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Study of Optical Property of CD Doped PBS Nanocrystalline Thin Films Fabricated by Chemical Bath Deposition Technique

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Abstract: The Cd doped PbS (CdPbS) nanocrystalline thin films were fabricated using glass substrate by chemical bath deposition technique at 50°C. The XRD analysis shows the nanocrystalline nature of Cd-doped PbS thin films. The crystallite size of Cd-doped PbS thin film was found to be 27.24 nm. The morphology of the films was examined by Scanning Electron Microscopy (SEM) and it shows the presence of crystallites having uniform size. The energy band gap increases with decrease of molarities of CdPbS nanocrystalline thin films.

Keywords: Thin Film, Chemical Bath Deposition, X-Ray Diffraction, Scanning Electron Microscopy, UV-Visible Spectrophotometer, Energy Band Gap

I. INNTRODUCTION

Lead sulfide (PbS) which is a direct band gap compound semiconductor of 0.4eV belonging to IV-VI group are widely used as infrared sensor [1]. The excitation Bohr radius of PbS is very large i.e.18 nm [2]. The strong quantum confinement of both electrons and holes observed in nanostructure is due to large excitation Bohr radius and consequently, the effective mass model with the modification of size of the particle can control the value of the energy band gap [3]. The applications of such semiconductor materials are found in radiation absorption [4], Selective sensors for Pb ²⁺ [5] and photography [6]. In addition to these, PbS has been utilized as photo resistance, humidity, solar control, temperature sensors, decorative coatings and diode lasers[7,8]. However, all these properties depend on nature of substrates and the condition of crystal growth. This leads many researchers to employ different deposition technique in order to study such material. The most commonly employed techniques are microwave heating [9,10] electro deposition [11,12], chemical bath deposition [13-17] and spray pyrolysis [18]. The properties of photo conductivity of PbS nanocrystalline thin films have been investigated [19]. The addition of metal ions to this material decreases the size of the particle thereby increasing its energy gap. Because of these reasons, it becomes an excellent candidate for opto-electronic applications in the fields such as solar cell, IR detectors, light emitting and photography[20,21]. The doping of Cd and Ni in PbS thin films produces a significant shift in the forbidden energy band gap with energy range, 0.15 to 0.5eV and 1.4 to 2.4 [22]. The significant effects in energy band gap due to doping of metal ions makes it suitable for detector and solar applications. As chemical bath deposition technique has the advantages such as low cost, low temperature requirement, suitable for large scale deposition areas, controllable properties of thin film through adjustable deposition parameters and the ability to deposit thin films on different types of substrates as compared to other methods, it is a good and convenient one for preparation of PbS nanocrystalline thin films [23]. Because of these reasons, chemical bath deposition technique is employed in the present investigations also. The Cd doped PbS nanocrystalline thin film was characterized by XRD, SEM and optical property was studied with the help of uv-visible spectrophotometer.

II. EXPERIMENTAL DETAILS

The Cd-doped PbS thin films were deposited by Chemical Bath Deposition Technique on glass substrate. The glass substrates were first washed with liquid detergent and rinsed thoroughly in double distilled water and then it is placed in boiled water for a few minutes. They were finally immersed into acetone for 15 minutes and then dried in an oven.

The materials used for deposition of Cd doped PbS nanocrystalline thin films are lead acetate as source material of lead ion, thiourea as the source of sulphur ion and cadmium acetate as the source of cadmium ion respectively. The lead acetate solution of 0.1M was prepared with double distilled water stirring separately at 50°C until a clear solution is obtained. The p^H value of lead

acetate solution is maintained at 10 by adding the ammonia solution to it drop by drop slowly. The equimolar solution of Thiourea (0.1M) was then added to the solutions and the resulting mixture solution is further stirred slowly at the same temperature. Again solution of cadmium acetate (1wt%) was added to the precursor mixture solution of lead acetate and thiourea maintaining the same p^H value. Four ultrasonically cleaned glass substrates were vertically immersed in the solution using a suitable substrate holder for 24 h for deposition of Cd doped PbS thin films at room temperature. Similarly, Cd doped PbS nanocrystalline thin films of 0.15M, 0.2M and 0.25M were fabricated. The as deposited films were taken out and washed thoroughly in distilled water several times and dried in air and then put in a dessicator. The overall chemical reaction taking place is as follows. $\frac{1}{2}[Pb(CH_3COO)_2] + \frac{1}{2}Cd^{2+} + CS(NH_2)_2 \rightarrow Pb_{1-x}Cd_xS + 2CH_3COOH + CH_2N_2$

