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Characterizations of Antimony Tri-Sulfide Chemically Deposited with Silicotungstic Acid

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ABSTRACT

A new chemical deposition method has been developed to prepare photoconducting n-Sb2S3 thin polycrystalline films. The solution composition of the deposition bath was 0.025M potassium antimonyl tartarate, 0.4M triethanolamine, 0.025M thiocacetic acid, and 5×10^-7M silicotungstic acid (STA), respectively. The as-deposited and the annealed films were characterized through x-ray diffraction, neutron activation analysis, and the optical absorption investigations. The photoelectrochemical performances of these films were examined. The best photoresponse was observed on the film prepared from a chemical bath containing 5×10^-2M STA.

Photoconducting antimony tri-sulfide thin films are generally prepared by vacuum evaporation (1) or by sintering technique (2) using powdered Sb2S3 compound as the starting material. This creates the difficulty of achieving the stoichiometric films due to wide differences of the vapor pressures of the constituents at the deposition temperature. Recently there has arisen a sustained effort to produce different chalcogenide thin films by simple and inexpensive chemical deposition methods. Other than Cd-chalogenides (3, 4), this method is applied to produce good quality, stoichiometric layered semiconductors such as MoS2 (4, 5) and MoSe2 (6). The method has also been proven to be the least expensive, low-temperature method, non-polluting, and with an ease for making films of large area of any configuration. Among the different metal sulfides, antimony tri-sulfide finds special applications in vidicon devices (7,8), microwave devices (9), switching devices (10) and various optoelectroni c devices (11).

The activation of electrode surfaces by heteropolyacids (HPAs), e.g., H3SiW12O40 or H3PW12O40 has been well established and largely used in the electrocatalysis of the hydrogen evolution reaction at modified semiconductor or metal electrode surfaces (12, 13). The significant improvement of the hydrogen evolution reaction kinetics has also been observed on electrodeposited nickel with various HPAs whereas the electrode fabricated without HPAs do not show any improvement (14, 15). These interesting results have prompted us to examine the effects of incorporating silicotungstic acid (SiW12O402-; STA) in the chemical deposition bath of antimony trisulfide thin films.

In this paper we report a new chemical method for the deposition of Sb2S3 thin films and their characterizations using x-ray diffraction, neutron activation analysis, optical absorption, resistivity and Hall effect studies, and the photoelectrochemical (PEC) measurements. The pronounced effect of STA incorporated films were determined from this study.

Results and Discussion

The structural features of the films deposited with and without STA are shown in Fig. 1. The as-deposited film in both the cases, with or without 5×10^-7M STA showed a broad x-ray diffractogram of an Sb2S3 film suggesting that they have an amorphous structure. But the annealed samples (300~ for 1 h, N2 atmosphere) showed x-ray spectra of the different Sb2S3 films deposited on SnO2 coated glass substrates and used for this study. The chemical composition of the different films was determined from the neutron activation analysis. Optical absorption spectra of the different Sb2S3 films deposited on SnO2 coated glass substrates were recorded from 950 to 540 nm by a Shimadzu UV/VIS spectrophotometer at 300 K. The optical bandgap of the as-deposited and annealed films with and without STA incorporated films were determined from this study.

Resistivity and Hall effect measurements were carried out by four-point probe van der Pauw method. Conducting silver paint was used for electrical contact. The I-V characteristics have been found to be linear within the voltage range of study (20 V) showing the ohmic nature of the contact Sb2S3 films. The photoelectrochemical (PEC) measurements were conducted on a standard three-electrode cell geometry. A large area graphite electrode was used as a counterelectrode. The working redox electrolyte was 0.01M I2 and 1M KI and was gassed thoroughly before and during the experiments. The Sb2S3 film surfaces which are not contacted with the electrolyte were covered by microtop lacquer adhesives. The PEC cell was illuminated with a broad band tungsten halogen lamp (Fibre-Lite). The intensity of illumination was calibrated using Oriel solar simulator radio meter (Model 81020).

Experimental Procedure

Thin films of Sb2S3 were deposited onto SnO2 coated glass substrates from an aqueous solution of 0.025M potassium antimonyl tartarate (BDH, AR), 0.4M triethanolamine (BDH, AR), 0.5M ammonia, and 0.025M thiocacetic acid (BDH, AR) under a magnetic stirrer. Before use, the SnO2-coated glass slides were cleaned ultrasonically in isopropyl alcohol and dried in pure N2 atmosphere. The cleaned substrates were then clamped vertically in the plating solution at 300 K. During the Sb2S3 film formation, the solution color changed progressively from light to deep yellow and then orange-red at which a thick deposition of Sb2S3 films (~1.0 μm) were formed on the substrates. After 60 h, the slides were removed and washed thoroughly by water and dried in air. In case of STA-incorporated Sb2S3 films, the same procedure was adopted except 5×10^-7M STA has been used in the chemical bath. The coated glass slides were then introduced into an oven maintained at 300°C for 1 h in N2 atmosphere. The composition and the crystalline status of the as-deposited and the annealed films with and without STA were examined from the powder x-ray diffractograms with a Philips X-ray diffractometer. The Sb2S3 powder was collected by scraping off the SnO2-coated glass substrates and used for this study.

