R in table 2 and the average value obtained from the SEM micrograph for the film of thickness 400 nm shows that the value obtained by the SEM is too much larger. This can easily be explained by saying that crystallites in the SEM micrographs are aggregates which consist of a collection of smaller particles.

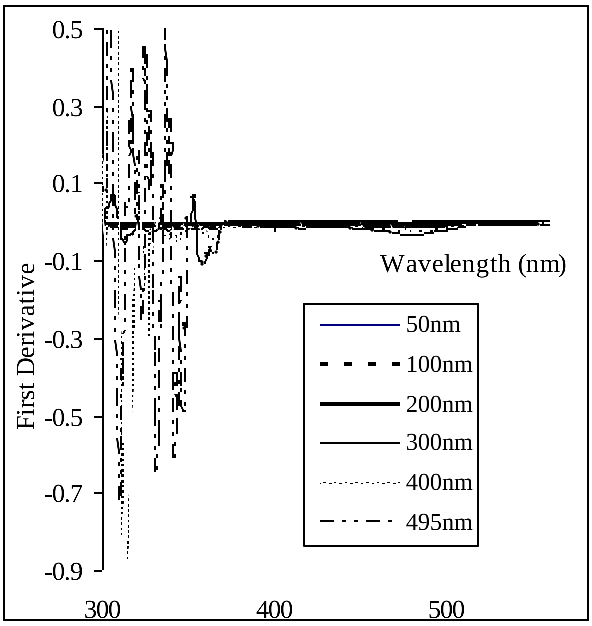


Figure 6. The first derivative of the absorbance curves of CdS thin films of different thickness

Table 1. Values of E_{gn} estimated from Fig.6 and the calculated values of the nanocrystallites' radii for film of thickness 300 nm

No.	Position of the minima (nm)	$E_g = hc/\lambda$ (eV)	R(nm)
1	478	2.594	11.4
2	365	3.397	4.5
3	353.5	3.508	4.2
4	337	3.670	3.9
5	325.5	3.810	3.6
6	315.5	3.930	3.4

Table 2. Values of E_{gn} estimated from Fig.6 and the calculated values of the nanocrystallites' radii for film of thickness 400 nm.

No.	Position of the minima (nm)	$E_g = hc/\lambda$ (eV)	R(nm)
1	478	2.594	11.4
2	416.5	2.977	6.1
3	382	3.246	4.9
4	365	3.397	4.5
5	344	3.605	4.0
6	314	3.949	3.4
7	301.5	4.113	3.2

5. Conclusions

Nanocrystalline cadmium sulfide CdS thin films were produced by thermal evaporation on glass substrates at ambient temperature. The films were characterized by recording their XRD diffractograms, SEM observations, EDAX spectra and transmittance measurements. XRD diffractograms and SEM micrographs revealed the nano-crystalline nature of the films. EDAX spectra showed that the films are cadmium rich and that they contain oxygen. The transmittance and absorbance curves confirmed the presence of quantum dots. The bandgap energy for the different nanocrystallites E_{gn} was estimated from the first derivative of the absorbance. These values of bandgap energy were used to calculate the paticles' sizes according to the hyperbolic model. The estimated values of the optical band gap are found to be 2.594-4.113 eV, corresponding to nanocrystallites of radii 11.4-3.2 for CdS film of thickness 300 and 400 nm. These results are compared with the results obtained by XRD diffractograms and SEM images.

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