



Structure and temperature dependence of conduction mechanisms in hot wall deposited CuInSe₂ thin films and effect of back contact layer in CuInSe₂ based solar cells

S. Agilan^{a,b}, D. Mangalaraj^{b,*}, Sa.K. Narayandass^b, G. Mohan Rao^c, S. Velumani^d

^a Department of physics, Coimbatore Institute of Technology, Coimbatore, India

^b Department of Physics, Bharathiar University, Coimbatore, India

^c Department of Instrumentation, Indian Institute of Science, Bangalore, India

^d Department of Electrical Engineering (SEES), CINVESTAV, Mexico City, D.F., 07360, Mexico

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Copper indium diselenide (CuInSe₂) was prepared by direct reaction of high purity elemental Copper, Indium and Selenium. CuInSe₂ thin films were prepared on well-cleaned glass substrates by a hot wall deposition technique. The X-ray diffraction studies revealed that all the deposited films are poly crystalline in nature, single phase and exhibit chalcopyrite structure. The crystallites were found to have a preferred orientation along the (112) direction. Structural parameters of CuInSe₂ thin films coated with higher substrate temperatures were also studied. As the substrate temperature increases the grain size increases. The resistivity is found to decrease with increase in temperature. Two types of conduction mechanisms are present in the hot wall deposited CuInSe₂ films. In the temperature region below 215 K the conduction is due to a variable range hopping mechanism and in the temperature region above 215 K the conduction is due to a thermally activated process. It is observed that the solar cell with molybdenum as back contact has low series resistance (R_s), high shunt resistance (R_{sh}) and large fill factor (FF) when compared with CuInSe₂ based solar cells with other back contact material layers.

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1. Introduction

CuInSe₂ (copper indium diselenide) is a promising material for thin film solar cells because of its extraordinary radiation stability [1]. CuInSe₂ is a semiconducting compound which belongs to the I–III–VI₂ chalcopyrite family. It is convenient to view the chalcopyrite structure in terms of two interpenetrating sub-lattices in which I–III atomic positions, which act as cations, rest on the other sub-lattice [2]. CuInSe₂ films possess certain exceptional material characteristics including band-gap, absorption coefficient and minority carrier diffusion length which are particularly suitable for photovoltaic applications. They can be prepared with *n*- and *p*-type conductivity and therefore both homo-junction and hetero-junction potential exists for this material [3]. The relation between the energy gap and the lattice constant of isovalent chalcopyrite materials and the material requirements for CuInSe₂ solar cells are analyzed by Konovalov [4]. Copper indium diselenide thin films have been deposited by several techniques including sputtering [5], molecular

beam epitaxy [6], two stage process [7] and vacuum evaporation [8]. More homogeneous and larger area CuInSe₂ thin films have been deposited by a simple closed space vapour transport technique [9].

Hot wall epitaxy has become a popular and reliable technique among different techniques available for the deposition of thin films. The hot wall deposition method yields high quality epitaxial thin films with smooth surfaces under conditions very close to thermodynamic equilibrium. Hot wall deposited CdTe thin films exhibited superior luminescence properties when compared to MBE and MOCVD films [10]. In the present study, stoichiometric CuInSe₂ thin films have been deposited on to well-cleaned glass plates by the hot wall deposition technique.

2. Experimental details

Bulk CuInSe₂ compound was synthesized by direct reaction of high purity (99.999%) elemental copper, indium and selenium with 1:1:2 ratio. The prepared bulk CuInSe₂ compound was evaporated and deposited onto well-cleaned glass substrates by the hot wall deposition technique. The schematic diagram of the hot wall experimental set up is shown in Fig. 1. The main feature of the system is the heated linear quartz tube, which serves to enclose and direct the

* Corresponding author.

E-mail address: dmrj800@yahoo.com (D. Mangalaraj).

