

Structural and Optical Properties of Sulphurised Ag₂S Thin Films

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Abstract: Thin films of silver (Ag) were thermally evaporated onto glass substrates. The films were then sulphurised using a simple chemical sulphurisation method with sulphurisation temperatures in the range 300°C to 350°C. The sulphurised films were then annealed using annealing temperatures in the range 250 °C to 350 °C. X-ray Diffractometer (XRD) and optical data are given for the as-sulphurised and the annealed layers. The structural and optical properties of the as-sulphurised layers show a poor crystallinity and weak transmission. However, annealing improved the crystallinity of the layers such that sharp X-ray diffraction peaks belonging to the acanthite phase was observed from X-ray diffractometry analysis. The annealed films had direct energy bandgap with energy bandgap in the range 2.10 eV to 2.20 eV

Keywords: Annealing, sulphurisation, Energy bandgap, Window layers.

1 Introduction

The urge to establish suitable window layers for fabrication of some optoelectronic devices such as solar cells has been a subject of research for years. Window layers suitable for solar cell fabrication are known to have energy bandgap ≥ 2.0 eV [1]. Some authors have shown that Ag₂S can be used in solar cells as window layers since it has energy band gap in the range 2.2 eV to 2.3 eV [2, 3]. Though recently, attention has shifted to other window layer materials such as ZnO, CdS, CdSe, SnS₂, more investigations on sulphides of silver is still a step in the right direction since the energy bandgap is within the range where it can be utilised as window layers, selective coatings, photoconductive devices and infrared millimeter wave devices [4, 5].

Silver sulphides can be fabricated using low-cost deposition techniques such as SILAR (successive ionic layer reaction and adsorption) [6-11], solution growth techniques [4, 12], chemical bath deposition [13, 14, 15], thermal evaporation [16, 17, 18], electro-deposition [19, 20], molecular beam epitaxy (MBE) [21], gamma irradiation [22], aerosol assisted chemical vapour deposition [23] and sulphurisation method [24]. Recently, researchers are adopting new methods of using noble metal nano-particles dispersed in the semiconducting film as a way of harnessing the light trapping potentials of these semiconductors [25, 26]. Some noble metal nano-particles such as silver (Ag), gold (Au), aluminum (Al) and copper

(Cu) embedded in a dielectric/semiconducting medium do show interesting optical properties and have gained a lot of attention due to their potential applications in plasmonic solar cells [27], surface plasmon enhanced sensors, and photonic devices [28]. Pustovit and Shahbazyan [29] noted that amongst all other noble metals, that silver nanoparticles gave the best localized surface plasmon resonance response, thus making it potential candidate for various optoelectronic applications. Thin films of Ag₂S have been reported to exhibit a p-conductivity type [2, 17] and n-conductivity type [9,30-31], thus giving room for more flexibility to device design. Solar cells with solar conversion efficiency $> 1.5\%$ has been reported [11]. Many authors have observed direct energy band gap for Ag₂S thin films independent of the deposition techniques [4, 13-16].

In this study, we have tried to improve the properties of sulphides of silver as a step toward producing more efficient devices. The structural and optical properties of the sulphurised and annealed layers are reported.

2 Experimental Procedures

Thin films of Ag were deposited on ultrasonically clean glass substrates using the thermal evaporation method with substrate temperature in the range 200 °C –300 °C. The depositions were carried out in a thermal evaporation system operating in the 10⁻⁵ to 10⁻⁶ Torr range of vacuum pressures. Other deposition variables were kept constant. The films were then subjected to a simple chemical sulphurisation method with sulphurisation temperatures in

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the range 300 °C – 350 °C. The sulphurised layers were then annealed using annealing temperatures between 250°C to 350°C and sulphurisation times between 60 min to 90 min.

The layers were then characterised using a Philips P.W 1500 X-ray Diffractometer with a CuK_α radiation source ($\lambda = 0.15406$ nm) to determine the phases present and the crystal structure of each phase. The film thickness was measured using the thickness monitor incorporated in the thermal evaporation system. The optical transmittance and reflectance versus wavelength measurements were measured in the wavelength range of 200 nm to 1000 nm using the Unico UV-2102 PC spectrophotometer.

3 Results

Physical observations of the films show that they were typically brownish-black in colour. Fig.1 gives a typical XRD diffractogram for Ag_2S films sulphurised at 350 °C and annealed at 250 °C. From the XRD pattern shown on Fig. 1, it is clear that the film is polycrystalline, due to the presence of the Bragg's peaks corresponding to (120), (-121), (-212) and the (-141) planes respectively. The film crystallised in the acanthite structure and the observed (hkl) peaks were found to be consistent with the Powder Diffraction File 14-0072 [32]. Other research groups on silver sulphides [33, 34, 35], have observed similar crystal structure with such corresponding diffraction peaks for different/same deposition techniques. However, Ben Nasrallah et. al. [17] reported on Silver sulphide thin films annealed in a nitrogen atmosphere that are crystallised in the $\beta\text{-Ag}_2\text{S}$ phase with a $\langle 103 \rangle$ preferred orientation.

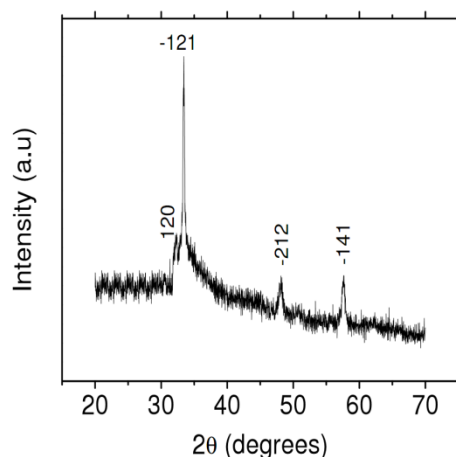


Fig.1 XRD diffractogram of Ag_2S films sulphurised at 350 °C and annealed at 250 °C.

