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Study of Photoluminescence and Photoconductivity Properties of Chemically Deposited Nanocrystalline PbS Thin Fims

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Abstract— *Nanocrystalline PbS thin films were deposited on glass substrates by Chemical Bath Deposition technique at room temperature. Lead acetate was used as the lead ion source and thiourea was used as the sulphur ion source. Plyvinyl alcohol (PVA) was used as the capping agent and ammonia as the complexing agent. The crystallite sizes of PbS is calculated by using Scherrer's formula. It was found that the size of the PbS crystallites varies in the range 9.0 – 18 nm for (111) orientation at four different molarities, which is much comparatively small as reported by earlier workers. The photoluminescence spectra of the films showed two peaks centered around 488 nm and 518 nm after excitation at 382 nm. The films in the present study were also found to exhibit positive photoconductivity. The electrical resistivity increases as molarity increases.*

Keywords— *Chemical Bath deposition Technique, substrate, quantum size, energy gap.*

1. INTRODUCTION

The Chemical Bath Deposition Technique is followed for deposition of PbS thin films on glass substrate at room temperature as the technique possesses a number of advantages such as low cost, low working temperature and easy coating of large surfaces as compared to other thin film deposition methods. Moreover, it is also found that CBD technique is very suitable for deposition of polycrystalline PbS thin films with good photoconductive properties [1]. Lead Sulphide(PbS) possesses relatively large excitation Bohr radius (18 nm) which gives a strong quantum confinement of both electrons and holes [2]. Lead Sulphide(PbS) belongs to binary IV-VI semiconductor material with direct narrow optical energy gap, 0.41 e V at 300 K. The energy band gap of PbS can be changed by changing the grain size of the nanocrystalline structure with lattice constant of 5.936 A ^{o} [3-5]. Quantum sized PbS can be used for making particularly electroluminescent devices such as light-emitting diodes, high-speed switching and IR detectors [1, 6]. PbS thin films can be used as high performance photoconductive detectors. Nanocrystalline PbS has good optical properties as compared to GaAs or CdS with a given particle size [7]. The present work aims to investigate the particle structure, surface morphology and optical, photoluminescence and photoconductivity prpoperties of PbS nanocrystalline thin films.

2. EXPERIMENTAL DETAILS

The cleaning of substrate surface is very important due to its effect on adherent thin film properties in Chemical Bath Deposition method. The glass substrates were first cleaned by liquid detergent and washed thoroughly in distilled water and then in boiling water. Finally, they were ultrasonically cleaned in acetone for 15 minutes and dried in an oven before deposition.

The lead acetate solutions of four different molarities (0.1, 0.15, 0.2, and 0.25M) were prepared with double distilled water and the same was added to an aqueous solution (2 Wt%) o of Polyvinyl alcohol(PVA) separately with constant stirring at 70 ^{o} C until a clear matrix solution is obtained. The p^{H} value of the matrix solutions was maintained at around 10.3 by slowly adding ammonia solution drop by drop. Then the equimolar solution of Thiourea was added to each of matrix solutions. The color of the resulting solution turned in to dark brown slowly. Four ultrasonically cleaned glass substrates were immersed vertically in the solution using a suitable substrate holder for 24 h for deposition of PbS thin films at room temperature. After deposition of PbS thin films, the glass substrate were taken out and washed thoroughly in distilled water several times and dried in air and then put in a dessicator.

The reaction mechanism which is responsible for deposition of PbS thin film by CBD method is as follows.

Step I. $Pb^{2+} + 4NH_3 \rightarrow Pb(NH_3)_4^{2+}$

Step II. $Pb(NH_3)_4^{2-} + S^{2-} + CH_2N_2 + 2H_2O \rightarrow PbS + 4NH_3 + CH_2N_2 + 2H_2O$.

