Progress Report No. 6

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

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ABSTRACT

Films of n-type CdTe:In have been deposited by hot-wall vacuum evaporation (HWVE) on 7059 glass substrates, BaF_2 single crystal substrates, metal (Pt, Cr, Mo, Al) coated glass substrates, and single crystal p-type CdTe substrates. Films deposited on 7059 glass show typically a dark resistivity of 2×10^5 ohm-cm and a light resistivity of 3×10^2 ohm-cm. With increasing In source temperature, the resistivity decreases, but actually increases slightly again if the T_{In} is raised above 600^oC. Photoexcitation increases the electron density but does not affect the electron mobility. It appears that the grains are depleted in the dark.

Films deposited on BaF_2 show dark resistivity of about 5 ohm-cm and light resistivity of about 2 ohm-cm, corresponding to electron densities of about 3×10^{16} cm^{-3} and electron mobilities of about 30 cm^2/V-sec. For doping levels above 10^{16} cm^{-3} photoexcitation increases the mobility, but not the electron density; it appears that the grains are not depleted in the dark in this case.

Cr coated 7059 glass makes an ohmic contact to n-type CdTe films. A Schottky diode formed with a 100A thick Au layer showed $V_{oc} = 0.46$ V, $J_{sc} = 9$ mA/cm^2 and a solar efficiency of about 2%.

An n/p homojunction device was made by HWVE deposition of a 1.5 μm thick n-type CdTe layer on a p-type CdTe single crystal substrate, reproducing the earlier cells made in this way in Linz. Values of $V_{oc} = 0.73$ V and $J_{sc} = 0.24$ mA/cm^2 (because of the thickness of the n-layer) were obtained. Modelling of the spectral response indicated $L_p = 0.28$ μm.

Grain boundary investigations showed the additive quality of two independent grain boundaries when measured in series, and tested the effects of "passivation" by Au, Cu, Li and H_2 in p-type CdTe grain boundaries, and In in n-type CdTe grain boundaries. Marked decreases in grain boundary resistance were observed after Li diffusion and H_2 diffusion in p-type CdTe.

INTRODUCTION

During this contract period the emphasis has been placed on growth and characterization of n-type CdTe:In films on various substrates in order to explore the effects of growth parameters on the photoelectronic and physical properties of the films. These films have been grown on substrates of 7059 glass, metal-coated 7059 glass, BaF_2 single crystals, and p-type CdTe:P single crystals. Although the principal thrust of our research is toward growth of polycrystalline films on amorphous substrates (such as glass or stainless steel), the analysis of such polycrystalline films is difficult. Since films grown on single crystal substrates have much larger grains with low angle grain boundaries, these are used as diagnostic tools to elucidate film properties that would otherwise be obscured by grain boundary phenomena. The most important of these properties are carrier density and diffusion length <u>inside</u> the grains. In many cases comparisons are made between films simultaneously grown on single crystal and amorphous substrates.

Low cost polycrystalline film solar cells will ultimately be deposited on glass, ceramic, or metal substrates. In the case of insulating substrates, a high conductivity layer that serves to collect current and to form the ohmic contact to the active layers must exist between the substrate and the CdTe film. To choose such a conductive layer or metal substrate, the following must be known: (1) the effects of the conducting layer on growth and properties of the film (i.e., growth rate, grain size, doping density, etc.); (2) chemical reactions between the conducting layer and the CdTe layer at the growth temperature; and (3) the ohmic character of the contact thus formed. Therefore growth on metal-coated 7059 substrates has been initiated to answer these questions. Thin metal films (59-110A) were used so that large-scale chemical reactions would be observable and thick films of the same metals were used to eliminate series resistance effects for electrical characterization.

A particular research project along this line was carried out with the participation of Professor Nicola Romeo, a visitor from the University of Parma, and an authority on grapho-epitaxy. Thin CdTe films were deposited on Sb-Bi alloy films deposited on tantalum substrates. Grain sizes of the order of 20 μm were achieved. A manuscript has been submitted to the Journal of Vacuum Science and Technology, and a copy of this manuscript is included as an Appendix to this report.

Measurements of the electrical properties of grain boundaries in large grain single crystal material (bicrystals) are being continued to (1) provide input for modeling of the electrical transport in thin polycrystalline films, and (2) give information on possible grain boundary passivation methods.

HOT WALL VACUUM EVAPORATION OF n-TYPE CdTe:In LAYERS

CdTe Films on 7059 Glass Substrates

1. Growth

The growth conditions are listed in Table I. The CdTe source temperature was maintained at 575°C for all the films grown. The indium source temperature was varied between 540° and 680°C. Films were grown either under excess Te or excess Cd (T_{Cd} = 205-245°C; T_{Te} = 360°C). Substrate temperatures T_s in the range of 430° to 510°C were used. Above T_s = 480°C film nucleation and growth did not occur. The growth rate was typically of the order of 7 μm/h. The typical grain size is approximately 1 μm and X-ray diffractometer measurements indicate no preferential orientation of the grains. Microprobe analyses of these films indicate good stoichiometry and spectrophotometer traces show the expected optical transmission spectra.

2. Electrical Properties

The electrical characteristics of some representative samples are listed in Table II. Contacts of In were evaporated onto these films and the resistivity was measured using a four-point method. The dark resistivity varied between 10^8 and 10^5 ohm-cm for indium source temperature T_{In} between 540° and 680°C. Illumination with simulated AM1.5 sunlight caused the resistivity to drop by orders of magnitude with the lowest observed value being 225 ohm-cm. This is quite adequate for a solar cell absorber layer with complete coverage by the ohmic contact. The resistivity varies exponentially with 1/T with an activation energy ΔE. Dark values of the activation energy are between 0.79 and 0.48 eV, while illumination reduces the activation energy to 0.1 eV or less for all these films.

The variation of the electrical properties with excess Te or Cd was also examined. The results (shown in Table II) give no clear indication

TABLE I

Growth Conditions for CdTe Films

Film #	Substrate	T_{CdTe}, ^{o}C	T_{In}, ^{o}C	T_{Cd}, ^{o}C	T_{Te}, ^{o}C	T_{s}, ^{o}C	t, μm	Growth Rate, μm/h
1	7059 glass	575	540	-	360	430	2.0	8.0
2	7059 glass	575	540	-	360	470	2.0	8.0
3	7059 glass	575	540	-	360	510	0	0
4	7059 glass	575	540	-	360	480	0	0
5	7059 glass	575	540	245	-	430	3.0	12.0
6	7059 glass	575	540	245	-	470	0	0
7	7059 glass	575	630	245	-	450	1.3	5.2
8	7059 glass	575	680	245	-	450	2.1	6.3
9A	7059 glass	575	680	250	-	450	0.9	6.8
9B	p-CdTe crystal	575	680	250	-	450	1.5	11.3
10B	7059 glass	575	590	245	-	450	1.8	5.4
11B	7059 glass	550	590	245	-	450		
12A	7059 glass	575	590	245	-	450	1.6	1.9
12B	Pt/7059 glass	575	590	245	-	450	1.6	1.9
13	7059 glass	575	590	205	-	450	1.8	5.4
14	7059 glass	575	590	220	-	450	2.5	7.5
19A	Pt/7059 glass	560	561	250	-	470		
19B	Cr/7059 glass	560	561	250	-	470		
20A	Mo/7059 glass	565	561	250	-	470	0	0
20B	Cr/7059 glass	565	561	250	-	470		
21B	Cr/7059 glass	561	510	245	-	480		
22	Al/7059 glass	570	581	250	-	455		
23	Al/7059 glass	575	575	250	-	455		
24	Al/7059 glass	525	525	250	-	455		
26	Cr/7059 glass	570	590	250	-	470		

TABLE II

Electrical Properties of Representative CdTe Films on 7059 Glass at 300°K

Film #	Resistivity, ohm-cm Dark	Resistivity, ohm-cm Light (AM 1.5)	Activation Energy of Resistivity, eV Dark	Activation Energy of Resistivity, eV Light (AM 1.5)
1	3.3×10^8	3.5×10^4		
2		2.3×10^4		
5	1.7×10^8	2.0×10^4	0.79	0.10
7	6×10^4	5.0×10^2	0.48	0.08
8	1.6×10^5	1.8×10^3	0.40	
9	5.5×10^5	6.3×10^2		
10	7.0×10^4	2.2×10^2	0.48	0.05
12	2.1×10^6	6.4×10^2	0.56	0.04
12	2.1×10^5	3.3×10^2	0.49	0.04
14	4.2×10^5	5.8×10^2	0.48	

of the influence of the Te or Cd source for an In source temperature of 540°C. A simple calculation shows that the Cd and Te pressures supplied by the CdTe source are of the same order of magnitude as the vapor pressure of the excess Cd or Te sources at 245° and 360°C respectively. Therefore a lowering of the excess element source temperature should not result in a strong variation of the vapor species above the substrate.

The film resistivity as a function of the indium source temperature is plotted in Figure 1. The resistivity has a plateau for T_{In} of about 600°C, and further increase of T_{In} does not result in a reduction of the resistivity.

Hall effect measurements indicate carrier densities of 10^{11} cm^{-3} in the dark. Figure 2 shows a plot of the electron density and mobility as a function of layer resistivity under varying light intensity. The mobility is not changed by illumination, whereas the electron density changes by orders of magnitude. It may be concluded, therefore, that the photoconductivity of these CdTe films on glass results entirely from a change in the density of free electrons.

CdTe Films on BaF_2

1. Growth

The purpose of the growth of CdTe layers on BaF_2 substrates was to obtain large grain CdTe films and to compare the electrical properties of these films with those grown on 7059 glass substrates.

The films were grown on air-cleaved (111) BaF_2 substrates. BaF_2 is an insulator with high optical transmission in the visible range, a lattice constant of 6.2A compared to 6.48A for CdTe, and a thermal expansion coefficient three times larger than than of CdTe.

The growth conditions are listed in Table III. The substrate temperatures used are in the range 450-480°C, while typical CdTe source

