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PREPARATION AND PROPERTIES OF EVAPORATED CdTe FILMS

COMPARED WITH SINGLE CRYSTAL CdTe

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ABSTRACT

The hot-wall vacuum evaporation system is finally coming down to operating condition and the first films are expected in early December.

CdTe homojunction cells were theoretically modelled and to some extent tested experimentally using the n-type CdTe film on p-type CdTe crystal homojunction cells previously deposited at Linz. Modelling emphasizes the known importance of surface recombination velocity for such homojunction cells. The n-type layer on the experimental cell was thinned by etching from 5 micrometers to 1.5 micrometers, with a corresponding increase in short-circuit current from 0.1 to 1 mA/cm^2 This behavior is as theoretically expected; to obtain a short-circuit current of 11 mA/cm^2, as required for a 10% cell, requires a thickness of about 0.2 micrometers for a surface recombination velocity of 10^6 cm/sec and other realistic cell parameters.

By doping experiments on single crystal CdTe, it has been shown that the hole density does decrease when the P dopant density is decreased below a critical value in CdTe:P crystals, thus eliminating the possibility that the major acceptors in the P-doped crystals were not P impurity. Attempts to heavily dope CdTe with As were less successful, but this may be due to the use of elemental As as the dopant in this case rather than a compound of the dopant. Cs was shown to be an effective dopant of CdTe and resistivities as low as 0.3 ohm-cm corresponding to hole densities in the low 10^{17} cm^{-3} range were obtained.

An apparent correlation between the low-temperature barrier height associated with a grain boundary in CdTe and the angle of mismatch between the two grains has been observed. Improved capacitance of grain boundary measurements should yield defect densities.

EVAPORATED CdTe FILMS

Hot-Wall Vacuum Evaporation System

The mechanical and electrical construction of the HWVE system will have been completed by the end of November, and the parts will have been sent to be cleaned for vacuum before reassembly. Figures 1 through 4 show the system. All remaining supplies, substrates, and source materials have been obtained and the first films are expected to be deposited in early December.

Solar Cell Modeling

Previous analysis shows that a n- on p-CdTe homojunction must have a short circuit current J_{sc} greater than 11 mA/cm^2, a reverse saturation current J_o less than 10^{-9} A/cm^2 ($J_o = 3 \times 10^{-10}$ A/cm^2 was measured on the device described in Progress Report No. 1), in order to produce a solar cell with greater than 10% efficiency.

Conservative values for materials properties were assumed for the modeled solar cell. The minority carrier diffusion lengths were chosen to be 0.8 micrometers each. (This is smaller than the values of L_n = 1.8 μm and L_p = 1.2 μm reported upon measurement in Progress Report No. 1.) Mobilities were taken to be 39 cm^2/V-sec for holes and 390 cm^2/V-sec for electrons. The base layer thickness (p-type) was taken to be 10 micrometers. J_o was assumed to be 3×10^{-10} A/cm^2. The model was based on the solution to the continuity equations as described in Hovel's book.[1] A computer program (HP 85) was developed for the analysis.

Figure 5 shows the relationship between thickness and J_{sc} for several different values of the surface recombination velocity S_p. The continuous lines are for a device with a depletion layer of 0.1 micrometers. The circles at a thickness of 0.25 micrometers are for a

