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Optical properties of Pulse Plated $CuInSe_2$ Thin Films

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Abstract*— Copper indium selenide (CIS) films were deposited by the pulse plating technique at different duty cycles in the range of 6 – 50 % and at a constant current density of 5 mA cm^{-2}. The films exhibited single phase copper indium selenide. The grain size increased with decrease of duty cycle. Optical band gap of the films increased from 1.05– 1.17 eV with increase of duty cycle. Optical constants (refractive index, n, and extinction co-efficient, k) of the films have been obtained in the wavelength range 1150 - 2650 nm by using spectrophotometric measurement. The obtained results concerning the absorption index yield the energy gap in addition to the type of the allowed optical transitions. N/m* ratio has been obtained from refractive index data. The dispersion of refractive index is analyzed by using a single oscillator model.

***Index Terms*—Electronic material, Optical properties, Semiconductors, thin films.**

I. INTRODUCTION

In recent years, copper indium diselenide (cis) with a i–iii–vi_2 ternary chalcopyrite structure has excited extensive interest for its desirable physical properties such as a direct band gap at ~1.0 ev and a high absorption coefficient of $>10^5$ cm^{-1} at photon energies above the band gap, which make it ideal for fabrication of high efficiency polycrystalline thin film photovoltaic devices [1]. There are multiple techniques currently available for the preparation of cis thin films, i.e. Co-evaporation [2], sputtering [3], spray pyrolysis [4], molecular beam epitaxy [5], etc. Among these, electrodeposition is considered to be a promising approach from the viewpoint of non-vacuum large area thin film production. Up to now, laboratory cell efficiency of more than 11% cis devices have been already developed using electrodeposited films at irdep [6]. Earlier two or three potential pulse electrodepsition method has been successfully employed for the deposition of cis films. In this work, we report for the first time results on optical properties of pulse plated cis films deposited at different duty cycles. In pulse electrodeposition [6] 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:

Duty cycle (%) = (on time) / (on time + off time) x 100 ----------- (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. Pulse plating technique has distinct advantages compared to conventional electrode position 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 electrode position of metals and alloys it is possible to exercise greater control over the properties of electrodeposits and to improve them by modifying their microstructures [7]. 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 [8].

II. EXPERIMENTAL METHODS

CIS films were deposited on indium tin oxide coated glass substrates (5 ohm/ sq) at different duty cycles in the range of 6 – 50 %. Deposition current density was kept constant at 5 mA cm^{-2} in the present work. The total deposition time was 60 min. the precursors used were AR grade 0.3 M of each $CuCl_2$ and $InCl_3$, along with 0.1 M of SeO_2. Thickness of the films estimated by Mitutoyo surface profilometer varied in the range of 800 to 1200 nm with decrease of duty cycle. The films were characterized by Xpert panalytical X-ray diffraction unit with CuK_α radiation. Optical measurements were recorded using a Hitachi U3400 UV-VIS-IR spectrophotometer. Composition of the films was estimated by EDAX attachment to JOEL SEM.

III. RESULTS AND DISCUSSION

The typical XRD patterns of CIS films deposited at different duty cycles are shown in Fig.1. The XRD patterns exhibit the chalcopyrite structure which is easily identified for the films (JCPDS card no. 00-040-1487). The films deposited at duty cycles more than 15 % show a poor crystallinity with weak and broadened diffraction peaks as shown in the figure.1. As the duty cycle decreases below 15 %, the

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diffraction peaks become sharp and the peak intensity is also greatly enhanced. Three well defined characteristic peaks at 26.6°, 44.1° and 52.4° correspond to the diffraction of the (112), (204) and (312) planes, respectively were observed for higher duty cycles. For duty cycles less than 15 %, two additional peaks corresponding to (400) and (316) were observed. The crystallite size was determined from Scherrer's equation

Crystallite size = 0.94λ / (βcosθ) ……….(1)

Where λ is the wavelength of CuKα x-rays (1.541Å), β is the full width at half maximum and θ is the Bragg angle. The crystallite size increased from 10 to 40 nm with decrease of duty cycle.