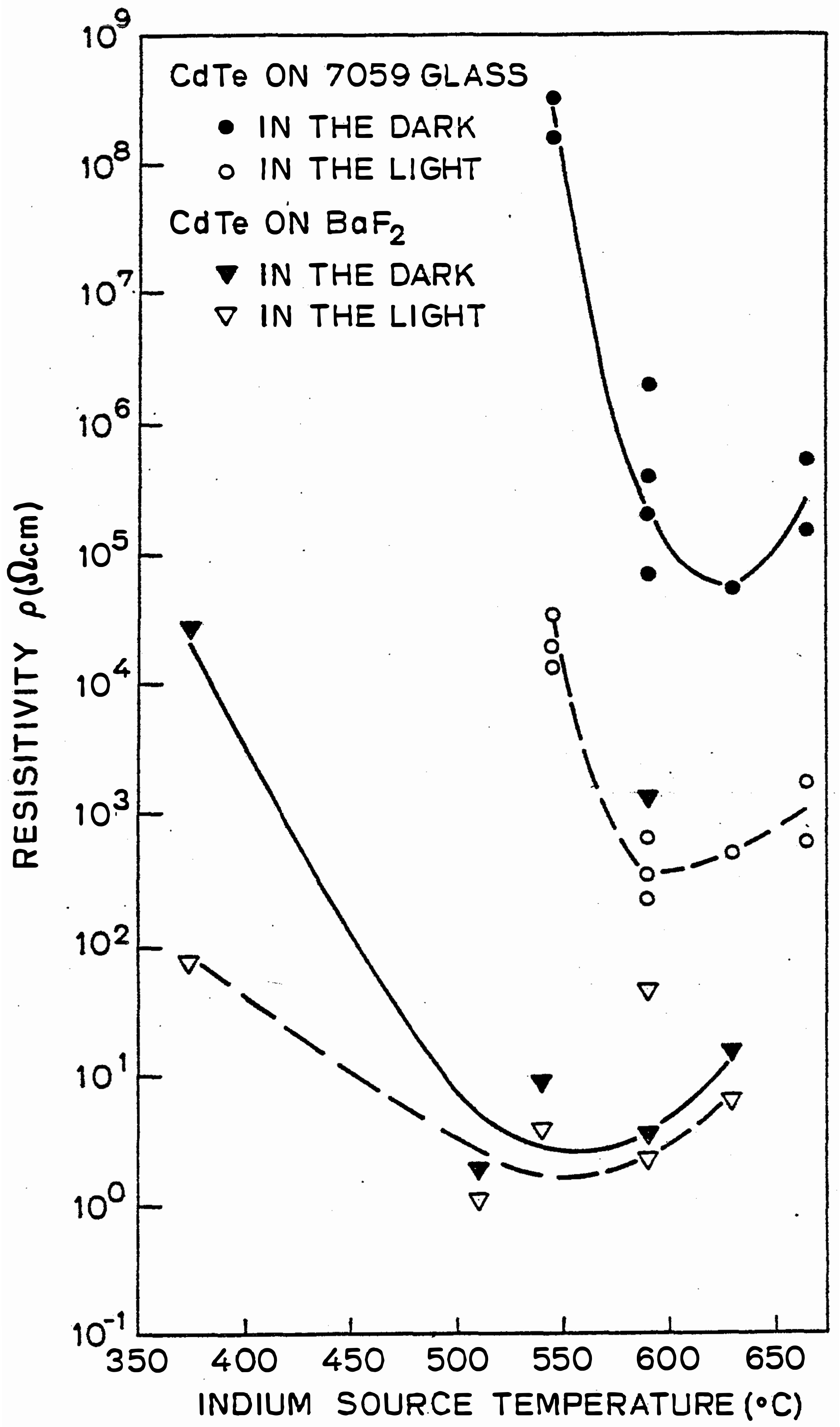

Figure 1. The dark and light resistivity of CdTe films grown on 7059 glass substrates, and on single crystal BaF$_2$ substrates as a function of the temperature of the indium reservoir T .

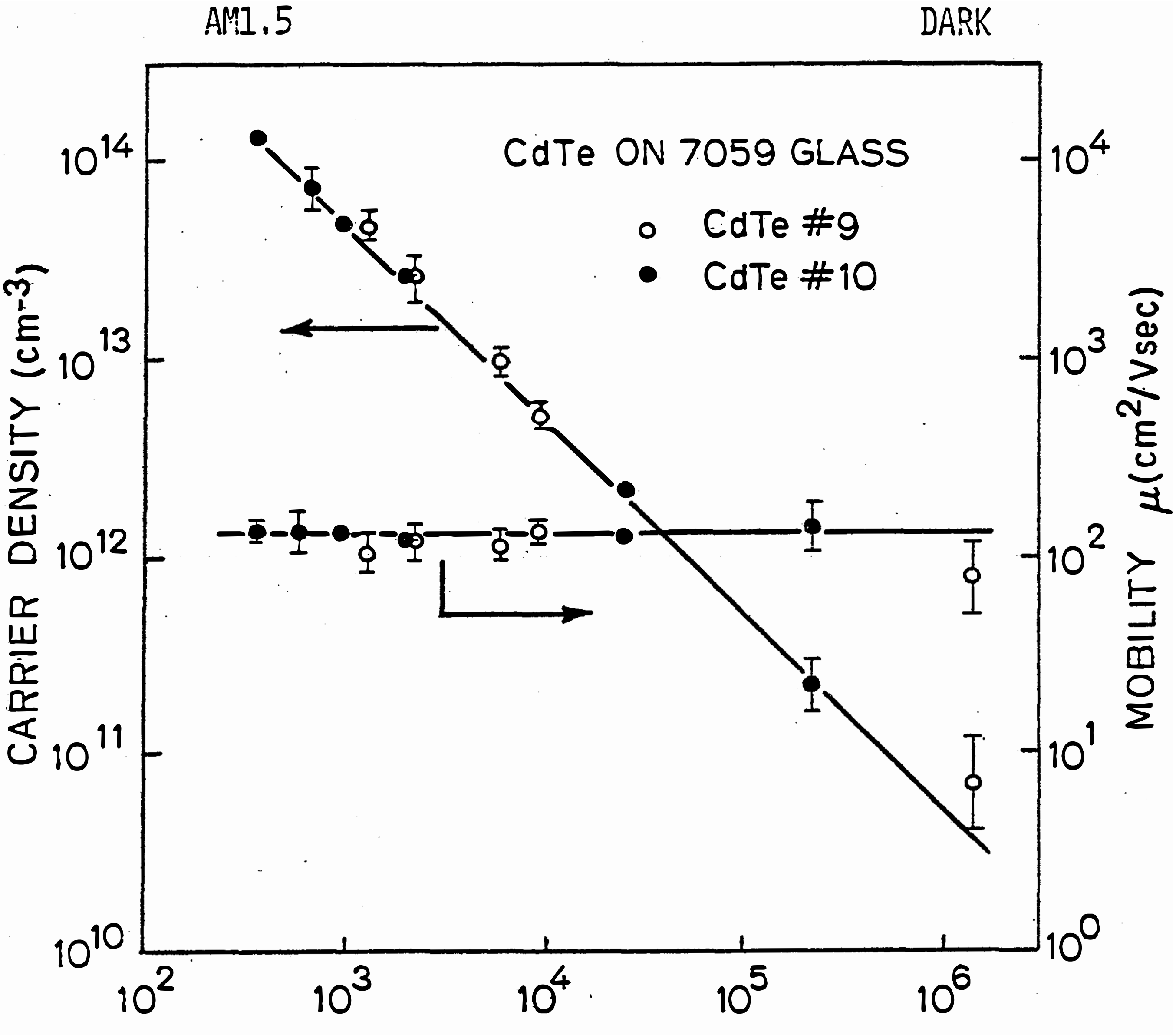

Figure 2. Variation of the electron density and mobility under optical excitation for CdTe films grown on 7059 glass substrates.

TABLE III

Growth Conditions and Characteristic Properties of CdTe Films on BaF_2 Substrates

Film #	T_{CdTe}, °C	T_{In}, °C	T_{Cd}, °C	T_s, °C	t, μm	Growth Rate, μm/h	Resistivity, ohm-cm[a]		Hall Measurements		
							Dark	Light(AM1.5)	ρ,ohm-cm	n,cm^{-3}	μ_n,cm^2/V-sec
10A	575	590	245	450	1.8	5.4	1400	47			
11A	550	590	245	450	0	0					
15	560	630	245	480	1.15	1.15	16	6	12.3	$1.7x10^{16}$	30
16	560	590	245	480	0.92	0.6	3.5	2.1	3.3	$3.9x10^{16}$	48
17	562	540	245	480	2.3	1.4	9.1	3.8	10.0	$3.0x10^{16}$	21
18	562	510	245	480	1.1	0.7	1.8	1.1	0.7	$1.0x10^{17}$	86
21	561	510	245	480	0[b]	0					
25	562	374	245	480	0.84	0.5			$2.9x10^4$	$2.5x10^{15}$[c]	35[c]

[a] Measured by four-point probe method.

[b] Deposition occured, but film peeled off after growth.

[c] These values were obtained from photo-Hall effect measurements under illumination.

temperatures were 550-575°C. The Cd reservoir temperature was maintained at 245°C, and the In temperature was varied between 374° and 630°C.

For the typical surface morphology of CdTe layer growth at T_s = 480°C, as shown in Figure 3, one observes a featureless background with shallow pyramids arising from it. These pyramids originate from defects in the crystal.[1] The distribution of the pyramids over the film surface is nonuniform and the layers of the pyramids are typically in the range of 30 μm. X-ray diffractometer measurements indicate a potential orientation of the grains in the (111) direction. BaF_2 has a cubic structure and the cleaved surface is (111) oriented.

2. Electrical Properties

The electrical properties of these films were obtained using a four-point measurement for resistivity and the Van der Pauw geometry for Hall measurements. The results are summarized in Table III. Both methods give the same result for the resistivity. The resistivity changes from 10^4 to 1 ohm-cm with T_{In} between 320° and 630°C, as also shown in Figure 1. The variation of the resistivity for T_{In} greater than 500°C is similar to that for the CdTe layers grown on 7059 glass substrates. The change of resistivity for the low-resistivity films under illumination is much less pronounced than for the CdTe samples on glass substrates.

The resistivity of film #10A grown on BaF_2 simultaneously with a film #10B on 7059 glass at T_s = 450°C, is more than an order of magnitude lower than for sample #10B. On the other hand, a film grown at T_s = 480°C and at the same indium temperature (e.g., film #16) had an even smaller resistivity than sample #10A. The resistivity of film #10A varies with temperature according to an activation energy of 0.25 eV in the dark, compared with an activation energy of 0.06 eV for a film deposited at T_s = 480°C (e.g., film # 15). These results show

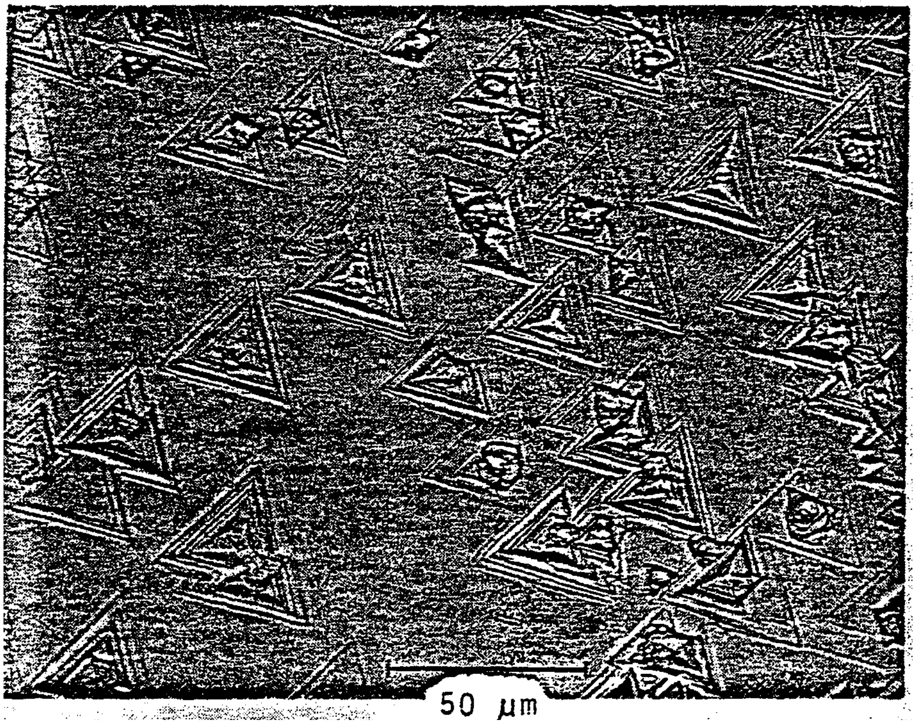

Figure 3. Surface morphology of a CdTe film grown on BaF_2 at T_s = 480°C and a growth rate of 1.4 μm/h. Magnification: 500X

