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# Electrodeposited CuInSe$_2$ Thin Film Junctions

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## ABSTRACT

We have investigated thin films and junctions based on copper indium diselenide (CIS) which have been grown by electrochemical deposition. CIS is a leading candidate for use in polycrystalline thin film photovoltaic solar cells. Electrodeposition is a cost-effective method for producing thin-film CIS. We have produced both $p$ and $n$ type CIS thin films from the same aqueous solution by simply varying the deposition potential. A CIS $pn$ junction was deposited using a step-function potential. Stoichiometry of the single layer films was determined by energy dispersive spectroscopy. Carrier densities of these films increased with deviation from stoichiometry, as determined by the capacitance versus voltage dependence of Schottky contacts. Optical bandgaps for the single layer films as determined by transmission spectrocopy were also found to increase with deviation from stoichiometry. Rectifying current versus voltage characteristics were demonstrated for the Schottky barriers and for the $pn$ junction.

## INTRODUCTION

Copper indium diselenide (CIS) is one of the best optical absorber materials used in polycrystalline thin film photovoltaic solar cells [1]. This is due to its favorable electrical and optical properties, stability, and inexpensive means of production. Conversion efficiencies of 17.8% have been achieved for a vapor deposited CIS based solar cell [2]. Electrochemical deposition is an inexpensive alternative to the standard vapor deposition techniques for producing thin-film CIS [3].

Stoichiometric variation in polycrystalline CIS leads to a high concentration of electrically active native defects. Small variations from a Cu-to-In ratio of unity have been shown to result in large changes in the carrier density [4]. In fact, the semiconductor type changes from $n$ to $p$ as the Cu to In ratio changes from less than one to greater than one. However, CIS has been shown to be electrically and structurally stable over a wide range of stoichiometries and their associated native defect concentrations [5]. This behavior has been recently explained in terms of electrically inactive and ordered defect pairs [6].

The stoichiometry of our electrodeposited thin films is potentiostatically controlled. We have previously shown that the Cu-to-In ratio will demonstrate a linear dependance with deposition potential over a fairly wide range [7]. Therefore, we are able to deposit thin films with different electrical, optical properties, and semiconductor type from the same aqueous solution by simply changing the deposition voltage [8].

The optical band gap of CIS can be calculated from its absorption spectrum assuming a direct energy gap [9]. CIS has been shown to have a low electron effective mass

$(m_e{}^*=0.09\ m_e)$ [10]. Therefore, these materials become degenerate at low electron carrier densities and we would expect a Burstein-Moss shift in the optical bandgap [11]. This effect has been observed in CIS single crystals grown by the vertical Bridgman method [12].

The current versus voltage (I-V) characteristics can be used to determine the barrier heights of metal to CIS junctions. For an ideal Schottky contact with an n-type semiconductor, the barrier height $q\phi_B$ is the difference in the metal work function $q\phi_m$ and the semiconductor electron affinity $q\chi$.

$$q\phi_B = q(\phi_m - \chi)$$ (1)

When the metal work function is comparable to or smaller than the semiconductor's electron affinity we would expect an ohmic contact for an n-type semiconductor. In the case of a p-type semiconductor, the barrier height is the difference between the metal work function and the sum of the electron affinity and the bandgap. Assuming ideal junctions and an Al work function of 4.28 eV [13], electron affinity of 4.48 eV and a CIS bandgap of 1eV [14], we would expect Al to make an ohmic contact on n-type CIS and a Schottky contact to p-type CIS, with a barrier height of around 1.2 eV. However, if there is a large density of surface states, the barrier height is determined by the semiconductor surface and is independent of the metal work function [13]. Schottky barrier junctions have been produced on both $n$ and $p$ type CIS (Au and Al, respectively) [14].

