Radial Heterojunction Solar Cell Consisting of n-type Rutile Nanowire Array Infiltrated by p-type CdTe

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ABSTRACT

We report a p-n heterojunction solid-state solar cell completely fabricated by simple and tunable solution-based processing. The solar cell comprised of *p*-type CdTe that was electrochemically deposited onto hydrothermally synthesized vertically oriented arrays of *n*-type rutile TiO_2 nanowire arrays (RNWAs), which were grown on fluorine doped tin oxide (FTO)-coated transparent conductive glass substrates. Morphological studies revealed the TiO_2 nanowires to be completely infiltrated by the CdTe. The solid-state solar cell exhibited an open circuit voltage of 0.6 V, short-circuit current of 3.57 $mAcm^{-2}$, a fill factor of 44 % and a power conversion efficiency of 0.96%.

KEYWORDS: Solvothermal growth; photovoltaic; electrodeposition; monocrystalline nanowires; mobility;

1. INTRODUCTION

Photovoltaic (PV) solar energy conversion is not only a renewable power source but also increasingly competitive with fossil fuel based energy sources on a dollar per watt basis. Even though technology for solar cells has enabled increase in efficiency and costs have been minimized, the quest for newer materials and architectures is driving research efforts worldwide.[1-4] There are few reports on TiO_2 nanostructures made of rutile as contrasted with anatase for photovoltaic applications due to the inferior electron mobility in rutile.[5-7] However rutile possesses certain desired characteristics for improving performance in light harvesting devices such as a lower electron affinity than anatase enabling easier electron injection and a higher refractive index enabling stronger scattering and confinement of light.[8, 9] CdTe exhibits a near-optimal electronic bandgap around 1.4 eV at 300K,[10] and also has a high optical absorption coefficient.[10-13] Consequently, CdTe solar cell efficiencies have reached values as high as 21 % and this technology has been commercialized by First Solar Inc. and others.[14] It is important to note that commercial solar cells based on *p*-type CdTe absorbers use *n*-type CdS as the window layer, and employ vacuum deposition to form thin films of both CdS and CdTe. Solution processing is potentially much more inexpensive than vacuum deposition and also capable of higher through-put but the optoelectronic quality of solution-based CdTe films is much more variable. Therefore the fabrication and testing of alternative solar cell configurations employing solution-grown CdTe remain a subject of ongoing research.

Prior reports of TiO_2/CdTe solar cells include: *n*-type disordered porous anatase TiO_2 coated with 150-250 nm of *p*-type absorber CdTe layer that exhibited 2% efficiency;[15] core-shell structure of anatase phase TiO_2 nantubes coated with electrodeposited CdTe with 0.1% efficiency;[16] and sputtered CdTe/TiO_2 nanowires heterojunction core–shell solar cell with an efficiency of 0.12%;[17] While we report a higher efficiency than similar FTO/TiO_2/CdTe solar cells, this is the first report of a solar cell architecture, which is comprised of hydrothermally formed vertically oriented *n*–type rutile TiO_2 nanowires grown on FTO glass and has a top layer of electrodeposited *p*–type CdTe.

2. EXPERIMENTAL DETAILS

TiO_2 nanowires were grown hydrothermally on FTO (2.5 x 1 cm) substrates, details of which are given elsewhere.[9] Vertically oriented, small diameter RNWAs were grown using a solution containing 5 ml of de-ionized (DI) water, 2.5 ml hydrochloric acid, 2.5 ml acetic acid and 0.2 ml titanium butoxide, loaded into a Parr acid digestion vessel and subjected to 180 ^{0}C for 4 hours. CdTe was electrodeposited on FTO/TiO_2 substrate by a two-electrode electrodeposition method in this study in a non-aqueous electrolyte prepared by dissolving cadmium sulfate (0.5 M) and tellurium dioxide (0.02 M) in ethylene glycol, and using a platinum anode at a pH of 1.5. The electrolyte was maintained at 140 °C during the electrodeposition process, and the voltage was maintained at 3 V. This was followed by $CdCl_2$ treatment, which consisted of 5 seconds of immersion of the as-electrodeposited samples in saturated $CdCl_2$/methanol solution. Upon removal from the $CdCl_2$/methanol solution, heat treatment was applied to the CdTe deposited RNWAs at 400 °C. Solar cells were fabricated by depositing 10 nm Cu and 40 nm Au contacts by thermal evaporation through a shadow mask, in order to form contact electrodes. Structural characterization was carried out by means of X-ray diffraction (XRD) while morphology was studied using field emission scanning electron microscopy (FESEM). Transmission electron microscopy (TEM) was performed at an acceleration voltage of 200 kV. Optical properties were measured by ultraviolet-visible (UV-Vis) spectroscopy and photoluminescence (PL) spectroscopy. The resistivity and mobility of the films were examined using a four point probe and a Hall effect measurement system. Finally the solar cell performance, i.e. I-V characteristics, of the TiO_2/CdTe device was tested by a semiconductor parameter analyzer using illumination from a class A solar simulator (AM 1.5G) with an output light intensity of 100 mW/cm^2 (1 sun). The illumination contact area for the device was 0.031 cm^2.

