



Analysis of Structural and Electrical Properties of Aluminium Doped Lead Sulphide (PbS) Thin Films Prepared by CBD Method.

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Received: 15. 07. 2013 Accepted: 20. 12. 2013

Abstract

We have deposited PbS and Al doped PbS thin films by chemical bath deposition. Lead acetate and thiourea were used as sources of Pb^{2+} and S^{2-} respectively. The films were deposited at a pH of 12.5. The deposited films were further annealed at three different temperatures 250 p C, 300 p C, 350 p C. The structural analysis reveals that PbS has a preferential growth at (200) planes and high crystalline PbS were obtained when the films were annealed at 300p C. Crystallite size for all the films varies from 30 to 50 nm. SEM analysis shows almost dense spherical and uniform grains were distributed upon the surface of the film. The Aluminium concentration were varied from (1,2,3 and 4 at %). The electrical conductivity of the Al doped PbS films increases upto to 3 at % and then it decreases at 4 at %. All films exhibits highly stable p-type behavior with maximum conductivity for 3% Al doped PbS films which is $13.32(\Omega cm)^{-1}$. Thereby it is concluded that 3% Al is the opimum concentration for the doping for PbS films and can be used for the application of IR detectors and sensors.

Keywords: Chemical bath deposition (CBD); PbS.q

1. INTRODUCTION

Lead sulphide (PbS) is an important direct narrow gap semiconductor material with an approximate energy band gap of 0.4 eV at 300 K and a relatively large excitation Bohr radius of 18 nm (Chattarki *et al.* 2012; Thangavel *et al.* 2012; Abbas *et al.* 2011; Preetha *et al.* 2012; Kumar *et al.* 2009). These properties make PbS very suitable for infrared detection application. This material has also been used in many fields such as photography, and solar absorption. In addition, PbS has been utilized as photo resistance, diode lasers, humidity and temperature sensors, decorative and solar control coatings. These properties have been correlated with the growth conditions and the nature of substrates (Fern'andez-Lima *et al.* 2007).

Lead sulfide (PbS) belongs to IV-VI group and is an important semiconductor with a narrow band gap. This semiconductor has a narrow band gap (0.41 eV) and a strong quantum-size effect in nanocrystalline form (Seghaier *et al.* 2006).

2. EXPERIMENT

Chemical bath deposition (CBD) is a very attractive method for deposition of polycrystalline thin films such as PbS thin films with good photoconductive properties. By CBD method, the dimensions of the crystallites can be controlled by varying the deposition parameters: reaction time, temperature, pH and presence of impurities in the solution. Chemical bath deposition CBD technique requires relatively mild conditions, cost effective, scalable and technically straight forward. In the last decade, there has been a renewed interest in this method, mainly associated with

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its remarkable success in depositing semiconductor layers in thin film photovoltaic cells. By CBD the dimensions of the crystallites can be varied by controlling deposition parameters.

PbS thin films were grown on soda lime glass slide substrates by CBD technique. Lead acetate and thiourea were used as sources of Pb^{2+} and S^{2-} respectively. Triethanolamine is used as complexing agent. The deposition was done using a reactive solution prepared in 100ml beaker containing lead acetate. This reactive solution was mixed in aqueous solution of thiourea. The pH of the solution is set to 12.5 using sodium hydroxide [NaOH]. Triethanolamine was used as a stabilizing agent. Double distilled water was added to the solution to achieve a volume of 100 ml. For doping of Al concentration aluminium Chloride hexahydrate is used. Now the reaction mixture is stirred well for ten minutes using a magnetic stirrer. Cleaned substrates were immersed vertically into the solution.

