



Fabrication of amorphous Sb_2S_3 films by chemical deposition

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Abstract

A simple, non-polluting and economical electrodeless chemical deposition technique for fabricating amorphous Sb_2S_3 films on glass or clear polymer substrates is described. The technique is based on hydrolytic decomposition of antimony thiosulfate compounds in aqueous media and is convenient for large area depositions at room temperature. Glassy, transparent and uniform amorphous films with yellow to orange colors were produced. The terminal thickness of the films from a single bath was $\sim 0.4 \mu\text{m}$. The X-ray diffractograph of the annealed films showed that orthorhombic Sb_2S_3 crystallizes within the amorphous phase upon annealing in air at 170–220°C for several hours. The optical band-gap of as-deposited amorphous films and annealed, partially crystallized films were found to be $2.48 \pm 0.02 \text{ eV}$ and $1.80 \pm 0.02 \text{ eV}$, respectively. The sheet resistance of 0.1–0.4 μm thick amorphous films was of the order of $10^{12} \Omega/\text{square}$ and two orders of magnitude less for the annealed films. Post-deposition immersion of the films in aqueous AgNO_3 solutions decreased the resistance by up to five orders of magnitude.

1. Introduction

Amorphous semiconductors have been a subject of special interest for years [1,2]. Of the amorphous chalcogenides, As_2S_3 and As_2Se_3 have received most attention [3–6], while, to our knowledge, relatively little attention has been paid to amorphous Sb_2S_3 [7,8].

Metal chalcogenides can be deposited as thin coatings by various techniques, such as sublima-

tion, vacuum evaporation and spray pyrolysis [9].

Thin films of metal chalcogenides can also be deposited by electrodeless chemical deposition from aqueous solutions [10–13]. This method has the advantage of being simple and economical. Further, it is non-polluting and convenient for large area depositions.

The main goal of this work is to present a simple and inexpensive technique for fabricating amorphous Sb_2S_3 thin films in aqueous media. The difficulty of using antimony salts in water media is caused by their strong tendency to hydrolyze, resulting in precipitation of basic insoluble salts. It is probably for this reason that methanolic solutions of SbCl_3 were used in the ‘dip-dry’ technique reported in Ref. [8], requiring many dips and dries before Sb_2S_3 could be de-

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posited onto a glass substrate. In order to avoid hydrolytic precipitation of antimony(III) basic salts in water media, one has to work in very acidic solutions, which are inconvenient for film deposition. Another way of avoiding basic salt precipitation is to complex the Sb^{3+} ions with a suitable agent. This has been employed in the present technique. Further, unlike most of the reports where complexing of heavy metal ions has been used in chemical baths for deposition of similar chalcogenides [11,14,15] by using a common complexing agent such as triethanolamine, EDTA and citric acid, and then another chalcogenide source agent, such as thiourea, thioacetamide or selenosulfate, in the technique described here the two required agents were replaced by a single one, namely sodium thiosulfate, which is both a complexing agent for Sb^{3+} and at the same time a source of sulfide ions upon hydrolysis. In this way, an inexpensive method for fabricating amorphous Sb_2S_3 coatings is achieved. Additionally, the deposited material is expected to be of a higher purity, since fewer chemicals are used in the present process. This technique is non-polluting, since practically no waste is produced and no toxic gasses evolve in the process. This technique was used to deposit amorphous Sb_2S_3 on glass and polymer substrates. Use of a glass substrate enables optical and annealing studies of the deposited material, while thin films deposited on organic polymer sheets have potential utility as materials for electrical and electro-optical devices requiring elastic and transparent substrates.

2. Experimental

2.1. Substrate preparation

Poor adhesion of the coating material onto the substrate surface is often a problem. For this reason, special attention was paid to preparation of substrates. Standard microscope glass slides, $75 \times 25 \times 1.0$ mm, as well as pieces of ordinary 3.0 mm thick window glass sheets were used as glass substrates. These were first washed with soap in warm water, then soaked in chromic acid

overnight, washed with distilled water and dried in air before use. Polymer substrates were strips cut from polymer transparency sheets (T2783, Sigma Chem. Co.), washed with soap in warm water and then soaked in 0.03% aqueous solution of tin(II) chloride for a few minutes. This ensures a uniform wetting of the polymer surface and in a way activates it for film deposition. The strips were then washed with distilled water and dried in air before use.

