Fabrication and performance of a monolithic dye-sensitized TiO_2/Cu(In,Ga)Se_2 thin film tandem solar cell

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Tandem solar cells using different bandgap absorbers allow efficient photovoltaic conversion in a wide range of the solar spectrum. The optical gaps of the dye-sensitized solar cell and the Cu(In,Ga)Se_2 solar cell are ideal for application in double-junction devices and a mechanically stacked device has been reported recently. We report on the monolithic integration of these subcells to cut optical losses at needless interfaces and material costs, achieving 12.2% conversion efficiency at full sunlight. The high open-circuit voltage confirms the series connection, but corrosion of the Cu(In,Ga)Se_2 cell by the redox mediator (I^-/I_3^- couple) of the dye-sensitized cell and an associated voltage loss (≈140 mV) limits performance. © *2009 American Institute of Physics*.
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The development of inexpensive and efficient solar cells is a key objective of photovoltaic research. The power conversion efficiency of solar cells can be extended beyond the Shockley–Queisser limit for a single-junction device[1] by using multiple subcells in a tandem device, thus shifting the absorption onset to longer wavelengths and reducing thermalization losses.[2,3] Very high efficiencies (>40% at concentrated sunlight) can be achieved with epitaxially grown triple-junction devices,[4] but the fabrication of efficient tandem cells using low-cost thin film technologies remains a challenge.[5–7] In a series-connected double-junction device the ideal optical bandgaps are around 1.6–1.7 eV for the top cell and 1.0–1.1 eV for the bottom cell.[8] The absorption characteristics of the dye-sensitized solar cell (DSC) and the Cu(In,Ga)Se_2 (CIGS) solar cell closely match these requirements. Hence, a wide range of the solar spectrum can be harvested by efficiently converting high energy photons in a top DSC and transmitted low energy photons in an underlying CIGS cell. Our groups have thus recently reported on a mechanically stacked device consisting of a DSC on top of a CIGS cell, yielding a conversion efficiency of over 15%.[9] This demonstrated the possibility of combining DSCs with CIGS thin film cells, but the drawbacks of the stacked setup are reflection losses at the stack interface and absorption losses of low energy photons in the conducting glass of the top cell. In this letter we present a *monolithic* DSC/CIGS setup to cut optical losses from the superfluous layers and interfaces and to reduce material and manufacturing costs.

The monolithic device consists of a mesoporous dye-sensitized TiO_2 film, which is directly sandwiched with a platinized CIGS solar cell using a spacer (Fig. 1), thus avoiding the back glass electrode commonly used in the DSC. The void is filled through a hole in the top electrode with an acetonitrile based electrolyte containing the I^-/I_3^- redox couple. The *p*-type CIGS absorber (~1 μm) was grown by sequential coevaporation of elements using a three-stage evaporation process[10] on a soda-lime glass substrate, coated with a 1 μm thick dc-sputtered layer of molybdenum, and covered with an *n*-type CdS window layer (50 nm). The detailed fabrication procedure is given elsewhere.[11] The front contact, a 600 nm thick layer of In_2O_3:Sn (ITO), was covered with a transparent layer (<1 nm) of sputtered Pt particles. A 8 μm thick film of 20 nm sized TiO_2 particles was screen-printed on a SnO_2:F (FTO) conducting glass electrode (10 Ω/□) and sensitized by immersing it overnight in a solution of 0.3 mM of C101 dye[12] and 0.3 mM 3α, 7α-dihydroxy-5β-cholanic acid. The detailed fabrication procedure for the TiO_2 paste and film has been described elsewhere.[13]

As shown by external quantum efficiency (EQE) measurements (Fig. 2), the DSC converts light in the visible region with an onset at 780 nm (optical gap of 1.6 eV) and the CIGS converts the remaining light up to 1160 nm (optical gap of 1.1 eV). The subcells in the monolithic tandem are

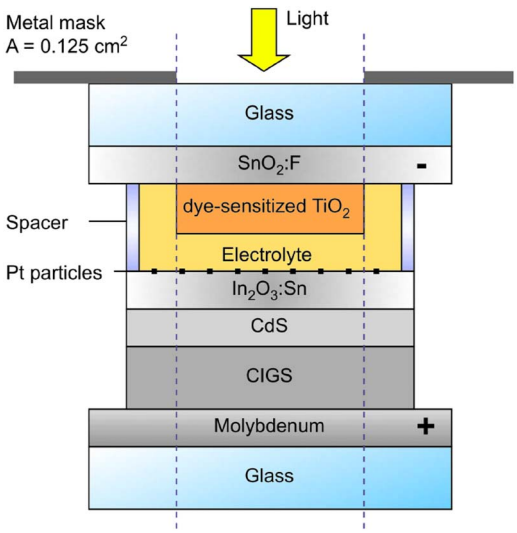

FIG. 1. (Color online) Schematic of the monolithic device structure using a dye-sensitized mesoporous TiO_2 film as top absorber of visible light and a Cu(In,Ga)Se_2 (CIGS) bottom absorber of transmitted near infrared light.

