Role of complexing agents on chemical bath deposited PbS thin film characterization

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Abstract In the present work, lead sulphide thin films have been grown on soda lime glass substrates by chemical bath deposition technique using three different complexing agents, namely triethanolamine, diethanolamine and hexamine. Aqueous solutions of lead acetate complexed with the above mentioned ligands were used as cationic precursor and thioacetamide as anionic precursor. The structural, morphological, optical and electrical properties of the as-prepared samples were investigated and compared by means of X-ray diffraction (XRD), Scanning electron microscopy (SEM), optical and electrical studies. The films were well crystallized and highly adherent to the substrate with face centered cubic structure. The average crystallite size was found to be in the range 15-20 nm. The SEM micrographs showed variations in morphology. Optical studies revealed that the direct band gap energy was in the range of 1.65-2.27 eV. The transmittance and reflectance in IR region was respectively in the range of 14%-47% and 25-45%. Optical constants of all films were determined by absorbance and reflection measurements. The room temperature conductivity of the PbS thin films were in the range 9.67x10^-9 (Ω-Cm)^-1-3.29x10^-6 (Ω-Cm)^-1. The optical band gap energy has inverse relation with grain size and electrical conductivity is closely related to structural parameters like grain size, crystallinity and microstrain. PbS thin film using hexamine as complexing agent was proved to be the best in structural, optical and electrical properties. In this attempt we establish that the use of different complexing agents have immense effect on structural, morphological, optoelectronic and transport properties of PbS thin films.

1. Introduction

The semiconductor chalcogenides of IV-VI group have recently attained considerable attention due to their simplicity in preparation and wide applications [1-3]. PbS with a narrow direct band gap energy of 0.41 eV can be used as a very good IR detector [4-6]. CBD is a very apposite method for the preparation of poly crystalline PbS thin films [7]. This process uses a controlled chemical reaction to achieve thin film deposition by precipitation. It is necessary to eliminate spontaneous precipitation in order to form a thin film by a controlled ion-by-ion reaction. This can be achieved by using a fairly

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stable complex of the metal ions which provides a controlled number of the free ions. A complexation reaction with a metal ion involves the replacement of one or more of the coordinated solvent molecules by other nucleophilic groups. In the metal complexes, the metal ions are bonded to one or more neutral molecules or anions so as to define the integral structural unit. The molecules or ions bonded to the central metal ion are called ligands.

In CBD, an aqueous solution of a metal complex when mixed with a solution of chalcogen bearing compound, precipitation of chalcogen occurs under certain conditions. When the precipitation is controlled, the compound gets deposited on clean substrates or other nucleating centers present in the solution. By choosing an appropriate complexing agent, the concentration of the metal ions is controlled by the concentration of the complexing agent. The kinetics of growth of a thin film in this process is determined by the ion-by-ion deposition of the chalcogenide on nucleating sites on the immersed surfaces. Initially, the film growth rate is negligible because an incubation period is required for the formation of critical nuclei from a homogeneous system onto a clean surface. Once nucleation occurs, the rate rises rapidly until the rate of deposition equals the rate of dissolution. Consequently the film attains a terminal thickness. The metal (M^{2+}) ion concentration decreases with increasing concentration of the complexing ions. Consequently, the rate of reaction and hence precipitation is reduced leading to a larger terminal thickness of the film.

In this research work, our main goal is to demarcate the role of complexing agents in the CBD grown PbS thin films. As complexing agents are one of the crucial chemical additives in preparation of thin films, we used a range of organic complexing agents with carboxylate and ammonia groups. The complexing agents under investigation are Hexamine (HA), Triethanolamine (TEA) and Diethanolamine (DEA). TEA N(CH2CH2OH)3, is an organic compound that is both a tertiary amine and a triol. A triol is a molecule with three alcohol groups. Like other amines, triethanolamine is a strong base. DEA, is an organic compound with the formula HN(CH2CH2OH)2. This colourless liquid is polyfunctional, being a secondary amine and a diol. Like other organic amines, diethanolamine acts as a weak base. Reflecting the hydrophilic character of the alcohol groups, DEA is soluble in water, and is even hygroscopic. HA is a heterocyclic organic compound with the formula (CH2)6N4. This white crystalline compound is highly soluble in water and polar organic solvents. Hexamine forms additive or complex compounds with metal salt. These additives are chemically neutral for those areas in which these grades are used.

The role of three complexing agents on structural, optical, surface morphological and electrical properties of as-deposited PbS thin films is highlighted in this work. We have carried out X-ray diffraction (XRD), Optical spectroscopy, Scanning electron microscopy (SEM) and two probe conductivity measurements for thin film characterization.