2.2. Deposition of Sb_2S_3

Thin films of amorphous Sb_2S_3 were deposited onto glass and polymer substrates from a chemical bath of the following composition. Approximately 4.0 g of solid SbCl_3 were dissolved in ~ 8 ml glacial acetic acid in a 250 ml beaker and 1.0M aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ was slowly introduced with constant stirring until a clear solution was obtained. As much as 100 ml of 1.0M sodium thiosulfate may be needed. The solution was then transferred into a 700 ml glass or plastic container and ~ 450 ml cold ($\sim 12^\circ\text{C}$) distilled water was added. The pH of the bath should be ~ 3 and can be adjusted with diluted acetic acid, if necessary. Previously cleaned and activated substrates were then introduced into the bath. As many as 15 standard microscope glass slides, inserted in plastics report binders, could be placed into a bath, as could larger pieces of ordinary glass. The chemical decomposition of the thiosulfate compounds of antimony in the bath begins in about ~ 20 min at room temperature. Yellow–orange precipitate begins to fill the bath container and thin films of the same color start to grow on the substrate surface(s). On vertically supported substrates, films deposited on both sides, while on horizontally mounted substrates films deposited only at the surface facing downward. To ensure good adherence of the films, the substrates need to be in the bath for at least 5 h. Depending on the desired thickness, the film growth can continue for up to 24 h. It is important to note that cold water should be used for the chemical bath, otherwise at temperatures $\geq 20^\circ\text{C}$ precipitation starts immediately, resulting in absence of film growth. The as-deposited films

were glassy, uniform and transparent, and bright yellow to orange in appearance.

2.3. Post-deposition treatment

In order to improve the conductivity of the semi-insulating as-deposited amorphous Sb_2S_3 films, they were immersed in aqueous AgNO_3 solution containing 0.3 g AgNO_3 in 50 ml distilled water for a variable time and at different temperatures, to allow ion exchange between Sb^{3+} and Ag^+ . In this way, Ag^+ was implanted into Sb_2S_3 , resulting in Ag-doped Sb_2S_3 films of suitable conductivity for opto-electronic applications.

3. Results

The deposited film material was identified by X-ray diffractometry. A 0.3 μm thick film deposited on glass was annealed in air, at 170°C for 6 h and an X-ray diffractograph (XRD) using nickel filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.54050 \times 10^{-10}$ m) was taken (Fig. 1). The XRD shows that a crystallization process has begun within the amorphous material. The labeled peaks in the XRD were compared against the standard JCPDS powder diffraction data set #42-1393 for Sb_2S_3

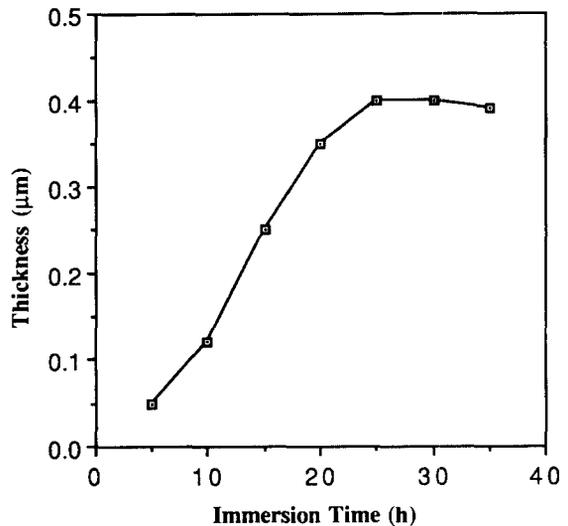


Fig. 2. Film thickness as a function of immersion time.

from the 1-42 Database. The crystallized material is thus identified as orthorhombic Sb_2S_3 .

