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SYNTHESIS OF MULTILAYERED CdS THIN FILMS ON AMORPHOUS GLASS SUBSTRATES BY SPIN COATING

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Abstract

Single layered and multilayered CdS films were synthesized using spin coating technique at spin speeds of 900, 1200 and 2000 rpm for 30s. Samples were subsequently annealed at 100, 200, 300 400 and 500 °C for one hour in order to form the phase of CdS. Structural properties of spin coated CdS films were characterized using polarization microscopy and XRF. Optical properties were investigated using UV visible spectrometer. The optical band gap for CdS sampled prepared at different annealing temperatures and different PEG concentrations were determined. In addition, films with 1 to 4 layers were fabricated by spin coating. The variation of optical band gap with number of layers in multilayered structure was studied. Optical band gap decreases with annealing temperature, PEG concentration and number of layers.

Keywords: CdS, optical band gap, XRF, spin coating, thin films

1. Introduction:

Cadmium sulfide (CdS) is a n-type yellowish semiconductor material with direct band gap 2.42 eV at 300 K. CdS is one of the most important II-VI semiconductors. The structure of CdS is solid hexagonal or cubic crystal. Thin films of CdS can be used as window material of CdS/CdTe solar cells and other electro optical devices. The crystallographic, morphological, optical and electrical properties of CdS layer depend on the film preparation parameters. CdS films have been prepared using many different techniques such as vacuum evaporation¹, electron beam evaporation method², chemical bath deposition³ and screen printing. CdS is the most suitable hetero-junction window material for CdS/CdTe because of its large band gap. The refractive index of CdS nanoparticles is lower than its bulk state due to the quantum confinement effect, and CdS layers exhibit the wave guiding properties. Concentration and synthesis technique determine properties of CdS related nanoparticles and quantum dots. The quantum dots are considered as promising candidates for optoelectronic applications including light emitting diodes (LED). Several methods have been used to fabricate nanostructured materials in solar energy conversion. Quantum dots can be used as frequency converters to match the spectrum of the incoming radiation to the spectral efficiency of the solar cell. Highly crystalline and transparent CdS films have been deposited on a glass substrate by electron beam evaporation technique. The structural and optical properties of the films were investigated. The X-ray diffraction analysis revealed that the CdS films have a hexagonal structure and exhibit preferred orientation along the (002) plane. UV-visible spectra of CdS films indicate that the absorption edge becomes steeper, and the band gap present fluctuation changes in the range of 2.389–2.448 eV as the substrate temperature increased².

CdS indicates some magnetic properties⁴. Magnetic thin films also find potential applications in memory and microwave devices. Second and third order perturbed Heisenberg Hamiltonian was used to describe the magnetic properties of ferromagnetic and ferrite films by us⁵⁻⁷. Thin films of Lithium mixed ferrite, multi walled carbon nanotubes, Cu₂O/CuO layers, Nickel ferrite and copper oxide have been fabricated⁸⁻¹². Previously electrical properties of semiconductor particles doped with salts have been investigated by us¹³. In this report, the structural and optical properties of spin coated CdS single and multilayered films have been explained.

2. Experimental:

Five chemical compounds were used in the preparation of the solution for the sol-gel spin coating process. When considering these five chemical compounds two chemical compound used as additive of solution and other three were used as Cd and S agents and solvent. In the preparation process, CdS was embedded in polyethylene glycol based solution. A polyethylene glycol (PEG 400, Merck) sol was prepared by mixing 0.6 ml of PEG with 8.9 ml of ethanol and 0.5 ml of acetic acid while stirring for one hour. Cadmium hydroxide and thiourea were used as the Cd and S supply agents, respectively. These agents were dissolved in ethanol while stirring for one hour. After that, this prepared solution was slowly added to the PEG sol with vigorous stirring and was stirred for four hours to obtain the final solution for thin film deposition. The spin-coating technique was used to prepare thin films on amorphous glass substrates. The samples were prepared at rotation speeds of 900, 1200 and 2000 rpm. The films have been post-annealed in air at 100, 200, 300 400 and 500 °C for one hour in order to remove the solvent and residual organics.

The optical properties of samples were investigated using UV-1800 SHIMATZU double beam UV/Visible spectrometer. Uniformity of films was investigated using Universal Trinocular Polarizing Microscope (Euromex Universal Polarizing Microscope ME.2895). Composition of films was determined using X-ray fluorescence (XRF) method by means of Helmut Fischer X- ray analyzer.

