

# Solution Processing of CdTe Nanocrystals for Thin-film Solar Cells

W. Yoon<sup>1</sup>, E. E. Foos<sup>1</sup>, M. P. Lumb<sup>1,2</sup> and J. G. Tischler<sup>1</sup>

<sup>1</sup>U.S. Naval Research Laboratory, 4555 Overlook Avenue S.W., Washington, DC 20375 United States

<sup>2</sup>School of Engineering and Applied Science, The George Washington University, 725 23<sup>rd</sup> Street NW, Washington, DC 20052 United States

**Abstract** — We describe solution-processed sintered nanocrystal solar cells. As the absorber layer, thin-films of CdTe nanocrystals were deposited using a layer-by-layer spin coating process. For Schottky barrier solar cells (ITO/CdTe/Ca/Al), an efficiency of  $3.0 \pm 0.3\%$  with  $V_{oc} = 0.53 \pm 0.03$  V,  $J_{sc} = 13.2 \pm 0.2$  mA/cm<sup>2</sup>, and FF =  $43.1 \pm 4.2\%$  was measured under AM1.5G conditions. In order to overcome the limitations associated with the Schottky barrier structure, heterojunction solar cells incorporating solution-processed CdSe nanocrystals as an *n*-type layer were fabricated and characterized. Under darkness, heterojunction devices (ITO/CdTe/CdSe/Al) showed an improved current rectification ratio of  $4.53 \times 10^2$  at  $\pm 1$  V in comparison to Schottky barrier solar cells, indicating that a well-defined junction is formed between CdSe and CdTe. Under illumination (AM1.5G), the devices exhibited an average efficiency of  $\sim 2\%$  with  $V_{oc} = 0.50 \pm 0.02$  V.

**Index Terms** — solution, nanocrystal, thin-film, CdTe, heterostructure, photovoltaic,

## I. INTRODUCTION

Thin-films assembled from colloidal inorganic nanocrystals provide an excellent opportunity for the development of low cost, large area and high-throughput solar cell technologies. While the solution synthesis used to isolate these nanocrystals is applicable to a wide variety of II-VI and IV-VI materials [1-3], CdTe is particularly well suited for thin film solar cells due to a high optical absorption coefficient and an optimal bandgap of 1.45 eV that maximizes photovoltaic energy conversion in the visible spectrum [4].

Since the first report by Gur *et al.* [3] on solution-processed inorganic solar cells using colloidal CdTe and CdSe nanorods, the highest efficiencies of  $\sim 5\%$  have been achieved from a Schottky barrier structure based on colloidal CdTe nanorods [5]. More recently, Jasieniak *et al.* exploited CdTe nanocrystal films to fabricate CdTe/ZnO heterojunction solar cells with improved efficiencies of  $\sim 7\%$  [6].

In this work, we focus on thin-film solar cells prepared using CdTe nanocrystals in a layer-by-layer solution process. Using this material as the absorber layer, we fabricate thin-film solar cells and examine several different device architectures designed to maximize efficiency.

## II. EXPERIMENTAL

CdTe and CdSe nanocrystals were synthesized in solution from Cd oleate and Se/trioctylphosphine [6][7],[7]. Following isolation, the material was dispersed in pyridine at 90 °C for 18 hours, precipitated from hexane, and dissolved in 1:1 (v/v) pyridine:1-propanol at an approximate concentration of 30 mg/mL. These solutions were centrifuged to remove any insoluble solid, and then used directly for spin coating.

The film formation is as described in [6]. Briefly, colloidal nanocrystals were spin coated at 800-900 rpm, followed by drying at 150 °C for 2 min. The sample was then immersed in a 60 °C saturated solution of CdCl<sub>2</sub> in MeOH, rinsed two times with iPrOH, blown dry with N<sub>2</sub>, and annealed at 400 °C for 10 sec. All procedures were performed in air. This process was repeated until the desired film thickness had been achieved. The nanocrystal film thicknesses were measured using a MicroXAM interferometric profilometer, and film morphology was characterized using both SEM and optical profilometry.

