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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-Sb<sub>2</sub>S<sub>3</sub> thin polycrystalline films. The solution composition of the deposition bath was 0.025M potassium antimonyl tartarate, 0.4M triethanolamine, 0.025M thioacetamide, and  $5 \times 10^{-7}$ M 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  $5 \times 10^{-7}$ M STA.

Photoconducting antimony tri-sulfide thin films are generally prepared by vacuum evaporation (1) or by sintering technique (2) using powdered Sb<sub>2</sub>S<sub>3</sub> 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-chalcogenides (3, 4), this method is applied to produce good quality, stoichiometric layered semiconductors such as MoS<sub>2</sub> (4, 5) and MoSe<sub>2</sub> (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 optoelectronic devices (11).

The activation of electrode surfaces by heteropolyacids (HPAs), e.g., H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> or H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> 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 (SiW<sub>12</sub>O<sub>40</sub><sup>4-</sup>; STA) in the chemical deposition bath of antimony trisulfide thin films.

In this paper we report a new chemical method for the deposition of Sb<sub>2</sub>S<sub>3</sub> 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 with a nominal concentration of  $5 \times 10^{-7}$ M in the chemical deposition bath have been studied along with the effect of annealing.

## Experimental Procedure

Thin films of Sb<sub>2</sub>S<sub>3</sub> were deposited onto SnO<sub>2</sub>-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 thioacetamide (BDH, AR) under a magnetic stirrer. Before use, the SnO<sub>2</sub>-coated glass slides were cleaned ultrasonically in isopropyl alcohol and dried in pure N<sub>2</sub> atmosphere. The cleaned substrates were then clamped vertically in the plating solution at 300 K. During the Sb<sub>2</sub>S<sub>3</sub> film formation, the solution color changed progressively from light to deep yellow and then orange-red at which a thick deposition of Sb<sub>2</sub>S<sub>3</sub> films ( $\approx 1.0 \mu\text{m}$ ) 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 Sb<sub>2</sub>S<sub>3</sub> films, the same procedure was adopted except  $5 \times 10^{-7}$ M 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 N<sub>2</sub> 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 Sb<sub>2</sub>S<sub>3</sub> powder was collected by scrapping off the SnO<sub>2</sub>-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 Sb<sub>2</sub>S<sub>3</sub> films deposited on SnO<sub>2</sub> 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 Sb<sub>2</sub>S<sub>3</sub> 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 I<sub>2</sub> and 1M KI and degassed thoroughly before and during the experiments. The Sb<sub>2</sub>S<sub>3</sub> 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).

## 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  $5 \times 10^{-7}$ M STA showed a broad x-ray spectrum (Fig. 1a) suggesting that they have an amorphous structure. But the annealed samples (300°C for 1 h, N<sub>2</sub> atmosphere) showed well-defined crystallographic planes (Fig. 1b) and these were identified in the recordings (16). The structural features are consistent with an orthorhombic cell with lattice constants  $a_0 = 11.269$ ,  $b_0 = 11.299$ , and  $c_0 = 3.824$ . Figure 1c

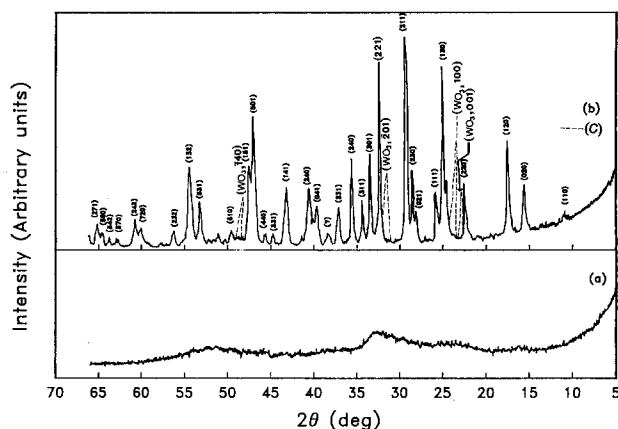


Fig. 1. X-ray diffractograph of an Sb<sub>2</sub>S<sub>3</sub> film scrapped off the glass substrates: (a) as deposited film with and without  $5 \times 10^{-7}$ M STA; (b) with annealing at 300°C for 1 h in N<sub>2</sub> atmosphere (without STA) and (c) same as (b) but with  $5 \times 10^{-7}$ M STA.

