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Photoconductive Properties of Pulse Plated In_2Se_3 Films

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Abstract: ***In_2Se_3 films were pulse electrodeposited on tin oxide coated glass substrates at different duty cycles for the first time. The films were single phase with crystallite size in the range of 15 – 40 nm. The strain and dislocation density decreased with increase of duty cycle. Post annealing increased the crystallite size from 40 nm to 115 nm. The films exhibited photoconductivity.***

Keywords: thin films, electronic material, pulse plating

1. Introduction

In_2Se_3 (Indium Selenide, IS) has a direct band gap, with enormous potential utilization in photovoltaic cells and other optoelectronic devices [1]. The In_2Se_3 consists of some well-known phases, including the layered structure (α-phase), rhombohedral structure (β-phase), defect wurtzite structure (γ-phase) and anisotropic structure (κ-phase). Among these, the γ-phase presents a band gap of 1.8 eV [1], which is suitable for buffer layer in CIS solar cells [2]. The films obtained by a large number of techniques, such as chemical bath deposition [3], electrodeposition [4] and sol gel [5], are composed of at least two low temperature phases. Three preparation methods for growing high performance single phase In_2Se_3 thin films have been reported until now, including solid state reaction (SSR) [6], molecule beam epitaxy (MBE) [7] and metal organic chemical vapor deposition (MOCVD) [8]. In this work, single phase γ-In_2Se_3 thin films were deposited by the pulse electrodeposition technique for the first time. In this paper, results obtained on photoconductive properties of In_2Se_3 films deposited at different duty cycles are presented and discussed.

In pulse electrodeposition [10,11] the potential or current is alternated swiftly between two different values. This results in a series of pulses of equal amplitude, duration and polarity, separated by zero current. Each pulse consists of an ON-time (T_{ON}) during which potential and/current is applied, and an OFF-time (T_{OFF}) during which zero current is applied. It is possible to control the deposited film composition and thickness in an atomic order by regulating the pulse amplitude and width. They favor the initiation of grain nuclei and greatly increase the number of grains per unit area resulting in finer grained deposit with better properties than conventionally plated coatings. The sum of the ON and OFF times constitute one pulse cycle. The duty cycle is defined as follows:

$$\text{Duty Cycle (\%)} = (\text{ON time}) / (\text{ON time} + \text{OFF time}) \times 100 \quad \text{----------- (1)}$$

A duty cycle of 100% corresponds to conventional plating because OFF time is zero. In practice, pulse plating usually involves a duty cycle of 5% or greater. During the ON time, the concentration of the metal ions to be deposited is reduced within a certain distance from the cathode surface. This so-called diffusion layer pulsates with the same frequency as the applied pulse current. Its thickness is also related to i_p, but reaches a limiting value governed primarily by the diffusion coefficient of the metal ions. During the OFF time the concentration of the metal ions build up again by diffusion from the bulk electrolyte and will reach the equilibrium concentration of the bulk electrolyte if enough time is allowed. These variables result in two important characteristic features of pulse plating which make it useful for alloy plating as well as property changes as mentioned earlier.

Pulse plating technique has distinct advantages compared to conventional electrodeposition namely, crack free, hard deposits and fine grained films with more uniformity, lower porosity and better adhesion. it is well known that by using pulse current for electrodeposition of metals and alloys it is possible to exercise greater control over the properties of electrodeposits and to improve them by modifying their microstructures [12]. It has been reported that a significant reduction in internal stress could be obtained when pulse current was used, compared to the use of conventional direct current [13].