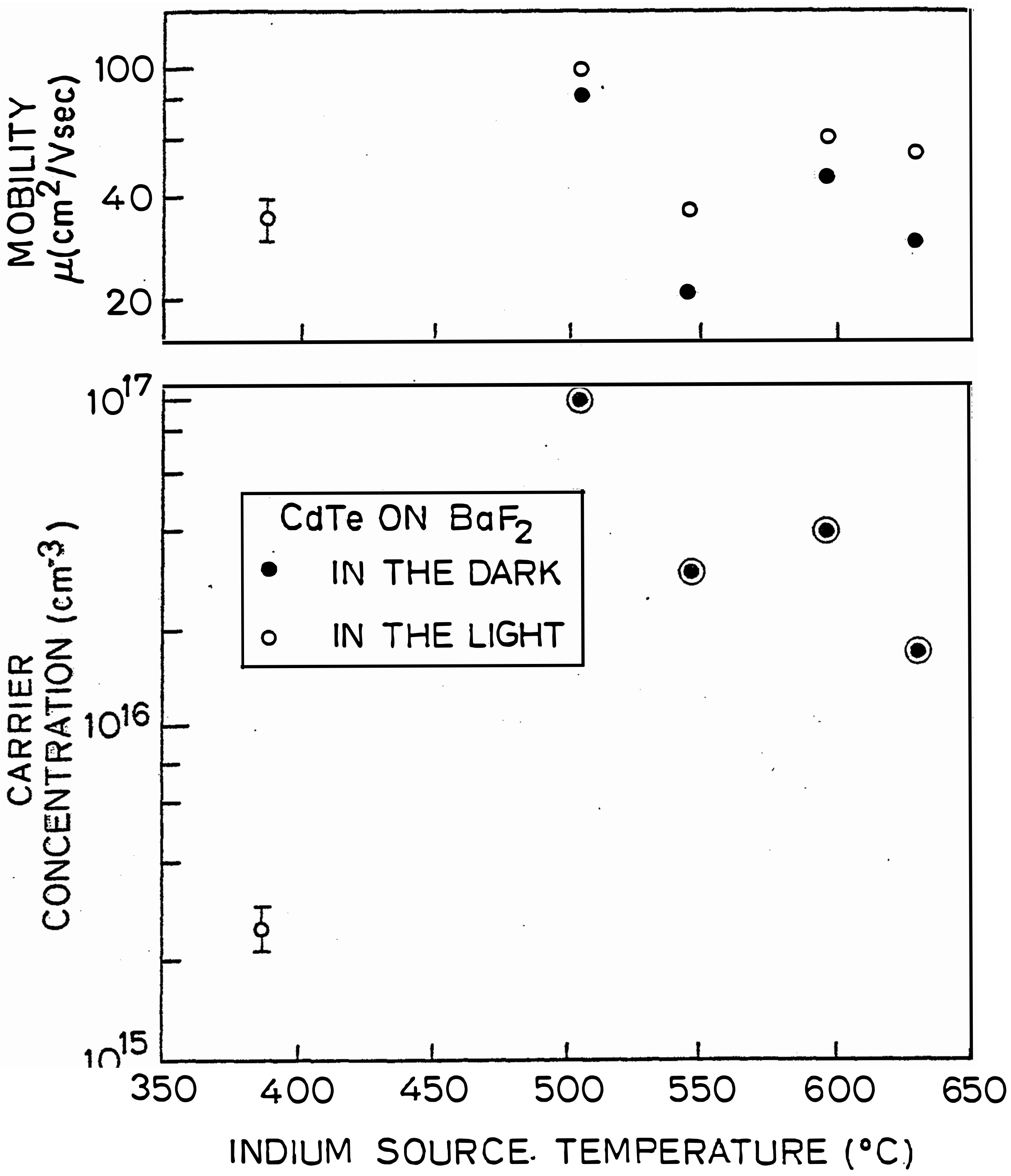

Figure 4. (a) The electron mobility, and (b) the electron density of CdTe layers on BaF_2 as a function of the indium source temperature T_{In}. The solid dots are dark measurements and the open circles are measurements under 80 mW/cm^2 of white light.

that the grain boundary effects are more pronounced in this sample than for films grown at a higher substrate temperature.

The electron density and mobility as a function of T_{In} are shown in Figure 4. We were unable to measure the dark value of the electron density for the most photosensitive sample (#25) grown at T_{In} = 374°C. By varying the light intensity one observes a change in the mobility, but no change in the electron density. We assume, therefore, that the experimental point for sample #25 represents also the electron density in the dark.

For doping levels above 10^{16} cm^{-3} the density of electrons does not change with illumination, whereas the mobility increases. The electron density in CdTe #18 was also determined from capacitance vs voltage data for a Au Schottky barrier, and is in good agreement with the Hall measurement. Electron densities above 10^{16} cm^{-3} for T_{In} greater than 500°C were also found in the earlier research on hot-wall vacuum evaporation of CdTe films at Linz.

Qualitative Electronic Transport Model for Polycrystalline n-type CdTe Films

Although the CdTe layers on glass and on BaF_2 were grown at similar indium temperatures, the electron density differs by several orders of magnitude (10^{11} cm^{-3} on glass compared to 10^{16} cm^{-3} on BaF_2). This result can be explained by the grain boundary transport proposed by Seto[2] and Baccarani.[3] These authors showed that the grains in small grain size films (such as CdTe on 7059 glass) can be completely depleted, and the density of free carriers is reduced by orders of magnitude. On the other hand, the carrier density in large grain films (such as CdTe on BaF_2) approaches the bulk doping density.

Illumination modulates the density of trapped charge at the grain boundaries. For layers with completely depleted grains, the increase in conductivity with illumination can result almost entirely from an

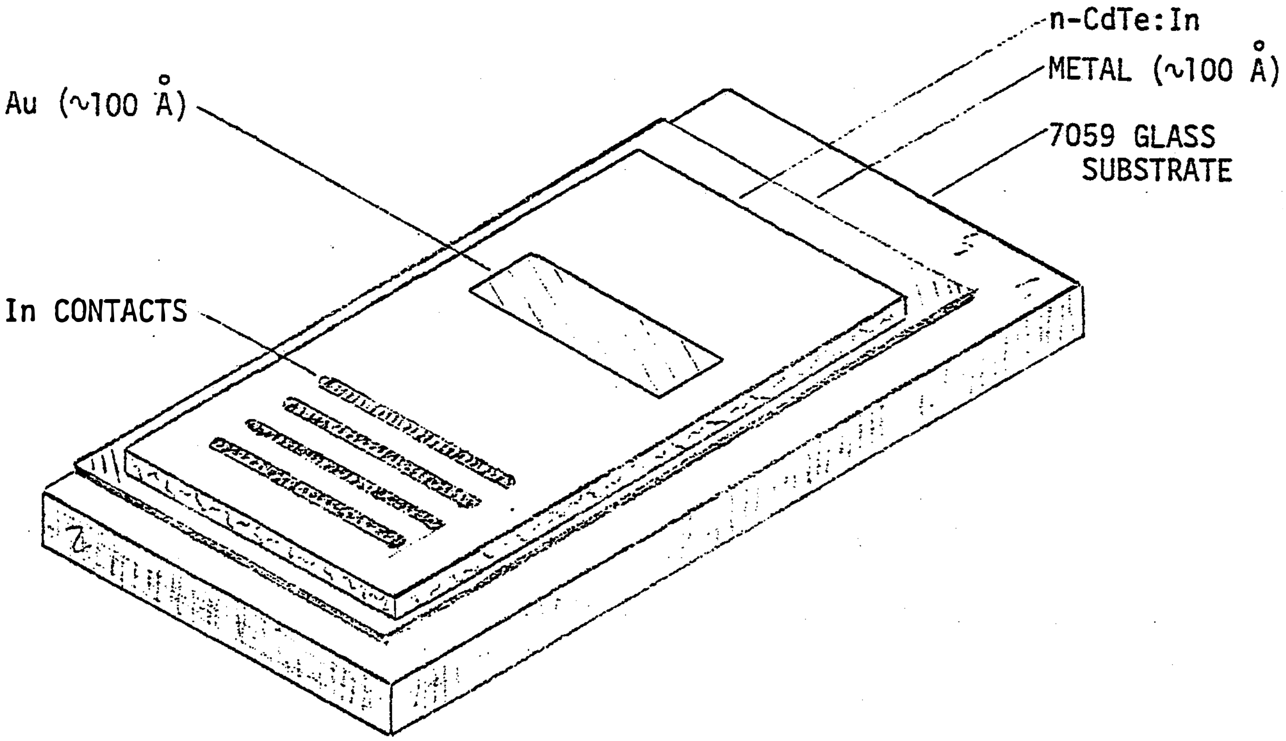

Fig. 5 . Geometry of devices fabricated on metal-coated 7059 glass.

increase in the carrier density, whereas in the case of partly depleted grains the modulation of the grain boundary barrier height changes the mobility.[4] This is in agreement with our experimental results.

A more quantitative electrical transport computer model for polycrystalline CdTe films is being formulated.

CdTe Films on Metal/7059-Glass Substrates

Films of CdTe:In were deposited on substrates of metal-coated 7059 glass in order to observe the effects on film growth and to determine the feasibility of ohmic back-contact formation. The substrates were prepared by deposition of films of Pt, Cr, and Mo on 7059 glass substrates by electron beam evaporation. Thin metal films, 50 to 100A thick, were chosen so that: (1) large scale chemical interactions between metal and CdTe would be directly observable, and (2) illumination of the CdTe through the metal film would be possible. Thicker films, greater than 5000A, were used for electrical characterization when series resistance was a problem.

The growth parameters of these CdTe films are included in Table I. Samples with metal-coated glass substrates were grown at higher substrate temperatures (470°C), allowing comparison of these films with those grown under similar conditions on BaF_2. The interaction energy between CdTe and Cr or Pt appears to be larger than that of either Mo/7059 or 7059 alone, since no deposition occurred on the latter substrates at 470°C.

The n-CdTe:In layers were greater than 1 μm thick and appeared to be extremely uniform; these films had a grain size of 1 to 2 μm and a grain structure similar to samples grown on 7059 glass without metal. There did not appear to be any appreciable diffusion of the subtrate metal into the CdTe layer or chemical reaction, since the thin metal layers remained bright and without defects.

Strip contacts of In were applied (Figure 5) to serve as ohmic contacts and thin (100A) Au dots with area of 3 mm^2 were applied to the top surface of the CdTe grown on the Cr-coated substrates to serve as diagnostic diodes. The Cr-coated 7059 substrates are the most completely characterized to date. The In strips made ohmic contact to the n-CdTe:In as expected. Measurements of resistivity through the film using the top In contacts and the back Cr contact (which proved to be a low resistance contact) yielded an upper bound for the bulk n-CdTe resistivity of 1.3×10^4 ohm-cm in the dark (without accounting for any possible contact resistance).

The dark log J vs V plot for sample #19 is shown in Figure 6; the values of A and J_o are 2.1 and 5×10^{-6} A/cm^2 respectively. Light and dark I vs V plots are shown in Figure 7. The 100A Au layer forming the junction barrier absorbs 30 to 50% of the incident light. The measured values for J_{sc} and V_{oc} at an illumination of AM 1.5 are 9 mA/cm^2 and 0.46 V respectively. The measured value of V_{oc} is in reasonable agreement with the value calculated from

$$V_{oc} = \frac{A\,kT}{q} \ln\{(J_{sc}/J_o) + 1\} \qquad (1)$$

which yields a value of 0.41 V. The fill factor is 0.41 and the solar efficiency was 1.9% for this cell. Samples #19 and #20, grown under similar conditions, showed almost the same photovoltaic parameters.

Capacitance vs voltage measurements at 10 kHz on sample #19 yielded a barrier height of 0.42 V and a carrier density of 10^{15} cm^{-3} as indicated in Figure 8.