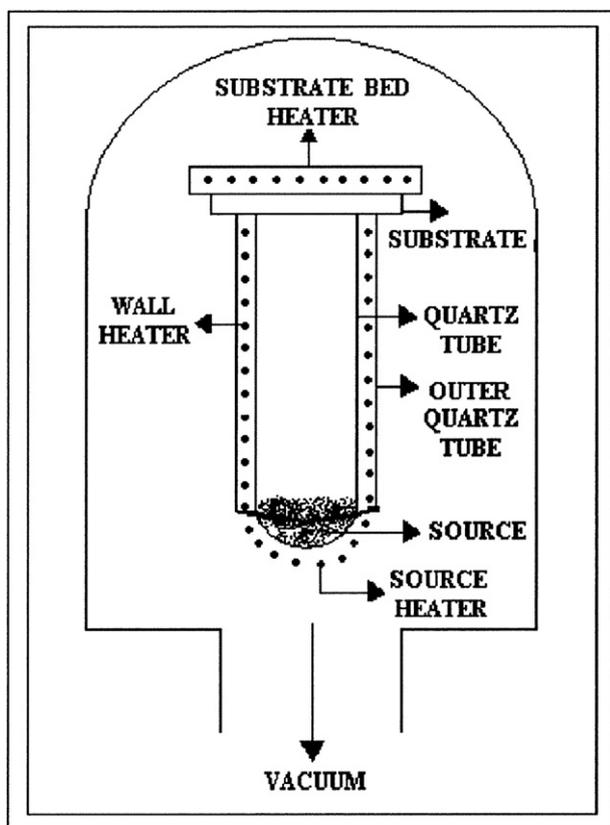


Fig. 1. Schematic diagram of the hot wall experimental set up.

vapour from source to substrate. Kanthal wire wound closely along the length of the quartz tube was used to heat the tube wall. CuInSe_2 thin films were deposited onto the well-cleaned glass substrates, using the quartz tube with the source and wall temperatures around 1270 K. The thicknesses of the films were determined using a gravimetric method and confirmed by a multiple beam interferometry technique. The structure of the films was studied using X-ray diffractometer model Philips PW 3710 with CuK_α radiation. Chemical constituents present in the deposited films were estimated using a scanning electron microscope (SEM) attached with Energy Dispersive X-ray Analysis (EDAX) (Model 7060 Oxford Instruments (Cambridge).) The electrical resistance of CuInSe_2 thin films of different thicknesses (410–910 nm) was measured under a vacuum of the order of 10^{-3} mbar. The electrical contacts required for resistance measurement were made with silver dots above the CuInSe_2 thin films. The silver dots were evaporated using a mask in a vacuum coating unit (Hind Hivac, Model 12A4, Bangalore, India) with a vacuum of the order of 10^{-5} mbar. The electrical resistance was measured in the temperature range 70–340 K using a Keithley 614 electrometer as an ohm-meter. CuInSe_2 thin films were illuminated using a tungsten lamp (230 V, 1250 W Philips). The intensity of illumination on the solar cell was measured using a suryamapi (CEL, India). The current and voltage were measured using optical power meter [70310, Oriol Instruments, USA] and an electrometer (Keithley 2001), respectively.

3. Results and discussion

3.1. Structural properties of CuInSe_2 thin films

For thermal equilibrium in a hot wall system, the direct transmission of molecules should be minimum and molecules must

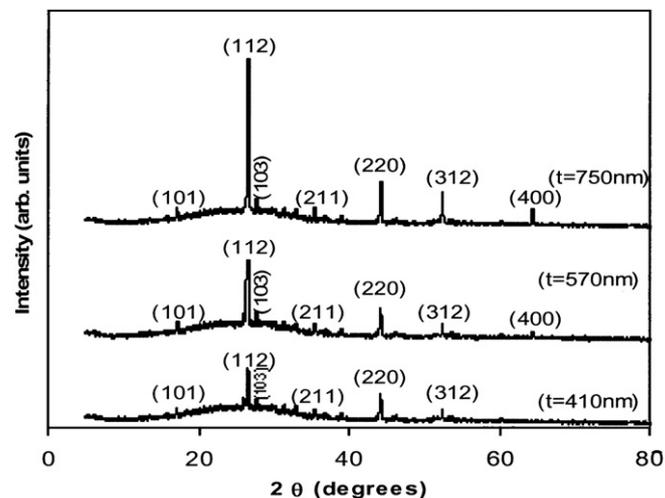


Fig. 2. X-ray diffraction pattern of CuInSe_2 thin films of different thicknesses deposited using a quartz tube of length 0.11 m.

attain thermal equilibrium with the heated wall before they reach the substrate. For larger tube lengths, the number of wall collisions suffered by molecules is sufficient for the molecules to attain thermal equilibrium before they reach substrate and direct transmission is minimum. The molecular flux density distribution at the substrate may also be uniform for larger tube lengths.