2. Experimental Methods

In_2Se_3 films were deposited on titanium and Indium tin oxide substrates at 80°C. The films were deposited at different duty cycles and at a deposition potential of – 0.8 V(SCE). The precursors used were 0.1 M $InCl_3$, 0.001M SeO_2 in diethylene glycol. Thickness of the films measured by Surface profilometer was in the range of 400 nm to 800 nm. The films were characterized by x-ray diffraction technique using Philips x-ray unit and CuK_α radiation. Optical properties were studied using U3500 Hitachi spectrophotometer. Surface topography was measured by Atomic force microscope

3. Results and Discussion

Fig. 1 shows the X-ray diffraction peaks of In_2Se_3 thin films deposited at different duty cycles. Four peaks corresponding to (110),(006),(116) and (300) of γ-In_2Se_3 (JCPDS 40-1407). The peaks increase in intensity with duty cycle. The resulting values are a=7.1154Å and c=19.4293Å, which are consistent with the standard values (JCPDS40-1407). The crystallite size, dislocation density and strain were calcuated by considering high intense diffraction peaks of the deposited films using the following equations and the values are tabulated in Table 1.

$$D = K\lambda / \beta\cos\theta \qquad (1)$$

where K is the shape factor, θ is theBragg's angle, λ is the wavelength of X-rays used and β is the width of the peak at the half of the maximum peak intensity.The dislocation density (δ) was determined using Williamson and Smallman's formula [9]. The dislocation density was calculated from the crystal- lite size of the deposited samples. The increase in crystallite size is due to the aggregation or coalescence of small nanocrystalline particles.

$$\delta = 1/D^2 \qquad (2)$$

The line broadening gets reduced because of increase in crystallite size and decrease in strain of the material. The strain(ε) is obtained using the relation

$$\varepsilon = (\beta\cos\theta)/4 \qquad (3)$$

In order to induce photoactivity the films were post heat treated at different temperatures in argon atmosphere for 20 min in the temperature range of 450 - 550°C. Fig.2 show the XRD pattern of the films deposited at 50 % duty cycle and post heated at different temperatures. It is observed that the peaks become sharp due to recrystallization. The microstructural parameters of the post heat treated films are shown in Table.2. The crystallite size of the In_2Se_3 films increases from 30 nm to 60 nm with increase of duty cycle (Table.1) and also with heat treatment temperature.

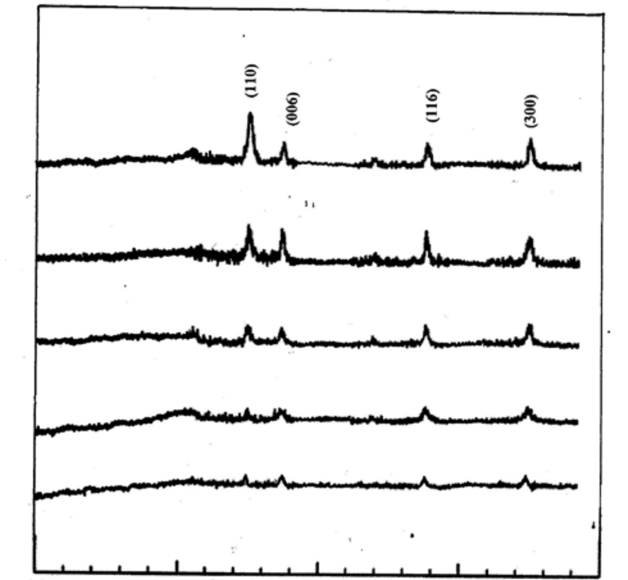

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Figure 1: X-ray diffraction pattern of γ – In_2Se_3 films deposited at different duty cycles (Top most) 50 % (Bottom most) 6 %. Duty cycle increases from bottom to top