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

Film	Atomic compositions (%)		Resistivity ( $\rho$ , $\Omega$ cm)	Carrier concentration ( $N_d$ , $\text{cm}^{-3}$ )	Mobility ( $\text{cm}^2/\text{V}\cdot\text{s}$ )	Grain sizes ( $\mu\text{m}$ )
	Sb	S				
(a) $\text{Sb}_2\text{S}_3$ film as-deposited	34.3	65.7	$3.8 \times 10^8$	—	—	$0.12 \pm 0.02$
(b) Film (a), annealed	36.2	63.8	$5.3 \times 10^6$	$1.2 \times 10^{12}$	9.8	$0.82 \pm 0.1$
(c) STA incorporated film, annealed	38.6	61.4	$5.0 \times 10^6$	$2.4 \times 10^{12}$	9.2	$1.02 \pm 0.2$

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

A comparison of the atomic percentage of Sb and S present in the different films are given in Table I. In order to optimize measurement conditions, the powdered sample (scrapped off the substrates) of about 1 mg was irradiated at least three times with the flux of  $10^{12}$  neutrons/ $\text{cm}^2/\text{s}$  and counted four times with the liquid nitrogen cooled Ge gamma ray detector. The measured accuracy was estimated to be  $\pm 5\%$ . 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  $5 \times 10^{-7} \text{M}$  STA and subsequently annealed ( $300^\circ\text{C}$ , 1 h) in  $\text{N}_2$  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  $\text{N}_2$  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.

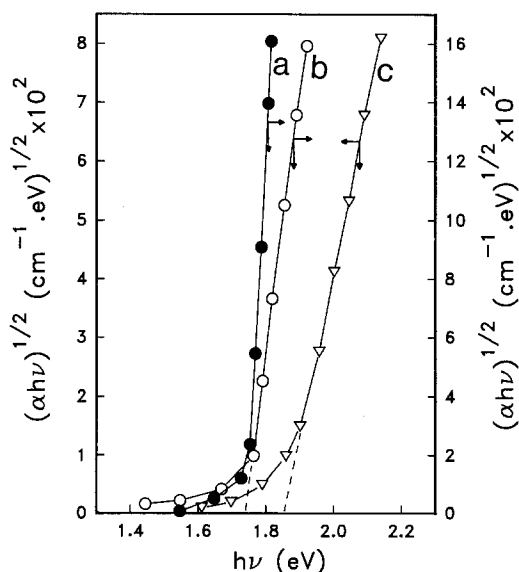
Figure 2 shows the optical absorption  $(\alpha h\nu)^{1/2}$  vs. incident photon energy ( $h\nu$ ) curves for  $\text{Sb}_2\text{S}_3$  films with (Fig. 2a) and without (Fig. 2b) STA incorporated annealed in  $\text{N}_2$  atmosphere. The plots are found to be linear, suggesting that the bandgaps of the  $\text{Sb}_2\text{S}_3$  films are indirect in nature. Extrapolation of these curves to zero absorption coefficient gives the optical energy gap of the  $\text{Sb}_2\text{S}_3$  films, which are 1.85 eV for the as-deposited unannealed (Fig. 2c) and 1.74 eV for the annealed sample. The decrease in  $E_g$  after heat treatment may be due to increase in effective grain size and in the closer stoichiometric composition on annealing. The later value of  $E_g$  agrees closely with the value of 1.77 eV for polycrystalline  $\text{Sb}_2\text{S}_3$  films (17).

The solar cell characteristics of the annealed sample with and without STA was evaluated at a constant illumination intensity of  $40 \text{ mW}/\text{cm}^2$  and is shown in Fig. 3. The as-deposited  $\text{Sb}_2\text{S}_3$  film without STA showed poor I-V characteristic (Fig. 3). But after annealing the films ( $300^\circ\text{C}$  in  $\text{N}_2$  atmosphere) the I-V properties improved significantly (Fig. 3b). This is mainly due to the influences of annealing of the films causing a significant in-

