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CHARACTERIZATION OF CHEMICALLY-DEPOSITED SILVER SULFIDE THIN FILMS

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Ag_2S thin films have been deposited onto fluorinated tin oxide (FTO)-coated conducting glass substrates using chemical bath deposition (CBD) method. Photoelectrochemical (PEC) cell, optical properties, surface morphology, structural properties, compositional analysis and electrical properties of Ag_2S thin films have been investigated. The PEC measurements indicate that the deposited Ag_2S layers are n-type in electrical conduction. The transmittance of deposited layer is obtained to be about 13–87%. The absorbance of the films is found to decrease with increasing wavelength. The band gap of the Ag_2S thin film is estimated to be 1.8 eV. It is observed from scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements that the substrates are well-covered with the deposited Ag_2S layers without cracks and pinholes. The grain size of Ag_2S thin films is estimated from SEM measurements to be in the range 100–210 nm. The mean roughness of Ag_2S films is found from AFM measurements to be in the range 7.20–15 nm. X-ray diffraction shows that the films are well-crystallized and the deposited layers are mainly consisting of Ag_2S phase with (-103) preferential plane. EDX analysis shows that a nearly stoichiometric composition of Ag_2S is obtained. The resistivity is estimated to be in the range 3.5–7.0 Ω-cm.

Keywords: Thin film; chemical bath deposition; silver sulfide.

1. Introduction

Metal chalcogenides have been studied intensively over the past three decades in view of their actual and potential applications. Considerable work has been done on the photovoltaic[1] and photoconducting[2] properties of silver sulfide thin films. In the visible and near IR region, Ag_2S barrier layers are used as detectors. Recently, the use of Ag_2S in the electrochemical photovoltaic (ECPV) storage cells as a storage

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electrode has created much interest as the current storage efficiency of Ag/Ag_2S couple is about 90%.[3,4]

Preparation of Ag_2S films has been carried out by a number of chemical methods. Dhumure and Lokhande have reported the chemical deposition of Ag_2S films from acidic solutions containing thioacetamide and thiosulphate.[5–8] Thin films of Ag_2S have been deposited by Mangalam *et al.* at $pH = 8 - 10$ using thiourea as a sulfur source.[2] Ristova and Toshev deposited Ag_2S films by successive immersion in silver thiosulfate complex solution and then in hot thiourea at $pH = 8 - 11$.[9]

This paper reports a study of silver sulfide (Ag_2S) thin films on flourinated tin oxide (FTO)-coated conducting glass substrates by chemical bath deposition (CBD) technique using sodium thiosulfate and silver nitrate as sulfur and silver sources, respectively.

2. Experimental Details

2.1. *Substrate preparation*

The FTO-coated conducting glass substrates having sheet resistance 7 ohm per square area were used as substrates to deposit Ag_2S films. Due to poor adhesion of silver sulfide films on untreated substrates, a special pre-treatment of the substrates was undertaken to ensure uniformity and good adhesion. The substrates were first treated with chromic acid overnight and washed with distilled water. Then the substrates were soaked in 0.3% aqueous solution of $SnCl_2$ for about 10 min, rinsed with distilled water and dried in air. In addition, the treated glass slides were annealed at 220–250°C for about 20 min and cooled to room temperature before use. Annealing of $SnCl_2$– treated glass substrates creates an ultra-thin layer of SnO_2 on the substrate surface, which proved to be an excellent solution to the problem of poor adhesion.

2.2. *Film depositions and chemical reaction for CBD technique*

Typically, 0.05 M solution of silver nitrate ($AgNO_3$) was placed in a beaker by dissolving silver nitrate in distilled water. Then ammonium hydroxide (NH_4OH) was gradually added with constant magnetic stirring until the forming precipitate is dissolved. At that point, 0.05 M sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) was introduced into the beaker. The substrates were vertically supported against the walls of the beaker and the bath was kept at 50°C on a hot plate with stirring for about 45 min. Samples were prepared using the above mentioned method at different bath temperatures and pH values with and without stirring. The as-deposited films were immersed in distilled water for 10 min, dried in air and preserved for basic characterizations.

