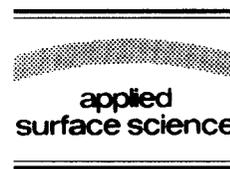




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Solution growth and characterization of silver sulfide films

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Abstract

Silver sulfide (Ag_2S) thin films were grown by an electroless chemical deposition technique at 50°C and $\text{pH} = 10$. Silver ions were first complexed by ammonia, and then sodium thiosulfate solution was introduced. Upon hydrolytic decomposition, uniform thin silver sulfide films were grown on either glass or polyester substrates. X-ray studies confirmed that the deposited material was Ag_2S . Optical studies were carried out in the spectral region $0.3\text{--}2.5\ \mu\text{m}$. The absorption coefficient of the films was found to decrease with increasing wavelength, which makes the Ag_2S films suitable as IR detectors. The optical band-gap energy of the films was found to be $2.2\ \text{eV}$. The resistivity was $14\text{--}20\ \Omega \cdot \text{m}$, and the films were of p-type.

1. Introduction

Thin-film technology continues to attract the interest of scientists. As new device applications are being discovered, the study of thin-film materials is greatly arousing the interest of material scientists. A great number of semiconducting, metallic or insulating thin films have already found applications in industry, medical science, space science, etc. Inexpensive and pollution-free techniques are becoming an imperative in today's fabrication of thin films and related devices. At present, a wide variety of thin-film deposition techniques are in use, broadly classified as Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), Electro-Chemical Deposition (ECD), electroless or solution growth techniques.

The latter is generally considered to be the least expensive, as it requires no special equipment.

This paper reports a simple solution growth technique for fabrication of silver sulfide (Ag_2S) thin films, as well as a basic characterization of the as-deposited material. The chemicals used for the bath are inexpensive, and the precipitate is silver sulfide of high purity, which could further be used wherever this bulk material is in use, e.g., ion-selective electrodes, infrared detectors, etc.

Silver sulfide is known to be a mixed ionic–electronic conductor [1,2]. The two common forms of silver sulfide are the low-temperature α phase, which is monoclinic (P21/c) and the high-temperature β phase, which is cubic (1m3m). The transformation temperature is about 177°C . Both phases are mixed conductors and exhibit nonstoichiometry on the order of 10^{-5} for the α phase and 10^{-3} for the β phase [3]. Silver sulfide, as well as other silver chalcogenides are good prospective photoelectric and thermoelectric materials. Ag_2S and Ag_2Se have been

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used in IR detectors, photoconductors, photovoltaic cells, electrochemical storage cells, etc. [4,5]. The superionic conductivity in α -Ag₂S has also been well studied [6], as well as its photovoltaic and photoconductive properties [4,7].

Thin films of Ag₂S have been deposited by Mangalam et al. [8] at pH = 8–10 using thiourea as a sulfur source, also by Dhumhure and Lokhande in acidic medium using thioacetamide as a sulfur source [9]. In yet another report [10], Ag₂S films have been deposited by successive immersion in silver thiosulfate complex solution and then in hot thiourea at pH = 8–11.

This work presents a simple solution growth technique for fabrication of silver sulfide thin films with the use of common and inexpensive chemicals for the bath. Silver ions are introduced into a sodium thiosulfate bath in the form of diammino complex. The silver–thiosulfate system was studied in more detail with respect to thin-film formation and optimal growth conditions are reported. The basic morphological, optical and electrical characteristics of the films are also reported.

2. Experimental details

2.1. Substrate preparation

Standard microscope glass slides, 75 mm × 26 mm × 1 mm or transparent polyester films (commonly used as overhead transparencies) were used as substrates. Due to poor adhesion of the silver sulfide films on untreated substrates, a special pre-treatment of the substrates was undertaken to ensure uniformity and good adhesion. The glass substrates were first treated with chromic acid overnight and washed with distilled water. Then the glass slides were soaked in 0.3% aqueous solution of SnCl₂ for 10 min, rinsed with distilled water and dried in air. In addition, the treated glass slides were annealed at 220–250°C for 20 min and cooled to room temperature before use. Annealing of the SnCl₂-treated glass substrates creates an ultra-thin layer of SnO₂ on the substrate surface, which proved to be an excellent solution to the problem of poor adherence. The polyester substrates were first treated in diluted chromic acid for 1

h, washed with distilled water and soaked in 0.3% SnCl₂ for 10 min, rinsed with distilled water and dried in air before use. In this case an ultra-thin layer of Sn(OH)₂ is created on the substrate surface, which also initiates good adherence.

