PROGRESS TOWARDS HIGH EFFICIENCY, THIN FILM CdTe SOLAR CELLS

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ABSTRACT

This paper describes work investigating high rate CdTe film deposition by close-space vapor transport (CSVT), leading to greater than 10% efficient, 4 cm^2 tin oxide/CdTe solar cells. Under 100 mW/cm^2 AM 1.5 global spectrum, a 10.5% cell had values of 28.1 mA/cm^2 J_{SC}, 0.663 V V_{OC}, and 0.563 fill factor. Major accomplishments include: (1) completely non-vacuum processing; (2) simple transparent conductive oxide (TC)/CdTe cells without need of a CdS window layer; and (3) screen-printed back contacts.

INTRODUCTION

Cadmium telluride 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 formation of a variety of junction structures, and to 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. Emphasis for the front conductive layer was on the use of a wide band gap transparent conductor such as tin oxide without the need for an intermediate CdS layer. Non-vacuum processes, namely atmospheric CSVT for the CdTe and screen printing for the back contact, were emphasized for their simplicity and ability to be easily scaled to large areas. The paper will present the results of the individual layer studies and then the results for the different solar cells.

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BACKGROUND

CSVT CdTe films for solar cells have been studied by different groups [2-6]. Research at Stanford University examined the CdTe CSVT process and the resultant film properties [2-4]. Kodak has emphasized the development of CdS/CdTe solar cells and modules with special emphasis on low pressure CSVT in the presence of oxygen [5-9]. Notably Kodak reported 75 mW/cm^2 simulated AM 2 efficiencies of 10.5% for 0.1 cm^2 thin CdS/CdTe cells deposited at about 1 torr pressure [5].

EXPERIMENTAL SET-UP

A schematic of a CSVT deposition apparatus is illustrated 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

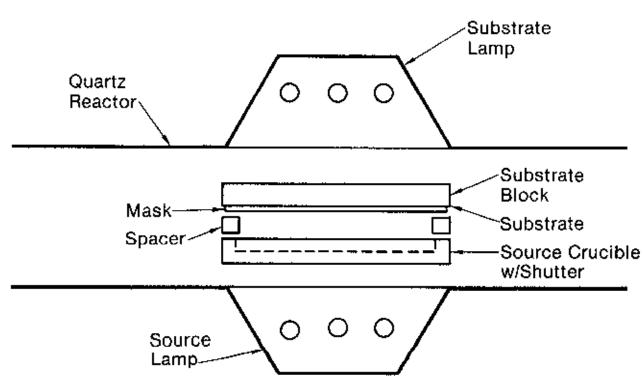

Fig. 1. Side view of CSVT deposition chamber.

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at which it transports across and deposits on a cooler substrate, usually by diffusion [3].

In our laboratory, purified graphite crucibles with optional shutters hold the source materials and Aremco machinable ceramic spacers support the substrates, typically 10 cm x 10 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, Eurotherm Model 984/931 temperature controllers, quartz halogen photolamps, a Tylan Hyoxyl Model 481 mass flow controller and a Tylan Tymer 16 programmer.

A second station complex for 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 gas flow. Eurotherm Model 984 temperature controllers with Time Trol SCR power supplies control banks of quartz infrared heat lamps.

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) were measured for different heat treatment conditions. For 1 atm H_2, temperatures of 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 readily reduces 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 He or H_2 from either a polycrystalline plate (CVD, Inc.) or from powder (MRC Marz grade, 325 mesh) which sinters itself into a block during CSVT. Typical conditions are 700°C source and 300°C substrate temperatures for 2 minutes in helium.

Figures 2 and 3 show the optical transmissions of thick (1.95 microns) and thin (0.041 micron) CSVT CdS deposited on TO coated 7059 glass. The thick CdS shows the abrupt CdS absorption edge at 520 nm and 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 the additional optical transmission above the CdS absorption edge due to its thinness.

