

# Influence of thermal treatment temperatures on CdTe nanocrystal films and photoelectric properties of ITO/CdTe/Al\*

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**Abstract:** The influence of sintering temperatures on solution-processed cadmium telluride (CdTe) nanocrystal films is studied in order to maximize the performance of CdTe/Al Schottky nanocrystal solar cells. The best overall performance of 2.67% efficiency at air mass 1.5 was achieved from devices with CdTe films sintered at 350 °C. X-ray diffraction, scanning electron microscopy and UV-vis absorption measurements show that the CdTe nanocrystal grains began to grow remarkably well when sintering temperatures increased to 350 °C. By analyzing the current–voltage characteristics, we find that the short-circuit current densities of devices increase with sintering temperatures ranging from 200 to 400 °C, but, the over-sintered (450 °C) treatment induces the shunting of devices.

**Key words:** solar cells; nanocrystal; sintering temperature

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## 1. Introduction

The development of cheap, efficient, and economically viable solar cells is an important challenge for renewable and clean energy solutions. Solution-processed photovoltaics based on colloidal semiconductor nanocrystals offer the possibility of achieving this goal. Semiconductor nanocrystals exhibit many unique properties, which have implications for solar cells. Quantum confined semiconductor nanocrystals exhibiting multi-exciton generation are being explored for next generation high efficiency solar cells<sup>[1]</sup>. In addition, semiconductor nanocrystals are used as precursors to yield dense bulk semiconductor films via an ultra-low-cost fabrication route to solar cells by taking the advantage of solution-based processes<sup>[2]</sup>. Recently, many photovoltaic devices have been fabricated from sintered films<sup>[3–5]</sup> or unsintered nanocrystal arrays<sup>[6–10]</sup>.

CdTe has become a candidate for solar cells since the 1950s due to its direct band gap of 1.5 eV<sup>[11,12]</sup>. Gur and co-workers were among the first to exploit the advantage of semiconductor nanocrystal solar cells by employing additional chemical and thermal treatments<sup>[2]</sup>. They fabricated cadmium telluride/cadmium selenide (CdTe/CdSe) and sintered inorganic solar cells from colloidal CdTe and CdSe nanorods with power conversion efficiencies as high as 2.9%. And then, Olson *et al.* reported Schottky solar cells with a power conversion efficiency of 5%, fabricated from a single layer of p-type CdTe colloidal nanocrystals<sup>[3]</sup>. More recently, Jasieniak *et al.* fabricated cadmium telluride/zinc oxide (CdTe/ZnO) thin-film solar cells with an efficiency of 6.9% from inorganic nanocrystal inks by adopting a simple layer-by-layer approach<sup>[13]</sup>. An important approach toward realizing significant improvements to

this performance is to enhance the carrier transport efficiency. The CdCl<sub>2</sub> solution treatment on CdTe films is routinely used to enhance the electronic properties of CdTe, and reports are available on CdCl<sub>2</sub>-treated CdTe films formed by closed space sublimation<sup>[14]</sup>, chemical bath deposition<sup>[15]</sup>, close-space vapor transport<sup>[16]</sup>, electro deposition<sup>[17]</sup> and thermal evaporation<sup>[18]</sup>.

However, little work has been done on the influence of sintering treatments with the presence of CdCl<sub>2</sub> on solution-processed CdTe nanocrystal films and solar cells. Hence an attempt has been made in this paper to study the structural, surface morphology and optical properties of CdTe films sintered at different temperatures in the presence of CdCl<sub>2</sub>, and research the influences on the current–voltage characteristics of CdTe/Al Schottky nanocrystal solar cells.

## 2. Experiment

CdTe nanocrystals were prepared according to previous procedures as described in Ref. [13], and Figure 1 shows the transmission electron microscope (TEM) image of the CdTe synthesised. Before fabricating the devices, a CdTe nanocrystal solution was filtered to create ultrathin, flexible films. We fabricated the devices with the structure of ITO/CdTe/Al and the processes were as follows.

### 2.1. Fabrication of as-cast devices

The solution of CdTe nanocrystals was spun-coat onto ITO-coated glass substrates at 1000 rpm (revolutions per minute) for 50 s, then the substrate was placed on a hot plate at 150 °C for 2 min. This process was repeated a number of times until the desired thickness was achieved. The solar cells were