2.2. Film deposition and characterization

Typically, 0.85 g AgNO₃ (~0.05 mol) were placed in a 100 cm³ beaker and dissolved in a little distilled water. Then ammonium hydroxide (NH₄OH, 1 : 1) was gradually added with constant stirring, just until the forming precipitate dissolved. At that point, sodium thiosulfate was introduced into the beaker and the rest distilled water to make a total volume of 80 cm³. The amount of sodium thiosulfate was varied in such a way as to match molar ratios of silver to thiosulfate 1 : 1, 1 : 2 and 1 : 3. In this way, the role of thiosulfate as a sulfur-generating agent was studied. The substrates were vertically supported against the walls of the beaker and the bath was brought and kept at 50°C on a hot plate with magnetic stirrer. Films of Ag₂S were grown in these baths for a period of time up to 45 min, both with and without stirring.

The as-deposited films were immersed in distilled water for 10 min, dried in air and preserved for further investigation.

The deposited material was identified by X-ray diffractometry, employing nickel-filtered Cu K α radiation ($\lambda = 1.54050 \times 10^{-10}$ m), on a JEOL Model JDX Diffractometer. The surface morphology of the films was studied by a Scanning Electron Microscope (SEM), on a JEOL S840. Optical transmission and absorption spectra were taken on a CARY 5 UV–VIS–NIR spectrophotometer in the spectral range 0.3–2.5 μ m. The sheet resistance of the films was measured between two gold-pasted electrodes, 1 cm in length and 1 cm apart. Resistivity was then calculated taking into account the film thickness. The film thickness was determined by weighing equally colored parts and assuming the same density as that of bulk silver sulfide (7.3 g cm⁻³). The gravimetric way of determining the thickness was found satisfactory after a comparison against ellipsometric determinations performed on several samples of Ag₂S films. The observed differences were within 10%.

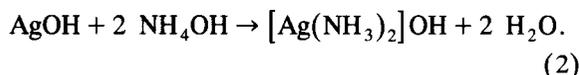
3. Results and discussion

3.1. The chemistry of the technique

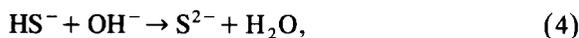
The following chemical processes are considered to take place in the deposition of the silver sulfide films. First, silver ions are complexed by NH_4OH , as follows:



in excess of NH_4OH :



As the amino complex undergoes thermal decomposition, Ag^+ ions are being released in the bath. At the same time, the thiosulfate ions undergo hydrolytic decomposition, releasing sulfide ions in basic media, according to:



The silver ions then combine with the sulfide ions to give Ag_2S :



The solubility product of silver sulfide is 1.6×10^{-49} [11] and its ionic product in the solutions employed in this work greatly exceeds this value, satisfying the condition for precipitation of Ag_2S .

3.2. Optimal growth conditions

The growth of silver sulfide films was studied at $\text{pH} = 10$ and $t = 50^\circ\text{C}$ with variable concentrations of thiosulfate with or without stirring. At lower pH values the growth is slow, while at higher pH values non-uniform films are grown. The chemical processes involved are substantially slower at room temperature and film deposition can take up to 24 h. A growth temperature of $45\text{--}50^\circ\text{C}$ was found to be optimal and films with thicknesses up to $0.2 \mu\text{m}$ could be deposited from a single bath in about 35 min. Thicker films can be obtained, if necessary, by re-introducing the initially deposited films into a fresh bath. Molar ratios of silver to thiosulfate of 1:3 or higher thiosulfate lead eventually to no pre-

