CdTe Schottky diodes from colloidal nanocrystals

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(Received 17 December 2009; accepted 2 May 2010; published online 15 June 2010)

We have fabricated ultrathin photovoltaic cadmium telluride (CdTe) film solar cells from colloidal nanorod solutions with a power conversion efficiency of 5.0% and internal quantum efficiency approaching unity near the band edge. Sintering of the CdTe nanorod films was necessary to facilitate grain growth and enhanced optical absorption. By analyzing electrode dependence, capacitance-voltage, temperature dependence, and current-voltage characteristics, the device performance is shown to be dominated by the formation of a p-CdTe/Al Schottky junction. The reduced need for material and cheaper processing make this an attractive technology for solar power generation. © 2010 American Institute of Physics. [doi:10.1063/1.3440384]

Recently, ultrathin (<500 nm) photovoltaic films have been fabricated from layers of sintered1,2 and unsintered3,4 nanocrystals. Colloidal nanocrystals provide a method of depositing cadmium telluride (CdTe) from solution and enable the study of ultrathin CdTe films. Because nanocrystals have lowered melting points, 5 they may also provide a means to lowered processing temperatures. Producing reasonable efficiencies with a few hundred nanometers CdTe simultaneously reduces cadmium and tellurium materials costs by a factor of 10 or more6 and simplifies the CdTe deposition procedure.

While previous reports have shown power efficiencies >2% in spun cast nanoparticle p-type CdTe heterojunctions, with cadmium selenide (CdSe) or cadmium sulfide (CdS) serving as the n-type material, Schottky devices with comparable efficiencies have not been reported heretofore. The lack of efficient Schottky devices from CdTe colloidal thin films has suggested that CdTe nanoparticles devices operate primarily as donor:acceptor heterojunctions that require a p-type and an n-type nanoparticle layer. Here, we report on Schottky solar cells with 5% power efficiency fabricated from a single layer of p-type CdTe colloidal nanoparticles, opening up the possibility of high efficiency ultrathin solar cells that do not require a window (i.e., n-type) layer.

The nanoparticle thin films are fabricated by spin-casting CdTe nanorods (approximately 5 x 2 nm2) onto clean indium-tin-oxide (ITO) coated substrates. The resulting film is coated with cadmium chloride (CdCl2), sintered at 400 °C, and then rinsed in hot water to remove any remaining CdCl2. Aluminum contacts are then evaporated onto the films with no attempt to further improve the CdTe/metal interface. Under illumination, electrons are excited and collected at the aluminum contact. Holes are collected through the ITO. As others1,2,7,9 have seen, sintering with CdCl2 vapors resulted in grain growth (see inset in Fig. 1). Grain growth would remove energetic barriers at grain boundaries,10 improving carrier transport. The final grain size, observed by scanning electron microscope (SEM), is about 50 to 100 nm, approximately an order smaller than those seen with other vacuum deposition technologies, but this is unsurprising as those technologies deposit CdTe with micron-scale grains before CdCl2 treatment.

The CdCl2 treatment also modifies the optical absorption in two ways, as shown in Fig. 1. The absorption redshifts due to loss of quantum confinement and an overall increase in optical absorption occurs. Many other studies note increased absorption near the band edge,7,9 but the change in the absorption properties we observe is likely to be caused by the shift from weak quantum confinement of the unsintered films to the bulklike behavior of the sintered films. Our photothermal deflection spectroscopy measurements reveal both a large change in band gap structure, consistent with this shift from quantum confined to bulk behavior, and a substantial increase in trap distribution with sintering. CdTe films used in traditional CdS/CdTe solar cells are typically over a micron thick, which is sufficient to absorb all light in its band-width, but full absorption does not occur on the scale of the minority carrier diffusion length.11 Electrons absorbed far from the CdS/CdTe interface are more likely to recombine in p-type CdTe than those collected close to the interface. Increasing the optical density of CdTe would increase collection of these carriers by reducing the distance they must travel, resulting in improved device efficiency across the visible spectrum with slightly more improvement in the red. This sort of EQE enhancement after exposure to CdCl2 has been observed by Ringel et al.12

