

## PROGRESS TOWARDS HIGH EFFICIENCY THIN FILM CdTe SOLAR CELLS

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### Summary

This paper describes work investigating high rate cadmium telluride (CdTe) film deposition by close-space vapor transport, leading to 4 cm<sup>2</sup> tin oxide/CdTe solar cells of efficiency greater than 10%. Under a 100 mW cm<sup>-2</sup> air mass 1.5 global spectrum, a cell of efficiency 10.5% had a short-circuit current of 28.1 mA cm<sup>-2</sup>, an open circuit voltage of 0.663 V and a fill factor of 0.563. Our major achievements include (1) the use of completely non-vacuum processing, (2) the fabrication of simple transparent conductive oxide/CdTe cells without need of a CdS window layer, and (3) screen-printed back contacts.

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### 1. Introduction

Cadmium telluride (CdTe) has long been identified as a strong candidate for low-cost thin film photovoltaic application because of its direct band gap and its ability to be doped n and p type, permitting the formation of a variety of junction structures, and because it may be deposited by a variety of techniques ranging from vacuum evaporation and chemical vapor deposition to electrodeposition and screen printing [1].

The objective of this work is to achieve high efficiency CdTe solar cells using low-cost simple high throughput processing. The device configuration selected was a glass superstrate where the light enters through the glass into the cell consisting of three layers, namely a front conductive window layer, a CdTe absorption layer and a back-contact layer. For the front conductive layer, emphasis was placed on the use of a wide band gap transparent conductor such as tin oxide without the need for an intermediate CdS layer.

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Non-vacuum processes, namely atmospheric close-space vapor transport (CSVTV) for the CdTe and screen printing for the back contact, were chosen for their simplicity and ability to be easily scaled to large areas. This paper first presents the results of the individual layer studies and then the results for the different solar cells.

## 2. Background

CSVTV CdTe films for solar cells have been studied by various groups [2 - 6]. Research at Stanford University examined the CdTe CSVTV process and the resultant film properties [2 - 4]. Kodak has concentrated on the development of CdS/CdTe solar cells and modules with special emphasis on low pressure CSVTV in the presence of oxygen [5 - 9]. Notably, Kodak reported  $75 \text{ mW cm}^{-2}$  simulated air mass (AM) 2 efficiencies of 10.5% for  $0.1 \text{ cm}^2$  thin CdS/CdTe cells deposited at about 1 Torr pressure [5].

## 3. Experimental set-up

A CSVTV deposition apparatus is illustrated schematically in Fig. 1 where the spacing between the source and substrate is usually less than 1 cm. The source material is heated to a temperature at which it is transported across the space, usually by diffusion, and deposited on a cooler substrate [3].

In our laboratory, purified graphite crucibles with optional shutters hold the source materials, and Aremco machinable ceramic spacers support the substrates, typically  $10 \text{ cm} \times 10 \text{ cm}$  in size. Computer control allows independent control of gas flows, chamber pressure and source and substrate temperatures.

One station is used to investigate the effects of chamber pressure on film growth. Components include a Leybold Heraeus Trivac D8AC dual-stage vacuum pump for corrosive applications, a Vacuum General Model 80-1 pressure regulator and a Model 80-6B capacitance manometer readout,

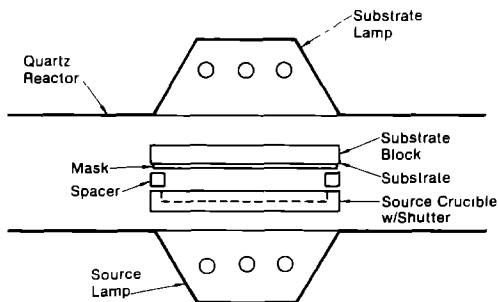


Fig. 1. Side view of CSVTV deposition chamber

Eurotherm Model 984/931 temperature controllers, quartz-halogen photo-lamps, a Tylan Hyoxyl Model 481 mass flow controller and a Tylan Tymer 16 programmer.

A second station complex for the investigation of atmospheric film deposition uses an IBM XT computer coupled to a Keithley DAS Series 510 data acquisition system. Unit Instruments UFC 1000 mass flow controllers with a URS 100 readout control the gas flow. Eurotherm Model 984 temperature controllers with Time Trol SCR power supplies control banks of quartz IR heat lamps.