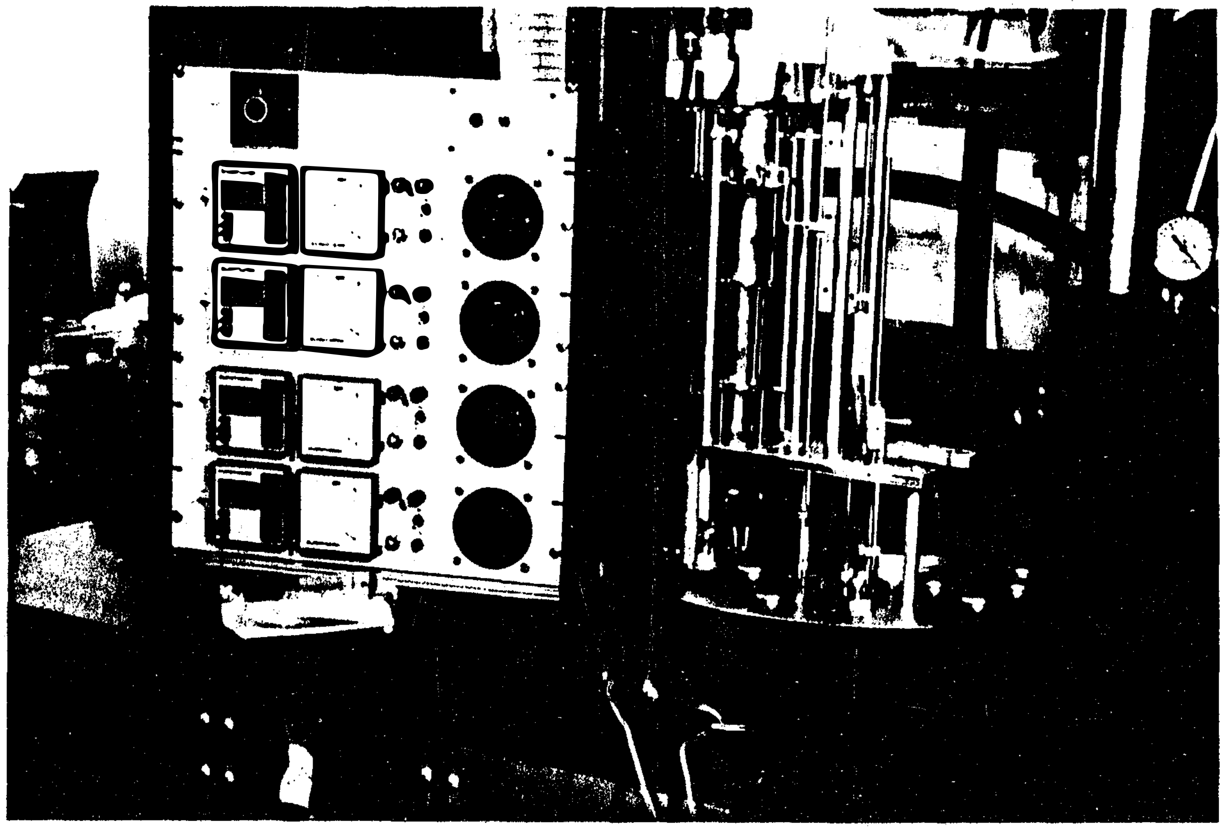

Fig. 1. Overall view of HWVE system. Rack contains four Eurotherm Model 983 temperature controllers, variacs for load matching, and temperature scan unit for recording values for all four sections as a function of time. The four zone furnace is contained in a Varian 3118 diffusion pumped vacuum system.

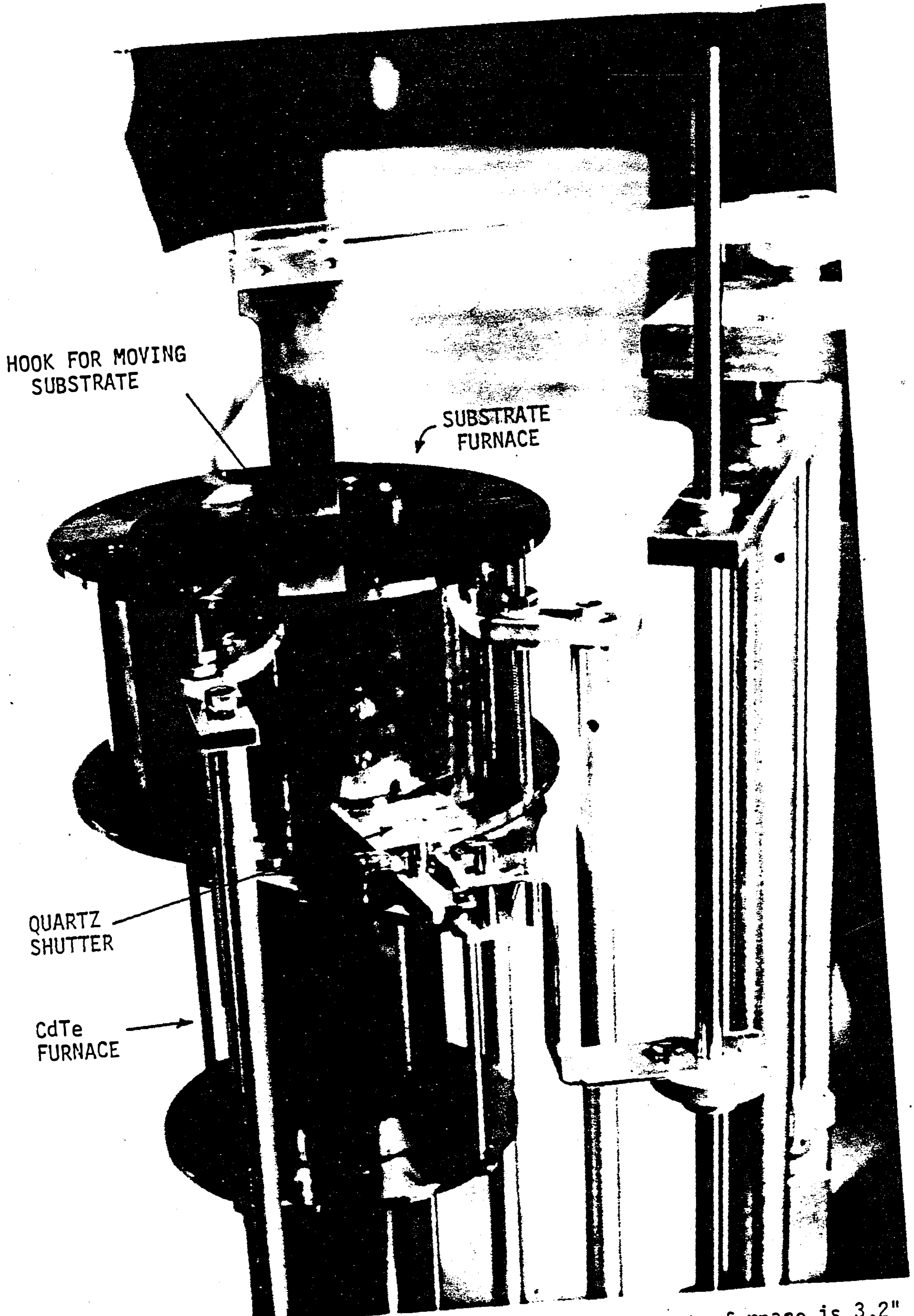

Fig. 2. Close-up of HWVE unit (hole in top of substrate furnace is 3.2" in diameter). Heat-shielded furnace lid is not shown here.