The thicknesses of the films were determined by ellipsometry and found to be between 0.05 and 0.4 μm , depending on the immersion time. A plot of the thickness of Sb_2S_3 films as a function of the immersion time is shown in Fig. 2. Under the experimental conditions described above, a terminal thickness of about 0.4 μm was reached after 24 h immersion time from a single bath. Thicker

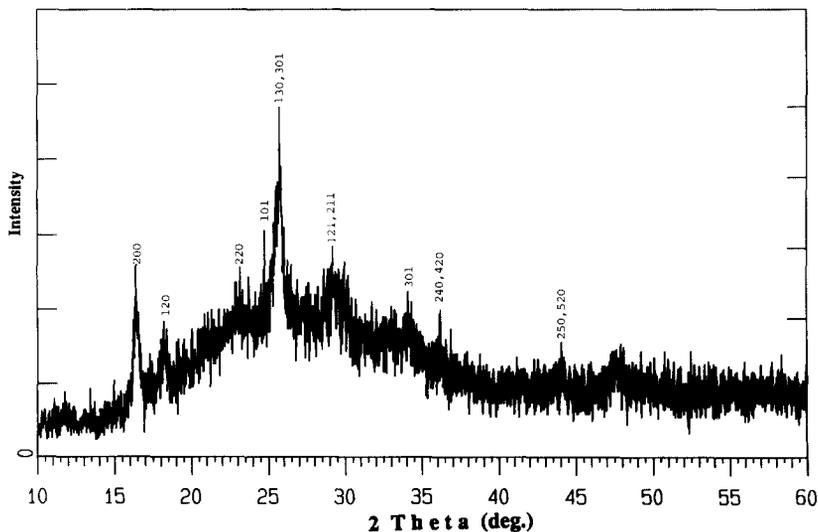


Fig. 1. X-ray diffractograph of a 0.3 μm thick Sb_2S_3 film on glass substrate. The film was annealed in air for 6 h at 170°C.

films can be deposited by re-immersing the films into a fresh bath.

The optical characteristics of both the as-deposited and annealed films were studied by spectrophotometers (Cary 5 and a CP6-300 Pye Unicam) in the spectral interval between 300 and 2500 nm wavelength. The transmission spectra of a 0.3 μm thick film prior to and after annealing are shown in Fig. 3. The anneal was carried out in air, for 6 h at 170°C.

The band-gap energy of the as-deposited Sb_2S_3 amorphous films was found to be 2.48 ± 0.02 eV (see Fig. 4, curve 1). The plot for determination of the band gap energy for the annealed, partially crystallized films, is shown in Fig. 4, curve 2. Two straight lines can be drawn, giving band-gap energies of 2.05 ± 0.05 and 1.76 ± 0.02 eV.

No photoconductivity was observed in the as-deposited amorphous films. On the other hand, the annealed films were photoconductive, and a plot of the spectral sensitivity is presented in Fig. 5. Two maxima were observed, corresponding to 2.11 ± 0.03 and 1.85 ± 0.03 eV, respectively.

The sheet resistances of the films were determined by an electrometer (Keithley 616). As-deposited 0.3 μm thick amorphous films exhibited sheet resistances of the order of 10^{12} Ω /square, while the same films, after annealing for 6 h at 170°C, had sheet resistances of the order of 10^{10} Ω /square. Thermoelectric probe measurements with both film materials showed negative thermopower, indicating that Sb_2S_3 exhibits n-type

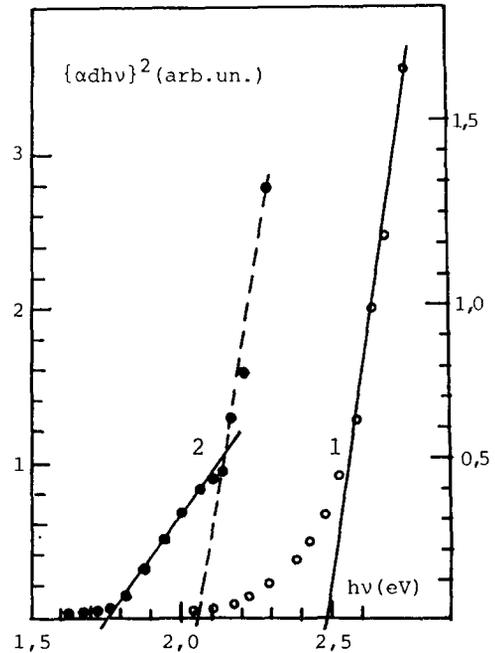


Fig. 4. Graphical determination of the optical band-gap energies for Sb_2S_3 films: 1, before annealing; 2, after annealing in air for 6 h at 170°C.

conductivity [16]. The sheet resistances of the as-deposited and then Ag-doped films are presented in Table 1.