Two aspects of the electrical characteristics of this Au/CdTe junction (#10) suggest that it is more complex than a simple Schottky diode. First, the diode factor is 2.2, rather than the value of 1.0 as expected for a simple Schottky diode. Second, the V_{oc} is larger than the barrier height measured by C-V techniques. This suggests the presence of a thin insulating layer between the Au and the n-CdTe:In film and/or the involvement of considerable depletion region recombination

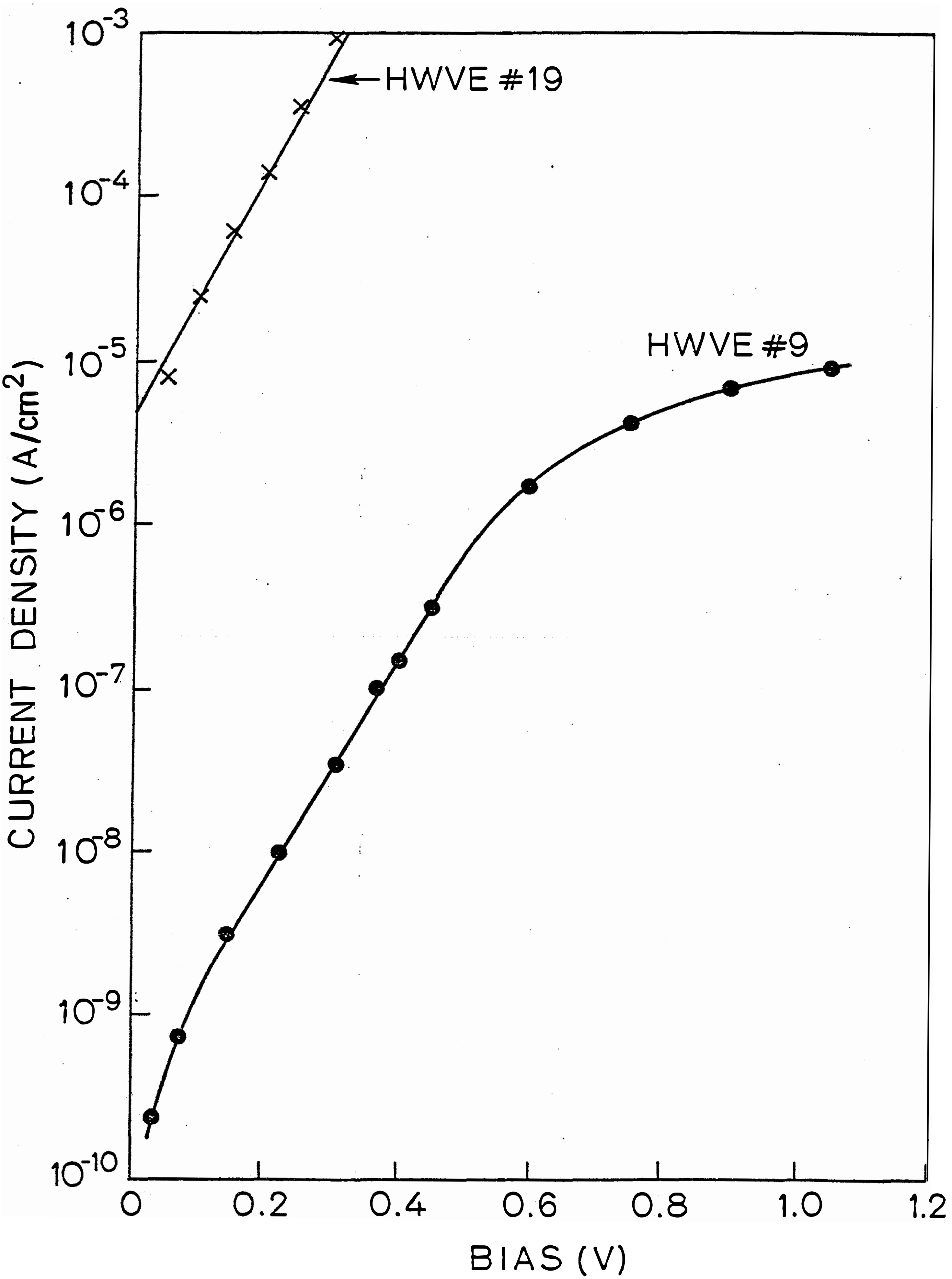

Figure 6. Dark J-V characteristics for an n/p homojunction (HWVE #9) and

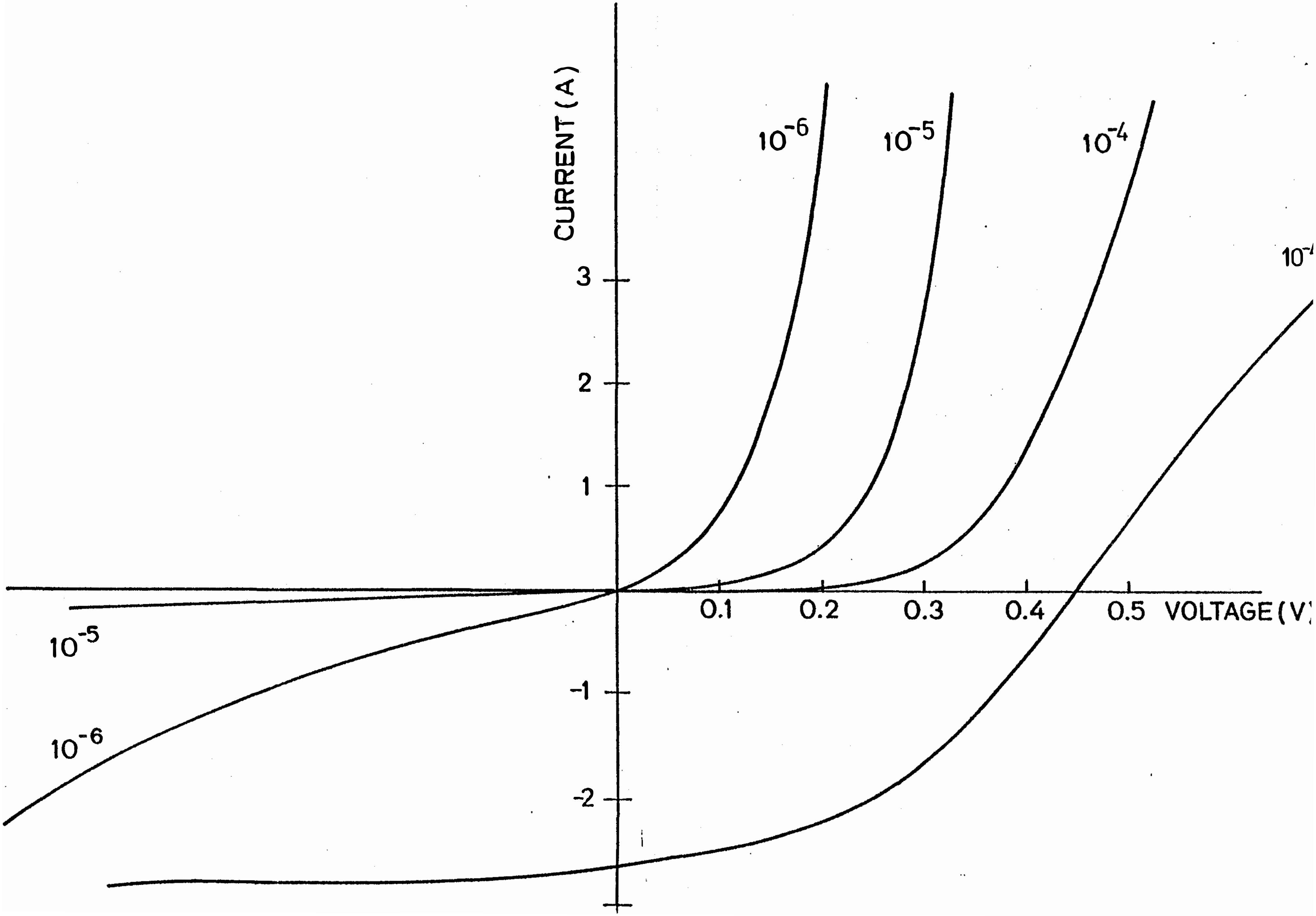

Figure 7. Dark and light (AM 1.5) I-V characteristics for Au/n-CdTe(HWVE #19). Area = 3 mm^2. V_{oc} = 0.46 V, J_{sc} = 9 mA/cm^2, ff = 0.41.

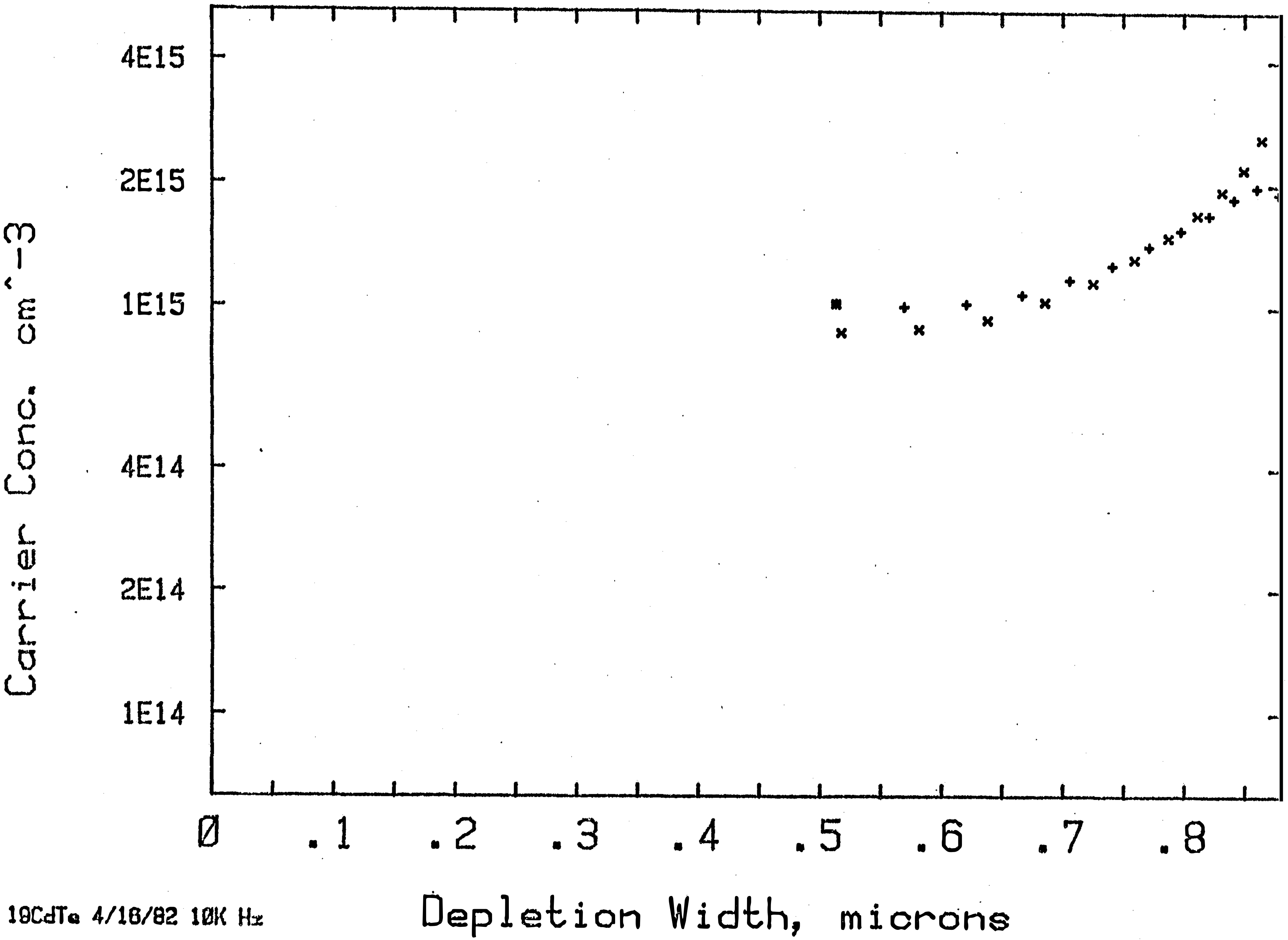

Figure 8. Electron density vs depth for

in the junction transport.

Through the film resistivity measurements made on n-CdTe:In on a Pt(50A)-coated 7059 glass substrate indicated that the Pt alo makes a relatively low resistance contact, although with some rectifying characteristics. Au/n-CdTe/Pt diodes proved difficult to characterize due to the large series resistance of the thin Pt layer, however.

