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Studies on electrodeposited silver selenide thin film by double exposure holographic interferometry

S.J. Pawar*, P.P. Chikode, V.J. Fulari, M.B. Dongare

Materials Research and Holography Laboratory, Department of Physics, Shivaji University, Kolhapur, India

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Abstract

Silver selenide (Ag_2Se) thin film has been electrodeposited at room temperature from an aqueous acidic bath containing silver nitrate ($AgNO_3$) and selenium dioxide (SeO_2) as precursor salt with ethylene diamine tetra-acetic acid (EDTA) as a complexing agent. The electrodeposition of Ag_2Se thin film was carried out by varying the time of deposition. The influences of preparative parameters on growth of Ag_2Se thin film have been studied. This electrodeposited film has been characterized by X-ray diffraction (XRD) for their structural studies. Surface morphological study of Ag_2Se thin film was carried out by scanning electron microscope (SEM). The determination of thickness and stress of the Ag_2Se thin film was carried out by double exposure holographic interferometry (DEHI) technique. Band gap of Ag_2Se thin film was calculated by using UV–vis spectrophotometer.

Keywords: Electrodeposition; Ag_2Se; XRD; SEM and holography

1. Introduction

Thin film of Ag_2Se is an $A_2^{I}B^{IV}$ group compound semiconductor. It shows a polymorphic-phase transition at 406 K. The low-temperature phase orthorhombic β-Ag_2Se is a narrow band gap semiconductor. Its high-temperature phase of cubic α-Ag_2Se shows the properties of a metal and is a well-known super ionic conductor [1–3]. Infrared sensors, photolithographic layer, electrochemical storage cells, electrochemical potential memory devices, etc. can be activated by Ag_2Se [4,5]. Thin film of Ag_2Se can be used as a promising material for technological application in magnetic field sensing devices [6–8].

These Ag_2Se thin films were deposited by vacuum evaporation [9], solid vapour phase reaction and chemical bath deposition [10]. Electrodeposition technique is a very effective and convenient method for deposition of Ag_2Se thin film. [11]. Thin film of Ag_2Se was prepared by chemical bath deposition [12]. The structural, optical and electrical properties of Ag_2Se thin film were reported by number of investigators [13–15]. Compositional and surface studies of Ag_2Se thin film was reported by number of workers [16,17]. Abundant literature is available on preparation and characterization of Ag_2Se thin films by various techniques. But there is no report available on studies of Ag_2Se thin films by holographic interferometry technique. This manuscript discussed the preparation of Ag_2Se thin films by electrodeposition from an acidic aqueous bath containing $AgNO_3$, SeO_2 as precursor salts with EDTA as a complexing agent. Deposited thin films of Ag_2Se have been studied by X-ray diffraction, scanning electron microscopy (SEM), holographic Interferometry and UV–VIS spectrometer for optical absorption.

2. Experimental

Silver Selenide thin films were cathodically electrodeposited from aqueous solution containing 0.01 M $AgNO_3$, 0.05 M EDTA and 0.005 M SeO_2. Silver nitrate ($AgNO_3$, 99.9%) and selenium dioxide (SeO_2, LR-grade) were used without further purification. EDTA was used as a Complexing agent in the bath in order to control the rate of reaction.

Thin film electrodeposition was carried out using a three-electrode system with a saturated calomel electrode (SCE) as the reference electrode. The well cleaned, mirror polished, stainless steel plate as a working electrode with graphite as a counter electrode. Applied potentials were measured with respect to SCE. The fluorine doped tin oxide (FTO) substrates were cleaned

* Corresponding author. Tel.: +91 231 2690571; fax: +91 231 2691533.
E-mail addresses: sachinpawar91@yahoo.co.in (S.J. Pawar), mbdongre202@yahoo.co.in (M.B. Dongare).

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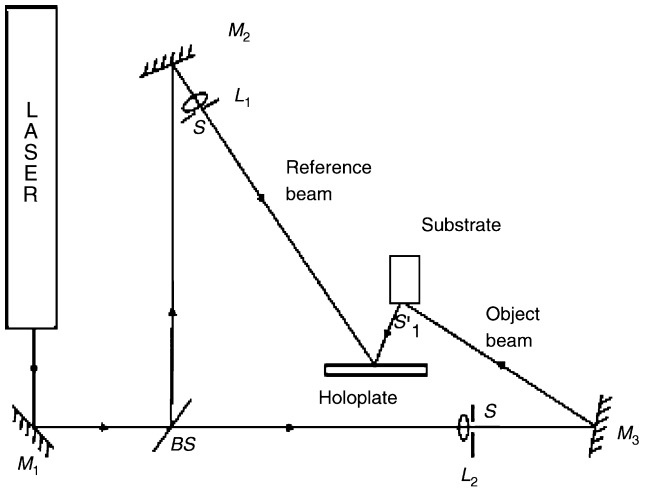

Fig. 1. Experimental setup for recording the hologram.

ultrasonically in 0.1 M NaOH, double distilled water, acetone and finally cleaned in double distilled water. The films deposited at optimized preparative parameters are a dark grayish color and well adhering to the substrates.

