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Properties of pulse plated SnSe films

K. Ananthi · K. Thilakavathy · N. Muthukumarasamy · S. Dhanapandian · K. R. Murali

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Abstract In this work, the pulse electrodeposition technique has been employed for the first time to deposit SnSe films from a bath containing Analar grade 50 mM tin chloride ($SnCl_4$) and 5 mM SeO_2. The XRD profile of SnSe thin films deposited at different duty cycles indicate the peaks corresponding to SnSe. Atomic force microscopy studies indicated that the surface roughness increased from 0.5 to 1.5 nm with duty cycle. The transmission spectra exhibited interference fringes. The value of refractive index at 780 nm was 2.1, this value decreased to 1.95 with decrease of duty cycle. The room temperature resistivity increased from 0.1 to 10 Ωcm with decrease of duty cycle. Photo electrochemical cell studies were made using the films deposited at different duty cycles. For duty cycles greater than 15% photo output was observed. For a film deposited at 50% duty cycle, 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. Capacitance voltage measurements indicated $V_{fb} = 0.67$ V (SCE) and p type, carrier density $= 6.98 \times 10^{16}$ cm^{-3}.

1 Introduction

The IV–VI compound, tin selenide (SnSe) has received considerable attention due to its applications in a variety of devices. SnSe thin films were deposited by different methods like thermal evaporation [1, 2], flash evaporation [3], hot wall epitaxy [4], reactive evaporation [5], electrodeposition [6], laser ablation [7], chemical bath deposition (CBD) [8], chemical synthesis [9, 10] and electrochemical atomic layer epitaxy (ECALE) [11], to study various physical properties. The decisive requirements for the efficient performance of the devices are compositional uniformity and crystallinity. Further, the technique adopted should be simple and cost effective. Every technique has its own merits and demerits. In this investigation, SnSe films were deposited for the first time using the pulse electrodeposition technique.

2 Experimental methods

SnSe films were deposited by the pulse electrodeposition technique at room temperature from a bath containing Analar grade 50 mM tin chloride ($SnCl_4$) and 5 mM SeO_2. The deposition potential was maintained at −0.9 V (SCE). Tin oxide coated glass (5.0 Ω sq^{-1}) 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 to 1,000 nm as the duty cycle increased from 6 to 50%. Structural, optical, electrical and photoelectrochemical (PEC) properties of the films were studied. For PEC studies 1 M polysulphide was used as the redox electrolyte.

3 Results and discussion

The XRD patterns of SnSe thin films (Fig. 1), deposited at different duty cycles indicate the peaks around $2\theta = 30°$

K. Ananthi · K. Thilakavathy · N. Muthukumarasamy
Department of Physics, CIT, Coimbatore, India

S. Dhanapandian
Department of Physics, Annamalai University, Chidambaram, India

K. R. Murali (✉)
ECMS Division, CSIR-CECRI, Karaikudi, India
e-mail: muraliramkrish@gmail.com

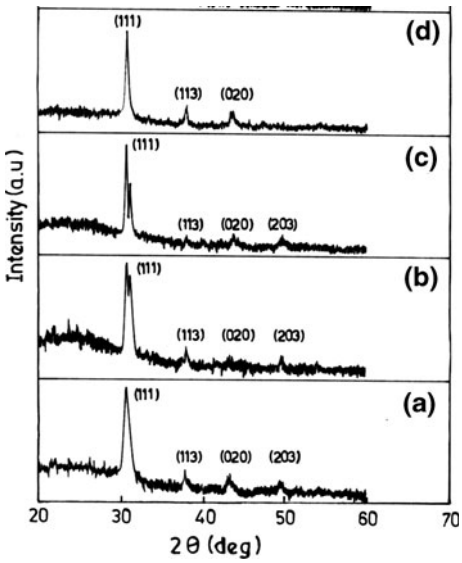

Fig. 1 XRD pattern of SnSe films deposited at different duty cycles **a** 9%, **b** 15%, **c** 33%, **d** 50%

corresponding to (111) reflection, along with three other very weak diffraction peaks corresponding to (113), (020), (203) reflections, which confirms the polycrystalline nature of the film. A similar preferred orientation of grains along the (111) plane in SnSe film was observed in the evaporated SnSe thin films. The analysis of the diffraction patterns also suggests that the SnSe thin-film has orthorhombic structure with lattice parameters $a = b = 0.429$ nm and $c = 0.523$ nm. The XRD data of the films matches well with JCPDS data card no. 32-1392. Furthermore, it is observed that as the duty cycle increases, the intensity of the diffraction peaks increase. This could be linked with the grain-growth with increase in duty cycle. The crystallite size was estimated by using Scherrer's equation and it was found to increase from 37 to 78 nm with increase of duty cycle. Energy dispersive X-ray spectra of SnSe thin films revealed that the Sn and Se contents depend critically on the duty cycle. It is seen that the SnSe thin films formed at duty cycles less than 50% contained a slight excess of selenium. The films deposited at 50% duty cycle was nearly stoichiometric and the calculated atomic percentages (at%) of tin and selenium are 50.19 and 49.81, respectively (Fig. 2).

