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GROWTH OF CDS NANOSTRUCTURES BY NEW SOL GEL ROUTE AND ITS OPTICAL CHARACTERIZATION

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Abstract- Cadmium Sulphide nanostructures are prepared with new sol gel route by direct reduction of sulpher and its reaction with cadmium chloride in the sol. The sol was consisting of non aqueous mixture of cadmium chloride, thiourea and complexed by TEA. The solution was stirred well and heated to about 60 ^{o}C for one hour and kept for another 24 hours at sufficiently lower temperature to initiate the reaction. Green yellowish gel was obtained and characterized by optical spectrophotometer. The step like nature in transmission and band gap curves could be due to discrete energy levels in nanomaterials. To obtain the films the CdS paste was screen printed on glass substrate and annealed at 300 ^{o}C for few hours. Optical studies suggest that, the CdS particles are either of thickness of few nanometer range and/or grain size of nanometer range. This paper includes details about new sol gel technique and optical characterization of particles and films.

Key words - CdS films, sol gel, optical properties, solar cells

INTRODUCTION

Smaller and faster is the technological demand of our times and this creates a need for suitable materials and processing techniques. Thin films play an important role in fulfilling this need for a long time. Nanotechnology is further added new dimension to it. The CdS semiconductor having direct band gap 2.42 eV [1], exhibit interesting properties has spectrally pure very narrow emission spectra and the emission colour is simply tuned by changing their size. Direct band gap at room temperature provide a wide range of potential optoelectronic applications such as laser materials, transducers, photoconducting cells, photosensors, optical wave-guides and non-linear integrated optical devices. Due to the high material cost involved there is a major drive toward developing polycrystalline compound semiconductors, especially in the form of thin films.

CdS thin films has been obtained by several methods such as electrodeposition, vacuum evaporation, sputtering, screen printing, photochemical deposition, CBD, spray pyrolysis and sol gel[2-10], However the basic problem with CdS is to obtain uniformity over a large area and stoichiometry. Sol gel method is one of the newest chemical methods to produce thin-film and powder. The technique appears to be a relatively simple, inexpensive method to prepare a homogeneous film with controlled composition and useful for large area industrial applications. Now a days nanocrystalline materials opened a new era of electronic applications since material properties could be changed by changing the crystallite size of the films. Band gap of the varies with particles size and particle size depends on deposition parameters like pH of the solution. In this paper we have discussed the optical characterization of sol gel deposited CdS Nanostructures at various pH values.

EXPERIMENTAL DETAILS

Cadmium Sulphide nanopowder and films are prepared with new sol gel route by direct deduction of sulpher and its reaction with cadmium chloride in the sol. The sol was consisting of non aqueous mixture of cadmium chloride, thiourea and complexed by TEA. The pH of the solution was maintained by ammonia solution. The solution was stirred well and heated to about 60 ^{o}C for one hour and kept for another 24 hours at sufficiently lower temperature to initiate the reaction. Green yellowish gel was obtained. CdS particles were obtained by centrifuge the gel. CdS films were obtained on glass substrates by screen printing. Large number of samples were obtained at various pH values. It has been observed that the reaction occurs only in basic region (ph>7).

The effect of pH on the CdS nanoparticles has been studied. The transmission data were obtained by UV-Vis spectrophotometer 119 Systronics. The optical transmission of CdS films on glass substrates was measured at near normal incidence in the 300-800 nm wavelength ranges. Optical band gap energy (Eg) was determined graphically after extrapolation of the plot at α

=0 using the standard expression for direct transiotion between two parabolic bands $(\alpha h\nu)^2 = A(h\nu - E_g)$.

RESULTS AND DISCUSSION

Green yellowish samples were obtained from the gel after one day. Some of the samples were heated at different temperatures and different time intervals. Color of the samples changes from green to dark yellow on slow heating of these samples could be due to particle size of CdS.