The double exposure holographic interferometry (DEHI) technique was used for the thickness and stress measurement of the Ag_2Se thin film. The experimental set up for recording hologram of the thin film is as shown in Fig. 1. Light from the laser source is incident on mirror M_1 and then passed through beam splitter BS. The 50% of light is transmitted and incident on mirror M_3. Through spatial filter assembly L_2 it illuminates the stainless steel substrate. Scattered light from the stainless steel substrate is taken on holographic plate, which is called as object beam. And the 50% reflected beam is incident on mirror M_2. It is directly incident on the holographic plate through spatial filter assembly L_1, which is called as reference beam. Initially steel substrate was recorded on holographic plate without deposition of the film. Secondly the holographic plate was exposed again by depositing Ag_2Se thin film say for 15 min. It is reconstructed in the same angle as that of recording.

These deposited thin films at optimized preparative parameters were annealed at the temperature 300 °C for 120–180 min at the interval of 20 min and then these cooled Ag_2Se films was done slowly down to room temperature in the Muffel furnace. The phase formation was characterized by X-ray diffraction (XRD), which is performed on a PW-3710 diffractometer using Cu Kα radiations. Surface morphology of these films was studied using a JEOL-JSM 6360 Japan, scanning electron microscope (SEM). The optical band gap of the material was determined by UV–VIS spectrophotometer in the wavelength range (λ) of 350–950 nm.

3. Result and discussion

3.1. X-ray diffraction studies

The structural identification of Ag_2Se thin film was studied by XRD technique. The XRD was carried out in the range of

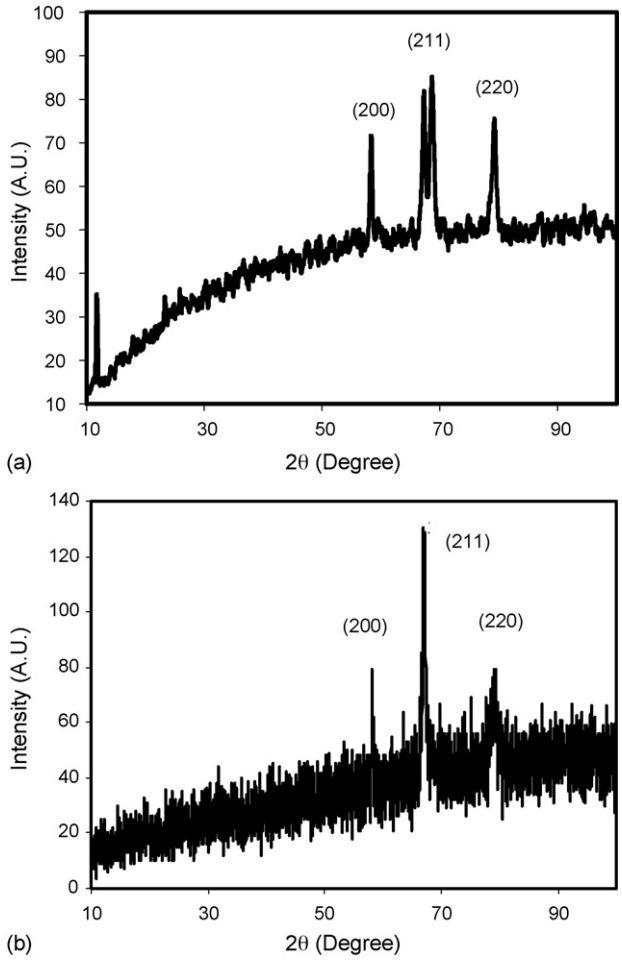

Fig. 2. X-ray diffraction of silver selenide thin film. (a) As deposited and (b) annealed at 300 °C.

diffraction angle 2θ between 10° and 100°. The entire pattern consisted of a broad hump and no clear characteristic peaks of Silver Selenide, indicating that the samples are amorphous in nature.