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Table 1. Deposition conditions for PBS and Al doped PBS at 1%, 2%, 3 %, and 4 % by Chemical Bath Deposition (CBD)

Sample	Lead Acetate (in gms)	NaOH (in gms)	Thiourea (in gms)	TEA (in ml)	AlCl ₃ (in gms)	Dipping time (in mins)	Dipping temperature (°C)
PbS 300	2.6	0.8	0.76	1	—	30	70
PbS Al 1%	2.574	0.8	0.76	1	0.026	30	70
PbS Al 2%	2.548	0.8	0.76	1	0.052	30	70
PbS Al 3%	2.522	0.8	0.76	1	0.078	30	70
PbS Al 4%	2.496	0.8	0.76	1	0.104	30	70

3. RESULTS & DISCUSSION

3.1 Structural studies

X-Ray diffraction spectra of the samples were recorded using RIGAKU ULTIMA-III X diffractometer. Fig.1 shows the XRD spectra of undoped PbS at annealing temperatures 250 °C, 300 °C, 350 °C respectively.

It is observed that PbS films which were annealed at 300 °C shows very good crystallinity with well packed 3D form and the preferred orientation of growth is along the (200) direction. Hence it is observed that the 300 °C is the optimized annealing temperature for PbS films. By keeping 300 °C as constant the Al concentration is varied from 1%, 2%, 3% and 4% in the PbS films and the corresponding XRD pattern is shown in Fig.2.

The crystallite size of the films were calculated using the Scherrer's formula, $D = k\lambda/\beta \cos\theta$, where λ is the wavelength of CuK_α radiation (1.5406 Å), k is shape factor (0.9), θ is the Bragg's diffraction angle and β is the broadening of the diffraction line (FWHM). The crystallite size is found to be varying from 30 to 50 nm. Both the results are compared with standard JCPDS (78-1901) and confirms the cubic PbS structure.

3.2 Morphological Studies

Scanning electron micrographs (SEM) are recorded for different deposition timings. Fig.3 shows the SEM image of the deposited PbS thin films upon the glass substrates at 30 minutes deposition time. The image shows almost dense spherical and uniform grains distributed on the surface.

3.3 Electrical Studies

Hall Effect measurements were performed in order to investigate the electrical properties of the PbS thin films. It is observed that with doping the resistivity

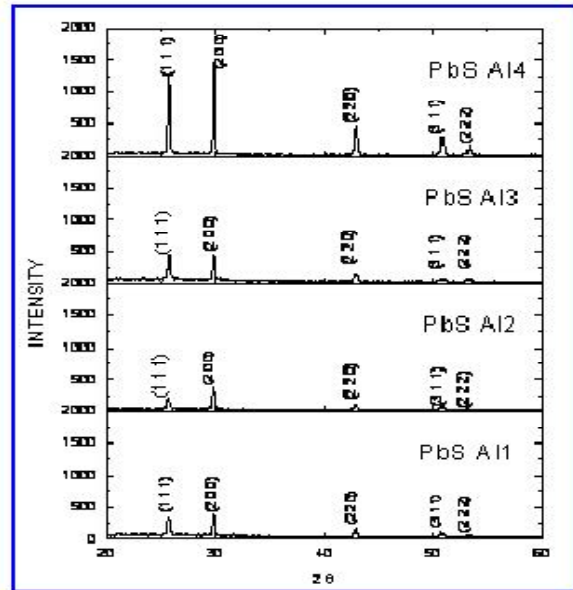


Fig. 1: XRD spectra of PbS undoped films with varying annealing temperature.

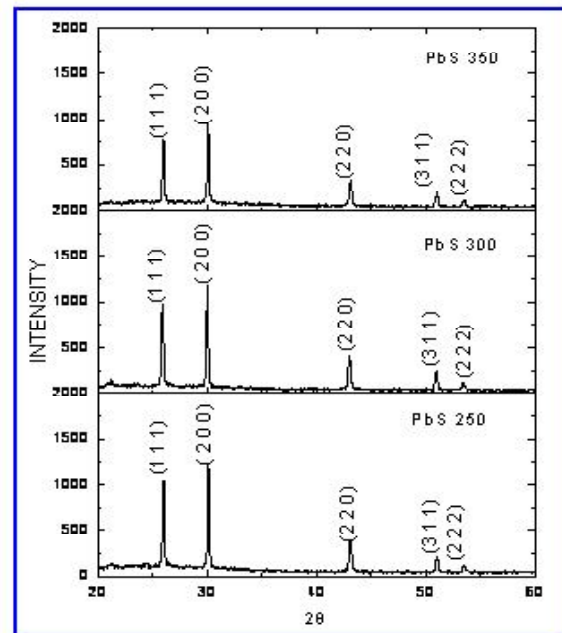


Fig. 2: XRD pattern of Al doped PbS films with varying Al concentration.

