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Studies on structural, morphological and optical behavior of chemically deposited $Cd_{0.5}Pb_{0.5}S$ thin films

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ABSTRACT

The present paper reports the preparation of $Cd_{0.5}Pb_{0.5}S$ thin films via a simple and inexpensive chemical bath deposition technique. Various preparation conditions were optimized for the deposition of good quality $Cd_{0.5}Pb_{0.5}S$ thin films. The structural, morphological and optical properties of these films are discussed. The structural studies confirmed the polycrystalline nature of material with cubic structure. Using scanning electron microscopy, the surface morphology of the films was studied. The optical band gap of the film gets modified during annealing. The chemical composition of these thin films was studied by energy dispersive spectroscopy. The optical band gap energy for as-deposited and annealed $Cd_{0.5}Pb_{0.5}S$ thin films were calculated and found in the range of 2.6 to 2.05 eV.

1. Introduction

In the recent years, a rapid growth in the field of thin film science as a major research area has been noticed worldwide. A continuous research and development of innovative thin film processing techniques has increased the importance of coatings and synthesis of new materials for various industrial and technological applications. Consequently, there is a need of basic research activities in the future, to increase knowledge, understanding and to develop predictive calibers for relating fundamental properties of microstructures and performance of thin films in various basic and applied prospects. At present, II–IV–VI group ternary semiconductor inorganic compounds, in the form of thin films have attracted a great deal of attention due to their potential applications, both from the fundamental and applied point of view.

Cadmium lead sulfide (CdPbS) is one of the promising material, belongs to II–IV–VI group ternary semiconductor materials, which have large range of application as gas and humidity sensors [1], solar control coatings [2], IR detectors [3], optoelectronics [4] and photo electrochemical (PEC) solar cells [5,6]. Obaid et al. studied structural, optical and electrical properties of CdS/PbS thin films for its solar cell application [7]. Skyllas-Kazacos et al. gave detailed data on high Cd mole fraction in chemical bath [8]. Nill et al. fabricated $Pb_{0.98}Cd_{0.02}S$ for its application as diode lasers in ultra-high resolution spectroscopy [9].

A variety of techniques have been employed to synthesize the thin films including successive ionic layer adsorption and reaction (SILAR) [10], electro deposition [11], spray pyrolysis [12], vacuum deposition [13], sputtering [14] and chemical bath deposition (CBD) [15–17]. Among these techniques, CBD has been used to deposit metal chalcogenide thin films since long back due to feasibility of routine deposition of nano-structured films and owing to strong advantage. It is the occurrence of moderately slow chemical reaction in the reaction bath results into a solid product deposited on the immersed substrates. It is a very ideal technique for industrial adaptation as the involvement of low deposition temperature, inexpensive equipment setup and ease of deposition on any size and shape of substrate via chemical route. By this technique, pinhole free thin solid films can be grown easily on the suitable substrate, since the basic building blocks are ions instead of atoms [18]. Moreover, this technique has an ability to deposit the thin films on different substrates and flexibility of tuning thin film properties by controlling and adjusting the deposition parameters [19]. A comparative study between various deposition techniques and CBD (including present work) has been given in Table 1.

The most recognized manifestation of nanoparticles is tunability of band gaps with increase or decrease in crystal size. Annealing is one of the important tools for tuning the band gaps and as such its effect on the crystallite size and structure is of remarkable significance [20]. Annealing not only increases the crystal size but also

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Table 1
A comparative study on previously reported techniques and present work.