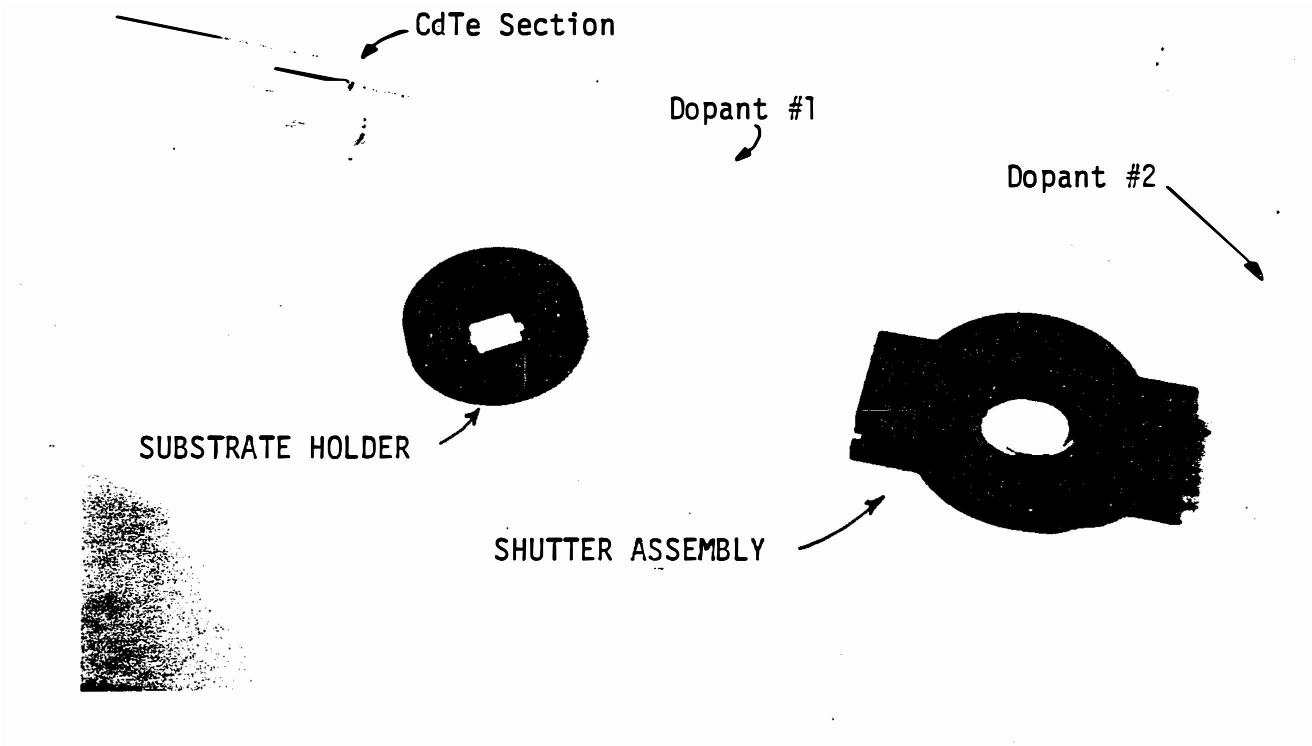

Fig. 3. Quartz HWVE furnace liner, graphite substrate holder, and shutter assembly. Top of liner fits in groove in bottom of shutter assembly.

