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OPTICAL CHARACTERISTICS OF PULSE PLATED $CuInS_2$ FILMS

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***Abstract*— Copper indium sulphide films were deposited by the pulse plating technique with different OFF times in the range of 5s – 30s and at a constant current density of 5 mA cm-2. The films exhibited single phase copper indium sulphide. The grain size increased with decrease of OFF time. Optical band gap of the films increased from 1.44– 1.497 eV with decrease of OFF time. Optical constants (refractive index, n, and extinction co-efficient, k) of the films have been obtained in the wavelength range 800 - 1700 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.**

***Key words*— Electronic material, Optical properties, Semiconductors, thin films.**

I.INTRODUCTION

The chalcopyrite compound family Cu(In,Ga)(Se,S)2 provides some of the most efficient thin film solar cells [1]. This is mainly due to the high light absorption coefficient of these compounds and a band gap value between 1 and 2.4 eV, which is suitable for photovoltaic application [2]. High efficiencies above 19% have been achieved in laboratory using chalcopyrite based solar cells [2]. The main problem is the use of a toxic selenium gas treatment. Many studies are presently focused on the use of sulfured compounds such as CuInS2. Efficiency of 12.5% [3] has been obtained using CuInS2 thin film based solar cells. Numerous methods such as chemical vapor deposition (CVD) [4], spray pyrolysis [5], vacuum evaporation [6] and sputtering [7] have been used for the preparation of CuInS2. However, these methods usually involve expensive precursors, complicated apparatus and even some toxic byproducts. Electrodeposition is a low-cost, ambient temperature and convenient technique, thus it is appealing for the formation of complex compound semiconductors. In this work, the pulse electrodeposition technique has been employed for the deposition of CuInS2 films. Optical constants were evaluated and the refractive index data was analyzsed using single oscillatoir model.

In pulse electrodeposition [8,9] 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 (TON) during which potential and/current is applied, and an OFF-time (TOFF) 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 ip, 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 [10]. 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 [11].

II.MATERIALS AND METHODS

CuInS2 films were pulse electrodeposited at 5 mA cm-2, ON time of 5s at room temperature and with different OFF times in the range of 5 – 30s. Tin oxide coated glass substrates were used. The total deposition time was kept constant at 30 min. Thickness of the films measured by Mitutoyo surface profilometer was in the range of 525 nm – 1450 nm with decrease of duty cycle. The films were characterized by Xpertpanalytical x-ray diffraction unit with Cukα radiation. Optical measurements were recorded using an Hitachi UV–Vis-IR spectro-photometer. Composition of the films was estimated by EDS attachment to JOEL SEM.

III.RESULTS AND DISCUSSION

The typical XRD patterns of CIS films deposited with different OFF times exhibit the chalcopyrite structure which is easily identified for the films (JCPDS card no. 00-040-1487). The films deposited at lower OFF time, show a poor crystallinity with weak and broadened diffraction peaks as shown in figure.1. As the OFF time increases, the diffraction peaks become sharp and the peak intensity is also greatly enhanced. Three well defined characteristic peaks correspond to the diffraction of the (112), (204) and (312) planes were observed. The crystallite size was determined from Scherrer's equation

Crystallite size = 0.94λ / (βcosθ) …….(2)

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 20 to 80 nm with increase of OFF time from 5s to 30s (Table-I). The formation of large grains at longer OFF-times can be plausibly explained by desorption of some species during the longer OFF-times which activates the growth centers and results in grain growth. Also the adatoms at longer OFF-times have sufficient time to migrate over the crystal surface and enhance the grain growth process. Puippe [12] obtained grain coarsening during pulse plating of copper and gold deposits at long OFF-time while the current ON time and pulse current density were held constant. They explained this trend in terms of a recrystallization process and argued that coarse grains are thermodynamically more stable and longer offtime provides enough time for the system to stabilize and therefore grain growth takes place. Similar behaviour has been observed in pulse plated zinc films [13].