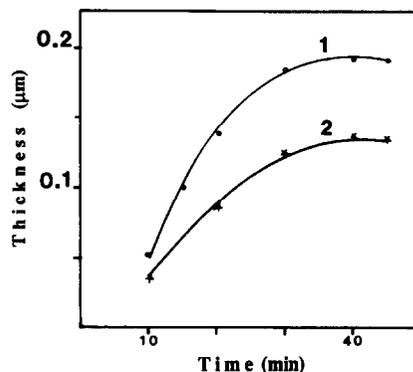


Fig. 1. Film thickness for Ag_2S as a function of deposition time: (1) 1:1, (2) 1:2 silver-to-thiosulfate molar ratio.

cipitation at all. The most probable reason for this is the complexation of Ag^+ ions by thiosulfate. It is known that silver ions form a complex compound with thiosulfate, $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$, with an instability constant $\text{pK} = 13.60$ [12]. And since thiosulfate in this case is present in excess, it is reasonable to assume that all silver ions are complexed by it. Eventually, this complex does not decompose under the experimental conditions employed in this work. It was observed, however, that upon boiling, some Ag_2S precipitates from these baths, but no films could be produced. Films were grown successfully at molar ratios 1:1 and 1:2 and the dependence of terminal film thickness versus deposition time for these ratios is shown in Fig. 1. Since best results were achieved at silver to thiosulfate molar ratio 1:1, films examined in this work were grown from this bath. Stirring was found to have little effect on the film growth. Slightly less uniform, i.e., unequally colored films were produced when stirring was not applied. The films used for characterization of physical properties were obtained with stirring of the baths.

3.3. Physical properties of the films

Identification of the deposited film material was done by X-ray diffractometry (XRD). For this purpose, a Ag_2S film was annealed for 3 h at 150°C and an XRD pattern was recorded (see Fig. 2). After comparison of the obtained XRD against the standard JCPDS-ICDD files from PDF-2 Sets 1–42

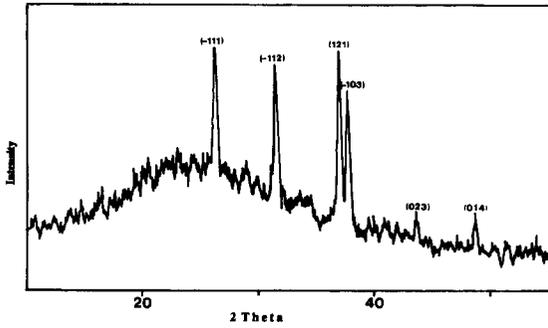


Fig. 2. X-ray diffraction pattern of a Ag_2S thin film, annealed for 3 h at 150°C .

Database, it was found to match with the standard XRD file #14-72 of synthetic Ag_2S (the monoclinic aconthite). A SEM micrograph of Ag_2S film on glass substrate was also taken (see Fig. 3). It shows that the substrate is well covered with the deposited material. The randomly protruding nodules observed on the SEM were occurring during the taking of the micrographs. It is possible that the energy applied was initiating these, due to the mixed ionic–electronic nature of the silver sulfide.

Optical studies of the silver sulfide films were carried out in the spectral range $0.3\text{--}2.5\ \mu\text{m}$. Part of the absorption spectrum is shown in Fig. 4, and extrapolation of the absorption edge gives an estimated value for the band-gap energy (E_g) of about

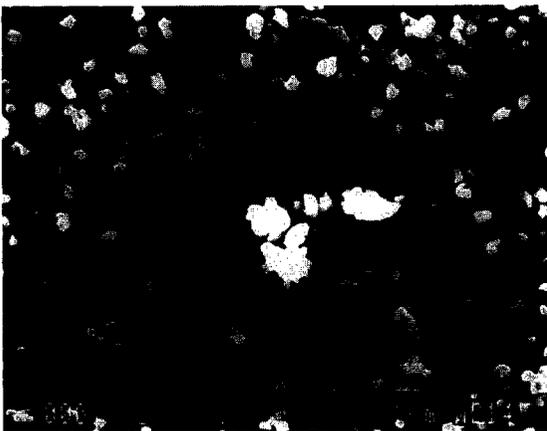


Fig. 3. SEM micrograph of a Ag_2S film on glass substrate. Magnification $10000\times$.