The X-ray diffraction pattern of CuInSe_2 thin films of different thicknesses deposited using a quartz tube of optimized length 0.11 m is shown in Fig. 2. All the deposited CuInSe_2 films are found to be polycrystalline in nature exhibiting chalcopyrite structure. The crystallites are found to have peak orientations along (101), (112), (103), (211), (220), (312) and (400) directions. Microstructural parameters of the deposited CuInSe_2 films have been evaluated and are given in Table 1. It is observed that the grain size increases but the strain and dislocation density decrease with increase of film thickness. A similar peak orientation, dependence of grain size, strain and dislocation density on film thickness has been reported by earlier researchers [11,12]. The presence of (101), (103) and (211) diffraction peaks confirm the chalcopyrite structure in the deposited films [13,14].

The EDAX pattern of a CuInSe_2 thin film deposited using 0.11 m tube length is shown in Fig. 3. It is found that the elemental composition in the deposited film is almost maintained as in the bulk and is copper: 24.653 atomic%, indium: 24.288 atomic% and selenium: 51.059 atomic%. The presence of high copper content increases the grain size, in turn yielding good poly crystallites [15,16]. Results of X-ray diffraction studies and the EDAX carried out on CuInSe_2 thin films deposited using the hot wall arrangement and tube of length 0.11 m clearly show that the deposited films are of good quality suitable for fabrication of CuInSe_2 based solar cells. CuInSe_2 thin films with Cu/In ratio greater than one have been reported by Menna et al. [17] as suitable for high efficiency devices.

The X-ray diffraction pattern of the CuInSe_2 films deposited at different substrate temperatures using a quartz tube of length 0.11 m is shown in Fig. 4. Films deposited at substrate temperatures of 423, 523 and 673 K are found to exhibit crystalline structure with orientation of the crystallites along (112), (220) and (312) directions. As the substrate temperature is increased, the films are found to show a highly preferred orientation along the (112) direction. Micro structural parameters of the CuInSe_2 thin films deposited at different substrate temperatures are given in Table 2. Since the strain and dislocation density are manifestations of a dislocation network in the films, the decrease in both of these parameters with

Table 1
The microstructural parameters of the deposited CuInSe₂ films of different thicknesses.

Film thickness (nm)	Lattice parameter		c/a ratio	Tetragonal distortion 2-c/a	Grain size D (nm)	Dislocation density $\times 10^{14}$ lin/m ²	Strain $\epsilon \times 10^{-4}$
	a Å	c Å					
410	5.779	11.623	2.0112	-0.0112	89.37	1.252	4.507
570	5.780	11.621	2.0105	-0.0105	162.75	0.378	2.475
750	5.785	11.613	2.0074	-0.0074	243.68	0.168	1.653

the increase of the substrate temperature, indicates the formation of high quality films. The tetragonal distortion is also found to decrease as the substrate temperature increases. Fig. 5(a) and (b) are the SEM micrographs of CuInSe₂ thin films of thickness 410 nm, as-deposited and for a substrate temperature of 673 K, respectively. Increase in substrate temperature leads to increase in the grain size of the CuInSe₂ thin films.

3.2. Temperature dependence of DC conduction in CuInSe₂ thin films

The variation of resistance with temperature in CuInSe₂ films of different thicknesses deposited onto glass substrates by the hot wall deposition technique have been studied in the temperature range 70–340 K. Fig. 6 shows the temperature dependence of resistivity of CuInSe₂ films of different thicknesses. The resistivity is found to decrease with increase in temperature which confirms the semiconductor nature of the deposited CuInSe₂ films. The plot also reveals that the resistance of the films depends strongly on thickness; the resistance of the thicker film is found to be comparatively less than that for thinner films. This is due to the presence of large grains with less strain and fewer dislocations in the thicker films [18].

