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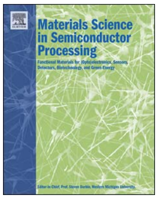

Temperature dependent charge transport mechanisms in highly crystalline *p*-PbS cubic nanocrystals grown by chemical bath deposition

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ABSTRACT

Lead sulfide nanocrystal films, comprising of well faceted 350 nm cubic-nanocrystals are tailored by ion-flux controlled chemical bath deposition at 50 °C to 80 °C bath temperatures. These possess compact (111) oriented nanocubic morphology and exhibit significantly improved electrical and opto-electronic properties as necessary for emerging next generation solar energy conversion applications. All films are of *p*-type nature and concurrently possess high carrier mobility (μ), high hole concentration (p) and low electrical resistivity (ρ) at room temperature. In particular, for films grown at 75 °C, high values of $\mu = 29.3\ \mathrm{cm^2V^{-1}s^{-1}}$, $p = 8.1\times10^{17}\ \mathrm{cm^{-3}}$ and $\rho = 0.26\ \Omega\ \mathrm{cm}$ are observed on the same nanocubic film. At high temperatures ($T > 150$ K), the charge transport is governed by thermally activated band conduction and nearest-neighbour hopping conduction. However, at lower temperatures ($T < 150$ K), both Mott variable-range hopping (VRH) and Efros–Shklovskii (ES) VRH type hopping are prevalent. PbS films grown at 75 °C have the lowest thermal activation energy. The distinct crossover from Mott-VRH to ES-VRH conduction process is observed at ~ 80 K. The observed decrease in Mott temperature with increase in bath temperature has been attributed to the lesser defects and enhanced density of states at Fermi level, which suggest the reduction in activation energy of the films beneficial for improved cell performance. Prevalence of conduction mechanisms is correlated with growth process.

1. Introduction

Semiconductor nanocrystals have emerged as the promising novel materials for efficient conversion of solar energy into electricity and chemical energy through solar cells, photoelectrochemical cells and photocatalysis [1–6]. Nanocrystalline semiconductors possess numerous distinguishing features such as controlled and scalable synthesis, large surface to volume ratio, size-customizable optical and electronic properties, efficient broadband absorption and self-assembled nano-architectures [1,7–13]. Additionally, nanostructured architectures such as nanowires, nanorods and nanocubes suppress reflection and improve solar photon absorption fraction via light trapping and scattering, which allows use of lesser absorber material and considerably large effective junction area compared to the planar architecture [1,7,10,11]. Moreover, these nanocrystalline materials have been contemplated to be more efficient solar absorber layer materials in comparison with their bulk counterparts because of the capability to deal with hot carriers and enhanced multiple exciton generation (MEG), i.e. generation of multiple free carriers on absorption of single high energy photon. The quantum confinement (quantization) effect arising due to nanocrystal grain size less than or comparable to the Bohr exciton radius (the characteristic dimension of carrier wavefunction in the semiconducting material) causes enhanced Coulomb interaction between carriers. The MEG process facilitated by Coulomb interaction is superior in such confined nanostructures as compared to the bulk materials [1,2,7,8,14]. The maximum theoretical efficiency with MEG in Shockley-Queisser limit is estimated to be 44%, considerably higher than 33% of the single junction limit [1,8,14]. Thus, photon absorber material should have smaller bulk energy band gap and a large Bohr exciton radius for efficient MEG and hence improved solar energy conversion. Therefore, the low energy band gap inorganic nanocrystals such as Pb(S, Se, Te), In(Sb, As) are a few promising materials for application in excitonic and multi-junction thin film solar cells [1,7,8].

Among these, PbS (consisting of natural abundant elements) has emerged as an appropriate low-cost *p*-type absorber layer material for photovoltaic applications because of its stability and low toxicity compared to other lead chalcogenides. The intrinsic *p*-type semiconducting nature of undoped PbS thin films is considered to originate from the native defects i.e. structural imperfections and shallow accepter levels due to Pb vacancies [V_{Pb}] [15,16]. The large relativistic splitting in band structure of PbS makes it favourable for band gap engineering [17]. PbS exhibits inimitable properties [10,18–20]

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comprising narrow infrared direct band gap (~0.41 eV at the L symmetric point of the first Brillouin zone), tunable energy gap from near-infrared (NIR) to visible region, high optical dielectric constant (ε_{PbS} = 17.2), small effective carrier mass (which causes large blue shift in absorption edge), a large Bohr exciton radius ~18 nm (which allows strong confinement effects even for large size grains), multiple exciton generation effect and proper band edge alignment (Type-II, as required for better carrier transport) with various *n*-type metal oxides. Moreover, the exceptional third order nonlinear optical properties of PbS nanocrystals make it suitable for potential applications in optical and optoelectronic devices [21].

Various heterojunctions based on PbS nanocrystals as absorber layer i.e. ZnO/PbS [22–25], TiO_2/PbS [26,27] and CdS/PbS [28,29] have been demonstrated for the improvement in solar energy conversion in next generation photovoltaics. The solar energy conversion depends on three essential aspects: absorption of solar flux; excitation and separation of charge carriers; and transport of these photo-excited carriers to respective electrodes. The former aspect is governed by the band gap of the material (tunable via nanocrystal size) and later two aspects are critically affected by crystal structure, crystal-facets, shape/size/texture of nanocrystals and associated defects [10,30,31]. High photocurrent requires the enhancement in solar flux absorption, in particular, in NIR region [7]. In addition, a better charge carrier separation and transport necessitates high quality well crystalline semiconductor nanocrystals with suitable morphology, low activation energy and high conductivity as well as large carrier mobility. The low resistivity, high carrier mobility and small activation energy promotes low series resistance and suppressed charge recombination at grain boundaries, that contribute to high efficiency of solar cells [1,2,10]. Also, for small activation energy, there should be large density of localized states near Fermi level which is directly related with high concentration of shallow acceptor cation vacancies. Large value of shallow acceptors may decrease the grain boundary potential by passivating the electronic states at grain boundaries [32].

