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Studies on Characterization of Nanocrystalline Silver Sulphide Thin Films Deposited by Chemical Bath Deposition (CBD) and Successive Ionic Layer Adsorption and Reaction (SILAR) method

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ABSTRACT

Nanocrystalline Silver Sulphide thin films were deposited at room temperature on glass substrate by two techniques: Chemical Bath Deposition (CBD) and Successive Ionic Layer Adsorption and Reaction (SILAR) technique. Silver nitrate and thiourea were used as basic precursors in both cases. The films were characterized by X-ray diffraction, scanning electron microscope and optical absorption measurements. X-ray diffraction patterns showed that both the films, as prepared, are of monoclinic (acanthite) structure with composition Ag_2S. The average crystallite size of the films prepared by CBD and SILAR technique is found to be 25.61 nm and 21.38 nm, respectively. The optical properties were studied by measuring the absorption spectra. The band gap is 1.78 eV and 2.09 eV for the nanocrystalline Ag_2S thin films prepared by CBD and SILAR technique respectively. It is observed from scanning electron microscopy (SEM) that the substrates are well-covered with the deposited Ag_2S layers without cracks and pinholes.

Keywords: Thin films, Chemical bath deposition, X-Ray diffraction, Optical Properties.

INTRODUCTION

In recent years, metal chalcogenide semiconducting thin films have received much attention due to their world-wide applications in various fields of science and technology [1]. Silver sulphide Ag_2S is an important chalcogenide compound which has been investigated for its numerous applications. Silver sulphide (Ag_2S) belongs to I–VI compound semiconductor materials with monoclinic crystal structure. The semiconductor silver sulfide has promising photoelectric and

thermoelectric properties [2, 3]. Silver sulphides (Ag_2S) have been used in IR detectors [4], photoconductors, photovoltaic cells, electrochemical storage cells [5, 6], etc. It is also well known as a mixed ionic and electronic conductor at high temperatures above 200^oC [7]. Considerable efforts on synthesis and properties characterization of silver sulphide have being done and their potential application areas have being developed. Various techniques such as chemical bath deposition (CBD) [8, 9], spray pyrolysis deposition (SPD) [10], successive ionic layer adsorption and reaction (SILAR) [11], molecular beam epitaxy (MBE) [12], thermal evaporation [13], sol-gel and ion implantation techniques[14], gamma irradiation [16] etc. have been reported for the preparation of silver sulphide thin films. Among these, chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) has become the favoured route because of its simpleness, low cost, scaleablity and reproducibility [17]. In this work, a simple chemical bath deposition and successive ionic layer adsorption and reaction technique is selected to prepare silver sulphide (Ag_2S) thin films with the use of common and inexpensive chemicals for the bath, as well as a basic characterization of the as-deposited material.

MATERIALS AND METHODS

Experimental

Commercially available, optically pure glass plates (25mm x 75mm x 1.35mm) were used as the substrate to deposit nanocrystalline Ag_2S thin films by chemical bath deposition and successive ionic layer adsorption and reaction technique. Before the deposition of Ag_2S thin films on glass substrates, a cleaning process was applied to the substrates. Initially the glass substrates were put into a beaker containing distilled water and kept there for 10 min to remove contaminants such as dust on their surfaces. Then they were taken from the beaker and dried. Then the substrates were degreased by chromic acid and rinsed with deionised water.

The deposition of nanocrystalline Ag_2S films by using the CBD technique in a silver nitrate – ammonia–thiourea system consist of: complexation of silver cations by ammonia and the consecutive reaction with the sulphide ions provided by hydrolysis of thiourea. The chemical bath contains aqueous solution of 20ml of 0.1M silver nitrate and 20ml of 0.6M thiourea. Aqueous ammonia was added into this solution to adjust the pH at the desired value (≈10). Then, mixture is stirred well. This reaction mixture was transferred into a beaker, in which the substrates were kept vertically. The deposition was carried out in a 100 ml beaker at a room temperature for a deposition time of 30 minute. Thereafter substrate coated with Ag_2S was removed, rinsed with distilled water, and dried in open air at room temperature for 15 minute. Film obtained was uniform, well adherent and blackish gray in color. The thickness of the optimized thin films was ≈140 nm.