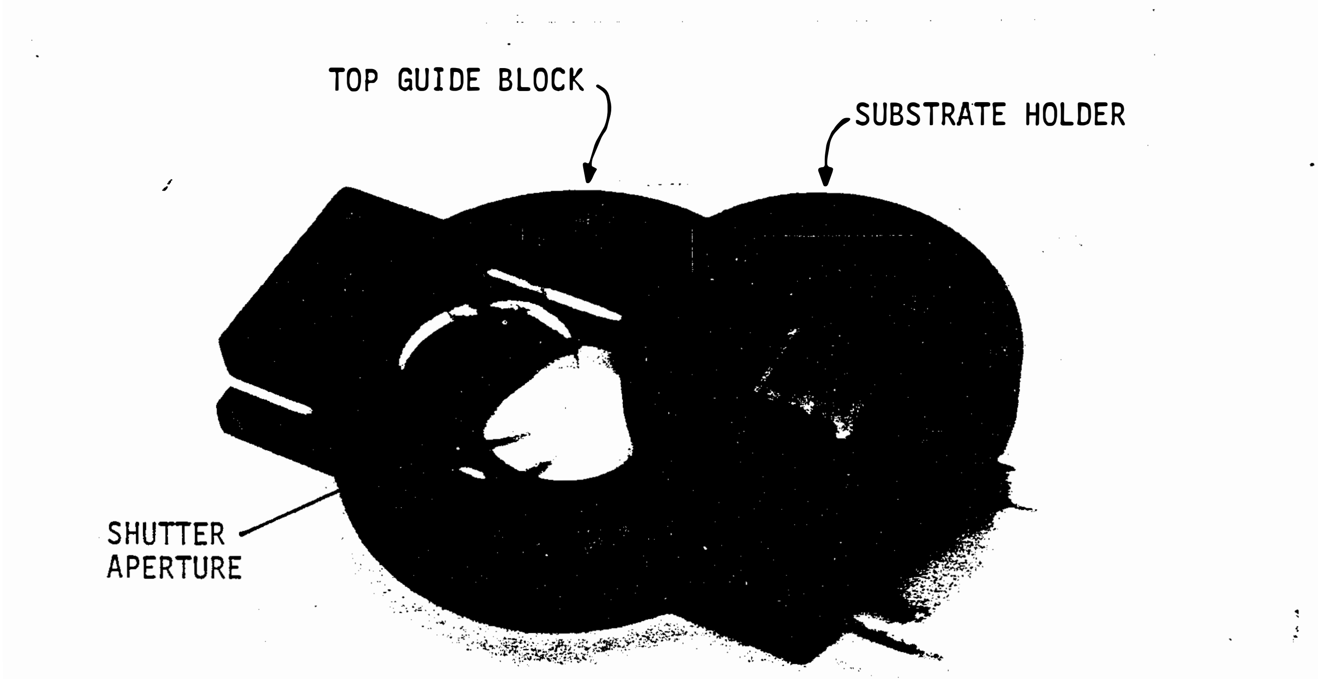

Fig. 4. Shutter assembly. Shutter aperture is 3/4" diameter and substrate size is 1.2 x 1.2 cm^2. Top guide block has hole to fit thermocouple that can contact substrate if desired.