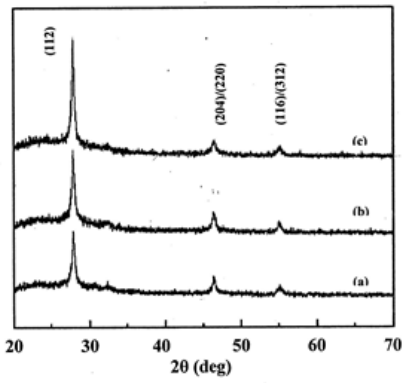

Fig.1 X-ray diffraction pattern of CuInS2 films deposited with different OFF times (a) 30s (b) 20s (c) 5s

OFF Time (s)	Lattice parameters		Grain size (nm)
	"a" (Å)	"c" (Å)	
5	5.58	11.04	20
20	5.55	11.05	45
30	5.54	11.03	80

TABLE.I Structural parameters of CuInS2 films deposited with different OFF times

Composition of the films was estimated by recording the EDS spectrum of the films deposited with different OFF time (Table-II). Fig.2 shows the EDS spectrum of CuInS2 films deposited with 5s OFF time. It is observed that films deposited with longer OFF time were copper rich. As the OFF time decreased, the films became stochiometric. For the films deposited with 5s OFF time, Cu/In ratio was 1.00. This is due to the fact that at longer OFF time, more flux of copper ions are available for deposition compared to the flux of copper ions at lower OFF time, which results in higher concentration of copper thus increasing the Cu/In ratio. Based on the defect chemistry model of ternary compounds, compositional deviations of the CuInS2 can be expressed by non-stoichiometry parameter {y = [2S/(Cu + 3In)] – 1}. The parameter Δy is related to the electronic defects. For Δy > 0, the film has a p-type conductivity and it has an n-type conductivity for Δy < 0. In this study the value of Δy is greater than zero and the films exhibit p-type conductivity.

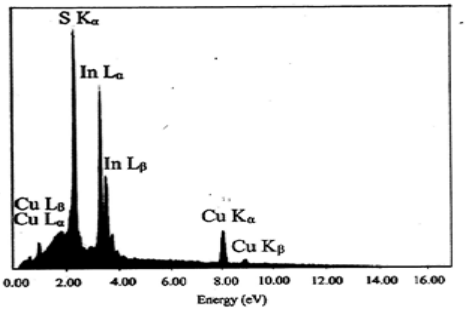

Fig.2 EDS spectrum of CuInS2 films deposited with 30s OFF time

Fig.3 shows the transmission spectra of the CuInS2 films deposited at 50% duty cycle. The spectrum exhibits interference fringes and the value of the refractive index was estimated by the envelope method [14] as follows:

n = [N + (N2 – ns 2)]2 ……(2)

N = (ns2 + 1)/2 + 2 ns (Tmax - Tmin)/ Tmax Tmin……..(3)

where ns is the refractive index of the substrate, Tmax and Tmin 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 2.43 – 2.62 at 800 nm. Variation refractive index with wavelength is shown in Fig.4. The value of the absorption co-efficient (α) was calculated using the relation

α = 1/d ln { (n-1)(n-ns)/(n + 1)(n – ns)} [(Tmax/Tmin)2 + 1]/[(Tmax/Tmin)2 - 1].……(4)

where 'd ' is the thickness of the film and the other parameters have the usual meaning as given for equation(4). The band gap of the film was estimated to be 1.42 eV from a plot of (αhν)2 vs hν (Fig.5). The values of the band gap and refractice index agree well with the earlier report [15].

OFF Time (s)	Composition (at %)			Cu/In	Δy
	Cu	In	S		
30	25.56	23.85	50.59	1.07	0.04
20	24.87	24.56	50.57	1.01	0.03
5	24.71	24.71	50.58	1.00	0.02