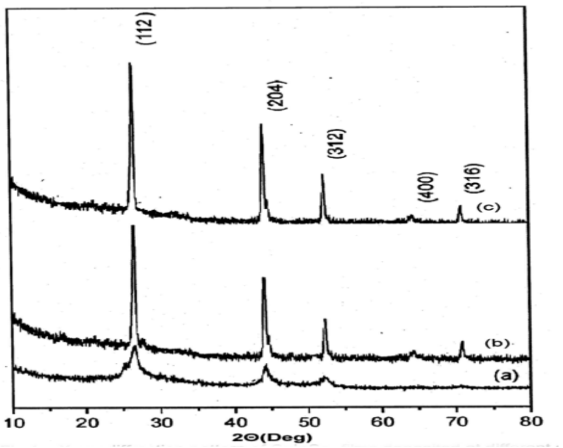

Fig.1 – X-ray diffraction pattern of $CuInSe_2$ films deposited at different duty cycles (a) 50 % (b) 33 % (c) 6 %

Table.1 Lattice parameters of $CuInSe_2$ films deposited at different duty cycles.

Duty cycle (%)	Lattice parameters (Å) (a)	(c)	Grain size (nm)
6	5.785	11.58	40
15	5.787	11.60	34
33	5.787	11.60	26
50	5.788	11.61	10

Composition of the films was estimated by recording the EDS spectrum of the films deposited at different duty cycles. Fig.2 shows the EDS spectrum of $CuInSe_2$ films deposited at 50 % duty cycle. The composition of the films deposited at different duty cycles is shown in Table-2. It is observed that films deposited at lower duty cycles were copper rich. For the films deposited at 6 % and 15 % duty cycle, the Cu/In ratio was 1.07 and 1.01 respectively. As the duty cycle increased, the films became stochiometric. For the films deposited at 33 % duty cycle, Cu/In ratio was 1.001. At 50 % duty cycle, the Cu/In ratio was less than unity, 0.99.This is due to the fact that at higher duty cycles, more flux of indium ions are available for deposition compared to the flux of indium ions at lower duty cycles, which results in higher concentration of Indium thus decreasing the Cu/In ratio. Based on the defect chemistry model of ternary compounds, compositional deviations of the $CuInSe_2$ can be expressed by non-stoichiometry parameter ($\Delta y = [2Se/(Cu + 3In)] - 1$). The parameter Δy is related to the electronic defects. For $\Delta y > 0$, the film has a p-type conductivity and it has an n-type conductivity for $\Delta y < 0$. In this study the value of Δy is greater than zero and the films exhibit p-type conductivity.

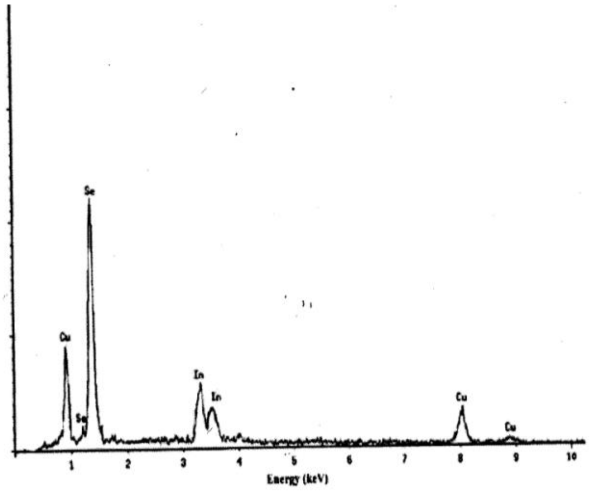

Fig.2 – EDS spectrum of CIS films deposited at 50 % duty cycle

Table- 2. Composition of $CuInSe_2$ films deposited at different duty cycles

Duty cycle (%)	Cu (at.%)	In (at.%)	Se (at.%)	Cu/In	Δy
6	25.56	23.85	50.59	1.07	1.04
15	24.87	24.56	50.57	1.01	1.03
33	24.74	24.71	50.55	1.001	1.02
50	24.62	24.91	50.47	0.99	1.02

