

Nanocrystalline dye-sensitized solar cell/copper indium gallium selenide thin-film tandem showing greater than 15% conversion efficiency

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Multijunction stacked (tandem) solar cells can increase the overall photovoltaic conversion efficiency by optimal utilization of the solar spectrum in individual cells. We demonstrate that a photovoltaic tandem cell comprising a nanocrystalline dye-sensitized solar cell as a top cell for high-energy photons and a copper indium gallium selenide thin-film bottom cell for lower-energy photons produces AM 1.5 solar to electric conversion efficiencies greater than 15%. © 2006 American Institute of Physics. [DOI: 10.1063/1.2203965]

Contrary to conventional solar cells, the nanocrystalline dye-sensitized solar cell (DSC) can be designed by appropriate choice of the sensitizer to absorb incident photons in selective spectral regions of the solar spectrum while maintaining high transparency in the remaining wavelength range.^{1–5} A further advantage of DSCs is that their optical transmission and short-circuit photocurrent can be readily adjusted by changing the film thickness, pore size, and the dye loading. This, along with the ease of forming a layered structure, for example, by producing the mesoscopic oxide films using screen printing or doctor blading methods, renders the DSC particularly well suited for the fabrication of tandem solar cell structures for an optimal utilization of the solar spectrum. Several previous publications have dealt with the use of stacked DSC configurations where two dyes absorbing different parts of the solar spectrum were employed as sensitizers.^{6–10} A preliminary conference report describing a tandem configuration using a DSC top cell has also appeared, producing a V_{oc} of over 2 V and an efficiency¹¹ of 15%. The record conversion efficiency of a single junction DSC stands currently at 11.3%.¹²

The optoelectronic properties of Cu(In,Ga)Se_2 (called CIGS) materials render it a highly attractive candidate for the bottom cell in a tandem configuration.¹³ The band gap of the CIGS semiconductor can be tailored in the range of 1.04–1.67 eV, but the high-efficiency solar cells use a composition corresponding to about 1.25 eV. These solar cells can be grown on a variety of substrates. A record efficiency of 19.5% has been achieved by NREL (USA) for solar cells grown on glass substrates, while flexible CIGS achieved 17.2% on stainless steel (Daystar, USA) and 14.1% on polymer foil (ETH Zürich, Switzerland). The NREL polycrystal-

line thin-film group recently demonstrated a four-terminal polycrystalline thin-film tandem cell consisting of a CdTe-based top cell and a CIS-based bottom cell with an efficiency¹⁴ of 15.3%. Here, we report on a tandem cell combining a DSC top cell with a thin-film CIGS bottom cell that allows realizing conversion efficiencies greater than 15%.

The DSC was produced according to a previously published procedure¹⁵ except that the sensitizer was $\text{Ru}(4,4'\text{-dicarboxylic acid-2,2'-bipyridine})_2(\text{NCS})_2$, coded N-719, and that a transparent single layer consisting of 20 nm sized TiO_2 particles was employed instead of the light scattering bilayer structure used in high-performance DSCs. The 12 μm thick film was deposited by screen printing on float glass covered with a conducting fluoride-doped tin dioxide (FTO) layer (TEC 15, sheet resistance 15 Ω/sq obtained from LOF). Due to the small TiO_2 particle size, the dye-covered nanocrystalline film itself shows negligible light

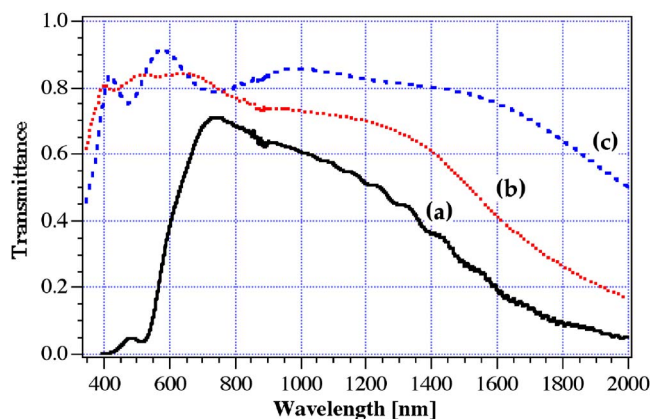


FIG. 1. (Color online) Optical transmission spectra including the diffuse part measured with an Ulbricht sphere of ITO glass (c), FTO glass (b), and the DSC with mesoporous TiO_2 sensitized by a N-719 analog dye (a). The front and back contacts of this cell are made of FTO glass.