The samples were then pumped down in vacuum ( $\sim 10^{-7}$  Torr) and completed by the shadowmask evaporation of a Ca (20 nm)/Al (80 nm) electrode for the Schottky barrier solar cells, or 100 nm of Al in the case of the heterojunction cells. The current density–voltage (*J*–*V*) measurements were performed with a semiconductor characterization system (Agilent 4156C) in air without any device encapsulation under the spectral output from a 150 W solar simulator (Newport) using an AM 1.5G filter. The irradiance (100 mW/cm<sup>2</sup>) of the solar simulator was adjusted using a standard Si photodetector (818-SL-L) that had been cross-calibrated by a reference Si cell traceable to the National Renewable Energy Laboratory (NREL). Solar cell device simulation was conducted using Crosslight (CrossLight Software, Inc.)

## III. RESULTS AND DISCUSSION

For as-deposited films of CdTe nanocrystals, the first absorption peak was observed at  $\sim 634$  nm (not shown), indicating the quantum confined electronic structure of the nanocrystals remains intact in the absence of any sintering process at elevated temperature. However, when the CdCl<sub>2</sub>

treated films were annealed at 400 °C, the absorption onset redshifted to ~850 nm (Fig. 1), consistent with bulk CdTe.

The SEM image shown in inset (a) of Fig. 1 is representative of the solution-processed sintered CdTe films using CdCl<sub>2</sub> treatment. Although the absorption spectra of the CdTe nanocrystal films is similar with that of bulk CdTe, the grain size was estimated to be only about ~100 nm. This grain size is significantly smaller than in conventional polycrystalline CdTe layers, where grain sizes are on the order of 1 μm [4]. Optical profilometry revealed smooth and pin-hole free surfaces with no large surface features, as shown in inset (b) of Fig. 1. The root mean square (RMS) roughness of the CdTe surface was determined to be ~3.9 nm.

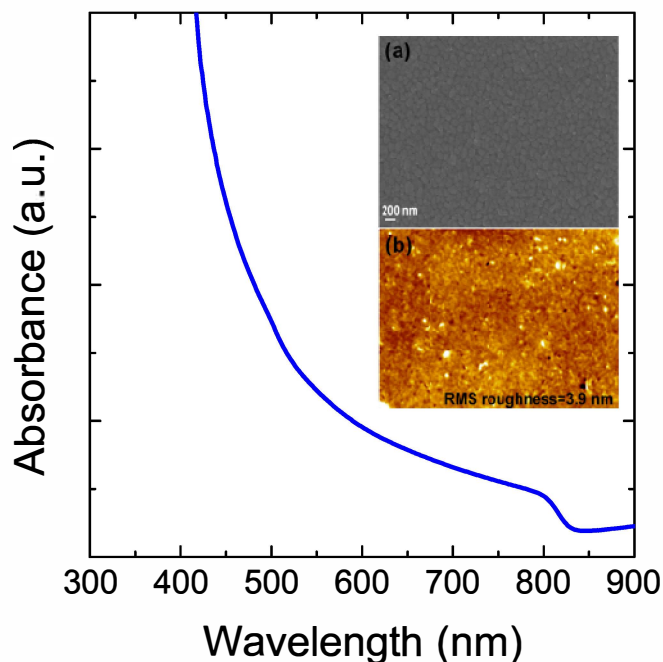


Fig. 1. Absorption spectra of CdTe nanocrystal films (~0.45 μm thick) assembled using a layer-by-layer spin-coating process. Following the solution deposition, films were sintered at 400 °C using a CdCl<sub>2</sub> treatment. The insets show (a) SEM image and (b) optical profilometer image (86.2 μm × 64.1 μm) of the corresponding CdTe nanocrystal films.