The current density versus voltage for a Schottky barrier can be expressed as

$$J \approx J_S\, e^{(qV/nkT)} \quad \text{for } V >> kT/q$$ (2)

where $J_s$ is the saturation current density and $n$ is the ideality factor. The ideality factor is very close to unity at low dopings and high temperature. However, it can depart substantially from unity when doping is increased or the temperature is lowered [15]. The barrier height can be determined using

$$\phi_B = \frac{kT}{q}\ln\left(\frac{A^{**}T^2}{J_S}\right)$$ (3)

where $A^{**}$ is the effective Richardson constant which can be estimated based on the effective mass [13].

The capacitance of an ideal Schottky barrier as a function of reverse bias voltage can be expressed as

$$C = A\left[q\varepsilon_s N_d \Big/ 2\left(V_{bi} - \left(\frac{kT}{q}\right) - V\right)\right]^{\frac{1}{2}}$$ (4)

where $A$ is the junction area, $\varepsilon_0$ is the dielectric constant, $N_d$ is the semiconductor doping density, and $V_{bi}$ is the built-in voltage [13]. Therefore, the slope of $1/C^2$ vs. V can be used to determine the doping density.

The Shockley ideal $pn$ junction diode equation follows the same form as equation (2) above. The ideality factor is determined for the forward bias current and equals 2 when the

recombination current dominates and equals 1 when the diffusion current dominates. When both currents are comparable, $n$ has a value between 1 and 2 [13].

## EXPERIMENT

A series of one micron thick films were electrodeposited on mechanically polished Mo substrates using deposition potentials ranging from $-1.0$ to $-1.4$ V versus a saturated calomel electrode (SCE). An analogous set of films was also deposited on indium tin oxide (ITO) coated glass. The deposition solutions consisted of 1mM $CuSO_4$, 10 mM $In_2(SO_4)_3$, 5 mM $SeO_2$, and 25 mM Na-citrate.

The deposition potentials used to deposit our thin films were based upon the results of cyclic voltammetry. These cyclic voltammograms and depositions were generated and monitored by a Keithley 236 Source/Measure Unit interfaced to a personal computer and a EG&G 362 Scanning Potentiostat. The composition of the resulting films were characterized by energy dispersive spectroscopy (EDS).

The thickness of the films was calculated using the following equation based on Faraday's law

$$ T = \frac{1}{n\ F\ A} \left( \frac{i\ t\ M}{\rho} \right) \tag{5} $$

where $n$ is the number of electrons transferred, $F$ is Faraday's number, $A$ is the electrode area, $i$ is the applied current, $t$ is the deposition time, M is the formula weight, and $\rho$ is the density [16]. For our calculations, we used the formula weight (336.28 g/mol) and density (5.77 g/cm$^3$) of intrinsic CIS [17]. This is an approximation, since the formula weight and density vary with composition. The number of electrons transferred was taken as 13 according to the total electrode reaction:

$$ Cu^{2+} + In^{3+} + 2SeO_3^{2-} + 12H^+ + 13e^- \rightarrow CuInSe_2 + 6H_2O \tag{6} $$
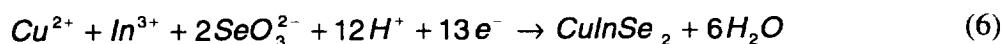
The absorption coefficient versus photon energy of the films deposited on ITO was determined from transmittance measurements in a Perkin Elmer Lambda 19 spectrophotometer. Optical bandgaps were detemined from the absorption coefficient data using linear least-squares analysis and assuming a direct bandgap dependence [9].

Schottky barriers were made on the series of films on Mo by thermal evaporation of aluminum using a positive photo-resist mask of 0.00095 cm$^2$ pads. Current versus voltage (I-V) measurements were performed on these junctions to determine their barrier heights. Capacitance versus voltage (C-V) measurements were used to determine the carrier density of the films.

