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Effect of thioglycerol capping on morphology and structure of chemically deposited CdS:NaF,La films

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Abstract

This paper reports the effect of thioglycerol as capping agent for synthesis of lanthanum (La) doped nanocrystalline CdS semiconducting films on the glass substrate by means of chemical bath deposition (CBD), with $Cd(CH_3COO)_2$ as Cadmium (Cd) ion source, and $(NH_2)_2CS$ as sulphur (S) ion source. Long, rod like structures is observed in SEM micrographs of the films. XRD studies show the existence of both hexagonal and cubic phases. Increase in FWHM is observed for smaller particle due to nanocrystalline effect. UV-VIS absorption studies show shift of absorption edge towards lower wavelength side.

Keywords: II-VI semiconductors, chemical bath deposition method, photoluminescence spectra, nanocrystalline materials.PACS: 71.55.GS, 61.82.RX, 81.15.L

INTRODUCTION

The most common II-VI semiconductor nanoparticles, are cadmium chalcogenide nanocrystals (CdTe, CdSe and CdS). Gao et al. [2] found that reactions in presence of thiols (mercaptans), which contain SH group attached to carbon atom, result in surface modification of the nanoparticles and reduction of the non-radiative local surface traps which, in turn, lead to an enhancement of the quantum yield of the excitonic transitions. Thioglycerol is one such thiols and has been found to act as capping agent [3]. Methanol is used as solvent for thioglycerol. II-VI semiconductor nanoparticles have been fabricated by various methods like sol-gel, electrostatic deposition [4, 5], solvent growth [6], DC magnetron sputtering [7] and chemical deposition [8–11] methods. In the present work La doped CdS photo luminescent nanoparticles have been synthesised by simple Chemical bath deposition (CBD) technique which is a low-cost method, for producing uniform, adherent and reproducible films.

Further, Lanthanide ions possess fascinating optical properties and their discovery, first industrial uses and present high technological applications are largely governed by their interaction with light. A host is usually necessary to dilute the optically active ions and prevent rapid non-radiative processes from occurring, i.e., all of the energy being lost as heat. Hosts are usually insulators, but semiconductors can also serve as hosts for optically active ions, as long as the luminescent excited state does not overlap with the conduction band leading to quenching. The present paper reports effect of thioglycerol as capping agent which results in surface modification crystal size reduction in La doped CdS films prepared by CBD method using. Results of SEM, XRD and Optical absorption studies are presented and discussed.

EXPERIMENTAL

Film preparation

In this study CdS nanocrystalline films were prepared on glass substrate by CBD technique. The microscopic glass slides of dimensions 24 × 75 mm was used as substrates. These slides were first cleaned with H_2SO_4, acetone, double distilled water and ultrasonic cleaner. Then, the dried glass slides were dipped vertically into a mixture of solutions of 1M Cadmium-acetate, TEA, 30% aq. Ammonia and Thiourea. 0.01 M NaF and varied molar concentrations (0.001 M, .005 M, 0.01 M, and 0.05 M) of Lanthanum Nitrate as an impurity were also added to the solution. All solutions were prepared in double distilled water.

Bhushan and co-workers [15, 16] reported that NaF acts as flux as in its absence the inclusion of rare earth impurities were not much effective. The capping agent thioglycerol with methanol (TGM) in 1:1 ratio were then added to the original mixture of solutions, since this ratio gave better results. The films were then formed on glass substrate by dipping the substrate in this mixture at the temperature of 60°C in constant temperature water bath for 60 min. The samples were then washed with double distilled water and dried at room temperature. The pH value of this mixture was found to vary from 11.2 at beginning to 10.9 at the end of deposition.SEM and XRD studies were made at IUC-DAE, Indore, India, using a JEOL JSM 5600 scanning electron microscope and a Rigaku RUZHR X-Ray diffractometer (CuK$_\alpha$ radiation, $\lambda = 0.154$ nm). The optical absorption spectra were studied by using a Shimadzu (UV-VIS) Pharma Spec-1700 Spectrophotometer.

RESULTS AND DISCUSSION

The films prepared on glass substrate in this study are synthesised by a simple chemical bath deposition approach. The films are deposited as a result of precipitation followed by condensation from a solution of the precursors. Organic molecule “capping agent” Thioglycerol was added in different volumes in order to limit the growth of the particles and control their size [17, 18]. Films deposited on glass substrates were rinsed with double distilled water and dried at room temperature. The samples thus prepared exhibited a change in particle colour from dark yellow in case of thin film (without capping agent) to light yellow, and finally pale yellow for increased volume of TGM in the precursor solution [19].

The SEM micrographs (Figure1) show the morphological features of CdS:NaF,La at 0.2 ml and 0.7ml volume of TGM.

Platelets type structure appears when only a small amount of TGM is added to the precursor solution. But with increase in TGM volume to 0.7ml structure changes to pointed petals type. Some sharp needle structure can also be observed (indicated by arrows).