#### 4. Window layer studies

A superstrate design requires the window layer to be compatible with the CdTe film deposition conditions and other subsequent processing. Tin oxide (TO), indium tin oxide (ITO) and CdS window layers were evaluated. Optical transmission and X-ray diffraction (XRD) measurements were carried out under different heat treatment conditions. Under 1 atm hydrogen, temperatures of the exposed TO should not exceed 450 °C, otherwise XRD indicates the reduction of the TO to elemental tin with a consequent loss in optical transmission. Annealing TO in 1 Torr oxygen at 500 °C has no effect on its properties. ITO is readily reduced in hydrogen at lower temperatures (around 400 °C) and was not considered further as a superstrate window layer.

CdS is a well-known window layer for CdTe solar cells. CSVT CdS films are deposited in helium or hydrogen from either a polycrystalline plate (CVD, Inc.) or from a powder (MRC Marz grade, 325 mesh) which sinters itself into a block during CSVT. Typical conditions are source and substrate temperatures of 700 °C and 300 °C respectively for 2 min in helium.

Figures 2 and 3 show the optical transmissions of thick (1.95 µm) and thin (0.041 µm) CdS deposited by CSVT onto TO-coated Corning 7059 glass. The thick CdS shows an abrupt CdS absorption edge at 520 nm and a reduced reflection loss due to a textured CdS surface morphology. The TO plasma absorption edge causes the transmission loss at long wavelengths. The thin sample shows additional optical transmission above the CdS absorption edge owing to its thinness.

#### 5. CdTe film deposition

The CdTe source is a sintered block formed during CSVT from ground CdTe powder (Alpha ultrapure no. 87821). Figure 4 shows the CdTe growth rate *vs.* temperature in hydrogen at 1 atm and at 1 Torr, indicating rates of 0.15 and 10 µm min<sup>-1</sup> respectively at 700 °C. The deposition rate *R* (µm min<sup>-1</sup>) is expressed by the following equation:

$$R = R_0 \exp \left( -\frac{\Delta E}{kT} \right) \quad (1)$$

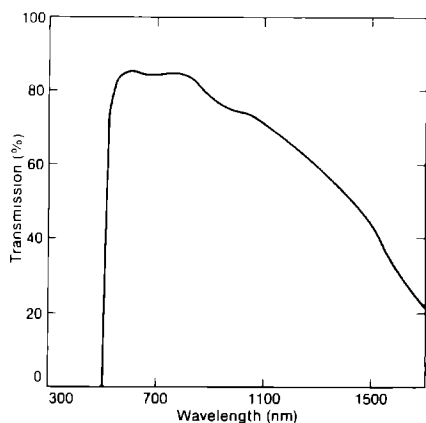


Fig. 2. Optical transmission of a 1.95  $\mu\text{m}$  thick CSVT CdS film on a 7059/TO substrate

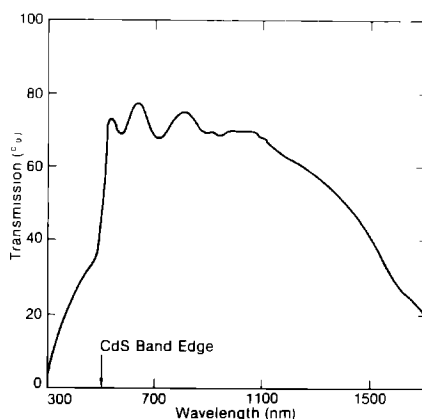


Fig. 3. Optical transmission of a 0.041  $\mu\text{m}$  thick CSVT CdS film on a 7059/TO substrate.

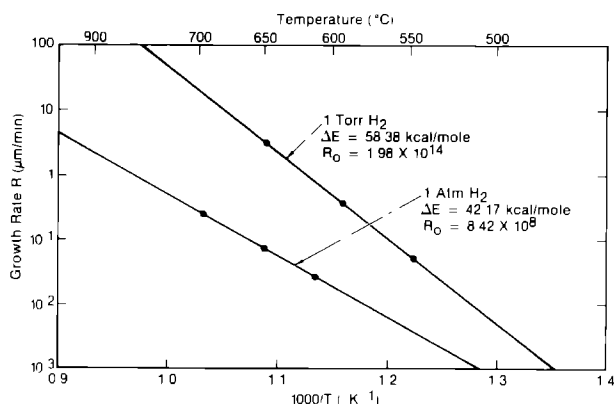


Fig. 4. CSVT CdTe growth rate  $R$  ( $\mu\text{m min}^{-1}$ ) vs. source temperature at 1 Torr and 1 atm pressure in hydrogen ( $R = R_0 \exp(-\Delta E/kT)$ ).

where  $R_0 = 1.98 \times 10^{14}$  at 1 Torr and  $R_0 = 8.42 \times 10^8$  at 1 atm;  $\Delta E = 58.38 \text{ kcal mol}^{-1}$  (2.53 eV) at 1 Torr and  $\Delta E = 42.17 \text{ kcal mol}^{-1}$  (1.82 eV) at 1 atm.