Four samples (HWVE #22, #23, and #24A and B) were grown on Al coated 7059 glass substrates (1.3 μm Al deposited by rf sputtering). Samples #24A and #24B were prepared on substrates that had been annealed in a partical pressure of Cd (10^{-2} mm Hg) for 45 minutes in situ prior to the n-CdTe:In deposition. The Cd partial pressure anneal was used to prevent the diffusion of Cd from the growing n-CdTe:In film into the aluminum[5] by saturating the Al with Cd. In all cases (#23, 24A and B) either a very resistive contact or a diode was formed. Diodes between the Al-coated 7059 substrate and the n-CdTe:In had A factors of about 3.

The formation of a low resistance contact between Cr and n-CdTe:In is expected since the indicated barrier height (using a work function of 4.5 eV for Cr) is only 0.1 to 0.2 eV. However, the formation of a low resistance contact to Pt is quite unexpected since a barrier height of 1.3 eV is calculated, and other workers have measured barrier heights of 0.6 to 0.7 eV (usually slightly larger than the Au/n-CdTe barrier). Similarly the high resistance and/or diode contacts formed when n-CdTe is deposited on Al are surprising. The work function of Al indicates a barrier height of less than 0.1 eV; in addition Al is an n-type dopant in CdTe. These results, although quite preliminary, suggest either than the out-diffusion of Cd forms an insulating region in the CdTe adjacent to the Al or that a compound (e.g., Al_2Te_3, a semiconductor with bandgap of about 2.5 eV) forms between the Al and the n-CdTe at high growth temperatures.

DEVICES: n-CdTe:In LAYERS ON p-CdTe:P SINGLE CRYSTAL SUBSTRATES

In previous Progress Reports results were reported on n/p homojunctions formed by HWVE deposition of n-CdTe:In layers at Linz, Austria, on p-CdTe:P single crystal substrates supplied by Stanford. In order to reproduce and refine these results, similar devices were made by deposition with the Stanford HWVE system. The properties of these junctions, with thinner n-type layers, show good agreement with spectral response modeling and provide estimates of the minority carrier diffusion length L_p in these materials.

A large-grain (3 to 5 mm) polycrystalline p-CdTe:P substrate was prepared by mechanical polishing and then etching a 1 mm thick wafer with a 5% Br:MeOh etch. The growth conditions for the film on this substrates (sample #9) were chosen to be similar to samples #1 through #8 grown on 7059 glass, thus providing a large grain epitaxial thin film material with which the small grain (0.5 to 1 μm) films on 7059 glass could be compared (Figure 9).

Ohmic contacts to the n-CdTe film were fabricated by the deposition of In stripes by vacuum evaporation followed by annealing in H_2 for 10 minutes to finish the contacting. Then Cu:Au alloy contacts were deposited on the surface of the p-CdTe previously etched with $H_2SO_4:K_2Cr_2O_7:H_2O$, thus forming ohmic contacts to the p-side of the cell.

The bulk resistivity of the grown n-CdTe:In layer was 2500 ohm-cm in the dark and 2.5 ohm-cm under simulated AM 1.5 solar illumination. For comparison, the resistivities of samples grown on glass under similar conditions were 3×10^5 ohm-cm in the dark, and 10^3 ohm-cm in the light.

Dark log J vs V measurements (Figure 6) reveal normal diode behavior with an A factor of 2.3 and $J_o = 3 \times 10^{-10}$ A/cm^2. Under simulated AM 1.5 illumination, the values of V_{oc} and J_{sc} were 0.73 V and 0.24 mA/cm^2

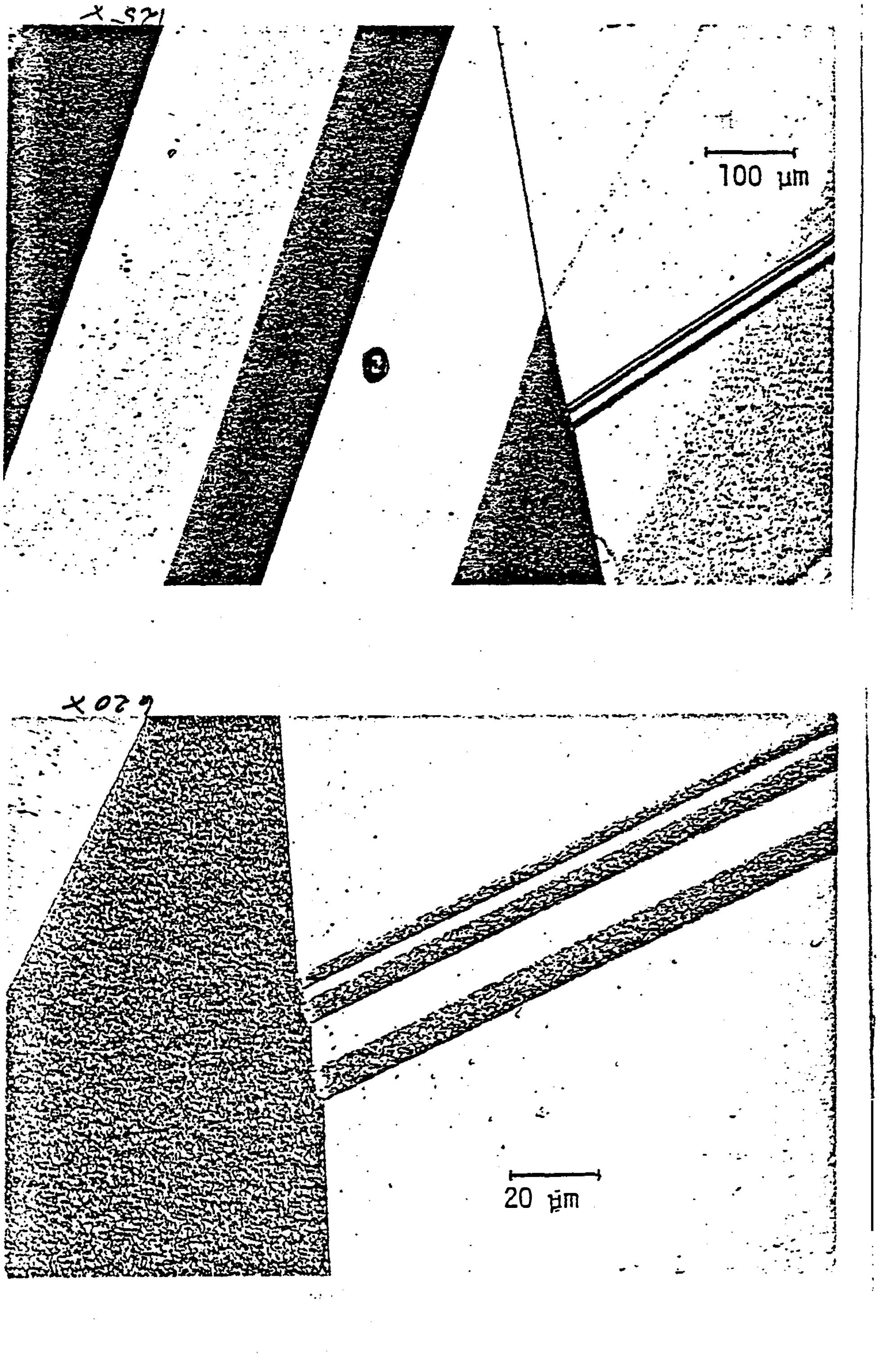

Figure 9. Optical micrographs of n-CdTe layer grown on a p-type single crystal CdTe substrate (HWVE #9).

respectively (Figure 10). The low fill factor is characteristic of the large series resistance of the film (about 5 times larger than that required for negligible R_s loss for this grid spacing). and the effect of a bias-voltage dependent light-generated current.

A laser scan of sample #9 provided by the Institute of Energy Conversion at the University of Delaware (Figure 11) shows the region of the front contact strips and a defect (grain boundary). The scan was taken with the diode in reverse bias (1 V) to amplify the collection features of the device. The defects are also apparent with zero applied bias. The laser scan is sensitive only to n-layer properties since the film thickness (1.5 μm) is much larger than the optical absorption length for the laser light (6228A) used (0.2 μm).

A grain boundary present in the CdTe substrate is reproduced in the HWVE grown n-layer (Figure 11) and is apparent as a resistive drop in the collection features of the laser scan. The n-layer collection region is seen to be rather small, in agreement with the high series resistance observed for this diode.

The spectral response measurement for this device was compared to those obtained by a theoretical model based on the equations found in Hovel's book.[6] The parameters chosen for the spectral response model were as follows: surface recombination velocity at the front surface, $S = 10^6$ cm/sec; thickness of the n-layer (junction depth), 1.5 μm; mobility of holes and electrons, 39 cm^2/V-sec and 100 cm^2/V-sec, respectively; depletion layer width, 0.1 μm; and diffusion length of the holes in the front layer L_p was taken as the major variational parameter in the modeling. As can be seen from Figure 12, the diode described above has a large sensitivity to the value of L_p with the quantum efficiency values for a diode with $L_p = 0.5$ μm being significantly larger than those for a similar diode with $L_p = 0.28$ μm. The model of a diode with $L_p = 0.28$ μm yielded an extremely good fit to

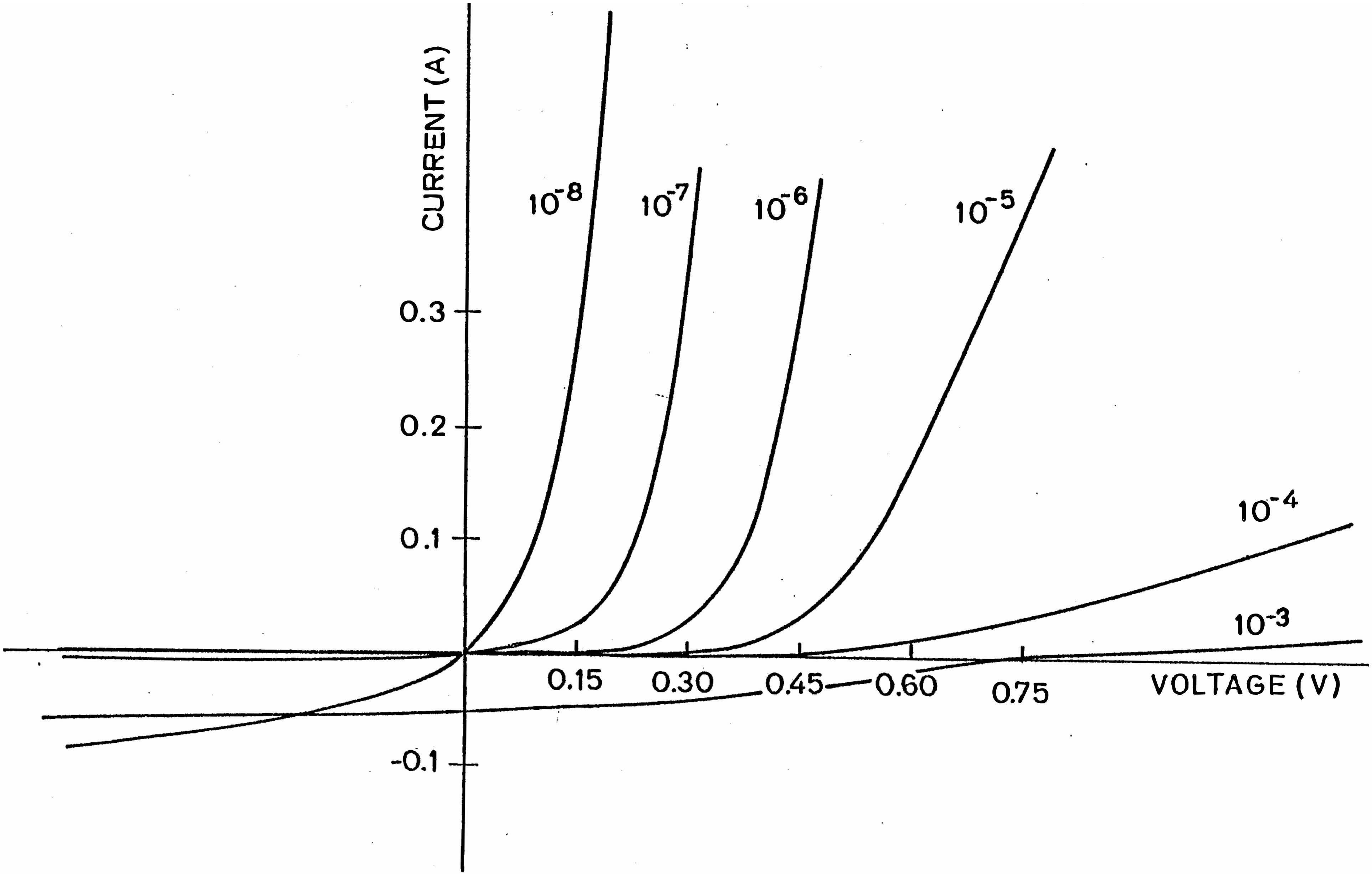

Figure 10. Dark and light (AM 1.5) I-V characteristics for an n/p homojunction CdTe (HWVE #9). Area = 0.25 cm^2. V_{oc} = 0.73 V, J_{sc} = 0.24 mA/cm^2, A = 2.3.

