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Synthesis of nanoflakes-like shapes of zinc sulfide grown at room temperature by electrodeposition method

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ABSTRACT

Zinc sulfide thin films were deposited on stainless steel and indium doped tin oxide substrates from an aqueous solution of $ZnSO_4$, and $Na_2S_2O_3$. This study reports the effect of bath conc. on the crystal structure, surface morphology, optical properties and compositional analysis of zinc sulfide nanostructured thin films. The electrodeposition time and bath concentration can be used to control the dimensions of the electrodeposited nanoflakes within nanometer range. Zinc sulfide thin films are polycrystalline with cubic crystal structure. SEM images indicate that the film surfaces are well-covered with zinc sulfide nanoflakes. The agglomeration of nanoflakes is enhanced due to the formation of large number of particles during growth process. A Raman shift of sample is detected at wave number 254 cm^{-1}. Typical film deposited with optimized bath concentration shows optical band gap of about 3.83 eV.

1. Introduction

Zinc sulfides are interesting because of their wide applications in many areas of modern technology such as photovoltaic solar cells due to their physical and chemical properties. Zinc sulfide is an n-type

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semiconductor with a wide direct band gap, mostly used for window layer in heterojunction photovoltaic solar cells [1]. Size dependent optical properties of zinc sulfide thin films are reported by Ubale et al. [2]. Blueshift of absorption band of zinc sulfide from the bulk was determined by John [3]. By thermal evaporation method Schottky barrier photodiode of zinc sulfide thin film have been fabricated [4]. Structural phase transformation and electronic stability properties of zinc sulfide is studied by Gangadharan et al. [5]. Photosensitivity of ZnS nanocrystalline thin films is studied and this photosensitivity decreases due to ageing and exposure to oxygen [6]. Single-crystal zinc sulfide nanoawls with strong green emissions are studied by Zhai et al. [7]. The quantum efficiency of fabricated cells can be improved by high band gap material like zinc sulfide, leading to an increase in short circuit current [8]. The growth mechanisms of ZnS thin films at room temperature can be improved using an aqueous medium containing an ammonium salt [9]. By a facile solution-chemical method ZnS core/shell heterostructures are fabricated [10]. P-type ZnS can also be obtained either by intrinsic or extrinsic doping [11,12]. Different structures of zinc sulfide such as nanotowers, submicrotubes, nanowires and nanoflakes were reported in literature [13–15]. According to literature survey it is seen that during the last two decades, methods like chemical and electrochemical conversion, precipitation, ion displacement and low temperature dip type for the preparation of zinc sulfide and their characterization have been reported by several authors but ours is very simple, isothermal process, less expensive method for fabrication zinc sulfide with nanoflakes of different dimensions.

2. Experimental

2.1. Film growth

The zinc sulfide nanoflakes were synthesized at room temperature by electrodeposition method. Thin films are deposited at room temperature which avoids oxidation and corrosion of metallic substrates. Chemical deposition results in smooth and homogeneous deposits are easily obtained since the basic construction of blocks is by ions instead of atoms. Preparative parameters such as deposition time and concentration of precursor were optimized. In the typical synthesis, (0.1 M) zinc sulfate ($ZnSO_4$) and (0.1 M) sodium thiosulfate ($Na_2S_2O_3$) are used as source of zinc and sulfate.

2.1.1. Bath (1)

Bath (1) is synthesized by taking mixture of 0.1 M of $ZnSO_4{\cdot}5H_2O$, 0.1 M of $Na_2S_2O_3{\cdot}5H_2O$, prepared in distilled water. For electrodeposition 30 ml synthesized bath is used as electrolyte.

2.1.2. Bath (2)

Bath (2) is synthesized by taking mixture of 0.2 M of $ZnSO_4{\cdot}5H_2O$, 0.2 M of $Na_2S_2O_3{\cdot}5H_2O$ prepared in distilled water. For electrodeposition 30 ml synthesized bath is used as electrolyte.

2.1.3. Bath (3)

Bath (3) is synthesized by taking mixture of 0.3 M of $ZnSO_4{\cdot}5H_2O$, 0.3 M of $Na_2S_2O_3{\cdot}5H_2O$ prepared in distilled water. For electrodeposition 30 ml synthesized bath is used as electrolyte.

The ultrasonically cleaned stainless steel and ITO substrate are used to prepare samples. All reagents were of analytical grade and used without further purification. Electrolytic bath contains 15 ml $ZnSO_4$ and 15 ml $Na_2S_2O_3$ as sources of Zn and S ions. Electrodeposition studies of zinc sulfide thin films were made using potentiostat (Princeton Perkin–Elmer, Applied Research Versa-stat-II; Model 250/270) in three-electrode configuration. Pure graphite plate was used as an anode, stainless steel was used as cathode and saturated calomel electrode (SCE) was used as reference electrode. The electrodeposition of zinc sulfide thin films was carried out at the deposition potential −0.7 V/SCE with current density of 3–4 mA/cm^2; for various bath concentrations without stirring and by keeping deposition time fixed. Gray colored, uniform and nearly stoichiometric zinc sulfide thin films were deposited by potentiostatic mode onto stainless steel and ITO (indium doped tin oxide) coated glass substrates for optimized preparative parameters. After deposition, the films were washed with double distilled water. The pH of the plating bath ranges between 3 and 4. In present work it is to be observed