STRUCTURAL, OPTICAL AND PHOTOELECTROCHEMICAL PROPERTIES OF PULSE PLATED $AgInSe_2$ FILMS

Murugan S.[1], Dhanapandian S.[2], Manoharan C.[2], Murali K.R.[3]

[1]Dept of Physics, AVC College (Autonomous), Mannanpandal, Mayiladuthurai, India
[2]Dept of Physics, Annamalai University, Chidambaram, India
[3]ECMS Division, CSIR-CECRI, Karaikudi, India
Email : [1]muraliramkrish @gmail.com

Abstract

In this work, the pulse electrodeposition technique has been employed for the first time to deposit $AgInSe_2$ films. $AgInSe_2$ films were deposited by the pulse electrodeposition technique at room temperature from a bath containing Analar grade 10 mM silver sulphate, 50 mM indium sulphate and 5 mM SeO_2. The deposition potential was maintained as – 0.98V (SCE). Tin oxide coated glass substrates (5.0 ohms/sq) was used as the substrate. The duty cycle was varied in the range of 6 – 50%. The XRD profile of the thin films deposited at different duty cycles indicate the peaks corresponding to $AgInSe_2$. The transmission spectra exhibited interference fringes. Refractive index decreased from 2.5 to 1.8 in the wavelength range of 500 – 1500 nm. The room temperature resistivity increased from 0.1 ohm cm to 10 ohm cm with decrease of duty cycle. Photoelectrochemical cell studies indicated an open circuit voltage of 0.55 V and a short circuit current density of 5.0 mA cm^{-2} at 60 mW cm^{-2} illumination for the films deposited at 50 % duty cycle.

Key words: I-III-VI_2, thin film, semiconductor, pulse plating

I. INTRODUCTION

$AgInSe_2$ is a member of the I–III–VI_2 group of semiconductors. In recent years, the ternary chalcopyrite semiconductors have been receiving considerable attention because of their adaptability, as an absorber component, in thin film solar cells. The I–III–VI_2 compounds are the ternary analogues of II–VI compounds. $AgInSe_2$ is a ternary analogue of CdSe, which has been used for a number of electronic devices. $AgInSe_2$ is a semiconductor with energy gap of 1.20 eV [1]. They crystallize in the chalcopyrite structure, which is closely related to zinc blend structure. Ternary chalcopyrite compounds have photovoltaic potential for solar cells since their optical band gap lies between 0.8 and 2.0 eV and they can be grown either n- or p-type [2]. The commonly used methods for preparing silver indium selenide thin films are flash evaporation [2–4], rf magnetron sputtering [5], thermal evaporation [6,7], electrodeposition [8], solution growth technique [9] and co-evaporation [10]. In the present work we employ bulk thermal evaporation technique in high vacuum. The objective of the present work is to deposit silver indium selenide by the pulse electrodeposition technique and study their properties. To our knowledge this is the first report on pulse electrodeposited $AgInSe_2$ films.

II. EXPERIMENTAL METHODS

$AgInSe_2$ films were deposited by the pulse electrodepsoition technique at room temperature from a bath containing Analar grade 10 mM silver sulphate, 50 mM Indium sulphate and 5 mM SeO_2. The deposition potential was maintained as – 0.98V (SCE). Tin oxide coated glass substrates (5.0 ohms/sq) was used as the substrate. The duty cycle was varied in the range of 6 – 50%. Thickness of the films measured by surface profilometer increased from 500 nm to 1000 nm as the duty cycle increased from 6 % to 50 %. Structural, optical and photoelectrochemical (PEC) properties of the films were studied. For PEC studies 1M polysulphide was used as the redox electrolyte.

