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CdTe Schottky diodes from colloidal nanocrystals

J. D. Olson, Y. W. Rodriguez, L. D. Yang, G. B. Alers, and S. A. Carter^{a)}
Department of Physics, University of California, Santa Cruz, California 95064, USA

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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 sintered^{1,2} and unsintered^{3,4} 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 $5 \times 2 \text{ nm}^2$) onto clean indium-tin-oxide (ITO) coated substrates. The resulting film is coated with cadmium chloride (CdCl_2), sintered at 400 °C, and then rinsed in hot water to remove any remaining CdCl_2 . 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 others^{1,2,7-9} have seen, sintering with CdCl_2 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 CdCl_2 treatment.⁸

The CdCl_2 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 bandwidth, 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 CdCl_2 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

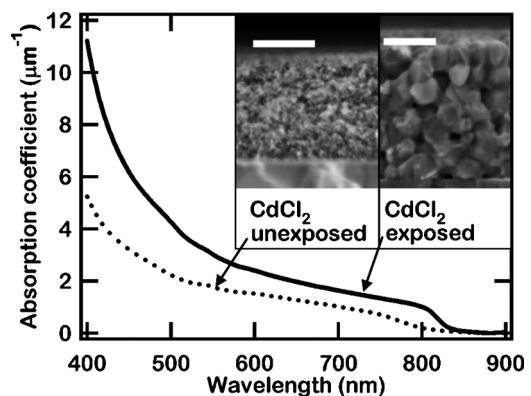


FIG. 1. Optical absorption measurements before (broken line) and after (solid line) exposure to CdCl_2 vapors at 400 °C. Optical absorption improves with CdCl_2 exposure. The inset displays SEM images of films before and after CdCl_2 treatment. The white scale bars represent 200 nm.

^{a)}Electronic mail: sacarter@ucsc.edu.

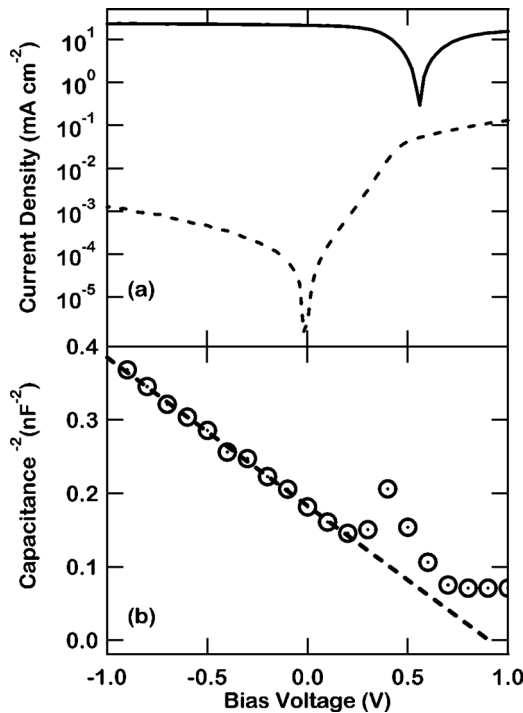


FIG. 2. (a) Light and dark current-voltage and (b) dark capacitance-voltage curves for optimized CdTe Schottky devices fabricated from spun-cast colloidal nanorods. Light curves were measured under simulated AM1.5G 100 mW cm^{-2} conditions. Photovoltaic parameters are as follows: J_{SC} 21.6 mA cm^{-2} , V_{OC} 540 mV , fill-factor 45.5% , PCE 5.3% . Adjusted for spectral mismatch, J_{SC} is 20.4 mA cm^{-2} , and PCE is 5.0% . C-V characteristics, taken at 50 Hz , are typical for a Schottky diode and suggest a carrier concentration around $7 \times 10^{16} \text{ cm}^{-3}$.

surface prior to ligand exchange suggest that our films are p-type. Studies of ligand exchange^{14–17} consistently reveal exchange efficiencies of 90% or less. Roughly one in five ions is a surface ion for a spherical 6 nm diameter nanocrystal.¹⁸ If we assume only 30% ligand coverage of surface ions as estimated by Kuno *et al.*,¹⁶ the sintered nanocrystal film would have a phosphorous content on the order of 10^{20} cm^{-3} . Although phosphorous is an effective p-dopant for CdTe, high concentrations of phosphorous are compensated leading to lower doping concentrations.¹⁹ X-ray fluorescence measurements of our films revealed an obvious phosphorous peak. Based on this analysis and our C-V data (presented below), we assume that our CdTe films are p-type.

