Progress Report No. 8

PREPARATION AND PROPERTIES OF EVAPORATED CdTe FILMS
COMPARSED WITH SINGLE-CRYSTAL CdTe

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ABSTRACT

The goal of our research is to develop efficient thin-film solar cells involving CdTe as the absorbing material using the method of hot-wall vacuum evaporation for CdTe film deposition. To be sure that we had removed all possible contamination of the apparatus due to indium impurity remaining from the deposition of n-type CdTe:In films, we carried out a series of undoped CdTe film depositions. These showed dark resistivity in the $10^7$ ohm-cm range and light resistivity in the $10^5$ ohm-cm range. No indication of indium contamination was obtained. Ampoules with small apertures were designed for the Zone 3 and Zone 4 of the furnace (dopant zone, and Cd or Te zone) to allow the temperatures of these zones to be raised near that of the substrate and thus prevent deposition of Te in these zones during a deposition run. Weighing these ampoules also provides a convenient test of material evaporated.

The first set of depositions with As impurity to produce p-type CdTe:As films was carried out. No large effect of As doping was observed in these early runs, but some system improvements have been made for the future.

A CdTe homojunction with a 0.15 µm n-type CdTe:In layer on a p-type CdTe:P single crystal substrate has been analyzed. Modelling of the spectral response of the quantum efficiency suggests the presence of a thin inactive layer at the surface, possibly a depletion layer in the n-type film. A value of $V_{oc} = 0.80$ V is obtained from In strips on the n-type film, and a value of $J_{sc} = 7$ mA/cm$^2$ (active area) without correction for reflection loss. Large values of the diode factor $A$ indicate non-simple homojunction structures.

A light spot scanning apparatus has been constructed using a He-Ne laser and a 4 µm optical fiber. This apparatus will be used to measure
the recombination characteristics of grain boundaries covered by transparent Schottky barriers.

The electrical conductivity of p-type CdTe films prepared by close-spaced vapor transport is markedly increased by heat treatment in H₂. Such a heat treatment has been shown to decrease the grain boundary resistance in p-CdTe bicrystals. Some recovery of the film resistivity is seen after 1 week in air. Interesting differences in spectral response of change in conductivity are seen between films before and after heat treatment, and between bulk CdTe and a single grain boundary in a CdTe bicrystal.
GROWTH AND CHARACTERIZATION OF UNDOPED CdTe FILMS

In the transition interval between our deposition of n-type CdTe:In films and our deposition of p-type CdTe films using As, P or Cs dopant, we have carried out some depositions of undoped CdTe films in order to provide basic information as reference and control for future research. A series of undoped CdTe films were deposited on 7059 glass and BaF$_2$ crystal substrates.

Growth

The growth conditions of these films are listed in Table I. Substrate temperatures in the range of 430 to 450°C were used, and the CdTe source temperature was between 570 and 575°C. These temperatures were also used for the growth of indium doped CdTe films. No material was positioned in Zone 3 (lower middle furnace) and Zone 4 (bottom furnace), except during the deposition of film # 66 which was grown with an extra Te source. The temperature of Zone 3 was varied between 306 and 525°C. At the beginning, the temperature for Zone 4 was 113°C; this was subsequently increased to 475°C. During the deposition of films # 61 and # 62, the two lower furnaces had been at temperatures low enough to allow deposition of Cd and Te. In order to avoid that deposition, the temperatures of these two furnaces were raised above the substrate temperature.

Samples # 62 and # 66 were grown simultaneously on glass and BaF$_2$. The grain size of the films on glass is typically about 1 μm and only slightly larger for films grown on BaF$_2$.