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:

$$AgNO_3 + NH_4OH \rightarrow AgOH + NH_4NO_3\,, \tag{1}$$

In excess of NH_4OH:

$$AgOH + 2\,NH_4OH \rightarrow [Ag(NH_3)_2]OH + 2\,H_2O\,, \tag{2}$$

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

$$S_2O_3^{2-} + OH^- \rightarrow HS^- + SO_4^{2-}\,, \tag{3}$$

$$HS^- + OH^- \rightarrow S^{2-} + H_2O\,, \tag{4}$$

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

$$2Ag^+ + S^{2-} \rightarrow Ag_2S\,, \tag{5}$$

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

2.3. *Film characterization*

Electrical conductivity type of Ag_2S thin films was investigated by photoelectrochemical (PEC) cell method. The optical measurements of Ag_2S thin films were performed using a UV-1201V spectrophotometer (Shimadzu Corp., Japan) in the spectral range 400–1100 nm. The surface morphology of Ag_2S thin films was investigated by scanning electron microscopy (SEM, using S-3400N HITACHI, JAPAN) and by atomic force microscopy (AFM, using a Nanoscope III, Scanning Probe Microscope). The X-ray diffraction (XRD) method was used to investigate the structural properties of the Ag_2S films using a Philips PW 3040 X' Pert PRO XRD system with Cu-K_α radiation using the wavelength of 1.5406 Å, operated at 40 kV and 30 mA. Compositional analysis was performed by energy dispersive X-ray analysis (EDXA) measurements. Electrical properties of the films were performed using four-point probe and two-point probe methods, respectively.

3. Results and Discussion

3.1. *Electrical conductivity type of* Ag_2S *films*

The electrical conductivity type of Ag_2S layers has been measured using photoelectrochemical (PEC) cell method.[11] The Ag_2S/FTO/glass and a carbon rod were partially immersed in a 10% NaCl solution, and these two electrodes were connected to a digital voltmeter. The photovoltage, created with white light illumination, was estimated by measuring the voltage under dark and illuminated conditions. Observation of few millivolts as the open circuit voltage is an indication of the formation of a good Schottky barrier at the solid/liquid junction. The deposited films are observed to be *n*-type in electrical conduction.

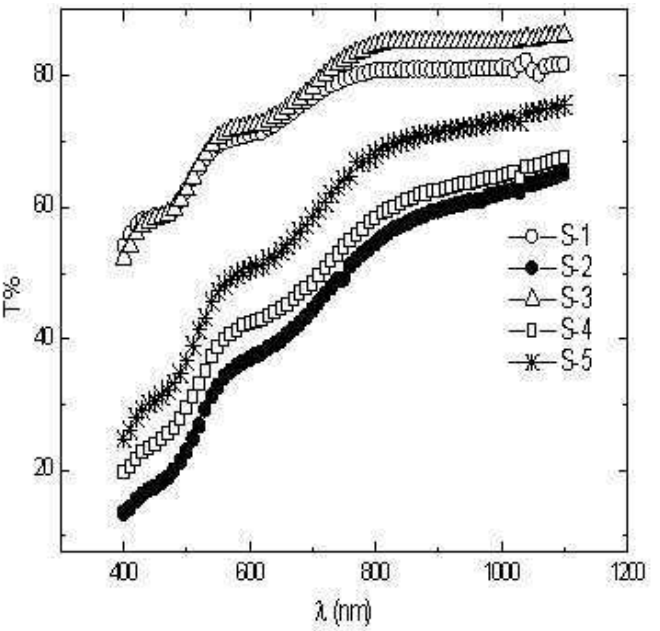

Fig. 1. The optical transmittance spectra of different as-deposited Ag_2S thin films.

3.2. *Optical properties*

3.2.1. *Transmittance measurements*

Figure 1 represents the variation of transmittance $T(\%)$ with wavelength in the spectral range 400–1100 nm of different Ag_2S films prepared at different conditions. Transmittance is obtained to be about 13–87% in the wavelength range 400–1100 nm. The spectra show that the transmittance increases with wavelength, which may be due to absorption by carrier in the degenerate films. In the near infrared region, the transmittance is very high. Therefore, the silver sulfide thin films have very low transmittance, 10–30% in the visible-UV region; low to moderate transmittance, 30–50% in the visible range and moderate to higher transmittance, 50–87% in the visible-infrared region. The behavior of higher transmittance obtained makes the materials suitable as an electro-conductive window coating.