TABLE- II Composition of CuInS2 films deposited at different duty cycles

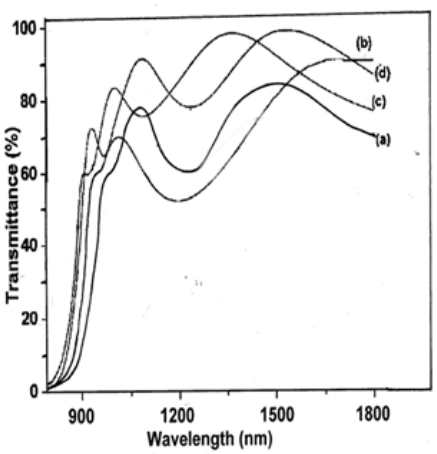

Fig.3 Transmission spectra of CuInS2 films deposited with different OFF Time (a) 30s (b) 20s (c) 10s (d) 5s

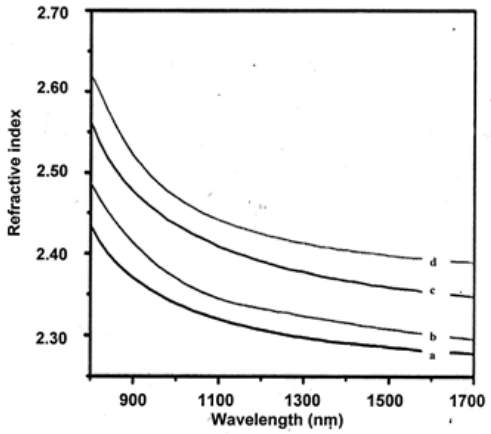

Fig.4 Variation of refractive index with wavelength for CuInS2 films deposited with different OFF times (a) 5s (b) 10s (c) 20s (d) 30s

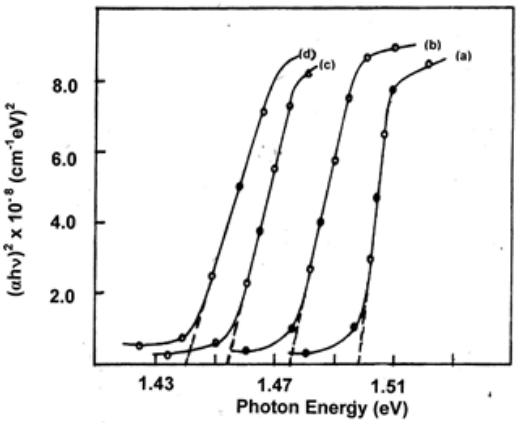

Fig.5 Tauc's plot of CuInS2 films deposited with different OFF times (a) 5s (b) 10s (c) 20s (d) 30s

Extinction coefficient (k) was determined from the absorption coefficient using the following relation. Fig.6 shows the variation of extinction coefficient with wavelength.

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

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.

In transparent region, the relation between the optical dielectric constant, ε1, the wavelength, λ, and the refractive index, n, is given by the following equation [16] :

$$\varepsilon 1 = n2 = \varepsilon L - D\,\lambda 2 \ldots\ldots\ldots\ldots\ldots(6)$$

where ε1 is the real part of the dielectric constant, εL 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;

$$D = (e2\ N)/ (4\pi 2\varepsilon 0\ m^*\ c2) \ldots\ldots\ldots\ldots..(7)$$

where e is the charge of the electron, N is the free charge carrier concentration, εo is the permittivity of free space, m* is the effective mass of the electron and c is the velocity of light [17] . Fig.7. shows the relation between n2 and λ2 for the copper indium sulphide thin films de[posited at different duty cycles. It is observed that the dependence ε1 (= n2), on λ2 is linear at longer wavelengths. Extrapolating the linear part of this dependence to zero wavelength gives the value of εL 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-III).

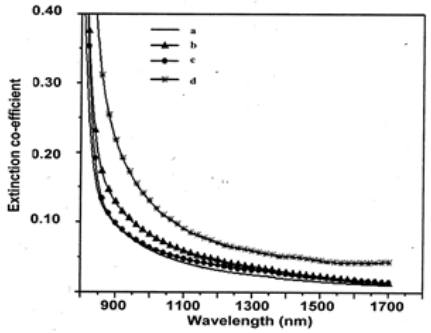

Fig.6 Variation of Extinction coefficient with wavelength for CuInS2 films deposited with different OFF time (a) 5s (b) 10s (c) 20s (d) 30s