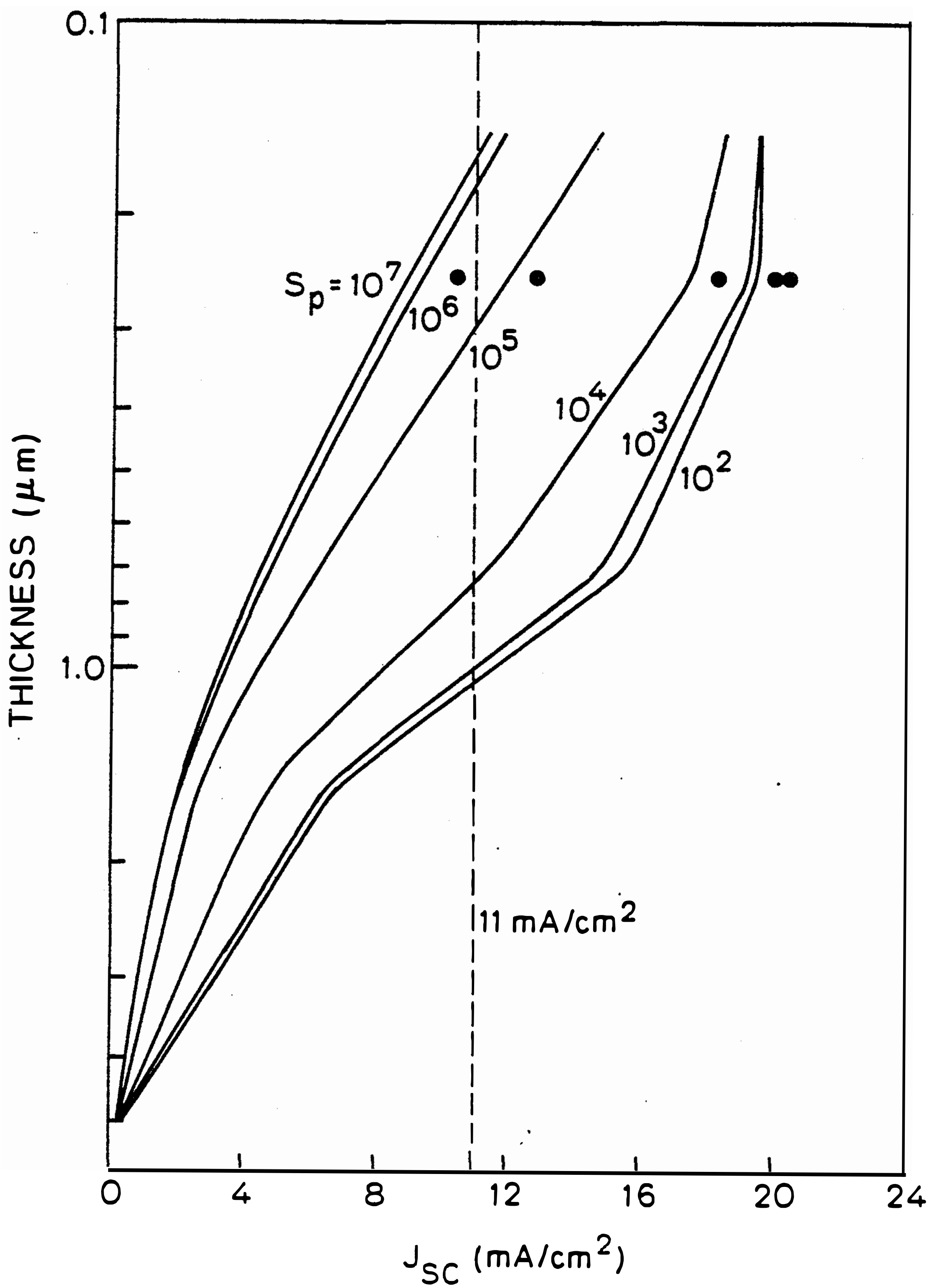

Figure 5. Short-circuit current J_{sc} vs n-CdTe thickness in an n-on-p homojunction structure for various surface recombination velocities S_p. A solar efficiency of 10% is indicated for J_{sc} = 11 mA/cm^2, given the values described in the text. Curves are for a depletion layer width of 0.1 μm. Dots show J_{sc} for an n-CdTe layer thickness of 0.25 μm for a depletion layer width of 0.8 μm.

device with depletion layer width of 0.8 micrometers. It is apparent from this analysis that S_p must be no greater than 10^5 cm/sec, and that the larger S_p is, the smaller the thickness must be. For ease of fabrication and avoidance of film defects, it is desirable to work with thicker films. However, with a growth rate of 0.15 μm/min (the rate observed at Linz for n-type films with the best properties), a thickness of several thousand Angstroms should be possible. Positive control of growth time is provided by the use of a smoothly-working shutter in the HWVE system, as shown in Figure 4.

The value of S_p most often cited in the literature for CdTe is 10^6 cm/sec. Techniques for reducing S_p for n-CdTe have not been extensively investigated. It is important to investigate the possibility of S_p by the use of various surface passivation techniques (application of front surface field and/or oxide layers), and we hope to be able to do this. The evaluation of such techniques could readily be carried out by the measurement of the quantum efficiency of a device with thickness of 0.7 micrometers and depletion layer of 0.1 micrometers for a monochromatic wavelength < 750 nm (see Figure 6) where high sensitivity to S_p is seen.

Characterization of CdTe Homojunctions

The short circuit currents J_{sc} of CdTe homojunctions (HWVE n-type CdTe on p-type single crystal substrates, previously described in earlier Progress Reports, and prepared at Linz) are of the order of 0.1 mA/cm^2. The low value of J_{sc} in this cells is attributed to the thick n-type layer, as corroborated by spectral response measurements showing a peak quantum efficiency of 2.8% at 825 nm. The thickness of the n-type layer is about 5 micrometers, as measured by an Alpha-step device and by SEM. Therefore a reduction of the n-type layer thickness should enhance the short-circuit current, as described above.