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shows the intense peak due to WO$_3$, which is incorporated in the Sb$_2$S$_3$ film during deposition.

Table I. Compositions, electrical properties, and grain sizes of the different films (for the experimental conditions, see the text).

<table>
<thead>
<tr>
<th>Film Description</th>
<th>Atomic Compositions (%)</th>
<th>Resistivity ((\mu, \Omega \text{ cm}))</th>
<th>Carrier Concentration ((N_c, \text{cm}^{-3}))</th>
<th>Mobility ((\text{cm}^2/\text{V-s}))</th>
<th>Grain Sizes ((\mu\text{m}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Sb$_2$S$_3$ film as-deposited</td>
<td>Sb 34.3, S 65.7</td>
<td>(3.8 \times 10^6)</td>
<td>--</td>
<td>0.12 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>(b) Film (a), annealed</td>
<td>Sb 36.2, S 63.8</td>
<td>(5.3 \times 10^6)</td>
<td>(1.2 \times 10^{12})</td>
<td>9.8</td>
<td>0.82 ± 0.1</td>
</tr>
<tr>
<td>(c) STA incorporated film, annealed</td>
<td>Sb 38.6, S 61.4</td>
<td>(5.0 \times 10^6)</td>
<td>(2.4 \times 10^{12})</td>
<td>9.2</td>
<td>1.02 ± 0.2</td>
</tr>
</tbody>
</table>

A comparison of the atomic percentage of Sb and S present in the different films is given in Table I. In order to optimize measurement conditions, the powdered sample (scraped off the substrates) of about 1 mg was irradiated at least three times with the flux of \(10^{12}\) neutrons/cm$^2$s and counted four times with the liquid nitrogen cooled Ge gamma ray detector. The measured accuracy was estimated to be ±5%. From the Table I, it is clear that a near-stoichiometric film could only be obtained when the film was prepared from a chemical bath containing \(5 \times 10^{-7}\) STA and subsequently annealed (300°C, 1 h) in N$_2$ atmosphere. The grain sizes obtained are also included in Table I. From the values of grain sizes, it is clear that largest grains are only achievable, when the films are prepared with STA and subsequently annealed in N$_2$ atmosphere.

Resistivity and Hall effect measurements were made at room temperature. Thermoelectric power measurements showed that the films are n-type. The resistivities, carrier concentrations, and mobilities of the different films are given in Table I.

Figure 2 shows the optical absorption (\(\alpha h\nu)^{1/2}\) vs. incident photon energy (\(h\nu\)) curves for Sb$_2$S$_3$ films with (Fig. 2a) and without (Fig. 2b) STA incorporated annealed in N$_2$ atmosphere. The plots are found to be linear, suggesting that the bandgaps of the Sb$_2$S$_3$ films are indirect in nature. Extrapolation of these curves to zero absorption coefficient gives the optical energy gap of the Sb$_2$S$_3$ films, which is 1.77 eV for polycrystalline Sb$_2$S$_3$ films (17).

The solar cell characteristics of the annealed sample with and without STA was evaluated at a constant illumination intensity of 40 mW/cm$^2$ and is shown in Fig. 3. The as-deposited Sb$_2$S$_3$ film without STA showed poor I-V characteristic (Fig. 3). But after annealing the films (300°C in N$_2$ atmosphere) the I-V properties improved significantly (Fig. 3b). This is mainly due to the influences of annealing of the films causing a significant increase in the effective grain sizes (cf, Table I) and a decrease in grain boundary area due to migration of smaller crystallites, and the joining of similarly oriented grains to form bigger crystallites. The decrease of effective grain boundary area decreases grain boundary scattering, surface scattering, and space charge scattering resulting much improved I-V characteristics. But STA incorporated and subsequent annealing in N$_2$ atmosphere, the Sb$_2$S$_3$ film showed the best I-V (Fig. 3c) characteristics with open-circuit voltage (\(V_{oc}\)) 540 mV, short-circuit photocurrent density (\(J_{sc}\)) 5.6 mA/cm$^2$, fill factor of 0.52 and cell efficiencies 3.9%, respectively. The significant improvement of the qualities of the films and the properties of PEC solar cells may be due to the influence of the STA (SiW$_{12}$O$_{42}$) used in the deposition bath. It has already been established ([12-15, 18, 19] and the references therein) that the PEC cell characteristics is not well understood and is the subject of current investigations.

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![Fig. 2. Variation of \((\alpha h\nu)^{1/2}\) vs. \((h\nu)\) plot: (a) Sb$_2$S$_3$ film prepared with \(5 \times 10^{-7}\) STA and annealed at 300°C for 1 h in N$_2$ atmosphere, (b) same as (a) but without STA; and (c) as-deposited film without STA. The optical absorption coefficient, \(\alpha\), is in cm$^{-1}$.](image)

![Fig. 3. The current (I)-voltage (V) characteristics of the n-Sb$_2$S$_3$/0.01M KI/C PEC cell, (a) as-deposited n-Sb$_2$S$_3$ electrode without STA; (b) same as (a) but annealed at 300°C in N$_2$ atmosphere for 1 h and (c) \(5 \times 10^{-7}\) STA incorporated Sb$_2$S$_3$ electrode and annealed at 300°C in N$_2$ atmosphere for 1 h.](image)
REFERENCES