3.2.2. *Absorbance measurements*

The optical absorbance of Ag_2S films was studied in the wavelength range 400–1100 nm. Figure 2 shows the variation of absorbance with wavelength for different as-deposited samples. It is observed that the absorbance 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.[1,4] The films become totally absorbing at $\lambda < 400$ nm.

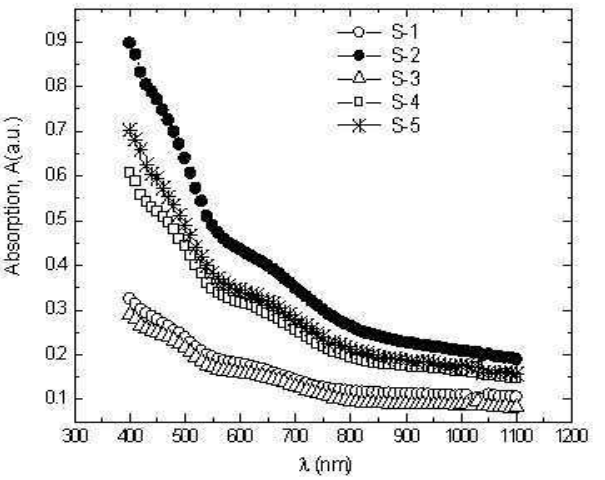

Fig. 2. The optical absorption spectra of different as-deposited Ag_2S thin films.

3.2.3. *Band gap measurements*

The band gap, E_g, for Ag_2S films was determined by plotting (absorbance, A)^2 versus photon energy, $h\nu$ (eV) graphs. Extrapolating the straight-line part of the curve in Fig. 3 to the energy axis, where (absorbance, A)$^2 = 0$, gives the value of band gap, E_g, for the Ag_2S thin films. The band gap for Ag_2S films was found to be 1.8 eV. A value of 2.3 eV has been found in another report,[12] where Ag_2S films were chemically deposited from thiourea baths.

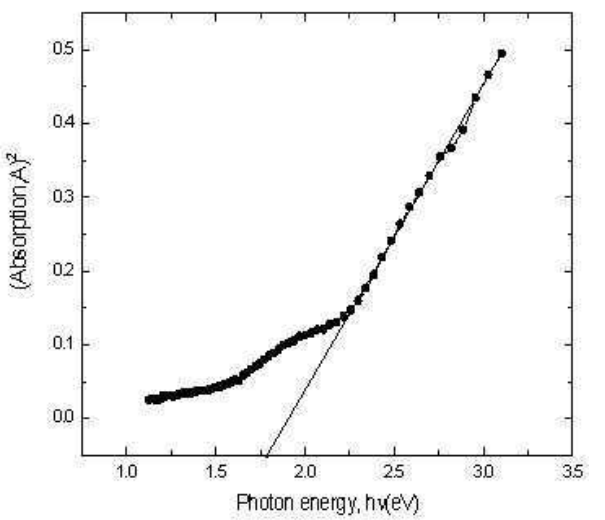

Fig. 3. Estimation of band gap, E_g of as-deposited Ag_2S thin film.

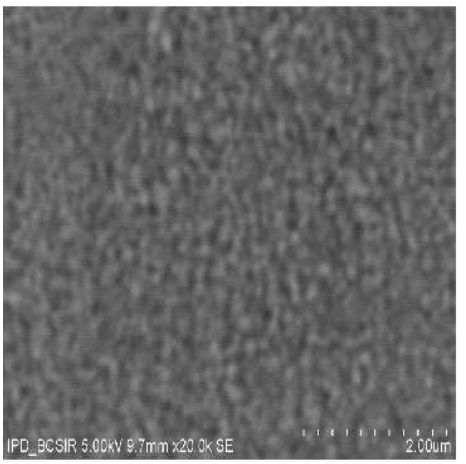

Fig. 4. SEM image of as-deposited Ag_2S thin film. Magnification 20000X.