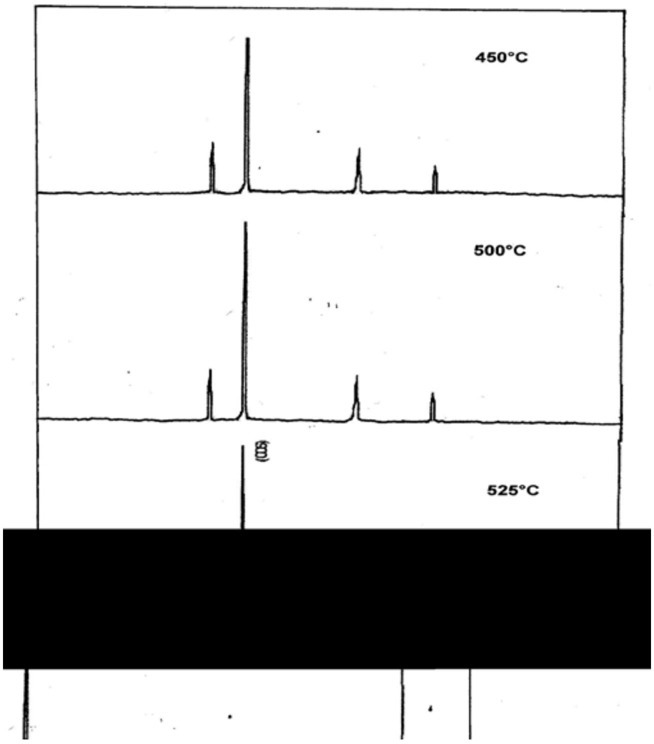

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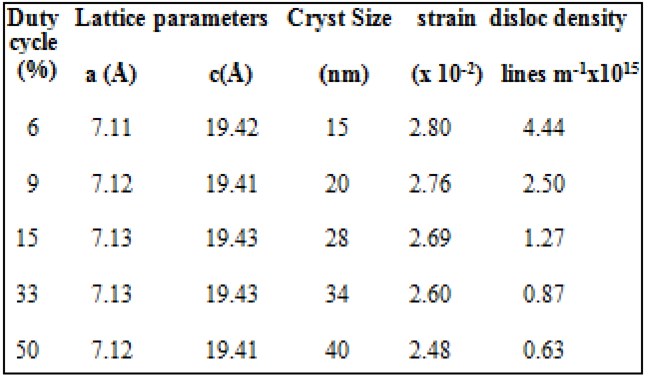
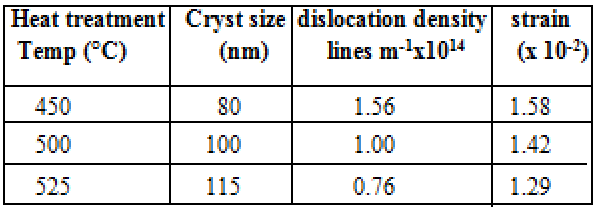
Figure 2: X-ray diffraction patterns of γ-In_2Se_3 films post annealed at different temperatures in argon atmosphere.

Table 1: Structural parameters of In_2Se_3 films deposited at different duty cycles



Duty cycle (%)	Lattice parameters a (Å)	c(Å)	Cryst Size (nm)	strain ($x\ 10^{-2}$)	disloc density lines $m^{-1}x10^{15}$
6	7.11	19.42	15	2.80	4.44
9	7.12	19.41	20	2.76	2.50
15	7.13	19.43	28	2.69	1.27
33	7.13	19.43	34	2.60	0.87
50	7.12	19.41	40	2.48	0.63

Table 2: Structural parameters of In_2Se_3 films deposited at 50 % duty cycle and post heat treated at different temperatures



Heat treatment Temp (°C)	Cryst size (nm)	dislocation density lines $m^{-1}x10^{14}$	strain ($x\ 10^{-2}$)
450	80	1.56	1.58
500	100	1.00	1.42
525	115	0.76	1.29

Composition of the films was studied by EDS analysis. The atomic ratio of approximately 2 :3 was observed in all cases. For the films deposited at lower duty cycles, there was a slight excess of Selenium. The atomic concentration was In – 38.50 %, Se – 41.50 % at 6 % duty cycle, with increase of duty cycle, the atomic concentration was In – 39.90 % and Se – 40.10 % at 50 % duty cycle. Fig.3 shows the EDS spectrum of In_2Se_3 films deposited at 50 % duty cycle.