Loba analytical reagent grade silver nitrate and thiourea were used in the deposition of nanocrystalline silver sulphide thin films by successive ionic layer adsorption and reaction technique. The cationic precursor for nanocrystalline Ag_2S thin film was 0.1M silver nitrate. The source for sulphide ions was 0.5M thiourea. To deposit nanocrystalline Ag_2S thin film one SILAR cycle involves the following four steps: a well-cleaned glass substrate is immersed in the first reaction vessel containing aqueous cation precursor 0.1M silver nitrate solution at pH ~5.

After the cation immersion, the substrate is moved to the rinsing vessel where it is washed with purified water. The sulphide ions were adsorbed from an aqueous 0.5M thiourea solution with pH ~10. After anion immersion the substrate was washed as described above; thus the first SILAR cycle is completed. Repeating these cycles a thin film with desired thickness is prepared. Therefore, we obtained a Ag_2S film of 135nm thickness by repeating such SILAR cycles 30 times. The cation and anion immersion times were 15 s and the rinsing time was 10 s. The temperature of the solutions was maintained at 27^{o}C. The preparative parameters used for the deposition of Ag_2S thin films are summarized in Table 1.

Table 1 Optimized preparative parameters for the deposition of Ag_2S thin films by SILAR

Parameters	Precursors solutions	
	Silver nitrate	Thiourea
Concentration (M)	0.1	0.1
pH	~ 5	~10
Immersion time (S)	15	15
Number of SILAR cycle	30	30
Temperature ^{o}C	27	27

The as-deposited thin films of Ag_2S were characterized for structural, optical and surface morphological studies. The Ag_2S film thickness was measured by weight difference method technique. X-ray diffraction (XRD) pattern of the film were recorded on a Bruker AXS, Germany (D8 Advanced) diffractometer in the scanning range 20–80◦ (2θ) using Cu Kα radiations with wavelength 1.5405A°. The elemental composition was determined by EDAX technique. The surface morphology was studied by scanning electron microscopy (SEM, JOEL-JSM-5600). Absorbance spectra were recorded in the range 200–1100 nm by means of Shimadzu UV-3101PC spectrophotometer.

Structural studies:

Fig. 1 shows a typical XRD pattern of nanocrystalline Ag_2S thin films prepared, by CBD and SILAR technique, on glass substrate at optimized preparative parameters. The data are further analyzed and it is found that nanocrystalline Ag_2S films deposited by CBD and SILAR technique are polycrystalline with monoclinic (acanthite) crystal structure. For Ag_2S thin films grown by CBD technique, it is seen that the XRD pattern exhibits a major peak reflection along the (1 1 1), (1 2 1), (1 2 1) and (0 3 1) planes. Other peaks corresponding to (1 0 1), (1 1 0), (1 1 1), (1 1 2), (1 2 0), (1 0 3) and (2 0 0) planes are observed with lower scattering intensity. From the XRD pattern of Ag_2S thin films deposited by SILAR technique, no substantial change in the peak intensity and peak position was observed. The observed 'd' values are compared with JCPDS data [18, 19] and are found to be in good agreement with the standard values as shown in table 2. The average crystallite size is calculated using the well known Scherrer's formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

where D is the crystallite size, β is the broadening of diffraction line measured at half of its maximum intensity (FWHM) and λ is the X-ray wavelength (1.5406Å). The calculated average

crystallite size is 25.61nm for the film deposited by CBD technique and 21.38 nm for the film deposited by SILAR technique at optimized preparative parameters.