Based on our EDS results, we attempted to deposit *pn* junction from a single aqueous solution using a step-function potential. A $-1.2$ V vs. SCE potential was applied for 900 s and then changed to $-1.3$ V for 90 s. This was done in an attempt to produce an approximately 0.1 µm n-type CIS layer on a 1.0 µm p-type CIS layer. A similar procedure was used to grow a *pn* junction with slightly different characteristics (e.g., majority carrier densities) using voltages of $-1.1$ and $-1.3$ V vs. SCE. Ohmic contacts were made to the top *n*-side of the junctions using thermal evaporation of aluminum and a shadow mask.

The I-V characteristics of the Schottky barriers and *pn* junctions were measured using a signatone wafer probing station and a Keithley 236 Source/Measure Unit interfaced to a 486 PC. The Keithley 236 is replaced by a Keithley 590 CV Analyzer in this setup to measure the C-V behavior of the Schottky barriers. The C-V measurements were performed at 1kHz.

## RESULTS

The cyclic voltammogram of the deposition bath identified the deposition potentials for the various atomic constituents. These atomic deposition potentials are indicated by the increases in the deposition current: Cu @ -0.4 V, Se @ –0.8 V, In @ -1.0 V (see Fig. 1). Therefore, films deposited at less negative potentials should have a larger Cu to In ratio. Comparing cyclic voltammetry of ITO working electrodes to those of Mo showed a shift of -1.0V.

SEM micrographs show that the series of thin films on Mo were polycrystalline and dense with a sub-micron grain size and a uniform thickness (see Fig. 2). However, surface roughness increased with more negative deposition potentials.

EDS analysis showed that the atomic percent of Se was between 50 and 53% for deposition potentials from -1.0 to -1.4 V vs. SCE. However, there is a large degree of variation in the Cu to In ratio in the films as a function of deposition potential (see Fig. 3). Based on these results, we would expect that those films deposited at potentials less negative than -1.2 V vs. SCE would be p-type, and those deposited at more negative potentials would be n-type [15].
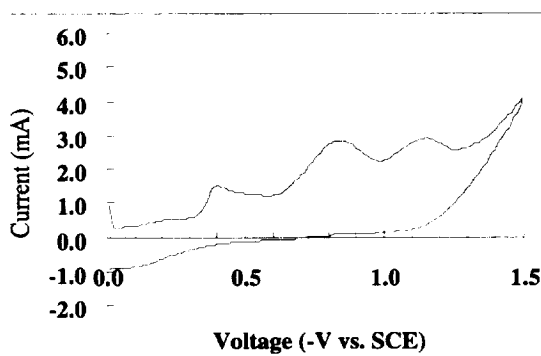


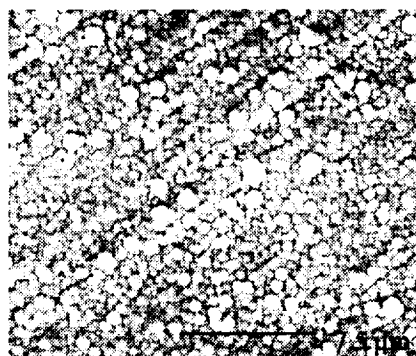Figure 1. Cyclic voltammogram of the deposition solution used in this study.



Figure 2. SEM micrograph of an -1.2 V as-deposited 1.0 μm thick CIS film.