S. nos.	Method/ technique used	Material	Precursor used	Temp. (°C)	Form	Remarks	Refs.
1	RF magnetron sputtering	PbS-QD/CdS heterojunction	PbO (99.9%), CdS (99.9%), hexane (anhy., 95%), ethyl alcohol (abs.), acetonitrile (anhy., 98%)	270	Thin films, grown on ITO coated glass substrates	Hexagonal wurtzite crystalline phase, CdS thin film with thickness of ~70 nm was used as optimized window layer for CdS/PbS-QD combination	[14]
6	Microwave assisted chemical bath deposition [MA-CBD (modified form of CBD)	n-CdS/p-PbS heterojunction	$CdCl_2$, CH_3COONH_4, $CS(NH_2)_2$, NaOH	80	Thin films, grown on ITO coated glass substrates	Nanocrystalline nature, uniform surface without the presence of voids, pinholes or cracks, polycrystalline with cubic structure, lattice mismatch was found to be very low indicating that the film has good crystalline quality	[16]
2	Metal organic chemical vapor deposition (MOCVD)	Pb–Cd–S	$Pb(CH_3COO)_2$, $Cd(CH_3COO)_2$, ammonium morpholinodithiocarbamate	400	Thin films, grown on glass substrates	Smooth and homogeneous surface morphology, with densely packed cubic grains, well distributed and adhered to the substrate without any crack, polycrystalline nature, having mixed phases, band gap value was obtained 2.17 eV	[29]
3	Spray pyrolysis	$Cd_{1-x}Pb_xS$	$Cd(CH_3COO)_2{\cdot}3H_2O$, $Pb(CH_3COO)_2{\cdot}2H_2O$, $CS(NH_2)_2$	300	Thin films, grown on glass substrates	Polycrystalline in nature, dense morphology with no voids or pinholes, wurtzite hexagonal structure, band gap decreased from 2.43 to 2.07 eV eith variation of x from 0.0 to 0.20	[30]
4	Cation exchange method	PbS/CdS	$Cd(CH_3COO)_2{\cdot}2H_2O$, oleic acid, phenyl ether, PbS nanoparticles (dispersed in toluene)	100	Core shell quantum dots	Cubic phase, blue shifts in absorption and PL peaks were observed with varying PL quantum yields, size dependent free carrier absorption (FCA) was observed, smaller PbS/CdS nanoprticles were found to exhibit greater FCA	[31]
5	Hybrid Passivation technique followed by standard layer-by-layer spin coating technique	CdS encapsulated PbS nanocrystals	CdO (99.99%), PbO (99.999%), $Na_2S{\cdot}9H_2O$ (98%), hexane (anhy., 95%), methanol (anhy., 99.8%), oleic acid (90%)		Thin films, grown on FTO coated glass substrates	Rock salt PbS and zinc blende CdS crystal phase, suppression of carrier scattering in matrix encapsulated nanocrystal films had relatively low density of surface defects at nanocrystal/matrix interface, rate of exciton dissociation and charge trapping exhibited either matrix encapsulation or cross-linking assembly strategies	[32]
7(a)	Chemical bath deposition (CBD)	$Cd_{0.825}Pb_{0.175}S$	$CdSO_4$, $PbSO_4$, $CS(NH_2)_2$, TEA	80	Thin films, grown on FTO coated glass substrates	Polycrystalline nature with mixed phases, dense and homogeneous morphology, film thickness and crystallite size affects the cell performance	[33]
(b)		$Cd_{0.5}Pb_{0.5}S$	$Cd(CH_3COO)_2{\cdot}2H_2O$, $Pb(CH_3COO)_2{\cdot}2H_2O$, $CdCl_2{\cdot}H_2O$, $CS(NH_2)_2$, 2-mercaptoethanol (2-ME), triethanolamine (TEA), ammonia solution (25%)	70	Thin films, grown on glass substrates	Cubic crystalline phase, 3-dimensional growth of films, spherical shaped grains with well defined boundaries, agglomeration of nanoparticles was obsereved at higher annealing temperature, increased absorption with increasing annealing temperature was due to increase in grain size, band gap energy was found in the range of 2.6 to 2.05 eV	Present work

refines the structure by making it homogeneous and improves the certain properties of the material to be annealed [21]. In the present work, the goal of our work was to prepare $Cd_{0.5}Pb_{0.5}S$ thin film in a cost effective way and to study the modifications of structural, morphological and optical characteristics of as-deposited samples on annealing at various temperatures. The enhancement of the above mentioned properties by annealing was highlighted in this work.

2. Experimental details

2.1. Materials

Cadmium acetate dihydrate [$Cd(CH_3COO)_2{\cdot}2H_2O$], lead acetate dehydrate [$Pb(CH_3COO)_2{\cdot}2H_2O$], cadmium chloride ($CdCl_2{\cdot}H_2O$), thiourea [$CS(NH_2)_2$], 2-mercaptoethanol (2-ME) and triethanolamine (TEA) were obtained from MERCK (Mumbai, India) and 25% ammonia solution was purchased from S. D. Fine-Chem Limited (Mumbai, India). All the reagents used were of AR grade and were used as received without any further purification. All the precursor solutions were prepared with deionized water. Commercially available microscopic glass slides (Blue Star, Polar Industrial Corporation, Mumbai) with the dimensions of 75 mm × 25mm × 2 mm were used as glass substrates. These substrates were boiled in chromic acid for 2 h, washed with deionized water followed by degreasing with acetone and finally ultrasonicated with deionized water for 15 min, before being used.

2.2. Preparation of $Cd_{0.5}Pb_{0.5}S$ thin films

The thin films of $Cd_{0.5}Pb_{0.5}S$ were deposited on glass substrates by chemical bath deposition (CBD) technique. The optimal reaction mixture for the deposition of $Cd_{0.5}Pb_{0.5}S$ thin films was obtained by mixing 7.5 mL of both 1 M cadmium acetate and lead acetate solutions with constant stirring by the means of magnetic stirrer for 2–3 min. After this, 5 mL of triethanolamine (TEA) was added drop wise. After stirring the mixture for few minutes, 20 mL of