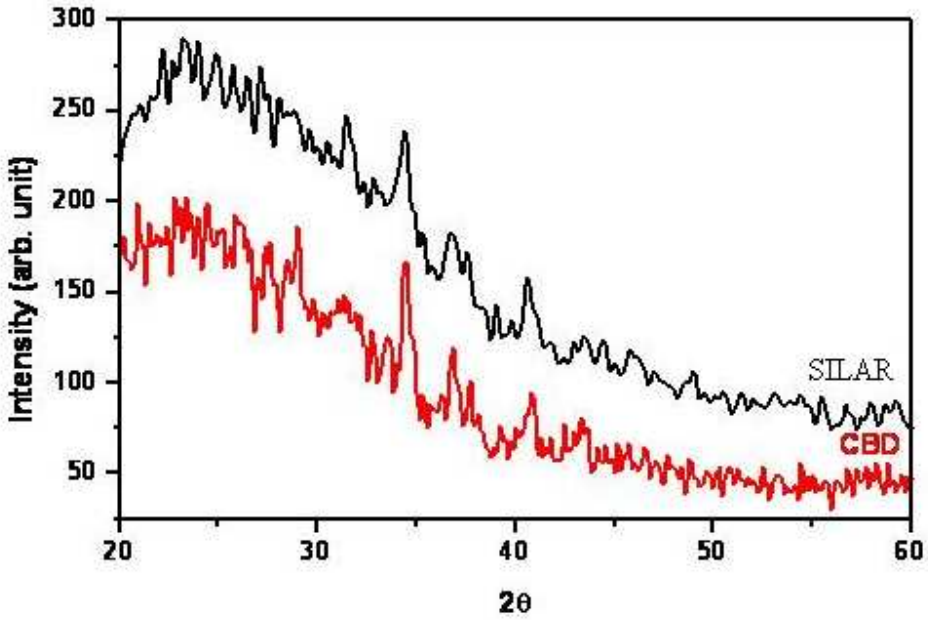
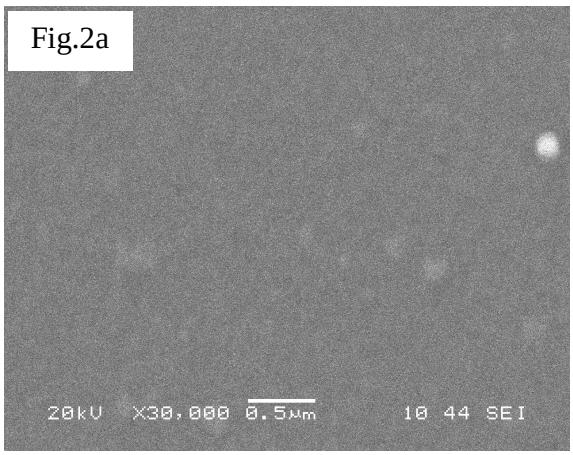


Fig.1 X-Ray diffraction pattern of Ag_2S thin films deposited by CBD and SILAR

Ag_2S by CBD				Ag_2S by SILAR			
2θ	Standard d value (Å)	Observed d value (Å)	(h k l)	2θ	Standard d value (Å)	Observed d value (Å)	(h k l)
22.81	3.96	3.90	$\bar{1}$ 0 1	22.18	3.96	4.00	$\bar{1}$ 0 2
24.50	3.57	3.63	1 1 0	24.95	3.58	3.57	$\bar{1}$ 1 1
25.95	3.44	3.43	$\bar{1}$ 1 1	25.75	3.44	3.45	$\bar{1}$ 1 2
28.95	3.08	3.08	1 1 1	31.54	2.67	2.63	$\bar{1}$ 2 1
31.44	2.84	2.84	$\bar{1}$ 1 2	34.38	2.61	2.61	$\bar{1}$ 2 2
33.56	2.66	2.67	1 2 0	36.82	2.44	2.44	1 2 0
34.44	2.61	2.60	$\bar{1}$ 2 1	40.60	2.21	2.22	0 3 1
36.89	2.44	2.43	1 2 1	43.49	2.07	2.07	0 2 3
37.81	2.38	2.38	$\bar{1}$ 0 3	44.42	2.05	2.04	1 0 2
40.82	2.21	2.21	0 3 1	45.78	1.98	1.98	$\bar{2}$ 0 4
43.42	2.08	2.08	2 0 0	49.01	1.85	1.86	$\bar{1}$ 3 3