When the deposited films were annealed at 350 °C for 60 min in ambient atmosphere, the amorphous films became polycrystalline. Fig. 2(a) and (b) shows XRD pattern of the as deposited and annealed films at 300 °C temperature. The '*d*' values (interplaner spacing) of XRD reflections were compared with standard '*d*' values taken for JCPDS data and is as shown in Table 1. The observed '*d*' values are in good agreement with the standard '*d*' values. And crystal structure fit into cubic with lattice constant 4.99 Å. The XRD patterns of annealed samples manifest that (2 0 0), (2 1 1) and (2 2 0) planes appear with relatively higher intensity.

Table 1
Calculated and standard '*d*' values by X-ray diffraction pattern

Serial number	Observed 'd' (Å)	Standard 'd' (Å)	(*h k l*)
1	2.4625	2.4915	(200)
2	2.0390	2.0343	(211)
3	1.7982	1.7617	(220)

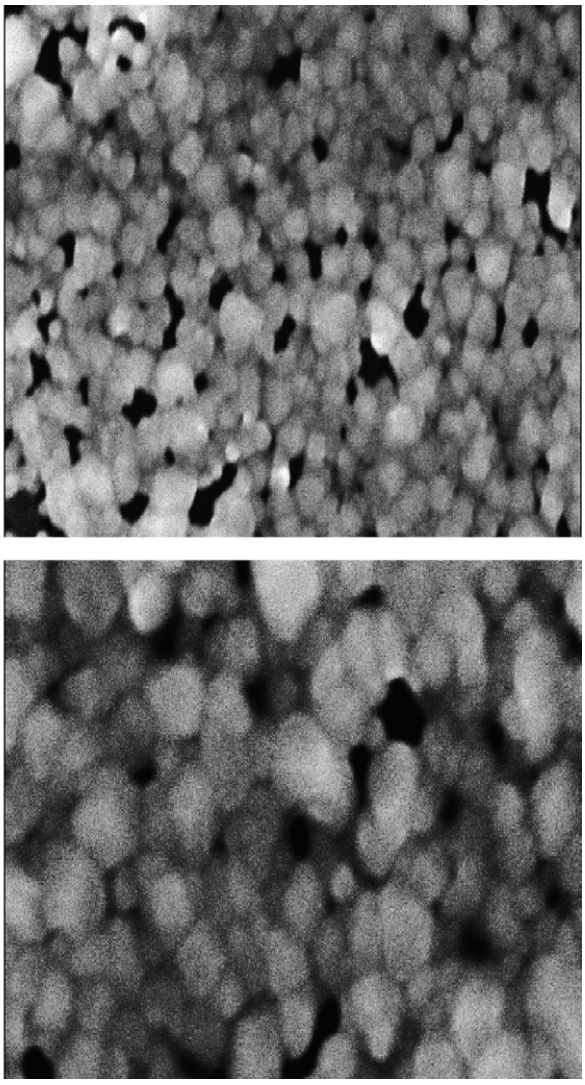

Fig. 3. SEM pictures of (a) as deposited and (b) after heat treatment of Ag_2Se thin film.

In order to determine the crystallite size a XRD scan was carried out for all the annealed samples between 27° and 29°. The crystallite size of Ag_2Se oriented (2 1 1) plane was estimated from well-known Scherer's formula [18]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where 'λ' is the wavelength of incident radiation, 'β' the intrinsic width of half maximum of peak having higher relative intensity and θ is the Bragg's diffraction angle of XRD peak. During the calculation of D values peak broadening due to instrument has been eliminated using standard LaB6 pattern. The crystallite size of as deposited Ag_2Se thin film was 37.4 nm and it increases after annealing and found to be 49.2 nm.

3.2. Scanning electron microscopy

The surface morphology of Ag_2Se thin film, as deposited and annealed at 300 °C is as shown in Fig. 3(a) and (b), respectively. The crystalline grains become globular and the diameters are in the range of 0.5–0.8 μm, which are larger than the crystallites of the corresponding as-deposited Ag_2Se thin film. This shows the increase in the grain size with respect to annealing temperature.

It was observed that the porosity decreases for annealed film. The films become more homogeneous and uniform due to heat treatment. The blank region depicts pores, which are less in annealed films.

3.3. Double exposure holographic interferometry (DEHI) technique

The great advantage of holographic interferometry technique is that distinct interference fringes appear even on a rough surface [19].

The DEHI technique records permanently a relative surface displacement of object occurring after a fixed interval of time. If, in interval between the exposures, we have deformed the surface slightly at certain places, the reconstructed image would be covered by interference fringes at these places [20,21]. This helps to investigate all changes in solid bodies, which are due to the form and quality of their surfaces [22].