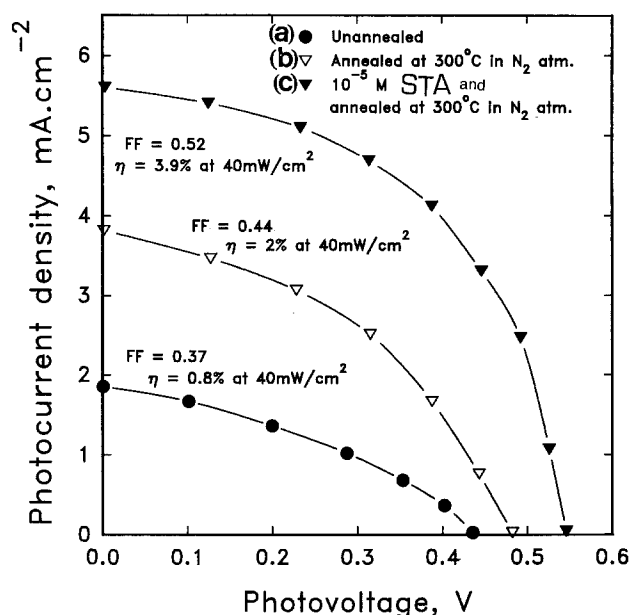
crease in the effective grain sizes (cf, Table I) and a decrease in grain boundary area due to migration of smaller crystallites, and the joining of similarly oriented grains to form bigger crystallites. The decrease of effective grain boundary area decreases grain boundary scattering, surface scattering, and space charge scattering resulting much improved I-V characteristics. But STA incorporated and subsequent annealing in  $\text{N}_2$  atmosphere, the  $\text{Sb}_2\text{S}_3$  film showed the best I-V (Fig. 3c) characteristics with open-circuit voltage ( $V_{oc}$ ) 540 mV, short-circuit photocurrent density ( $J_{sc}$ )  $5.6 \text{ mA}/\text{cm}^2$ , 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 ( $\text{SiW}_{12}\text{O}_{40}^{4-}$ ) used in the deposition bath. It has already been established [(12-15, 18, 19) and the references therein] that the modification of semiconductor surfaces with STA (12) and electrodeposition of metal with STA (14, 15, 18, 19) can produce good electrocatalytic interfaces for the PEC and for the hydrogen evolution reaction (HER), respectively. The improvement of the PEC characteristics and the qualities of the  $\text{Sb}_2\text{S}_3$  films deposited with STA may also be attributed to the induction of a favorable energy state within the bandgap favoring the charge-transfer kinetics at the electrode interface (20). The mechanism of the electrocatalytic activity of the STA on the improvement of the  $\text{Sb}_2\text{S}_3$  thin film properties and the PEC cell characteristics is not well understood and is the subject of current investigations. However, this communication demonstrates the feasibility of preparing semiconductor grade n- $\text{Sb}_2\text{S}_3$  thin films by an inexpensive chemical deposition route and the possibility of achieving photoactive electrode material for photovoltaic or PEC solar cells.

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



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

## REFERENCES

1. K. A. Mady, M. M. Elnahas, A. M. Farid, and H. S. Soliman, *Mater. Sci.*, **23**, 3636 (1988).
2. M. J. Chokalingam, K. N. Rao, N. Rangarajan, and C. V. Suryanarayana, *J. Phys. D: Appl. Phys.*, **3**, 1641 (1970).
3. K. C. Mandal, *J. Mater. Sci. Lett.*, **9**, 1203 (1990).
4. K. C. Mandal and A. Mondal, *J. Solid State Chem.*, **85**, 176 (1990).
5. T. K. Gupta, *Phys. Rev. B*, **43**, 5276 (1991).
6. K. C. Mandal and O. Savadogo, *J. Mater. Chem.*, **1**, 301 (1991).
7. S. V. Forgue, R. R. Goodrich, and A. C. Cope, *RCA Rev.*, **12**, 335 (1951).
8. A. D. Cope, U.S. Pat. 2,875,359 (1959).
9. J. Grigas, J. Meshkauskas, and A. Orliukas, *Phys. Status Solidi A*, **37**, K39 (1976).
10. M. S. Ablova, A. A. Andreev, T. T. Dedegkaev, B. T. Melekh, A. B. Peutsov, N. S. Shendel, and L. N. Shumilova, *Soviet Phys. Semicond.*, **10**, 629 (1976).
11. B. Roy, B. R. Chakraborty, R. Bhattacharya, and A. K. Dutta, *J. Solid State Commun.*, **25**, 937 (1978).
12. O. Savadogo, *Can. J. Chem.*, **67**, 382 (1989).
13. O. Savadogo, K. Amuzgar, and D. L. Piron, *Int. J. Hydrogen Energy*, **15**, 783 (1990).
14. O. Savadogo and C. Allard, *J. Appl. Electrochem.*, **21**, 73 (1991).
15. O. Savadogo and S. Lévesque, *ibid.*, **21**, 457 (1991).
16. Index to the Powder Diffraction File, JCPDS (1987).
17. A. Viehbeck and N. Hackerman, in "Photoelectrochemistry: Fundamental Processes and Measurement Techniques," W. L. Wallace, A. J. Nozik, S. K. Deb, and R. H. Wilson, Editors, PV 82-3, p. 478, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1982).
18. O. Savadogo and D. L. Piron, *Int. J. Hydrogen Energy*, **15**, 715 (1990).
19. O. Savadogo and C. Allard, *Can. Metal. Quart.*, **29**, 285 (1990).
20. O. Savadogo and K. C. Mandal, *Solar Energy Mater.*, In press.