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Effect of immersion cycles on structural, morphology and optoelectronic properties of nanocrystalline Ag_2S thin films deposited by SILAR technique

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Abstract: *The silver sulfide (Ag_2S) nanocrystalline thin films have been prepared on the glass substrate by successive ionic layer adsorption and reaction (SILAR) technique at 40 ^oC. Several sets of films were prepared by keeping number of cycles of immersion as 20, 30, 40, and 50 and the effects of number of immersion cycles on the structural properties and surface morphology together with the optical and electrical properties are studied. The XRD studies showed that the number of immersion cycles affect the crystallinity and the peak intensity of (1 2 0) plane increases with the immersion cycles. The morphology of the films was characterized by field emmission scanning electron microsopy (FE-SEM). All the thin films looked relatively smooth and homogeneous in field emmission scanning electron microsopy (FE-SEM) images. Optical properties of nanocrystalline Ag_2S thin films deposited on glass substrates for different number of cylces of immersion were studied. The optical investigations revealed that the transmittance in the visible region is found to be gradually decreased as the number of immersion cycles is increased from 20 to 50. It was found that the energy band gap decreased from 2.17 eV to 2.09 eV when the number of immersion cycles increased from 20 to 50. The resistivity of Ag_2S thin films decreases as the immersion cycles increases.*

Keywords: *Silver sulfide, nanocrystalline thin film, X-ray diffraction, optical properties, electrical properties.*

I. Introduction

Metal chalcogenide thin films has been studied extensively by various researchers, particularly for the fabrication of large area photodiode arrays, solar selective coatings, solar cell photoconductors, sensors, etc. [1]. Because of photoelectric and thermoelectric properties, silver sulfide is one of the important metal chalcogenide compound which has been investigated extensively for its various applications in different semiconducting devices [2]. Silver sulfide is well known for its applications in various optical and electronic devices such as IR detectors, photoconducting cells, solar selective coatings, photovoltaic cells and as a photosensitive material for recording media [3, 4]. Due to its bandgap of ~ 1.8 eV [5] and its optical absorption coefficient of ~ 10^4 cm^{-1} [6], Ag_2S have been useful for photoelectrochemical conversion. Recently, electorochemical photovoltaic storage cells with Ag_2S electrodes have been reported [7]. Such electrodes of silver sulfide in thin film form have been prepared by various deposition techniques such as, chemical bath deposition [8], successive ionic layer adsorption and reaction (SILAR) [2, 9], electroless chemical deposition technique [10], thermal evaporation [11], solution growth technique [12] and by aerosol assisted chemical vapor deposition (AACVD) [13]. Among all these deposition techniques chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) are the low cost deposition techniques. However for this particular study we have preferred SILAR technique for the deposition of silver sulfide thin films. Because SILAR technique is a simple, low cost, convenient and useful for large area industrial applications. Another advantage of SILAR method with respect to other methods is that SILAR does not require high quality substrates nor does it require vacuum at any stage, which is a great advantage if the method will be used for industrial application, the deposition rate and the thickness of the film can be easily controlled over a wide range by changing the deposition cycles [14]. To the best of our knowledge, it is the first report on the effect of immersion cycles on the properties of Ag_2S thin films by SILAR. The present article deals with the preparation of Ag_2S thin films and characterization of the films by XRD, FE-SEM and study of their optoelectronic properties.

II. Experimental procedure

Glass microslides of the dimensions 75mm x 25mm x 1.10mm is used as a substrate. Before deposition, the substrates were cleaned with double distilled water, boiled in chromic acid for 2h. Again, the substrates were washed with detergent, rinsed in acetone and finally ultrasonically cleaned with double distilled water. A.R. grade chemicals supplied by Loba Chemie Ltd., silver nitrate, thiourea and aq. Ammonia were used

in the deposition of silver sulfide (Ag_2S) thin film. The cationic precursor used for the deposition of Ag_2S films was 0.05M silver nitrate complexed with 25% aq. ammonia at pH~9. 0.05M thiourea is used as the source of sulpher ions with pH~6. The adsorption and reaction time in the Ag_2S film formation was 25s. Rinsing time was 15s. Thus, a single SILAR deposition cycle consisted of 25s adsorption of silver ions, 15s rinsing with double distilled water, 25s adsorption and reaction of sulpher ions with preadsorbed silver ions on the substrate and 15s rinsing with double distilled water. By repeating this procedure for different number of SILAR cycles viz. 20, 30, 40 and 50 cycles, Ag_2S films has been deposited. The deposition was carried out at 40°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