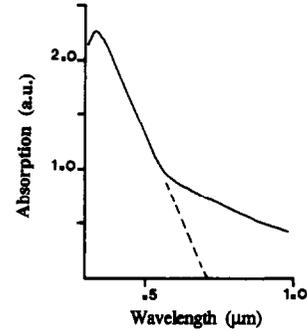


Fig. 4. Absorption optical spectrum of a Ag_2S film and estimated extrapolated E_g value (1.8 eV).

1.8 eV. More often, however, the E_g values are determined by fitting the absorptivities to the relation $\alpha(\nu)h\nu = \text{const.} \times (h\nu - E_g)^n$,

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 [13]. In this work, it was found that the best fit for the deposited Ag_2S films is obtained for $n = 1/2$. It follows that in the spectral range close to the absorption edge, a plot of $(\alpha h\nu)^2$ versus $h\nu$

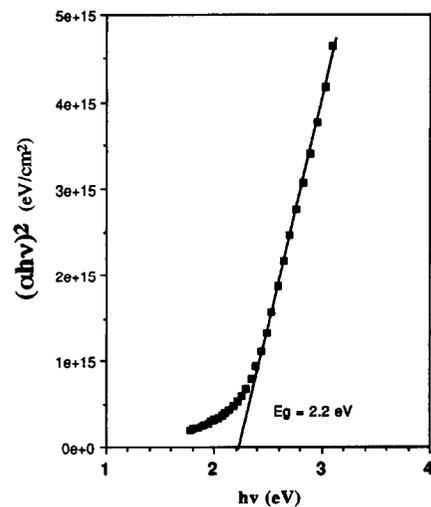


Fig. 5. Graphical determination of band-gap energy for Ag_2S films.

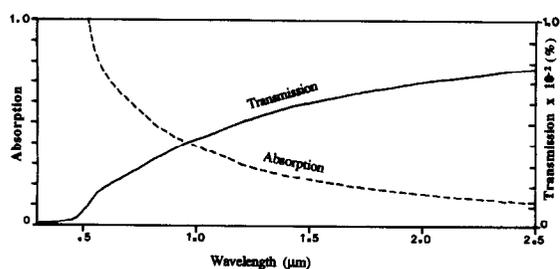


Fig. 6. Optical absorption and transmission spectrum of a Ag_2S film.

should result in a straight line intercepting the abscissa at $h\nu = E_g$. This exponent (1/2) indicates that the deposited material is a semiconductor with allowed direct band-to-band transitions. The E_g value for the Ag_2S deposited in this work, was found to be 2.2 eV, as shown in Fig. 5. A similar value of 2.3 eV has been found in another report [14] where Ag_2S films were chemically deposited from thiourea baths. Compared to the indirect band gap of 1.3 eV for bulk Ag_2S , these two values (e.g., 2.2 and 2.3 eV) for solution-grown Ag_2S thin films are significantly different, which may be due to the presence of amorphous phase, due to low-temperature depositions in both cases. It is also noteworthy that similar disparities have been found in chemically deposited Sb_2S_3 [15] and Cu_xS films [16].

Fig. 6 shows both the transmission and the absorption spectrum of silver sulfide films in the spectral range 0.3–2.5 μm . The terminal cross-over point for absorption and transmission is observed at 0.95 μm wavelength. It is also noteworthy that the absorption coefficient of the Ag_2S films increases continually from the near-infrared towards the visible region, which makes this material suitable for use in infrared detectors [4,5].

The electrical resistivity of the films was found to be 14–20 $\Omega \cdot \text{m}$, and the thermo-EMF polarity shows that the material has p-type conductivity.

4. Conclusions

Silver sulfide (Ag_2S) films were deposited on glass substrate or on polyester films by a simple

electroless chemical deposition technique. The silver ions were introduced in a thiosulfate bath in the form of its diammino complex. Uniform and specularly reflecting films were successfully deposited from baths in which the molar ratios of thiosulfate to silver did not exceed 2:1. The technique described here is convenient for both small- and large-area depositions and is virtually non-pollutive.

Acknowledgments

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