III. RESULTS AND DISCUSSION

The films deposited at different duty cycles were characterized by the X-ray diffraction (XRD) pattern (Fig. 1). All the reflections could be indexed as the tetragonal phase of $AgInSe_2$ with the lattice parameters a = 6:09A , c = 11:67A , which were very close to the reported data (JCPDS Cards, 35– 1099). As the duty cycle increased, the intensity of the peaks increased. Peaks corresponding to the (112), (220), (204), (312) and (116) reflections were observed. The height of the peak increased with duty cycle and the width of the peaks decreased with increase of duty cycle. No

characteristic peaks of other impurities, such as Ag_2Se or In_2Se_3, were detected in the pattern. The crystallite size was determined from Scherrer's equation

$$\text{Crystallite size} = 0.9\lambda/(\beta\cos\theta) \quad ...(1)$$

where λ is the wavelength of x-rays, β is the full width at half maximum and θ is the Bragg angle. The crystallite size was found to vary in the range of 5 to 12 nm with increase of duty cycle.

The microstructural parameters like dislocation density and strain were calculated from the XRD data. Strain (ε) and grain size (D) are calculated using the relation

$$\beta\cos\theta = \lambda/D - \varepsilon\sin\theta \quad ...(2)$$

where; λ is the wavelength of the radiation used (0.15418 nm), β the full width at half maximum, and θ the angle of diffraction.

$$\text{Dislocation density } (\delta) = 15\,\varepsilon/aD \quad ...(3)$$

Table 1. Microstructural parameters of the $AgInSe_2$ films deposited at different duty cycles.

Duty Cycle (%)	Grain size (nm)	Strain ($x10^{-3}$)	Dislocation Density (10^{14} lines/m)
6	5.0	1.97	9.6
9	7.0	1.56	5.48
15	9.0	1.35	0.69
33	11.0	1.14	0.38
50	12.0	1.01	0.20

Energy dispersive X-ray (EDAX) spectrum gives the elemental composition of the as prepared samples. It contains 29.29% of Ag, 20.76% of In and 49.95% Se. This indicates that the as prepared films were indium deficient. The indium sites can be occupied by Ag atoms, acting as donors

The morphological characterizations were made by a TEM (JEM 2000FX). TEM sample preparation for the observation of nanostructured thin films was done by the following procedures: 1. The film was scraped off from the tin oxide glass with a spatula into an agate mortar. 2. The finely milled powder was dispersed in 1:1 mixed solution of water and alcohol for an hour. 3. A small amount of the liquid taken from the surface of oxide dispersed solution was dropped on the microgrid of each TEM sample holder, which was then dried. Fig. 2 shows the Transmission electron micrographs of the films deposited at different duty cycles. It is observed that the grain size increases from 5 nm to 10 nm with increase of duty cycle from 6% to 50%.

