The role of cationic precursors in structural, morphological and optical properties of PbS thin films

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Abstract. Thin films of Lead sulphide (PbS) were grown on soda lime glass substrate by Successive Ionic Layer Adsorption and Reaction (SILAR) method using lead acetate, lead chloride, lead nitrate, and lead sulphate as cationic precursors and thioacetamide as sulphur source. The experiments were carried out at room temperature under normal pressure utilizing aqueous conditions. The structural and morphological aspects of the as prepared samples were investigated by means of XRD and SEM results. The prepared samples were polycrystalline with nanometer-sized grains and identified as galena type cubic structure (FCC). The values of average crystallite size were found to be in the range 22 to 30 nm. The SEM micrographs show variations in morphology. Optical studies revealed that the absorption edges of the films indicated strong blue shifts with respect to bulk sample. In this work, we establish that the cationic precursor sources and in turn the size of the crystallites affects the structural, morphological and optical properties of PbS thin films.

1. Introduction
Synthesis of binary metal chalcogenides of group IV-VI semiconductors in nanocrystalline form has attracted many researchers due to their size dependent optical and electrical properties [1, 2]. Application of PbS thin films as infrared detectors has been known for a long time [3]. In particular, during the last few years, research on the growth of nanoparticle PbS films has increased, for its technological applications in photo resistance, diode lasers, decorative coatings, and optoelectronic devices [4, 5]. In solar energy research, PbS thin films were examined for photothermal conversion applications [6].

In the present work we have utilized a simple modified chemical bath deposition method at room temperature named SILAR, first reported by Ristove et. al [7]. It is an aqueous solution growth technique based on sequential reactions at the substrate-solution interface for the deposition of the films. Since the complexed lead ecursor solution clearly affects the growth rate and orientation of PbS thin films, Triethanol amine (TEA) was used as complexing agent in this work along with different cationic precursors. This method offers the minimal waste generation since cationic and anionic
precursors is kept in different reaction baths. Thin film can be synthesized by means of self limiting chemical reactions from bath containing ionic species of the reactants. The aim of this paper was to study the structural, morphological and optical properties of the PbS thin films during SILAR growth.

2. Experimental details
The mechanism of formation of PbS thin films by SILAR technique has been discussed by Kanniainen et al [8]. Lead sulfide thin films were grown from lead acetate, lead chloride, lead nitrate, and Lead sulphate as cationic precursors, each complexed with TEA to have a pH 8 and thioacetamide with pH 4.7 as anionic precursor. The growth parameters and precursors used to deposit PbS thin films by the SILAR were presented in Table1. The cation–anion ratio 1:2 and the number of cycles 100 were maintained in all the cases. The films were appeared to be mirror-like and highly adherent. The as prepared samples were named as SAT8, SCD8, SNT8 and SST8 respectively. In our present work we have obtained the film thickness in the range 960-1360 nm by gravimetric method.

Table 1. The growth parameters and precursors for PbS thin film deposition.

| Cation solution          | pH   | Anion solution       | Dip.time (sec) | Rins.time (sec) |
|-------------------------|------|----------------------|----------------|-----------------|
| 0.1M Pb(CH₃COO)₂        | 8    | 0.2M thioacetamide   | 10             | 20              |
| 0.1M PbCl₂              | 8    | 0.2M thioacetamide   | 10             | 20              |
| 0.2M PbNO₃              | 8    | 0.4M thioacetamide   | 10             | 20              |
| 0.1M PbSO₄              | 8    | 0.2M thioacetamide   | 10             | 20              |

As-deposited samples were characterized for structural, morphological and optical properties. Structural studies were carried out using an X-ray diffractometer (Bruker AXS-8 advance) with CuKα radiation of wavelength 1.5406 Å as source. Morphological studies have been carried out by Scanning Electron Microscope (JEOL Model JSM6490). The optical characterization was done by taking absorption, transmission and reflection spectra of the samples using a Hitachi-U-3410 UV-Vis-NIR spectrophotometer.

3. Results and discussions

3.1 Structural studies
Figure 1 shows the X-ray diffraction pattern of Lead sulfide thin films. All the samples are polycrystalline with varying degree of orientation and having FCC structures. For SAT8 and SST8, (111) orientations are dominant whereas SCD8 and SNT8 cause the orientation along (200) direction. The crystallite size determined using Debye Scherrer formula is found to be varying between 22 to 30 nm. Lead Sulphide film prepared with Lead acetate as cation source are found to be highly crystalline and composed of largest crystallites as compared to other cationic sources.
3.2 Morphological studies

Figure 2 illustrates the SEM micrographs of PbS thin films. It can be seen that PbS thin films were uniform, homogeneous, with well defined grain boundaries and cover the substrate well without any voids, pinhole or cracks for SAT8 and SCD8. But agglomeration is noticed in other two samples. SAT8 sample shows densely packed grains of uniform size and this result is in accordance with very good crystallinity and largest crystallite size promoting three dimensional growths as seen in XRD results for this sample.

![SEM micrographs of PbS thin films](image)
3.3 Optical studies

Figure 3 shows the absorption, transmission and reflection spectra of PbS films using different cationic precursors. All the films show a gradually increasing absorbance throughout the visible region, which makes it possible for this material to be used in a photo electrochemical cell. The strong blue shift in the absorption threshold from the bulk indicates quantum confinement. SAT8 sample is having maximum absorption. This may be due to largest crystallite size and very good crystallinity shown by this sample as evidenced in XRD and SEM studies. Using Tauc relation, the optical band gap is calculated from the analysis of spectral dependence of absorption near fundamental absorption edge and is depicted in Figure 4. We have obtained direct band gap energies in the range 2.28 to 1.82 eV. SAT8 with largest thickness and crystallite size exhibits minimum band gap energy. Thus we were able to shift optical absorption onset from NIR region to visible region by using different cationic precursors.
Figure 3 Optical absorption, transmission and reflection spectra of SAT8, SCD8, SNT8 and SST8.

Figure 4 Direct band gap energy plot for PbS thin films SAT8, SCD8, SNT8 and SST8.

The transmission spectra indicate sharp band edge for all samples indicating good crystallinity of the film. In UV region samples are non transparent, indicating maximum absorption in this region. The transmittance increases with increase in wavelength. In IR region a maximum transmittance of 75% is observed for SNT8 where as a transmittance of only 20% is observed for SAT8. Reflectance spectra show a maximum value 65% for SAT8 and a minimum of 35% for SNT8 in near IR region. Lead sulphide thin film prepared with lead acetate as cationic precursor with very good structural, morphological and optical properties can be used as solar control coatings, since it is having low transmittance in UV region coupled with an appreciable reflectance in near IR region.

Conclusion

We have successfully utilized SILAR method for the synthesis of PbS thin films using different cationic precursors. XRD studies revealed the cubic structure of PbS with nanocrystallites in the range 22nm-30nm. SEM morphology was in compatible with structural analysis. The optical absorption edge was shifted from the infrared region to the visible region on account of quantum confinement arising from the nanostructured nature of the films. We were able to tailor optical band gap energy in the range of 1.82eV-2.28eV by changing the cationic precursor. The PbS thin films with good optical properties can be used in various photovoltaic applications such as absorbing layers in solar cell, solar control coatings, photo electrochemical cell etc.
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