PREPARATION AND PROPERTIES OF EVAPORATED CdTe FILMS
COMPARED 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 H_2. 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

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

* 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 $475^{o}C$ 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

Sample	# 67	# 68	# 69
T_{sub}, ^{o}C	436	430	430
T_{CdTe}, ^{o}C	571	575	575
$T_{Zone\ 3}$, ^{o}C	420 (empty)	420 (Cd)	480 (Cd)
$T_{Zone\ 4}$, ^{o}C (As)	457	457	457
Light resistivity, ohm-cm	4.9×10^4	5.1×10^4	2.2×10^5
Dark resistivity, ohm-cm	1.3×10^7	6.4×10^6	2.2×10^7
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[a]
Weight Change As ampoule, mg	1.1	1.1	1.1

[a] Evidence of capillary clogging; resolved by new design of ampoule.

CdTe HOMOJUNCTIONS

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 cm^2 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_{oc} = 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

Sample	# 9	# 38	# 45	# 57
p-CdTe:P substrate	55B	55B	55B	55B
Substrate thickness	1 - 2 mm	1 - 2 mm	1 - 2 mm	1 - 2 mm
Chemical etch	Br:MeOH	Br:MeOH	Br:MeOH	Br:MeOH
L_n, μm	0.5	0.5	0.5	0.5

HWVE Deposited n-CdTe

	# 9	# 38	# 45	# 57
T_{sub}, °C	450	450	450	450
T_{CdTe}, °C	575	575	575	575
T_{In}, °C	680	575	590	590
T_{Cd}, °C	245	245	245	245
L_p, μm	0.38	0.60	0.60	0.60
Thickness, μm	1.6	1.5	0.60	0.15

Front Contact	In Strips	In Strips	In Strips	ITO[a]	ZnO[b]	In Strips	ITO[a]
V_{oc}, V	0.73	0.71	0.725	0.59	0.485	0.80	0.67
J_{sc}, mA/cm^2 [c]	0.016	0.023	4.5[d]	4.1	4.8	7[e]	7.7
J_o, A/cm^2	3×10^{-10}	2×10^{-10}	8×10^{-10}	2×10^{-5}	3×10^{-5}	8×10^{-7}	9×10^{-6}
A	2.5	2.7	3.1	5.4	4.2	4.0	6.5