3. RESULTS AND DISCUSSION

Cross-section and top-view of the RNWA/CdTe structure are shown in Fig. 1 (a) and (b), respectively. Fig. 1 (a) shows a uniform CdTe layer of thickness ~150 to 200 nm at the top and also within the RNWAs. Fig. 1 (b) shows that the length of RNWAs is about 1 µm. The inset in Fig. 1 (b) is the top-view FESEM image of the RNWAs without deposited CdTe. Fig. 1 (c) is the TEM

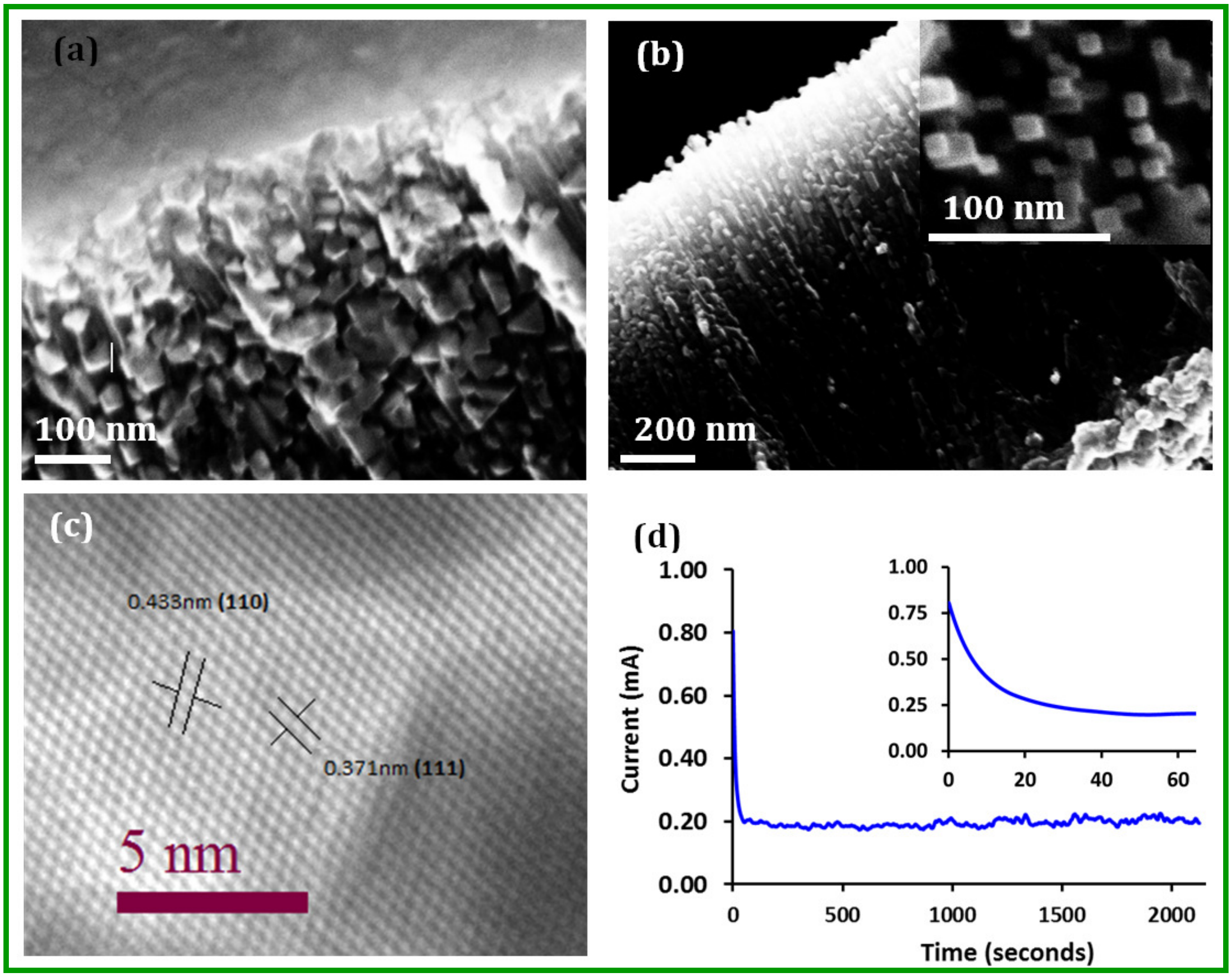

Figure 1. (a) and (b) are the cross-section FESEM images (c) is the TEM lattice image and (d) is the current transient of the CdTe electrodeposition process of the CdTe coated TiO_2 RNWAs.