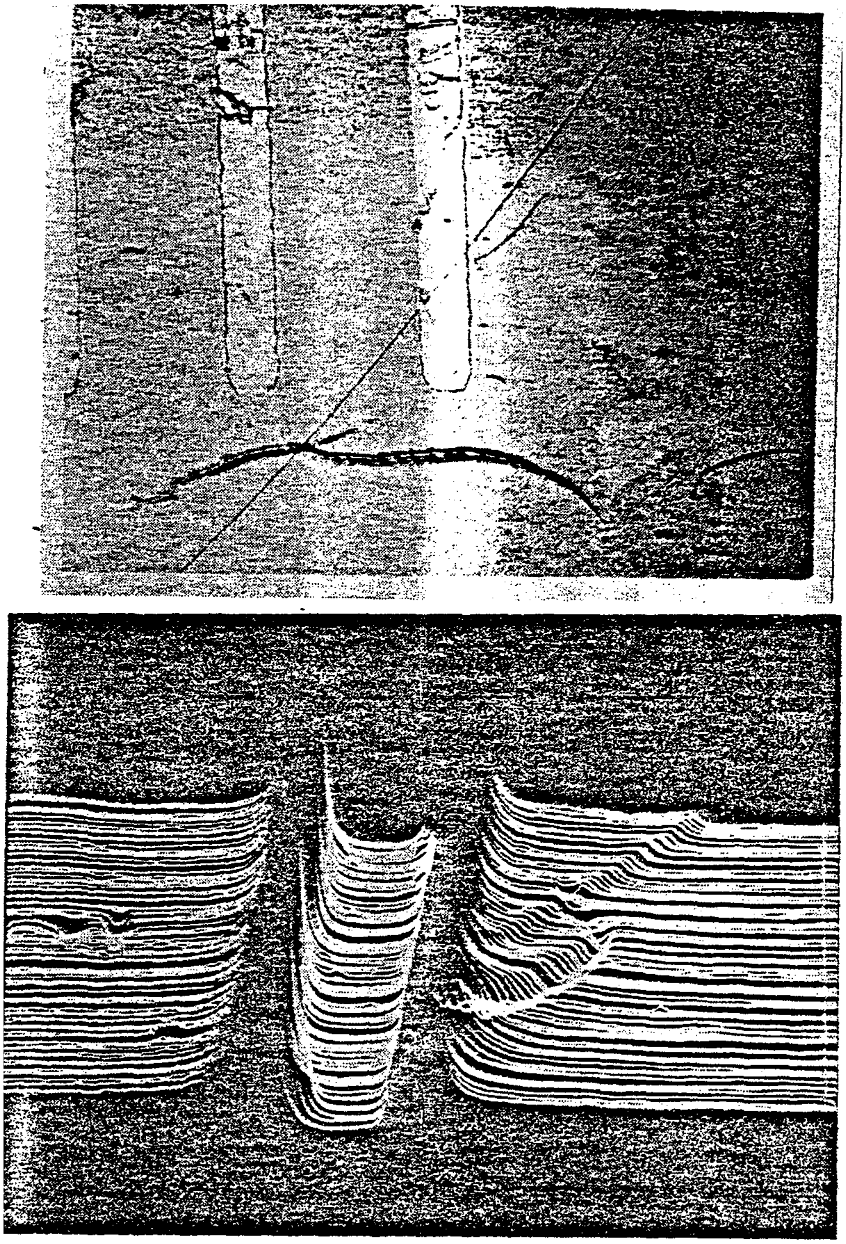

Figure 11. Laser scan of n/p homojunction (HWVE #9) in the region of a grain boundary seen in the optical micrograph. This grain boundary appears to be a simple resistive barrier to current collection.

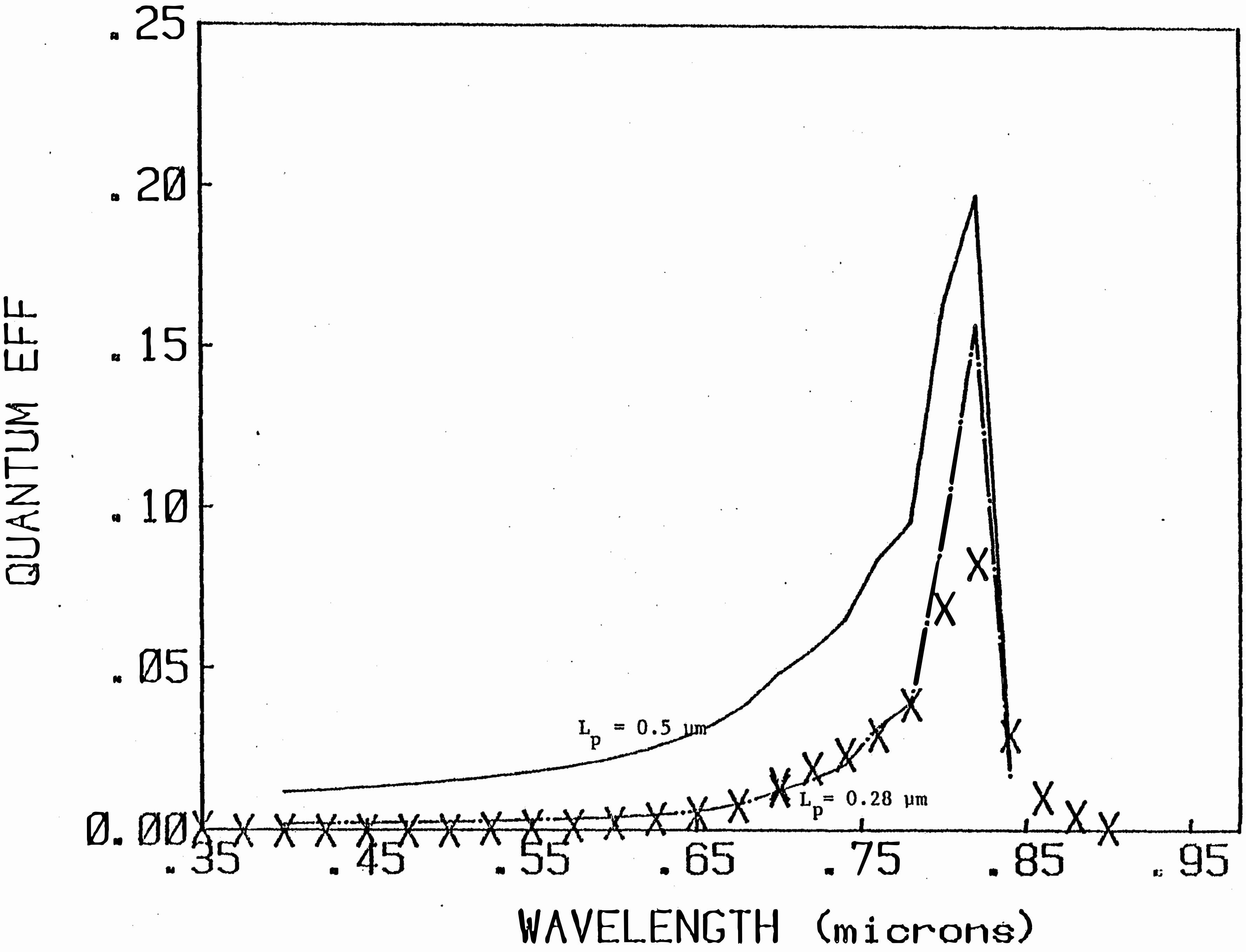

Figure 12. Calculated quantum efficiency vs wavelength for L_p = 0.28 μm

the measured efficiency of HWVE sample #9. This value for L_p is consistent with EBIC measurements which yielded a value of $L_p = 0.35$ µm. This value for L_p is in agreement with those determined by Mimila-Arroyo et al.[5] The most evident difference between this film and those described in Progress Report No. 1 which had a larger L_p, is a considerably higher T_{In}. It is possible that the same imperfections responsible for the photoconductivity (three orders of magnitude) are responsible for the reduced diffusion length.

The characteristics of the HWVE cells grown in Linz and at Stanford are compared in Table IV. A remarkable agreement in properties is evident. The values of $J_{sc} = 0.24$ mA/cm^2 and $V_{oc} = 0.73$ V are in fairly good agreement with the general diode equation given in Eq. (1).

TABLE IV

Comparison of p/n CdTe Homojunction Cells Prepared at Linz and Stanford

	Linz Original	Linz Thinned	Stanford
Substrates			
Boule	38b	38b	55b
p, cm^{-3}	10^{17}	10^{17}	3×10^{16}
Resistivity, ohm-cm	1.1	1.1	3
Growth Conditions			
T_s, °C	450	450	450
T_{CdTe}, °C	565	565	575
T_{In}, °C	560	560	680
T_{Cd}, °C	-	-	250
Thickness, μm	5	1.5	1.5
Growth rate, μm/h	7	7	11
Electrical Characteristics			
J_o, A/cm^2	3×10^{-10}	3×10^{-9}	3×10^{-10}
A	2.2	2.7	2.3
V_{oc}, V (AM 1.5)	0.62	0.67	0.73
J_{sc}, mA/cm^2 (AM 1.5)	0.15	0.19[a]	0.24
Spectral response	Maximum at 1.5 eV for all cases		
Fitting Parameters for Spectral Response Modeling			
Reflection, %		25	30
S, cm/sec	10^6	10^6	10^6

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[a] The extrapolation of J_{sc} measured at low light intensities gives a value of 1 mA/cm^2 at AM 1.5 simulated sunlight.

GRAIN BOUNDARY STUDIES

Recent research on the properties of grain boundaries in CdTe bicrystals has taken two directions: (1) the measurement of the properties of two grain boundaries in series, and (2) first attempts at grain boundary passivation.

An n-CdTe:In crystalline sample containing two grain boundaries in series was prepared and mounted on glass. The sample was approximately 10 x 2 x 0.5 mm^3 with a grain boundary area of 2 x 0.5 mm^2. Contact was made by evaporating 8 indium stripes, 2 each on either side of one boundary, and 4 on the remaining side of the second boundary (for measurement of bulk resistivity). This enabled all measurements to be made in a four-point mode. Measurements included I-V characteristics, resistivity activation energies obtained from I-V vs T (measured in both dark and light), and spectral response of grain boundary resistivity modulation by light. Measurements were corrected for bulk resistivity where necessary. All measurements were made for each boundary separately, followed by a measurement of the two in series. This knowledge is of substantial support in extending experimental results obtained from single grain boundary experiments to the properties of polycrystalline thin films.

