High efficiency thin-film CuIn$_{1-x}$Ga$_x$Se$_2$ photovoltaic cells using a Cd$_{1-x}$Zn$_x$S buffer layer

R. N. Bhattacharya, a) M. A. Contreras, B. Egaas, and R. N. Noufi
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401
A. Kanevce and J. R. Sites
Department of Physics, Colorado State University, Fort Collins, Colorado 80523

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The authors have fabricated 19.52% thin-film CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS)-based photovoltaic devices using single layer chemical bath deposited Cd$_{1-x}$Zn$_x$S (CdZnS) buffer layer. The efficiency equals the world record for any thin-film solar cell and is achieved with reduced optical absorption in the window layer. Using current-voltage, quantum efficiency, and capacitance-voltage measurements, the CIGS/CdZnS device parameters are directly compared with those of CIGS/CdS devices fabricated with equivalent absorbers. © 2006 American Institute of Physics. [DOI: 10.1063/1.2410230]

Of the thin-film photovoltaic devices that have been developed to date, those fabricated with CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) absorbers have shown the highest efficiencies. One of the critical elements of CIGS photovoltaic technology is the junction-formation step. At present, the preferred approach is to deposit a chemical-bath-deposited (CBD) CdS layer, which has resulted in a 19.5%-efficient device. Recently, single-layer CBD ZnS(OH) substituted for CBD CdS has demonstrated device efficiency up to 18.5%. In a separate report, multilayer (three layers) CBD ZnS(OH) also produced 18.6% device efficiency.

In this letter, we report 19.52%-efficient CIGS-based solar cells using a single-layer CBD CdZnS buffer layer, an efficiency equal to that reported in Ref. 1 using the standard CdS process. The CBD CdZnS thin films were obtained from a solution containing CdSO$_4$, ZnSO$_4$, thiourea, ammonia, water, and isopropanol. The compositional ratio of Cd:Zn was 80:20, as determined by inductively coupled plasma analysis. The CIGS/CdZnS devices were measured by the Cell Performance Characterization Group at NREL. The current-voltage (J-V) of the 19.52%-efficient CIGS/CdZnS device is shown in Fig. 1(a) and the quantum efficiency (QE) is shown in Fig. 1(b). The confirmed cell parameters are 0.705 V open-circuit voltage, 35.5 mA/cm$^2$ short-circuit current density, 77.9% fill factor, and 19.5% efficiency. It also appears that the commonly used $i$-ZnO layer is not necessary with the CdZnS buffer, which makes it a commercially favorable technique.

The CdZnS buffer layer allows greater numbers of high-energy photons to reach the junction, which increases the short-circuit current above that obtained for the CdS layer. This difference is clearly seen in Fig. 2, which compares the absolute external quantum efficiencies of CIGS/CdS and CIGS/CdZnS devices made with identical absorbers. It is evident from these measurements that significant (2 mA/cm$^2$) current is gained between 300 and 500 nm when the CdZnS buffer layer is used. Also seen in Fig. 2 is a small QE difference in the opposite direction for the longer wavelength photons, suggesting that the collection of deeper penetrating photons is slightly less. The identical long-wavelength cutoff in the two cases helps confirm that the absorbers are in fact identical. Additional information extracted from J-V measurements showed that the diode qual-

![FIG. 1. (a) Current-voltage characteristics: $V_{oc}=0.7052$ V, $I_{sc}=14.490$ mA, $J_{sc}=35.515$ mA/cm$^2$, fill factor=77.90%, and efficiency=19.52% and (b) QE characteristics of CBD CdZnS/CIGS devices.](image-url)
ity factor $A$, under both dark and light conditions, is slightly higher for cells with the CdZnS buffer ($A = 1.5$ vs $1.3$), and that with either buffer, losses due to series resistance or current leakage are very small.

Capacitance techniques were also used to compare the CdZnS and CdS cells. Again using identical buffers, Figs. 3(a) and 3(b) shows the frequency-dispersion comparison at four selected voltages. The turn-up at high frequency is an inductance effect, and only the data below $200$ kHz are used. At each voltage, the CdS curves are flatter, which implies that they are less affected by electronic defects in the depletion region. Figure 3(c) shows the carrier density deduced from capacitance-voltage ($C-V$) measurements for the same two cells. The $C-V$ curve for the CdS cell was closer to the classic dependence: $A^2/C^2$ is a linear function of voltage, the curve is flatter, and it extrapolates to a reasonable value near $1$ V, where $A$ is the effective area of the device. The capacitance-voltage curve for the CdZnS device was less linear, and capacitance variation with voltage was stronger. The free-carrier density derived from $C-V$ measurements in CIGS/CdS device is about three times higher then in the CdZnS device.

The use of a CdZnS buffer with CIGS solar cells has achieved an important step forward in that it has significantly reduced short-wavelength absorption with only a small impact on junction quality. It seems highly likely that further optimization of the CdZnS process will restore the modest impact on junction quality and will lead to increases in voltage and fill factor while maintaining the higher current achieved here. Hence, the near-term prospects for CIGS cells with efficiency exceeding $20\%$ would appear to be quite favorable.

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FIG. 2. External quantum efficiency curves for CdZnS device and the equivalent CdS device normalized to $J_{sc}$ measurements of $35.5$ and $34.0$ mA/cm$^2$, respectively.

FIG. 3. Comparison of frequency dependence in capacitance for (a) CdZnS and (b) CdS buffers. (c) Comparison of carrier density derived from $C^{-2}$ vs $V$ at $100$ kHz.