3. Results and Discussion:

The best possible structure was obtained at spin speed of 900 rpm. So all the samples were spin coated for a duration of 30s at 900 rpm. In this process, CdS concentration of the solution was changed in three steps (1, 0.5 and 0.25) mol/dm³. Thereafter, thin film structure was fabricated at spin speed of 900 rpm for 30s, and films were subsequently annealed. Then the best possible concentration of CdS was found using polarization microscopy imaging and transmittance variation of the thin film structure. Transmittance variation was measured using the UV/Visible Spectroscopy in the transmittance mode. Figure 1 shows the polarization microscope images. Table 1 indicates the variation of transmittance with CdS concentration. According to these data, 0.5mol/dm³ is the best CdS concentration to create thin film structure.

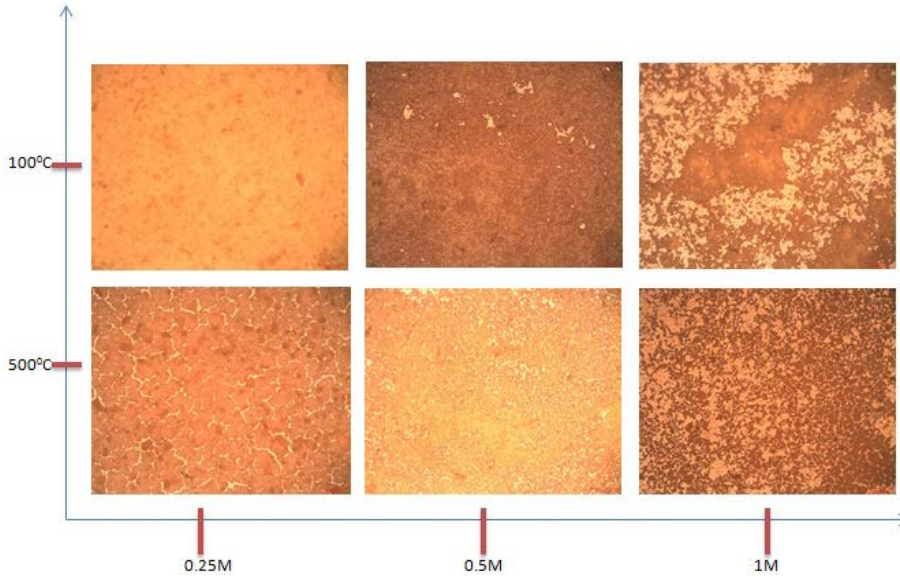
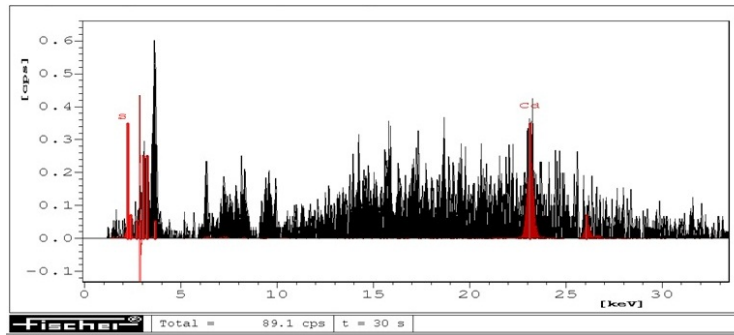


Figure 1: Polarization microscopic images of thin film structure with different CdS concentrations and annealed at 100 and 500°C.

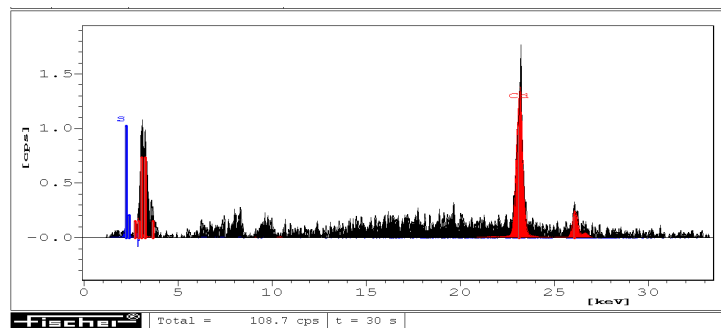
Concentration (mol/dm ³)	Transmittance
0.25	40-50%
0.5	30-40%
1.0	20-30%

Table 1: Transmittance variation with CdS concentration.

XRF spectrum was employed to detect the existence of Cd and S in the film sample. XRF peak at the 2.4 and 23 KeV are due to the S and Cd, respectively.



(a)



(b)

Figure 2: XRF Spectroscopy for PEG .1ml, 0.5M CdS annealed at (a) 100°C and (b) 500°C.

