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Polycrystalline thin films of antimony selenide via chemical bath deposition and post deposition treatments

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Abstract

We report a method for obtaining thin films of polycrystalline antimony selenide via chemical bath deposition followed by heating the thin films at 573 K in selenium vapor. The thin films deposited from chemical baths containing one or more soluble complexes of antimony, and selenosulfate initially did not show X-ray diffraction (XRD) patterns corresponding to crystalline antimony selenide. Composition of the films, studied by energy dispersive X-ray analyses indicated selenium deficiency. Heating these films in presence of selenium vapor at 573 K under nitrogen (2000 mTorr) resulted in an enrichment of Se in the films. XRD peaks of such films matched Sb_2Se_3. Evaluation of band gap from optical spectra of such films shows absorption due to indirect transition occurring in the range of 1–1.2 eV. The films are photosensitive, with dark conductivity of about 2×10^{-8} $(\Omega\ \mathrm{cm})^{-1}$ and photoconductivity, about 10^{-6} $(\Omega\ \mathrm{cm})^{-1}$ under tungsten halogen lamp illumination with intensity of 700 W m^{-2}. An estimate for the mobility life time product for the film is 4×10^{-9} $cm^2\ V^{-1}$.

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Keywords: X-ray diffraction; Chemical deposition; Antimony selenide; Photoconductivity

1. Introduction

Antimony(III) selenide has a ribbon-like polymeric structure in which each Sb-atom and each Se-atom is bound to three atoms of the opposite kind that are then held together in the crystal (orthorhombic, a=11.62 Å, b=11.77 Å, c=3.962 Å) by weak secondary bonds [1]. Optical band gaps due to both direct and indirect transitions in the range of 1 to 1.13 eV and thermal energy gap of 1–1.32 eV are reported for the material [1,2]. This makes it suitable for use as an absorber material in polycrystalline thin film solar cells [3]. A photoelectrochemical solar cell, employing antimony selenide thin film as photoanode, has shown short-circuit current of ~0.45 mA/cm^2 and open circuit voltage of ~0.37 V [4].

Polycrystalline thin films of the material have been prepared by vacuum evaporation [5], spray pyrolysis [6] and electrodeposition [7] methods, but the films obtained by chemical bath deposition are reported as amorphous [2,8]. In general, the films of V_2VI_3 compounds obtained by chemical bath method are amorphous, showing high resistivity (~10^8 Ω cm) and optical band gaps that are larger than those reported for the material in the bulk [9]. Quantum confinement effect arising from the small grain size in thin film semiconductors [9,10] is considered as the cause for the latter. Heating the films has been found to enhance crystallinity, thus permitting structural characterization of the material by X-ray diffraction (XRD) [9]. In this paper we report that thin films obtained from chemical baths of soluble tartrato-, citrato- or thiosulfato-complexes of antimony and sodium selenosulfate are constituted by antimony oxide in addition to antimony selenide, but the former could be converted to crystalline Sb_2Se_3 when heated at 573 K in presence of Se-vapor. The structural, optical and electrical properties of the films are reported.

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2. Experimental details

2.1. Materials employed

Antimony trichloride, $SbCl_3$, and aqueous ammonia, NH_3(aq), (30%) of Fermont chemicals, selenium powder of Alfa chemicals, and potassium antimony tartrate, triethanolamine, sodium citrate, and sodium thiosulfate of Baker Analyzed Reagents were utilized in the preparation of the chemical baths. Corning microscope glass slides of 1 mm thickness were used as substrates. These were cleaned well using detergent solution and water and dried prior to their use as substrates.