Fig.1 show the Optical transmission spectra for chemical bath deposited CdS films deposited at different pH value from 8.0 to 10 (Sample CdS-A for pH 8; Sample CdS-B for pH 9 and Sample CdS-C for pH 10). All the films shows more than 70% transmission for wavelength longer than 500 nm The pattern of interference films suggests that films are adherent and have enough homogeneous uniform thickness.

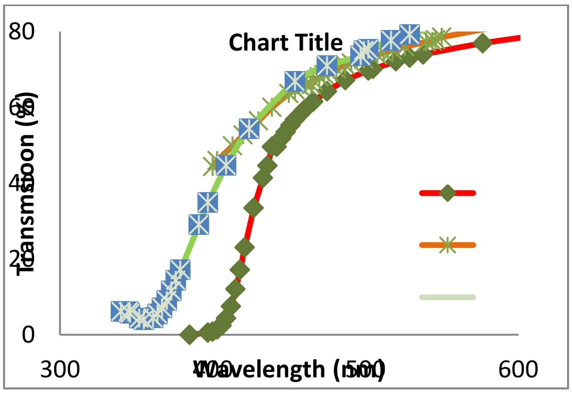

FIG. 1-Transmission curves for sol gel deposited CdS thin films at different pH values (CdS-A pH 8; CdS-B pH 9; and CdS-C pH-10).

The spectra shows that that the absorbance edges are blue shifted with respect to the bulk CdS, indicating quantum confinement effect in nanoparticles. For high pH values shifting of absorption edge is more pronounced. Variation of % spectral transmission with photon wavelength is also shown in Table 1.

For calculating energy band gap of the CdS films the transmission spectra is used. The corresponding $(\alpha h\nu)^2$ versus photon energy $h\nu$ plot for various pH values were shown in the Fig 2, Fig. 3 and Fig.4. Linearity of the plots indicates that material is of direct band gap nature. The extrapolation of the straight line gives the direct band gap of the material. These figures clearly show a shift in the band gap of the CdS on increasing the pH. The transmission and band gap curve also show a step like nature in the region where absorption occurs. This step like nature could be due to the discrete energy levels and step like density of states for nanomaterials instead of quasicontinuous levels in the conduction and valance band for bulk materials. From the band gap information the size of the cdS nanoparticles were calculated using the effective mass approximation (EMA) method and following the equation [11]

$$E_{gb} - E_{gs} = \left[\left(h^2\pi^2 / 2R^2 \right) \frac{1}{m*} \right]$$

In the above equation m^* is the effective mass of the specimen, E_{gb} is the bulk band gap and E_{gs} is the band gap of the sample. From the calculation it is found that the particle size decreases with the increase of the pH. The observations are shown in the table 2.

The films exhibit good transparency in the visible and infrared region. The refractive index n at for a sample is calculated using envelope curve method [12]. The Expression for refractive index is given by

$$n = [N + (N^2 - n_S^s)^{\frac{1}{2}}]^{1/2}$$

$$Where\ N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{N_{sN_S^2}}{2}$$

The extinction coefficient k can be obtained from the experimental expression [13].

$$\boldsymbol{k = \frac{a\lambda}{4\pi d}}$$

Where α is the absorption coefficient and and t is film thickness. It has been seen that although extinction coefficient value varies with wavelength, the refractive index value remain fairly constant for the wavelength. It can be seen that n first increases, then decreases and finally stabilizes with increasing λ. These trends suggest the presence of an absorption band at a wavelength bellow 400 nm. This shows that the nanostructured thin films prepared in this study may give protection to optical devices that operate within visible region or for reducing the radiation exposure in the substrate within the ultraviolet region.

