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High-efficiency solar cells based on Cu(InAl)Se_2 thin films

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A Cu(InAl)Se_2 solar cell with 16.9% efficiency is demonstrated using a Cu(InAl)Se_2 thin film deposited by four-source elemental evaporation and a device structure of glass/Mo/Cu(InAl)Se_2/CdS/ZnO/indium tin oxide/(Ni/Algrid)/MgF_2. A key to high efficiency is improved adhesion between the Cu(InAl)Se_2 and the Mo back contact layer, provided by a 5-nm-thick Ga interlayer, which enabled the Cu(InAl)Se_2 to be deposited at a 530 °C substrate temperature. Film and device properties are compared to Cu(InGa)Se_2 with the same band gap of 1.16 eV. The solar cells have similar behavior, with performance limited by recombination through trap states in the space charge region in the Cu(InAl)Se_2 or Cu(InGa)Se_2 layer. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1499990]

The Cu(InGa)Se_2 thin films in high efficiency solar cells typically have Ga/(In+Ga)≈0.1–0.3 giving a band gap (E_g)=1.1–1.2 eV. Significant effort has been made to develop high efficiency solar cells based on wider band gap $CuInSe_2$ alloys by replacing In with Ga, or Se with S. The goal is improved module performance resulting from the tradeoff between higher voltage and lower current at maximum power which can allow fewer scribes for monolithic integration or reduced losses in the transparent conducting oxide layer. Further, wider band gaps could be used to develop multijunction devices with even higher efficiency. However, with band gaps greater than 1.3 eV, the efficiency of Cu(InGa)Se_2 devices is limited by a degradation of the electronic properties of the Cu(InGa)Se_2 layer leading to losses in fill factor (FF) and open circuit voltage (V_{OC}).[1,2]

We have recently reported on Cu(InAl)Se_2 films deposited by multisource elemental evaporation, in which the band gap can be varied from 1.0 to 2.7 eV.[3,4] Solar cells with 11% efficiency were fabricated, but poor adhesion limited the substrate temperature (T_{SS}) used for the growth of the Cu(InAl)Se_2 film which restricted the cell efficiency. In this letter, a method to improve the adhesion, allowing higher T_{SS}, is presented and a Cu(InAl)Se_2 based solar cell with 16.9% efficiency is demonstrated. Film and device properties are compared to Cu(InGa)Se_2 with the same band gap of 1.16 eV.

Cu(InAl)Se_2 and Cu(InGa)Se_2 films were deposited by elemental evaporation on Mo-coated soda lime glass at T_{SS} =530 and 550 °C, respectively. The films were 2.0–2.5 μm thick. The ratio of Al or Ga to In was adjusted so that the films had the same band gap. Delivery rates of all metals were constant during the 60 min film growth and secondary ion mass spectroscopy (SIMS) depth profile measurements confirmed that the films have uniform composition and, therefore, band gap. At substrate temperatures greater than 450 °C, the Cu(InAl)Se_2 did not adhere well to the glass/Mo substrate. It has been previously shown that the addition of Ga to $CuInSe_2$ films improves their adhesion to Mo.[5] Therefore, a 5-nm-thick Ga film was sputtered onto the Mo prior to the growth of Cu(InAl)Se_2. This resulted in improved adhesion and allowed films to be deposited at T_{SS}=530 °C. SIMS measurements showed that the Ga is distributed through the Cu(InAl)Se_2 film, but it accounts for only 0.3 at. % of the Cu(InAl)Se_2. All Cu(InGa)Se_2 films exhibited good adhesion.

The compositions of Cu(InAl)Se_2 and Cu(InGa)Se_2 films were determined by energy dispersive x-ray spectroscopy (EDS) and are shown in Table I. The ratios $x \equiv$ Al/(In+Al) and Ga/(In+Ga) were 0.13 and 0.26, respectively, for films with E_g=1.16 eV. For the Cu(InAl)Se_2, the optical absorption coefficient (α) was determined by spectroscopic ellipsometry[4] and E_g was obtained from the intercept of $(\alpha E)^2$ plotted versus E. The band gap for Cu(InGa)Se_2 was determined from the composition as in previous work.[1] Scanning electron microscopy characterization of the surface and the cross section of the films shows similar surface morphology with columnar grains for both films, and cross-sectional grain width in the range of ~1 μm.