The temperature dependence of the dark resistance was measured in the temperature interval 300 to 600 K. The linear plots of $\ln R$ vs. $1/T$ are shown in Fig. 6. The activation energies cor-

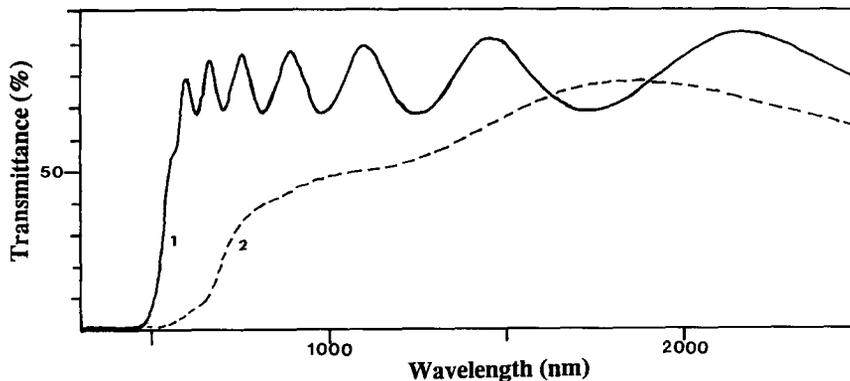


Fig. 3. Optical transmission spectra of a 0.3 μm thick Sb_2S_3 film: 1, before annealing; 2, after annealing in air for 6 h at 170°C.

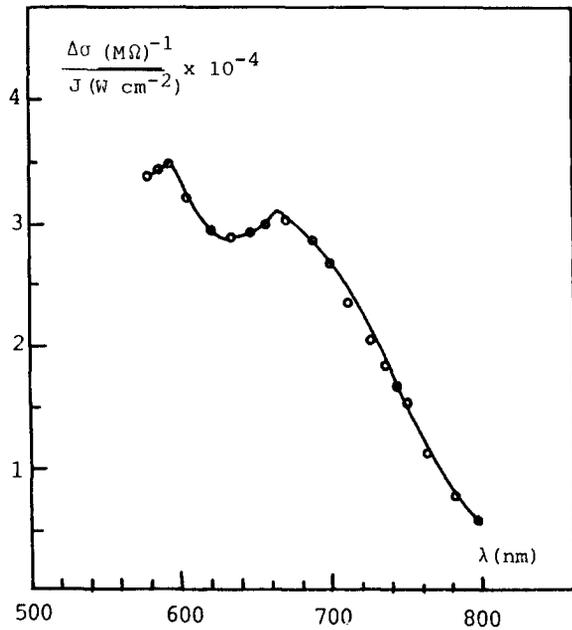


Fig. 5. Spectral sensitivity of the photoconductivity response for Sb_2S_3 films annealed in air for 6 h at $170^\circ C$.

Table 1
Post-deposition Ag-doping of as-deposited Sb_2S_3 films, to increase conductivity

Temperature ($^\circ C$)	Dip time (h)	Sheet resistance ($M\Omega$ /square)	Film thickness (μm)
20	0.0	10^6	0.22
	24	50	
	48	30	
50	0.25	500	0.24
	0.50	100	
	20	30	
75	0.25	100	0.23
	0.5	50	
	2.0	30	

responding to slopes 1 and 2 in Fig. 6 are 1.76 ± 0.03 and 1.54 ± 0.03 eV, respectively, for the as-deposited and annealed films.