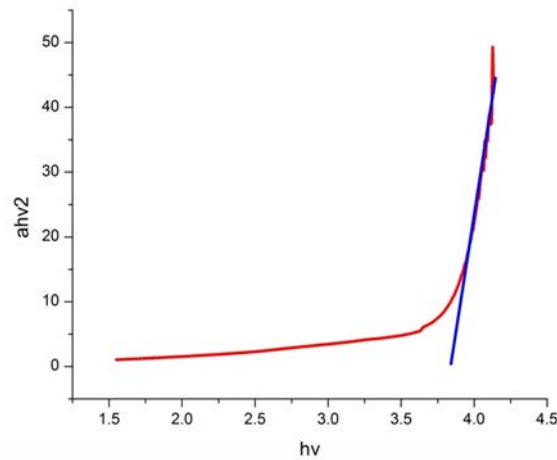
As next step, the polyethylene glycol (PEG) concentration was changed and characterized the sample using UV/Visible Spectroscopy. In this step, the PEG amount was varied in three steps (0.05, 0.1 and 0.15 ml). For this process, a constant amount of CdS solution (5 ml of .5mol/dm³ CdS) was used to prepare each sample. Thereafter, thin films were synthesized by spin coating technique with spin speed 900 rpm for 30s. The samples were subsequently annealed at five different temperature values with an increment of 100 °C (100, 200, 300, 400 and 500 °C) for a 1 hour duration. After measuring the UV/Visible absorption Spectrum, the optical band gap values were calculated using the equation:

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2}$$

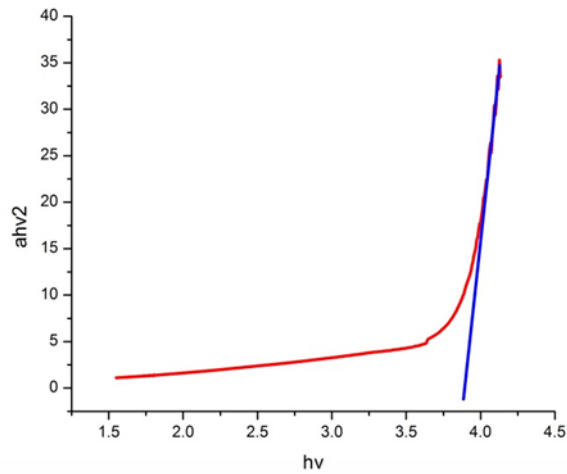
Here α , $h\nu$ and A are absorption coefficient, photon energy and a constant, respectively.

Annealing temperature (°C)	PEG amount (ml)	Optical band gap (eV)
100	0.05	3.82
200	0.05	3.82
300	0.05	3.83
400	0.05	3.82
500	0.05	3.82
100	0.10	3.74
200	0.10	3.73
300	0.10	3.69
400	0.10	3.72
500	0.10	3.71
100	0.15	3.39
200	0.15	3.34
300	0.15	3.34
400	0.15	3.27
500	0.15	3.27

Table 2: Optical band gap variation with annealing temperature and PEG concentration.



(a)



(b)

Figure 3: a) The graph of $(\alpha hv)^2$ vs. $h\nu$ (Photon Energy) for a thin film (PEG .05ml, 0.5M CdS, annealed at 100 °C) (Other preparation conditions: Spin speed = 900 rpm; Spin time duration = 30sec.; Annealing time duration = 1 hour)
 b) The graph of $(\alpha hv)^2$ vs. $h\nu$ (Photon Energy) for a thin film (PEG .05ml, 0.5M CdS, annealed at 500 °C) (Other preparation conditions: Spin speed = 900 rpm; Spin time duration = 30 sec.; Annealing time duration = 1 hour)