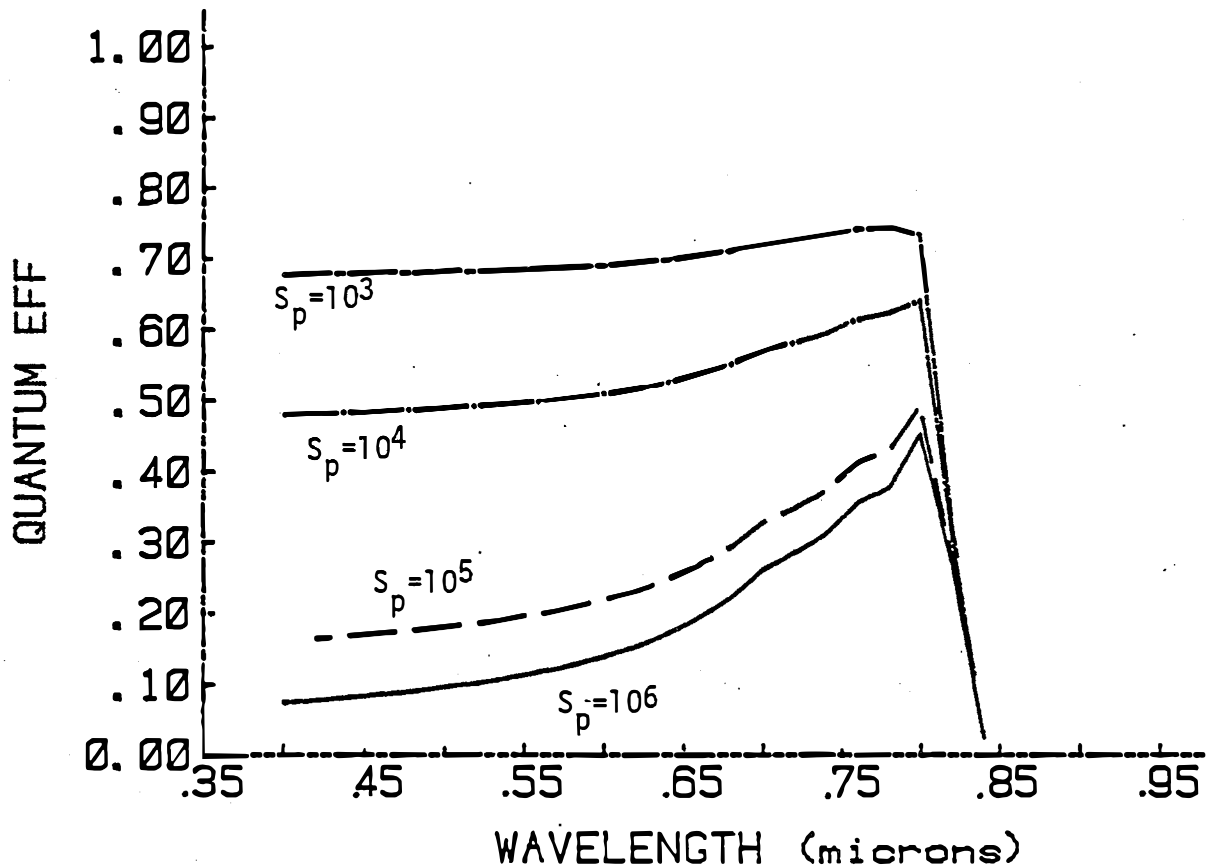

Figure 6. Quantum efficiency as a function of wavelength for various surface recombination velocities for a 0.7 μm thick n-type CdTe layer on a p-type CdTe substrate, and a depletion layer thickness of 0.1 μm.

An investigation was undertaken to determine the effect of variation of n-type layer thickness on spectral response experimentally. Contacts of In on the n-CdTe and of CuAu on the p-type CdTe were deposited by vacuum evaporation. The contact resistivity of the CuAu contacts was 0.4 ohm-cm^2. Then the contact areas were covered with Lacomit. By etching the n-type CdTe film with a 1% Br-MeOH etch, the junction depth was reduced to about 1.5 micrometers. A scan of the etched area with a He-Ne laser with beam diameter of about 1 mm indicated that the n-type layer was continuous over the whole surface. To explore the effect of spreading resistance, the short-circuit current J_{sc} was measured for various light intensities of AM1.5 simulated sunlight with neutral density filters. Figure 7 shows the short-circuit current as a function of the current produced by a Si standard cell. The experimental data indicate that for currents larger than 10^{-5} A/cm^2 a loss of current occurs; this is the result of a spreading resistance due to the unoptimized indium contact configuration. The extrapolation of the short-circuit current measured at low light intensities gives a value of J_{sc} = 1 mA/cm^2 at AM1.5 simulated sunlight.

Figure 8 shows the spectral response of the CdTe cell. These measurements indicate a peak quantum efficiency of 16% at a wavelength of 810 nm (the data are not corrected for reflection losses). Using the measured values of the quantum efficiency from Figure 7, we calculated a value of J_{sc} = 1.3 mA/cm^2 for AM1.5 illumination, which is in good agreement with the extrapolated value of J_{sc} from Figure 6. (The spectrum of our simulator differs slightly from the true solar spectrum.)

The spectral response was modelled using the formulas given by Hovel.[1] The minority carrier diffusion length measured by EBIC gives values of 0.8 micrometers for electrons and holes. A hole diffusion coefficient D_p = 1.6 cm^2/sec was estimated by assuming that the ratio of electron to hole mobility is about 10 and an electron mobility of 600 cm^2/V-sec, as measured