Barrera-Calva et. al. [24] reported on Ag_2S thin films that crystallised in the acanthite phase, exhibited low intensity diffraction peaks that occurred at Bragg's angle of 34.48° , 36.56° , and 44.28° corresponding to the $\langle 100 \rangle$, $\langle 112 \rangle$, and the $\langle 103 \rangle$ directions respectively. The difference in such

crystal structural observation could be attributed to a deviation from stoichiometry of the constituent elements of the film and/or different annealing conditions/environment.

Data extracted from the XRD diffractograms were used to calculate the crystallite size D , by applying the Scherer's formula given as [36-37]:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (1)$$

Where D is the crystallite size, λ is the wavelength of the CuK_α radiation source given as ($\lambda = 0.15406$ nm), β is the full width at half maximum of the most prominent diffraction peak and θ is the Bragg's angle.

The crystallite size was in the range 0.0025 nm to 0.0016 nm. The crystallite size was found to be slightly higher for the layers annealed at 250 °C. This could be due to a fragmentation of the crystallites at the higher annealing temperatures and/or a re-evaporation of sulphur during the annealing process.

Fig.2 gives a typical transmittance versus wavelength spectrum for Ag_2S films sulphurised at 350 °C and annealed at 250 °C. The transmittances versus wavelength measurements were taken in the range 200 nm – 1000 nm. The film show a very good transmittance with a sharp fall in the fundamental edge, indicating the absence of the other secondary phases of sulphides of silver such as Ag_2S_2 , Ag_2S_3 or Ag_3S_3 . From the transmittance measurements, some optical constants such as the energy bandgap were deduced. The energy bandgap was calculated using the relation [38-39],

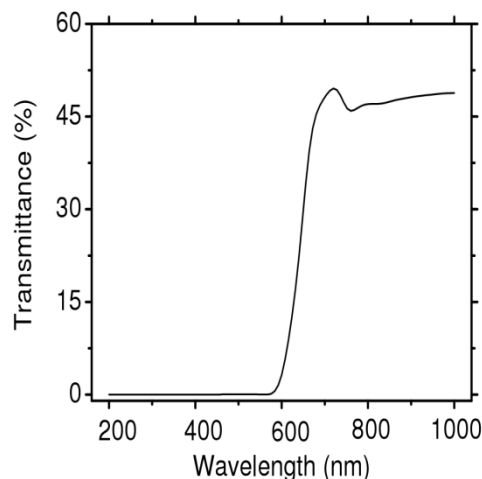


Fig.2 Transmittance vs. Wavelength spectrum of Ag_2S films sulphurised at 350 °C and annealed at 250 °C.

$$ahv = B(hv - E_g)^n \quad (2)$$

Where B is an energy independent constant and $n = 0.5$ for direct allowed transition and 1.5 for direct forbidden transitions.

The optical energy bandgap was direct, with an energy bandgap of 2.10 eV and 2.20 eV respectively. Other authors have reported values of direct energy band gap \geq 2.0 eV [2, 3].

The slightly higher value obtained in this study could be due to a loss of stoichiometry during the sulphurisation/annealing process. As indicated earlier, Ag_2S displays an amphoteric character hence it can be used as an absorber or window layers depending on the energy bandgap of the layers. Some authors have reported energy bandgap in the range 1.0 eV to 1.5 eV [4, 14, 17, 29, 40].

The value obtained in this study suggests a possible use of Ag_2S thin films as a window layer in photovoltaic solar cell devices or for other solar thermal devices. Jadhav et. al. [31] reported low power conversion efficiency for a Ag_2S thin films of n-conductivity type fabricated using a modified chemical bath deposition method and noted that this was due to high series resistance and low shunt resistance of the cell, coupled with high density of interface states, thus leading to high recombination mechanism in the device.

4 Discussions

Thin films of Ag_2S has been grown using the sulphurisation method. The structural studies show that films with polycrystalline structure can be obtained. The films crystallised in the acanthite form. The optical energy band gap was direct, and within the range suitable for various optoelectronic and solar thermal/photovoltaic applications.

5 Conclusions

Using the thermal evaporation method, silver thin films were deposited on glass substrates, and further sulphurised using a simple sulphurisation method to produce Ag_2S thin films. From structural studies, X-ray analysis show that the films were of the acanthite phase belonging to the Powder Diffraction File 14-0072. The films were polycrystalline and showed $\langle hkl \rangle$ directions corresponding to $\langle 120 \rangle$, $\langle -121 \rangle$, $\langle -212 \rangle$ and the $\langle -141 \rangle$ respectively. The optical energy bandgap was direct, with energy bandgap between 2.10 eV to 2.20 eV.

This value is within the range suitable for window layers in solar cell fabrication and also for other solar thermal applications or transparent conducting devices. The findings reported herein is a fundamental step toward obtaining the necessary conditions for fabrication of more suitable and efficient window layers for application in photovoltaic solar cell devices. It will also serve as a useful guide in fabricating several solar thermal devices, infra-red detectors and other optoelectronic devices. Our future work will focus on the use of these layers to make heterojunction devices with improved solar conversion efficiency.

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