Electrical Properties

Evaporated indium and gold contacts were used for the resistivity measurements. The dark resistivity as obtained from 2-point and 4-point measurements is uniformly high, ranging from $10^7$ to $10^8$ ohm-cm, as indicated
# TABLE I

Growth Conditions and Electrical Properties of Undoped CdTe Films

<table>
<thead>
<tr>
<th>#</th>
<th>Substrate</th>
<th>$T_{\text{sub}}, ^\circ \text{C}$</th>
<th>$T_{\text{CdTe}}, ^\circ \text{C}$</th>
<th>$T_{3\text{rd}}, ^\circ \text{C}$</th>
<th>$T_{4\text{th}}, ^\circ \text{C}$</th>
<th>Thickness, $\mu$m</th>
<th>Growth Rate, $\mu$m/h</th>
<th>Resistivity, ohm-cm Dark</th>
<th>Resistivity, ohm-cm Light (AM 1.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>7059 Glass</td>
<td>454</td>
<td>575</td>
<td>306</td>
<td>113</td>
<td>4.7</td>
<td>4.7</td>
<td>$2.1 \times 10^7$</td>
<td>$5.6 \times 10^4$</td>
</tr>
<tr>
<td>62B</td>
<td>BaF$_2$</td>
<td>452</td>
<td>574</td>
<td>338</td>
<td>300</td>
<td>7.8</td>
<td>19.5</td>
<td>$3 \times 10^7$</td>
<td>$1.8 \times 10^5$</td>
</tr>
<tr>
<td>62A</td>
<td>7059 Glass</td>
<td>452</td>
<td>574</td>
<td>338</td>
<td>300</td>
<td>4.9</td>
<td>12.3</td>
<td>$5 \times 10^7$</td>
<td>$1.5 \times 10^5$</td>
</tr>
<tr>
<td>63</td>
<td>7059 Glass</td>
<td>442</td>
<td>575</td>
<td>525</td>
<td>475</td>
<td>5.5</td>
<td>11.0</td>
<td>$9 \times 10^6$</td>
<td>$7.5 \times 10^4$</td>
</tr>
<tr>
<td>64</td>
<td>7059 Glass</td>
<td>432</td>
<td>575</td>
<td>525</td>
<td>475</td>
<td>8.0</td>
<td>16.0</td>
<td>$7.1 \times 10^7$</td>
<td>$1.6 \times 10^5$</td>
</tr>
<tr>
<td>65</td>
<td>7059 Glass</td>
<td>434</td>
<td>570</td>
<td>525</td>
<td>475</td>
<td>3.5</td>
<td>8.7</td>
<td>$1.1 \times 10^8$</td>
<td>$2.2 \times 10^5$</td>
</tr>
<tr>
<td>66B</td>
<td>BaF$_2$</td>
<td>435</td>
<td>571</td>
<td>526</td>
<td>431</td>
<td>3.1</td>
<td>6.2</td>
<td>$5 \times 10^7$</td>
<td>$3.6 \times 10^5$</td>
</tr>
<tr>
<td>66A</td>
<td>7059 Glass</td>
<td>435</td>
<td>571</td>
<td>526</td>
<td>431</td>
<td>2.7</td>
<td>5.4</td>
<td>$9 \times 10^7$</td>
<td>$1.3 \times 10^5$</td>
</tr>
</tbody>
</table>

* Grown with extra Te source in the 4th Zone.
in Table I. The results obtained from both methods are in good agreement and are independent of the metal used to make contact to the CdTe films. The resistivity seems also not to be affected by the temperature profile of the HWVE apparatus, and no appreciable change of the resistivity with excess Te was observed.

Under simulated sunlight (AM 1.5) the resistivity dropped to approximately $10^5$ ohm-cm. This value is one to three orders of magnitude higher than the resistivity measured for CdTe films on glass when doped with indium during the deposition. The conductivity in the dark of sample # 66 increases exponentially with an activation energy of 0.65 eV; in the light the activation energy is greatly reduced to 0.17 eV.

Discussion

Before beginning this series, the source container, shutter blocks and substrate holder were replaced to prevent contamination by indium from past runs. The top furnace was completely disassembled and cleaned, and new shutter blocks were designed to reduce leakage of the retort. The fact that the undoped films described above were more resistive than those grown with indium doping indicates low residual indium impurity in the system.