lattice spacing image, which shows lattice spacing that are typical to (110) plane of rutile TiO_2 and (111) plane of CdTe. Fig. 1 (d) is the current transient plot for electrodeposition of CdTe, which follows an exponential decay profile in the first minute (as shown in the inset) and thereafter follows a rather flat pattern. Fig. 2 (c) shows the XRD pattern for electrodeposited CdTe on the rutile TiO_2 nanowires layer. The X-ray diffractogram demonstrates the presence of CdTe as well as rutile phase TiO_2. The observed peaks, indexed in Fig. 2 (c), are consistent with TEM spacing (Fig. 1 (c)), and are associated with FTO, TiO_2 and CdTe.[18]

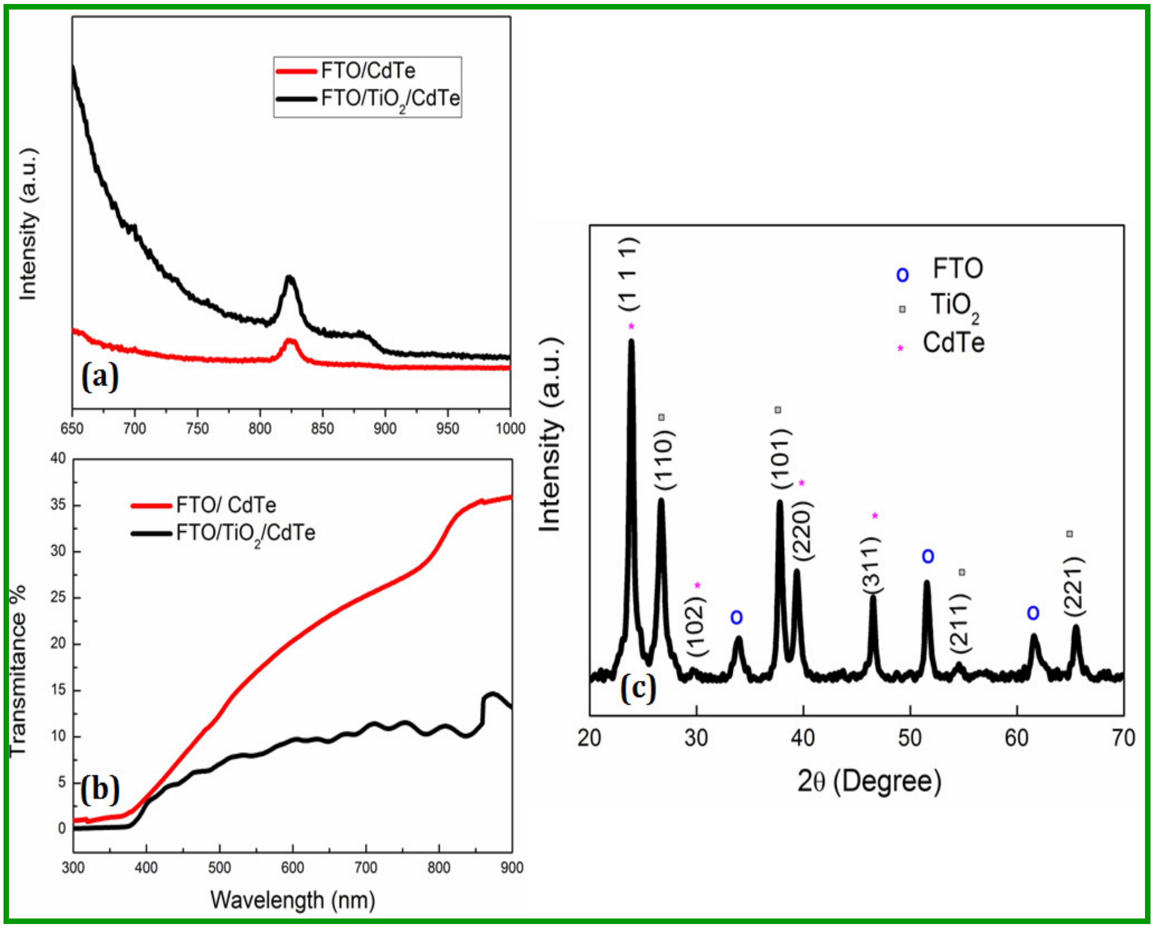

Figure 2. (a) PL spectra and (b) UV-Vis spectra for FTO/CdTe and FTO/TiO$_2$/CdTe; (c) XRD patterns for FTO/TiO$_2$/CdTe.