Morphological studies:

The scanning electron micrographs of the nanocrystalline Ag_2S thin films, prepared from chemical bath deposition and SILAR technique, of thickness 140 nm and 135 nm respectively are shown in Fig.2a and Fig.2b at 30000 magnification. SEM micrographs reveals that the film is well adherent, homogeneous and well covered to the substrate surface without any cracks or pinholes for both cases. Some of the grains show an agglomerated morphology. There is no much difference among these two samples



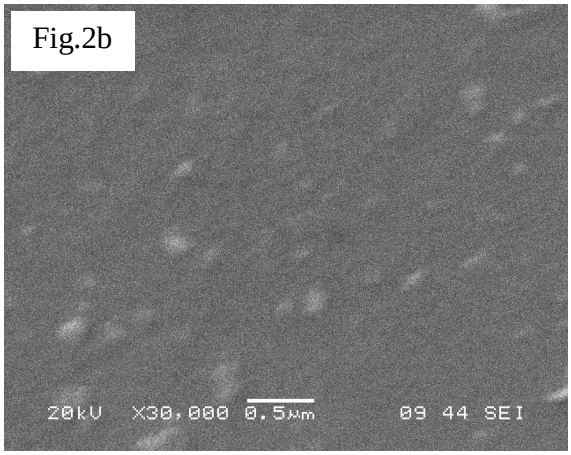


Fig.2a and 2b SEM micrographs of Ag_2S thin films deposited by CBD and SILAR respectively

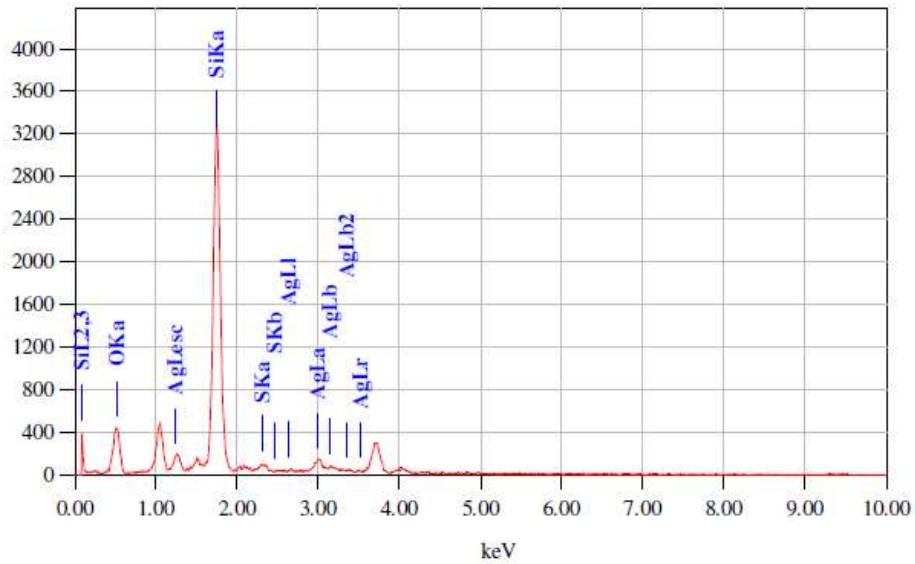


Fig.3 EDAX spectra for Ag_2S thin films deposited by CBD

Optical studies:

The absorption spectrum of as-deposited film has been recorded at room temperature without considering losses due to reflection and transmission. Fig.4a and 4b shows a plot of absorption coefficient versus wavelength for nanocrystalline Ag_2S thin films, prepared from chemical bath deposition and SILAR technique respectively. The absorption coefficient is of the order of 10 cm^{-1}. The spectrum shows absorption edge at around 800 nm and 620nm wavelength for CBD and SILAR grown nanocrystalline Ag_2S thin films. The edge is seen to be strongly blue shifted.