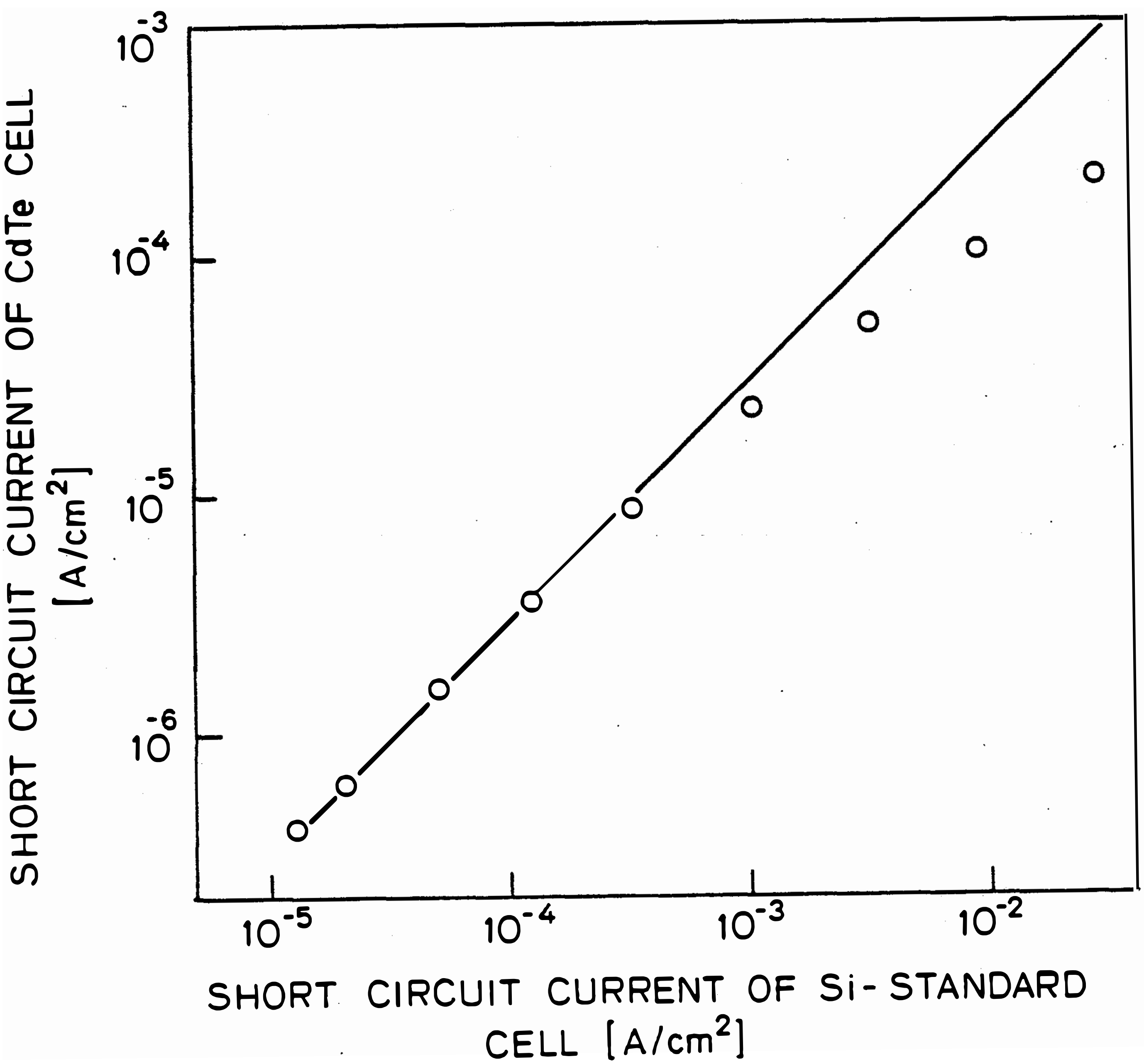

Figure 7. The short-circuit current of the CdTe homojunction as a function of the light current of a Si standard cell.