Parameters	**Precursors solutions**	
	Silver nitrate ($AgNO_3$)	**Thiourea ($CS(NH_2)_2$)**
Concentration (M)	0.05	0.05
pH	9	6
Immersion time (s)	25	25
Temperature (°C)	40	40

The SILAR coated thin films of Ag_2S were characterised for structural, morphology, optical and electrical properties. X-ray diffraction (XRD) patterns of the films were recorded on a Bruker AXS, Germany (D8 Advanced) diffractometer in the scanning range 20-80° (2θ) using CuKα radiations with wavelength 1.5405 Å. S-48500 Type-II (HITACHI HIGH TECHNOLOGY CORPORATION Tokyo, Japan) field emission scanning electron microscope (FESEM) with an energy dispersive spectrometer (EDS) attachment was used for the determination of morphology and chemical composition. To study the optical characteristics of the film, absorbance and transmittance spectra were recorded in the range 400-900 nm by means of JASCO UV-VIS spectrophotometer (V-630). The resistivity of the Ag_2S thin films was determined by two-probe method.

III. Result and discussion

In order to study the growth rate, SILAR coated Ag_2S thin films were deposited for various immersion cycles on glass substrates. Fig.1 represents Ag_2S film thickness as a function of the immersion cycles. It is found that the film thickness increases with the deposition cycles.

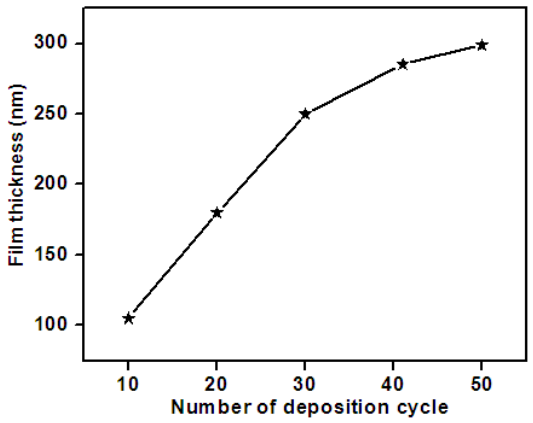

Fig. 1 Plot of thickness of the Ag_2S thin film as a function of deposition cycles.

In order to study crystal structure of Ag_2S thin film deposited by SILAR technique, X-ray diffractogram of the film on the glass substrate was examined. The X-ray diffraction (XRD) pattern of SILAR deposited Ag_2S thin films with 20, 30, 40 and 50 immersion cycles are as shown in figures 2a, b, c, d respectively. The XRD patterns clearly showed the influence of the immersion cycles on the crystallinity of the films. For all Ag_2S films, the monoclinic crystal structure characterized with (1 2 0) plane as preferred orientation, is identified [15]. Similar result was observed by Nasrallah et.al. for unannealed Ag_2S thin films prepared by sequential thermal evaporation method [16]. Other diffractions peaks are also visible in the XRD pattern of Ag_2S films. The peaks at 2θ = 33.81°, 34.89°, 38.73°, 43.78° and 45.04° referred to the ($\bar{1}$ 2 1), (0 2 2), (1 1 1), ($\bar{2}$ 0 2) and (1 2 1) orientations of the monoclinic phase of the Ag_2S. The XRD peaks corresponding to monoclinic Ag_2S became more intense as number of immersion cycles increases from 20 to 50. No shift in the peak position was found with the increase of immersion cycles. The crystallite size (D) of the films has been evaluated from the high intensity peak at 2θ = 37.54° by using Scherrer's formula [17]:

$$D = \frac{k\lambda}{\beta\cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where k is constant (0.94), λ is the wavelength of X-ray, β is the full width at half of the peak maximum in radians and θ is Bragg's angle. It is observed that the crystallite size increases from 31.6 nm to 35 nm as immersion cycle's increases from 20 to 50.