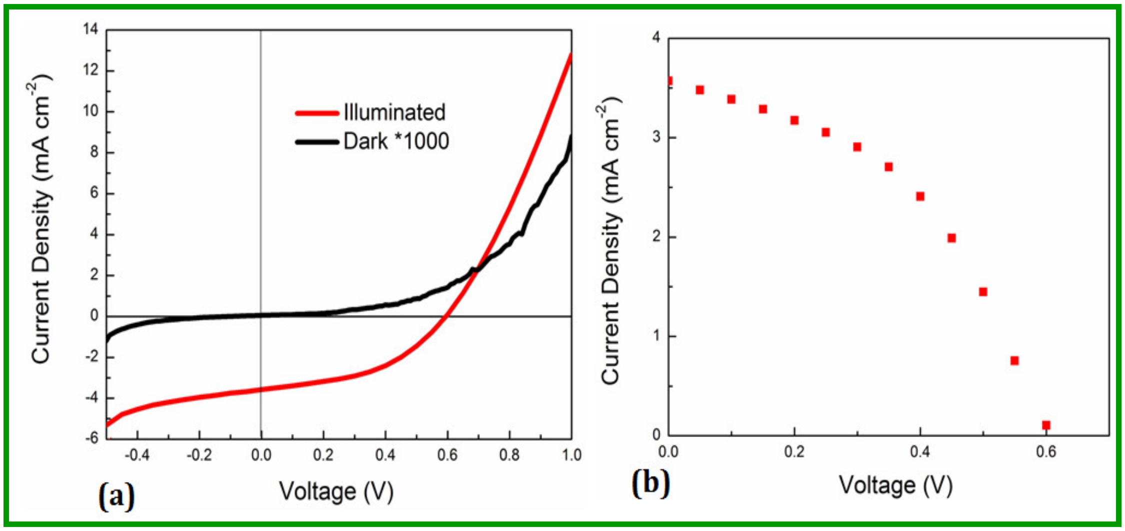

Figure 3. (a) J–V characteristics of the TiO$_2$/CdTe solar cell and (b) Photocurrent density vs potential for extraction of the maximum power conversion efficiency.

The UV-Vis transmission spectra for FTO/CdTe and FTO/TiO_2/CdTe structures are given in Fig. 2 (b). The FTO/CdTe structure is far more transparent than FTO/RNWA/CdTe in the visible wavelength range. The observed results demonstrates the light-trapping role of TiO_2 nanowires in the structure.[19] As-grown CdTe films on FTO were found to be *n*-type initially with an electron mobility of ~14 $cm^2V^{-1}s^{-1}$, and became *p*-type following $CdCl_2$ treatment and annealing. A narrow full-width-at-half maximum (FWHM) in the PL spectra in Figure 2 (a) is indicative of the narrow size distribution of CdTe crystallites. The observed peak at ~825 nm corresponds to the CdTe bandgap of 1.5 eV, which is close to the optimum value for photovoltaic performance (1.4 eV).[20]

The current−voltage characteristics of the solar cell, both in dark and under illumination, are provided in Fig. 3. The cell was illuminated from the FTO side. The existence of a *p-n* junction for TiO_2/CdTe can be observed from Fig 3 (a). The photovoltaic behavior of device is evident from the rectification of current, and also from the comparison of the I-V curve of the dark and illuminated conditions, as illustrated in Fig. 3 (a). The open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) and power conversion efficiency (EF) were extracted to be 0.6 V, 3.57 $mA.cm^{-2}$, 44% and 0.96% respectively. The series resistance (R_s) and shunt resistance (R_{sh}) values, determined from the slope of I-V curve at V_{oc} and J_{sc} were found to be 58 Ωcm and 548 Ωcm respectively. R_s is due to both bulk material and contacts of the device, where R_{sh} is due to leakage in the cell, which may be due to presence of surface and bulk defects.

4. CONCLUSIONS

This is the first report of solar cell consisting of a heterojunction of electrodeposited *p*-type CdTe with *n*-type rutile TiO_2 nanowires arrays. Enhanced light absorption was observed in the FTO/TiO_2 nanowires/CdTe configuration as compared to FTO/CdTe. Low cost and simplicity of the solution based route employed in the synthesis of the component *n*-type and *p*-type layers of the solar cell, imply the availability of schemes for further improvement of solar cell performance made out of these materials.

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GRAPHICAL ABSTRACT

Radial heterojunction solar cell was formed by n-type rutile TiO_2 nanowire arrays grown on glass and infiltrated by p-type CdTe. Enhanced light absorption, low-cost and simplicity of fabrication process, are hallmarks of the materials and processing methodologies employed for fabrication of the solar cell. The solar cell exhibits promising photovoltaic performance with potential further improvement.