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Deposition of morphology-tailored PbS thin films by surfactant-enhanced aerosol assisted chemical vapor deposition

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ABSTRACT

In this work, we report the results of deposition of PbS thin films using single molecular precursor, *bis*(*O*-isobutylxanthato)lead(II), in the presence of additives namely: sodium dodecyl sulfate (SDS), Tween and Triton x-100, via aerosol assisted chemical vapor deposition (AACVD). The as-deposited PbS thin films are highly crystalline and exhibited superior adhesion to glass substrates. Powder X-ray diffraction (XRD) analysis confirmed the formation of pure cubic phase of PbS. Thin films deposited using 0.4 mM Triton X-100 as additive resulted in wire like structures while 0.8 mM Triton X-100 deposited thin films comprised of predominantly shoe shaped structures. Further, increase in concentration (1.2 mM) of Triton X-100 deposited films having rod like morphology. The scanning electron microscopy (SEM) confirmed that in the presence of SDS, thin films consist of spherical shaped crystallites. Energy dispersive X-ray spectroscopy (EDX) and X-ray photon electron microscopy (XPS) of as-deposited PbS thin films was used to study chemical composition of thin films.

1. Introduction

Nanostructured semiconductor materials (NSMs) have been extensively studied and explored for potential applications [1–3] in solar cell devices [4], self-cleaning coatings [5,6] and photocatalysis [7,8]. The unusual properties of NSMs are size as well as morphology dependent [9]. It has been observed that a slight variation in shape may have substantial effect on desired properties [4,6]. The efficiency of the dye sensitized solar cell can be increased up to 10 folds using vertically aligned ZnO nanorods [6,8,10]. Similarly, catalytic activity may be enhanced greatly by controlling the morphology of certain facets e.g.; (111) & (100) which are responsible for catalytic activity of the material, making the material a more active catalyst [3,7,8]. Therefore, the development of morphologically-controlled synthetic routes for nanostructured materials is necessary to explore their potential as more efficient and smart materials. A widely adopted approach for morphologically controlled synthesis is the solution based route to manipulate kinetic factors of growth using polymers, surfactants or by altering pH/or growth temperature [11–14]. Surfactants play an important role in controlling the morphology of nanoparticles. They contain metal coordinating groups as well as solvophilic groups. The metal coordinating groups are generally electron donating which coordinate well with electron poor metal atoms in nanocrystals. This surfactant-metal interaction prevents the aggregation and further growth on surfactant bound facets of nanocrystals. The tail of surfactant extends to solvent and therefore determine the solubility of nanocrystals, which in most cases is hydrophobic in nature. In addition to nanocrystal binding, a surfactant also forms a complex with the reactive monomer species and plays its role in obtaining control over nanocrystal growth [15]. A number of cationic/non-ionic surfactants have been explored extensively to study their role in tailoring the shape of as-prepared nanoparticles [3,11–13]. However, the solution based synthesis involves complex procedures and reaction conditions and relatively longer reaction time is required. Therefore, a simple, fast and cost effective route is required to meet economic and industrial needs.

Chemical vapor deposition is a simple technique to grow thin films on a wide variety of substrates [16]. Over the past few decades, this technique has been extensively explored by various

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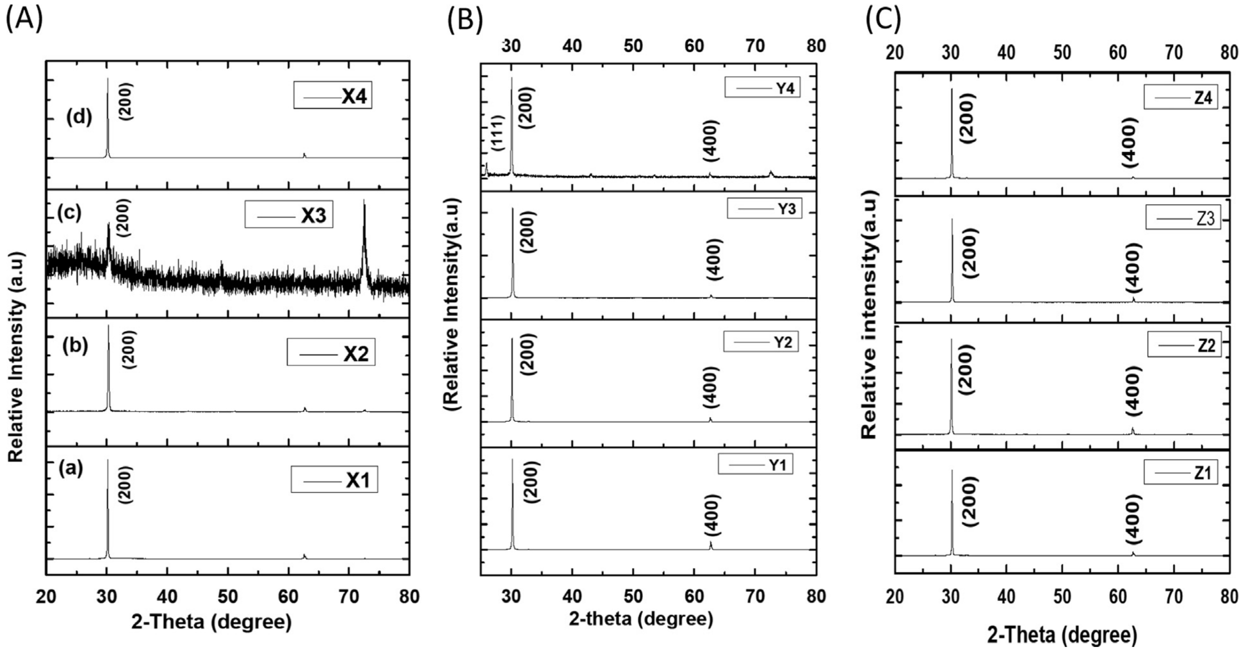