Fig.3 shows the transmission spectra of the $CuInSe_2$ films deposited at 50% duty cycle. The spectrum exhibits interference fringes and the value of the refractive index was estimated by the envelope method [10] as follows:

$$n = [N + (N^2 - n_s^{\ 2})]^2 \ \ldots\ldots\ldots(2)$$

$$N = (n_s^2 + 1)/2 + 2\, n_s\, (T_{max} - T_{min}) / (T_{max}\ T_{min}) \ldots\ldots\ldots(3)$$

where n_s is the refractive index of the substrate, T_{max} and T_{min} are the maximum and minimum transmittances at the same wavelength in the fitted envelope curve on a transmittance spectrum. The value of the refractive index calculated from the above equations was in the range of 2.45 – 2.65 at 1150 nm for the films deposited at different duty cycles. The refractive index decreases with wavelength (FIg.4). The value of the absorption co-efficient (α) was calculated using the relation

$$\alpha = 1/d \ \ln \{ (n-1)(n-n_s)/(n + 1)(n - n_s)\} \ [(T_{max}/T_{min})^2 + 1]/[(T_{max}/T_{min})^2 - 1] \ldots\ldots(4)$$

where 'd ' is the thickness of the film and the other parameters have the usual meaning as given for equation (3). The band

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gap of the films increased from 1.05 eV to 1.17 eV as the duty cycle decreased (from$(\alpha h\nu)^2$ vs hν plot)(Fig.5). The increase in band gap at lower duty cycles is due to the small crystallites. The values of the band gap agree well with the earlier report [11]. Extinction coefficient (k) was determined from the absorption coefficient using the following relation. Fig.6 shows the variation of extinction coefficient with wavelength.

$$k = \alpha\lambda/4\pi \qquad (5)$$

where α is the absorption coefficient and λ is the wavelength. As seen from the figure, the extinction coefficient decreases with the increase in the wavelength. The decrease in extinction coefficient with increase in wavelength shows that the fraction of light lost due to scattering and absorbance decreases.

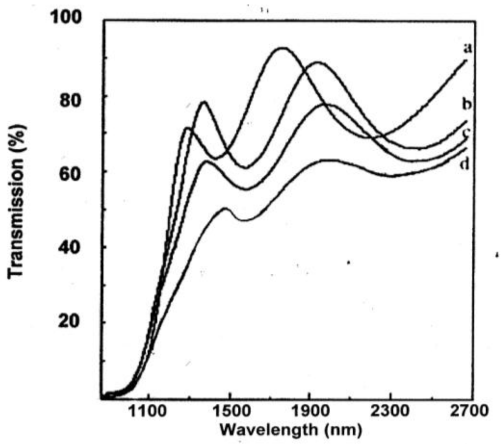

Fig.3 – Transmission spectra of CIS films deposited at different duty cycles (a)50 % (b) 33 % (c) 15 % (d) 6 %

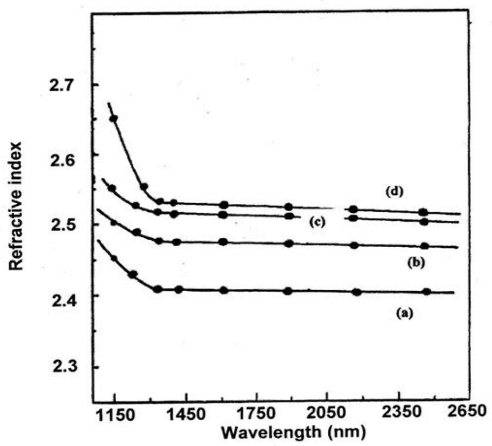

Fig.4 – Variation of refractive index with wavelength for CIS Films deposited at different duty cycles (a) 50 % (b) 33 % (c) 15 % (d) 6 %