[a] Annealed for 2 min at 240°C in air to obtain transparency.
[b] Annealed for 8 min at 450°C in air.
[c] For active area, but without correction for reflection.
[d] Based on an active area extening L_p 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.
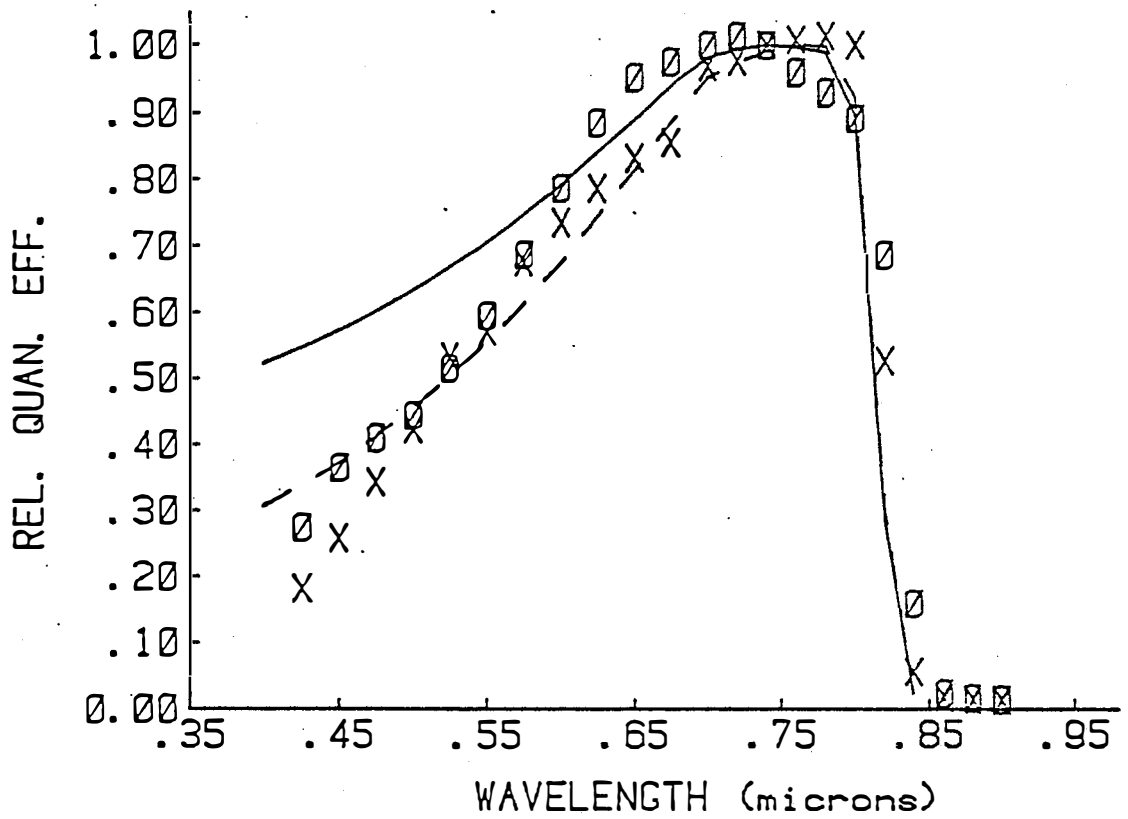
Figure 1. The relative quantum efficiency measured for homojunction
57 for indium strip contacts (X) and for an ITO
