

STRUCTURAL AND ELECTRICAL CHARACTERISTICS OF SILVER SELENIDE THIN FILMS

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Thin films of silver selenide have been prepared by chemical bath deposition technique at substrate temperature of 300K. The films were characterized by X-ray diffraction and four point probe techniques. Silver selenide thin films are polycrystalline with orthorhombic structure, confirmed by x-ray diffractogram. The deposition parameters were optimized to obtain good quality thin films.

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1. Introduction

Silver selenide, a group I-VI semiconductor compound is a mixed ionic conductor (Santosh Kumar and Pradeep 2002). Ag_2Se undergoes a polymorphic phase transition, a low-temperature orthorhombic phase ($\beta\text{-Ag}_2\text{Se}$) at 0 K, and a high temperature cubic phase ($\alpha\text{-Ag}_2\text{Se}$) with a transition temperature of 135 °C (Santosh Kumar and Pradeep 2002 and Schoen *et al*, 2007). Silver selenide exhibits many interesting and useful properties (Sreenivas *et al*, 1987). A low temperature phase ($\beta\text{-Ag}_2\text{Se}$) is a narrow band gap and n-type semiconductor (Ferhat and Nagao 2000) with resistivity of 10^3 and 10^4 Ωcm (Shukla *et al* 1981). $\beta\text{-Ag}_2\text{Se}$ is used as a photosensitizer in photographic films and in thermochromic materials due to its relatively high Seebeck coefficient, low lattice thermal conductivity, and high electrical conductivity (Cui *et al*, 2003). A high temperature phase ($\alpha\text{-Ag}_2\text{Se}$) is a superionic conductor. It finds application in solid electrolytes in photochargeable secondary batteries (Kobayashi 1990).

Xu *et al*, (1977) observed that silver selenide has linear magnetoresistance effect of 370% at 4.5K and more than 100% at room temperature. Manoharan *et al*, (2001) found a magnetoresistance effect of 250% at 4.2K. Large magnetoresistance has also been reported by Elliot (1998) for a non stoichiometric derivative of Ag_2Se solid.

Many techniques have been used for the preparation of silver selenide thin films. Sharma *et al*, (1990) prepared the films by chemical bath deposition technique. Okabe and Ura (1994) reported flash evaporation technique. Santhosh Kumar and Pradeep (2002) used the reactive evaporation to prepare silver selenide thin film. Kreutzbruck *et al*, (2005) adopted thermal evaporation and pulsed laser deposition technique to deposit the film. Pandiaraman *et al*, (2011) prepared silver selenide by thermal evaporation. In the present case, we prepared thin films of silver selenide by chemical bath deposition technique.

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2. Experimental

Silver selenide thin films were deposited on a glass substrate using chemical bath deposition method. The substrates were previously degreased in trioxonitrate (V) acid, washed with detergent, rinsed with distilled water and dried in air. During deposition process, an aqueous solution of silver trioxonitrate (V) [AgNO_3] was used as silver source, selenium trioxo sulphate(V) [SeSO_3] was the selenide source triethanolamine[TEA] acted as complexing agent. All the solutions were prepared in deionised water. For deposition, 10ml of 0.5M silver trioxonitrate (V) was complexed with 0.5M triethanolamine agent of different concentrations (2.5-12mls). To this, 10ml of 1M selenium trioxo sulphate (V) was added slowly to the reaction mixture. The pH was adjusted to 11.0 by addition of 10ml 30% ammonia. The cleaned glass substrate was vertically immersed in the reaction bath at room temperature. After the deposition time of 10hrs, the substrate was taken out of the reaction bath, washed with distilled water and dried in air.

The structural properties of the films were investigated by X-ray diffraction using CuK_α ($\lambda=1.5406\text{\AA}$) radiation. The electrical properties were measured using four point probes.