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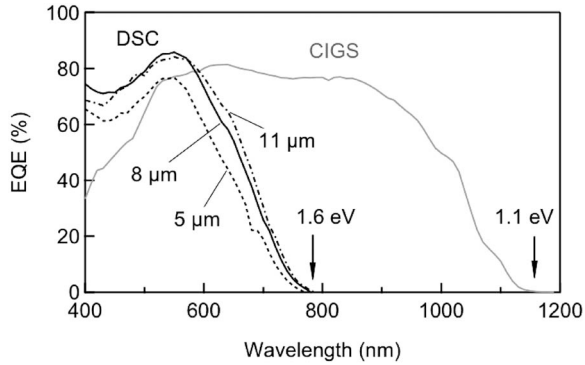

FIG. 2. The EQE of the DSC and CIGS shows ideal onsets for use in a tandem device. The EQE of the DSC can be fine-tuned with variation of the TiO_2 film thickness.

electrically connected in series. The charges generated in the subcells recombine at the catalytic Pt particles[14] on the electrolyte/ITO interface, that is, the "holes" from the top cell (oxidized I_3^- ions) react with electrons from the bottom cell via $I_3^- + 2e^- \rightarrow 3I^-$. It is thus crucial to match the current densities of the subcells to minimize electronic losses. The current density of the DSC can be tuned with choice of the sensitizer, by variation in the optical bandgap, and film thickness, by variation in the optical path length. Here we use a Ru-complex sensitizer with a suitable optical gap and a high molar extinction coefficient[12] to achieve large short-circuit currents at full sunlight on thin transparent TiO_2 films, ranging from 13.6 mA cm^{-2} (5 μm film) to 16.2 mA cm^{-2} (11 μm film). The current density of the CIGS cell can be tuned with variation of the bandgap by changing the In/Ga ratio in the absorber.[11]

The monolithic setup omits the transparent conductive oxide (TCO) back electrode of the DSC to avoid reflection and free charge carrier absorption losses.[15] We show an estimate for the enhancement in photocurrent with a monolithic setup compared to a mechanically stacked setup from the comparison of the transmission spectra of a DSC with a FTO back contact and a microscope glass back contact (Fig. 3). Transmittance spectra were measured on a custom-built setup using a chopped white light probe and a monochromator to detect the transmitted light via a lock-in amplifier. In the visible range, the transmittance of the two devices is attenuated by the dye absorption onset at 780 nm and the absorption of I_3^- ions around 400 nm. The transmittance

TABLE I. Photovoltaic performance of the DSC/CIGS monolithic device and the subcells (AM 1.5G, 100 mW cm^{-2}). A Ni/Al grid was evaporated on the CIGS cell to improve charge carrier collection.

Test device	Efficiency (%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	Fill factor (-)
DSC (FTO back contact)	8.4	0.74	−15.3	0.74
CIGS (unfiltered)	11.6	0.62	−27.3	0.68
DSC/CIGS monolithic	12.2	1.22	−13.9	0.72

losses above 780 nm are entirely due to absorption by free charge carriers in the FTO and reflection losses at interfaces. The replacement of the FTO back electrode with a microscope slide leads to an increase in transmittance of up to 20% in the infrared region and to an overall integrated increase of 24%. The short-circuit current (J_{sc}) of a "DSC filtered" CIGS cell can be estimated from integration of the product of the EQE of the CIGS cell with the transmittance spectrum of the DSC and the AM 1.5G reference spectrum. The integrated current of the CIGS cell in Fig. 2 is J_{sc}=27.6 mA cm^{-2} and reduces to J_{sc}=10.9 mA cm^{-2} with the DSC/FTO filter and to J_{sc}=13.1 mA cm^{-2} with a DSC/glass filter. Even though this calculation underestimates the effective current of the CIGS cell in a monolithic device by at least 4% (reflection losses at the electrolyte/glass/air interfaces are not deduced), it gives a lower limit for the increase in photocurrent expected (~20%), which can be exploited with a current-matching top DSC.