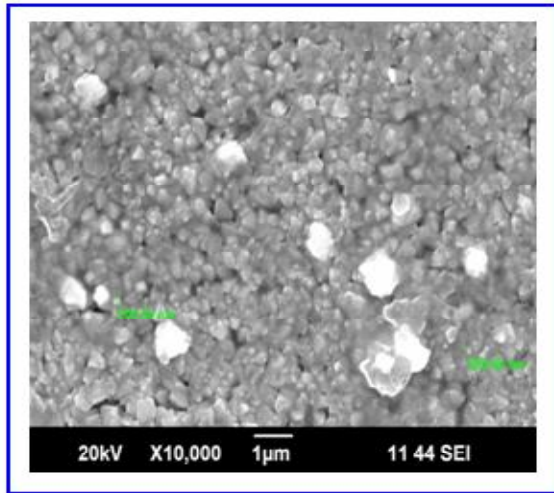


Fig. 3: SEM micrograph of PbS film

decreases from the order of 10^{-1} to $10^{-2} \Omega \text{ cm}$. Preetha *et al.* [4] reported that the electrical conductivity is strongly affected by Al doping. The similar results is observed for our Al doped PbS films where we can see increased conductivity up to the concentration upto Al 3 at %. There is a slight decrease in conductivity by doping Al 4% and hence we conclude that Al 3% is the optimum concentration for doping in PbS. All the samples exhibit p-type behavior.

The increase in conductivity shows that the Al^{3+} ions incorporated into Pb atoms. There is two possibility of valence state for Pb ions. The first possibility is Pb^{2+} while the other being Pb^{4+} . The ionic radii of Al^{3+} (0.068 nm) is closer to the ionic radii of Pb^{4+} (0.0775nm) and hence it gets incorporated easily in the Pb site. Since the electrical conductivity increases as well as maintaining the p-type behavior, it is expected that Al^{3+} ions incorporated in Pb^{4+} ions. Activation energy is the energy required to raise the conduction electron from impurity level to the conduction band and it is given by $R = R_0 \exp(-E_a/kT)$ Where E_a the activation energy in eV, k is the Boltzmann constant and T is the absolute temperature. We can calculate the activation energy by plotting $\ln(R)$ Vs $1000/T$ (also known as the Arrhenius plot) and finding the slope. Fig.4 and Fig.5 shows the

Arrhenius plot of the undoped and Al doped PbS films for different concentrations respectively and Table 2 shows the activation energy for corresponding undoped and Al doped PbS thin films. The measured values of conductivity, carrier concentration and mobility are shown in the Table 3.

Table 2. Shows the activation energy(meV) at higher and lower temperature for undoped PbS and Al doped PbS for different concentrations.

Composition	Activation Energy Low Temperature Region(meV)	Activation Energy High Temperature Region(meV)
PbS at 250 °C	98.9	115.8
PbS at 300 °C	83.8	81.2
PbS at 350 °C	92.3	106.7
PbS (Al 1 %)	86.0	80.9
PbS (Al 2 %)	68.9	85.0
PbS (Al 3 %)	70.0	71.2
PbS (Al 4 %)	70.7	71.6

Table 3. Variation of concentration, conductivity, mobility, hall coefficient and carrier type of various samples