3. Results and discussion

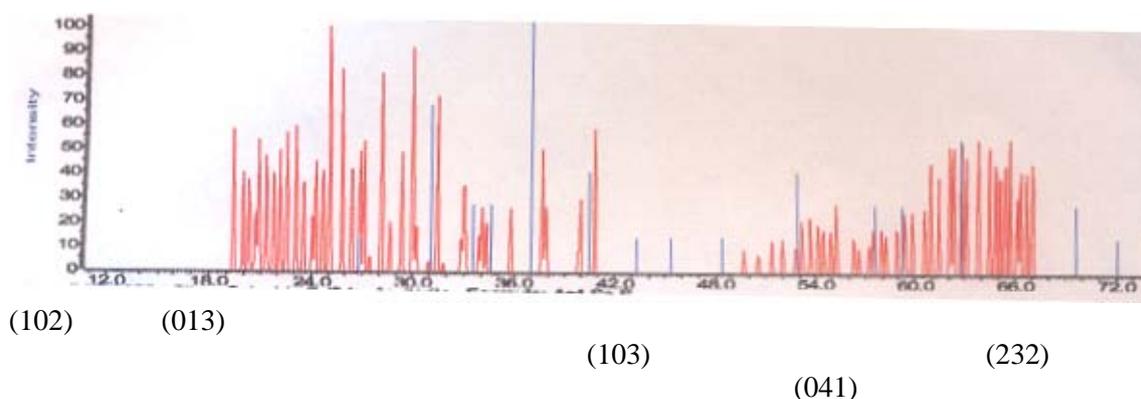


Fig. 3.1 XRD patterns of Ag_2Se thin film.

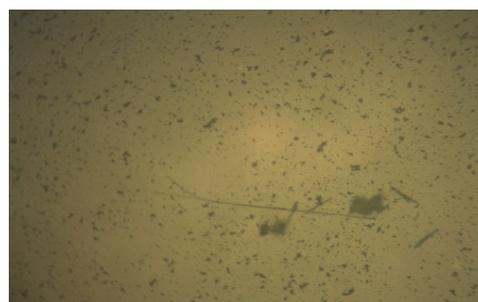
Fig. 3.1 shows the x-ray diffraction of silver selenide thin film prepared at room temperature. The structural studies on silver selenide thin films reveals the existence of (102), (013), (103), (041) and (232) planes of reflections of orthorhombic phase with lattice constant of $a = 4.33\text{\AA}$, $b = 7.09\text{\AA}$ and $c = 7.76\text{\AA}$ which are very close to the reported values by Santhosh *et al*, (2002) and Gates *et al* (2001) who reported the XRD pattern showing (002), (013), (004) and (014) planes of reflections of orthorhombic phase of Ag_2Se prepared by reactive evaporation. The XRD analysis shows that the film contains 80.7% of silver, 13.4% of selenium and 7.1% of sulphide suggesting that the films are rich in silver. The sulphide detected in the film is believed to have come from the chemicals used as some chemicals are not 100% pure. Kurlkarni *et al*, (1995) obtained a film of orientations (002), (111), (210) and (204) using chemical bath method. Damodara and Karunakara (1989) reported XRD pattern of Ag_2Se by vacuum evaporation method showing only (002) and (004) plane. Pandiaraman *et al*, (2010) obtained an XRD pattern of Ag_2Se by thermal evaporation method showing (002) and (040) planes of reflections. Huaqiang *et al*, (2010) reported XRD pattern of Ag_2Se by solvothermal method showing (120), (112), (121), (013), (122), (113) and (201) planes of reflections of orthorhombic phase of $\beta\text{-Ag}_2\text{Se}$ with lattice constants of $a=4.333\text{\AA}$, $b=7.062\text{\AA}$, and $c=7.764\text{\AA}$. The grain size of the films has been calculated using Scherer formula. Table 3.1 shows the XRD data for Ag_2Se thin film prepared at room temperature with the thickness.

