Preparation of ZnS and SnS Nanopowders by Modified SILAR Technique

S. Patra, S. Mondal, and P. Mitra

Department of Physics The University of Burdwan, Golapbag, Burdwan – 713104, West Bengal e-mail: <u>mitrapartha1@rediffmail.com; bu_pm@yahoo.com</u>

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ABSTRACT

Nanocrystalline powders of zinc sulphide (ZnS) and tin sulphide (SnS) were prepared by modified SILAR (successive ion layer adsorption and reaction) technique. The technique involves multiple dipping of a substrate in cationic and anionic precursors. All the synthesized powders were found to contain nanocrytsalline grains. Broad humps at 26.9° for ZnS and 31.55° for SnS were observed in XRD patterns. The corresponding reflection plane was (101) in both cases. The presence of broad humps (large FWHM) confirms the presence of nanocrystalline grains. The particle size estimated using X-ray line broadening method was ~1.6 nm for ZnS and ~1.4 nm for SnS. However, instrumental broadening and strain broadening was not taken into account during particle size estimation. Large shift in bandgap energy values were observed compared to bulk values of the materials indicating quantum confinement. The bandgap energies were 4.08 eV for ZnS and 1.32 eV for SnS.

Keywords: ZnS, SnS, Nanopowder, SILAR

1. Introduction

The synthesis and characterization of zinc sulphide and tin sulphide via different techniques have attracted considerable attention due to their potential applications. The II-VI group of sulphides has distinctive features of high ionicity (compared to Si, Ge and III-V compounds), large band gap, and transparency in the visible region. In this regard zinc sulphide (ZnS) deserves a special mention because of its large optical band gap, in fact, the highest (>3.6 eV) among all II-VI compound semiconductors. ZnS has got applications in photoluminescent and electroluminescent devices and more recently as n-type window layer heterojunction solar cell [1]. SnS, on the other hand, is an indirect semiconducting material with bandgap energy $\sim 1.2 \text{ eV}$ and has potential applications in current controlled devices, sensor and laser devices, switching devices and photovoltaic devices [2]. We have earlier reported preparation of ZnS and SnS thin films by SILAR [3-4]. In SILAR technique thin films are obtained by immersing the substrate into separately placed

cationic and anionic precursors. Between every immersion it is rinsed in distilled water or ion exchanged water.

For deposition of ZnS thin films, zinc acetate was use as zinc ion releasing source (cation) and thiourea was used as sulpher ion releasing source (anion). Both anionic and cationic precursors were kept at room temperature. In case of SnS, tin chloride solution kept at 80°C and sodium sulphide solution kept at room temperature were used as cationic and anionic precursors respectively.

In the present work, we have used modified SILAR technique to get nanocrystalline powders of ZnS and SnS. The modified SILAR deposition from aqueous solutions is a very promising method because of its simplicity and economy. The aim of the present work is to promote interest in SILAR method as applied to preparation of nanocrystalline metal sulphide powders. The structural and optical characterizations of the synthesized powders were carried out using x-ray powder diffractometer and UV-VIS spectrophotometer.

2. Experimental

Zinc sulphide powder was synthesized by dipping a precleaned glass substrate in 0.1 M $ZnCl_2$ solution and 0.1 M Na_2S solution both kept at room temperature. The substrate was kept overnight in chromic acid and this was followed by rinsing in distilled water and ultrasonic cleaning in equivolume mixture of acetone and alcohol in an ultrasonic cleaner. The zinc chloride bath, used for deposition of ZnS was prepared by adding ZnCl₂ (Merck) in deionized water. Similarly sodium sulphide flakes (Merck) was added in deionized water to prepare the Na₂S bath. Zinc chloride does not dissolve completely in water. So during synthesis, the ZnCl₂ bath was continuously stirred using a magnetic stirrer. The solution of sodium sulphide was however stable and no stirring were required. Dipping of the substrate in cationic and anionic precursors leads to a very weakly adherent ZnS film that could be easily scratched from the substrate. The powder was thoroughly washed repeatedly in deionized water.

For SnS, the substrate was dipped in 0.1M stannous chloride $(SnCl_2)$ solution and 0.1 M ammonium sulphide $[(NH_4)_2S]$ solution both kept at room temperature. A very thin and weakly adherent film of SnS is formed on the substrate which could be easily scratched.

Dipping of the substrate in cationic precursors leads to the absorption of metal (M^{2+}) ions and subsequent dipping in anionic precursors leads to the absorption of sulpher (S^{2-}) ions. The reaction on the substrate leading to the formation of metal sulphide can be represented as

 $M^{2+} + S^{2-} \rightarrow MS$

X-ray diffraction (XRD) with CuK_{α} radiation (λ =1.5418 Å) was made for structural characterization of the synthesized powders of ZnS and SnS. Transmission spectrum was recorded in UV-VIS-NIR spectrophotometer (JASCO V-570).