III. RESULTS AND DISCUSSION

A. Structural Study

The structural characterization was done by an X-ray diffractometer (Bruker D8 Advance) in the 2θ range, 20-80 using CuKa radiation of wavelength $\lambda=1.5406\text{A}^\circ$. The XRD patterns of Cd-doped PbS (CdPbS) thin films (0.1M) is shown in figure 1. The XRD Pattern of Cd doped PbS has face centered cubic structure as confirmed by JCPDS Data card and the peaks correspond to (111), (200) and (220) corrected crystal planes. The narrow peaks in the XRD Pattern of CdPbS indicate that the materials have good crystallinity and they are preferentially oriented along the (200) direction. A significant boardening is observed for for (111), (200), (220) orientations due to doping of cadmium. Consequently, it confirms the presence of a phase transformation due to doping of Cd into PbS lattice [24]. The lattice d- spacing is calculated by using Bragg's Law, $\lambda=2d\text{Sin}\theta$. For (200) orientation, the lattice d-spacing of CdPbS is found to be 2.99946 Å which is smaller than that of pure PbS. This indicates that there is a decrease in the value of lattice d-spacing due to doping of Cd which is in agreement with the literature reported earlier [25] and this confirms the formation of CdPbS thin film. The lattice constant is also calculated by using the relation

$$a = d (h^2 + k^2 + l^2)^{1/2}$$

The lattice constants of CdPbSare found to be 5.9989 Å for (200) orientation. The crystallite sizes of CdPbS are calculated by using Scherrer's formula,

$$D = \frac{K \lambda}{\beta \cos \theta}$$

where K is a constant (= 0.94), β is the full width at half maximum (FWHM) of the diffraction peak corresponding to a particular crystal plane. The size of CdPbS crystal for (200) orientation is found to be 27.24 nm which is also smaller than that of pure PbS crystal. Thus, the doping of cadmium also decreases the crystallite size which is in line with reports of earlier workers [26].

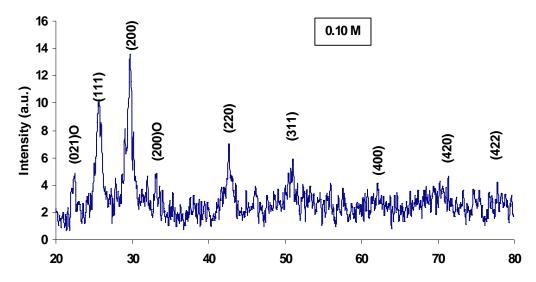


Figure 1. XRD pattern of CdPbS nanocrystalline thin film for 0.1M.

B. SEM Analysis

The morphology of Cd doped PbS (CdPbS) thin films deposited on glass substrate was examined by scanning electron microscopy (SEM). The SEM micrograph image of CdPbS nanocrystalline thin film is shown in figures 2. The (CdPbS) nanocrystalline thin film is continuous with uniform cyrstallite size.

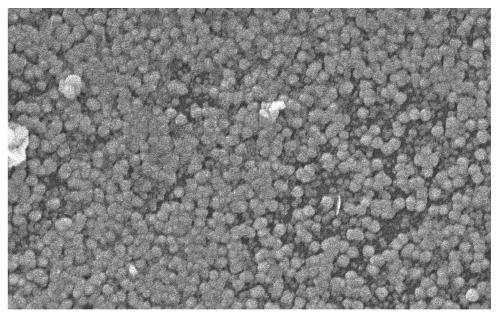


Figure 2. SEM micrograph of CdPbS nanocrystalline thin film (0.1 M)

C. Optical Property

The UV absorption spectra of CdPbS thin films for different molarities taken at room temperature are shown in Figure 3. The absorption coefficient of direct band gap semiconductor is given by $\alpha = c (h\nu - E_g)^{1/2} /h\nu$ where α is absorption coefficient, c a constant, $h\nu$ incident photon energy and E_g the band gap. Graphs between $h\nu$ vs $(\alpha h\nu)^2$ is plotted for different films which is shown in figure 4 and the intercepts of the extrapolated straight line at the $(\alpha h\nu)^2 = 0$ axis gives the value of the E_g of the material. The values of E_g so obtained vary from 0.42 to 0.47 eV indicating increase of band gap with decrease of molarities.

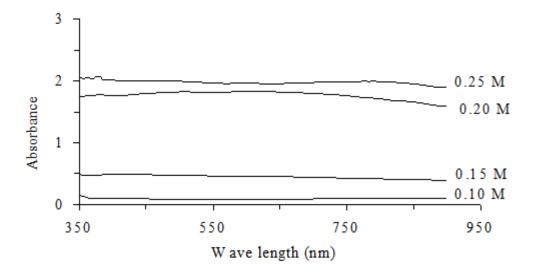


Figure 3. UV absorption spectra of CdPbS thin films for different molarities.

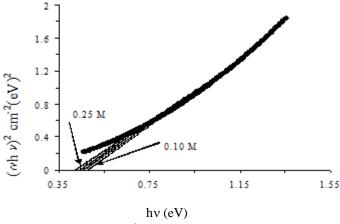


Figure . 4 Plot of $hv \sim (\alpha hv)^2$ of PbS thin films for different molarities.

IV. CONCLUSION

In the present study, the chemical bath deposition technique is employed for fabrication of Cd doped PbS (CdPbS) nanocrystalline thin films. From XRD analysis, it is observed that the crystallite size of CdPbS nanocrystalline thin films are found smaller than that of pure PbS nanocrystalline thin film and show good crystallinity. The SEM image shows the presence of cyrstallites having uniform size. The values of energy band gap, E_g vary from 0.42 to 0.47 eV indicating the increase of energy band gap with decrease of molarities of CdPbS nanocrystalline thin films.

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