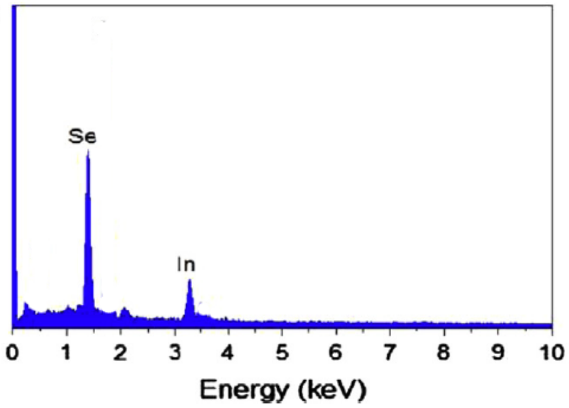
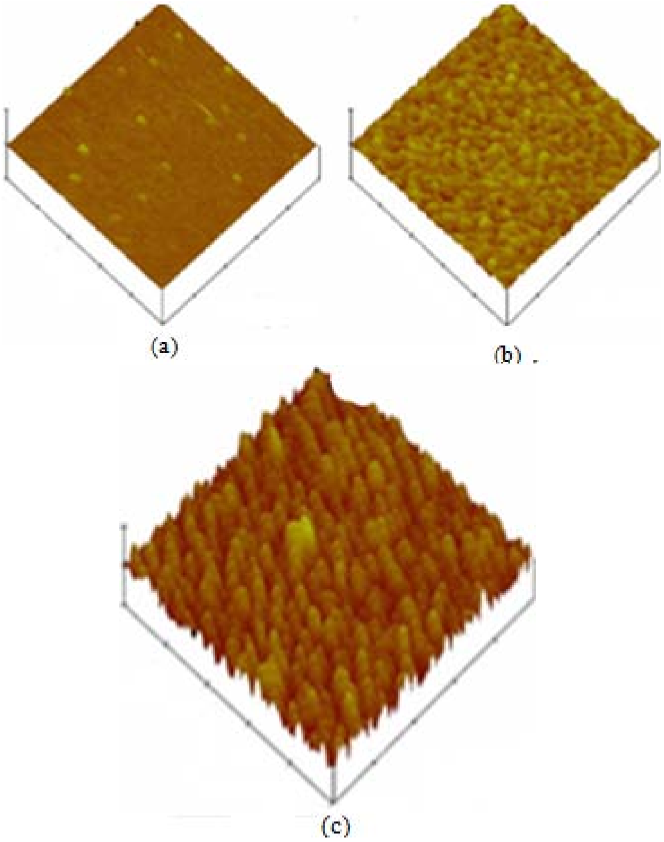


Figure 3: EDS spectrum of In_2Se_3 film deposited at 50 % duty cycle

Surface morphology of the films deposited at different duty cycles was studied by Atomic force microscope. Fig.4 shows the atomic force micrographs of the films.



Area – 1000 nm x 1000 nm, Z – ! div - 20 nm

Figure 4: AFM of In_2Se_3 films deposited at different duty cycles (a) 9 % (b) 33 % (c) 50 %

For measuring the photoconducting properties, the surface of the films were vacuum evaporated with Indium contact on the edges of the film. It is observed that the films deposited at 50 % duty cycle exhibited the maximum photosensitivity; hence further studies were carried out on these films. Fig.5 shows the variation of photosensitivity (PS**)** with intensity of illumination for the films prepared at different duty cycles.

It was observed from the figure, as the intensity of illumination increases, the corresponding photosensitivity also increases. Of all the annealing temperatures, the cells prepared with films annealed at 550°C exhibited maximum photosensitivity. The dependence of PS on light intensity at room temperature can be described in terms of the oxygen absorption effects at high annealing temperatures. The thermal release of oxygen from the surface is the possible mechanism, which is always dominant for cells annealed in Argon and hence both the dark and photoconductivity are increased.