Fig. 7 shows the variation of electrical conductivity of CuInSe₂ films with the inverse of absolute temperature. The plot is a linearly varying one and therefore the measured experimental data fits the relation,

$$\sigma = \sigma_0 \exp(-E_a/k_B T). \quad (1)$$

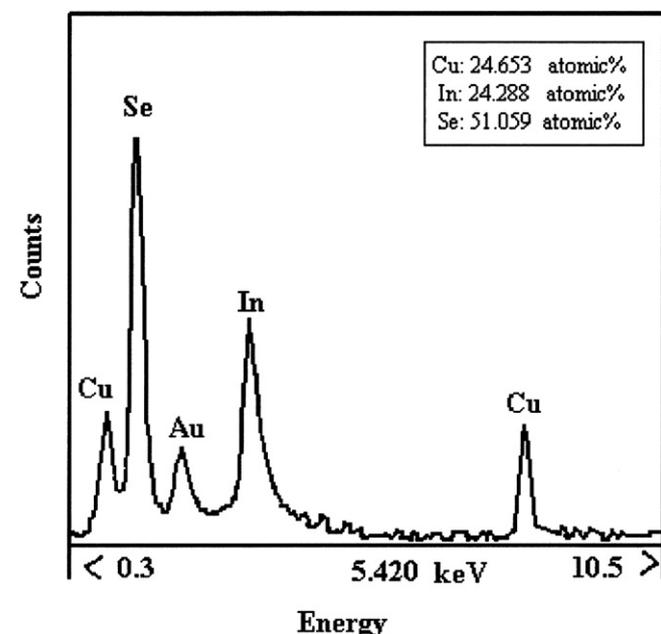


Fig. 3. The EDAX pattern of a CuInSe₂ thin film deposited using a 0.11 m tube length.

The increase in conductivity is very gradual and small in the room temperature range. Similar observations have been reported by several workers [2,19,20]. In extrinsic semiconductors, there will be additional energy levels in the band-gap which will be localized and close to either the conduction band or valance band. Since the energy difference between these levels and band edges is very small, a slight thermal excitation is sufficient to donate or accept electrons and, thereby increase the electrical conductivity in the film. The presence of two regions with different slopes in the plot suggests that there are two types of conduction mechanism present in the CuInSe₂ films deposited by a hot wall deposition technique. The point of inflection is found to be around 215 K. In the temperature region below 215 K, the conduction is due to a variable range hopping mechanism and in the temperature region above 215 K, it is due to a thermally activated process. From the plot it is clear, that, for temperatures greater than 215 K, the electrical conductivity varies linearly with temperature and so the electrical data fits the relation $\sigma = \sigma_0 \exp(-\Delta E/k_B T)$ therefore, the conductivity is attributed to thermal excitation of charge carriers from grain boundaries to the neutral region of grains. The activation energies associated with the hot wall deposited CuInSe₂ films at two different temperatures are shown in Table 3. The two different activation energies of low and high value obtained for temperatures 135 K (below 215 K) and 313 K (above 215 K) can be attributed to the hopping conduction mechanism and thermally activated process respectively. Similar characteristics have been reported for CuInSe₂ films by earlier workers [19,21,22].

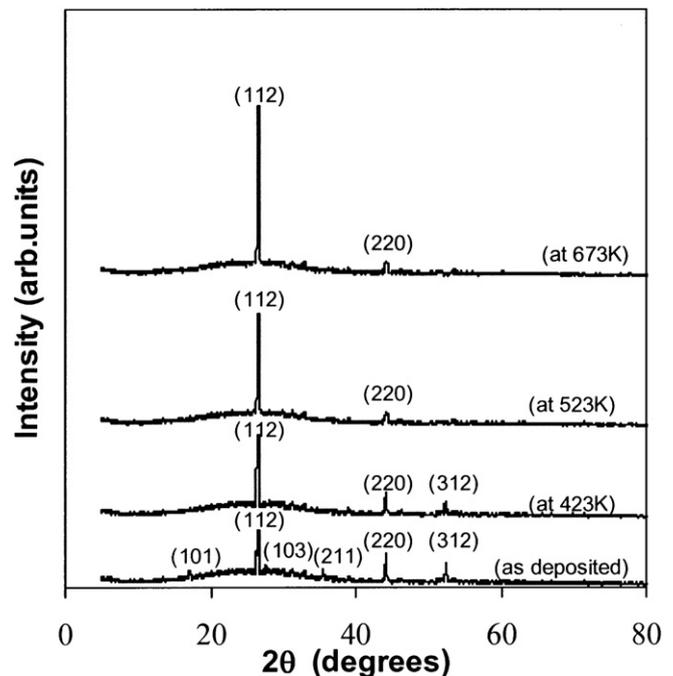


Fig. 4. The X-ray diffraction pattern of the CuInSe₂ films deposited at different substrate temperatures.

Table 2
Micro structural parameters of the CuInSe₂ thin films deposited at different substrate temperatures.

