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Growth and characterization of nanocrystalline PbS:Li thin films

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ABSTRACT

The structural, electrical and opto-electronic properties of PbS thin films doped with Li^+ ion were investigated. The crystallite size showed a strong dependence on Li doping, the crystal size changed from 36 nm to 12 nm due to Li incorporation in PbS. Optical band gap showed a shift in the range ~1.5–2.3 eV with Li incorporation. Urbach tailing in the band gap was observed and the Urbach energy has a dependence on the amount of incorporated Li. SEM images showed a notable change in grain size with Li doping, however the morphology changes from large grains to agglomerations of smaller grains when doped with Li. The electric conductivity of the films showed a dependence on Li doping, reached a maximum value and later decreased for higher Li containing films. The doped samples showed better photosensitivity.

1. Introduction

The band gap of PbS can be tuned in the range 0.4–5.0 eV [1] via size control, which makes it a promising material for optoelectronic applications including telecommunications [2], LEDs [3], lasers [4], photodetectors [5], and photovoltaic devices [6–9]. Alkali metals are monovalent cations that can substitute Pb^{2+} supplying free carriers in the structure for application in solar cells [10]. PbS is a semiconductor material with a E_g of 0.4 eV in bulk, and relatively large exciton Bohr radius of 18 nm [11], which allows strong quantum confinement of both electrons and holes. The value of the E_g can be simply controlled by modifying the grain size (GS) and this is achieved by controlling systematically the deposition temperature and doping [12]. The absorption edge has been found to blue shifted significantly as particle size reduced. Also polycrystalline PbS thin films showed good photoconductive properties, these properties have been correlated with the synthesis method, thickness, composition and structure.

Various methods for the preparation of PbS nanocrystals have been reported such as SILAR [13], chemosynthesis [14], Chemical bath deposition (CBD) [10], etc. In the present report, PbS and PbS:Li films were prepared by CBD, which involves the immersion of a glass substrate in alkaline lead–thiourea yielding PbS films of 100–500 nm thickness. CBD method has

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become an attractive technique for the growth of films due to several advantages compared to other techniques, including scalability to large area, low cost, ability to deposit thin films on different substrates, and flexibility of tuning thin film properties simply by controlling and adjusting the deposition parameters. In addition CBD allows easy incorporation and control of the dopants as well as the reproducibility of the samples. In the present work we are reporting CBD preparation of PbS:Li thin films, and the structural, morphological, electrical, optical, and opto-electronic properties of the deposited films as a function of Li^+ concentration. A systematic investigation of the CBD prepared PbS:Li will enhance the knowledge about the Li^+ incorporation in PbS and associated changes in grain size and quantum confinement effects.

2. Experimental

2.1. Chemical reactions and film deposition

Chemical reactions for the growth of doped and undoped PbS films were determined by employing the reported cell potential values in basic media. The cell potential and the Gibbs free energy are related through the Nernst equations: $\Delta G^\circ = -n\tau\varepsilon^\circ$ [10]. The slow process at the substrate surface take place predominantly over direct hydrolysis of thiourea in the bulk of the reaction bath as follows:

$$SC(NH_2)_2 + 3OH^- \Leftrightarrow CO_3^{2-} + S^{2-} + 7H^+ \quad (1)$$

$$[Pb(NH_3)_4]^{2+} + S^{2-} \Leftrightarrow PbS + 4NH_3$$

$$\Delta G^o = +362.88\ \text{KJ} \quad (2)$$

Li^+ ion is generated by the dissociation of Li(OH) according to

$$LiOH \Leftrightarrow Li^+ + OH^-$$

$$\Delta G^o = +140.08\text{KJ} \quad (3)$$

PbS doping is happened according to the following reaction

$$[Pb(NH_3)_4]^{2+} + S^{2-} + Li(OH) \Leftrightarrow PbSLi^+ + 4NH_3 + OH^-$$

$$\Delta G^o = +592.96\text{KJ} \quad (4)$$

Finally, according to the numerical value of $\Delta G^\circ > 0$, it is concluded that Li is incorporated in the PbS as Li^+ ion.

Experimental details for depositing PbS:Li films are similar to those reported in previous work [14,15]. The PbS bath contained $Pb(CH_3CO_3)_2$ (0.04M), KOH (0.2 M), NH_4NO_3 (1.3 M), and $SC(NH_2)_2$ (0.3 M). Thin films with eight different volume levels of Li doping ($V_{[Li]}$) were obtained by the addition in situ of 1–8 ml of $Li(NO_3)$(0.04M) to the above bath. The different batches of solutions were stirred well and kept at 40 ± 2 °C during 30 min. The adequate molarity of 0.04 of the doping solution was determined experimentally on the basis of film adherence. The samples were labelled as PbS for undoped film and PbS:Li1–PbS:Li8 for doped films, where the numbers 1–8 corresponds to the volume (ml) of $Li(NO_3)$ added to the PbS bath.

2.2. Material characterization

The structural characterization was carried out using the X-ray diffraction (XRD) patterns recorded on a Bruker D8 Discover Diffractometer, using the Cu K_α line. Morphological features were investigated using a Hitachi S5500 FESEM. The optical absorption spectra were recorded using a UV-Vis-NIR Varian 5000 Spectrophotometer, the photoresponse of the films were studied using a computerized homebuilt system.

3. Results and discussion

Fig. 1 shows the SEM images of two typical samples; (a) pure PbS, and (b) PbSLi6, which is the film deposited from the PbS bath containing 6 ml of $Li(NO_3)$(0.04M) as discussed in section 2.1. The effect of doping is very clear, grain size was significantly lowered and the film surface feature agglomeration of large numbers of smaller grains. Fig. 1(a) resembles the typical morphology of PbS obtained by CBD [16,17].

Fig. 2 (a) shows the X-ray diffractograms of pure PbS as well as the PbS:Li films. All the diffraction peaks corresponds to the PbS as reported previously [17]. According to reference pattern JCPDS 05–0592 the PbS crystallizes in the cubic (zinc-blende) phase.