X-ray diffraction (XRD) measurements with Bragg–Brentano (θ–2θ configuration) focusing geometry and Cu $K\alpha$ radiation show that the Cu(InAl)Se_2 and Cu(InGa)Se_2 films are single phase and nearly randomly oriented. Figure 1 compares the (112) reflections for $CuInSe_2$, Cu(InAl)Se_2, and Cu(InGa)Se_2. The lattice spacing d(112) and full width at half maximum (FWHM) are included in Table I. In each case, the variation in lattice spacing with Al and Ga content follows Vegards law,[4] but the shift in d(112) from $CuInSe_2$,

TABLE I. Results of EDS and XRD measurements on Cu(InAl)Se_2 and Cu(InGa)Se_2 films.

Sample	Cu	In	Al or Ga	Se	x	d(112) (Å)	FWHM (°)
Cu(InAl)Se_2	23.5	23.0	3.5	50.0	0.13	3.324	0.14
Cu(InGa)Se_2	24.1	19.7	6.9	49.3	0.26	3.312	0.13

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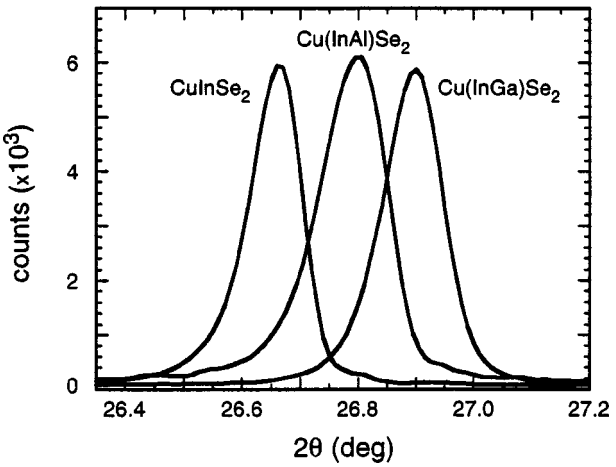

FIG. 1. XRD scans of the (112) peaks of the $Cu(InAl)Se_2$ and $Cu(InGa)Se_2$ films and a $CuInSe_2$ film for comparison.

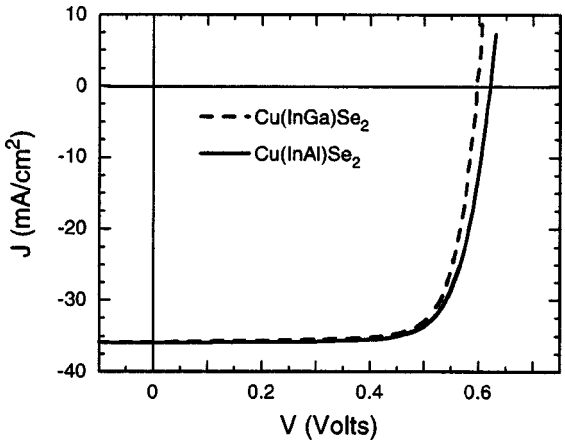

FIG. 2. Current–voltage curves for the $Cu(InAl)Se_2$ and $Cu(InGa)Se_2$ devices.

with $d(112)=3.343$ Å, is smaller for the $Cu(InAl)Se_2$ film than for the $Cu(InGa)Se_2$. This shows that alloying with Al allows the band gap to be increased with less variation in lattice spacing than with Ga. The FWHM for all films is comparable to the instrumental broadening of 0.11° which indicates that compositional variations are small, with a maximum variation in x of $\pm 2\%$.

Solar cells were fabricated with the structure glass/Mo/[$Cu(InAl)Se_2$ or $Cu(InGa)Se_2$]/CdS/ZnO/indium tin oxide (ITO)/MgF_2 with a Ni/Al collection grid. The CdS was deposited with a thickness of ~40 nm by chemical bath deposition. ZnO and ITO were deposited by rf sputtering, with the ITO having a sheet resistance of 25Ω/□. The MgF_2 antireflection layers and grids were deposited by electron-beam evaporation. Current–voltage ($J-V$) characteristics were measured at the National Renewable Energy Laboratory (NREL) under standard conditions (100 mW/cm^2, 25 °C; ASTM: E 892 Global). The open circuit voltage (V_{OC}), short circuit current (J_{SC}), and efficiency (η) are listed in Table II. The $J-V$ and quantum efficiency (QE) curves, also measured at NREL, are shown in Figs. 2 and 3. The cells have comparable efficiency with slightly higher V_{OC} and lower FF for the $Cu(InAl)Se_2$ device. The QE curves are nearly indistinguishable, in agreement with the cells having the same band gap and J_{SC}.

