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Low Temperature Route For Synthesis Of Silver Selenide Thin Films And Their Properties: Annealing Effect

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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 di-amine 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). Band gap of Ag_2Se thin film was calculated by using UV-Visible spectrophotometer.

KEYWORDS

Electrodeposition;
Ag_2Se;
XRD;
SEM.

INTRODUCTION

Thin film of Ag_2Se is an $A_2^IB^{IV}$ 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 it 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 film was 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) and UV-VIS Spectrometer for optical absorption.

EXPERIMENTAL

Silver Selenide thin films were cathodically electrodeposited from aqueous solution containing 0.01M $AgNO_3$, 0.05M EDTA and 0.005M 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 ultrasonically in 0.1M 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.

These deposited thin films at optimized preparative parameters were annealed at the temperature 300^0C for 120 min to 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 CuKα 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) 350-950 nm.

RESULT AND DISCUSSION

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 diffraction angle 2q between 10^0-100^0. 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 350^0 C for 60 min. in ambient atmosphere, the amorphous films became polycrystalline. Figure 1a and b shows XRD pattern of the as deposited and annealed films at 300^oC temperature. The 'd' values (interplaner spacing) of XRD reflections were compared with standard'd' values taken for JCPDS data and is as shown 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 A^0. The XRD patterns of annealed samples manifest that (200), (211) and (220) planes appear with relatively higher intensity.

In order to determine the crystallite size a XRD scan was carried out for all the annealed samples between 27^0 and 29^0. The crystallite size of Ag_2Se oriented (211) plane was estimated from well-known Scherer's formula[18].

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

TABLE 1: Calculated and standard 'd' values by X-ray diffraction pattern

Sr. No.	Observed 'd' A^0	Standard 'd' A^0	(hkl)
1	2.4625	2.4915	(200)
2	2.0390	2.0343	(211)
3	1.7982	1.7617	(220)

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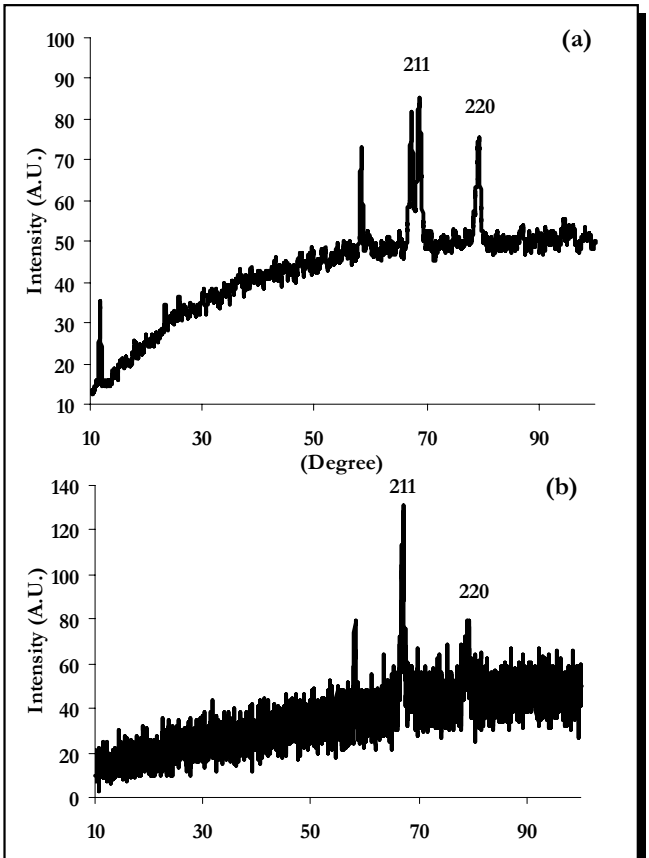

Figure 1: X-ray diffraction of silver selenide thin film. (a) As deposited (b) Annealed at 300°C.