Current-voltage (I-V) characteristics for a champion device are shown in Fig. 2(a). I-V characteristics were measured under simulated AM1.5G 100 mW cm^{-2} conditions. Our resulting power efficiency is 5.3% , with 5.0% obtained after correcting for spectral mismatch. This CdTe device had a thickness of 360 nm —about 10% of the material used in more established CdTe deposition techniques. This thickness is on the order of the minority carrier diffusion length,¹¹ allowing for a high probability of photon collection and transport of minority carriers across the full device thickness.

These I-V curves displayed two characteristics common among the films we studied: current roll-over above the open-circuit voltage (V_{OC}) and a dark current several orders of magnitude lower than the light current. The extremely low dark currents, similar to those seen by Gur *et al.*,¹ can be explained by a lack of charge carriers and/or poor electrical transport in the dark. Chakrabarti *et al.*¹⁰ showed that tunneling barriers at grain boundaries are higher and broader in the

dark than in the light impeding current. An alternative explanation for the low dark current is that back-to-back Schottky junctions are formed, namely, ITO/p-CdTe and p-CdTe/Al,²⁰ and that one of the junctions breaks down upon exposure to light. In support of this analysis, we were also able to make working Schottky devices consisting of ITO/p-CdTe/Au where the Schottky contact is ITO/p-CdTe; however, open circuit voltage were lower ($\sim 0.2 \text{ V}$) and power efficiencies never exceeded 2% for this devices structure. The interface of ITO with semiconductors is known to be strongly impacted by the exposure to elevated temperatures, such as the $400 \text{ }^\circ\text{C}$ sintering temperatures, due to increased oxygen deficiency and indium diffusion at the interface.²¹ Such a dopant-segregation layer adjacent to a Schottky contact has recently been shown to result in strong band bending, enhanced tunneling current, and effective lowering of the effective Schottky barrier height.²² This reduced barrier could enable the ITO/p-CdTe junction to undergo tunneling-current breakdown upon exposure to light, leaving the p-CdTe/Al junction (formed after the sintering steps) as the working Schottky barrier.

We note that while high efficiency ITO/p-CdTe solar cells have been reported in the literature,²⁰ they were abandoned (in favor of n-CdS/p-CdTe) due to lack of reproducibility over the ITO/p-CdTe interface. We found our devices based on ITO/p-CdTe/Au to be less reproducible also, presumably due to the impact of the sintering step on the ITO. 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;²³ 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,²⁴ 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,²⁵ 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,²⁶ described by $C \sim (\epsilon \epsilon_0 N_d / 2)^{1/2} [V - (kT/q)]^{1/2}$ where N_d is the donor density, V is the voltage, T is the temperature, and ϵ is the dielectric constant. Deep traps, surface states, and non-Ohmic contacts make C-V profiling quantitatively challenging on CdTe,^{27,28} but our measured profile does match the expected linear dependence of C^{-2} on V in reverse bias and yields quantitatively reasonable numbers around $7 \times 10^{16} \text{ cm}^{-3}$ 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 $\sim 1 \text{ eV}$, 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-

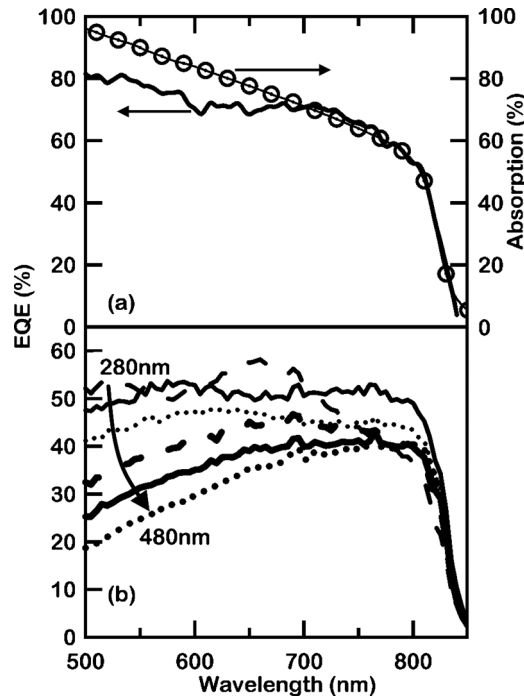


FIG. 3. External quantum efficiency for a champion CdTe Schottky device fabricated from spun-cast colloidal nanorods compared with optical absorption (a) and film thickness (b).

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 photoaction; 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 nanorods 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-portion 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.

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