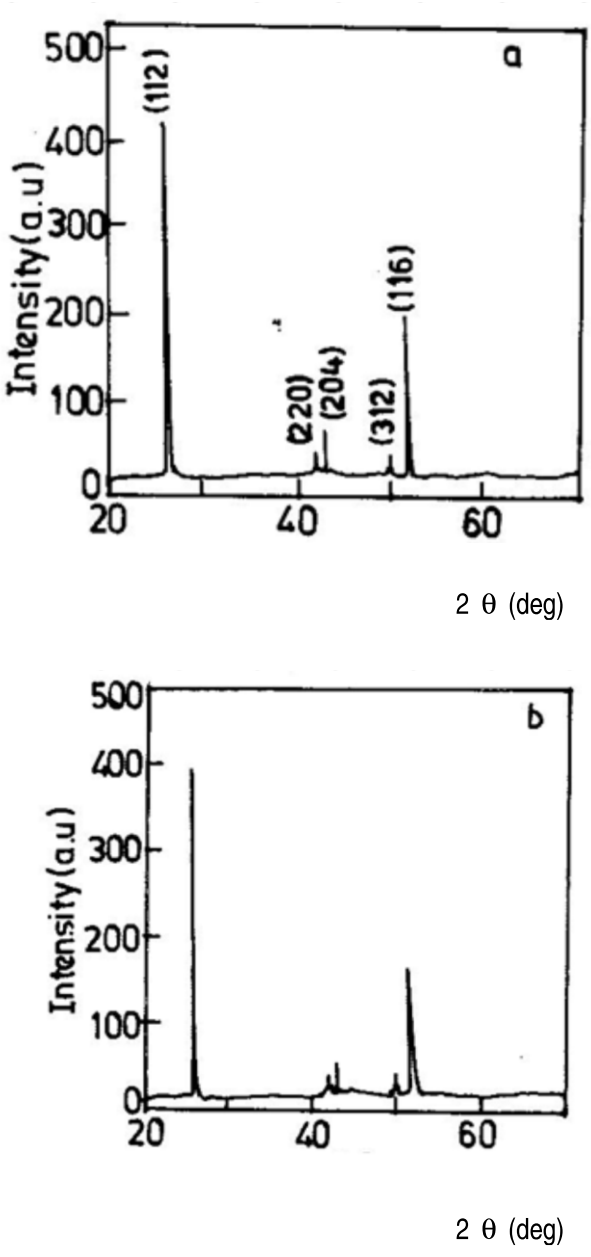

Fig. 1. XRD pattern of $AgInSe_2$ films deposited at different duty cycles (a) 9% (b) 50%

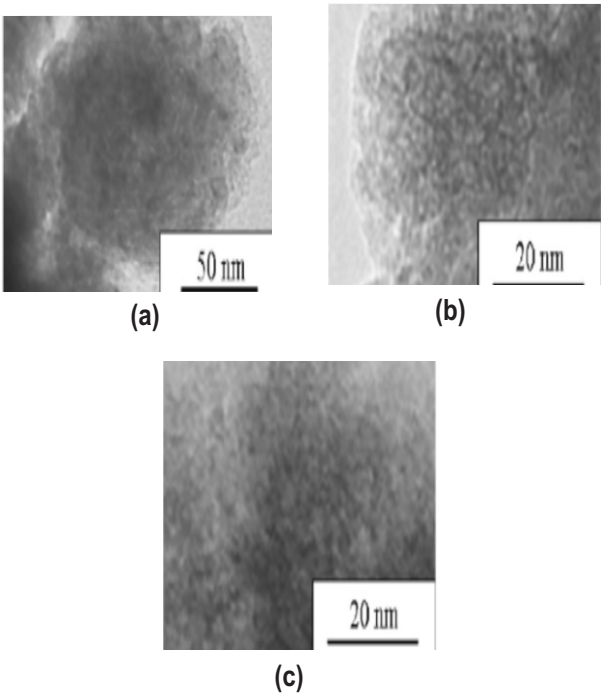

Fig. 2. Transmission Electron micrograph of $AgInSe_2$ films deposited at different duty cycles
(a) 50% (b) 33% (c) 5%

Fig. 3. shows transmittance spectra at RT of $AgInSe_2$ thin films deposited at different duty cycles. Fundamental absorption edges around 700 nm are observed in all samples. Interference can be observed in all samples, which is evidence that good uniformity thin films were produced. The value of the refractive index was calculated by the envelope method using the following relations

$$n = [N + (N^2 - n_s^2)]^2 \quad ...(1)$$

$$N = (n_s^2 + 1)/2 + 2n_s(T_{max} - T_{min})/T_{max}\ T_{min} \quad ...(2)$$

The refractive index decreased from 2.60 to 1.80 with increase of wavelength from 500 nm to 1200 nm. This result is similar to that observed by Santhosh Kumar et al [10]

Fig. 4 shows photon energy vs. $(\alpha h\nu)^2$ plot of $AgInSe_2$ thin films deposited at different duty cycles, with α and hv being the absorption coefficient and photon energy, respectively. Bandgap energy (Eg) can be calculated using the following equation for estimating the absorption coefficient (α)

$$\alpha = A/h\nu\,(h\nu - E_g)^{1/2} \quad ...(2)$$

A bandgap energy of 1.172 eV can be obtained using $\alpha h\nu = 0$. Other thin film references report the bandgap to be 1.21 eV [8] or 1.25 eV [11]. It is assumed that the discrepancies are due to differences in carrier concentration and/or Ag/In composition ratios.