Substrate temperature K	Lattice parameter		c/a ratio	Tetragonal distortion 2-c/a	Grain size D (nm)	Dislocation density × 10 ¹⁴ lin/m ²	Strain ε × 10 ⁻⁴
	a Å	c Å					
370 (As deposited)	5.779	11.623	2.0112	-0.0112	89.37	1.252	4.5071
423	5.778	11.616	2.0104	-0.0104	147.29	0.461	2.7345
523	5.784	11.621	2.0092	-0.0092	234.65	0.182	1.7213
673	5.786	11.617	2.0077	-0.0077	346.73	0.083	1.1616

From Table 3 it is observed that the activation energy associated with hot wall deposited CuInSe₂ films decreases considerably with increase in film thickness and the hence indicates semiconducting behavior of the deposited films. The decrease in activation energy also suggests that the grain boundary scattering contribution reduces significantly as thickness increases.

The plot of log (σT^{1/2}) versus T^{-1/4} shown in Fig. 8, represents conductivity below 215 K. As the plot is a linearly varying one, the experimental data fits into the relation given by Mott [23]

$$\sigma = \sigma_0 T^{-1/2} \exp\left[-(T_0/T)^{1/4}\right] \quad (2)$$

The conduction mechanism in the temperature range below 215 K can be considered as a variable range hopping conduction

mechanism. The parameters T₀ and T₀/T for CuInSe₂ films of different thicknesses have been calculated using the above expression and are given in Table 4. As T₀/T values are greater than 1, it can be easily confirmed that the conductivity mechanism in the hot wall deposited CuInSe₂ films is variable range hopping in the temperature range below 215 K [24–26].

3.3. Effect of back contact in CuInSe₂ based solar cells

The back contact plays an important role in solar cell device fabrication. The requirements for a good back contact material for CuInSe₂ solar cells are manifold. The contact layer must function as

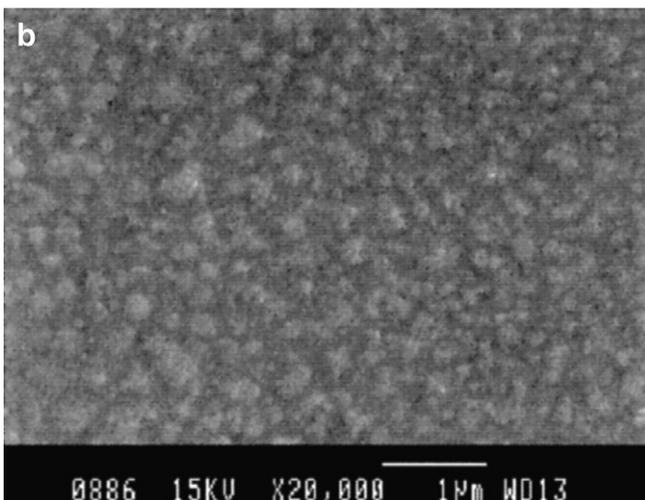
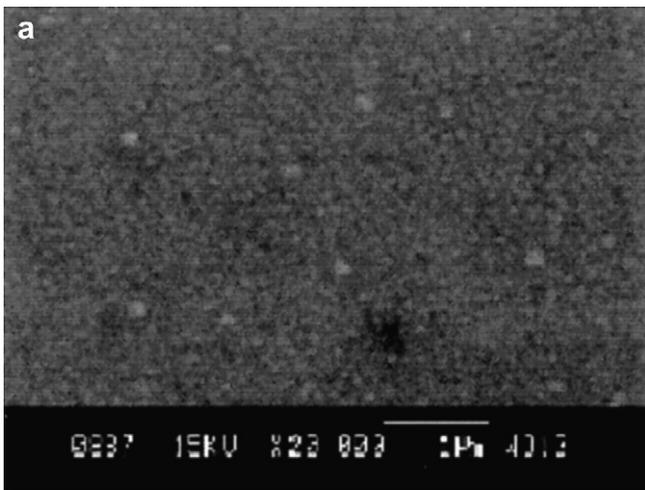


Fig. 5. (a). SEM micrograph of the as-deposited CuInSe₂ thin film with a thickness of 410 nm. (b). SEM micrograph of the CuInSe₂ thin film with a thickness of 410 nm deposited at a substrate temperature of 673 K.