According to the single-effective oscillator model proposed by Wemple and DiDomenico [18], the optical data can be described by an excellent approximation using the relation

$$n2 - 1 = (EdE0)/ (E02 - E2) \ldots\ldots\ldots\ldots(8)$$

where E = hν is the photon energy, n is the refractive index, E0 is the single-effective oscillator energy and Ed is the dispersion energy which is a measure of the average strength of the inter band optical transitions. Plotting (n2 − 1)-1 against E2 gives the oscillator parameters by fitting a straight line. Figure.8 shows the plot of (n2 − 1)-1 vs E2 for the films deposited at different duty cycles. The values of E0 and Ed can then be calculated from the slope (E0Ed)-1 and the intercept on the vertical axis (E0/Ed). The values of the static refractive index (n0) can be calculated by extrapolating the Wemple – DiDomenico dispersion equation (8) to E → 0. The calculated values of n0 are 2.28, 2.32, 2.37 and 2.40 for the films deposited with different OFF time. The calculated values of n0, E0 and Ed are listed in table 3. In addition, the optical band gap (Eg) determined from the Wemple–DiDomenico dispersion parameter E0 using the relation Eg = E0/1.4, 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 [19].

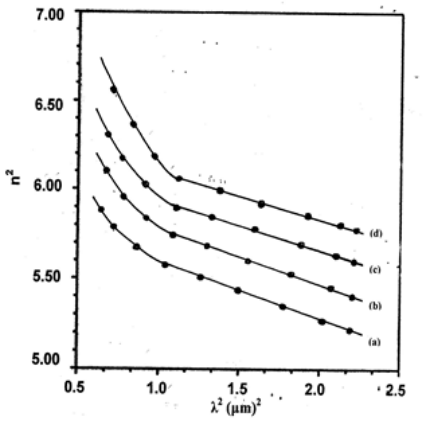

Fig.7 Variation of n2 vs λ2 for CuInS2 films deposited with different OFF Time (a) 5s (b) 10s (c) 20s (d) 30s

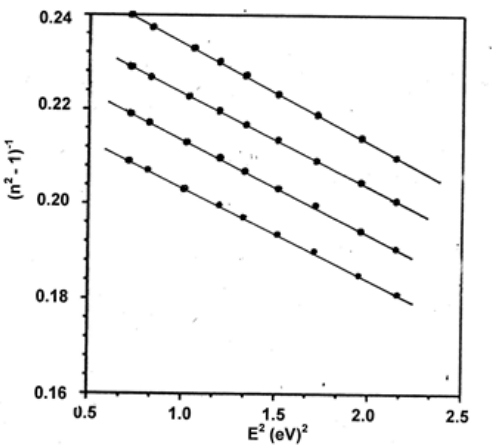

Fig.8 Variation of (n2 – 1)-1 vs E2 for CuInS2 films deposited with different OFF time Top to bottom 30s, 20s, 10s, 5s

M−1 and M−3 are the Moments of the Optical Spectra for the Copper Indium Sulphide thin films, which were obtained from the following relations [19],

E02 = M-1/ M-3 ……..(9)

Ed2 = M-13 / M-3 ……(10)

The single-oscillator parameters Eo and Ed are related to the imaginary component εi 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.

OFF Time (s)	n_0	E_0 (eV)	E_d (eV)	E_g (eV)	N/m* x 10^{45} (cm^{-1} gm^{-1})
5	2.28	2.096	9.98	1.497	3.97
10	2.32	2.062	9,52	1.473	3.72
20	2.37	2.037	8.93	1.455	3.54
30	2.40	2.015	8.46	1.44	2.93

TABLE III Values of single oscillator energy (E0), dispersion energy (Ed), N/m* for CuInS2 films deposited with different OFF time

OFF Time (s)	M_{-1}	M_{-3} $(eV)^{-2}$
5	4.76	1.084
10	4.62	1.08
20	4.38	1.06
30	4.20	1.03

TABLE IV Values of M-1 and M-3 of CuInS2 films deposited with different OFF time

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