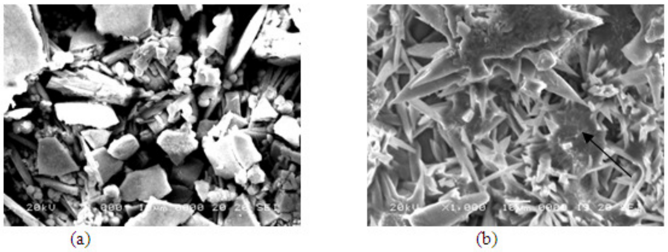

Fig 1. Effect of TGM on morphological features of CdS:NaF,LaF films with:

a) 0.2ml TGM ; b) 0.7ml TGM;

Figure 2 shows the nanocrystalline effect in the XRD pattern of CdS:NaF,La films for 0.2 ml and 0.7 ml volumes of TGM. Increase in TGM volume in the precursor solution causes broadening of several diffraction peaks. Figure 5 shows broadening of $(210)_c$, $(102)_h$, $(003)_h$ and $(110)_h$ lines. In this figure range of angles is limited from 26° to 46°, so that the broadening can be seen clearly. This is a consequence of particle size reduction.

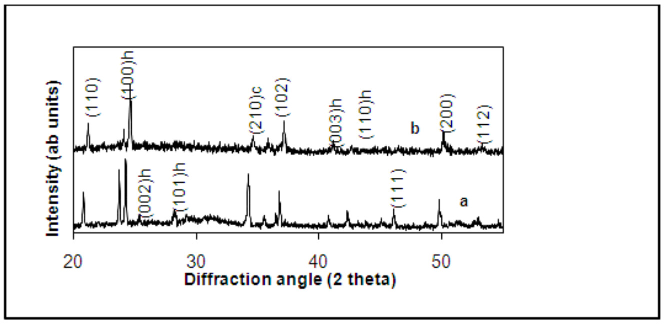

Fig 2. X-ray diffractrograms of some La doped nanocrystalline CdS films. Plot (a) is for CdS:NaF,La + 0.2 ml TGM; and (b) is for CdS:NaF,La + 0.7 ml TGM.

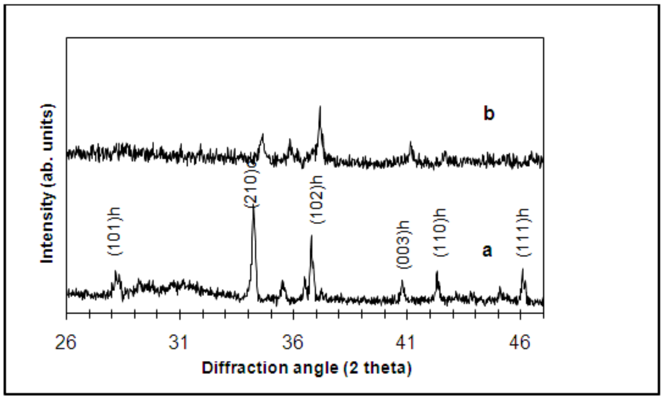

Fig 3. Broadening of diffraction lines (lying within the 2θ range 26°–46°, as seen in Figure (2)) (a) CdS:NaF,La + 0.2 ml TGM; (b) CdS:NaF,La + 0.7 ml TGM.

The XRD data along with calculated and standard values of lattice constants are shown in Table 1. As mentioned above, films examined show combination of hexagonal and cubic phases and the values of lattice constants are quite close to reported values. Using the Debye-Scherer's formula [21]

$$L = \frac{0.94\ \lambda}{\beta_{1/2}\cos\ \theta} \qquad (1)$$

where L is the particle size, λ is the X-ray wavelength used, $\beta_{1/2}$ is the full width at half maxima (FWHM) of the diffraction peak and θ is the angle of diffraction. Particle sizes were calculated for $(210)_c$, $(102)_h$, $(003)_h$, $(110)_h$ peaks of CdS:NaF,La with 0.2 ml and 0.7 ml volumes of TGM and the corresponding values are as follows: 48 nm, 88 nm, 45 nm, 55 nm and 20 nm, 27 nm, 21 nm, 29 nm at two volumes, respectively. Thus, it is apparent that increasing volume of capping agent enhances reduction in particle size. It should be further noted that according to this formula at constant θ, FWHM ($\beta_{1/2}$) should increase with reduction in particle size as observed in the present case.

Table 2. XRD data of different nanocrystalline CdS films (deposition time = 60 min;temperature of deposition = 60 °C).