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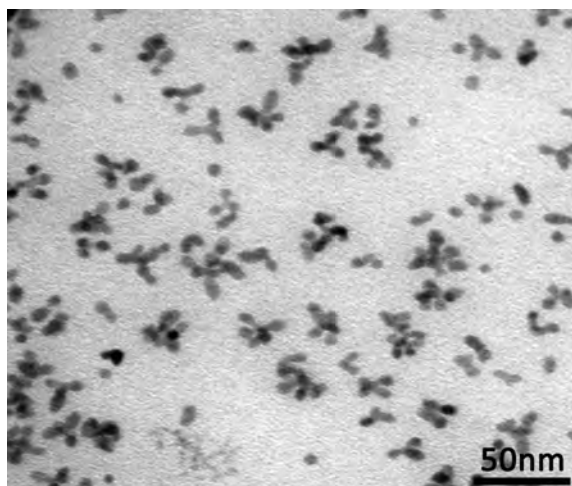


Fig. 1. TEM image of CdTe nanocrystals.

then produced by thermally depositing 120 nm of aluminum cathode on top.

## 2.2. Fabrication of sintered devices with CdCl<sub>2</sub>

The fabrication process of the devices is similar to that of the as-cast devices, except that the substrate was immediately dipped into a 60 °C saturated CdCl<sub>2</sub> methanol solution after each annealing, rinsed gently with 1-propanol, dried under a nitrogen stream, and finally the CdTe nanocrystal films were sintered by placing the substrates onto a hot plate at different temperatures (200, 300, 350, 400, 450 °C).

## 2.3. Measurement and characterization

The surface morphologies of CdTe films were investigated by SEM using a JSM 7401 electron microscope and the UV-vis absorption spectra were obtained on a Shimadzu-UV 3101 spectrophotometer. The crystallographic phase was monitored by a Philips PZ 3710 X-ray diffractometer using monochromatic CuK $\alpha_1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in a scanning angle range of 10°–80° ( $2\theta$ ). The current–voltage characteristics of the devices were measured by a Keithley 2410 sourcemeter controlled by a computer at air mass 1.5. All the measurements were carried out under ambient conditions at room temperature.

## 3. Results and discussion

The XRD patterns of CdTe nanocrystal films with different treatments are shown in Fig. 2. It is clearly seen that the three diffraction peaks correspond to (111), (220), and (311) planes, which can be indexed to cubic zincblende CdTe (JCPDS Card No. 65-1082, lattice parameter  $a = 6.481 \text{ \AA}$ ). This demonstrates that the lattice structure of CdTe nanocrystals did not change with sintering in the presence of CdCl<sub>2</sub>, which is different from results reported previously<sup>[19, 20]</sup>. CdTe films of as-cast sintered at low temperatures (200, 300 °C) have a similar XRD pattern, and the widened diffraction lines of these samples demonstrate the nano-scale size of their particles as shown in Fig. 1. However, when the sintering temperature increased to

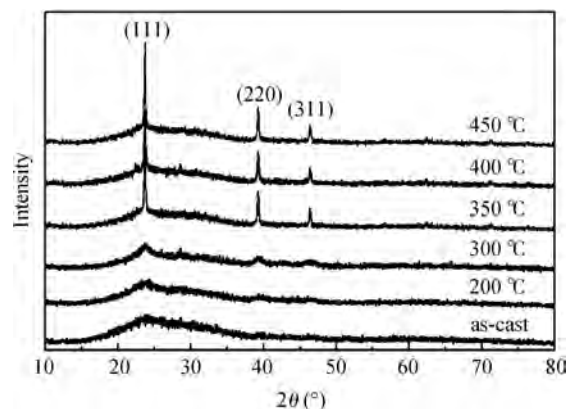


Fig. 2. XRD patterns of CdTe nanocrystal films.

350 °C or higher, the diffraction lines of the CdTe films became intense, which indicates the CdTe particle's higher crystallinity and bigger size. The crystallite sizes ( $D$ ) were calculated using the Scherrer formula from the full-width at half-maximum (FWHM) ( $w$ ) of the XRD peaks<sup>[21, 22]</sup>:

$$D = \frac{0.94\lambda}{w \cos \theta}, \quad (1)$$

where  $\lambda$  is wavelength of the X-ray and  $\theta$  is Bragg angle. Average grain sizes for the CdTe films of as-cast, sintered at low temperatures (200, 300 °C) were about 4 nm, 5 nm and 7 nm; for the high temperatures (350, 400, 450 °C), those were estimated to be 35 nm, 45 nm and 50 nm, respectively.

The SEM images of the as-obtained CdTe nanocrystal films are shown in Fig. 3. It can be seen clearly that the films sintered at low temperatures (Figs. 3(b) and 3(c)) have a similar surface morphology to the as-cast film (Fig. 3(a)). From their SEM images we cannot find clear profiles of the CdTe nanocrystals because their sizes are below the SEM detection limit, which is consistent with the results of XRD. Samples sintered at high temperatures (Figs. 3(d)–3(f)) exhibit remarkable grain growth. The reason of this remarkable growth is unclear. We guess that it may be due to the ripening of the CdTe nanocrystals when the sintering temperature is increased to 350 °C, as the melting temperature of the nanocrystals drops as their size decreases<sup>[23]</sup>. While the higher temperature leads to a bigger nanocrystal melt, this promotes nanocrystal growth further. Also, the increase of nanocrystal size with sintering temperature is consistent with the results of XRD.