In transparent region, the relation between the optical dielectric constant, ε_1, the wavelength, λ, and the refractive index, n, is given by the following equation [12] :

$$\varepsilon_1 = n^2 = \varepsilon_L - D\lambda^2 \qquad (6)$$

Where ε_1 is the real part of the dielectric constant, ε_L is the lattice dielectric constant or (the high- frequency dielectric constant) and D is a constant depending on the ratio of carrier concentration to the effective mass;

$$D = (e^2 N)/(4\pi^2\varepsilon_0 m^* c^2) \qquad (7)$$

where e is the charge of the electron, N is the free charge carrier concentration, ε_o is the permittivity of free space, m* is the effective mass of the electron and c is the velocity of light [13] . Fig.7. shows the relation between n^2 and λ^2 for the CIS thin films de[posited at different duty cycles. It is observed that the dependence ε_1 (= n^2), on λ^2 is linear at longer wavelengths. Extrapolating the linear part of this dependence to zero wavelength gives the value of ε_L and from the slope of this linear part, the constant D can be obtained, from which the value (N /m*) for the thin films can be obtained (Table-3).

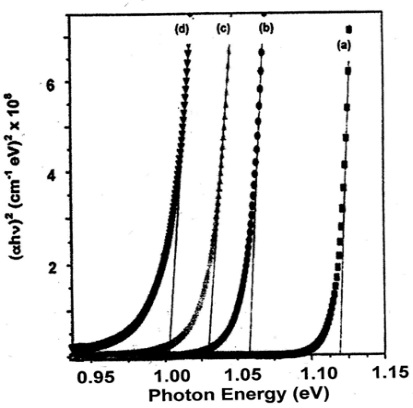

Fig. 5 – Tauc's plot of CIS films deposited at different duty cycles (a) 50 % (b) 33 % (c) 15 % (d) 6 %

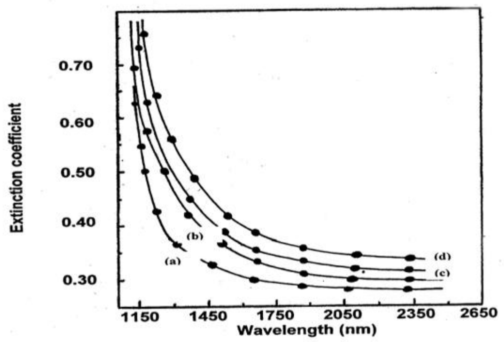

Fig.6 – Variation of extinction co-efficient of CIS films deposited at different duty cycles (a) 6 % (b) 15 % (c) 33 % (d) 50 %

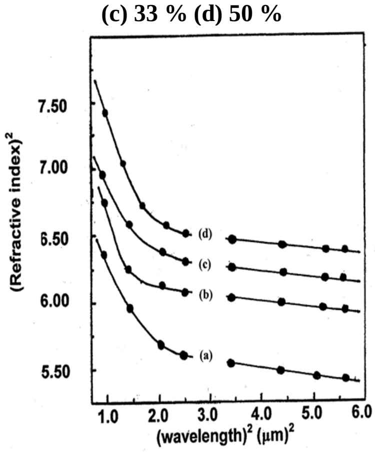

Fig.7 – Variation of square of refractive index with square of wavelength of CIS films deposited at different duty cycles (a) 50 % (b) 33 % (c) 15 % (d) 6 %