front contact (Ø). The solid curve was generated
by modelling a homojunction with a front layer thickness
of 0.15 μm and a depletion region of 0.2 μm. The dashed
curve was generated by 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
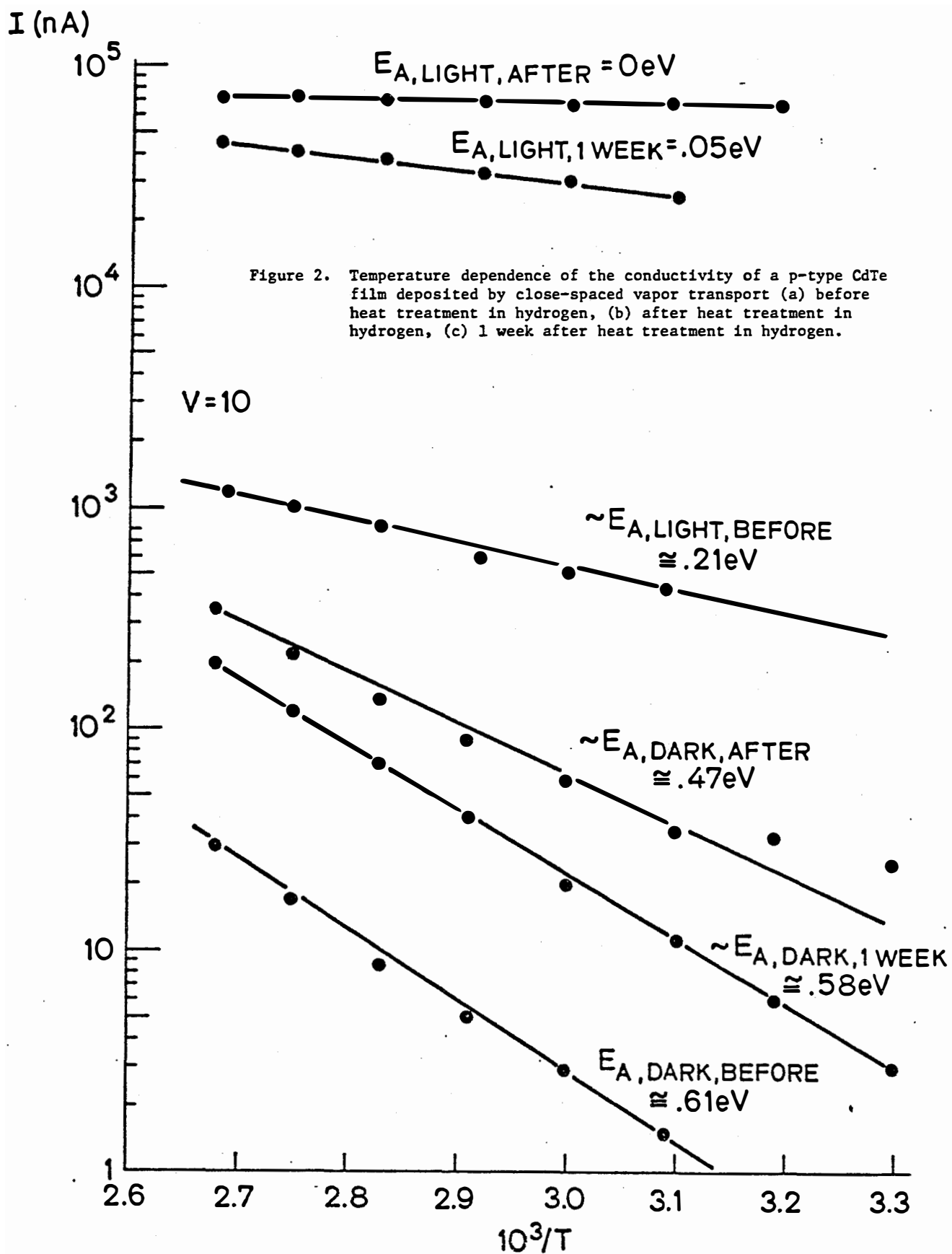devices of Report No. 7.
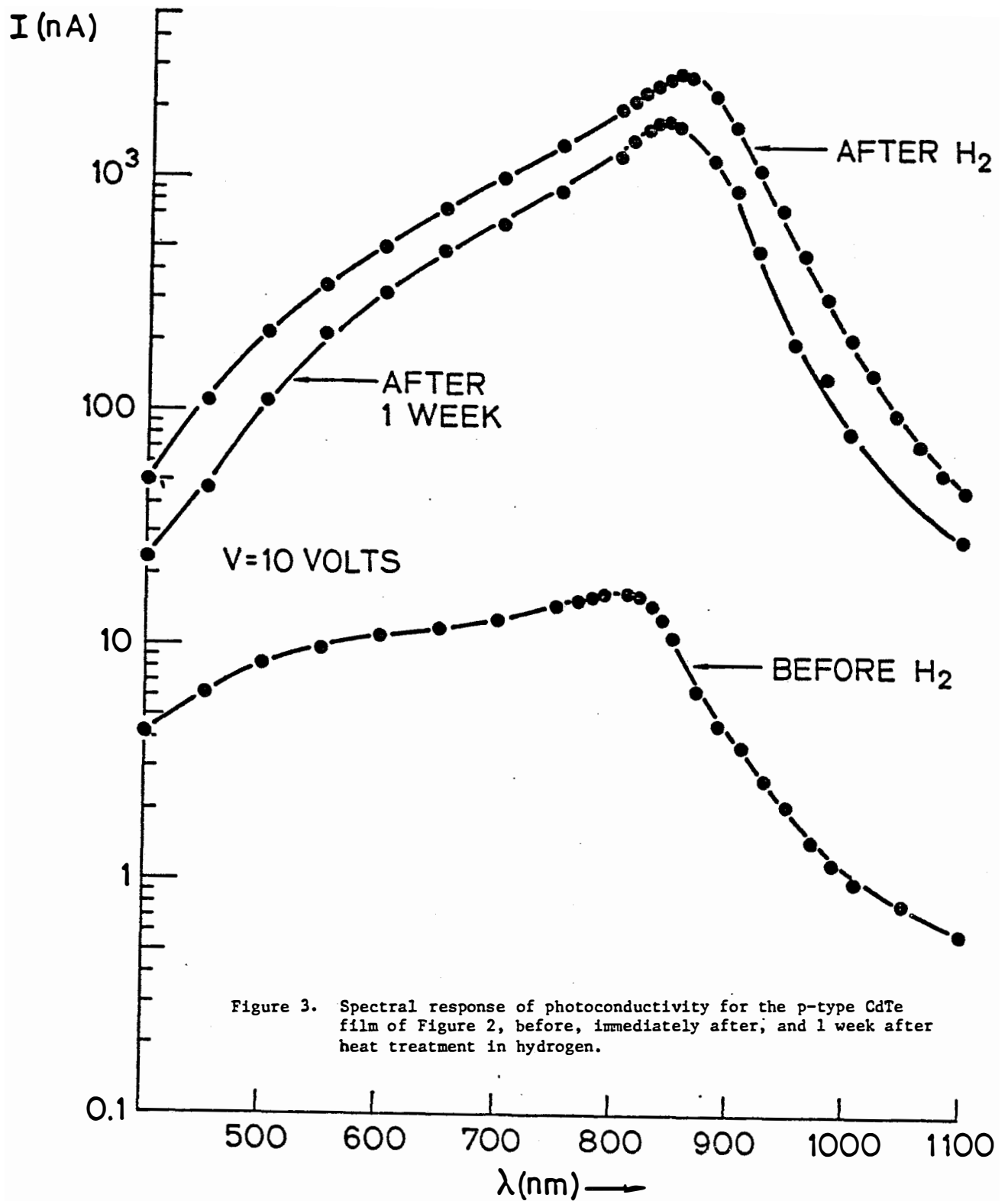
GRAIN BOUNDARY RESEARCH