3.3. *Surface morphology*

3.3.1. *Scanning electron microscopy (SEM)*

Figure 4 shows SEM image of as-deposited silver sulfide (Ag_2S) thin film on FTO-coated glass substrate; it consists of closely packed grains. It shows that the substrate is well-covered with the deposited material without cracks and pinholes. The scanning electron microscopy (SEM) study of Ag_2S films reveals that the films formed are homogeneous and uniform. The grain size of the Ag_2S thin films was observed to be 100–210 nm.

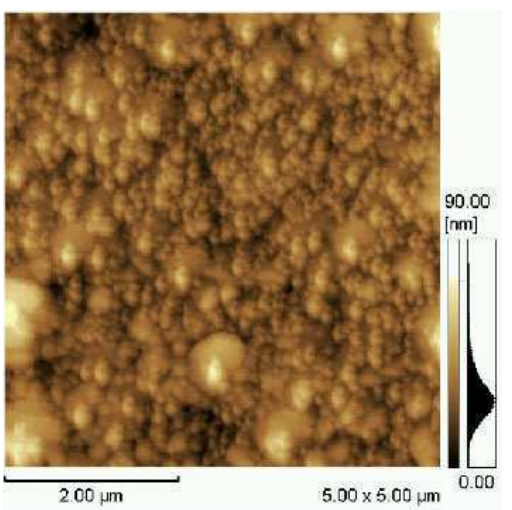

Fig. 5. 2D AFM image of as-deposited silver sulfide thin film with the scan area of 5×5 μm^2.

3.3.2. *Atomic force microscopy (AFM)*

The surface morphology of the silver sulfide (Ag_2S) films deposited onto FTO-coated glass substrate was studied by atomic force microscopy (AFM). Two-dimensional AFM image of as-deposited CBD silver sulfide (Ag_2S) thin film is shown in Fig. 5 for the scan areas of 5×5 μm^2. It seems that the overall film surface is almost smooth. The mean roughness of Ag_2S film was observed to be 7.2–15 nm.

3.4. *Structural properties*

The X-ray diffraction (XRD) method was used to investigate the structural properties of Ag_2S films. Figure 6 shows the X-ray diffraction pattern of Ag_2S thin films after annealing at 175°C for about an hour. Several well-defined peaks are observed in the XRD pattern. The observed peak positions are due to reflection from (111), (012), ($\bar{1}$12), ($\bar{1}$03), (040) and ($\bar{1}$05).[13,14] ($\bar{1}$03) plane becomes very strong and the full width at half-maximum (FWHM) becomes very small showing a good crystalline state of the film.[14] The X-ray diffraction parameters for Ag_2S films are given in Table 1.

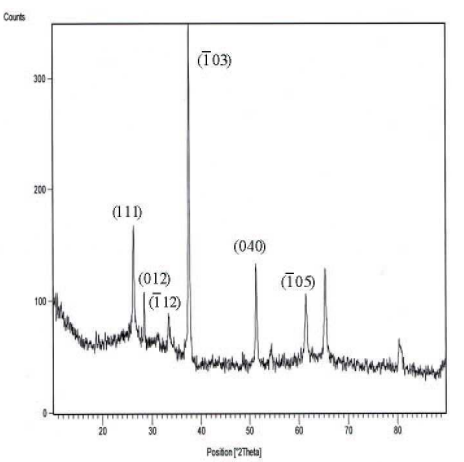

Fig. 6. X-ray diffraction pattern of Ag_2S thin film, annealed for 1 h at 175°C.

Table 1. X-ray diffraction parameters of Ag_2S thin films.

Angle (2θ)	d-spacing (Å)	Planes (hkl)	FWHM	Relative Intensity (%)
26.32	3.386	111	0.276	33.96
28.45	3.137	012	0.157	14.61
33.48	2.677	$\bar{1}$12	0.472	8.27
37.58	2.393	$\bar{1}$03	0.256	100
54.27	1.690	040	0.945	3.35
61.48	1.508	$\bar{1}$05	0.394	17.76

Table 2. EDX analysis of Ag_2S films.