The holograms were recorded on holographic plates (Kodak 8E 75 HD) for different time intervals. The holographic plate was processed and replaced only in the reference wave path. The reconstructed image of substrate was observed with the reference beam, which shows the fringes localized on its surface as shown in Fig. 4. The double exposure holographic interferometry (DEHI) technique was used to study thin film thickness and stress parameter of the Ag_2Se films [23].

While recording the hologram, the substrate is illuminated with a beam of light making an angle θ_1 with the normal and it is viewed at an angle θ_2 during reconstruction, the reconstructed image has a superimposed fringe pattern corresponding to a displacement of the surface [24].

The displacement (d) of the surface, in normal direction is given by:

$$d = \frac{n\lambda}{\cos\theta_1 + \cos\theta_2} \tag{2}$$

where n is the total number of fringes and λ is the wavelength of light.

In general, the angles θ_1 and θ_2 are sufficiently smaller. So that:

$$d = \frac{n\lambda}{2} \tag{3}$$

After counting the relevant number of fringes directly from the hologram, we have determined the displacement of a point on the surface of the object, i.e., information of the object surface.

The property of thin film depends on a very large extent upon their mechanical stability, which in turn is dependent on the intrinsic stresses developed during deposition. The importance of understanding the stress in thin film is a good review given by Campbell et al. [25]. The simple non-destructive technique for the quantitative measurement of stress in thin films

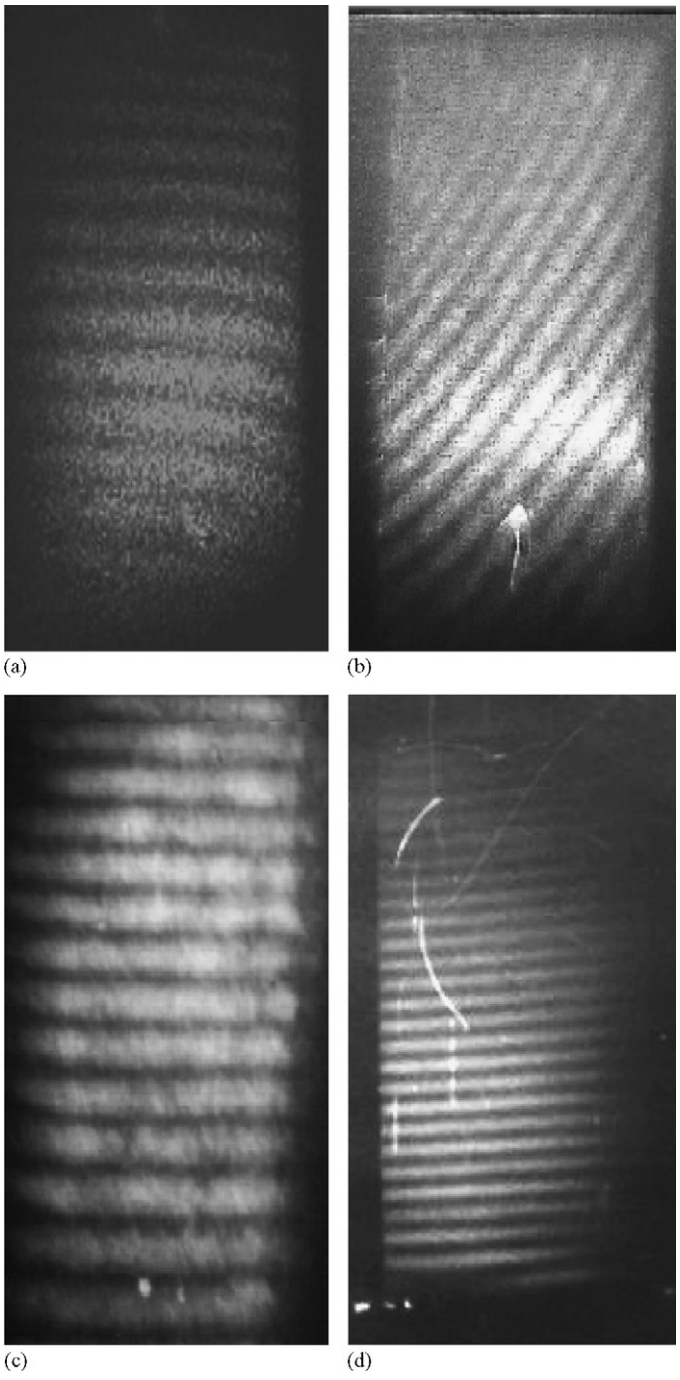

Fig. 4. Reconstructed images of substrate from holograms for deposition times: (a) 15 min, (b) 20 min, (c) 25 min and (d) 30 min.