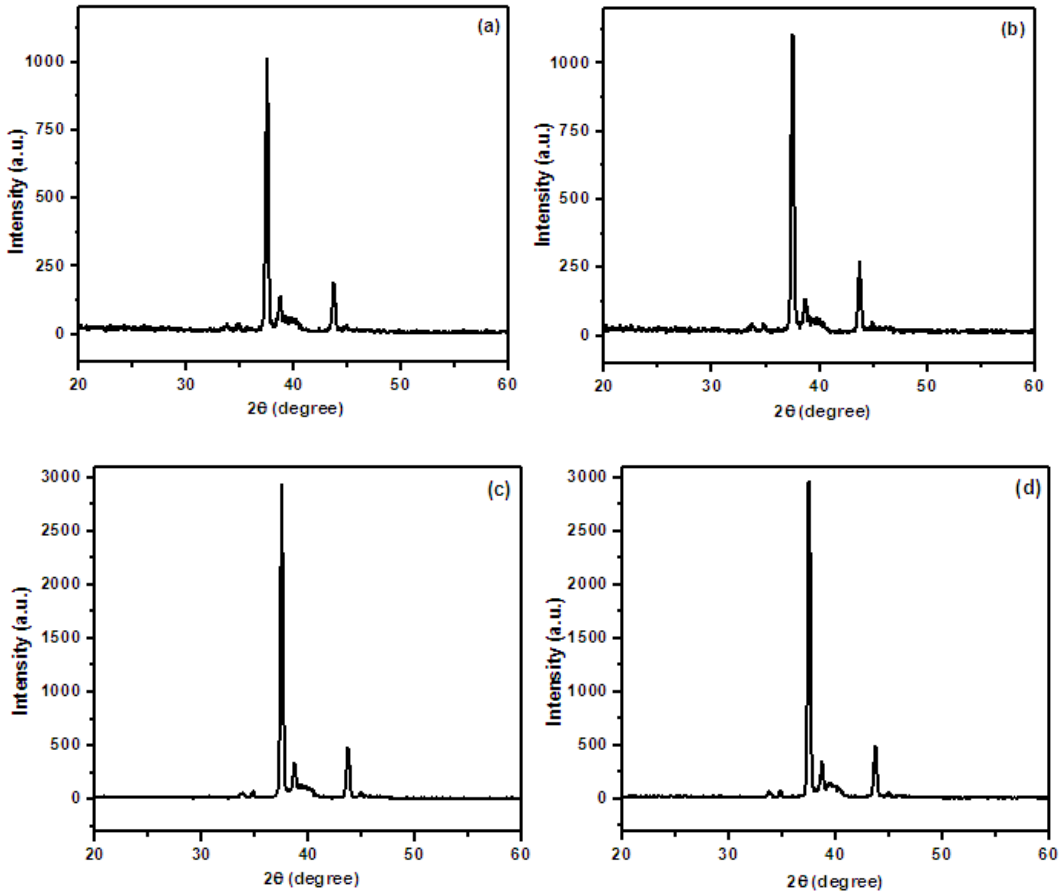

Fig. 2 XRD pattern of Ag_2S thin film synthesized with: a) 20, b) 30, c) 40 and d) 50 immersion cycles.

Field Emission Scanning Electron Microscopy (FE-SEM) was used to investigate the effect of the immersion cycles on thin film surface properties because the surface properties directly affect the electrical and optical properties of the films [18]. The FE-SEM images of the Ag_2S thin films deposited with different immersion cycles are presented in Fig. 3a-d. It is observed from fig. 3a-d that all the thin films were homogenous, without cracks or holes and with dense surface morphology covering entire substrate surface area. It can also be seen from FE-SEM images that the films were composed of a large number of spherical nanoparticles. Improvement in the crystallinity was found with increase of immersion cycles.