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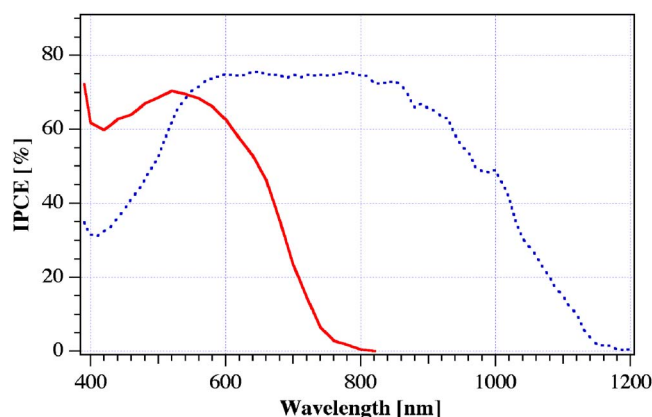


FIG. 2. (Color online) Spectral response curves of the photocurrent for a DSC top cell (bold line) and a red and near IR sensitive bottom cell (dotted line). The external quantum efficiency (incident photon to current conversion efficiency) is plotted as a function of wavelength of the incident light.

absorption or scattering above 1.65 eV, which corresponds to the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap of the sensitizer. However, the FTO glass does absorb in the near IR wavelength region above 1000 nm, thereby reducing significantly the photocurrent drawn by the bottom cell. The diffuse transmission spectra for a DSC using FTO glass both as front and back contacts are shown in Fig. 1, along with the individual spectra for FTO and tin-doped indium oxide (ITO) glass. Clearly the ITO has a much larger window in the near IR extending to 1600 nm, while the FTO absorbs light of wavelength >800 nm. In order to reduce these optical losses, the DSCs described below employed FTO only for the front contact, while the counter electrode is made of ITO glass. The development of a model to quantify the various losses in the tandem device, including the major optical loss deriving from the various types of conducting glasses, is presently underway.

The CIGS cell was fabricated by depositing a stack of polycrystalline layers of ZnO:Al/ZnO/CdS/CIGS/Mo on a soda-lime glass substrate, although metal or polyimide foils can also be used as a substrate. The details of the solar cell processing have been described elsewhere,^{16,17} but a brief description is the following. About $1\ \mu\text{m}$ thick Mo back electrical contact layer was deposited by dc sputtering and

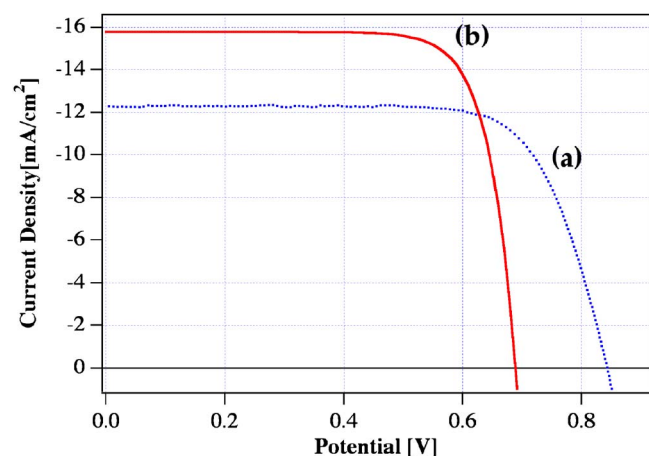


FIG. 3. (Color online) Photovoltaic performance of (a) top DSC and (b) bottom CIGS cells, measured by using a four-wire tandem configuration.

