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Room temperature chemical synthesis of lead selenide thin films with preferred orientation

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Abstract

Room temperature chemical synthesis of PbSe thin films was carried out from aqueous ammoniacal solution using $Pb(CH_3COO)_2$ as Pb^{2+} and Na_2SeSO_3 as Se^{2-} ion sources. The films were characterized by a various techniques including, X-ray diffraction (XRD), energy dispersive X-ray analysis (EDAX), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HR-TEM), selected area electron diffraction (SAED), Fast Fourier transform (FFT) and UV–vis-NIR techniques. The study revealed that the PbSe thin film consists of preferentially oriented nanocubes with energy band gap of 0.5 eV.

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1. Introduction

Fabrication of nano-to-microscopic-scale inorganic materials with special size and morphology are of great interest for material chemistry due to their importance in basic scientific research and potential applications [1]. Semiconductor nanocrystallites have been extensively investigated during the last decade because of their potential applications in many areas of technological importance [2]. Certain nanocrystals shows size dependent optical and electronic properties, which make them intriguing candidates for the wide applications in thermoelectric cooling, optical fibers, optical recording, solar cells, light emitting diodes, sensors, laser, superionic materials, thin film transistors, gamma ray detectors and biological labeling [3].

Lead selenide (PbSe) is one of the most attractive semiconducting materials for a wide variety of applications in IR detectors, photographic plates, photographic absorber, laser and so forth [4,5]. During the past two decades PbSe has also been used the object of an enquiry into nanosized effects [6]. PbSe have been synthesized by various methods, including photochemical [6], sonochemical [7], electrochemical atomic layer epitaxy [8], pulsed laser deposition [9], chemical bath deposition [10,11], vacuum deposition [12], electrodeposition [13,14], pulse sonochemical method [15] and successive ionic layer adsorption and reaction method [16]. The structural, optical, morphological and electrical characteristics depend on the method of preparation. Generally, each method has its advantages and limits. Among the various other methods, chemical bath deposition (CBD) method provides a promising way for the synthesis of metal chalcogenide nanocrystals due to its low cost, high yield and potential for large-scale production of thin films, at relatively low temperatures that do not require any special set-up and/or any sophisticated instrument as well. Also, CBD method has been used extensively to generate novel materials with unusual properties, since it forms the

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nanocrystalline materials with much smaller size and higher surface area at relatively low temperatures and atmospheric pressures than those operated for other methods. Also the thin films and bulk precipitates are of a relatively high purity and can be used for various devices applications.

In the present paper, we report the chemical synthesis using CBD method and characterizations of nanocrystalline PbSe thin films. The aim of present work is to simplify and economize the preparation of high purity nanocrystalline PbSe thin films, from single chemical bath using fewer chemicals at room temperature (300 K).

2. Experimental section

2.1. PbSe film formation

The PbSe thin films were deposited on amorphous glass substrates using analytical grade $Pb(CH_3COO)_2$, 25% NH_4OH and freshly prepared Na_2SeSO_3 solutions [17]. All the chemicals were purchased from S.D. Fine Chem. Ltd., India and used without further purification. It is recommended to make smaller volume of Na_2SeSO_3 stock solution and use it within 1–2 days for better results.

The optimized preparative parameters and experimental details are as follows: 25 ml of $Pb(CH_3COO)_2$ (0.2 M) solution was taken in a 100 ml capacity glass beaker, and then ammonia solution was slowly added with a constant stirring. Initially, the solution became milky turbid due to the formation of $Pb(OH)_2$. Further addition of excess ammonia dissolved turbidity to a certain extent. Then 25 ml of freshly prepared Na_2SeSO_3 (0.13 M) solution was added slowly with a constant stirring. The final solution was stirred with glass rod for few second and then transferred to another beaker containing the cleaned glass substrates, inclined vertically at 20° to the wall of beaker. The bath solution was kept in an open air and deposition was allowed to proceed at room temperature without stirring. The substrates coated with the PbSe thin films were taken out from the bath, dried in air and preserved in an airtight plastic container before examining the properties. The as-deposited films were uniform, specularly reflective (mirror-like) and extremely adherent to the glass substrates. The color of the film when viewed under white light appeared to be dark gray metallic (graphite like). The film deposition was carried out practically for about 28 h and the thickness of film was approximately 0.86 μm.