Fig. 4a and 4b shows absorbance and transmittance spectra obtained from Ag_2S thin film deposited with different immersion cycles, in the range of 400 to 900 nm. It is observed from the absorbance spectra that there is a red shift in the absorption edge as the SILAR growth cycles is increased, indicating a decrease in the optical bandgap. It is also observed from the transmittance spectra that for lesser immersion cycles (20), the average transmittance in the visible region is found to be 48% and it decreases gradually to about 27% for the higher immersion cycles (50). This variation in transmittance can be correlated with the thickness of the film as the thickness of the film is in direct proportion with the number of immersion cycles which may cause a gradual decrease in the optical transmission [19]. The theory of optical absorption gives the relation between the absorption coefficient α and the photon energy hν, for direct allowed transition as [20],

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

where hν is the photon energy, E_g is the optical bandgap, A is a constant. For allowed direct transitions, n = ½ and allowed indirect transitions n = 2. Fig. 5a-d shows a plot of $(\alpha h\nu)^2$ versus hν for films deposited with

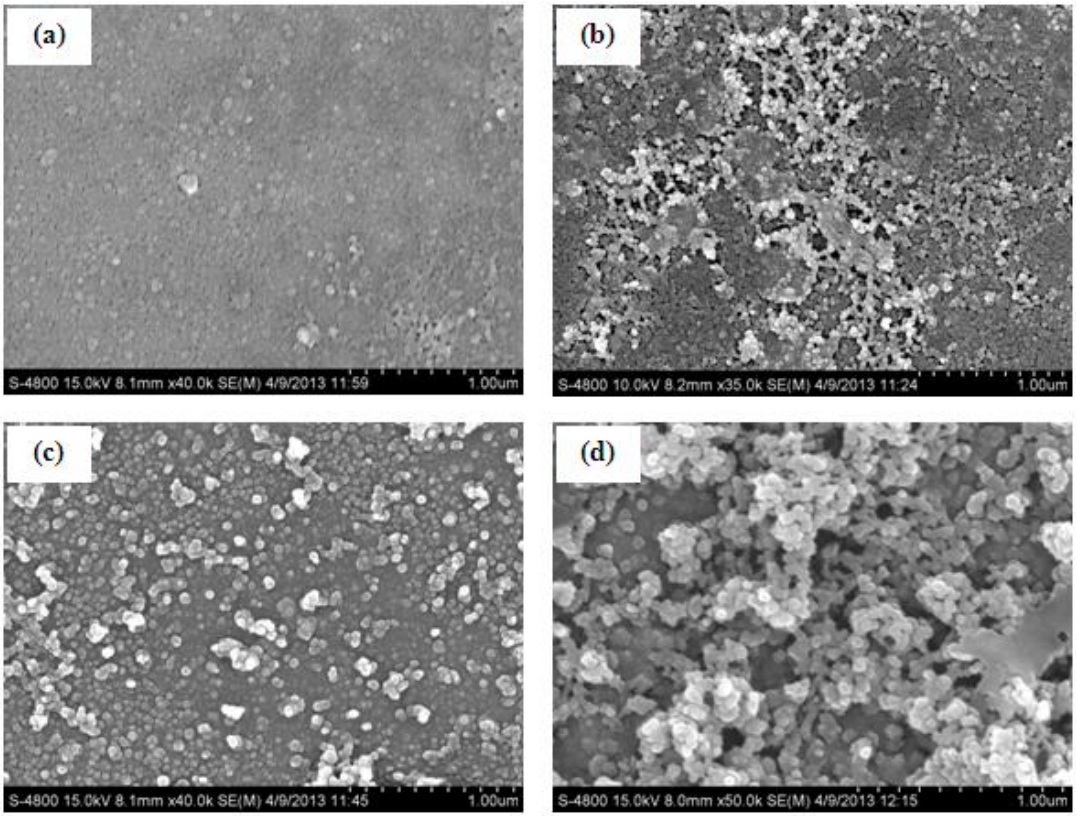

Fig. 3 Surface Morphology of Ag_2S thin film synthesized with: a) 20, b) 30, c) 40 and d) 50 immersion cycles.