After samples # 62 had been prepared, it was noted that Zone 4 showed a metallic-appearing deposit. Microprobe analysis indicated that this deposit was primarily tellurium. Subsequent runs in which the temperature of Zone 4 was increased to 475°C showed no tellurium deposit. Deposition of Te during the run in this way probably causes departures from stoichiometry conditions that are undesirable, particularly in the subsequent doping experiments to make p-type CdTe which may be sensitive to stoichiometry.
The control of stoichiometry during the growth of p-type films poses a problem also, since most p-type dopants (As, P, Cs) are high vapor pressure species requiring source temperatures of about 300°C, which would allow deposition of tellurium in this region. To solve this problem, quartz ampoules with small apertures were designed to contain the high vapor pressure dopants. The ampoule is a small quartz tube (0.3 cm OD and 2 cm long) with a capillary nozzle (0.005 - 0.010 cm ID and 1 cm long). The ampoule design permits source temperatures in the 400° to 500°C range while maintaining a throughput equal to that of a source (without ampoule) in the 200° to 300°C range. An additional advantage is the ability to weigh the ampoule with its source material before and after each run to obtain a direct measurement of how much the material has been evaporated during the run.
GROWTH OF p-TYPE CdTe FILMS

Films # 67, 68 and 69 were deposited with an arsenic source ampoule in Zone 4 at 457°C. The pressure inside the ampoule is approximately 10 Torr; the resulting pressure in the source container is about $10^{-5}$ Torr, a factor of one thousand less than the pressure of cadmium and tellurium (Te$_2$) over CdTe at the CdTe source temperature of 575°C. Films #68 and #69 were deposited with excess Cd, this excess cadmium being introduced in an ampoule in Zone 3. It is probable that, in the absence of a Cd or Te source, the vapor in the source container is Te rich, since Cd would be lost at any leak at a higher rate than Te$_2$. For effective As incorporation on Te sites, the growing film must have a sufficient density of Te vacancies, but an excess of Te vacancies will act as donors and compensate the conductivity. Preliminary results with As doping and excess Cd are shown in Table II for films #68 and #69. No large effects of As doping are indicated in these preliminary runs.
### TABLE II

Properties of CdTe Films Deposited with As Dopant

<table>
<thead>
<tr>
<th>Sample</th>
<th># 67</th>
<th># 68</th>
<th># 69</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{sub}}, ^\circ \text{C}$</td>
<td>436</td>
<td>430</td>
<td>430</td>
</tr>
<tr>
<td>$T_{\text{CdTe}}, ^\circ \text{C}$</td>
<td>571</td>
<td>575</td>
<td>575</td>
</tr>
<tr>
<td>$T_{\text{Zone 3}}, ^\circ \text{C}$ (empty)</td>
<td>420 (Cd)</td>
<td>420 (Cd)</td>
<td>480 (Cd)</td>
</tr>
<tr>
<td>$T_{\text{Zone 4}}, ^\circ \text{C}$ (As)</td>
<td>457</td>
<td>457</td>
<td>457</td>
</tr>
</tbody>
</table>

|Light resistivity, ohm-em| $4.9 \times 10^4$| $5.1 \times 10^4$| $2.2 \times 10^5$
|Dark resistivity, ohm-em| $1.3 \times 10^7$| $6.4 \times 10^6$| $2.2 \times 10^7$

|Thickness, μm| 3  | 4  | 2.5  |

|Growth Rate, μm/h| 6  | 8  | 5    |

|Weight Change CdTe, mg| 100  | 100  | 100  |

|Weight Change Cd ampoule, mg| No ampoule| 0.5  | 0.1<sup>a</sup> |

|Weight Change As ampoule, mg| 1.1  | 1.1  | 1.1  |

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<sup>a</sup> Evidence of capillary clogging; resolved by new design of ampoule.
The properties of homojunctions of CdTe prepared by HWVE deposition
n-CdTe:In films on p-CdTe single crystal substrates are summarized in
Table III. Cell # 57 has two areas: (1) an area where an ITO transparent
contact was applied to the grown n-type layer to aid in current
collection, and (2) an adjoining area where current was collected
through an indium strip contact only. Cells other than # 57 have been
described in previous Progress Reports.

Cell # 57 was prepared in the way that other cells in Table III
were prepared, using a substrate of p-CdTe:P from boule # 55B. The
deposition time for the n-type layer was reduced to 40 sec to yield an
expected n-layer thickness of approximately 0.15 μm. ITO was
deposited over an area of about 0.12 cm² and was annealed in air for
2 min at 240°C to achieve high conductivity and transparency. Indium
strip contacts were applied to both the area where the ITO was present
and to an area of the n-type layer without ITO (these regions are
listed separately in Table III).