The results are summarized in Table V. Bulk resistivity was 0.2 ohm-cm, corresponding to $n = 4 \times 10^{17}$ cm^{-3}. The I-V curves were measured over a range of voltages from +0.13 V to - 0.13 V, yielding linear characteristics. The resistance offered by both boundaries in series is nearly additive, except for a small difference introduced by the bulk resistance. The dark resistivity activation energy measured for the two boundaries in series is intermediate between the values measured for the two boundaries separately. The dark current is about 200 to 800 times larger than would be expected from a simple thermionic emission model with

TABLE V

Properties of Grain Boundaries in Series in n-CdTe:In

Property	Isolated Grain Boundary 1	Isolated Grain Boundary 2	Grain Boundaries 1 + 2 in Series
Dark Resistivity[a], ohm-cm^2	0.06	0.12	0.21
Dark Resistivity Activation Energy, eV	0.11	0.19	0.16
Light Resistivity Activation Energy, eV[b]	0.00	0.08	0.05
Light R/Dark R[c]	0.53	0.57	0.62

[a] Bulk resistivity = 0.2 ohm-cm

[b] For illumination with 60 mW/cm^2 white light

[c] Measured with a monochromator with photon energy at bandgap of CdTe

two non-interacting boundaries. Under 60 mW/cm^2 of white-light illumination, the barrier of one of the grain boundaries appeared to be completed removed. The spectral response of boundary resistivity modulation by light was measured for each boundary separately and then in series; resistances were additive at all wavelengths. Table V gives measured resistances for bandgap illumination as representative results.

The investigation of grain boundary passivation began with the evaporation and diffusion of several elements into grain boundaries, and with heat treatment in hydrogen. Samples of similar size were prepared in the same way as the sample used in the dual grain boundary measurements. Four p-type and one n-type bicrystal were investigated. Cu:Au contact stripes were evaporated on either side of the grain boundary for the p-type samples, and In stripes were evaporated on the n-type sample. Grain boundary I-V characteristics, light and dark activation energies, spectral response of grain boundary resistivity modulation, and bulk resistivity were measured for all samples both before and after "passivation." The elements diffused into the p-type samples were chosen because they act as acceptor impurities within bulk single crystal CdTe and thus might be expected to compensate the original donor imperfection states present at p-type boundaries and reduce the barrier present: Cu, Au and Li (because of its high atomic mobility and reactivity). Each element was applied in a stripe covering the grain boundary by vacuum evaporation, and was then diffused for 30 min at 500°C. Heating was performed in a H_2 atmosphere, so it is not clear what effect the H_2 had in conjunction with the intended diffusing element. Heat treatment in H_2 alone is discussed subsequently.

From Table VI it can be seen that after Au diffusion the dark resistivity decreased by a factor of two, and the dark activation energy decreased substantially. The indicated increase in bulk resistivity is curious since Au should act as an acceptor in the bulk.

TABLE VI

Preliminary Experiments on Grain Boundary Passivation in CdTe Bicrystals

	Au in p-CdTe		Cu in p-CdTe		Li in p-CdTe		In in n-CdTe		H_2 in p-CdTe	
Properties	Before	After	Before	After	Before	After	Before	After	Before	After
Dark Resistance, ohm-cm^2	$1.2x10^3$	$4.2x10^2$	$7.5x10^2$	$1.7x10^5$	$6.3x10^2$	98	0.12	55	$3.5x10^3$	20
Dark Resistance Activation Energy, eV	0.54	0.33	0.61	0.56	0.55	0.25	0.19	0.18	0.57	0.24
Light Resistance Activation Energy, eV[a]	0.33	0.31	0.39	0.56	0.26	0.15	0.08	0.00	0.42	0.00
(Light R) ÷ (Dark R)[b]	0.19	0.86	0.2	1	0.2	0.71	0.57	0.32	0.25	0.34
Bulk Resistivity, ohm-cm	10^2	$2.7x10^3$	$2x10^2$	$3x10^4$	$1.5x10^2$	90	0.2	0.25	10^2	10^2

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[a] For white light of 60 mW/cm^2 intensity

[b] Measured with a monochromator with photon energy equal to the bandgap

Table VI shows the results after Cu diffusion. Both bulk and grain boundary resistivity increased substantially. These results are not currently understood, although they do indicate that Cu is not a good choice for passivating impurity.

Table VI shows the results after Li diffusion. The dark resistivity is reduced by a factor of six, and the dark activation energy has been reduced by more than a factor of two. The bulk resistivity is also decreased. These results indicate that Li may be a promising passivating agent for grain boundaries in p-type CdTe.

Table VI gives the data for the diffusion of In into an n-type grain boundary, where the In was selected to compensate the acceptor imperfection states at the grain boundary. A large increase in grain boundary resistivity is caused by the In diffusion treatment, although the activation energy for grain boundary resistivity is virtually unaffected.

Table VI gives the results for H_2 heat treatment alone on grain boundary properties in p-type CdTe. The grain boundary resistivity is reduced by more than two orders of magnitude, while the activation energy is reduced by more than a factor of two. This large reaction to H_2 treatment makes it of interest as a passivating agent, although the permanence of the effect must be further tested. These results also indicate that future investigations of impurity diffusion into grain boundaries should be carried out in vacuum or an inert atmosphere.

FUTURE PLANS

Current plans for research in the next quarter include the following.

1. Correlation of properties of films grown on 7059 glass, BaF_2, and CdTe at the same growth conditions (simultaneous growth).

2. Determination of film properties as a function of substrate temperature, at constant growth rate and thickness (BaF_2 and 7059 glass substrates, simultaneous growth).

3. Minority carrier diffusion length vs T_{In} and T_s. Measurements to be made on internal grains for large grain material (on BaF_2) by EBIC; films on p-CdTe by spectral response modeling.

4. Grain size studies to be carried out: (a) EBIC-resolved grain size for films on 7059 glass, BaF_2, and p-CdTe by EBIC through thin Au Schottky barrier (beam perpendicular to film plane); (b) SEM on same films to correlate surface morphology to EBIC image; (c) SEM on cleaved or broken samples (beam parallel to film plane); (d) effects of oxidation and other passivation on EBIC-resolved grain image.

5. Determination of the effect of excess Cd or excess Te at the highest T_{In}.

6. Characterization of grown grain boundaries (e.g., n-CdTe film grown on p-CdTe substrate containing a grain boundary that will propagate up through the film) by EBIC and capacitance (good possibility for passivation experiments).

7. Development of a quantitative computer model for electronic transport in n-CdTe polycrystalline films.

8. Stockpiling of n-CdTe films for substrates for subsequent work.

9. Preparation for p-type growth: complete modification to HWVE system (sample table, contact evaporation station, Meissner trap, RGA).

10. Studies of recombination at grain boundaries using EBIC on

single boundaries, and light spot scanning using optical fibers if possible.

11. Measurement of the temperature dependence of grain boundary capacitance to relate conductivity activation energies to internal barrier height, and thus to charged interface state density.

12. Continued passivation studies, including annealing in H_2, air, and vacuum for both p- and n-type bicrystals and n-type polycrystalline thin films.

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LARGE GRAIN CdTe THIN FILMS ON Sb-Bi ALLOY COATED Ta SUBSTRATES

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ABSTRACT

Description is given of the preparation and structural properties of thin CdTe films deposited on two Sb-Bi alloys with compositions of 60% and 70% by weight of Sb on Ta substrates, at temperatures just below that of the melting temperature of the alloys, 380° and 430°C respectively. The Sb-Bi alloy films grow with an (003) preferential orientation that matches the (111) plane of CdTe, and are expected to provide low-resistance ohmic contacts to p-type CdTe in solar cell applications. The grain size of the CdTe films was about 2 μm when deposited at 350°C on the 60% Sb alloy; after vacuum annealing of the deposited film for 10-15 h at 350°C, the grain size of both the Sb-Bi film and of the CdTe film increased to about 20 μm. With controlled conductivity, CdTe films deposited in this way should make ideal solar cell components.

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Introduction

The large scale application of solar cells requires a decrease in their cost by a factor of about thirty. One of the most promising ways to reach this goal consists of the preparation of solar cells in an all thin film form on low cost substrates. Unfortunately, low cost substrates, such as glass or steel, are amorphous or fine grain polycrystalline in strucutre, and for this reason seem not to be suitable for the preparation of large grain and oriented semiconductor thin films as are required in high efficiency solar cells. Recently, a new method that could allow one to overcome such an obstacle, called Quasi-Rheotaxy, has been reported.[1] It consists of the deposition of thin semiconductor films on low cost substrates such as steel coated by a few micrometers thick layer of a metal that is kept at a temperature below, but close to, its melting point. According to a recent melting theory,[2] a material close to its melting point exhibits a liquid-like diffusion coefficient on its surface. Therefore a thin film growing on such a material can take advantage of the high surface diffusion coefficient, and can grow with large and oriented crystalline grains. Quasi-Rheotaxy has already been used for the preparation of CdTe thin films on Bi and Pb[1,3,4] and a homojunction solar cell with a conversion efficiency of 2% has been prepared on Pb coated substrates.[4] However, because of its high absorption coefficient and high surface recombination velocity, CdTe is more suitably used as a p-type absorber in a heterojunction rather than a homojunction cell.

In the case of a heterojunction cell, the metal substrate has to be chosen to make low-resistance ohmic contact to the p-type CdTe. The only metals that have suitable melting points and simultaneously could behave as ohmic contacts since there are p-type dopants for CdTe are Bi and Sb. Their melting points are 271° and 630°C respectively, and they are completely miscible in all their compositions.[5] Therefore the melting point of the Sb-Bi alloy varies continuously between 271 and 630°C. But, since the vapor pressure of both Sb and Bi approaches 10^{-5} Torr at about 400°C, and as a consequence the alloy evaporates at this temperature, its use as a substrate is possible only at temperatures lower than 400°C.

In this investigation, we have explored the preparation and the structural properties of CdTe deposited on two Sb-Bi alloys with compositions of 60% and 70% by weight of Sb. The melting points of these two alloys are about 380° and 430°C respectively.[5]

Substrates

Tantalum has been chosen as a substrate for the Sb-Bi alloy because its thermal expansion coefficient, which is 6.5×10^{-6} cm $^{o}C^{-1}$ is not far from that of Sb, which is 9×10^{-6} cm $^{o}C^{-1}$. In addition, it has been observed that the sticking coefficient on Ta is larger than for less expensive substrates such as steel. Before being used, Ta substrates have been polished with fine grain sandpaper and then with 0.3 μm and 0.05 μm Al_2O_3. In order to get a shiny surface, a few minutes of HF etch followed by a further polish with 0.05 μm Al_2O_3 was necessary.

Alloy Preparation

Both alloys have been prepared using the following procedure. Exact amounts of Sb and Bi were sealed in an evacuated quartz ampoule. The ampoule was placed in an inclined furnace to get all the material at the bottom of the ampoule. The furnace temperature was increased to about 700°C, a temperature higher than the melting point of either Sb or Bi. The ampoule was kept at 700°C for about 1 h in order to get a complete mixture of the two elements. Subsequently the temperature was decreased to 350°C, a temperature at which both alloys are solid; the ampoule was held at this temperature for about 48 h to insure good composition uniformity.

Thin Film Preparation

Both Sb-Bi alloy and CdTe thin films were evaporated in a conventional vacuum system containing a rotatable substrate holder that could be heated to 430°C. Since the vapor pressures of Sb and Bi are not far from each other at the evaporation temperature of between 800 and 1200°C, no large difference is expected between the alloy composition of the source and the film even though the alloy decomposes during evaporation. Microprobe analysis of Sb-Bi films deposited in this way confirmed that differences in composition between source and film were in the range of 5%. The thickness of the Sb-Bi films are about 3 to 4 μm.