The activation energy and pressure dependence agree with those reported elsewhere [2, 3]. The growth in a helium ambient is similar to that reported in ref. 3. The amount of oxygen added must be kept low because substantial oxidation of the CdTe source can result, suppressing the CSVT process. Satisfactory levels are about 2.2% oxygen in helium at 1 atm or about 1 Torr of oxygen at low pressure.

The properties of CdTe films are strongly dependent on both the temperature and the type of substrate. Four substrates were evaluated: (1) 7059 glass; (2) 7059/TO; (3) 7059/CdS; and (4) 7059/TO/CdS. For substrate temperatures of 550  $^{\circ}\text{C}$ , the substrates without CdS gave gray-black deposits with an optical transmission, below the CdTe band gap, of less than 5% and

XRD indicated the presence of both cubic and hexagonal CdTe. The substrates with CdS gave gray deposits with an optical transmission, below the band gap, of about 40% and XRD showed only cubic CdTe. Increasing the substrate temperature to 600 °C resulted in cubic CdTe for all substrates and an optical transmission, below the band gap, of about 67%, which is nearly ideal considering reflection losses.

## 6. Back contacts

Stable low resistance p-type electrical contacting to CdTe is an art which is not well understood. One technique is to chemically etch the CdTe to form a  $p^+$  tellurium-rich surface, then to deposit the back metallization, usually high work function metals such as gold or nickel [10 - 12]. Temperature studies on single-crystal CdTe indicate that current transport at these contacts is controlled by tunneling. Excessive heat treatment of the contacts will cause chemical reactions in which the metal tellurides are formed. The presence of surface oxide tends to give high contact resistance [10].

Chemical etches typically use either sulfuric acid, designated etch A, or nitric acid, designated etch B. An example of etch A is a saturated chromate etch (77 ml saturated  $K_2Cr_2O_7$ :25 ml  $H_2SO_4$ ) [10 - 12]. An example of etch B is 1.25 ml  $HNO_3$ :100 ml  $H_3PO_4$  [13, 14].

The etching rate of etch A ( $10 \mu m \min^{-1}$  for single-crystal CdTe) is too high for thin films, but is satisfactory at one-tenth dilution. An Auger depth profile of CdTe etched using etch B (Fig. 5) shows the tellurium-rich surface which probes  $p^+$  with a hot-point probe. The surface oxide can be removed with KOH.

Surface doping the CdTe with an acceptor to make it p type also facilitates formation of low resistance contacts. Introducing small amounts of copper has been successfully demonstrated at both Stanford University and

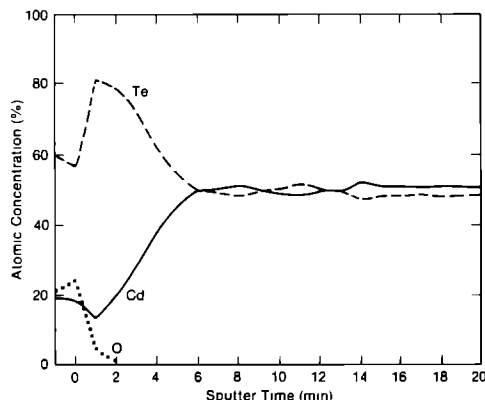


Fig. 5. Auger depth profile of a CdTe surface etched with etch B (1.25 ml  $HNO_3$  100 ml  $H_3PO_4$ )

by Matsushita [11, 15]. Alternatively, a  $p^+$  interlayer such as PbTe, SnTe, HgTe or other low band gap tellurides between the CdTe and metallization can form low resistance contacts.

A number of the above contacting schemes were demonstrated in our laboratory including gold, nickel, PbTe/Au, graphite-silver (C-Ag) and PbTe/C-Ag, with and without prior surface treatments. Screen-printed C-Ag (Electrodag 426SS) paste contacts are significant for their simplicity.