Figure 3 shows XPS spectrum of the sample in the region of Sn3d signal, which corresponds to the Sn doublet. No obvious peaks for selenium oxide are observed indicating high product purity. The two strong peaks at 486.05 and 53.55 eV correspond to $Sn3d_{5/2}$ and Se3d binding energy for SnSe, respectively. This result is close to that of bulk SnSe [12]. The contents of Sn and Se are quantized by $Sn3d_{5/2}$ and Se3d peak areas and an average composition of $Sn_{0.98}Se$ is obtained.

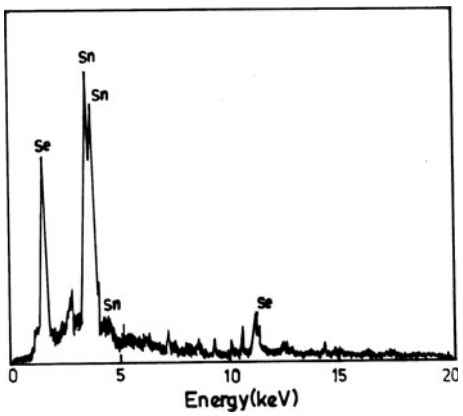

Fig. 2 EDAX spectrum of SnSe film deposited at a duty cycle of 50%

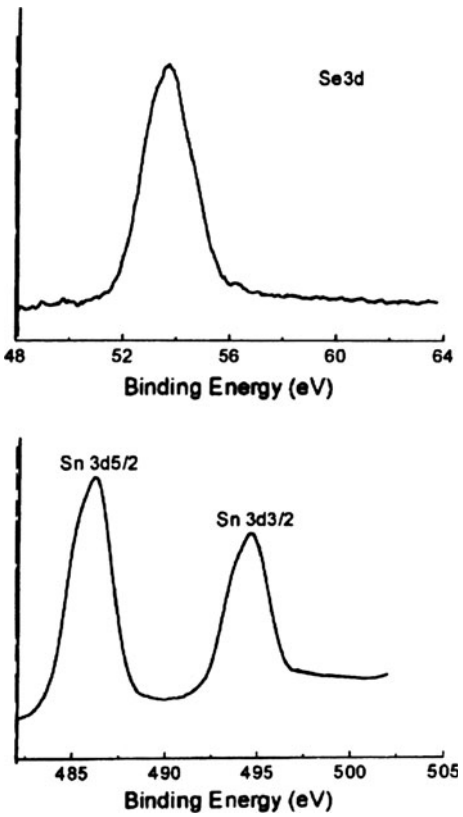

Fig. 3 XPS spectrum of SnSe films deposited at 50% duty cycle

Surface morphology of the films deposited at different duty cycles studied by Atomic force microscope indicated that the surface roughness increased from 0.5 to 1.5 nm and the grain size increased from 40 to 80 nm respectively with increase of duty cycle (Fig. 4). These results are similar to that observed from XRD data.

Transmission measurements were made in the wavelength range 750–2,300 nm. The spectra exhibited interference fringes (Fig. 5). Refractive index of the films was

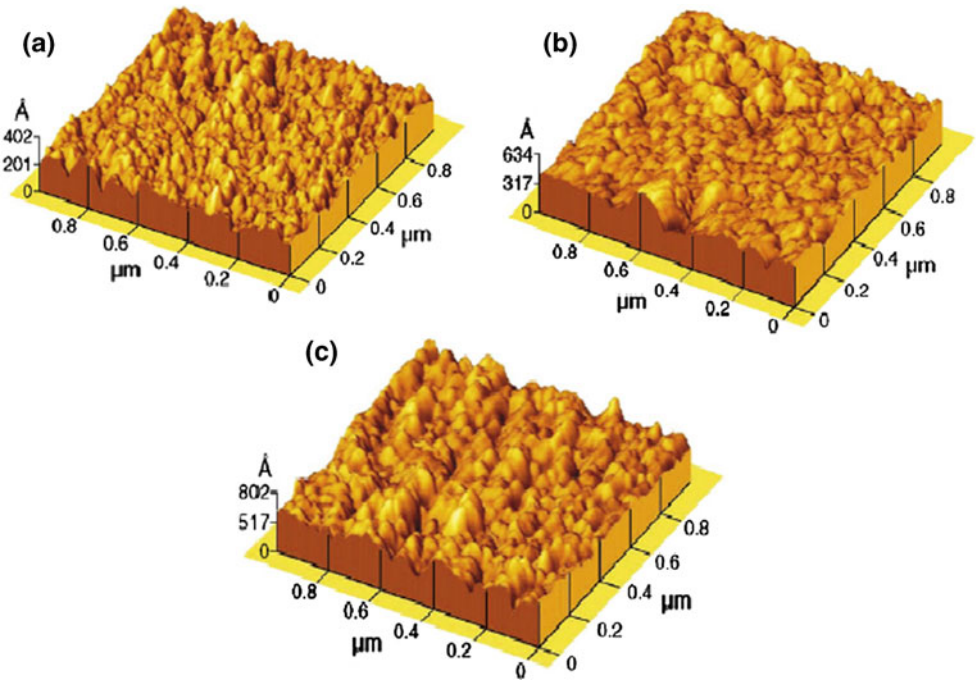

Fig. 4 Atomic force micrograph of SnSe films deposited at different duty cycles **a** 5%, **b** 33%, **c** 50%