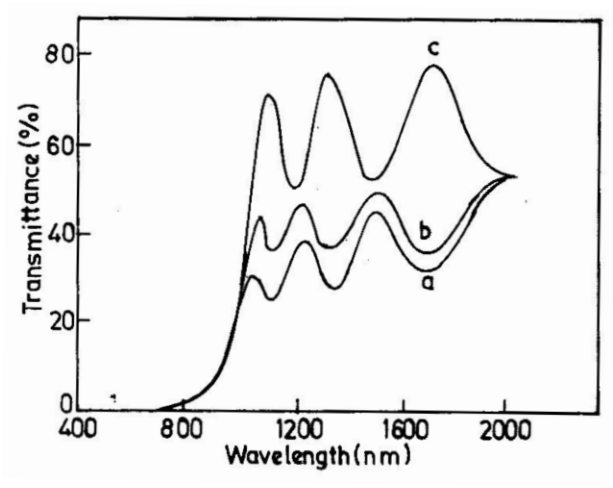

Fig. 3. Transmission spectra of $AginSe_2$ films deposited at different duty cycles
(a) 15% (b) 33% (c) 50%

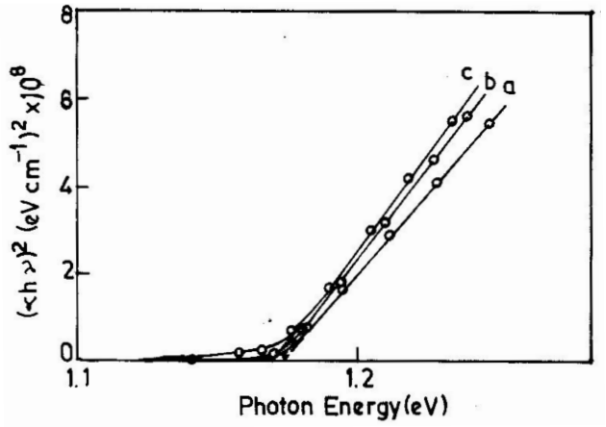

Fig. 4. $((\alpha h\nu)^2$ vs hv plot of $AgInSe_2$ films deposited at different duty cycles
(a) 15% (b) 33% (c) 50%

Photoelectrochemical cell studies were made using 0.5 M KI and 0.05 M I_2 as the redox electrolyte. Graphite was used as the counter electrode. The films deposited at lower duty cycles exhibited very poor photo output after post annealing in Argon atmosphere. Films deposited at lower duty cycles exhibited low output. For a film deposited at 50% duty cycle, an open

circuit voltage of 0.48 V and a short circuit current density of 3.8 mA cm^{-2} at 60 mW cm^{-2} illumination (Fig. 5). The photooutput is higher than earlier report [12].

The photoelectrodes were photoetched in 1 : 100 HCl, by shorting the photoelectrode and the counter electrode under an illumination of 100 mW cm^{-2}. The photocurrent and photovoltage increased with photoetching upto 80s, beyond which the parameters decrease due to the reduction in thickness. The output parameters after photoetching are V_{oc} = 0.65 V, J_{sc} = 7.0 mA cm^{-2}. Photoecthing causes an increase in surface area and also etches defects that are not accessible by chemical etching.