CdTe was evaporated from a single source with a temperatue of about 640°C. A growth rate of about 5A/sec was obtained in this way when the substrate was kept a a distance of about 18 cm from the source. Pure CdTe powder, Li-doped CdTe, and P-doped CdTe were used for source material. A typical CdTe film thickness was 4 μm. When the 60% Sb alloy was used, the procedure for the CdTe deposition on Sb-Bi alloy on Ta substrates was as follows. The Ta substrate temperature was increased to 350°C, close to the alloy melting point. Then, the substrate was rotated above the Sb-Bi alloy source and the alloy was evaporated. After the alloy deposition, in some cases the alloy film was vacuum annealed for 10-15 h at 350°C before the CdTe deposition. In other cases the CdTe was deposited immediately after Sb-Bi deposition. When the 70% Sb alloy was used, the procedure was the same except that the substrate temperature was 400°C.

Results

CdTe thin films deposited on un-annealed 60% Sb-content Sb-Bi alloy at 350°C shows a grain size between 2 and 3 μm, while the Sb-Bi alloy thin film average grain size is about 1 μm. Micrographs taken with a scanning electron microscope are shown in Figures 1 and 2.

Figure 1 shows an Sb-Bi film deposited on Ta at 350°C, while Figure 2 shows a CdTe film deposited at 350°C on this Sb-Bi alloy. A microprobe analysis made on the surface of the CdTe film indicates neither Sb nor Bi, suggesting that the alloy has not penetrated to at least 1 μm from the CdTe surface, which is approximately the penetration depth of the microprobe.

Both CdTe and Sb-Bi alloy thin films are preferentially oriented. CdTe is preferentially oriented in the (111) direction, while the Sb-Bi alloy is preferentially oriented in the (003) direction. Since the Sb-Bi alloy has the hexagonal structure, its (003) plane has the same crystallographic structure as the CdTe (111) plane. If Vegard's Law is regarded as valid for the lattice constants of the Sb-Bi alloy, a mismatch of about 4% is expected between the lattice constant of the CdTe (111) plane and that of the 60% Sb-content Sb-Bi alloy (003) plane. The structural similarity between the Sb-Bi alloy and the CdTe growth planes is another factor that makes the Sb-Bi alloy a suitable substrate for CdTe thin film deposition.

An interesting result was obtained when the Sb-Bi alloy film was vacuum annealed for 10-15 h at 350°C before the CdTe deposition. In this case, the grain size of both the Sb-Bi alloy and the CdTe thin films increased by about one order of magnitude with respect to the case in which the Sb-Bi films were not annealed. An SEM micrograph of a CdTe film deposited on an Sb-Bi alloy after vacuum annealing for 15 h is shown in Figure 3. This large grain size increase could be caused both by the atomic mobility which the alloy exhibits when it is kept at a temperature close to its melting point, and to the re-evaporation of less-ordered zones, since the vapor pressure of both Sb and Bi is of the order of 10^{-6} Torr at the annealing temperature. Similar results have been obtained with the 70% Sb-content alloy when it was annealed at 400°C. In this case, however, the annealing was carried out for 4 h in a hydrogen atmosphere to avoid re-evaporation of the Sb-Bi alloy film.

In spite of the fact that p-type CdTe sources have been used in some cases, all the CdTe films deposited to date have had a high resistivity of about 10^8 to 10^9 ohm-cm. This result is probably caused by loss of the dopant during the period of increasing source temperature up to the deposition value. Low resistivity, p-type films should be obtainable by adding another source with dopant like Sb, P, As, or Cs to the evaporation system. Instead of the dopant, a Te source could also be used to achieve p-type behavior through non-stoichiometry; this approach has been reported to yield films with resistivity of 10^2 to 10^3 ohm cm.[4]

Conclusions

Sb-Bi alloys with Sb-content of 60% and 70% are suitable substrates for the growth of large and preferentially oriented crystalline grain CdTe films. They exhibit the following favorable characteristics:

1. Their melting points are in the range in which CdTe films are generally deposited. CdTe films grown on them at a temperature close to their melting points can take advantage of the high surface diffusion coefficient that is displayed by a material kept close to its melting point.

2. They display a vapor pressure at temperatures close to their melting points that is suitable for re-evaporation of disordered zones if a prolonged annealing is carried out.

3. They grow with the (003) preferential oreintation that matches the (111) planes of CdTe.

4. They are expected to make a low-resistance ohmic contact to p-type CdTe since they are p-type dopants in CdTe.

If low-resistivity p-type CdTe films can be prepared on such Sb-Bi alloy substrates, an all thin film heterojunction solar cell using indium-tin oxide or cadmium sulfide for the window material can be easily be achieved. Since CdTe films on Sb-Bi alloys display large grain sizes with a preferential (111) orientation, a high efficiency thin film solar cell seems feasible.

Acknowledgments

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Figure Captions

Figure 1. SEM micrograph of a 60% Sb-content Sb-Bi alloy thin film deposited on Ta kept at 350°C.

Figure 2. SEM micrograph of a CdTe thin film deposited on the Sb-Bi alloy thin film shown in Figure 1.

Figure 3. SEM micrograph of a CdTe thin film deposited on a 60% Sb-content Sb-Bi alloy thin film previously evaporated and vacuum annealed for 15 h on a Ta substrate.

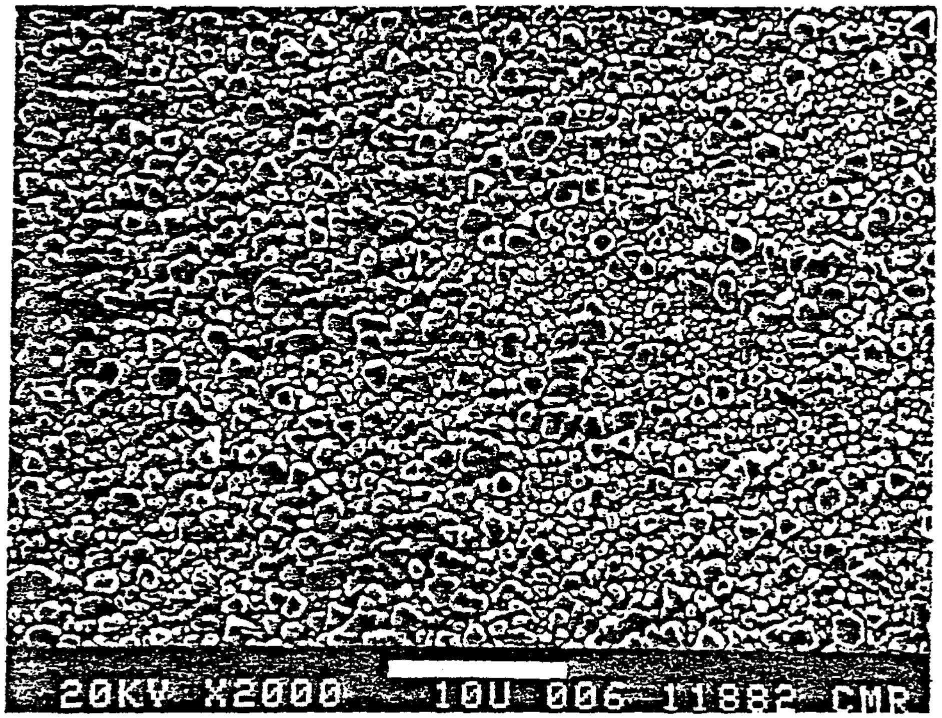

fig. 1

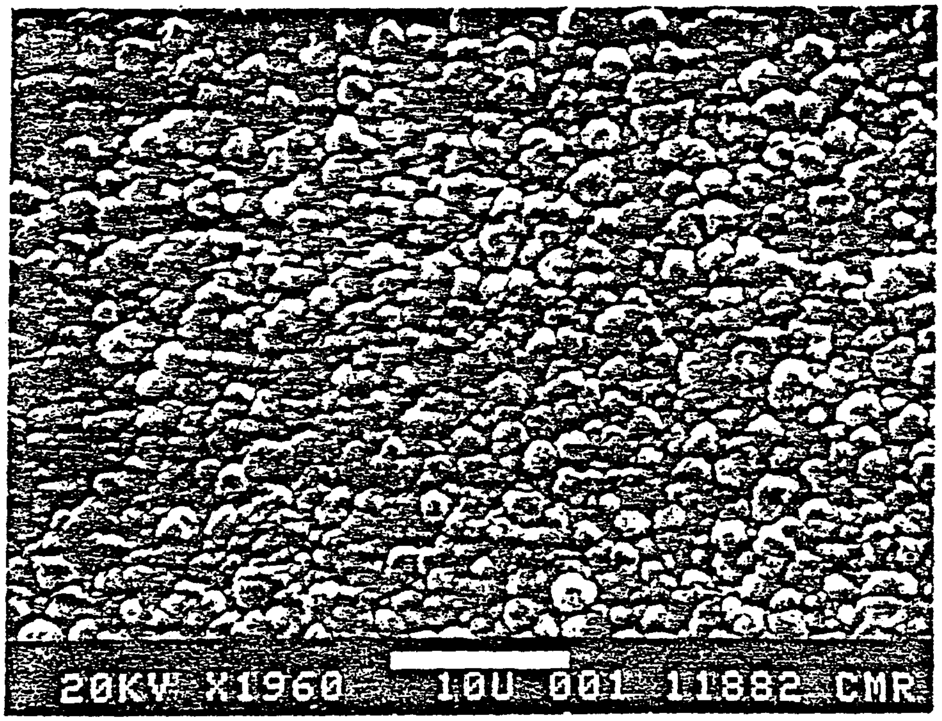

fig 2.

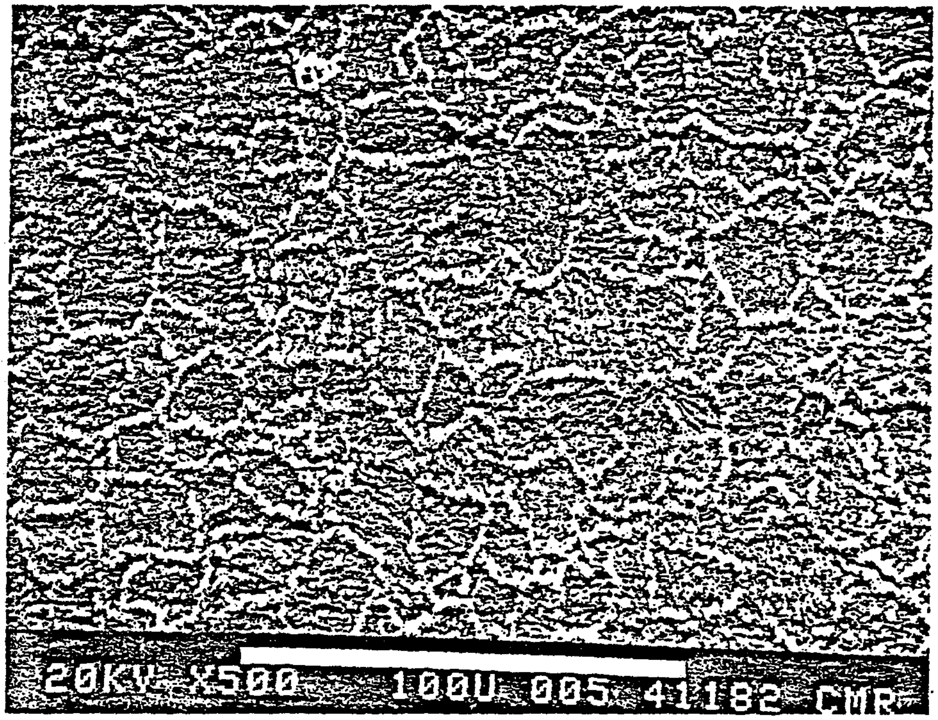

fig 3