Figure 4 shows the absorption spectra of the CdTe nanocrystal films. The arrow displays a transition from a quantum-confined regime to bulk. When the sintering temperatures range from 350 to 450 °C, the absorption peaks of the films are located at a similar wavelength of 820 nm. This demonstrates that these films exhibit bulk properties, as expected by the results of XRD and SEM. The shoulder of the nanocrystals UV-vis spectra is caused by the first excitonic transition. As the energy levels of the excitonic transitions are a function of particle size, the position of these shoulders can be used to evaluate the particle sizes. The shoulders occur at 680 nm, 700 nm and 740 nm for films of as-cast, sintered at 200 °C and sintered at 300 °C, respectively. Employing a tight-binding calculation, this corresponds to average particle sizes

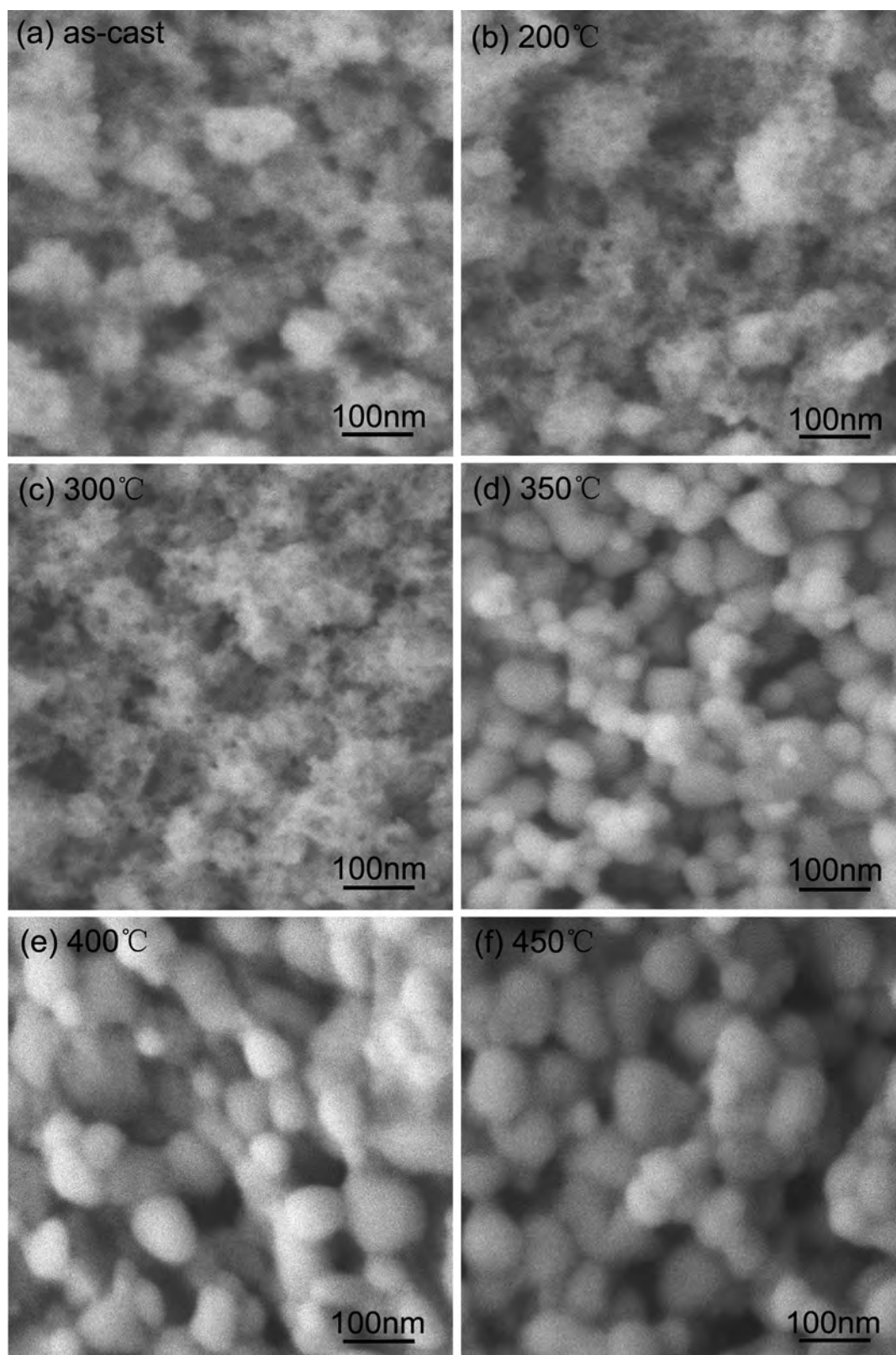


Fig. 3. SEM images of the CdTe nanocrystal films.

of 3.9 nm, 4.8 nm and 5.7 nm, according to the data obtained by Lippens<sup>[24]</sup>. These values are near the diameters obtained from the XRD data.