Using these layer-by-layer spin coated CdTe nanocrystal films, Schottky barrier solar cells (ITO/CdTe/Ca/Al) were fabricated and characterized. The inset in Fig. 2 shows a schematic of the device structure. The devices showed an efficiency of 3.0±0.3% with  $V_{oc}$  = 0.53±0.03 V,  $J_{sc}$  = 13.2±0.2 mA/cm<sup>2</sup> and FF=43.1±4.2% measured under AM 1.5G filtered spectral illumination at an incident intensity of 100 mW/cm<sup>2</sup> (Fig. 2). In this structure, a Schottky barrier is formed at the junction between the thermally deposited Ca electrode and the *p*-type CdTe nanocrystal

layer (~0.45 μm thick). The depletion width induced by the Schottky metal contact is estimated to be ~0.3 μm as shown in the inset of Fig. 2. The performance of these devices is comparable to solar cells with an identical structure prepared from CdTe nanorods where an uncertified efficiency of ~5% was reported [5].

These colloidal nanocrystal Schottky barrier solar cells, however, suffer from limited open-circuit voltages because of an independent barrier height regardless of the work function of the metal used [2]. The latter is attributed to the Fermi level pinning at the interface between the semiconductor nanocrystal films and the Schottky contact, resulting from a large number of traps associated with defects at the nanocrystal surfaces. These surface traps can also adversely affect the fill factor and the open-circuit voltage by creating additional parasitic current components, related to the interface states between the metal and the nanocrystal absorber layer. In addition, the thickness of the absorber layer in this structure is limited due to the formation of the Schottky junction at the back metal contact, making it difficult to balance light absorption with electron transport.

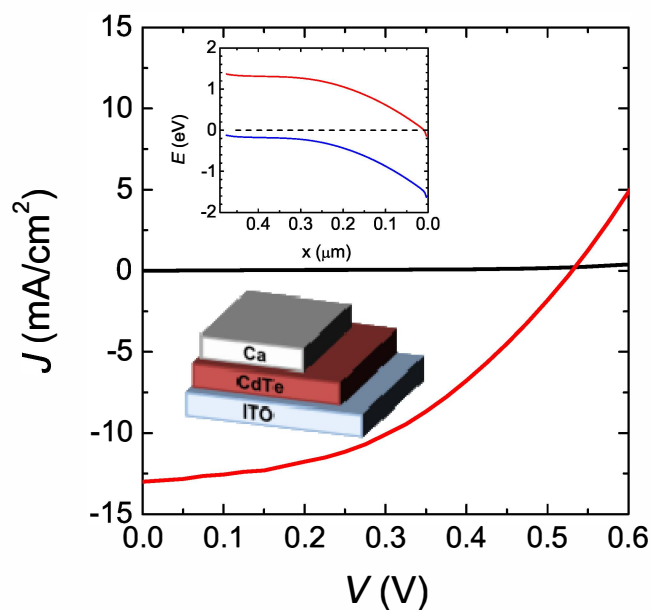


Fig. 2. *J-V* characteristics of CdTe nanocrystal Schottky barrier solar cell (ITO/CdTe/Ca/Al) under darkness (black) and AM 1.5G filtered spectral illumination at an incident intensity of 100 mW/cm<sup>2</sup> (red). The insets show the energy band model under zero bias showing the presence of a Schottky barrier and band bending in the conduction band (red) and valence band (blue) near the interface between the Ca contact and the CdTe nanocrystal film.

To overcome these limitations, heterojunction solar cells using solution-processed CdSe nanocrystals as an *n*-type layer were fabricated and characterized. The surface of

similarly prepared spin-coated CdSe layers was smooth with an RMS roughness of 2.7 nm. Due to the wider bandgap of CdSe in comparison CdTe, a bi-layer stack did not significantly enhance the optical absorption, as shown in Fig. 3a.