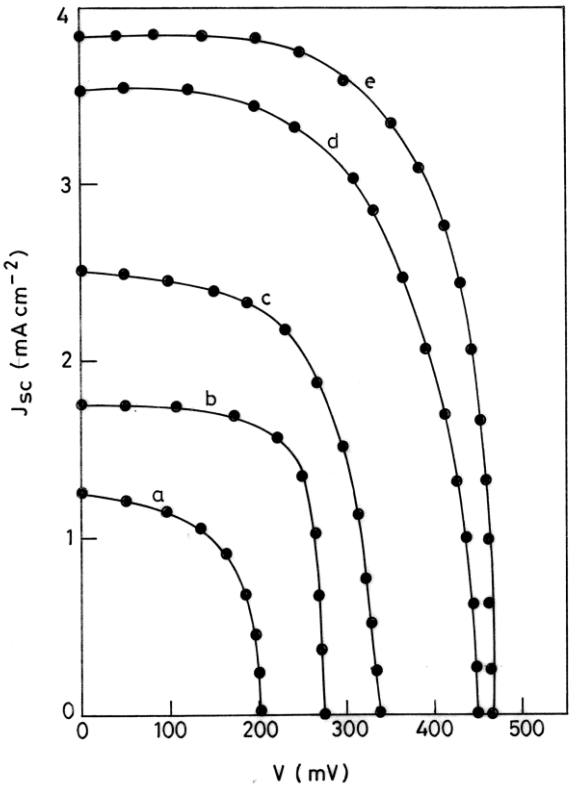

Fig. 5. Load characteristics of the photoelectrochemical cell made with $AgInSe_2$ film deposited at different duty cycle (a) 6% (b) 9% (c) 15% (d) 33% (e) 50%

Impedance spectroscopy (IS) is a powerful method of characterizing many of the electrical properties of materials and their interfaces with electronically conducting electrodes. A great strength of impedance spectroscopy is that, with appropriate data analysis, it is often possible to characterize the different electrically active regions in a material by demonstrating their existence and by their individual electric properties. The electrical characteristic of a material is exhibited by the appearance of semicircular arcs in the Nyquist plots. Fig. 6 shows the complex impedance plots (Nyquist plots) of $AgInSe_2$ films deposited at different duty cycles and taken over a wide frequency range (20 Hz – 1 MHz). It can be seen from the figure the existence of a single semicircle. This can be explained on the basis of reduction in grain size with doping. Indeed, nanomaterials consist of nanometer size grains which introduce more grain boundaries within the samples. As the particle size decrease with increasing duty cycle according to the X-ray diffraction results, the number of grain boundaries increases. Hence, the grain boundaries effect becomes more dominant over grain contribution and therefore giving one semicircle in the Nyquist plot. Each of the semicircles of Fig. 6 could be represented by a single parallel RC combination as shown in Fig. 6. The values of grain boundaries resistance (R_{gb}) at different duty cycles have been obtained from the intercept of the semicircular arcs on the real axis (Z'). The value of R_{gb} decreases from 990 ohms to 440 ohms with decrease of duty cycle.

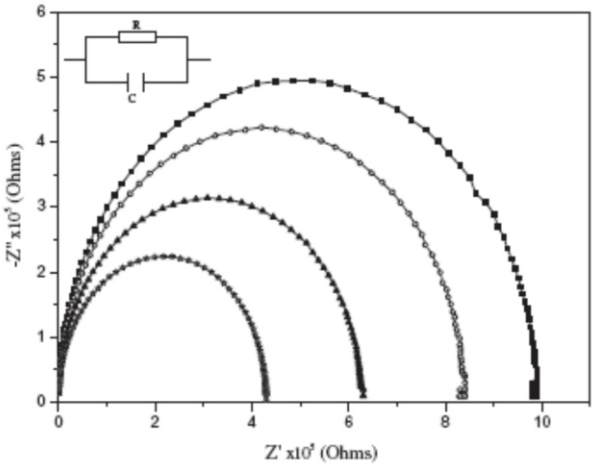

Fig. 6. Nyquist plot of $AgInSe_2$ films deposited at different duty cycles (a) 50% (b) 33% (c) 15% (d) 6%

IV. CONCLUSION

This study clearly illustrates that the pulse plating technique can be employed for the deposition of nanocrystalline $AgInSe_2$ films. Films possessing grain

size in the range of 5 nm to 10 nm can be prepared. Films with transmission around 80 % can be prepared. Preliminary studies indicate the use of these films in photoelectrochemical cells.The photo output is higher than earlier report.

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