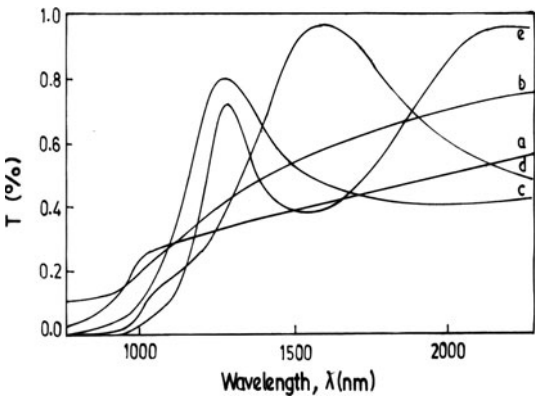

Fig. 5 Transmission spectra of SnSe films deposited at different duty cycles **a** 6%, **b** 9%, **c** 15%, **d** 33%, **e** 50%

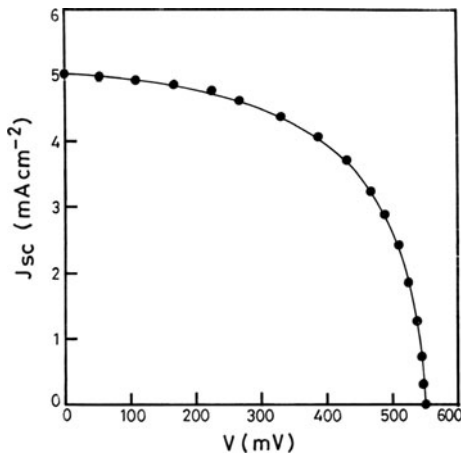

Fig. 6 Load characteristics of the photoelectrochemical cell made with SnSe film deposited at a duty cycle of 50%

calculated by the envelope method. The value of refractive index at 780 nm was 2.1, this value decreased to 1.95 with decrease of duty cycle. These values are in agreement with earlier reports. The band gap was estimated from the transmission spectra and it varied from 1.26 to 1.50 eV with decrease of duty cycle. This is understandable, since the grain size decreases with decrease of duty cycle, hence, the band gap value increases due to quantum size effects.

Electrical resistivity measurements were made by the two probe technique. Silver contacts were evaporated in the middle of the top surface of the film. The room temperature resistivity increased from 1.0 to 10 Ωcm with decrease of duty cycle. The resistivity values are lower than earlier reports.

Photo electrochemical cell studies were made using 1 M polysulphide (1 M S, 1 M Na_2S, 1 M NaOH) 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 duty cycles greater than 15% exhibited photo output. For a film deposited at 50% duty cycle, an open circuit voltage of 0.55 V and a short circuit current density of 5.0 mA cm^{-2} were observed for 60 mW cm^{-2} illumination (Fig. 6).

Capacitance–voltage measurements were made on the films deposited at 50% duty cycle. Figure 7 shows the $1/C^2$ versus V plot. The nature of the graph indicates p-type conductivity. Extrapolation of the graph to the voltage axis

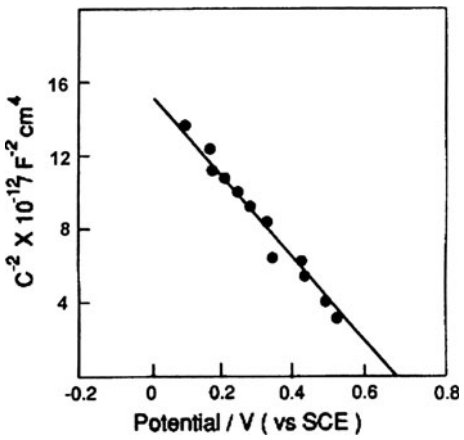

Fig. 7 Capacitance voltage plot of SnSe films deposited at 50% duty cycle

yields a Vfb = 0.67 V (SCE), the slope of the plot gives a p type, carrier density = 6.98×10^{16} cm^{-3}. Using the value of resistivity obtained from two probe measurements, the mobility value was calculated as 89 cm^2 V^{-1} s^{-1}. SnSe films exhibiting p-type behaviour was also reported earlier [8].

4 Conclusion

This study clearly illustrates that the pulse plating technique can be employed for the deposition of nanocrystalline SnSe films. Films with low resistivity in the range of 1.0–10 Ωcm can be deposited. Films with transmission around 80% can be prepared. Preliminary studies indicate the use of these films in photoelectrochemical cells.

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