The current–voltage characteristics for CdTe/Al Schottky solar cells are shown in Fig. 5, and the corresponding para-

eters are listed in Table 1. The device sintered at 350 °C exhibits its best performance with a power conversion efficiency of 2.67%, which is 8 times higher than the devices as-cast. Notably, the devices sintered at high temperatures showed an apparent improvement in total power conversion efficiencies ( $\eta$ )

Table 1. Performance characteristics of devices.

Devices	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{OC}$ (V)	FF	$\eta$ (%)
As-cast	1.72	0.51	0.33	0.29
200 °C	2.62	0.49	0.29	0.37
300 °C	3.57	0.50	0.31	0.55
350 °C	17.55	0.49	0.31	2.67
400 °C	19.86	0.45	0.28	2.50
450 °C	0	0	0	0

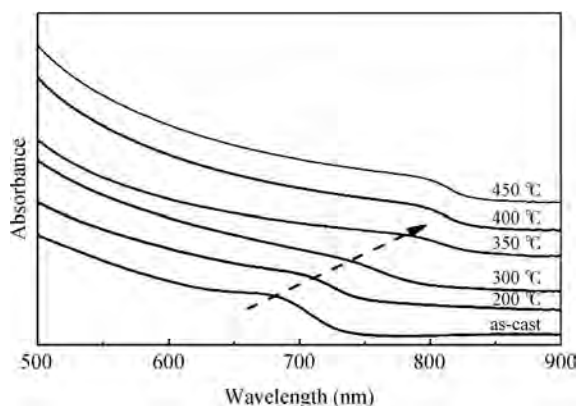


Fig. 4. UV-vis absorption spectra of the CdTe nanocrystal films.

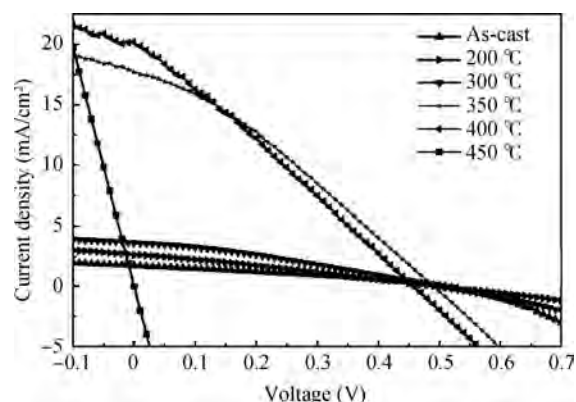


Fig. 5. Current–voltage curves for devices of ITO/CdTe/Al.

compared to the devices as-cast and sintered at low temperatures. While the open-circuit voltages ( $V_{OC}$ ) varied slightly, the short-circuit current density ( $J_{sc}$ ) of devices increased from 2.62 to 19.86 mA/cm<sup>2</sup> as sintering temperatures increased from 200 to 400 °C. This can be attributed to a good performance of electron transportation for the grain growth as described above. The grain growth removes energetic barriers at boundaries and decreases the time of electrons hopping between nanocrystals, improving electron transport. However, over-treatment (450 °C) in the sintering step results in shunting of the solar cells due to a conducting layer of cadmium-rich material along the grain boundaries, because the nanocrystal surfaces tend to be cadmium-rich<sup>[25]</sup> and the grain growth will drive defects to the grain boundaries.

#### 4. Conclusion

In summary, we have investigated the influence of sintering temperatures on the solution-processed CdTe nanocrystal

films and CdTe/Al Schottky solar cells. The best solar cell is achieved at a sintering temperature of 350 °C, with a power conversion efficiency of 2.67%. We find that with an increase of sintering temperature, the size of the CdTe nanocrystals enlarges while the quantum confinement effect degrades. At a sintering temperature of 350 °C, CdTe nanocrystals begin to grow remarkably well. The short-circuit current densities of the CdTe/Al Schottky nanocrystal solar cells increased with sintering temperatures ranging from 200 to 400 °C, while the open-circuit voltages varied slightly.

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