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3. RESULTS AND DISCUSSION

3.1 Structural Study

Structural characterization was done by XRD available at USIC, Gauhati University, Guwahati. Cu-K_α radiation of wavelength 1.5418 A^o was used to record the X-ray diffraction (XRD) patterns of the PbS thin films deposited at same temperatures for different molarities (0.10, 0.15, 0.20 and 0.25 M) with the value of 2θ ranging from 20^0 to 70^0 and a typical XRD pattern of 0.25 M is shown in Figure 1. The crystallography of the film is good and characterized by three principal peaks corresponding to (111), (200) and (222) corrected planes of the face-centered cubic structure of PbS. All the XRD patterns have face-centred cubic structure. The broaden diffraction profiles indicate the formation of PbS nanocrystals. The dominant and sharp peaks indicate that PbS nanocrystals are highly crystalline. The lattice constants for cubic phase is determined by using the relation

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

The lattice constant calculated from the above relation is found to vary from a = 5.959 to a = 6.030 Å for (111) orientation at four different molarities, which is slightly higher than the standard value (5.931 Å). The crystallite sizes of PbS is calculated by using Scherrer's formula,

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

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. It was found that the size of the PbS crystallites varies in the range 9.0 – 18 nm for (111) orientation at four different molarities, which is much comparatively small as reported by earlier workers [8,9]. Further, it was also found that the crystallite size decreases as the molarity increases for the same orientation (111)

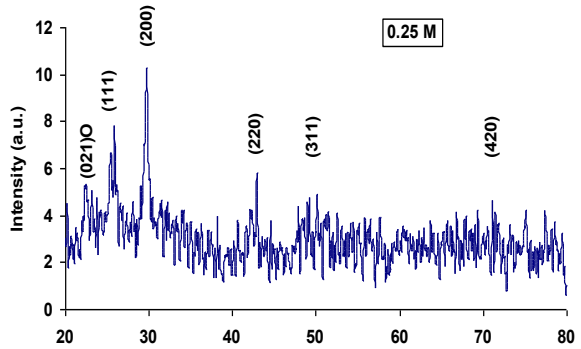

Fig. 1: XRD pattern of PbS thin film at 0.25M

3.2 SEM Analysis

The morphology of PbS thin films on glass substrate was examined by scanning electron microscopy (SEM). Figures (2-5) show the SEM micrograph image of PbS nanocrystallites at four different molarities. The surface of the film is smooth and covers to the glass substrate well and also clearly showing an abundance of cubical shaped crystallites of similar structure with formation of clusters here and there. The surface morphology of the nanocrystals is also found to be smooth and semispherical in structure.

3.4 Photoluminescence Spectra

The excitation and emission spectra of PbS nanocrystalline thin films at room temperature are shown in figure 6. In all cases of different molarities (0.1, 0.15, 0.2 and 0.25M), the excitation is monitored under the wavelength of 518 nm. It is found that a broad excitation from 200 – 4000 nm with two peaks at around 362 and 385 nm are observed. And also the emission spectra from 400 – 700 nm after excitation at 382 nm with two peaks at 488 and 518 nm are observed. The strong peak at 518 nm is due to a high level transition in PbS semiconductor crystallites. Emission bands at 518 nm are usually related to the transition of electrons from the conduction band edge to holes, tapped at interstitial Pb^{2+} sites [10]. There is another possibility that the observed peaks may correspond to transition into high-energy bands rather than excitonic transition.

3.3 Photoconductivity Measurement.

A suitable optical arrangement was made to illuminate the sample uniformly with white light of different intensities. A tungsten halogen lamp (250 W-24V) attached a parabolic focusing mirror was used as the white light source. The block diagram of the experimental set-up is shown in figure 11. The intensity of light was measured with the help of a sensitive digital Light Meter, Lutron Electronic Enterprise Co. Ltd. (Model: Lx – 103). High ambient temperature were achieved by means of a resistive heater connected to a stabilized power supply. The temperatures of thin films were measured with the help of a copper- constantan thermocouple coupled with Digital Multimeter, Omega Electronics, Jaipur, India. The dark currents (I_D) and the currents under illumination (I_L) were measured with the help of a Digital Picoammeter, SES Instruments Pvt. Ltd. Roorkee (Model : PDM-111) under different dc bias voltages. The pure silver probes were used for the measurements. The whole experimental set-up including the observer was housed inside a suitable sound proof dark room. The observations were taken preferably at night to avoid the high day time noise.