The In contact area (no ITO) on cell # 57 yielded the highest
V 폄 = 0.80 V of any junctions fabricated to date. The modelled spectral
response shown in Figure 1 for a n/p homojunction with a 0.15 μm
n-type layer does not correspond well to the measured spectral response
(particularly for short wavelengths). A better fit was obtained by
modelling that includes an inactive surface region (a region not
generating current, but absorbing light) of 0.08 μm in thickness,
a depletion region (region of total collection) of 0.3 μm in thickness,
and a typical p-type absorber. The thin inactive region might physically
correspond to a depletion region at the surface, resulting in a field
that sweeps minority carriers toward the surface rather than toward the
### TABLE III

**Properties of CdTe Homojunctions**

<table>
<thead>
<tr>
<th>Sample</th>
<th># 9</th>
<th># 38</th>
<th># 45</th>
<th># 57</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-CdTe:P substrate</td>
<td>55B</td>
<td>55B</td>
<td>55B</td>
<td>55B</td>
</tr>
<tr>
<td>Substrate thickness</td>
<td>1 - 2 mm</td>
<td>1 - 2 mm</td>
<td>1 - 2 mm</td>
<td>1 - 2 mm</td>
</tr>
<tr>
<td>Chemical etch</td>
<td>Br:MeOH</td>
<td>Br:MeOH</td>
<td>Br:MeOH</td>
<td>Br:MeOH</td>
</tr>
<tr>
<td>( L_n', \mu m )</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**HWVE Deposited n-CdTe**

| \( T_{sub}, ^\circ C \) | 450 | 450 | 450 | 450 |
| \( T_{CdTe}', ^\circ C \) | 575 | 575 | 575 | 575 |
| \( T_{In}', ^\circ C \) | 680 | 575 | 590 | 590 |
| \( T_{Cd}' , ^\circ C \) | 245 | 245 | 245 | 245 |
| \( L_p', \mu m \) | 0.38 | 0.60 | 0.60 | 0.60 |
| Thickness, \( \mu m \) | 1.6 | 1.5 | 0.60 | 0.15 |

<table>
<thead>
<tr>
<th>Front Contact</th>
<th>In Strips</th>
<th>In Strips</th>
<th>In Strips</th>
<th>ITO(^a)</th>
<th>ZnO(^b)</th>
<th>In Strips</th>
<th>ITO(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{oc}, V )</td>
<td>0.73</td>
<td>0.71</td>
<td>0.725</td>
<td>0.59</td>
<td>0.485</td>
<td>0.80</td>
<td>0.67</td>
</tr>
<tr>
<td>( J_{sc}, mA/cm^2 )(^c)</td>
<td>0.016</td>
<td>0.023</td>
<td>4.5(^d)</td>
<td>4.1</td>
<td>4.8</td>
<td>7(^e)</td>
<td>7.7</td>
</tr>
<tr>
<td>( J_0, A/cm^2 )</td>
<td>( 3 \times 10^{-10} )</td>
<td>( 2 \times 10^{-10} )</td>
<td>( 8 \times 10^{-10} )</td>
<td>( 2 \times 10^{-5} )</td>
<td>( 3 \times 10^{-5} )</td>
<td>( 8 \times 10^{-7} )</td>
<td>( 9 \times 10^{-6} )</td>
</tr>
<tr>
<td>( A )</td>
<td>2.5</td>
<td>2.7</td>
<td>3.1</td>
<td>5.4</td>
<td>4.2</td>
<td>4.0</td>
<td>6.5</td>
</tr>
</tbody>
</table>

\(^a\) Annealed for 2 min at 240\(^\circ\)C in air to obtain transparency.

\(^b\) Annealed for 8 min at 450\(^\circ\)C in air.

\(^c\) For active area, but without correction for reflection.

\(^d\) Based on an active area extending \( L_n' \) beyond the strip contact perimeter.

\(^e\) Based on integrated spectral response.
junction. The value of $J_{sc}$ obtained by integrating this modelled spectral response, assuming no reflection loss and active area, is 10.4 mA/cm$^2$.

The measured $A$ factor of 4.0 indicates that the device is not a simple homojunction.