## 7. Device development

The motivation in device research is to use simple, low-cost processes while maintaining high photovoltaic efficiency. Therefore, CSVT at 1 atm was chosen. One case evaluated includes a thin CdS interlayer between the TO and CdTe. Figure 6 shows the  $I$ - $V$  curve of a 9.5%, 4 cm<sup>2</sup> 7059/TO/CdS/CdTe/C-Ag cell with  $J_{sc}$ ,  $V_{oc}$  and FF values of 24.8 mA cm<sup>-2</sup>, 0.705 V and 0.54 respectively as measured under a xenon-arc solar simulator calibrated to 100 mW cm<sup>-2</sup> SERI AM 1.5 global spectrum.

The CdS and CdTe were deposited by CSVT and the C-Ag contact by screen printing. The CdS was grown with 700 °C source and 300 °C substrate temperatures for 2 min in 1 atm helium. The CdTe was then grown with 750 °C source and 550 °C substrate temperatures for 15 min in a helium ambient at 1 atm containing 2.2% oxygen. Next the back surface of the CdTe was etched for 30 s in etch B to form a tellurium-rich surface and the C-Ag back contact applied. The spectral response of the cell indicates a substantial blue response due to the thin CdS (Fig. 7). Some thinning of the CdS occurs by re-evaporation during the CdTe deposition.

Eliminating the CdS window layer further increases the blue response of the cell and reduces the number of process steps. Figure 8 shows the

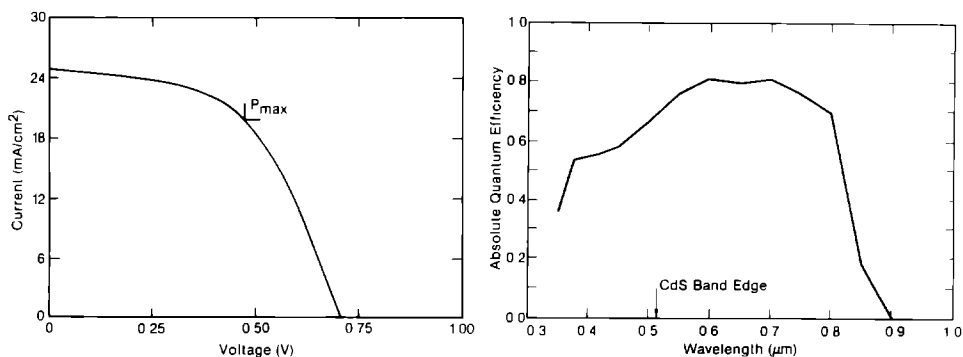


Fig 6. Current-voltage curve for a 1 atm 4 cm<sup>2</sup> 7059/TO/CdS/CdTe/C-Ag solar cell under simulated 100 mW cm<sup>-2</sup> SERI AM 1.5 global spectrum: efficiency, 9.5%;  $J_{sc}$  = 24.8 mA cm<sup>-2</sup>;  $V_{oc}$  = 0.705 V; FF = 0.540.

Fig 7. Spectral response curve for the 7059/TO/CdS/CdTe/C-Ag cell in Fig 6.

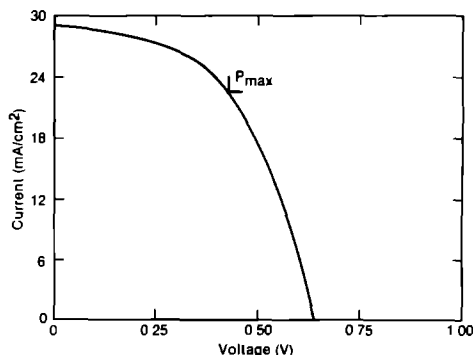
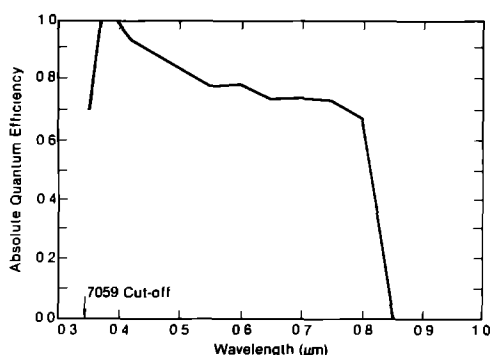


Fig. 8. Spectral response curve for a 1 atm 7059/TO/CdTe/C-Ag solar cell.