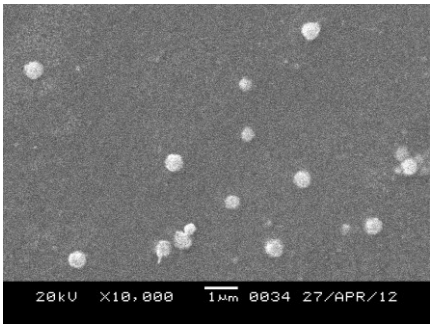

Fig. 2: SEM picture of PbS thin film at 0.1 M

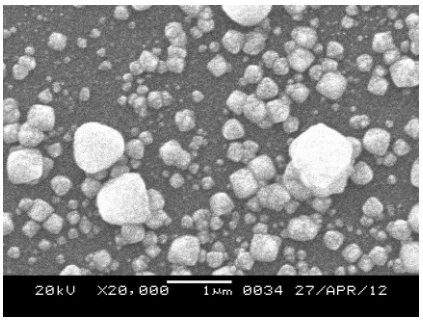

Fig. 3: SEM picture of PbS thin film at 0.15M

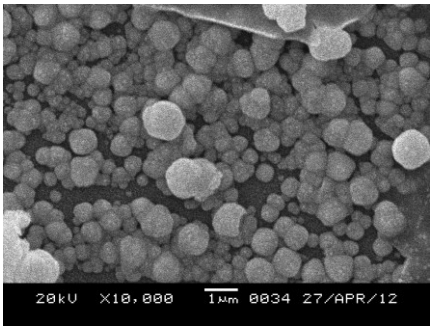

Fig. 4: SEM picture of PbS thin film at 0.2 M

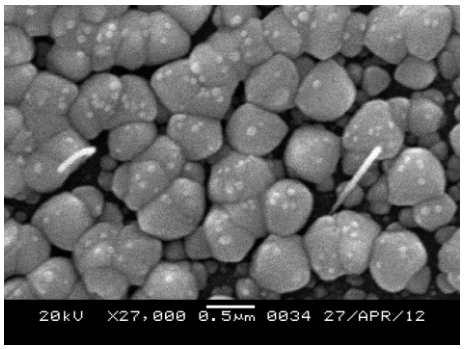

Fig. 5: SEM picture of PbS thin film at 0.25 M

3.5 Characteristics for Dark Current and Current Under Illumination.

The current and voltage characteristics of PbS nanocrystalline thin films at different molarity are shown in figures (8) in which 'a' represent current under illumination and 'b' represent dark current. In all cases, same intensity of incident light is used for illumination and same range of biasing voltage is also applied. In both cases, the current increases linearly after reaching a value of applied voltage 8V. However, the current under illumination increases rapidly as compared to dark current. The current under illumination is more than the dark current in all cases, which is termed as positive photoconductivity. This means that all the synthesized nanocrystalline thin films in the present study are found to exhibit positive photoconductivity. This may be attributed to generation of mobile charge carriers caused by absorption of photons [11].

3.6 Electrical Resistivity

The electrical resistivity of the films were determined by I-V characteristics curves using silver electrodes and their values were calculated using the relation, $R=\rho L/A$ where R is the resistance of the films and is measured by the slope of the I-V characteristic curves, A is the area of the film under investigation and L is the spacing between electrodes. The dark resistivity as well as the resistivity under illumination of the films were found to increase with increase in molarity in the range, 2.08 x 10^{-3} to 4.5 x 10^{-3} Ωm (in dark) and 1.78 x 10^{-3} to 3.12 x 10^{-3} Ωm(under illumination). This is because of the fact that in the present study, the crystallite size was found to decrease with increase in molarity which can be correlated with XRD result and SEM photo. The high resistance or

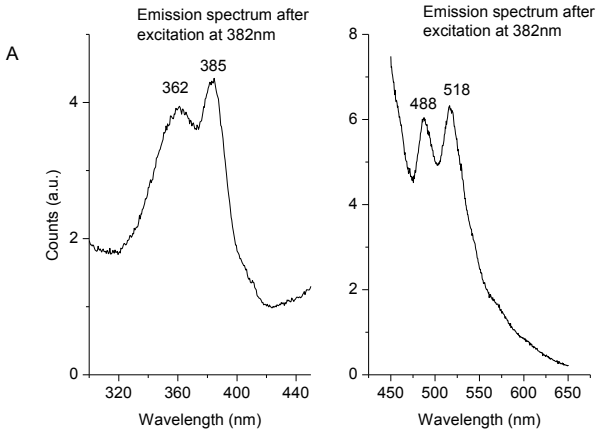

Fig. 6: Excitation and Emission of PbS nanocrystalline thin films.