2.2. Characterizations of PbSe films

The PbSe film thickness was measured with the commonly used gravimetrical weight-difference method, assuming density as that of a bulk PbSe (8.10 gm/cm^3). The deposited PbSe film was removed from the substrate surface by rubbing with cotton swab using 10% nitric acid to measure weight difference. The crystallographic study was carried out using a Phillips PW-1710 X-ray diffractometer using Cu Kα radiation ($\lambda_{\alpha1}$ = 1.5405 Å, $\lambda_{\alpha2}$ = 1.5433 Å, intensity ratio $\lambda_{\alpha2}/\lambda_{\alpha1}$ = 0.5) in the 2θ ranges from 10° to 100°, operated at 40 kV and 40 mA. The microstructure of the PbSe thin film on glass substrate was studied, using a scanning electron microscope (SEM) (Cambridge Stereoscan 250 MK-III) operated at 20 kV and working distance 10 mm. The PbSe films were coated with 100 Å gold–palladium (Au–Pd) layer using polaron SEM sputter coating unit E-2500, before taking SEM. Transmission electron microscope (TEM) and High-resolution transmission microscope (HR-TEM) analyses were performed with a Philips CM-12 electron microscope (point resolution 2.8 Å) attached with an EDAX analyzer to measure quantitatively the sample stoichiometry. To prepare TEM samples, the PbSe film deposited on glass substrate was scratched and dispersed in alcohol with ultrasonic stirring; then a small drop of the solution was placed on a Cu grid covered with a carbon film. A number of grids were prepared from the same sample in order to check reproducibility of the preparative procedures. The atomic force microscopy (AFM) unit (digital nanoscope) was used to study the surface morphology and surface roughness of the film. In order to study optical properties, optical absorption spectra were recorded in the wavelength range 300–3000 nm using UV–vis-NIR spectrophotometer (Hitachi model-330, Japan).

3. Results and discussion

3.1. Growth mechanism

Before describing the characterizing properties of the CBD PbSe films, the important mechanism of nucleation and growth of the PbSe crystallites have been described. Several factors such as concentrations of Pb^{2+} and Se^{2-} ion precursors, amount and strength of complexion, pH and temperature of the final bath, etc., determine the crystal size. The most important factor was whether a colloidal basic lead carbonate or hydroxide was present in the solution (depending on the amount and strength of the complexion). The presence of appreciable amounts of such a colloid resulted in a hydroxide-mediated mechanism and smaller PbSe crystal size. It mainly occurs when the Pb^{2+} ion complexes with low or small amount of complexion. In the absence of such a colloid (higher complexion concentration or stronger complexion), an ion-by-ion mechanism resulted in larger crystal size [18] for PbSe thin films. In the present research work, due to the formation of lead tetra-amine $[Pb(NH_3)_4{}^{2+}]$ complex the solution did not contain colloidal $Pb(OH)_2$ in the deposition solution. The low reaction temperature and unstirred chemical bath, slowly releases free Pb^{2+} and Se^{2-} ions from the stable precursors, favors nucleation and growth of PbSe films via the 'ion-by-ion' mechanism. It is likely that textured deposits form by the ion-by-ion mechanism and a pure cluster-by-cluster mechanism is less likely to result in strong texturing [19].

Chemical bath deposition of semiconductor thin films involves a nucleation/incubation phase followed by a growth phase and a terminal phase. Many of the chemically deposited thin films peel from the substrate at some stage of the growth phase before reaching terminal thickness [20]. In the present case PbSe films were extremely adhesive to the substrate and not peeled off from the substrate, though the deposition was carried out for prolonged time intervals. After certain time interval, powdery PbSe material was deposited over the