Fig. 9. Current-voltage curve for a 1 atm CSVT 4 cm<sup>2</sup> 7059/TO/CdTe/C-Ag solar cell under simulated 100 mW cm<sup>-2</sup> SERI AM 1.5 global spectrum:  $\eta = 9.7\%$ ;  $J_{sc} = 28.8$  mA cm<sup>-2</sup>;  $V_{oc} = 0.642$  V; FF = 0.524.

spectral response of a typical 7059/TO/CdTe/C-Ag cell fabricated using 1 atm CSVT CdTe in helium. Quantum efficiencies above unity near the TO cut-off are unexplained but have also been seen in other devices and may be due to avalanche effects or a light-dependent  $J_0$ . The best 4 cm<sup>2</sup> cell efficiency measured ( $\eta$ ) is 9.7% with  $J_{sc}$ ,  $V_{oc}$  and fill factor values of 28.8 mA cm<sup>-2</sup>, 0.642 V and 0.524 respectively (Fig. 9). The source and substrate temperature profiles during the CdTe growth of this cell are shown in Fig. 10. It should be noted that the 7059/TO substrate was kept below 400 °C to minimize TO reduction until the CdTe source reached 600 °C; then the substrate was quickly heated to 650 °C to improve initial film growth and cooled to 590 °C to complete the film growth. The resultant CdTe layer is 10.3 μm thick. No oxygen was used. During the CdTe growth, 200 ppm of PH<sub>3</sub> in helium were added. In addition, the CdTe was air annealed at 310 °C for 5 min before etching the back surface for 10 s in etch B and screen printing the C-Ag contact. Capacitance *vs.* voltage measurements of this device at 1 MHz give a straight line for  $1/C^2$  *vs.*  $V$  with a calculated carrier concentration of  $4 \times 10^{14}$  cm<sup>-3</sup> and a voltage intercept of 1.4 V.

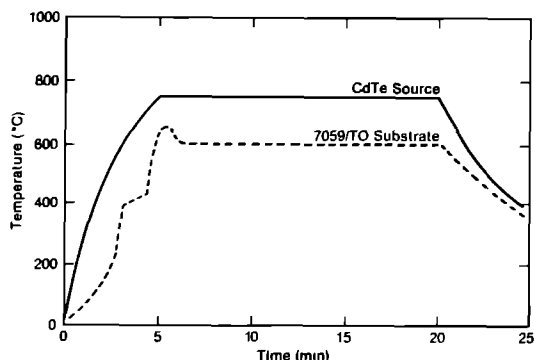


Fig. 10. Source and substrate temperature profiles for cell in Fig. 9.

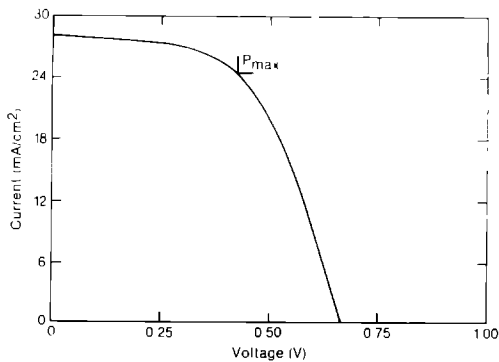


Fig. 11. Current-voltage curve for a 1 Torr 4 cm<sup>2</sup> 7059/TO/CdTe/C-Ag solar cell under simulated 100 mW cm<sup>-2</sup> SERI AM 1.5 global spectrum  $\eta = 10.5\%$ ;  $J_{sc} = 28.1 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.663 \text{ V}$ ; FF = 0.563

The best 4 cm<sup>2</sup> 7059/TO/CdTe/C-Ag cell is 10.5% efficient with  $J_{sc}$ ,  $V_{oc}$  and fill factor values of 28.1 mA cm<sup>-2</sup>, 0.663 V and 0.563 respectively (Fig. 11). The CdTe layer for this device was deposited at about 1 Torr pressure in oxygen for 2 min with source and substrate temperatures of 700 °C and 600 °C respectively.

## 8. Discussion

Our major achievements include the use of (1) completely non-vacuum processing over 10 cm × 10 cm areas, (2) the fabrication of simple transparent conductive oxide (TC)/CdTe cells without the need of a CdS window layer, and (3) screen-printed CdTe back contacts. Reducing losses due to shunting at pinholes, voltage-dependent photocarrier collection [10], back-contact resistance and trapping effects will result in improved values for the  $V_{oc}$ , fill factor and efficiency. With process and device optimization, efficiencies above 15% are projected.

## Acknowledgment

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