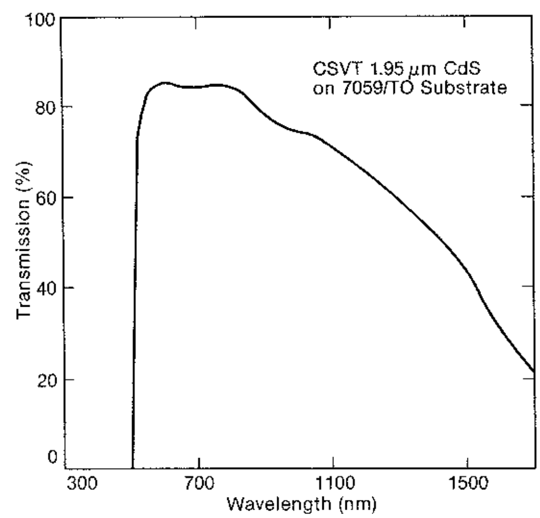

Fig. 2. Optical transmission of a 1.95 micron thick CSVT CdS film on a 7059/TO substrate.

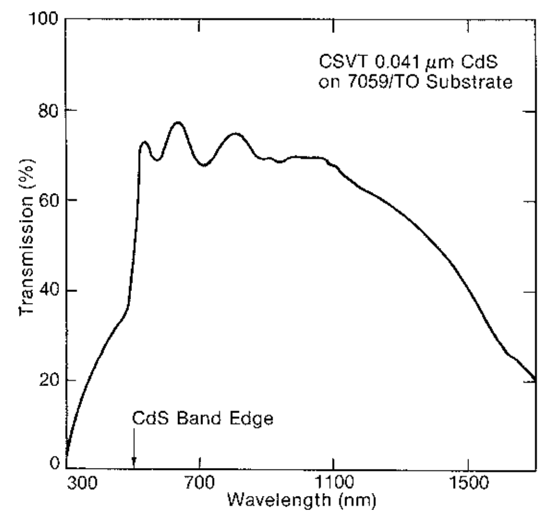

Fig. 3. Optical transmission of a 0.041 micron thick CSVT CdS film on a 7059/TO substrate.

CdTe FILM DEPOSITION

The CdTe source is a sintered block formed during CSVT from ground CdTe powder (Alpha ultrapure #87821). Figure 4 shows the CdTe growth rate versus temperature in H_2 at 1 atm and at 1 torr, indicating rates at 700°C of 0.15 and 10 micrometers/min respectively. The deposition rate R is expressed in the following equation:

$$R\ (\text{microns/min}) = R_o \exp(-\Delta E/kT) \qquad \text{Eq. 1}$$

where

$R_o = 1.98\times10^{14}$ at 1 torr
$= 8.42\times10^{8}$ at 1 atm

$\Delta E = 58.38$ kcal/mole (2.53 eV) at 1 torr
$= 42.17$ kcal/mole (1.82 eV) at 1 atm

The activation energy and pressure dependence agree with those reported elsewhere [2,3]. Growth in He ambient is similar to that reported in Ref. 3. Addition of oxygen must be kept low because it can result in substantial oxidation of the CdTe source, suppressing the CSVT process. Satisfactory levels are about 2.2% oxygen in He at 1 atm or about 1 torr of oxygen at low pressure.

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 550°C substrate temperatures, the substrates without CdS gave gray/black deposits with optical transmission below the CdTe band gap of less than 5% and XRD indicating both cubic and hexagonal CdTe. The substrates with CdS gave gray deposits with below band gap optical transmissions of about 40% and XRD showing only cubic CdTe. Increasing the substrate temperature to 600°C resulted in cubic CdTe for all substrates and below band gap optical transmission of about 67%, which is nearly ideal considering reflection losses.

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+ Te-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 current transport at these contacts is controlled by tunneling. Excessive heat treatment of the contacts will cause chemical reactions to form the metal tellurides. 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].