There are some reports on study the structural, morphological, optical and electrical behaviour of PbS thin films fabricated by chemical bath deposition technique [28,33–39]; and hardly any report on the temperature dependence of electrical transport behaviour of these films [39–41]. Moreover, many of these reports have used an additional inhibitor (triethanolamine, tri-sodium citrate, ethylene glycol etc.) to deposit the PbS thin films. Such films seem to suffer from less solar flux absorption and poor charge transport properties because of the inhibitor linked smaller grain size, that causes larger grain boundary scattering and possible formation of additional defects and trap states on the film surface/bulk [28,34–38,42]. Therefore it is essential to ascertain the nature of charge transport mechanisms prevailing in the semiconducting material and establish correlation with various material parameters for eventual optimization of the performance of solar cell [43].

In this work, we demonstrate a detailed study of temperature dependent behaviour of electrical conductivity over a broad temperature range from 20 to 300 K in PbS nanocubic films as potential photovoltaic absorber material and extraction of various conduction mechanisms operative in different temperature regimes. Chemical bath deposition (CBD), a facile, inexpensive, less time consuming, reproducible, low temperature and large-scale deposition technique [18,44,45] that has potential of harvesting better quality films with various possible nanoarchitectures (employing low ion-flux), is used for inhibitor-free growth of PbS thin films by simply varying the bath temperature from 50 °C to 80 °C. The novelty of this work is the designing of well oriented and faceted nanocubic PbS, as large as 350–400 nm, via ion-flux controlled facile chemical bath deposition and simple bath temperature tuning of nanocube-size. An hitherto unreported detailed study of such nanocubic films on the optoelectronic properties, charge transport behaviour and associated defects; securing concurrently tunable optical and electronic properties, simultaneous occurrence of very high carrier concentration and high carrier mobility with better inter grain conduction properties necessary for good solar absorber layer material for efficient energy conversion devices is the significant highlight of the work. A comprehensive study of charge transport mechanisms, correlation of defects with growth and optical absorption have been scrutinized.

2. Experimental

2.1. Synthesis of PbS thin films

PbS thin films were deposited on glass substrates employing CBD technique at different bath temperatures (T_B) ranging from 50 °C to 80 °C. All analytical grade reagents (Merck) were used without further purification. The reaction bath containing alkaline aqueous solution of 25 mM lead acetate [$Pb(CH_3COO)_2 \cdot 3H_2O$] as a source of lead ($Pb^{2+}$) ions and 50 mM thiourea [$SC(NH_2)_2$] as a source of sulfide (S^{2-}) ions was prepared for PbS deposition. It may be noted that for the present study, we have used 25 mM bath concentration which was earlier optimized and reported in our previous work [18] in which bath temperature was fixed at 75 °C. The main idea in the present work is to explore further tuning of the nanocubic films via bath temperature variation. Liquid ammonia was added slowly to bring the solution pH to 11. No additional inhibitor was used to control the reaction rate in the bath. The solution was stirred continuously for 30 min to ensure homogeneous mixing. The reaction bath was immersed into hot water bath placed on magnetic stirrer and maintained at the required temperature. The properly cleaned glass substrates were suspended vertically into the reaction bath with constant stirring during deposition. After deposition, the grown PbS films were rinsed ultrasonically in distilled water to remove the loosely adhered particles and then dried in ambient air. The obtained grayish-black color PbS films were specular (mirror-like), uniform and well adherent to the substrate.

2.2. Characterizations

Surface morphology of the as-prepared films was observed using field emission scanning electron microscopy (FESEM, FEI Quanta 200F SEM Model). The structure of the PbS films was examined using X-ray diffractometer (PANalytical X'Pert PRO model) equipped with CuK_α radiation (λ = 1.54 Å) in the 2θ range of 20° to 80° using Bragg-Brentano (θ– 2θ) configuration. The microstructure of the samples was observed using high resolution transmission electron microscopy (HRTEM, Tecnai G^2 F20 Twin), operated at 200 keV. The elemental composition of the synthesized PbS thin films was determined by the energy dispersive X-ray spectroscopy (EDX). Optical measurement of the samples in the range of wavelength 500–2500 nm was performed using Perkin Elmer Lambda 1050 UV–Vis–NIR spectrophotometer. The electrical parameters were obtained from room temperature Hall Effect measurements using van der Pauw configuration. The temperature dependent resistivity ρ(T) measurements were performed using closed cycle helium cryostat in the temperature range 20–300 K.

3. Results and discussion

3.1. Morphology and composition

Fig. 1 shows FESEM images of the inhibitor-free grown as-deposited PbS nanocrystal films revealing significant changes in morphology with increase in bath temperature. A subtle change in morphology is noticeable at bath temperatures above 60 °C. The micrographs also reveal that the films are quite compact and have uniform coverage on the substrate. The single crystal like nanocube morphology of the films seems to evolve with increasing bath temperature. Fig. 1a and b reveal PbS nanocrystals with rounded edges and small sizes ~100–150 nm in films deposited at lower bath temperatures. However, the bath temperature $T_B \geq 70$ °C results into (111) oriented and well-formed cubic