2. Experimental methods

PbS thin films were prepared on ultrasonically cleaned soda lime glass substrate by CBD technique. The reaction bath comprised of an aqueous solution containing 0.3M Lead acetate solution as metal source and equimolar solution of thioacetamide as sulphur source. To avoid precipitation of the bath, HA, TEA and DEA were used as complexing agents for metal source. All the reagents used were of analytical grade. Metal complex and sulphide ions migrate to the substrate surface, where they react to form PbS thin film. Highly adherent PbS thin films were taken out from the reaction bath after three hours. The films prepared by using different complexing agents, HA, TEA and DEA are denoted by PbSHA, PbSTEA and PbSDEA respectively.
The structural studies were carried out using X-ray diffractometer (Bruker AXS-8 advance) having CuKα radiation of wavelength 1.5406 Å as the source. The optical absorption was recorded using Hitachi-U-3410 UV-Vis-NIR spectrophotometer. Scanning Electron Microscopy (SEM) of the samples was recorded using a Hitachi (JEOL Model JSM6490) operating at an accelerating voltage of 25 kV. Conductivity measurements were done with the help of two probe using Keithley Source Measurement Unit (Model SMU Keithley 2400).

3. Results and discussions
3.1. Structural Studies. According to XRD pattern in Figure 1, all the PbS thin films were polycrystalline and have face centered cubic structure with (111) as preferred orientation plane. The average size of the crystallites obtained by Debye scher formula is in the range of 15-20 nm. Strong and narrow diffraction peaks with maximum intensity and crystallite size are obtained for PbSHA. DEA complexed thin film has very low crystallinity. The variation in crystallinity is due to the fact that the resulting concentrations of Pb²⁺ and S²⁻ in solution will be different for different complexing agents, thus leading to different deposition rates. When the effective concentrations of precursor ions are high and that of PbS particles is low, ions-by-ions deposition is dominant in CBD process; and it leads to uniform films as in PbSDEA. When HA is used, the clusters-by clusters deposition is dominant, which leads to the formation of thicker films. Micro strain of the samples is calculated using equation

\[ \varepsilon = \frac{(a_0 - a)}{a_0} \]  

Where ‘a₀’=5.936nm. Thin films prepared from HA exhibits minimum strain (0.012) and DEA based film has maximum strain (0.018), which leads to reduction in crystallinity. The above results confirm that the deposition using HA proved more favourable.

![X-ray diffraction pattern of as-prepared samples-PbSHA, PbSTEA, PbSDEA](image)

3.2. Morphological studies
Figure 2 shows the SEM micrograph of the PbS thin film samples. The micrograph reveals that the film surface is found to be densely packed with bigger grains for PbSHA and PbSTEA, indicating fast growth rate and size of the nano grains. Whereas the surface becomes less dense for PbSDEA. Maximum grain size is noticed in PbSHA and minimum for PbSDEA. Thus SEM results are in accordance with the XRD data.
3.3. Optical Properties

The optical absorbance, band gap, transmittance/ reflectance of the films were shown in Figure 3. According to Figure 3(a), the optical absorption edge shifts to lower wavelength with improvement in crystallinity ,which leads to a blue shift in band gap energy for PbSHA. The direct band gap energy calculated using Tauc’s relation is shown in Figure 3(b) and is in the range of 1.65-2.27 eV. The decrease in band gap of HA complexed PbS films may be attributed to the improvement in the crystalline quality of the films along with reduction in porosity, strain relief and increase of grain size.

As it can be seen in Figure 3(c), the transparencies of the PbS films in the visible region strongly depend on the complexing agent used in the CBD. HA complexed PbS film displays low transmission in the visible region; on the other hand, when the complexing agent is DEA, the transmission in the visible region is very high. PbS is normally used as the solar control coating material that is required to have low transmission in the visible region so that not much visible light can penetrate solar cells and appreciable reflectance in IR region   as in Figure 3 (d). PbSHA is a very acceptable material for this purpose. Morphologies of three PbS thin films are quite different, which affects the transmission of visible light. Evidently, the rough surface morphology will reduce the transmission in visible region. Moreover the variation in film thickness due to difference in deposition rates also contributes to different transmission and reflection.

Figure 3. Absorbance spectra and direct band gap energies of samples PbSHA, PbSTEA, PbSDEA

3.4. Electrical characterization

Figure 4 shows the typical I-V characteristic of the PbS thin films prepared with different cationic complexes. The measured conductivity of the PbS thin films are found to be in the range 9.67X10⁹ (Ω-cm)⁻¹ - 3.29X10⁹ (Ω-cm)⁻¹. The electrical conductivity is directly connected to crystallinity and grain size and it is inversely related to band gap and micro strain. Thus PbSHA shows maximum electrical conductivity. Lead sulphide thin film with hexamine as complexing agent has least micro strain, minimum optical band gap and maximum electrical conductivity.
Conclusion

In this study, we have presented chemical bath deposition method to synthesize PbS thin films using three different metal complexes. Structural analysis specifies that the best crystallinity and high adhesion of PbS on glass substrate is obtained by employing hexamine as complexing agent. The film grown in this condition was well crystallized, with minimum strain and optical band gap and maximum electrical conductivity. As an outcome of this work, the HA is proven to be very feasible for the preparation of PbS films which finds application as solar control coating.

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