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 H_2 at $500^{\circ}C$ for 5 min. This heat treatment produced a decrease in the room temperature dark resistivity from 4×10^7 ohm-cm to 9×10^5 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 10^3 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.

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
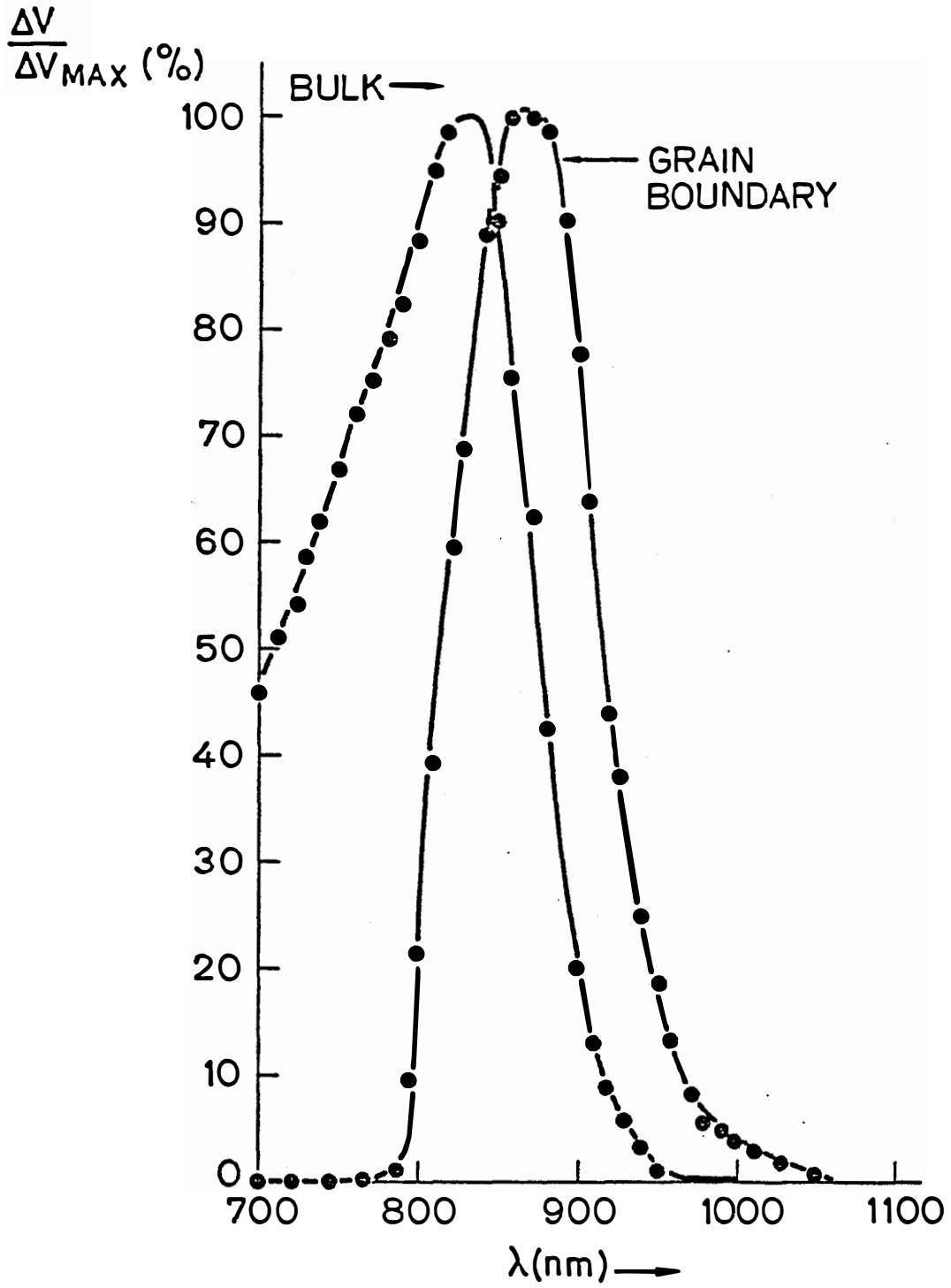
constant for the grain boundary than for the bulk.

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.