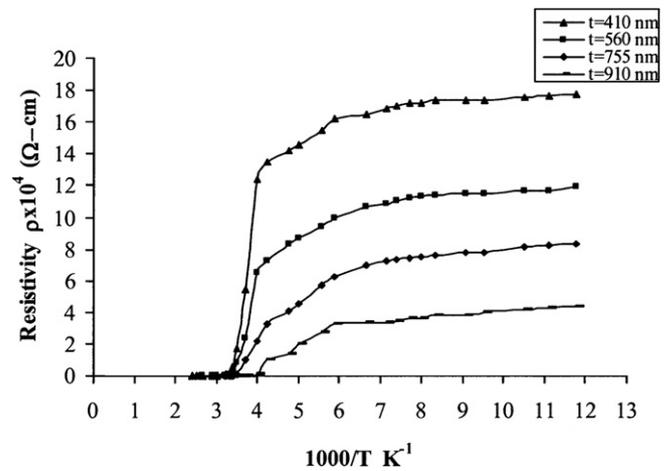


Fig. 6. Variation of resistivity of CuInSe₂ thin films of different thicknesses with inverse of absolute temperature.

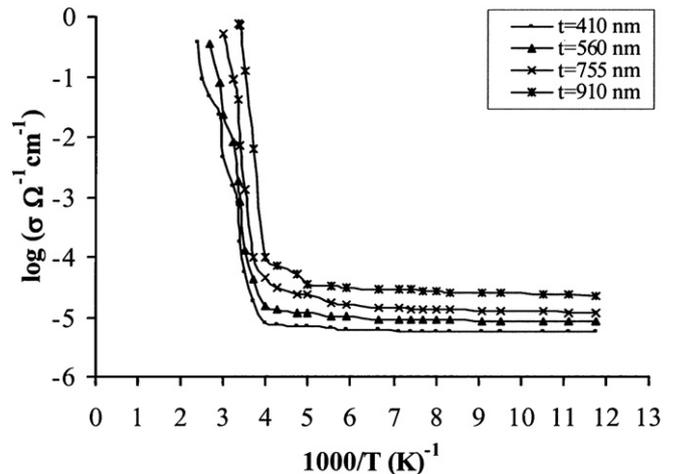


Fig. 7. Plot of lnσ (Ω⁻¹ cm⁻¹) versus 1000/T (K⁻¹) of CuInSe₂ thin films of different thicknesses.

Table 3

The activation energies of hot wall deposited CuInSe₂ films at two different temperatures.

Thickness (nm)	Temperature (K)	Activation energy (eV)
410	135	3.26×10^{-3}
	313	0.706
560	135	1.98×10^{-3}
	313	0.545
755	135	1.59×10^{-3}
	313	0.381
910	135	1.33×10^{-3}
	313	0.155

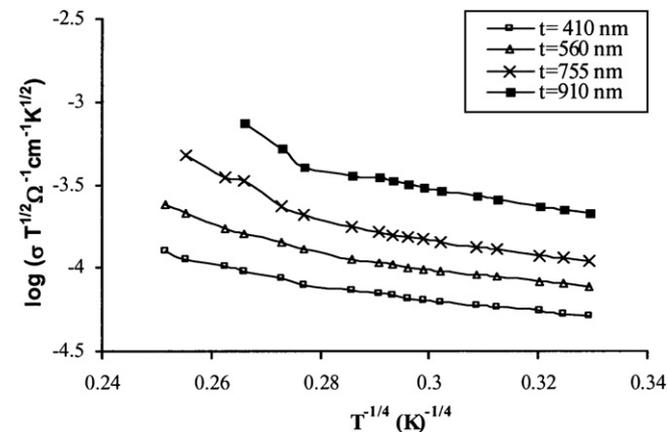


Fig. 8. Plot of $\ln(\sigma T^{1/2})$ ($\Omega^{-1} \text{cm}^{-1} \text{K}^{1/2}$) versus $T^{-1/4}$ ($\text{K}^{-1/4}$) of CuInSe₂ thin films of different thicknesses.

Table 4

The T_0 and T_0/T parameters of CuInSe₂ films of different thicknesses.