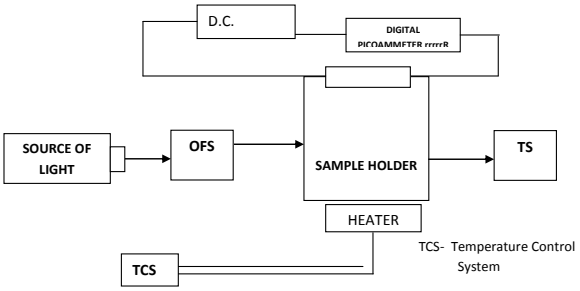

Fig. 7: Block Diagram of experimental set-up for photoconductivity measurement.

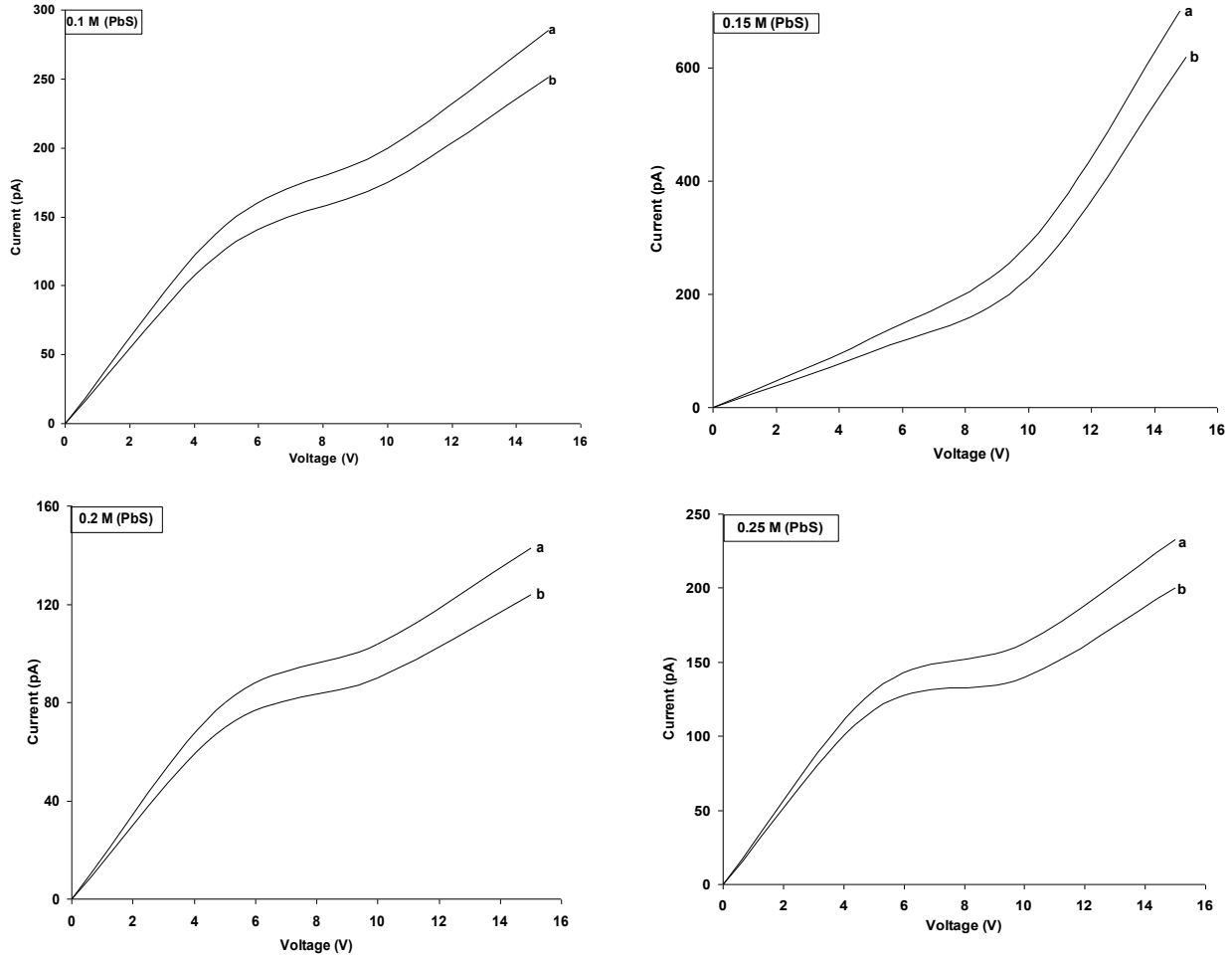

Fig. 8: I-V characteristics of PbS thin films (0.1, 0.15, 0.2 & 0.25 M) where 'a' represents Current under illumination 'b' represents Dark Current