The $J-V$ data were analyzed using a standard diode equation

$$J=J_0\exp\left[\frac{q}{AkT}(V-R_sJ)\right]-J_0-J_L+GV, \tag{1}$$

where J_0 is the forward current, A is the diode quality factor, J_L is the light generated current, R_S is the series resistance, and G is the shunt conductance. For the devices in this work, $G<1$ mS/cm^2 and can be neglected. R_S was determined from the intercept of a plot of the derivative dV/dJ vs $(J+J_{SC})^{-1}$, since, according to Eq. (1) with $J_L=J_{SC}$:

$$\frac{dV}{dJ}=R_s+\frac{AkT}{q}(J+J_{sc})^{-1}. \tag{2}$$

Using the value of R_S, listed in Table II, the semilogarithmic plot of $J+J_{SC}$ vs $V-R_SJ$ is shown for the two cells in Fig. 4. In each case the data is linear over more than an order of magnitude demonstrating a good fit to Eq. (1) with no significant loss due to voltage dependent collection of the light generated current. The slope and intercept in Fig. 4 give A and J_0, also listed in Table II. In addition, the temperature dependence of V_{OC} was measured at 10 K intervals from 218 to 318 K. For both cells, V_{OC} varied linearly with T and extrapolation to $T=0$ gave the band gap of 1.16 V. This shows that the recombination is in the absorber layer. Thus, the diode behavior of both devices is consistent with the forward diode current limited by Shockley–Read–Hall recombination through trap states within the space-charge region of the absorber.[6,7] The $Cu(InAl)Se_2$ device has larger A and smaller J_0 than the $Cu(InGa)Se_2$ which suggest differences in the defect distributions which control the recombination.

In conclusion, the adhesion of $Cu(InAl)Se_2$ films was improved by the addition of a 5-nm-thick Ga film on the glass/Mo substrate which allowed the films to be deposited at

TABLE II. Solar cell parameters and results of diode analysis.

Film	η (%)	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	R_S (Ω cm^2)	A	J_0 (mA/cm^2)
$Cu(InAl)Se_2$	16.9	621	36.0	75.5	0.5	1.5	1×10^{-5}
$Cu(InGa)Se_2$	16.5	593	35.8	77.7	0.1	1.4	2×10^{-6}

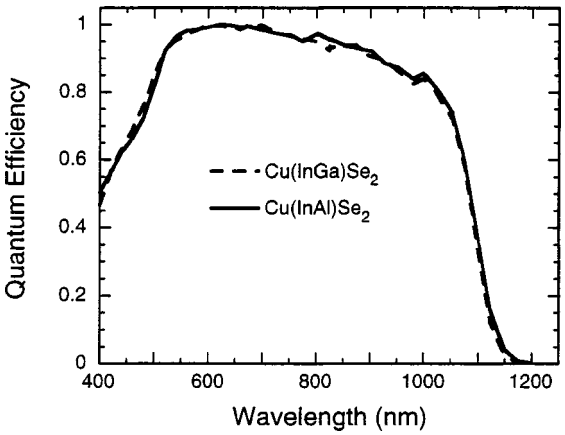

FIG. 3. Normalized quantum efficiency curves for the $Cu(InAl)Se_2$ and $Cu(InGa)Se_2$ devices.

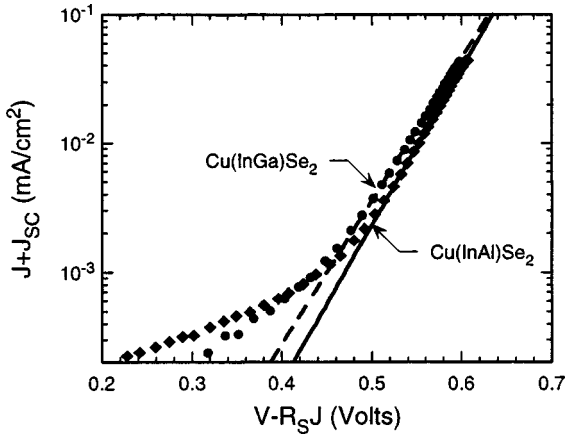

FIG. 4. Semi-logarithmic plot of $J+J_{SC}$ vs $V-R_SJ$ under illumination for the Cu(InAl)Se_2 and Cu(InGa)Se_2 devices.

a substrate temperature of 530 °C. The higher substrate temperature resulted in Cu(InAl)Se_2 with improved electronic properties and a solar cell with 16.9% efficiency was fabricated. The Cu(InAl)Se_2 solar cells diode characteristics are similar to Cu(InGa)Se_2 with the same band gap, limited by recombination through defect states in the absorber layer.

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