Elements	Atom (%)
Ag	67.98
S	32.02

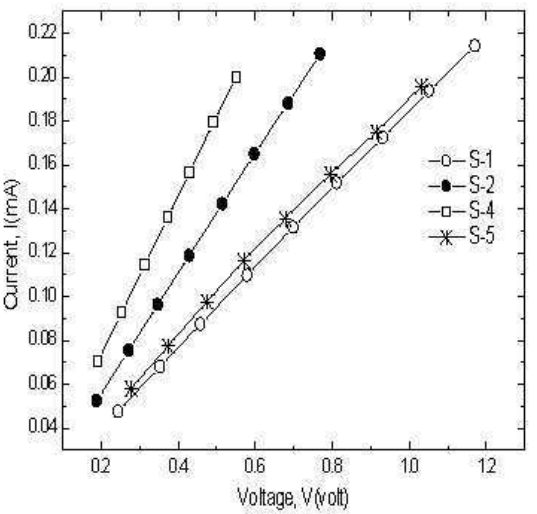

Fig. 7. I–V characteristic curve for different as-deposited samples.

3.5. *Energy dispersive X-ray analysis (EDXA) study*

EDXA study is carried out on Ag_2S thin films deposited on FTO-coated glass substrate for annealed samples at 175°C and results are presented in Table 2. For each sample, the atomic percentage of Ag and S elements is an average, which was taken in several zones of the material. It is obvious from these results that Ag_2S thin film has been grown with stoichiometric composition.

3.6. *Electrical properties*

3.6.1. *Resistivity measurement*

Four-point probe method is used to determine the resistivity of Ag_2S films. Figure 7 shows the I–V characteristic curves for different as-deposited samples. The I–V characteristics have been studied over the range of applied voltage (1–5 volt). The corresponding voltage drop, V, and current, I, across the sample was calculated. All the samples show the ohmic behavior in the measured voltages. Resistivity of Ag_2S films was observed from I–V data. All the samples show resistivity lying in the range 3.5–7.0 Ω-cm.

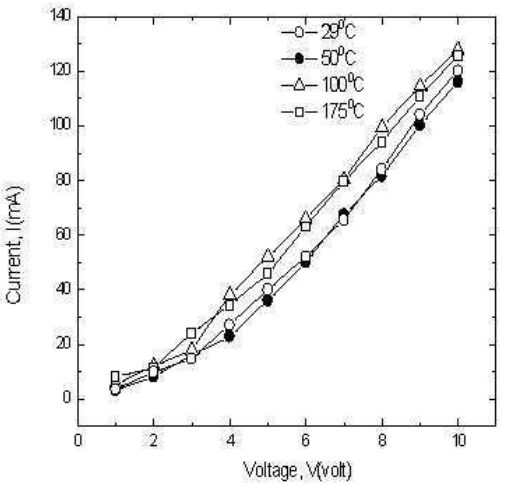

Fig. 8. The temperature dependent I–V characteristic curve following two-point probe method.

3.6.2. *Temperature dependent resistivity measurement*

The temperature dependent resistivity following I–V characteristic curve of the Ag_2S films was investigated using the two-point probe method. Since the resistivity depends only on the value of V/I obtained from the I–V characteristic curve for finite geometry of a given sample, we can conclude from the Fig. 8 that the resistivity decreases as the temperature increases for the Ag_2S thin films.

4. Conclusion

Good quality thin films of silver sulfide are deposited using low cost CBD technique. Sodium thiosulfate is used as a source of sulfide ions, and silver nitrate as a source of silver ions and NH_4OH was added to fix the pH of the solution. The grown Ag_2S films are observed to be *n*-type in electrical conduction. Transmittance is obtained to be about 13–87% in the wavelength range 400–1100 nm. The increases of transmittance with wavelength may be due to absorption by carrier in the degenerate films. The absorbance of the Ag_2S films increases continually from the near-infrared towards the visible region. The band gap of the Ag_2S thin films is found to be 1.8 eV. It is observed from SEM and AFM measurements that the substrates are well-covered with the deposited Ag_2S material without cracks and pinholes. The grain size of the Ag_2S films is observed to be 100–210 nm. The mean surface roughness of the Ag_2S film is observed to be 7.2–15 nm. The XRD analysis shows that the preferential plane of Ag_2S film is (-103) and stoichiometric Ag_2S film is deposited onto FTO-coated substrate. EDX analysis shows that Ag_2S thin films prepared has a nearly stoichiometric composition. The resistivity is estimated to be in the range 3.5–7.0 Ω-cm and the resistivity decreases as the temperature increases for Ag_2S thin films.

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