



Effect of hydrazine hydrate concentration on structural, surface morphological and optoelectronic properties of SILAR deposited PbSe thin films



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ABSTRACT

Lead Selenide (PbSe) thin films have been deposited by Successive Ionic Layer Adsorption and Reaction (SILAR) method to investigate the effect of hydrazine hydrate on film properties. The peak behavior of the X-ray diffractogram corroborates crystalline nature of PbSe thin films. The intensity of the major peaks attributable to PbSe improved at higher concentrations up to 5 ml HH and gets reduced for 7 ml HH. The average crystallite size is in the range 18.18–33.37 nm. The film surface of lower HH sample is composed of spherical grains which are arranged in a compact manner. On increasing HH some clusters appears on the surface of the film over a homogeneous background. The AFM micrographs show that the surfaces of the lead selenide thin films consist of dense distribution of nanoscale particles with a range of grain sizes. The roughness obtained is in the range 13.7–76.3 nm. Highly crystalline sample, 5HH exhibits very good topography. The direct band gap values are in the range 1.425–1.803 eV. Thus by varying HH we have been able to tune the band gaps over a wide range. The highly crystalline sample 5HH with least strain and excellent topography exhibits maximum conductivity.

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1. Introduction

Lead chalcogenide semiconductors (PbS, PbSe, and PbTe) have attracted particular attention as possible candidates for applications in photovoltaics and charge transport [1–5]. Quantum size effects can be clearly seen in this material, even in crystals up to several tens of nanometers in size due to the small effective mass of the excited electron–hole pair. Lead salt quantum dots can be

size-tuned to absorb strongly in the IR to near-IR wavelength range, an optical region of significance to solar energy conversion. The development of laser technology has opened new applications for IV–VI compounds. The laser diodes based on lead chalcogenides and their alloys are important sources for the tunable radiations in the mid infrared wavelength region. PbSe quantum dots are very attractive for mid-infrared optoelectronic device applications, such as photon detectors. It is used as a target material in infrared sensor, grating and various opto-electronic and photovoltaic devices [6–8]. Compared to II–VI materials, lead salts possess much higher dielectric constants (ϵ) and lower effective masses for the electron and the hole. These properties transform to large Bohr radii and, thus, strong quantum confinement effects.

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Moreover, high conductivity and charge carrier mobility have been observed in PbSe QD thin films.

Lead salts have known characteristics such as a small energy band gap, a positive temperature coefficient of the resistance and large carrier mobilities. The lead salts exhibit properties which are unusual and possibly unique, relative to other semiconductors and these unusual characteristics have obviously added to the stimulated study. A particularly remarkable feature of this group of materials is the relative stability of the lattice over a rather wide range of non-stoichiometry [9].

Low band gap semiconductors such as PbSe, PbS and PbTe are potential alternatives for shield materials. Also in recent years, because of relatively large Bohr exciton radius of 46 nm, wide range of band gap energy shifts have been demonstrated in PbSe from the bulk band gap of 0.28 eV [10]. It has emerged as one of the most prospective materials to be used as an efficient absorber of solar radiation in solar cell devices due to high optical absorption coefficient near optimum band gap energy, P type conduction mechanism and high environmental stability

Compound semiconductors based on selenium have been subjected to considerable research due to their technological importance in crystalline and polycrystalline forms. PbSe has a more recent history than PbS. The most important use of chemically deposited PbS and PbSe thin films was for photoconductive detectors [11,12]. Though a number of alternatives are available now, such detectors are also still in use. PbSe is one of the most attractive semiconducting materials for a wide variety of applications in IR detectors, photographic plates, photographic absorber, laser technology and so on [13,14].