Sample	Carrier concentration (cm^{-3})	Conductivity ($\Omega^{-1} \text{ cm}^{-1}$)	Hall Mobility ($\text{cm}^2/\text{V s}$)	Hall coefficient (cm^3/c) $\times 10^{-1}$	Carrier type
PbS 300	9.468×10^{19}	9.569	6.310	6.593	P
PbS Al 1at %	1.231×10^{19}	11.23	5.699	5.070	P
PbS Al 2at %	1.728×10^{19}	11.44	4.134	3.613	P
PbS Al 3at %	2.403×10^{19}	13.32	3.461	2.598	P
PbS Al 4at %	1.903×10^{19}	13.10	4.303	3.281	P

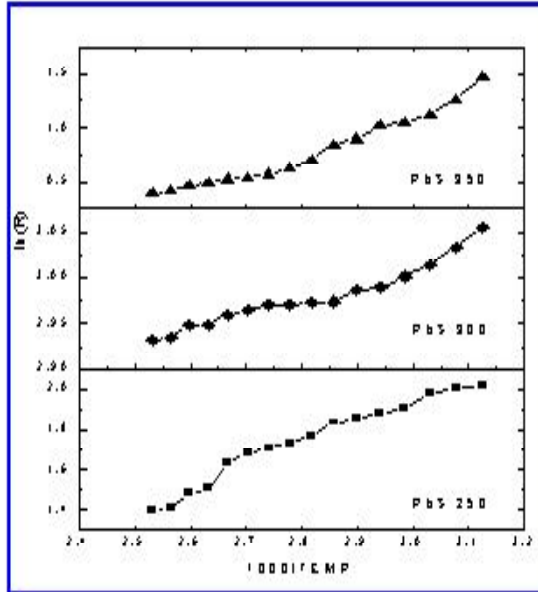


Fig. 4: $\ln R$ vs $1000/\text{temp}$ plot for undoped PbS

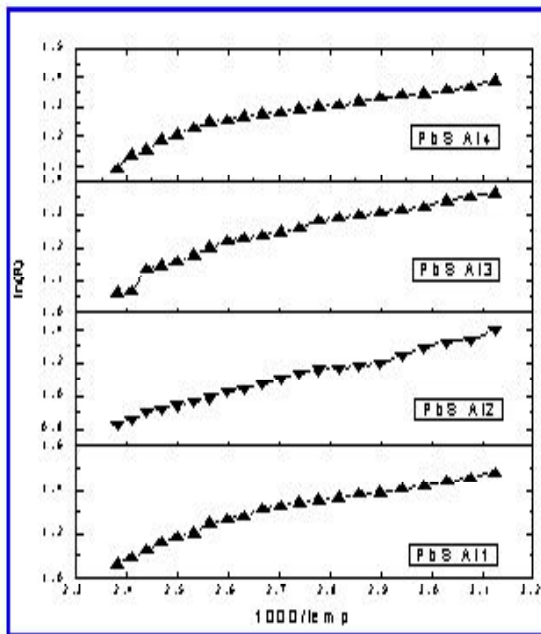


Fig. 5: $\ln R$ Vs $1000/T$ plot for Al doped PbS

4. CONCLUSION

The objective of Al doping on PbS thin films was achieved and its structural and electrical properties were studied. It was observed that the resulting films were homogeneous, well adhered to the substrate with darker surface like mirror and specularly reflecting. The average thickness of the thin films is 1 micron. All the deposited films exhibit p-type behaviour. The films had good crystallinity with well packed 3D form and the preferred orientation of growth was along the (200) direction. And there was an increase in conductivity from undoped sample to aluminium doped sample. With increasing Al concentration in PbS, the lattice structure becomes more and more ordered and thereby reduces the grain boundary scattering so that electrical conductivity increases. This could also be supported by the improvement in crystalline quality and higher reflectance with the increase in Al concentration. In the case of undoped PbS the activation energy is the least for PbS (300). Hence the annealing temperature $300\text{ }^{\circ}\text{C}$ is kept constant for all other doped samples. Also, while doping the activation energy found to increase at 4%. This may be due to the solubility of aluminium in the PbS solution. So we conclude that Al 3 at % is the optimum concentration for Al doping in PbS showing the maximum conductivity as well as behaving a stable p-type semiconductor. The deposited PbS films can be used in the field of IR sensors and detectors.

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