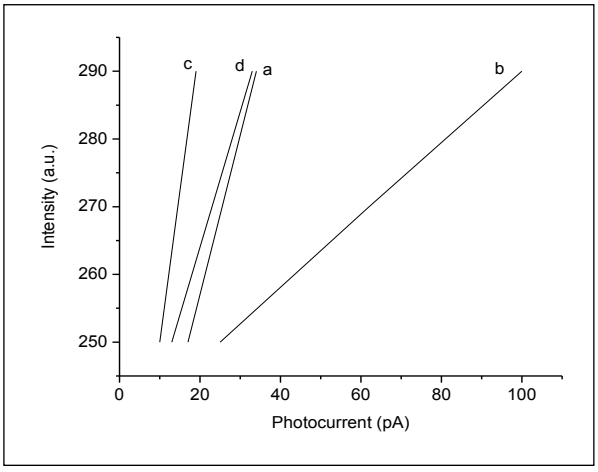

Fig. 9. Photocurrent vs Intensity of Illumination a,b,c,d corresponds to 0.1,.15,0.2,0.25 M

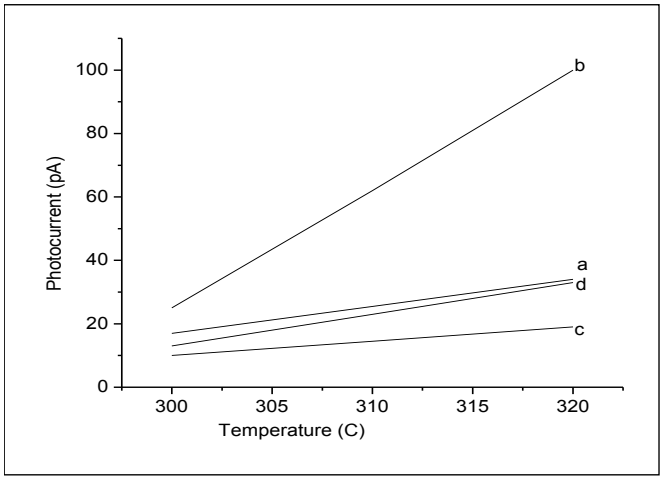

Fig. 10: Photocurrent vs Temperature a,b,c,d corresponds to 0.1,.15,0.2,0.25 M

resistivity of nanocrystalline film is due to the small crystallite sizes. The change in crystallite size will mainly affect the mobility of the carriers and so change the resistance or resistivity [12].

3.7 Effect of Incident Light and Temperature on Photocurrent

We define the photocurrent, $I_{ph} = I_L - I_D$, where I_L is the current under illumination and I_D is the current under dark.The variation of photocurrent with intensity of illumination under same biasing voltage at room temperature in all cases is shown in figure (9). The plot shows that the photocurrent increases almost linearly with increase in intensity of illumination in all cases. The variation of photocurrent with temperature under same biasing voltage and intensity of illumination in all cases is shown in figure (10). The plot shows that the photocurrent increases almost linearly with increase in temperature. This indicates the semiconductor nature of PVA capped PbS thin films synthesized by CBD technique.

4. CONCLUSION

PVA capped nanocrystalline PbS thin films were fabricated by chemical bath deposition (CBD) method on glass substrates. The nanostructure was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and PL spectroscopy. From XRD result the particle size are found to vary from 9.0 – 18 nm. SEM result shows the surface morphology of the nanocrystals is found to be smooth and cubical in structure. The photoluminescence spectra of the films showed two peaks centered around 488 nm and 518 nm after excitation at 382 nm. Photo conducting studies show photocurrent to be larger than the dark current for the same voltage. The electrical resistivity of the films increases as molarity increases indicating semiconductor nature.

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