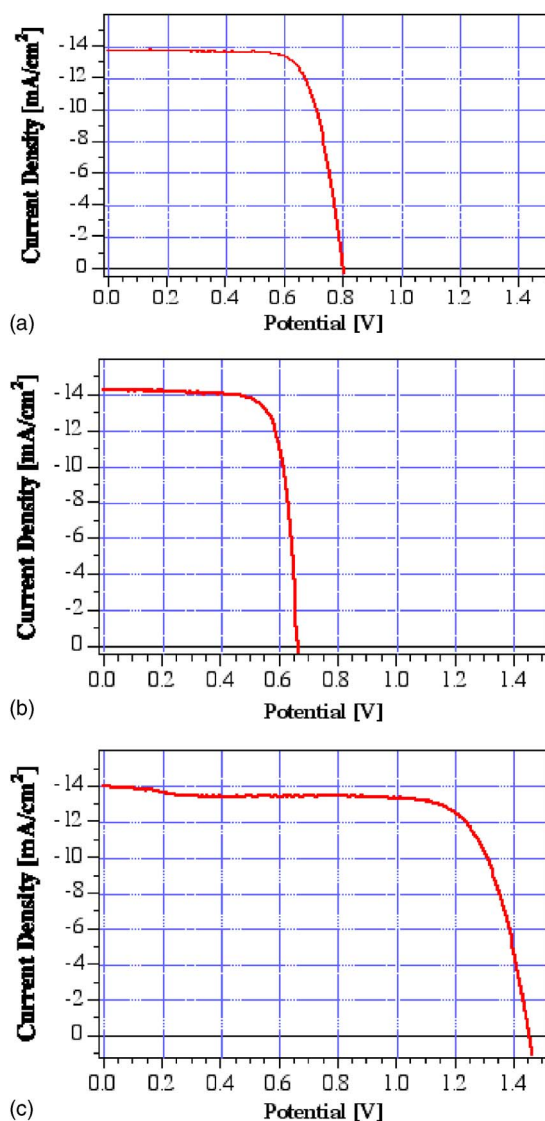


FIG. 4. (Color online) Photocurrent density-voltage characteristics under AM 1.5 full sunlight ($100\ \text{mW/cm}^2$) for a two-wire tandem DCS/CIGS cell. (a) J-V curve for the DSC top cell in the stack producing $J_{sc} = 13.66\ \text{mA/cm}^2$, $V_{oc} = 0.798\ \text{V}$, FF=0.75, and $\eta = 8.18\%$; (b) J-V curve for the CIGS bottom cell in the stack producing $J_{sc} = 14.3\ \text{mA/cm}^2$, $V_{oc} = 0.65\ \text{V}$, FF=0.77, and $\eta = 7.28\%$; and (c) two-terminal DSC/CIGS tandem cell producing $J_{sc} = 14.05\ \text{mA/cm}^2$, $V_{oc} = 1.45\ \text{V}$, FF=0.74, and $\eta = 15.09\%$.

then the CIGS absorber layer was grown by evaporation of Cu, In, Ga, and Se elements using a “three-stage” evaporation process. During the first stage of the absorber growth, the substrate temperature was kept at $400\ ^\circ\text{C}$, while during the second and third stages the substrate temperature was raised to about $580\ ^\circ\text{C}$. The solar cells were finished by a chemical bath deposition of a CdS buffer layer followed by rf sputtering of ZnO:Al/i-ZnO front contacts (200 nm thick) and electron beam evaporation of Ni-Al contact grids for better current collection. No antireflection (AR) coating was applied. The CIGS cell employed in the stack gave alone under exposure to simulated AM 1.5 sunlight a short-circuit photocurrent $J_{sc} = 26.8\ \text{mA/cm}^2$, an open-circuit photovoltage $V_{oc} = 698.5\ \text{mV}$, a fill factor (FF)=0.744, and a solar to electric power conversion efficiency $\eta = 13.9\%$.

Figure 2 shows typical photocurrent action spectra measured separately for a DSC and a CIGS cell. The external quantum efficiency (incident photon to current conversion

efficiency) is plotted as a function of wavelength of the light. The DSC shows a strong response in the UV, blue, and green wavelength domains. By contrast the CIGS cell exhibits high external quantum efficiencies in the red and near IR parts of the spectrum extending from 700 to 1150 nm where the DSC is insensitive to light. Thus, the spectral response of the two systems is complementary to each other and reveals the advantage of employing them in a tandem mode.

Superposition of the two cells produced a stack whose photovoltaic performance was tested under AM 1.5 sunlight. Results obtained from four contact measurements are shown in Fig. 3. The DSC top cell yielded $J_{sc}=12.22$ mA/cm², $V_{oc}=0.858$ V, FF=0.72, and $\eta=7.58\%$, while the corresponding parameters for the CIGS bottom cell are $J_{sc}=15.7$ mA/cm², $V_{oc}=0.689$ V, FF=0.75, and $\eta=8.17\%$ (efficiency lowering from 13.9% is due to light absorption by the DSC cell, while AM 1.5 power is originally used for efficiency calculation of the bottom cell alone). The combined conversion efficiency of 15.75% was significantly higher than that of the individual cells even though the FTO glass causes significant transmission losses in the near IR range, as discussed above.

An attempt was also made to realize a two-wire tandem cell by adapting the film thickness of the top cell in order to match the photocurrent of the CIGS bottom device. Results are shown in Fig. 4. Figure 4(a) gives the J - V curve for the DSC top cell in the stack yielding $J_{sc}=13.66$ mA/cm², $V_{oc}=0.798$ V, FF=0.75, and $\eta=8.18\%$, while Fig. 4(b) shows the J - V curve for the CIGS bottom cell in the stack producing $J_{sc}=14.3$ mA/cm², $V_{oc}=0.65$ V, FF=0.77, and $\eta=7.28\%$. Finally, when the two cells are connected in series to produce a two terminal DSC/CIGS tandem cell, the photovoltaic parameters are $J_{sc}=14.05$ mA/cm², $V_{oc}=1.45$ V, FF=0.74, and $\eta=15.09\%$. It is remarkable that such a high efficiency is obtained even though the photocurrents of the two cells were not perfectly matched, producing the hump in the J - V curve in Fig. 4(c), and there are significant optical losses in the stack. By adequately reducing the optical loss derived from the conducting glass, it is possible to optimize the cell voltages and also match the currents of the two cells

to higher values by tuning the spectral responses of the two cells in a mutually complimentary manner. Therefore, a large room for further improvement of this tandem system exists, which appears to be a promising configuration for realizing very high conversion efficiencies.

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