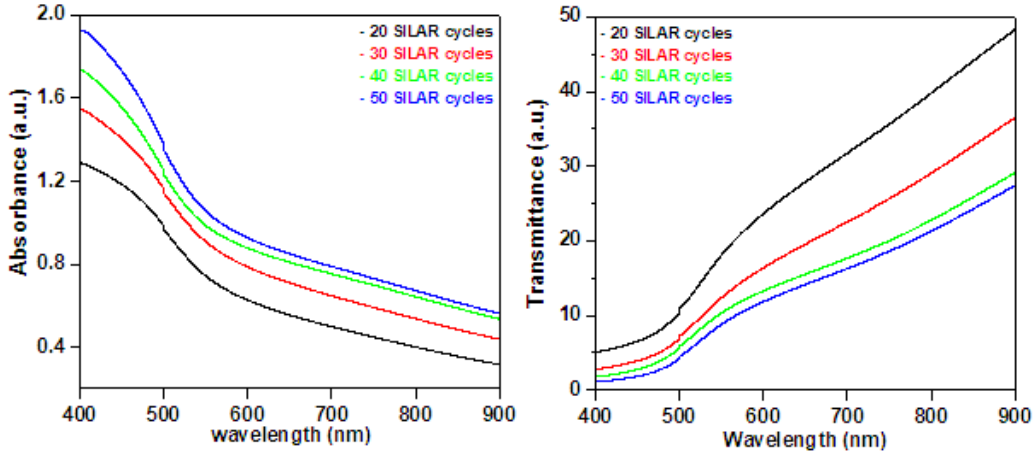

Fig. 4a and 4b Absorbance and transmittance with respect to wavelength for Ag_2S thin films synthesized with different immersion cycles.

20, 30, 40 and 50 immersion cycles which is linear at the absorption edge, confirming the direct band gap material. The linear fit of the plot indicate the existence of the allowed direct bandgap transition. The direct bandgap of Ag_2S thin films deposited with various immersion cycles are determined by extrapolating the linear portion of the curve on hν axis at $\alpha = 0$.

The band gap values for films deposited with 20, 30, 40 and 50 immersion cycles are estimated to be 2.17, 2.15, 2.11, and 2.09 eV respectively. These bandgap values were in good agreement with the earlier reported values of bandgap for Ag_2S thin films deposited by electroless chemical deposition technique [10]. It is obvious from the results (shown in fig. 6) that the optical band gap decreases with the increase in the immersion cycles which may be due to the quantum size effect and variation in the stoichiometry of the film [19].