CdTe can be doped either n-type or p-type,13 but the P-containing ligand (i.e., TOPO) present on the nanoparticle...
The optimized devices we have fabricated with p-CdTe/Al as the active junction are highly reproducible when the spun cast colloidal CdTe nanorod films exhibit nanoscale smoothness and when the sintering conditions are optimized. However, spinning rougher films from aggregated colloidal nanoparticle solutions and over-treating the CdTe colloidal thin films in the sintering step results in shunting. Thermoreflectance images, of over-treated films, reveal no significant temperature variations due to such defects, so this shunting is likely not due to pinholes. We believe a conducting layer of cadmium-rich material along grain boundaries is responsible for the shunting; nanocrystal surfaces tend to be cadmium-rich, and grain growth will drive defects to grain boundaries.

As shown in Fig. 2(b), capacitance-voltage (C-V) measurements taken in the dark suggest a Schottky barrier. As the reverse bias voltage extends the depletion region, capacitance drops, described by $C = \frac{q}{\epsilon e_{0} N_d} \frac{1}{V-(kT/q)^{1/2}}$, where $N_d$ is the donor density, $V$ is the voltage, $T$ is the temperature, and $\epsilon$ is the dielectric constant. Deep traps, surface states, and non-Ohmic contacts make C-V profiling quantitatively challenging on CdTe, but our measured profile does match the expected linear dependence of $C^{-2}$ on $V$ in reverse bias and yields quantitatively reasonable numbers around $7 \times 10^{16}$ cm$^{-3}$ for $N_d$. This C-V profile also places the rectifying barrier at the back contact, assuming p-type CdTe. Analysis of the temperature-dependence of the J-V curves support the Schottky analysis, with the best fits yielding an average CdTe/Al barrier height of $\sim 1$ eV, assuming a Gaussian distribution of barrier heights.

Figure 3(a) shows the self-consistent external quantum efficiency at short-circuit, and the optical absorption calculated for this thickness of CdTe using Beer–Lambert law. Near the band edge the internal quantum efficiency ap
proaches unity. Since the optical density is higher at blue wavelengths than red, blue light will be absorbed closer to the ITO than red light. External quantum efficiency measurements over a variety of thicknesses reveal that the current under blue illumination decreases as devices become thicker [See Fig. 3(b)]. This result confirms that the p-CdTe/Al contact is responsible for the photocurrent; minority carriers excited far from the rectifying electrode will be more likely to recombine.

To summarize, we have fabricated Schottky photovoltaic devices from spun-cast colloidal CdTe nanocrystals with over 5% power efficiency. These films are only 360 nm thick but have short-circuit current densities comparable with much thicker CdTe films. Compared to traditional CdTe photovoltaics, they also perform better in the blue-portions of the solar spectrum due to the lack of absorption from the window (CdS) layer. Further improvements to the contacts and sintering treatment could substantially increase \( V_{oc} \) and fill factor, producing ultrathin devices with competitive power efficiencies.

We would like to thank the Ali Shakouri group for providing thermoreflectance images and Anna Bezryadina for sharing her photothermal deflection spectroscopy results. We also thank Solexant for materials and the UC Discovery program for funding. Portions of this work were performed at the Molecular Foundry, Lawrence Berkeley National Laboratory, which is supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE AC02-05CH11231.

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23Over 20 substrates were fabricated with six devices per substrate, or over 120 devices in total. Over 24 devices were fabricated with power efficiencies within 10% (i.e., 4.5% to 5.5%) of the optimized results reported here. High reproducibility (i.e., over 80% of the devices repeated with less than 10% variation) was observed for devices consisting of similar thickness, nanoscale film smoothness, proper surface preparation, and optimized sintering conditions. Devices that were not sintered all worked but had very low \( J_{SC} \). Devices that were over-sintered or fabricated from aggregated nanoparticle solutions were almost always shunted. Approximately 200 nm was the minimum thickness to form nonsunted devices.