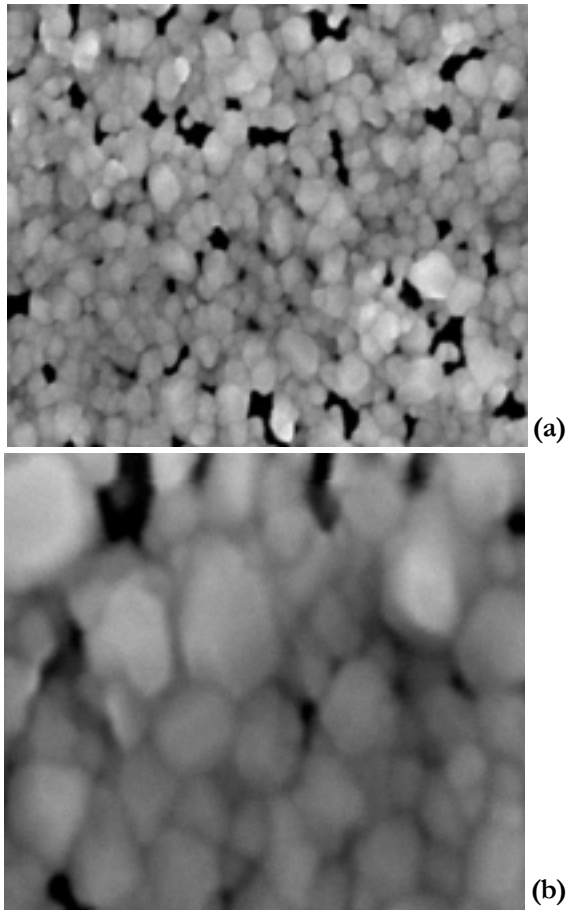

Figure 2: SEM pictures of (a) As deposited Ag_2Se thin film, (b) After heat treatment of Ag_2Se thin film

Where 'λ' is the wavelength of incident radiation, 'β' is the intrinsic width of half maximum of peak having higher relative intensity and θ is the Bragg's diffraction angle of XRD peak.

Scanning electron microscopy

The surface morphology of Ag_2Se thin film, as deposited and annealed at 300^0 C is as shown in figure 2a and b respectively. The crystalline grains become globular and the diameters are in the range of 0.5- 0.8μm 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.

Optical absorption studies

The optical absorption spectrum for all the as-

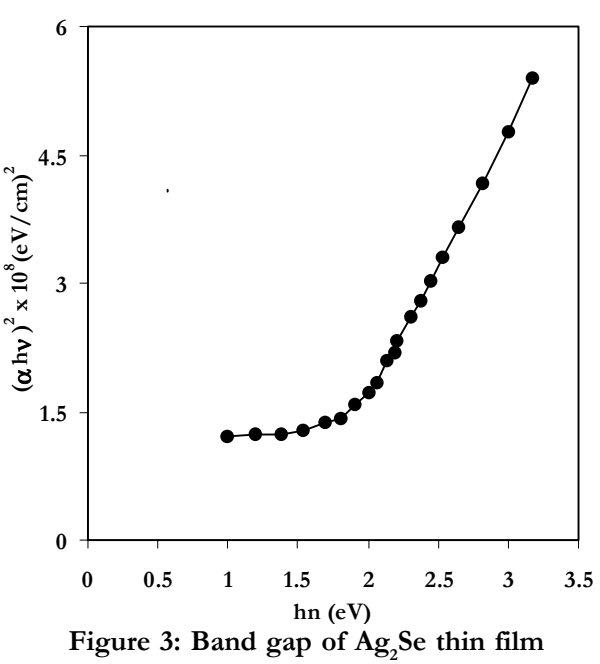

Figure 3: Band gap of Ag_2Se thin film

deposited and annealed samples was recorded in the wavelength range from 350-850 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[19],

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

Where E_g is the separation between bottom of conduction band and top of the valence band, $h\nu$ the photon energy, n & A which are constants. The nature of $(\alpha h\nu)^2$ Vs. $h\nu$ showed the direct type transition for Ag_2Se thin film and the energy band gap was found to be 1.62 eV.

CONCLUSIONS

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

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