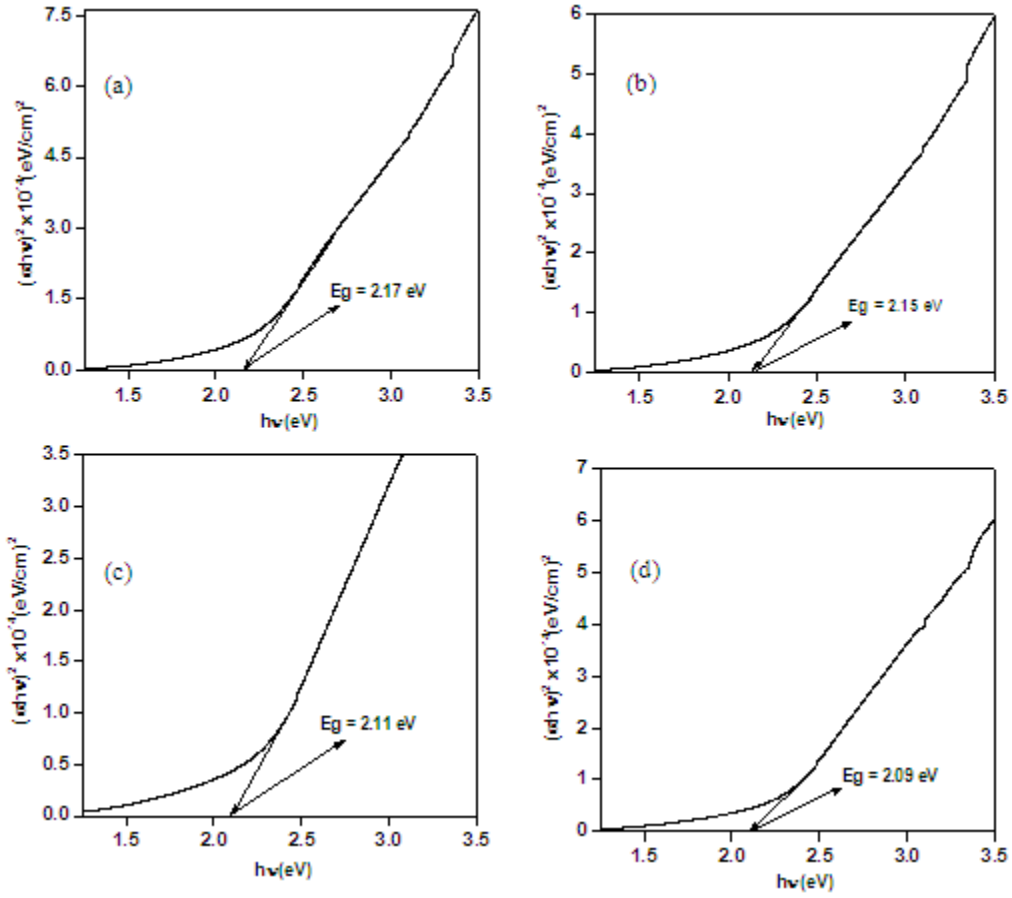

Fig. 5 Variation of $(\alpha h\nu)^2$ versus hν for Ag_2S thin films deposited with a) 20, b) 30, c) 40 and d) 50 immersion cycles.

The measurements on electrical resistivity of the Ag_2S thin film as a function of immersion cycles were carried out in the temperature range 300 - 423 K on rectangular-shaped samples with typical size of 1cm x 1cm, using a standard two point probe method. The variation of log ρ versus inverse of absolute temperature (1000/T) for the films deposited with different immersion cycles, shown in Fig. 7. The resistivity of all the films decreases with increase in temperature indicates semiconducting nature of the films [21]. The resistivity of the films decreased from 0.89 x 10^3 to 0.17 x 10^3 Ω.cm with increasing the immersion cycles. This decrease of resistivity with the immersion cycles might be due to the decrease of residual defects and increase of crystallite size in the films, which was observed in the XRD studies [22].

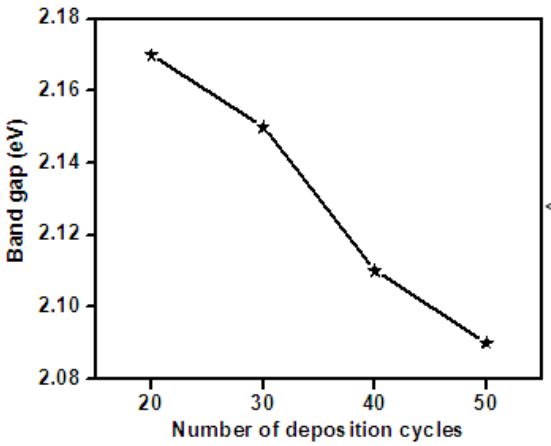

Fig. 6 Variation of energy bandgap as a function of immersion cycles.

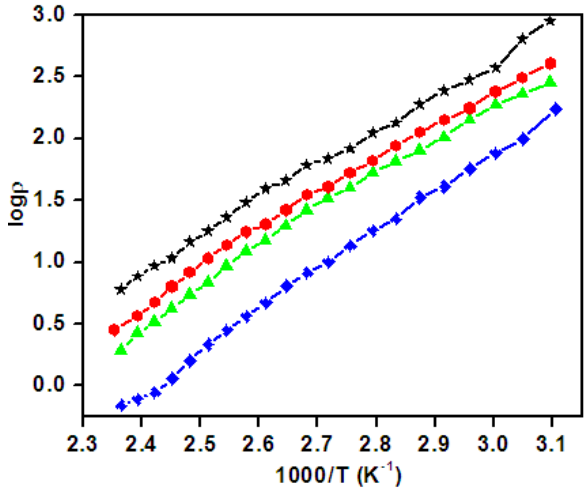

Fig. 7 Electrical resistivity as a function of Temperature

IV. Conclusion

Good quality silver sulfide (Ag_2S) thin films were deposited onto glass substrates by using SILAR technique as a function of immersion cycles varing from 20 to 50 in the interval of 10. XRD analysis revealed the monoclinic structure of Ag_2S thin films. Peak intensity increases with immersion cycles and thus the crystalline quality of the films gets better and the crystallite size increases with increase of immersion cycles. Surface properties of deposited thin films were improved with increasing immersion cycles. The band gap energy values reduced from 2.17 to 2.09 eV with increase in the immersion cycles. Electrical studies showed that the films are semiconducting which may be used in optoelectronic devices.

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