The ITO front contact provided a relatively large area device. The spectral response of this device is also shown in Figure 1. It was not modelled since the optical transmission of the ITO was not known as a function of wavelength. The measured peak response was shifted and considerably broadened. The $A$ factor for this ITO diode was 6.5, also indicating a non-simple homojunction.
Figure 1. The relative quantum efficiency measured for homojunction # 57 for indium strip contacts (X) and for an ITO front contact (Ø). The solid curve was generated by modelling a homojunction with a front layer thickness of 0.15 μm and a depletion region of 0.2 μm. The dashed curve was generated by modelling a device with a 0.08 μm inactive layer and a 0.3 μm depletion region. The modelling parameters were the same as used for the devices of Report No. 7.
Light Spot Scanning Apparatus

A light spot scanning apparatus has been constructed to enable us to measure the recombination characteristics of grain boundaries. Semi-transparent Schottky barriers are formed on polished and etched bicrystals, making certain to cover the intersection of the grain boundary with the crystal surface. A light spot is obtained by focussing a 15 mW He-Ne laser into a 4 μm diameter optical fiber. The focussed beam is chopped, and the short-circuit current generated is detected by a lock-in amplifier. Initial problems of a weak response signal have been overcome. Some dramatic effects have been initially observed; their interpretation is currently being considered and will be reported on later.

Grain Boundary Passivation on CdTe Film

Initial results observed on grain-boundary passivation in bicrystals of CdTe as the result of heat treatment in hydrogen were extended to thin film p-type CdTe grown on 7059 glass by the close-spaced vapor transport system by T. C. Anthony. A 4 μm thick film was annealed in H₂ at 500°C for 5 min. This heat treatment produced a decrease in the room temperature dark resistivity from 4 x 10⁷ ohm-cm to 9 x 10⁵ ohm-cm, a decrease in the dark conductivity activation energy from 0.61 eV to 0.47 eV (see Figure 2), and a decrease in the illuminated conductivity activation energy from 0.27 eV to approximately zero. Resistivity in the light after heat treatment was 10³ ohm-cm. Spectral response measurements made before and after heat treatment (see Figure 3) indicate a greatly enhanced light response after heat treatment. Also evident is a shift in the maximum response from 810 nm before heat treatment to 850 nm afterwards. This film was remeasured one week after the hydrogen heat treatment. As seen from Figures 2 and 3, a significant portion of
Figure 2. Temperature dependence of the conductivity of a p-type CdTe film deposited by close-spaced vapor transport (a) before heat treatment in hydrogen, (b) after heat treatment in hydrogen, (c) 1 week after heat treatment in hydrogen.

- $E_{A,LIGHT, AFTER} = 0$ eV
- $E_{A,LIGHT, 1 \text{ WEEK}} = 0.05$ eV
- $E_{A,DARK, BEFORE} \approx 0.21$ eV
- $E_{A,DARK, AFTER} \approx 0.47$ eV
- $E_{A,DARK, 1 \text{ WEEK}} \approx 0.58$ eV
- $E_{A,DARK, BEFORE} \approx 0.61$ eV
Figure 3. Spectral response of photoconductivity for the p-type CdTe film of Figure 2, before, immediately after, and 1 week after heat treatment in hydrogen.
the change induced by heat treatment had decayed away. Future experiments will include films stored in vacuum or an inert atmosphere to separate out possible removal of oxygen from grain boundaries by the hydrogen heat treatment from penetration of the grain boundaries by hydrogen itself. Thin layers of potential dopants will also be tested as to their effect on thin film properties.

AC techniques were applied to permit the comparison of the spectral response of photoconductivity in bulk CdTe with the spectral response of the increase in conductivity of a single grain boundary in a p-type CdTe bicrystal. The results are shown in Figure 4. The grain boundary response is shifted significantly to longer wavelengths, compared to the bulk response. Further analysis will determine whether this is a genuine extrinsic excitation in the grain boundary, or can be attributed to an optical effect with a different effective absorption constant for the grain boundary than for the bulk.
Figure 4. Comparison of the normalized spectral response of photoconductivity in bulk p-type CdTe with that for increase in conductivity of a single grain boundary in a CdTe bicrystal.