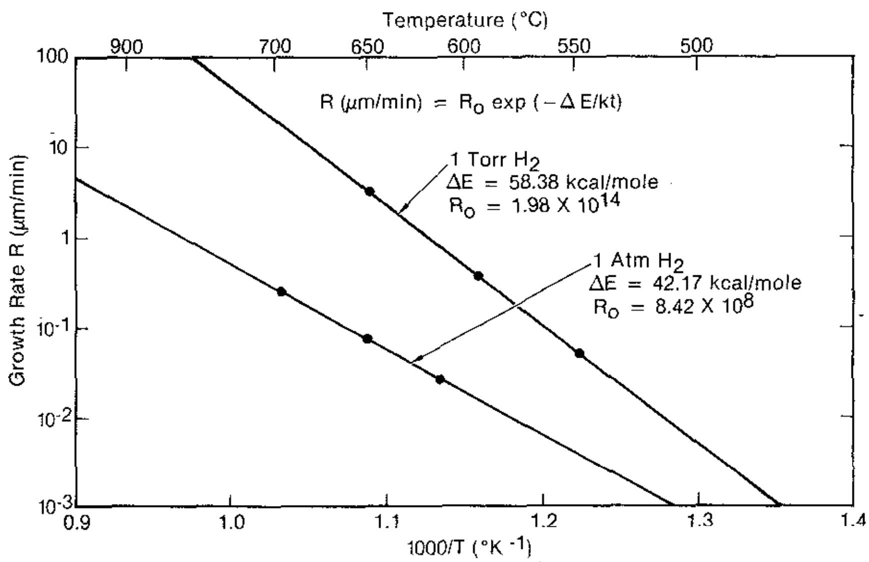

Fig. 4. CSVT CdTe growth rate vs. source temperature at 1 torr and 1 atm pressure in H_2.

The etch rate of Etch A (10 microns/min for single crystal CdTe) is too high for thin films, but is satisfactory in one-tenth dilution. An Auger depth profile of CdTe etched using Etch B (Fig. 5) shows the Te 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 by both Stanford University and 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 Au, Ni, 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 emphasized for their simplicity.

DEVICE DEVELOPMENT

The motivation in the device research is to use simple, low cost processes while maintaining high photovoltaic efficiency. As a result, CSVT at 1 atm is emphasized. 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^2 7059/TO/CdS/CdTe/C-Ag cell with J_{SC}, V_{OC}, and FF values of 24.8 mA/cm^2, 0.705 V, and 0.54 respectively as measured under a xenon-arc solar simulator calibrated to 100 mW/cm^2 SERI Air Mass 1.5 global spectrum.

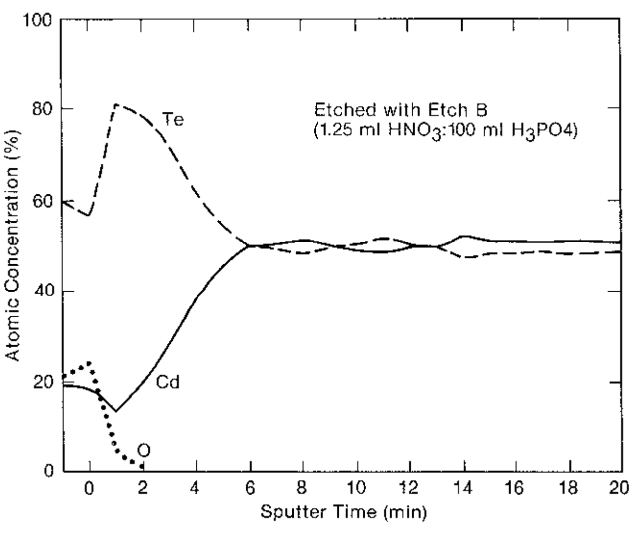

Fig. 5. Auger depth profile of a CdTe surface etched with Etch B.

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 minutes in 1 atm helium. The CdTe was then grown with 750°C source and 550°C substrate temperatures for 15 minutes in a 2.2% oxygen in helium 1 atm ambient. Next the back surface of the CdTe was etched for 30 sec in Etch B to form a Te rich surface and the C-Ag back contact applied. The spectral response of the cell indicates substantial blue response due to the thin CdS (Fig. 7). Some thinning of the CdS occurs by re-evaporation during the CdTe deposition.

