

## PHOTOELECTROCHEMICAL BEHAVIOUR OF PULSE PLATED SNSE FILMS

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### ABSTRACT

The IV-VI compounds are technologically important in view of their applications in detectors and IR lasers. In this work, the pulse – plating technique has been employed for the deposition of SnSe films at different duty cycles. The films were polycrystalline with peaks corresponding to the orthorhombic structure. The grain size varied in the range of 40 – 80 nm with increase of duty cycle. The surface roughness of the films varied from 0.5 to 1.5 nm. The band gap increased from 1.26 – 1.50 eV with duty cycle. Photoelectrochemical cell studies indicated 4.93% efficiency at 60 mW cm<sup>-2</sup> illumination after photoetching.

**Keywords:** IV – VI, SnSe, thin films, semiconductor, electronic material.

### I. INTRODUCTION

The electronic and optical properties of IV – VI compounds, make them attractive for their use in diverse technological applications such as cut-off devices and photovoltaic cells, and in the manufacture of infrared lasers [1,2] and detectors. They have also been studied for the evaluation of nanostructures etching [3]. In particular, SnS and SnSe have been used as shells for PbSe and PbS quantum dots, for the development of infrared-based devices. SnSe thin films have been deposited by different methods like vacuum evaporation [4], flash evaporation [5], hot wall epitaxy [6], reactive evaporation [7], electrodeposition [8], laser ablation [9], chemical bath deposition (CBD) [10] and electrochemical atomic layer epitaxy (ECALE) [11] to study various physical properties. In this investigation, SnSe films were deposited for the first time using the pulse electrodeposition.

### II. 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<sub>4</sub>) and 5 mM SeO<sub>2</sub>. The deposition potential was maintained as – 0.9V (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, electrical 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 XRD patterns of SnSe thin films (Fig. 1), deposited at different duty cycles indicate the peaks around  $2\theta = 30^\circ$  corresponding to (111) diffraction

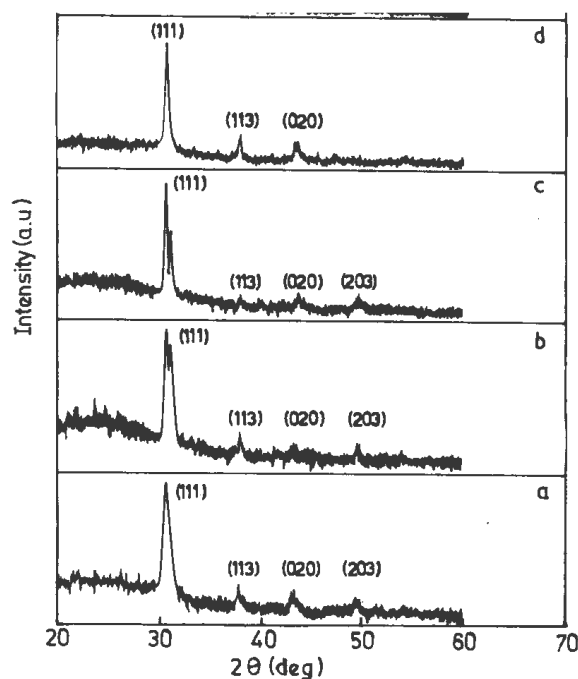


Fig. 1. XRD pattern of SnSe films deposited at different duty cycles  
(a) 9% (b) 15% (c) 33% (d) 50%

plane, along with three other very weak diffraction peaks viz. (113), (020), (203), 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 duty cycle increases the intensity of the diffraction peaks increases. 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 nm 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.

Strain ( $\epsilon$ ) and grain size ( $D$ ) are calculated using the relation

$$\beta \cos \theta = \lambda/D - \epsilon \sin \theta \quad \dots(1)$$

where;  $\lambda$  is the wavelength of the radiation used (0.15418 nm),  $\beta$  the full width at half maximum, and  $\theta$  the angle of diffraction. A graph is drawn between  $\beta \cos \theta$  and  $\sin \theta$  for various  $\theta$  values taken from the peaks of the corresponding plane (111). From the

**Table 1. Microstructural parameters of SnSe films deposited at different duty cycles**

Duty cycle (%) ( $10^{15}$ )	strain ( $\times 10^{-3}$ )	grain size (nm)	Dislocation density lines/m <sup>2</sup>
6	1.97	40	6.25
9	1.56	52	2.69
15	1.35	60	2.77
33	1.14	71	1.98
50	1.01	80	1.52

intercept and slope of the straight line plots, the particle size ( $D$ ) and strain ( $\epsilon$ ) in the film are calculated. The dislocation density ( $\delta$ ) is determined from the relation

Transmission measurements were made in the wavelength range 750 nm to 2300 nm. The spectra exhibited interference fringes (Fig. 2). Refractive index of the films was 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 bandgap was estimated from the transmission spectra and it varied from 1.26 eV to 1.50 eV with decrease of duty cycle. This is understandable, since the grain size decreases with decrease of duty cycle, hence, the bandgap value increases due to quantum size effects.