Analysis of the transmission spectra of the series of films deposited on ITO revealed a linear dependence of $(\alpha h v)^2$ versus photon energy, indicating a direct energy gap. Non-linear behavior occurred below 0.95 eV and was attributed to phonon related mechanisms. The optical band gap was found to increase for potentials less than and greater than –2.2 V vs. SCE (see Fig. 4). This change in optical bandgap is consistent with a Burstein-Moss shift, and indicates an increasing carrier density with deviation from stoichiometry. However, the linearity of $(\alpha h v)^2$ versus hv was also reduced as the Cu/In ratio deviated from unity, most likely due to the introduction of second phases.
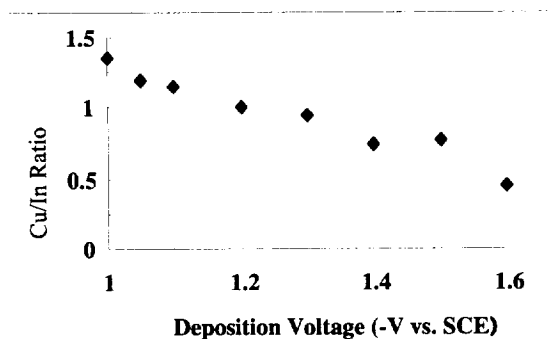
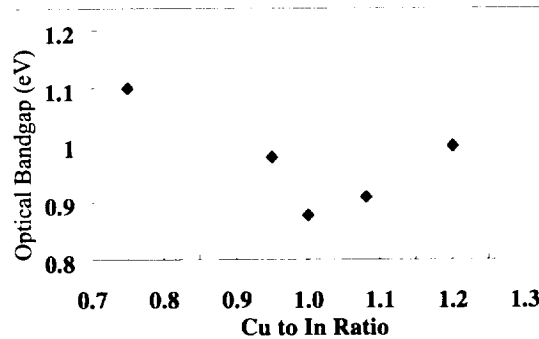Figure 3. Cu to In ratio versus deposition voltage of the as-deposited CIS films as determined by EDS.

Figure 4. Optical bandgap versus deposition potential.

The I-V behavior of the Al contacts on CIS films deposited at less negative potentials than -1.2 V vs. SCE showed the rectifying behavior of a Shottky barrier. This implies that these films were p-type. Al contacts on the films deposited at more negative potential that −1.2 V vs. SCE showed ohmic behavior indicative of n-type films. The semilog plots of current density versus voltage showed the anticipated linear behavior and yielded barrier heights between 0.55 and 0.64 eV, with ideality factors much greater than one (see Table I). A value for the hole effective mass of 0.71 was used in our calculations [1]. The measured barrier heights are much smaller than the theoretical prediction of 1.2 eV. The measured barrier heights of the Schottky barriers were found to decrease with increasing carrier density.

The capacitance versus voltage measurements of the Schottky barriers demonstrated linear $1/C^2$ vs. V behavior. The doping densities based on the least-square slopes were in good agreement with previous studies and our EDS results (see Table I). A value of 8.1 was used for the high frequency dielectric constant in our calculations [1].

Table I. Measured material properties versus deposition voltage
based on I-V and C-V results using Al contacts

| Deposition Voltage (-V vs. SCE) | Semiconductor Type | Barrier Height (eV) | Carrier Density |
|---|---|---|---|
| 1.00 | P | 0.56 | $1.1 \times 10^{21}$ |
| 1.05 | P | 0.60 | $7.3 \times 10^{20}$ |
| 1.10 | P | 0.64 | $2.8 \times 10^{20}$ |
| 1.20 | N | 0.0 | - |
| 1.30 | N | 0.0 | - |
| 1.40 | N | 0.0 | - |

The I-V results of the (-1.0/-1.3V) pn junction showed the anticipated rectifying behavior (see Figure 5). The immediate flow of current in the reverse bias direction is indicative of a "backward" diode [14]. This current is due to tunneling between degenerate or nearly degenerate semiconductors. This degeneracy is consistent with the above optical and Schottky barrier results. The (-1.1/-1.3V) pn junction showed less degeneracy as expected, with a more characteristic Schockley diode behavior [13].
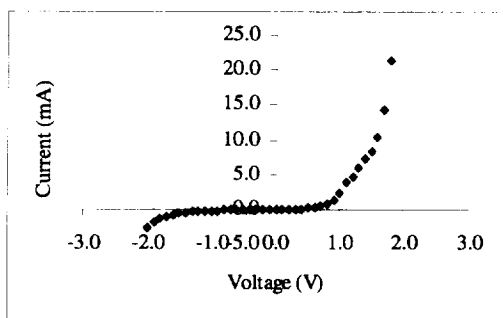
Figure 5. I-V behavior of a –1.0/-1.3 V
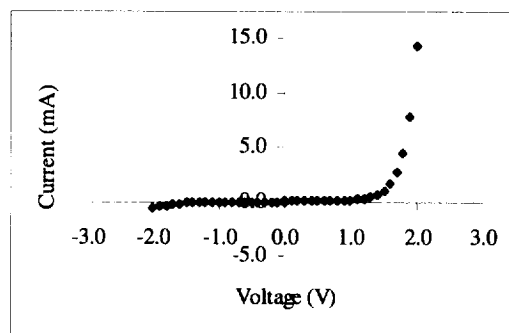CIS-based *pn* junction