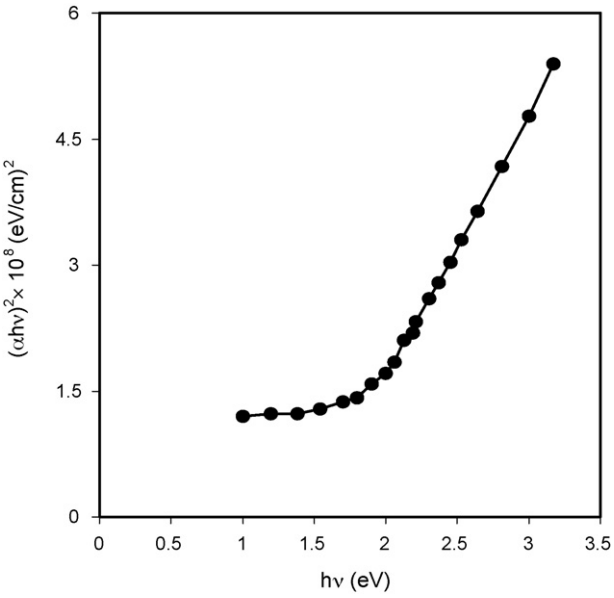

Fig. 5. Band gap of Ag_2Se thin film.

by the use of DEHI technique is reported by Magill and Young [26].

The stress applied to the stainless steel substrate is given by the formula [27,28]:

$$S = \frac{t_s^2 Y_s \Delta}{3l^2 d} \tag{4}$$

where S is the stress in dyne/cm^2, t_s the substrate thickness, Δ the deflection of the substrate equal to $4\lambda/2$, l the length of the substrate on which thin film deposited and Y_s is the Young's modulus of the substrate.

The thickness and stress have been determined by using the above relation and tabulated in Table 2.

3.4. Optical absorption studies

The optical absorption spectrum for all the as-deposited and annealed samples were recorded in the wavelength range from 350 to 850 nm at room temperature. The absorption coefficient for the film was found to be the order 10^4 cm^{-1}.

In order to confirm the nature of optical transmission in these samples, the optical data were analyzed using classical equation [29]:

$$\alpha = \frac{\alpha_0 (h\nu - E_g)^n}{h\nu} \tag{5}$$

Table 2
Thickness and stress of the thin film by double exposure holographic interferometry

Thin film	Deposition time (min)	Number of fringes	Thickness (μm)	Stress, S ($\times 10^9$ dyne/cm^2)
Ag_2Se	15	12	3.7968	0.125
	20	14	4.4296	0.1071
	25	18	5.6952	0.0833
	30	24	7.5936	0.0625

where E_g is the separation between bottom of the conduction band and top of the valence band, $h\nu$ the photon energy and n is a constant. Value of n depends on the probability of transition; it takes values as 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transition respectively. Thus if plot of $(\alpha h\nu)^2$ versus $(h\nu)$ is linear the transition is direct allowed. Extrapolation of the straight-line portion to zero absorption coefficient ($\alpha = 0$), leads to estimation of band gap energy (E_g) values. Fig. 5 shows variation of $(\alpha h\nu)^2$ as a function of photon energy $(h\nu)$. The optical band gap energy for Ag_2Se thin film was found to be 1.62 eV. The observed band gap energy is greater than the standard band gap (1.2 eV) of Ag_2Se material. The observed blue shift of 0.4 eV in the band gap energy can be attributed to size quantization in nanocrystalline semiconductor. This size quantization occurs due to localization of electrons and holes in a confined volume of the semiconductor nanocrystallites [30].

4. Conclusions

Electrodeposition for synthesis of Ag_2Se thin film is feasible technique. Nearly stoichiometric polycrystalline Ag_2 Se thin films were deposited from a bath containing $AgNO_3$ (0.01 M) and SeO_2 (0.005 M) with EDTA as complexing agent. Thin films deposited at optimized preparative parameters are dark grayish in color and well adherent to the substrates. After annealing the thin film shows improvement in the crystallinity.

DEHI was a useful technique for the determination of certain thin film parameters such as film thickness and the stress of the thin film deposited on the substrates. This is the easiest technique and gives better information as compared to other conventional techniques. We have used the DEHI technique for the characterization of Ag_2Se thin films deposited on a stainless steel substrate. It was observed that as the time of deposition increases, the number of fringes localized on the surface of stainless steel plate increases and consequently the fringe width decreases.

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