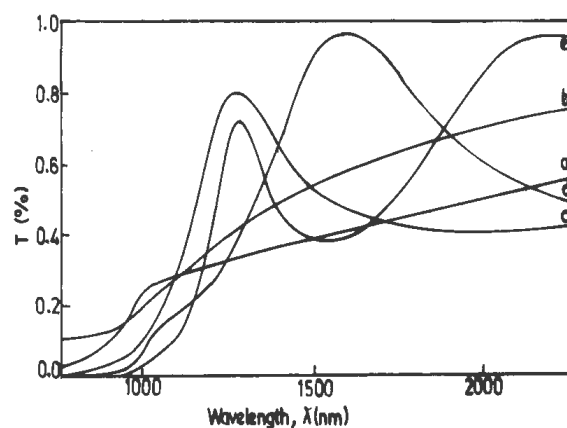


Fig. 2. Transmission spectra of SnSe films deposited at different duty cycles (a) 6% (b) 9% (c) 15% (d) 33% (e) 50%

Photoelectrochemical cell studies were made using 1 M polysulphide (1 MS, 1 M Na<sub>2</sub>S, 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<sup>-2</sup> at 60 mW cm<sup>-2</sup> illumination (Fig. 3).

Ideality factor of 1.85 and reverse saturation current of  $1.5 \times 10^{-7}$  A cm<sup>-2</sup> were obtained from the variation of open circuit voltage and short circuit current with intensity of illumination. The effect of photoetching on the PEC performance was studied by shorting the

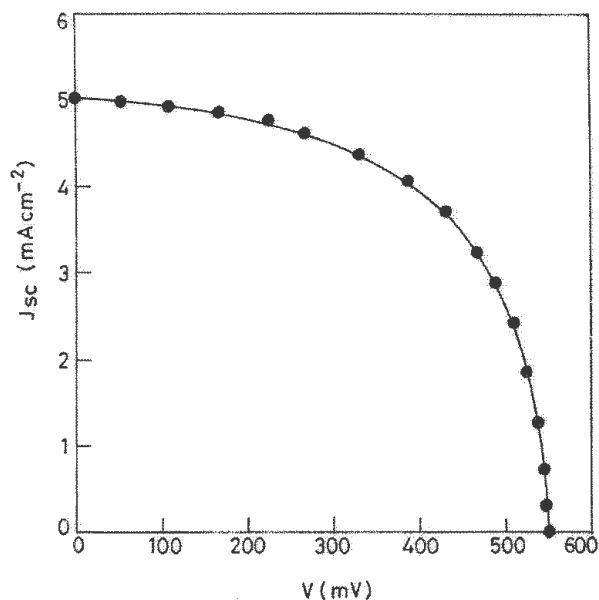


Fig. 3. Load characteristics of the photoelectrochemical cell made with SnSe film deposited at a duty cycle of 50%

photoelectrode and the graphite counter electrode under an illumination of  $80 \text{ mWcm}^{-2}$  in 1:100 HCl for different for different durations in the range 0 – 100 s. Both the photocurrent and photovoltage are found to increase upto 80 s photoetch, beyond which they begin to decrease (Fig. 5). Photoetching leads to selective attack of surface defects not accessible to chemical etchants. It is observed that during photoetching the  $V_{oc}$  increased from 0.55 V to 0.65 V and  $J_{sc}$  increased from  $5.00 \text{ mAcm}^{-2}$  to  $7.00 \text{ mAcm}^{-2}$ . The decrease in photocurrent and photovoltage beyond 80 s photoetching can be attributed to increase in surface area due to prolonged photoetching. The power output characteristics after 80 s photoetching indicates a  $V_{oc}$  of 0.65 V,  $J_{sc}$  of  $7.00 \text{ mA cm}^{-2}$ ,  $\eta$  of 0.65, of 4.93% for  $60 \text{ mWcm}^{-2}$  illumination.

#### IV. CONCLUSIONS

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 to 10 ohm cm can be deposited. Films with transmission around 80% can be prepared. Photoelectrodes exhibiting 4.93% efficiency after photoetching can be prepared

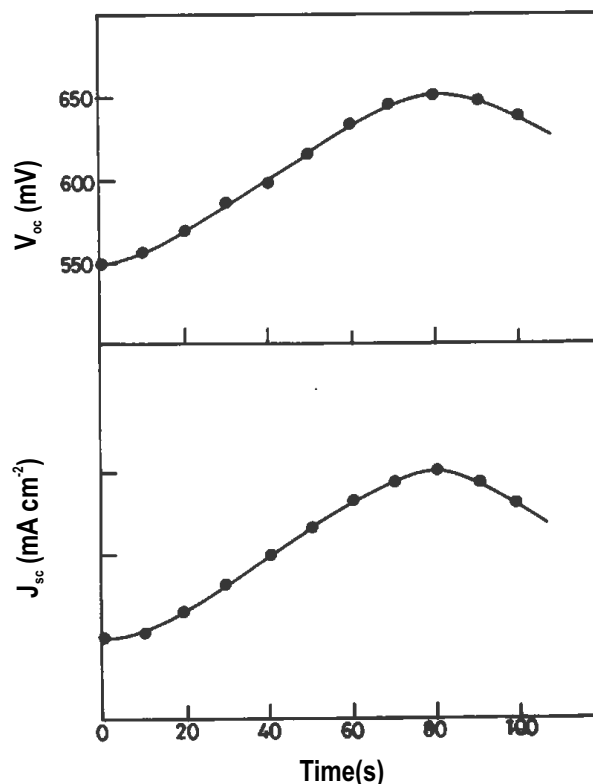


Fig. 4. Effect of Photoetching time on  $V_{oc}$  and  $J_{sc}$

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