Figure 6. I-V behavior of a –1.1/-1.3 V
CIS-based *pn* junction.

## CONCLUSIONS

The electrodeposited $Cu_xIn_{2-x}Se_2$ thin films were shown to have stoichiometries which varied linearly with the range of deposition potentials used in this study. The optical band gaps were found to be between 0.88 and 0.98 eV and increase with deviation from stoichiometry. Schottky barrier behavior was observed for Al contacts to films deposited at potentials less negative than –1.2 V. The results are in agreement with these films being p-type as indicated by our EDS results and previous studies on native defects in CIS. Current versus voltage measurements confirmed the ability to deposit a *pn* junction from a single aqueous solution using a step-function potential.

## REFERENCES

1. A. Rockett and R.W. Birkmire, *J. Appl. Phys.* **70**, R81(1991).
2. K. Zweibel, H. Ullal, and B. von Roedern, *25th IEEE PVSC* (IEEE, New York, 1996).
3. F.J. Pern, J. Goral, R.J. Matson, T.A. Gessert, and R. Noufi, *Solar Cells* **24**, 81 (1988)
4. S.P. Grindle, A.H. Clark, S. Rezaie-Serej, E. Falconer, J. Mcneily, and L.L. Kazmerski, *J. Appl. Phys.* **51**, 5464 (1980).
5. Copper Indium Diselenide for Photovoltaic Applications, edited by T.J. Couts, L.L. Kazmerski, and S. Wagner (Elsevier, Amsterdam, 1986).
6. S.B. Zhang, S.H. Wei, A. Zunger, *Phys. Rev. Lett.* **78**, 21 (1997).
7. R.P. Raffaelle, J.G. Mantovani, and R.B. Friedfeld, *Sol.Ener.Mat. & Sol.Cells* **46**, 201 (1997).
8. R.P. Raffaelle, J.G. Mantovani, R.B. Friedfeld, S.G. Bailey, and S.M. Hubbard, *26th IEEE Photovolt. Spec. Conf.* (IEEE, New York, 1997).
9. E.J. Johnson, *Semicond. and Semimet.* **3**, 153 (1967).
10. T. Irie, S. Endo, and S. Kimura, *Jpn. J. Appl. Phys.* **18**, 1303 (1979).
11. E. Burstein, *Phys. Rev.* **93**, 632 (1954); S. Moss, *Proc. Phys. Soc. B* **67**, 775 (1954).
12. C. Rincon and G. Sanchez Perez, *Solar Cells* **16**, 363 (1986).
13. S.M. Sze, *Physics of Semiconductor Devices* (John Wiley & Sons, Inc., New York, 1981).
14. H.M. Moller, *Semiconductors for Solar Cells* (Artech House, Boston, 1993).
15. C.Y. Chang and S.M. Sze, *Solid State Electron.*, **13**, 727 (1970).
16. D.S. Lashmore and M.P. Dariel, *J. Electrochem. Soc.* **135**, 1218 (1988).
17. R.C. Weast, ed., *CRC Handbook of Chem. and Phys.* (CRC, Boca Raton, FL, 1980).

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