Study of Effect of Different Capping Agents on the Optical Properties of CdS Nanocrystalline Films

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Abstract: ***Nanocrystalline CdS thin films were prepared by chemical bath deposition technique using different capping agents – Mercaptoethanol (MEL), Thioglycerol (TG), Thiophenol (TP) and Polyvinylpyrrolidone (PVP) for control of particle size. The effect of the different capping agents on the optical absorption spectra and transmittance spectra were studied. Shift in absorption edge to shorter wavelength is observed in all the nanocrystalline films in comparison to the bulk. However the PVP capped CdS films showed behavior similar to bulk. The values of Bandgap energy obtained from Tauc's plot were found to be greater than that of the bulk film. Transmittance spectral studies show that Thioglycerol capped CdS films exhibited very high transmittance and correspondingly low absorbance as compared to the other nanocrstalline films making it suitable for application as antireflection coatings in Solar cells. The values of Refractive Index and Extinction Coefficient were calculated from Transmittance spectra. The highest value of Refractive Index 'n' is for Thiophenol capped CdS films at around 400nm. Refractive Index decreases with increase in wavelength in all the films. The variation of Extinction Coefficient 'k' with wavelength shows a rise and fall which is directly related to the absorption of light. In the case of bulk film, the values of k are high (1.1-1.7).In Mercaptoethanol and Thioglycerol capped films 'k' decreases at around 440nm while in Thiophenol capped films it decreases at 500 nm and in PVP capped films at 560 nm which can be attributed to the absorption edge in these films.***

Keywords: CdS,Nanocrystalline films, Chemical bath deposition technique ,Capping agents, Antireflection coatings.

1. Introduction

Semiconductors nanoparticles are an important class of materials with variety of application like optoelectronic devices, photonic transducers[1], luminescence devices, biosensors etc [2].CdS is the one of the most important II-VI compound semiconductor which is of considerable interest in the fabrication of solar cell and other optoelectronic devices[3].A number of techniques have been employed in the synthesis of these nanomaterials like vaccum evaporation, molecular beam epitaxy, sputtering, chemical bath deposition, pulsed laser deposition[4]-[9].The use of different surface passivating agents/capping agents, can bring about control of growth, size distribution and improvement in the quality of crystallites synthesized using these techniques[10].The growth of a nanostructure is due to two processes namely Ostwald ripening and oriented attachment(OA)[11].It is reported that capping agents, as they directly modify the nanoparticle surface can largely influence the OA processes. The molecular weight of the capping ligand also makes a remarkable contribution in the assembly behaviours of the nanoparticles [11]. Exploiting these mechanisms using appropriate capping agents is an interesting and challenging aspect in the synthesis of nanostructure. These capping agents are also known to modify structural ,morphological and optical properties of the synthesized nano materials. In this paper we report the effect of different capping agents on the optical properties of CdS nanocrystalline films synthesized by chemical bath deposition technique, not reported earlier.

2. Materials and Methods

2.1 Sample preparation

The preparation by CBD method involves precipitation followed by condensation. The precipitates were prepared in 50ml beakers which were cleaned using HCl, acetone and distilled water. A mixture of solution of 1M Cadmium Acetate, Triethanolamine, Thiourea and aqueous Ammonia is prepared. Different capping agents were used in the present work namely Mercaptoethanol, Thioglycerol, Thiophenol and Polyvinylpyrollidone. In the Mercaptoethanol, Thioglycerol and Thiophenol capped films,.01ml Methanol was added for dissolving the capping agents. In polyvinylpyrollidone capped films methanol was not required. In the beginning when precipitation started, stirring was done using magnetic stirrer for 5 minutes. After that the deposition was made in static condition in the water bath at 60˚C. After deposition, the films were cleaned with distilled water, then dried by keeping them in open atmosphere at room temperature.

2.2 Measuring Instruments

The Optical Absorption and Transmittance studies were carried out using Ellico SL 210 UV–Vis Spectrophotometer.