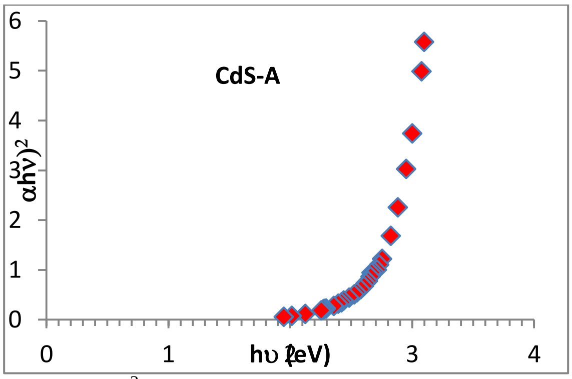

Fig. 2- $(\alpha h\nu)^2$ vs $h\nu$ graph for sol gel deposited CdS thin films for sample CdS -A (pH-8)

CONCLUSION

Cadmium Sulphide nanopowder and films are prepared with new sol gel route by direct reduction of sulpher and its reaction with cadmium chloride in the sol. Green yellowish samples were obtained from the gel after one day. Optical transmission spectra for chemical bath deposited CdS films deposited at different ph 8.0 to 10. films suggests that films are adherent, have enough uniform thickness and the absorbance edges are blue shifted with respect to the bulk CdS, indicating quantum confinement effect in nanoparticles. From the calculation it is found that the particle size decreases with the increase of the pH . The observations are shown in the table 1. The transmission and band gap curve also show a step like nature in the region where absorption occurs. This step like nature could be due to the discrete energy levels and step like density of states for nanomaterials instead of quasicontinuous levels in the conduction and valance band for bulk materials.

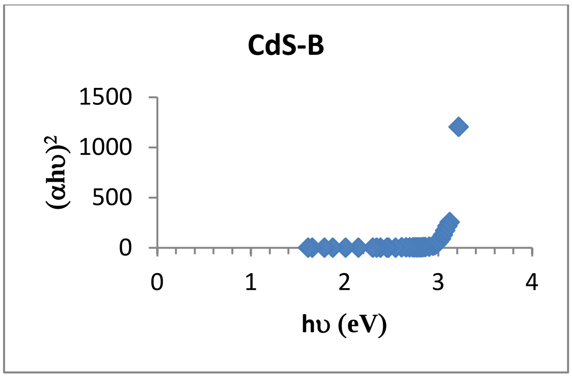

Fig. 3- $(\alpha h\nu)^2$ vs $h\nu$ graph for sol gel deposited CdS thin films for sample CdS –B (pH 9)

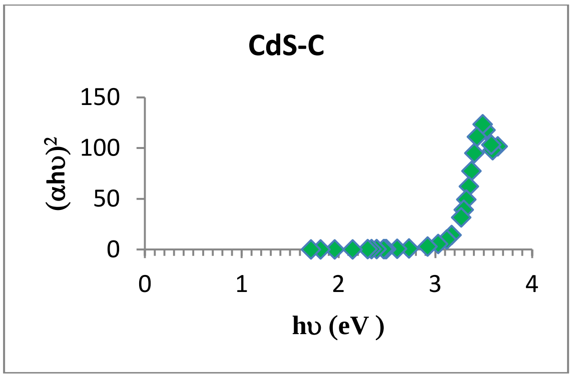

Fig. 4- $(\alpha h\nu)^2$ vs $h\nu$ graph for sol gel deposited CdS thin films for sample CdS –C (pH 10).

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Table 1-Variation of % spectral transmission with photon wavelength

Sample	350 nm	400 nm	450 nm	500 nm	550nm0	650nm	750nm
CdS -A	0	8	55.2	69.7	73.9	83.2	84
CdS -B	-	44.35	63.55	72.6	77.83	83.98	-
CdS -C	4.3	44.6	66.81	75.3	80.25	83.7	92

Table 2- Variation of size with pH

Sample	pH	Band gap from Uv-Vis (eV)	Shift in band gap (eV)	Grain Size (nm)
CdS -A	8	2.8	0.38	4.42
CdS -B	8.5	3.1	0.68	2.47
CdS-C	9.0	3.2	0.78	2.15