Table 3.1 Structural parameters of Ag_2Se thin films for T_8 and T_{14} with thickness.

| Reaction Bath | Thickness, t (μm) | (hkl) | (deg.) | | D (\AA) Measured | d (\AA) Standard | Lattice Constant, a (\AA) | FWHM (rad.) | Grain size, D(\AA) | Dislocation Density, $\delta \times 10^{-2}$ | Strain, $\epsilon \times 10^{-2}$ |
|---------------|--------------------------|-------|--------|-----------|-----------------------------|-----------------------------|--------------------------------------|-------------|-------------------------------|--|-----------------------------------|
| | | | | 2θ | | | | | | | |
| T_8 | 0.599 | 111 | 26.03 | 0.454 | 3.42 | 3.50 | 4.33 | 0.381 | 3.783 | 8.49 | 9.28 |
| | | 102 | 30.91 | 0.539 | 2.89 | 2.75 | 7.09 | 0.381 | 3.775 | 5.14 | 9.18 |
| | | 232 | 62.83 | 1.409 | 1.50 | 1.50 | 7.76 | 0.297 | 5.469 | 2.24 | 6.34 |
| T_{14} | 0.750 | 013 | 31.02 | 0.541 | 2.85 | 2.70 | 4.33 | 0.381 | 3.776 | 8.42 | 9.18 |
| | | 102 | 36.96 | 0.645 | 2.38 | 2.32 | 0.385 | 0.385 | 3.737 | 5.09 | 9.12 |
| | | 232 | 62.72 | 1.095 | 1.50 | 1.47 | 0.301 | 0.301 | 3.395 | 2.30 | 6.43 |

It was observed from table 3.1 that the average grain size for T_8 is 4.34\AA and that for T_{14} is 4.32\AA . The results from the table show that the crystal size of the film decreases with increase in thickness, but dislocation density and micro strain are also found to decrease.

The decrease in dislocation density and strain may be brought about by the decrease in imperfections and dislocations of the films while the decrease in grain size may be as a result of the trace of sulphide impurity that was found in the grown film. Films with small grain size show high resistivity. This can be explained in terms of scattering at the grain boundaries in addition to the bulk scattering centers. The reduction in the defect density makes the material suitable for doping and alloying with a range of materials and for junction device fabrication in solar cell.



T_8



T_{14}

Fig 3.2 Photomicrographs of Ag_2Se

Fig 3.2 shows the optical micrograph of Ag₂Se films. The surface of the silver selenide thin films was found to be uniform and exhibits polycrystalline nature. It was observed that film T₈ with thickness 0.599μm exhibits growth of small grains distributed across the surface of the substrate and T₁₄ with thickness 0.750μm exhibits growth of grains that are thicker than what was obtained in film T₈. The difference in the two films is clearly shown in fig.3.2. Both of them indicate uniform surface coverage and smooth texture. In thermally evaporated silver selenide thin films by Pandiaraman *et al*, (2010), the grains were found to be uniformly distributed from the recorded SEM image of the silver selenide thin films.

3.1.3 electrical properties of Ag₂Se thin films

The electrical properties of film were investigated using a standard four point probe technique. The arrangement was made in such a way that the voltage across the transverse distance of the film and corresponding value of the current were measured using silver paste to ensure good ohmic contact to the film. The relationship of the current and voltage values is dependent on the sheet resistivity, ρ_s of the material and is given by the expression:

$$\rho = \left(\frac{\pi}{\ln 2} \right) \frac{V}{I}$$

$$\text{where } \frac{\pi}{\ln 2} = 4.53$$

$$\rho = 4.53R$$

The results are shown in table 3.4

Table 3.2 Electrical properties of Ag₂Se film

| | |
|----------------------------------|-------------------------|
| Thickness, (μm) | 0.599 |
| Resistivity, ρ _s Ωm | 9.55 x 10 ⁶ |
| Conductivity, (Ωm) ⁻¹ | 1.04 x 10 ⁻⁷ |

The results show that Ag₂Se film has high resistivity and low electrical conductivity. The high resistivity is as a result of small crystallite size. Electric carriers moving through a thin film containing small grains would suffer extra scattering at the grain boundaries and therefore they have a reduced mean free path (Vospasroiu *et al*, 2005). The high resistivity made Ag₂Se suitable as window layer.

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