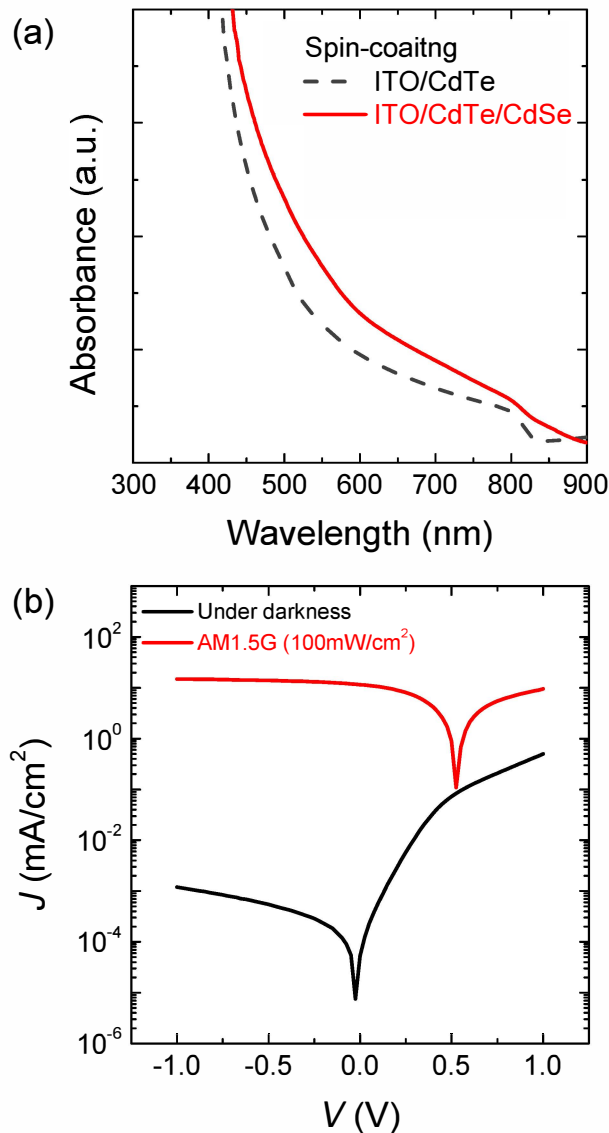


Fig. 3. (a) Absorption spectra of thin-films of CdTe/CdSe (red), where a solution-processed CdSe nanocrystal layer is deposited on the CdTe nanocrystal layer. The dashed line (grey) indicates the absorption spectrum of single layer of CdTe film for comparison. (b)  $J$ - $V$  characteristics of heterojunction solar cells (ITO/CdTe/CdSe/Al) under darkness (black) and AM 1.5G filtered spectral illumination at an incident intensity of 100 mW/cm<sup>2</sup> (red).

$J$ - $V$  characteristics of heterojunction solar cells (ITO/CdTe/ CdSe/Al) under darkness and illumination are

shown in Fig 3b. Under darkness, heterojunction devices showed an improved current rectification ratio of  $4.53 \times 10^2$  at  $\pm 1$  V in comparison to the Schottky barrier solar cells. The improved dark  $J$ - $V$  characteristics indicate that a well-defined junction is formed between the CdSe and the CdTe layers. Under illumination, the device exhibited an efficiency of 2.0% with average values of  $J_{sc}=10.3 \pm 1.1$  mA/cm<sup>2</sup>,  $V_{oc}=0.50 \pm 0.02$  V, and  $FF=31.7 \pm 3.1\%$ . The decreased FF are attributed to the increased series resistance resulting from the thick CdSe layer ( $\sim 0.35$   $\mu$ m).

#### IV. CONCLUSIONS

Both Schottky and heterojunction thin-film solar cell structures were fabricated using the layer-by-layer solution processing of CdTe nanocrystals. Smooth and pin-hole free CdTe layers were obtained in this approach by combining chemical and thermal treatment. Schottky barrier solar cells based on a single layer of CdTe yield efficiencies of  $\sim 3\%$  comparable to literature values. In addition, CdTe/CdSe heterojunction structures were prepared by spin-coating colloidal CdSe nanocrystals atop the CdTe layer. The improved dark  $J$ - $V$  characteristics suggest the formation of a well-defined junction between the CdSe and the CdTe layers. Under illumination, this latter device exhibits an average efficiency of  $\sim 2\%$ , which is limited by the series resistance of the thick CdSe layer.

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