3. Result and Discussion

3.1 Optical Absorption Spectra

The effect of the different capping agents on the optical absorption spectra were studied. Fig(1) shows Optical absorption Spectra of CdS films prepared with different capping agents. Shift in absorption edge to shorter wavelength is observed in all the nanocrystalline films in comparison to the bulk. However the PVP capped CdS films showed behavior similar to bulk. The Optical Absorption Coefficient α and band gap E_g (for direct band gap materials) are represented by the equation

$$\alpha=c(h\upsilon-E_g)^{1/2}/h\upsilon \text{ -----(1)}$$

where, E_g is the optical band gap and c is a constant. Thus a plot between $(\alpha h\upsilon)^2$ vs hυ (Tauc's plot) gives the band gap value E_g of the material. Fig(2) shows the Tauc's Plot of CdS films with different capping agents .The values of Band gap energy obtained from Tauc's plot are presented in table (1).The increase in the band gap with reduction in particle size (Quantum Confinement Effect) [12] is observed in all the capped films

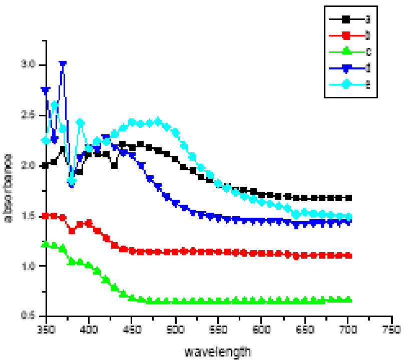

Fig: 1. Optical absorption Spectra of CdS films with different capping agents: 1. CdS bulk 2. CdS (with mercaptoethanol) 3. CdS (withThioglycerol) 4. CdS (withThiophenol) 5. CdS (with PVP)

Table 1: Optical bandgaps of the films

Sample	***Band Gap (eV)***
CdS bulk	**2.4**
CdS(with MEL)	**2.63**
CdS (with TG)	**2.8**
CdS (with TP)	**3.04**
CdS (with PVP)	**2.45**

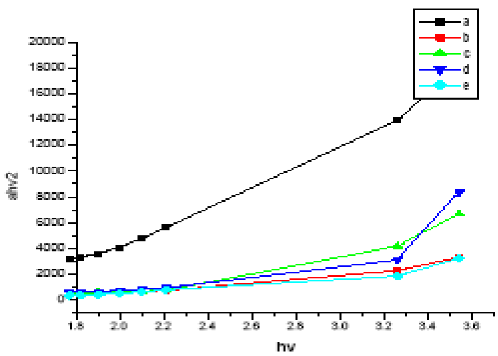

Fig: 2. Tauc's Plot of CdS films with different capping agents:1.CdS bulk 2.CdS (with mercaptoethanol) 3. CdS (with Thioglycerol) 4. CdS (withThiophenol) 5. CdS (with PVP)

3.2 Optical Transmittance Spectra

Fig(3) shows Optical transmittance Spectra of CdS films with different capping agents.Transmittance spectral studies show that Thioglycerol capped CdS films exhibited very high transmittance and correspondingly low absorbance as compared to the other nanocrstalline films making it suitable for application as antireflection coatings in Solar cells.The transmittance of other capped film was similar to that of the Bulk film.

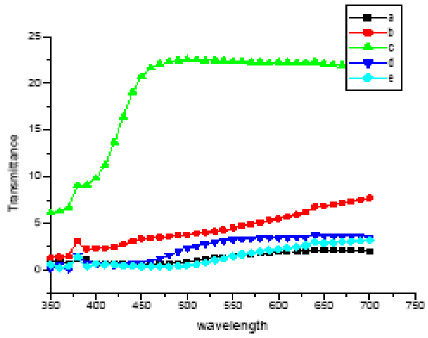

Fig: 3. Optical transmittance Spectra of CdS films with different capping agents: 1. CdS bulk 2. CdS (with mercaptoethanol) 3. CdS (withThioglycerol) 4.CdS (withThiophenol) 5.CdS(with PVP)