Fig.6 shows the variation in the photocurrent with illumination for the films deposited at different duty cycles. The high photosensitivity arises due to the presence of compensated acceptors, which act as sensitizing centers. As the excitation intensity is increased, these centers become more active and the photosensitivity sharply increases at some region of excitation. It is observed from the figure, that upto 5000 lux, the photocurrent varies linearly with illumination, becoming super linear above this intensity. The super linearity arises from the conversion of hole traps into recombination centers when the hole quasi Fermi level moves towards the valence band with an increase in light intensity. These recombination centers, which have higher capture cross sections for the holes than electrons, in conjunction with another set of recombination centers with equal capture cross sections for both the carriers, decrease the lifetime of the holes thereby increasing the lifetime of the electrons. While the hole traps are being converted into recombination centers, the electron lifetime is continuously increasing and the photocurrent varies super linearly with increasing light intensity [14]. The transition from linearity to super linearity occurs when the hole demarcation level is at the level of the recombination centers with equal capture cross section.

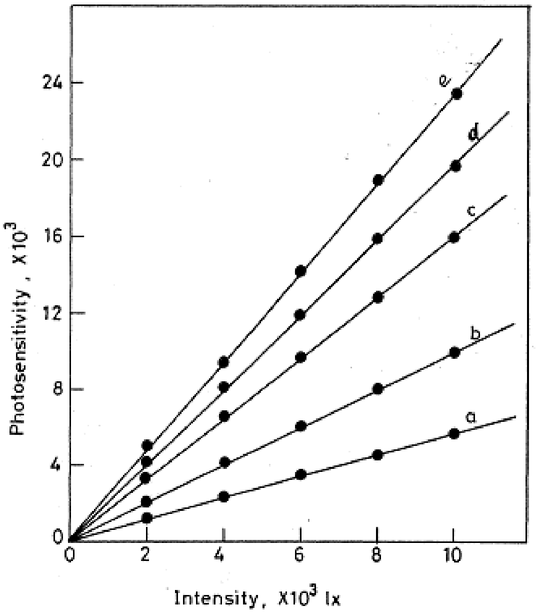


Figure 5: Variation of photosensitivity with illumination for the films deposited at different duty cycles (a) 6 % (b) 9 % (c) 15 % (d) 33 % (e) 50 %

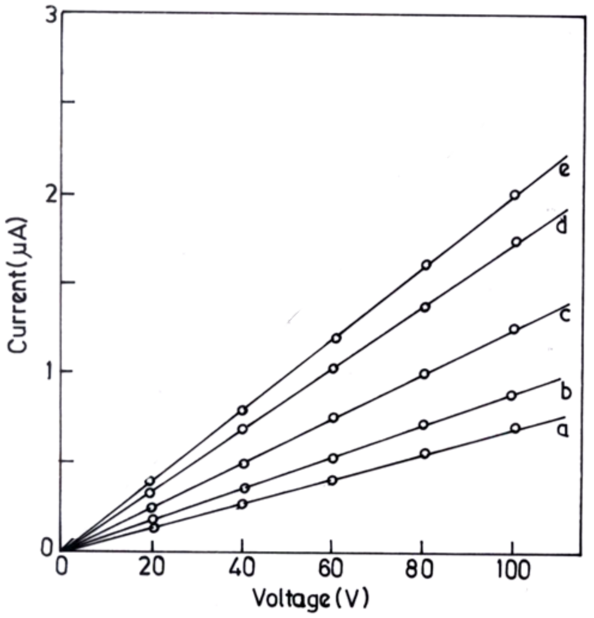


Figure 6: Variation of photocurrent with voltage for the films deposited at different duty cycles

4. Conclusion

Nanocrystalline films with crystallite size in the range of 15 nm – 40 nm can be obtained. Single phase In_2Se_3 films were prepared by the pulse electrodeposition technique. The films exhibit photoconductivity.

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