3. Results and Discussions

3.1 Preparation of ZnS and SnS powders

We have earlier reported the preparation of ZnS thin film by dipping a substrate in 0.1 M solutions of zinc acetate $[Zn(CH_3COO)_2]$ and 0.1M thiourea $[SC(NH_2)_2]$, both kept at room temperature [3]. Ammonia solution (NH_4OH) was used as complexing agent. A strongly adherent film resulted on the substrate. For the present case we have used 0.1M $ZnCl_2$ and 0.1M Na_2S as precursors. During each dipping, a part of the metal sulphide formed goes into the solution and the rest remains as a loosely adherent film on the substrate. For solution concentrations higher than 0.125M, the entire powder formed goes into the solution indicating complete detachment from substrate surface. It seems that choice of the precursor solutions and deposition parameters can be manipulated to give strongly adherent thin film or weakly adherent film which can easily scratched to give powder. The growth rate was high for ZnS powder and fifty dipping were performed. One complete dipping step involves dipping the substrate in cationic complex and then in anionic complex. A thick and very weakly adherent film (powder precipitate) results, which could be easily scratched from the substrate. The powder was subsequently washed repeatedly in deionized water.

For SnS synthesis, the precleaned substrate was first dipped in 0.1M stannous chloride $(SnCl_2)$ solution and then in 0.1 M ammonium sulphide $[(NH_4)_2S]$ solution both kept at room temperature. The growth rate was very low in this case and hundred dipping was performed. A very thin and weakly adherent film of SnS is formed which could be easily scratched. The light brown powder was thoroughly washed in deionized water. Similar to the case of ZnS, solution concentration in excess of 0.15M leads to complete detachment of powder from the substrate surface and the entire metal sulphide powder formed goes into the solution. Earlier we have reported that dipping in 0.1M SnCl₂ kept at 80°C and 0.1M Na₂S kept at room temperature leads to strongly adherent thin films of SnS [4].

3.2 Structural characterization

Figure 1 shows the XRD patterns of the zinc sulphide (ZnS) powder. The XRD was done after thorough washing of the synthesized powder in deionized water and heating the powder at 150°C for 2 hrs. The material was scanned in the range 20-90°. The peak at 26.9° corresponding to (101) plane is in good agreement with the Joint committee on powder diffraction standard (JCPDS) data belonging to hexagonal ZnS [5]. Other peaks of ZnS did not appear in the spectrum.

Figure 2 on the other hand shows the XRD pattern of SnS powder. The peak at 31.55° is in good agreement with the Joint committee on powder diffraction standard (JCPDS) data belonging to orthorhombic SnS [6]. The corresponding reflecting plane is (101).



Figure 1: XRD pattern of ZnS powder Figure 2: XRD pattern of SnS powder

The crystallite size was calculated by the X-ray line broadening method using the Scherrer formula [7]:

$$D = \frac{k\lambda}{\beta\cos\theta}$$

where λ is the wave length of radiation used (CuK_{α} in this case), k is the Scherrer constant, β is the full width at half maximum (FWHM) intensity of the diffraction peak for which the particle size is to be calculated, θ is the diffraction angle of the concerned diffraction peak and D is the Crystallite dimension (or particle size).

The value of observed broadening (β_o) for ZnS is 6.13° for peak at 26.9° and that for SnS is 6.62° for the peak at 31.55°. The corresponding values for particle sizes using Scherrer equation are ~1.6 nm for ZnS and ~1.4 nm for SnS respectively. While calculating the particle size, the instrumental broadening and strain broadening was not taken into account. In Scherrer equation, β represents the broadening due to particle size alone. In general the experimentally observed broadening (β_o) is the total contribution from particle size broadening [β], instrumental broadening (β_i) and strain broadening (β_c) and is represented as

$$\beta_o = \beta + \beta_i + \beta_s$$

For our present case, we have considered $\beta \cong \beta_o$ (without considering β_i and β_s). Thus the measured particle sizes are always on the low side and the actual particle size is higher than the values obtained. However, the observed broad hump (and therefore large FWHM) suggests that the synthesized materials are nanocrystalline in nature with very small particle size.



Figure 3: Optical transmission spectrum of ZnS



3.3 Optical studies

Transmission spectrum was recorded in a UV-VIS-NIR spectrophotometer (JASCO V-570). Figure 3 shows the transmission spectrum of ZnS. A sharp cut off is obtained at ~303 nm which corresponds to bandgap energy of 4.08 eV. Figure 4, on the other hand, shows the transmission spectrum of SnS. The bandgap energy could be obtained from the plot of $(\alpha hv)^2$ as a function of hv (Figure 5). Extrapolation of the line to the base line, where the value of $(\alpha hv)^2$ is zero, gives E_g as 1.32 eV. The values are on the higher side than those reported for bulk form of the materials [1-2] indicating a shift due to quantum confinement arising from lowering of particle size.

4. Conclusions

Nanocrystalline powders of ZnS and SnS can be prepared by modified SILAR technique. It seems that the technique can be extended for other metals sulphides as well. The technique is simple, cost effective and an easily scalable alternative to industrial level. The nanocrystalline powders so formed are extremely fine and their dimension is of the order of quantum dots, which is evident from large FWHM and large shift in bandgap energy values compared to bulk values. A detailed structural investigation of the materials is underway.

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Figure 5: $(\alpha hv)^2$ versus hv for SnS

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