To demonstrate the concept, the photovoltaic parameters of a monolithic DSC/CIGS device and its subcells are given in Table I. The conversion efficiency of the monolithic device (12.2%) slightly exceeds the performance of the CIGS cell (11.6%), justifying the monolithic approach to enhance device efficiency. The open-circuit voltage (V_{oc}) of the tandem device is close to the sum of the V_{oc}'s of the DSC and CIGS cell, confirming the series connection of the subcells. The J_{sc} of the tandem device is in good agreement with the estimate made using the transmittance spectrum in Fig. 3. The current density-voltage curves (Fig. 4) illustrate a drawback of the monolithic setup: the rectifying behavior in the dark and at a low light level is nonideal, suggesting internal electric shunt pathways. Indeed, the performance of the device degrades within hours; the V_{oc} and fill factor drop substantially. This is probably due to a corrosion of the CIGS cell by I_3^- ions in the electrolyte percolating through pinholes.

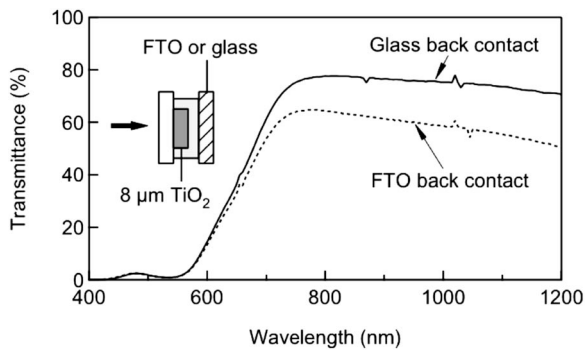

FIG. 3. Transmission spectra of a DSC with a platinized FTO back contact (15 Ω/□) and a microscope glass slide back contact. Omitting the FTO back electrode leads to a substantial increase in transmittance in the near infrared region.

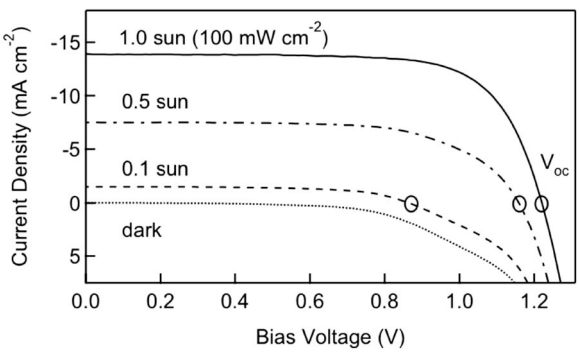

FIG. 4. Current density-voltage curve of a monolithic DSC/CIGS tandem device at various light intensities. Notice the nonideal rectification in the dark curve. The device was tested under simulated standard testing conditions (AM 1.5G) using a metal mask with an aperture area of 0.125 cm^2.

This hypothesis is supported by initial scanning electron micrograph studies showing cracks at grain boundaries in the CIGS absorber after exposure to the electrolyte for 40 min. The initial V_{oc} loss of 140 mV and the further degradation can be explained by a rapid corrosion of the *p-n* junction and shunting through the cracks. Further work to assess the precise degradation mechanism is underway.

Research on CIGS-based tandem cells is still in a preliminary stage and the efficiency of the tandem cell presented does not yet exceed state-of-the-art CIGS cells (up to 19%). However, the tandem cell concept is the key to enhance the performance of CIGS solar cells, provided that efficient and transparent top cells with an optical gap of 1.6–1.7 eV can be developed. We have shown that a monolithic DSC/CIGS tandem device has the potential for increased efficiency over a mechanically stacked device due to increased light transmission to the bottom cell and demonstrated a monolithic DSC/CIGS device with an initial efficiency of 12.2%. We expect to make full use of the optical advantages of this setup and to surpass the 15.1% efficiency benchmark given by the stacked device[9] with a suitable protective intermediate layer inhibiting the degradation mechanism at the electrolyte/CIGS interface. Substitution of the FTO front electrode with a high mobility TCO, e.g., In_2O_3:Ti (ITiO), which substantially reduces absorption losses in the near infrared,[16] and careful current-matching will further enhance the device performance.

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