d value (in Å)		Relative intensities		hkl	lattice const.(in Å)	
Obs.	Reported	Obs.	Reported		Obs.	Reported
CdS : NaF, La + 0.2 ml TGM						
3.5	3.58	25	75	(100)hCdS	a = 4.04	4.13
3.165	3.168	31	100	(101)hCdS	c = 6.86	6.71
3.47	3.35	13	59	(002)hCdS	c = 6.9	6.71
2.61	2.6	79	100	(210)cCdS	a = 5.83	5.818
2.44	2.45	57	25	(102)hCdS	c = 6.70	6.71
2.21	2.236	24	---	(003)hCdS	c = 6.63	6.71
2.06	2.068	15	57	(110)hCdS	a = 4.12	4.13
2.006	2.004	20	40	La		
1.968	1.95	32	20	(111)hCdS	c = 6.74	6.71
1.829	1.79	45	17	(200)hCdS	a = 5.783	4.13
1.7265	1.761	22	45	(112)hCdS	c = 6.716	6.71
4.2	4.11	47	100	(110)cCdS	a = 5.9	5.818
CdS : NaF, La + 0.7 ml TGM						
3.61	3.58	100	75	(100)hCdS	a = 4.17	4.13
2.587	2.6	31	---	(210)cCdS	a = 5.78	5.818
2.41	2.45	50	25	(102)hCdS	c = 6.51	6.71
2.19	2.23	24	---	(003)hCdS	c = 6.58	6.71
1.818	1.79	37	17	(200)hCdS	a = 4.18	4.818
2.8	2.79	23	30	La		
3.11	3.16	24	---	(101)hCdS	c = 6.13	6.71

The optical absorption spectra of CdS:NaF,La films deposited on glass substrate by CBD technique show shift in onset of absorption spectra towards the lower wavelength side on increasing the volume of TGM (see Figures 4), which confirms the particle size reduction. For direct band gap materials, the optical absorption coefficient α and the optical bandgap E_g are related by

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

where c is a constant [22]. Thus, the extrapolation of nonlinear plot between $(\alpha h\nu)^2$ as a function of $(h\nu)$ gives the band gap of the corresponding material. Tauc's $(\alpha h\nu)^2$ vs. $(h\nu)$ plots for La doped nanocrystalline films, are shown in Figure 5.

It is observed that the band gap increases from 2.34 eV (with 0.2 ml TGM) and 3.48 eV (with 0.7 ml TGM). It is apparent from all these observation that the band gap of material increases with increasing volume of TGM. Since the coalescence of particles is avoided, the particle size is expected to reduce more and more at higher volume of capping agents. Particularly, for thiophenol this kind of effect was reported by Herron and co-workers [23]. Such kind of absorption also supports the quantum confinement effect in nanocrystalline materials in which the electrons, holes and excitons have limited space to move and their motion is possible for definite values of energies. An important consequence of quantum confinement is blue shift in absorption spectrum which results due to increase in band gap of the materials. The particle size can be calculated from bandgap of material using effective mass approximation, given by the formula

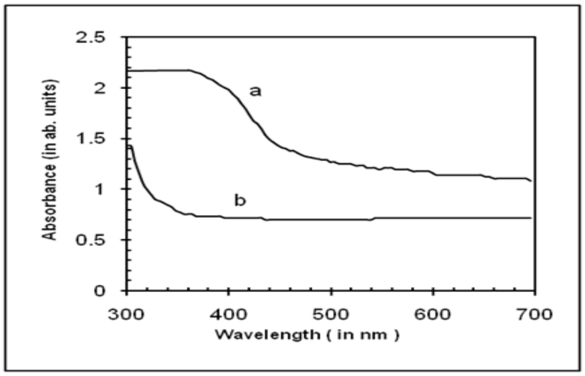

Fig 4. Optical absorption spectra of (a) CdS:NaF,La + 0.2 ml TGM; (b) CdS: NaF,La + 0.7 ml TGM.

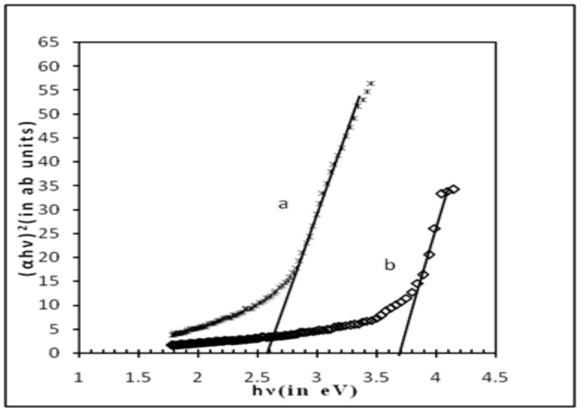

Fig 5. Tauc's plots of $(\alpha h\nu)^2$ as a function of ($h\nu$) for (a) CdS:NaF,La + 0.2 ml TGM; and (b) CdS:NaF,La + 0.7 ml TGM.

$$E_{gn} = E_{gb} + \frac{\hbar^2\pi^2}{2\mu R^2} \tag{3}$$

where E_{gn} is the band gap of nanocrystallites, E_{gb} is the band gap of the bulk semiconductor, R is the radius of particles and μ is the effective mass of electron [24]

CONCLUSIONS

The volume of TGM in the reaction mixture play a vital role in the preparation of CdS:NaF,La films by this technique, efficient photo luminescent La doped nanocrystalline CdS films have been prepared by optimising the concentration of Lanthanum Nitrate in the precursor solutions. SEM studies on pure and La doped nanocrystalline CdS films show cluster of long, rod like structures at higher volume (0.7 ml) of TGM. XRD studies show existence of both hexagonal and cubic phases in all the systems. At higher volume of TGM increase in FWHM of XRD peaks is observed suggesting a further reduction in particle sizes. The shift in onset of absorption spectra towards lower wavelength side in presence of TGM supports quantum confinement effect.

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