The synthesis of PbSe thin films has been carried out by variety of chemical deposition techniques [15–17]. The effect of preparative factors such as solution pH, deposition temperature, deposition time, nature of precursors, methods of preparation, nature of substrates, nature and concentration of complexing agents etc. have been thoroughly investigated by many researchers in order to obtain high quality, reproducible thin films. In most of the works high quality films were obtained by maintaining reaction bath at high temperature or post deposition treatments etc. [18,19]. Low temperature growth was also carried out [20]. In Chemical bath deposition technique precipitate formation is very high and quality of room temperature synthesized sample is poor. To improve this properties, in this work, PbSe thin films have been chemically deposited on soda lime glass substrates by utilizing a SILAR method at room temperature by varying the concentrations of hydrazine hydrate (HH) in the anionic precursor solution, which acts as a powerful reducing agent. The present work incorporates the study of the influence of HH on various structural, morphological, optical and electrical properties of the as deposited PbSe thin films. The obtained results regarding crystal structure, surface morphology, optical band gap and electrical conductivities were thoroughly investigated and correlated with the concentration of HH for specific photovoltaic applications.

2. Experimental methods

PbSe thin films were grown on soda lime glass substrates by the SILAR method at room temperature. All the

reagents used were of analytical grade (Merck). 0.1 M Lead acetate solution complexed with TEA was used as cationic precursor and the source of selenium ions was 0.025 M Na_2SeSO_3 solution. Na_2SeSO_3 was used to precipitate PbSe from solutions by mixing lead acetate and Na_2SeSO_3 solutions. The precipitation was rapid and film formation did not occur in normal case. Generally one or two metal ion complexing agents are added to the starting solution. The stable complex ion facilitates the slow release of free metal ions which react with the chalcogenide ions forming the desired film. Complexation was required to slow the reaction. Use of TEA as efficient complexant for lead chalcogenides has already been established in our previous works [21–23]. In order to prevent the formation of elemental selenium and to enhance the formation of Se^{2-} ions from Na_2SeSO_3 , 2 ml HH was used as reducing agent. The pH of the anionic precursor was adjusted to 11 with 4 M KOH and it was measured using pH meter with specification (systronics-mfg. Model No. pH 335). We have tried a range of pH but the optimized one with high quality thin film was for this particular pH of anionic precursor. So the pH of the anionic precursor was adjusted to 11 with 4 M KOH.

The dipping and rinsing time were optimized as 10 s and 20 s respectively. The number of deposition cycles was fixed to 100. Ultrasonically cleaned soda lime glass substrate was used for thin film deposition. The experiments were repeated under same conditions by adding 3 ml, 4 ml, 5 ml and 7 ml HH in the anionic solution. The samples were named as 2HH, 3HH, 4HH, 5HH and 7HH.

3. Results and discussion

3.1. Thin film growth mechanism

The formation of PbSe film depends on the rate of release of Pb^{2+} and Se^{2-} ions from the bound state. As a competent complexant, TEA forms $[\text{Pb}(\text{TEA})]^{2+}$ complex and thereby lowering the concentration of free Pb^{2+} ions below the level required for the precipitation of solid phase $\text{Pb}(\text{OH})_2$.

When glass substrate is first immersed in cationic precursor solution, Pb^{2+} ions are adsorbed on the surface of the substrate. Then on rinsing the substrate with distilled water, the excess unadsorbed ions are removed. When the substrate was immersed in anionic precursor solution, Se^{2-} ions react with the adsorbed Pb^{2+} ions to form PbSe on the substrate. Due to low solubility of lead selenide, a solid PbSe is formed by heterogeneous reaction. Then loosely bounded ions were removed on final step rinsing in distilled water. The immersion times and the cycles of operation were optimized after a number of trials and we obtained smooth grayish black PbSe thin films after hundred dipping cycles.

3.2. Structural studies

XRD patterns of films deposited at various HH concentrations are shown in Fig. 1. The peak behavior of the X-ray diffractogram corroborates crystalline nature of PbSe thin films. XRD pattern of all the PbSe thin films has sharp (111), (200) and (220) peaks and crystallized as

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