Thickness (nm)	Temperature (K)	T_0 (K)	T_0/T
410	215	2.444×10^3	11.368
	135	414.45	3.070
560	215	18.854×10^3	87.695
	135	545.59	4.041
755	215	95.451×10^3	443.958
	135	1013.57	7.508
910	215	175.43×10^3	815.965
	135	2653.20	19.65

a barrier that hinders diffusion of impurities from the substrate into the absorber [27]. For good electronic device properties, the formation of an ohmic contact for majority carriers (holes) from the p-type CuInSe₂ and a low recombination rate for the minority carriers (electrons) at the CuInSe₂/back contact interface is essential. Finally, a high optical reflectance is necessary to minimize optical losses. The electron-hole selectivity of the interface will drop as the band diagram approaches the flat band case, resulting in a back surface recombination under illumination [4].

In the present study, back contact metal layers of Mo, W, Ta and Cr ($\approx 1 \mu\text{m}$) were deposited separately onto chemically cleaned glass plate by electron beam evaporation p-CuInSe₂/n-CdS solar cells of area 50 mm² were fabricated on these metallic back contact layers by the hot wall deposition method. A silver grid was evaporated over n-CdS buffer layer which acts as a front contact for the fabricated cell. Fig. 9 shows the I–V characteristics of the fabricated solar cell with different back contacts. Solar cell parameters of the fabricated cells are given in Table 5. On comparing the parameters

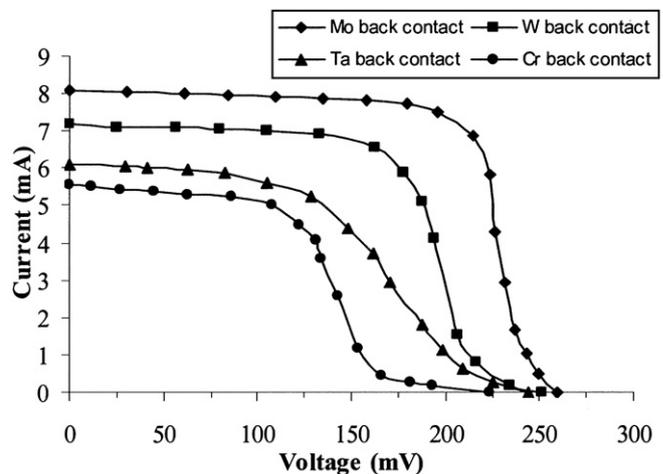


Fig. 9. I–V characteristics of the fabricated solar cell with different back contact layers.

Table 5

Solar cell parameters of the fabricated solar cells with different back contact layers.

Metallic back contact layer	V_{oc} mV	I_{sc} mA	R_{sh} Ω	R_s Ω	P_{max} mW	Fill factor
Mo	259.84	8.09	955	37	1.474	0.701
W	251.50	7.20	860	48	1.068	0.589
Ta	244.35	6.12	780	49	0.674	0.451
Cr	223.41	5.56	395	106	0.548	0.441

given in Table 5, it is observed that CuInSd based solar cells with molybdenum as back contact possess a lower series resistance (R_s), higher shunt resistance (R_{sh}), maximum Power P_{max} and higher fill factor (FF) values than the other cells with different metallic back contact layers.

In addition the deviation of the characteristic curve from the ideal curve near the open circuit region is highly reduced when molybdenum is used as back contact. Hence the molybdenum is the ubiquitous choice for back contact in CuInSe₂ device fabrication. The popularity of this material has repeatedly been demonstrated by its success in forming ohmic rather than rectifying contacts to CuInSe₂ and a higher resistance to selenium corrosion. However there may be a possibility for the formation of a Mo₂Se phase at the Mo–CuInSe₂ interface which could affect the CuInSe₂ film growth. Rockett et al. [28] suggested that this characteristic plays a significant role in adhesion at the Mo–CuInSe₂ interface and possibly in the subsequent growth of the CuInSe₂ film. Adhesion at the Mo–glass interface was not considered to be a serious problem.

4. Conclusion

By hot wall deposition technique, polycrystalline, single phase CuInSe₂ thin films were prepared on to well-cleaned glass substrates. The crystallites were found to have a preferred orientation along the (112) direction exhibiting a chalcopyrite structure. It is found that the grain size increases as the substrate temperature increases. Conduction in the hot wall deposited CuInSe₂ films is due to a variable range hopping mechanism below 215 K, while a thermally activated process is present above 215 K. Activation energy is found decrease as the thickness of the film increases. When compared with CuInSe₂ based solar cells with other back contact material layers, the solar cell with molybdenum as back contact has desirable and advantageous parameters which are suitable for high efficiency solar cells.

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