Fig. 1. XRD patterns of PbS thin films deposited in the presence of (A) SDS, (B) Triton X-100 and (C) Tween. Samples X1-Z1 were grown without the use of surfactant while X2-Z2, X3-Z3 and X4-X5 are thin films grown using precursor to surfactant mole ratios of 1:1, 1:2 and 1:3 respectively.

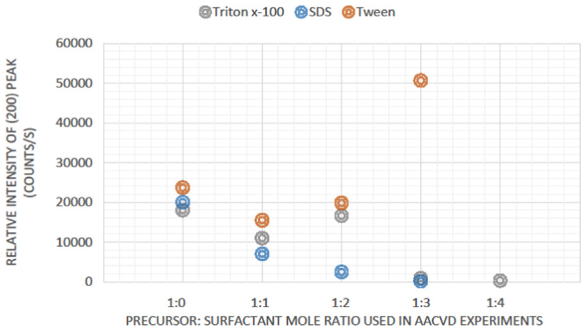

Fig. 2. Plot of relative intensity of (200) peak vs. precursor: surfactant mole ratio used in AACVD experiments.

research groups [17–19] (O'Brien et al. Ivan parkin et al. [20,21]. A number of new single molecular precursors have been designed and utilized to grow binary/or ternary phased materials [21]. Further, the efficiency of CVD technique has been improved by engineering new tools to perform CVD process (AACVD, LPCVD, and APCVD) [16,17,22].

One of the huge challenge in CVD deposited thin films is to control the size and morphology of as-deposited crystallites/grains [23,24]. Nature of substrates, deposition temperature and precursor types are key factors that influence the size/shape of particles in CVD deposited thin films [16]. Thus, reproducibility is a key limitation to grow desired thin films by AACVD method. To address this problem, here we report successful deposition of PbS thin films using a single source precursor, *bis*(*O*-isobutyldithiocarbonato)lead(II) in the presence of different surfactants, such as SDS (anionic), Triton X-100 and Tween (non-ionic), with the remarkable control over the morphology of as prepared PbS thin films. This approach is unique and may be extended to deposit thin films of other metal chalcogenides as well. Moreover, this approach is equally effective for single/or dual source precursors route. The as-deposited PbS thin films were crystalline and the change in morphology were investigated by field emission scanning electron microscopy (FE-SEM). The purity and chemical composition was studied by energy dispersive X-ray spectroscopy (EDX) and X-ray photon electron spectroscopy (XPS).

2. Experimental

The synthetic preparation of ligand was performed in an inert environment of nitrogen. All reagents were purchased from Sigma-Aldrich and were used as received without further purification. ^{1}H NMR spectrum was obtained by Bruker 300 MHz spectrometer. Infrared spectrum was obtained between range of 4000–200 cm^{-1}. Elemental analysis was performed which shows the ratio of different elements present in compound. TGA analysis was carried out at heating rate of 10 °C min^{-1}, under nitrogen environment at flow rate of 50 ml per minute from 30 °C to 500 °C. Thin films of lead chalcogenide deposited on glass substrates were characterized by XRD using Bruker diffractometer (Cu-Kα). Samples were scanned between 10° and 80° with a step size of 0.05. Thin films were carbon coated for SEM and EDX analysis. XPS experiments were performed using a Theta Probe Thermo VG Scientific spectrometer equipped with a micro spot monochromatized AlKα source and a 180° spherical sector analyzer with a two-dimensional electron detector. All the spectra were recorded in Constant Analyzer Energy (CAE) mode using a pass energy of 150 eV for survey and 100 eV for high resolution regions (C1s, O1s, S2p, Na1s, Cl2p, Pb4f). Calibration of the binding energy (BE) scale was performed by taking a suitable signal as internal reference. In particular, the reference peak was the first component of the C1s signal (BE = 284.8 eV). The spectra acquisition parameters (channel exposition, number of scans, analyzer parameters, etc.) were selected in order to provide the best energy resolution and signal/noise ratio.

Data analysis and curve-fit procedures were performed by means of Avantage 4.75 commercial software. The same peak lineshape parameters (Gaussian/Lorentzian ratio and full width at half maximum) values were employed for the curve fitting of components belonging to the same high-resolution spectrum. S2p high resolution spectrum was first of all processed removing the doublet minor components (i.e. S2p$_{1/2}$), exploiting an automatic computational routine provided by the Avantage software. Then, the resulting simplified S2p$_{3/2}$ spectrum underwent curve-fitting procedures. Effective Attenuation Length (EAL) taken into account was calculated using the software on the basis of the TPP-2 M