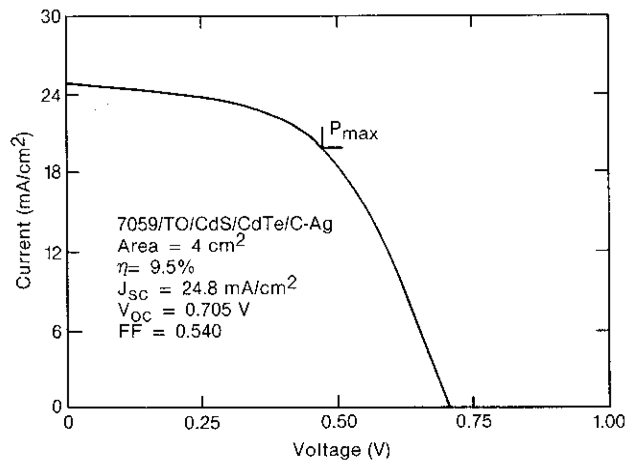

Fig. 6. Current-voltage curve for a 1 atm 4 cm^2 7059/TO/CdS/CdTe/C-Ag solar cell under simulated 100 mW/cm^2 SERI Air Mass 1.5 global spectrum.

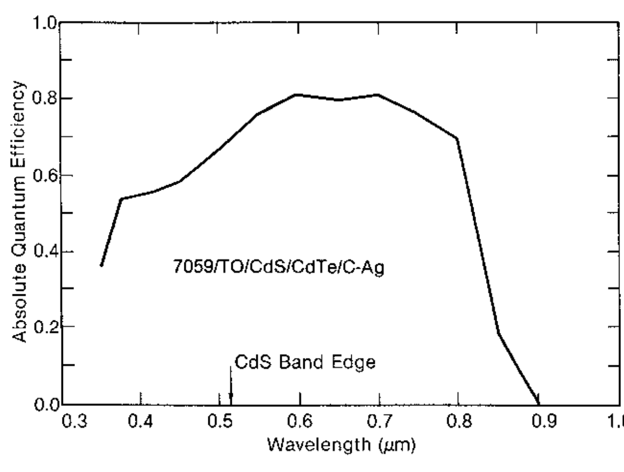

Fig. 7. Spectral response curve for cell in Fig. 6.

Eliminating the CdS window layer further increases the blue response of the cell and reduces the number of process steps. Figure 8 shows the spectral response of a typical 7059/TO/CdTe/C-Ag cell fabricated using 1 atm CSVT CdTe in He. 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_o. The best 4 cm^2 cell efficiency measured is 9.7% with J_{sc}, V_{oc}, and fill factor values of 28.8 mA/cm^2, 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. Note 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 microns thick. No oxygen was used. During the CdTe growth, 200 ppm of PH_3 in He was added. In addition, the CdTe was air annealed at 310°C for 5 minutes before etching the back surface for 10 sec in Etch B and screen printing the C-Ag contact. Capacitance versus voltage measurements of this device at 1 MHz give a straight line for $1/C^2$ versus V with a calculated carrier concentration of 4×10^{14} cm^{-3} and an voltage intercept of 1.4 V.

The best 4 cm^2 7059/TO/CdTe/C-Ag cell is 10.5% efficient with J_{sc}, V_{oc}, and fill factor values of 28.1 mA/cm^2, 0.663 V, and 0.563 respectively (Fig. 11). The CdTe

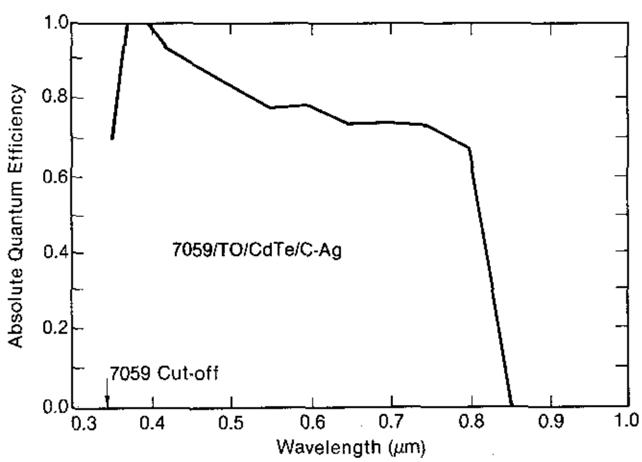

Fig. 8. Spectral response curve for a 1 atm 7059/TO/CdTe/C-Ag solar cell.