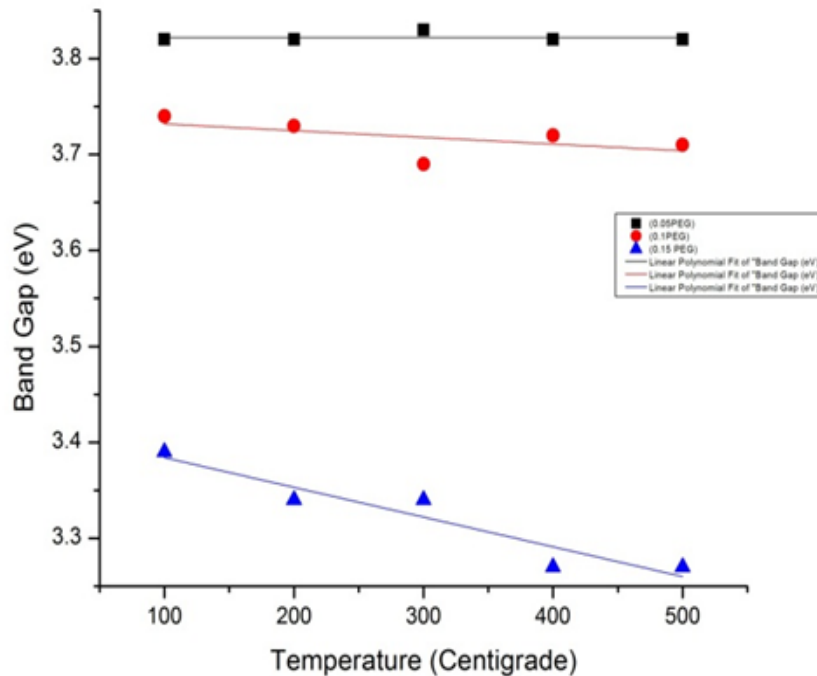


Figure 4: Optical band gap variations with annealing temperature. Here Square, circle and triangle in the graph represent 0.05, 0.10 and 0.15ml of PEG amounts, respectively.

According to the graph, the optical band gap decreases with the annealing temperature due to the increase of particle size with annealing temperature.

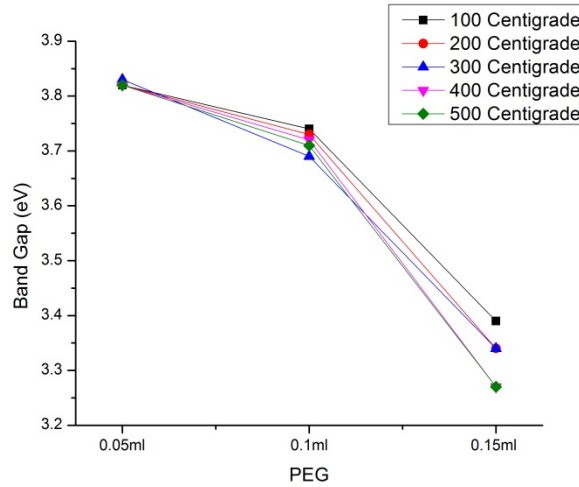


Figure 5: Optical band gap variations with PEG amount.

According to the graph, the optical band gap decreases with the PEG concentration due to the increase of particle size with the PEG concentration.

Multilayer structure of CdS was fabricated by depositing one CdS layer on another layer. To create this structure first the CdS solution was prepared by using PEG 0.15ml, 0.5M CdS, and then the thin film structure was created by spin coating with spin speed 900rpm for 30s. After annealing the sample at 300 °C for 30 minutes, the next coating was applied on the top of the first coating. By using this process, samples with 2 to 4 layers were fabricated. Finally the optical band gap variation was measured using UV/Visible spectroscopy.

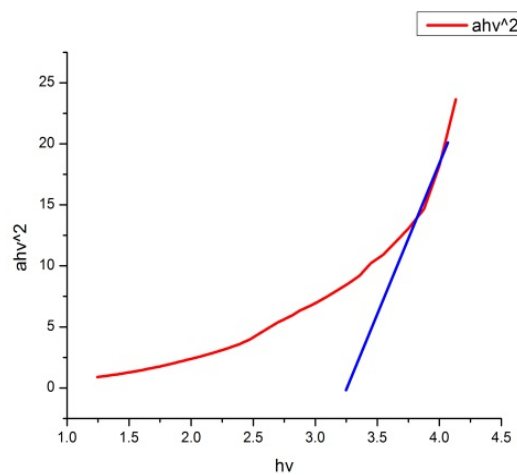


Figure 6: The graph of $(\alpha h\nu)^2$ vs. $h\nu$ (Photon Energy) for a thin film (PEG .15ml, 0.5mol/dm³ CdS film with two layers annealed at 300 °C).

The optical band gap value for films with one, two and three CdS layers are 3.35, 3.32 and 3.27 eV, respectively. Because the transmittance value is very low at higher thicknesses, the optical band

gap could not be determined for multilayered CdS films with four layers and above. The optical band gap gradually decreases with the thickness.

4. Conclusion:

According to the polarization microscopic data, the spin coated CdS films are fairly uniform at 0.5mol/dm^3 CdS concentration. XRF peaks at the 2.4 and 23 KeV indicate the existence of the S and Cd in the film sample, respectively. Optical band gap of film samples varies between 3.27 and 3.83 eV depending on the PEG amount and annealing temperature. The optical band gap of all the CdS films is higher than that of bulk CdS (2.42eV). Because the particle size in CdS films increases with the annealing temperature and PEG concentration, the optical band gap decreases with annealing temperature and PEG concentration. The optical band gap rapidly decreases with the annealing temperature at higher PEG concentration (0.15ml) compared to the lower PEG concentrations (0.05 and 0.1 ml). For all the annealing temperatures, the optical band gap slightly decreases from PEG concentration of 0.05 to 0.1ml. However, it rapidly decreases from PEG concentration of 0.1 to 0.15ml. Furthermore, the optical band gap decreases with the number of layers.

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