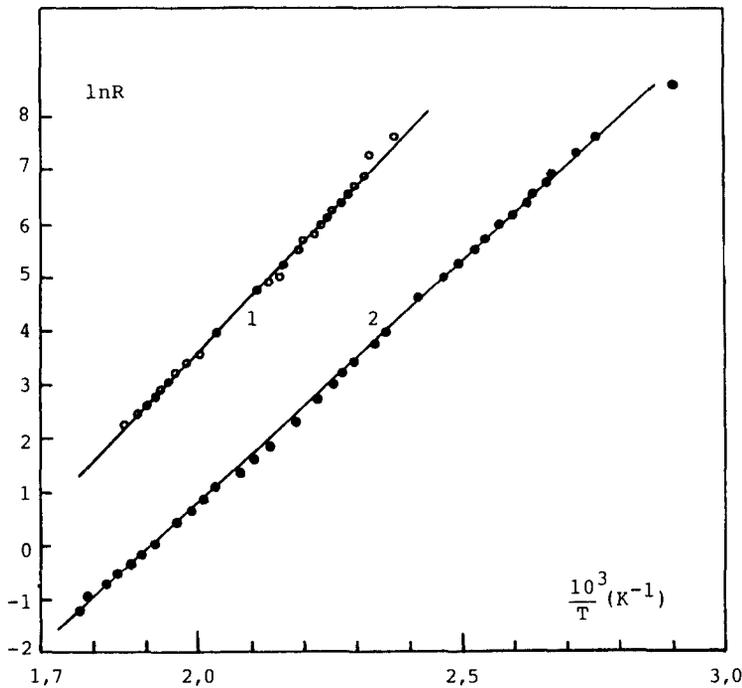


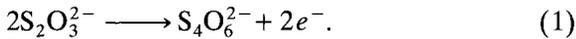
Fig. 6. Temperature dependence of the resistivity for a $0.3 \mu m$ thick Sb_2S_3 film: 1, before annealing; 2, after annealing in air for 6 h at $170^\circ C$.

4. Discussion

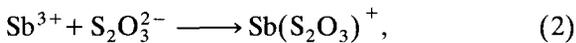
4.1. Chemical considerations

The deposition technique presented in this paper is based on hydrolytic decomposition of antimony(III) thiosulfate compounds formed in aqueous media. In fact, three characteristics of the thiosulfate ions were employed in this technique.

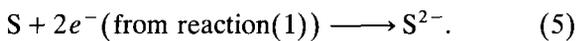
(1) The reducing ability of the thiosulfate ions, represented by the following half-cell reaction:



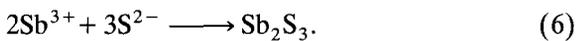
(2) The complexing ability of the thiosulfate ions, whereby successive antimony–thiosulfate complexes are formed in excess of the complexing ions, giving clear solutions:



(3) The ability of the thiosulfate ions to gradually release sulfide ions upon hydrolytic decomposition, in acidic media:



These sulfide ions then combine with the antimony(III) ions released from the thiosulfate complexes, upon hydrolysis, precipitating the amorphous, yellow–orange Sb_2S_3 :



The chemical bath described in the Experimental section was found to be optimal. At higher concentrations of the reactants (antimony(III) chloride and sodium thiosulfate), non-uniform films were produced and often peeled off the substrate upon rinsing with distilled water. A pH of ~ 3 was also experimentally established as the optimal pH. For $\text{pH} \leq 2.5$, adhesion is poor or altogether absent. At $\text{pH} \geq 4.0$, the solution turns turbid to milky, due to precipitation of antimony basic salts. If the bath parameters as described in the Experimental section are followed, the pH of the bath should be ~ 3 and no further adjustments are necessary. Excess use of glacial acetic

acid to dissolve SbCl_3 results in poor adhesion of the material to the substrate.

The optimal temperature for the chemical bath was found to be in the range $10\text{--}15^\circ\text{C}$. At lower temperatures, the hydrolytic decomposition of the antimony thiosulfate complexes slows, resulting in prolonged film formation. At temperatures $> 20^\circ\text{C}$, immediate precipitation of Sb_2S_3 occurs upon mixing of the bath components and no film deposition onto the substrates takes place.

4.2. Optical and electrical considerations

The optical transmission spectra (see Fig. 3) show that as-deposited Sb_2S_3 films exhibit a sharp absorption edge at ~ 500 nm wavelength. After annealing in air for 6 h at 170°C , the absorption edge shifts towards higher wavelengths, becoming less defined and less transparent throughout the visible–near infrared region.