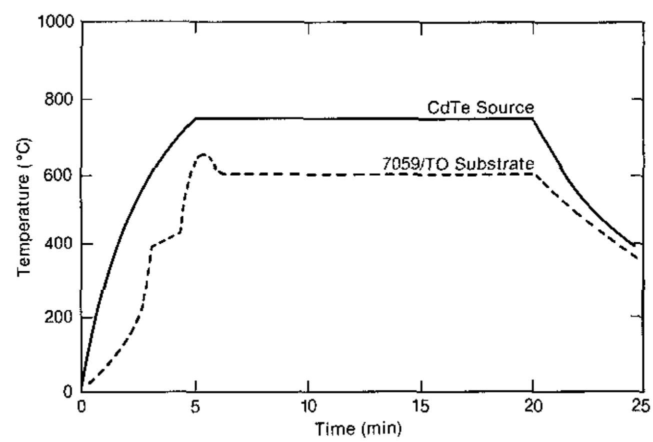

Fig. 10. Source and substrate temperature profiles for cell in Fig. 9.

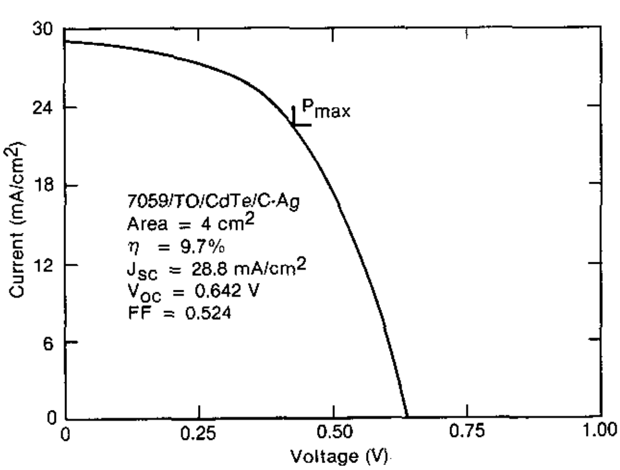

Fig. 9. Current-voltage curve for a 1 atm CSVT 4 cm^2 7059/TO/CdTe/C-Ag solar cell under simulated 100 mW/cm^2 SERI Air Mass 1.5 global spectrum.

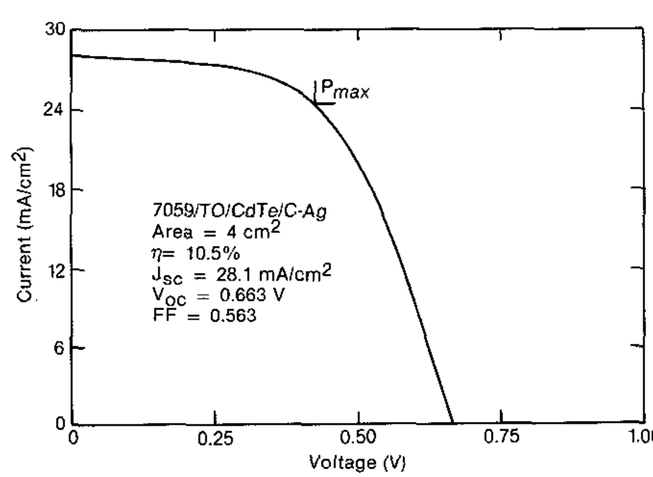

Fig. 11. Current-voltage curve for a 1 torr 4 cm^2 7059/TO/CdTe/C-Ag solar cell under simulated 100 mW/cm^2 SERI Air Mass 1.5 global spectrum.

layer for this device was deposited at about 1 torr pressure in oxygen for 2 minutes with source and substrate temperatures of 700°C and 600°C respectively.

DISCUSSION

Major accomplishments include: (1) completely non-vacuum processing over 10 cm x 10 cm areas; (2) 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 V_{OC}, fill factor, and efficiency. With process and device optimization, efficiencies above 15% are projected.

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