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According to the single-effective oscillator model proposed by Wemple and DiDomenico [14], the optical data can be described by an excellent approximation using the relation

$$n^2 - 1 = (E_d E_0)/(E_o^2 - E^2) \;\ldots\ldots\ldots\ldots(8)$$

where E = hν is the photon energy, n is the refractive index, E_0 is the single-effective oscillator energy and E_d is the dispersion energy which is a measure of the average strength of the inter band optical transitions. Plotting $(n^2 - 1)^{-1}$ against E^2 gives the oscillator parameters by fitting a straight line. Figure.8 shows the plot of $(n^2 - 1)^{-1}$ vs E^2 for the films deposited at different duty cycles. The values of E_0 and E_d can then be calculated from the slope $(E_0E_d)^{-1}$ and the intercept on the vertical axis (E_0/E_d). The values of the static refractive index (n_0) can be calculated by extrapolating the Wemple–DiDomenico dispersion equation (8) to E → 0. The calculated values of n_0 are 2.4, 2.47, 2.50 and 2.51 for the films deposited at different duty cycle. The calculated values of n_0, E_0 and E_d are listed in table 3. In addition, the optical band gap (E_g) determined from the Wemple–DiDomenico dispersion parameter E_0 using the relation $E_g = E_0/1.4$, are also in good agreement with the band gap values determined from Tauc's plot. This relationship is similar to earlier reports on thin films [15]

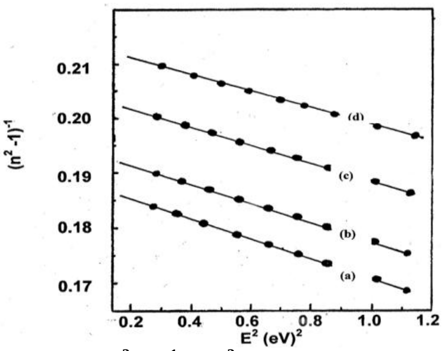

Fig.8 – Variation of $(n^2 -1)^{-1}$ vs E^2 plot of CIS films deposited at different duty cycles (a) 6 % (b) 15 % (c) 33 % (d) 50 %

Table-3 Values of single oscillator energy (E_0), dispersion energy (E_d), enrgy band gap (E_g) of films deposited at different duty cycles

Duty cycle (%)	n_0	E_0 (eV)	E_d (eV)	E_g (eV)	N/m* x 10^{46} (cm^{-3} gm^{-1})
6	2.51	1.40	6.66	1.00	1.6
15	2.50	1.44	7.35	1.03	1.3
33	2.47	1.48	7.77	1.06	1.2
50	2.40	1.58	8.37	1.13	1.1

M_{-1} and M_{-3} are the Moments of the Optical Spectra for the CIS thin films, which were obtained from the following relations [16],

$$E_0^2 = M_{-1}/M_{-3} \;\ldots\ldots\ldots\ldots(9)$$
$$E_d^2 = M^3_{-1}/M_{-3} \;\ldots\ldots\ldots\ldots(10)$$

The single-oscillator parameters E_o and E_d are related to the imaginary component ε_i of the complex dielectric constant. Thus, determining the moments is very important for developing optical applications of the optical material. The obtained values are given in Table 4. The obtained M_{-1} and M_{-3} moments increased with duty cycle.

Table-4. Values of M_{-1} and M_{-3} of CIS films deposited at different duty cycles

Duty cycle (%)	M_{-1}	M_{-3} (eV)$^{-2}$
6	6.66	3.39
15	10.61	5.11
33	11.50	5.25
50	13.23	5.30

IV. CONCLUSION

The optical constants and optical band gaps of CIS thin films deposited by the pulse plating technique onto tin oxide coated glass substrates at different duty cycles have been investigated by optical characterization method. X-ray diffraction results showed that the films were single phase. The direct band gaps of the films were in the range of 1.05 – 1.17 eV. The dispersion curves of the refractive index of the films obey single-oscillator model. The dispersion parameters of the films were determined and these values increase with duty cycle. The $M_{-1}$and M_{-3} optical moments of the films increase with the duty cycle.

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