Absorptivities of the films were fitted to the relation

$$\alpha(\nu)h\nu = \text{const.}(h\nu - E_g)^n, \quad (7)$$

where α is the absorption coefficient, h is Planck's constant, ν is frequency and E_g is the band-gap energy of the corresponding material. For direct transitions, $n = 1/2$ or $3/2$, depending on whether the transitions are allowed or forbidden. For indirect transitions, $n = 2$ for allowed transitions and 3 for forbidden [17]. We found that, for both the as-deposited and annealed films, $n = 1/2$, unlike in Ref. [8] where $n = 2$. It follows that in the spectral range close to the absorption edge, a plot of $(\alpha h\nu)^2$ vs. $h\nu$ should result in a straight line intercepting the abscissa at $h\nu = E_g$. This exponent (1/2) indicates that the deposited material is an amorphous semiconductor with allowed direct band-to-band transitions. There are earlier reports in literature [7,18] of a series of values for the energy gap of 1.88, 2.68, 2.88, 3.48, 3.86 and 5.25 eV for the crystalline phase of Sb_2S_3 . In our case, we believe that the different values of the energy gap are due to an amorphous–polycrystalline mixture within the annealed samples. For the same reason, we believe, two maxima were observed with our samples in

the spectral photosensitivity measurements (see Fig. 5), while Nayak et al. [8] report only one peak at 1.7 eV for crystalline Sb_2S_3 films prepared by the ‘dip–dry’ technique.

The thermal energy-gap values of 1.76 and 1.54 eV obtained for our as-deposited and annealed Sb_2S_3 films (shown in Fig. 6) are lower than the corresponding optically determined values. It is possible that the variety of band-gaps we observed are due to the different techniques employed for their determination, as well as to the variable amorphous to crystalline phase ratios in the samples.

Based on the sheet resistance of the amorphous Sb_2S_3 films, of the order of 10^{12} Ω /square for film thicknesses ~ 0.1 – 0.4 μm , we classify the material as a semi-insulator. After an anneal in air for 6 h at 170°C or 3 h at 220°C , the sheet resistance decreased for two orders of magnitude. In similar chalcogenides, such as Bi_2S_3 , for example, a similar change of two to three orders of magnitude was observed upon annealing amorphous films [13].

The resistivity of the Sb_2S_3 films being in the order of 10^5 – 10^3 Ω cm is very high for solar cells and other opto-electronic applications. Preliminary experiments with the purpose of increasing conductivity with Sb_2S_3 show that post-deposition immersion of the Sb_2S_3 amorphous films in aqueous solution of AgNO_3 increases the conductivity of the films by orders of magnitude. Ag^+ ions exchange with Sb^{3+} ions, displacing them in Sb_2S_3 and thus make the material more conductive. However, a saturation seems to occur as the sheet resistance drops to about 30 $\text{M}\Omega$ /square (see Table 1). These conductive Sb_2S_3 films can be used for solar cells and other opto-electronic applications. A slight change in color was also observed with the Ag^+ -doped films, as they changed from yellow–orange to orange–brown in appearance.

5. Conclusions

A simple solution-growth technique for fabricating amorphous Sb_2S_3 films on glass or transparent polymer substrates at room temperature

has been developed. The technique described in this paper proved that it was possible to choose an appropriate single chemical agent which would play the double role of a complexing agent and a sulfide generating agent. Sodium thiosulfate was found to be the ideal choice. Sb_2S_3 thin films were deposited from an aqueous chemical bath of just two components: SbCl_3 and $\text{Na}_2\text{S}_2\text{O}_3$. The technique is based on hydrolytic decomposition of antimony thiosulfate compounds in aqueous solutions. It was also shown that a substantial increase of conductivity can be achieved with the as-deposited Sb_2S_3 films by post-deposition treatment in aqueous AgNO_3 solutions. Annealing of the as-deposited films at 170°C for up to 6 h in air resulted in partial crystallization of the amorphous films, as confirmed by X-ray studies.

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