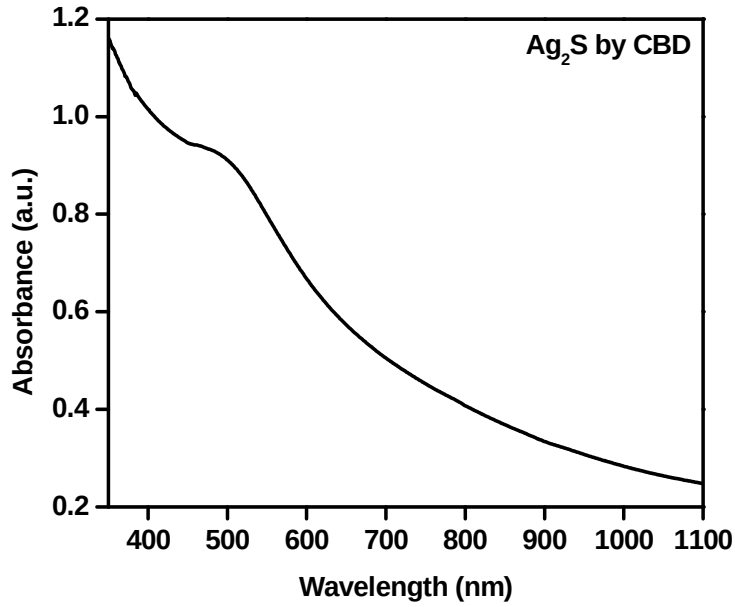


Fig.4a Absorbance spectra for Ag_2S thin films deposited by CBD

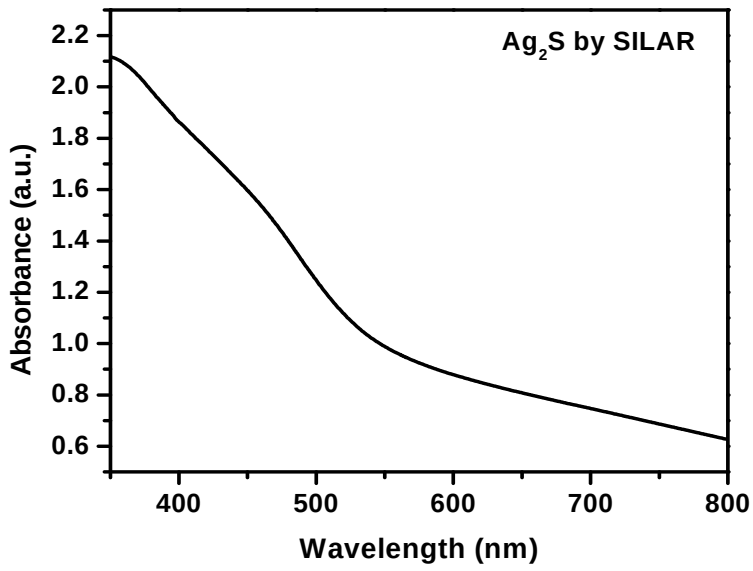


Fig.4b Absorbance spectra for Ag_2S thin films deposited by SILAR

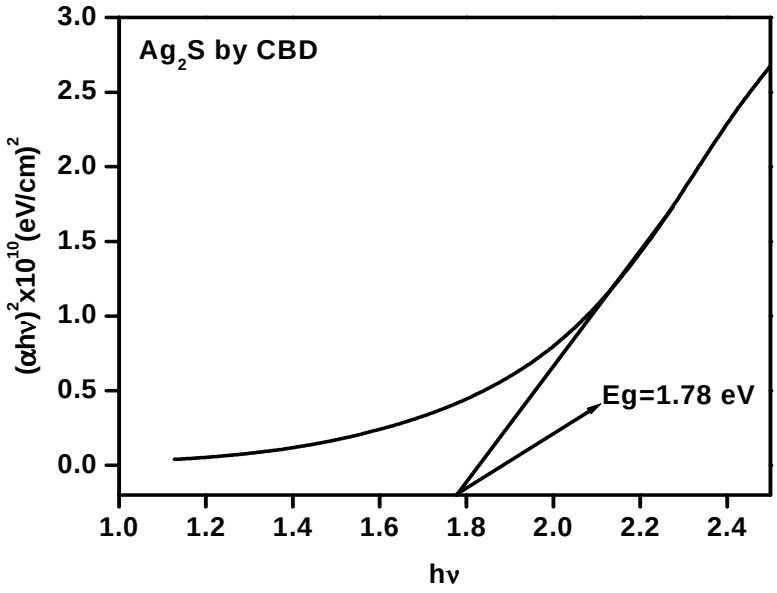


Fig. 5a Variation of $(\alpha h\nu)^2$ with photon energy (hν) for Ag_2S thin film dposited by CBD

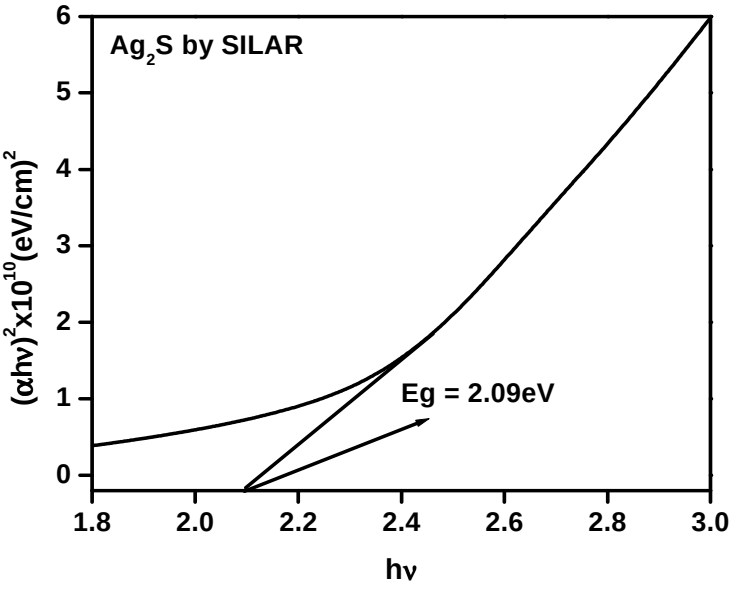


Fig. 5b Variation of $(\alpha h\nu)^2$ with photon energy (hν) for Ag_2S thin film dposited by SILAR

The band gap was obtained using the following equation for a semiconductor:

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad \text{.....(2)}$$

where A is a constant, α the absorption coefficient and n is equal to 1/2 for direct band gap semiconductors. The energy intercept of a plot $(\alpha h\nu)^2$ versus 'hν' (Fig.5a and 5b) gives 'E_g' for direct transition. The plot shows that the energy band gap is of the order of 1.78 eV and 2.09 eV for CBD and SILAR grown nanocrystalline Ag_2S thin films, which agrees well with the standard value reported for Ag_2S thin films deposited onto fluorinated tin oxide (FTO)-coated conducting glass substrate [20]. The greater band gap of silver sulphide film deposited by SILAR technique is might be due to the smaller crystallite size as compared to that deposited by chemical bath deposition technique.

CONCLUSION

In this work nanocrystalline Ag_2S thin films were prepared by Chemical Bath Deposition technique and Successive Ionic Layer Adsorption and Reaction (SILAR) technique at room temperature using silver nitrate –ammonia–thiourea system. The XRD studies of silver sulphide films deposited by CBD and SILAR techniques indicate that the deposited thin films are polycrystalline with monoclinic (acanthite) crystal structure and particle size is of the order of 25.61 nm and 21.38 nm respectively. The optical band gap of the films deposited by CBD and SILAR techniques are estimated using the optical absorption measurements and is found to be 1.78 eV and 2.09 eV respectively.

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