3.3 Determination of Optical Constants

The values of Refractive Index and Extinction Coefficient were calculated from Transmittance spectra. Refractive index (n) is a fundamental property of an optical material because of its close relationship to the electronic polarization of ions and the local field inside the materials [13].Evaluation of the refractive index of these materials is important for application in various integrated optic devices. In the present work the refractive indexes were determined using the well known Envelope method proposed by Swanepoel [14].Generally outside the region of fundamental absorption (hυ>Eg) or of free carrier absorption (for higher wavelength), the dispersion of n and k is not very large [15].Using the Envelope method, the refractive index of the film on a transparent substance can be evaluated from the transmittance spectra using the relation[16]

$$n=[N+(N^2-n_s^{\,2})^{1/2}]^{1/2} \text{ -------------(2)}$$

where,

$$N=2n_s\,(T_{max}-T_{min}/T_{max}\,T_{min})+(n_s^{\,2}+1)/2 \text{ --------------(3)}$$

and n_s is the refractive index of the substrate (n_s=1.52 for glass)

The extinction coefficient 'k' is a measure of the fraction of light lost due to scattering and absorption per unit distance in the participating medium. 'k' can be calculated from the relation[13,17]

$$k=\alpha\lambda/4\pi \text{ --------------(4)}$$

where α is the absorption coefficient.

Fig(4) shows variation of Refractive Index with wavelength of CdS films prepared with different capping agents.'n' is for Thiophenol capped CdS films at around 400nm. Refractive Index decreases with increase in wavelength in all the films.

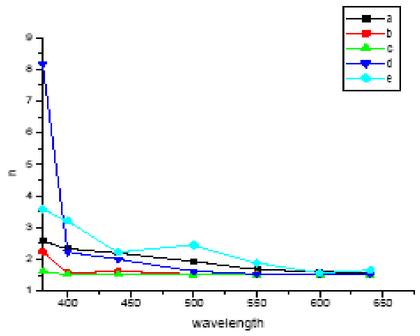

Fig: 4. Refractive Index of CdS films with different capping agents: 1. CdS bulk 2. CdS (with mercaptoethanol) 3. CdS (withThioglycerol) 4. CdS (withThiophenol) 5. CdS (with PVP)

Fig(5) shows the variation of Extinction Coefficient with wavelength of CdS films

Prepared with different capping agents. The variation shows a rise and fall which is directly related to the absorption of light. In the case of bulk film, the values of k are high (1.1-1.7). In Mercaptoethanol and Thioglycerol capped films 'k' decreases at around 440nm while in Thiophenol capped films it decreases at 500 nm and in PVP capped films at 560 nm which can be attributed to the absorption edge in these films.

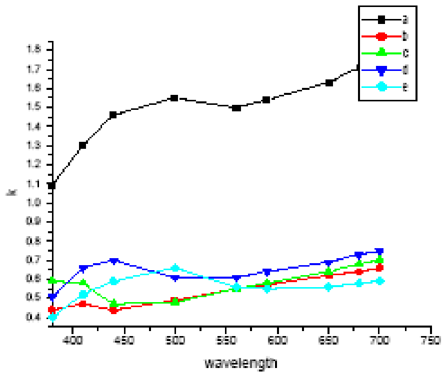

Fig: 5. Extinction Coefficient of CdS films with different capping agents: 1. CdS bulk 2. CdS (with mercaptoethanol) 3. CdS (withThioglycerol) 4. CdS (withThiophenol) 5. CdS (with PVP)

4. Conclusions

The optical properties of nanocrystalline CdS films prepared with different capping agents were studied. Quantum confinement effect is predominant in the nanocrystalline films which was observed by the blue shift in the absorption edge. Band gap values calculated from absorption spectra were found to be greater than the bulk film. Thioglycerol capped film showed high transmittance as compared to other nanocrystalline films. Refractive Index was found to decrease with increase in wavelength in all films. The extinction coefficient showed an initial increase and further decrease with wavelength which is related to the absorption edge in the films.

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