2.2. Deposition of thin films

Antimony(III) chloride does not dissolve in water, instead, precipitates as oxochloride, SbOCl. Clear solutions are formed in high concentrations of acids or alkalis, which when diluted precipitate oxosalts or hydroxide, respectively. The presence of strong ligands such as tartrate that form soluble complexes prevents the precipitation of basic salts in aqueous solutions. In the present study, we have used one or more of the ligands–citrate, triethanolamine and thiosulfate–to form soluble complexes of antimony in the deposition bath using $SbCl_3$ as the starting material. The other starting material, potassium antimony tartrate, is a soluble complex tartratoantimonate(III), $[Sb_2(C_4O_6H_2)_2]^{2-}$. The dissociation equilibria involving these complexes produce antimony(III) (aq) ions in the bath. Sodium selenosulfate was used as a source of selenide. This was prepared in the laboratory by refluxing 4 g of selenium powder and 12.5 g of sodium sulfite in 100 ml deionized water for 4 h, which resulted in a solution that was approximately 0.4 M in Na_2SeSO_3. Chemical baths of three different compositions, a), b) and c), were prepared:

a) To 25 ml of 0.1 M solution of potassium antimony tartrate was added with stirring 2 ml of approx. 3.7 M triethanolamine (50% dilution of as supplied reagent) followed by 20 ml of 30% ammonia (aq), 10 ml of 0.4 M sodium selenosulfate and the rest deionized water to take the volume to 100 ml.
b) To 1 g of antimony trichloride ($SbCl_3$) was added with stirring 37 ml of 1M solution of sodium citrate—a white precipitate formed initially dissolves in an excess of the reagent. Sequential addition, with stirring, of 20 ml of 30% ammonia (aq), 24 ml of approximately 0.4 M sodium selenosulfate and sufficient volume of deionized water took the volume to 100 ml.
c) To 500 mg of antimony trichloride was added 2.5 ml of acetone to dissolve it. This was followed by the addition of 20 ml of 1 M sodium citrate, 15 ml of 30% aqueous ammonia, 10 ml of 1 M sodium thiosulfate, 20 ml of 0.1 M sodium selenosulfate (prepared by diluting the 0.4 M solution above) and deionized water to take the volume to 100 ml.

In all the cases the solutions were clear and devoid of any precipitate at the beginning. Clean glass substrates were introduced vertically in the bath, supported against the wall of the beaker. Baths a) and b) with the substrates were placed in a Polyscience digital temperature controlled circulation bath maintained at 300 K and bath (c) was placed in a refrigerator (283 K). The depositions were allowed to proceed for different durations ranging from 1 to 6 h in the case of baths a) and b) and from 3–18 h in the case of bath c). At the end of these durations, the coated substrates were taken out of the baths, washed well with distilled water and dried by blowing hot air. Both sides of the substrates were coated with brown colored films, characteristic color of antimony selenide. The thin film deposited on the side of the substrate, which faced the wall of the beaker was chosen for characterization—the film from the other side was removed with cotton swabs moistened with dilute HCl. The thicknesses of the films were, for bath a): 0.1 μm (2 h)–0.4 μm (4 h); bath b): 0.2 μm (1 h)–0.7 μm (5 h) and bath c): 0.2 μm (3 h)–0.4 μm (18 h). An Alfa Step 100 (Tencor Inc., CA) was utilized for the measurement of thin film thickness.

2.3. Post-deposition treatments on the films

The thin films of approximate thickness 0.4 μm were heated to different temperatures in a vacuum oven (T-M High Vacuum Products) in a nitrogen atmosphere of 100 mTorr at 573 K for 1 h to facilitate structural and compositional modifications. To heat the films in presence of selenium, samples of size 2.5×2 cm^2 and weighed quantities 5 or 50 mg of selenium powder were placed adjacent to each other in a petri dish. The latter, covered with its lid, was placed in the vacuum oven and the chamber was evacuated to a pressure of 10 mTorr and simultaneously heated to 393 K to eliminate any trace of moisture from the samples. Subsequently, nitrogen was introduced into the chamber to a pressure of 2000 mTorr and the oven temperature was raised to 573 K. The heating lasted for 1800 s.

2.4. Characterization

XRD patterns of the films were recorded on a Rigaku D-Max X-ray diffractometer using Cu–K_α radiation. The elemental composition of the films was done by electron probe microanalysis in a Scanning Electron Microscope, model Carl Zeis DMS 940 A, over a sample area of approximately 300 $(\mu m)^2$. Optical transmittance (T%) and reflectance (R%) spectra of the films with air and a front aluminized mirror as references, respectively, were recorded on a Shimadzu UV-3101PC UV–VIS–NIR spectrophotometer. For the electrical measurements, a pair of coplanar