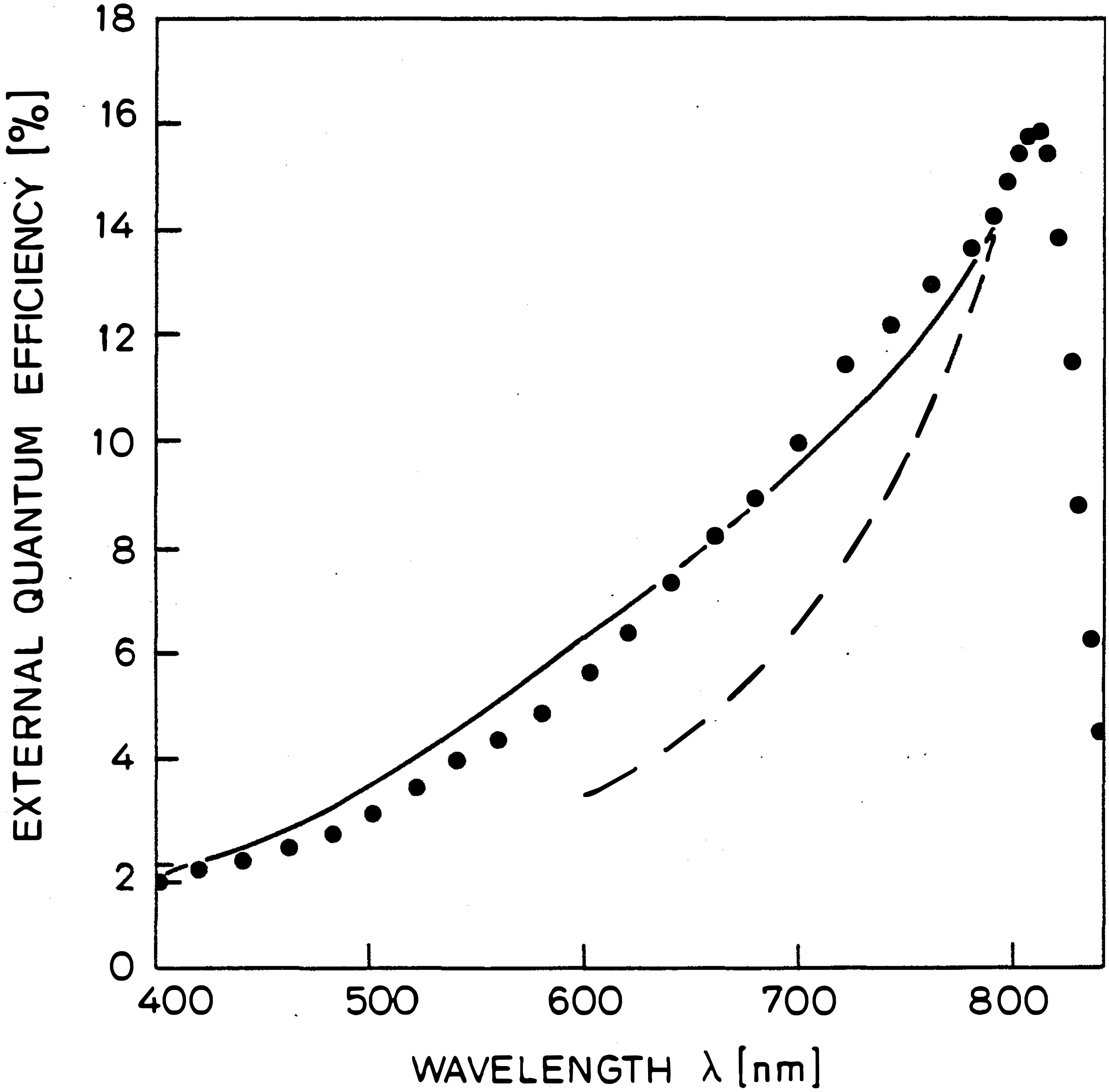

Figure 8. Comparison of the measured spectral response for a n-on-p CdTe homojunction with a 1.5 micrometer thick n-layer, with theoretical curves. The dashed line was calculated using absorption constant values for bulk crystals, whereas the solid curve was calculated using absorption constant values for thin films.

in n-CdTe films deposited onto semi-insulating CdTe bulk substrates. The value of the quantum efficiency at wavelengths shorter than 800 nm for a cell with a top layer of this thickness is not very sensitive to the space charge layer width. We also assumed a constant 25% reflection loss. Substituting these values, a front surface recombination velocity of 10^6 cm/sec, and a junction depth of 1.5 micrometers into Hovel's equation gives the solid curve in Figure 7 if values of the absorption constant reported for thin films are used,[2] and the dashed line if values of the absorption constant reported for bulk crystals are used.[3]

BULK CRYSTAL RESEARCH

Characterization of Crystals

Recently grown p-CdTe boules, two doped with As, one with P, and one with Cs, were characterized. Three single crystal specimens were cut from each boule (beginning, middle, and end). A four-point resistivity measurement was made on each sample. In addition, indium dots were evaporated onto each sample, and carrier densities were determined from $1/C^2$ vs V data obtained from the resulting Schottky barriers, correcting for contact capacitance. The results are summarized in Table I. Agreement between expected and measured doping levels is reasonably good in the P-doped and Cs-doped samples, although even for these samples the measured hole density appears to be two to six times too small, for consistency between the measured resistivity and the expected maximum hole mobility of about 40 cm^2/V-sec. The hole density in the As-doped samples (again about two to ten times too small for consistency with resistivity and expected mobility) is much less than would be expected for the heavy doping levels of As used. One significant difference needs to be tested out further: for doping by P and by Cs, compounds were used (Cd_3P_2 and Cs_2Te), whereas for doping by As, elemental

TABLE I

Measured Resistivity and Hole Densities for Single Crystal CdTe

Boule No.	Dopant	Doping Level in Growth, cm^{-3}		ρ, ohm-cm	$1/C^2$ vs V p, cm^{-3}	Calculated $\mu = 1/pq\rho$ cm^2/V-sec*
57	P	9×10^{14}	Beginning	43	2×10^{15}	72
			Middle	160	5×10^{14}	78
			End	82	6×10^{14}	127
58	As	4×10^{18}	Beginning	5	8×10^{15}	156
			Middle	12	7×10^{15}	74
			End	33	1.5×10^{15}	126
60	As	2×10^{18}	Beginning	63	6×10^{14}	165
			Middle	6	1×10^{16}	104
			End	9	2×10^{15}	347
61	Cs	5×10^{17}	Beginning	1.2	3×10^{16}	173
			Middle	2.5	2×10^{16}	125
			End	0.3	8×10^{16}	260

* Expected hole mobility is about 40 cm^2/V-sec.

As was used.

Properties of Grain Boundaries in Bicrystals

Research on grain boundaries was carried out in three areas. The first involved a continuation of capacitance measurements. An effort was made to increase the contact capacitance to such a value that it could be neglected, but this proved not to be possible. In the future, grain boundary capacitances may be measured on much thinner samples, thus increasing the ratio of contact area to grain boundary cross section area.

Capacitance was measured as a function of temperature for four different samples. All samples had a slight increase in capacitance between room temperature and 90°C, by a factor between 10% and 40%. Density of shallow defect states may be obtainable from these measurements in the future. A typical C vs T plot is given in Figure 9.

Laue X-ray back reflection images were taken for four samples. The orientation of each grain (relative to the normal of the sample surface which is perpendicular to the plane of the grain boundary) was determined, and the relative angle of mismatch calculated for each grain boundary. There appears to be a reasonable correlation between angle of mismatch and barrier height as indicated by the results summarized in Table II.

Figure 10 shows the temperature dependence of the grain boundary conductivity in dark and light for a typical sample. These results were described in the previous Progress Report but no actual data were given.

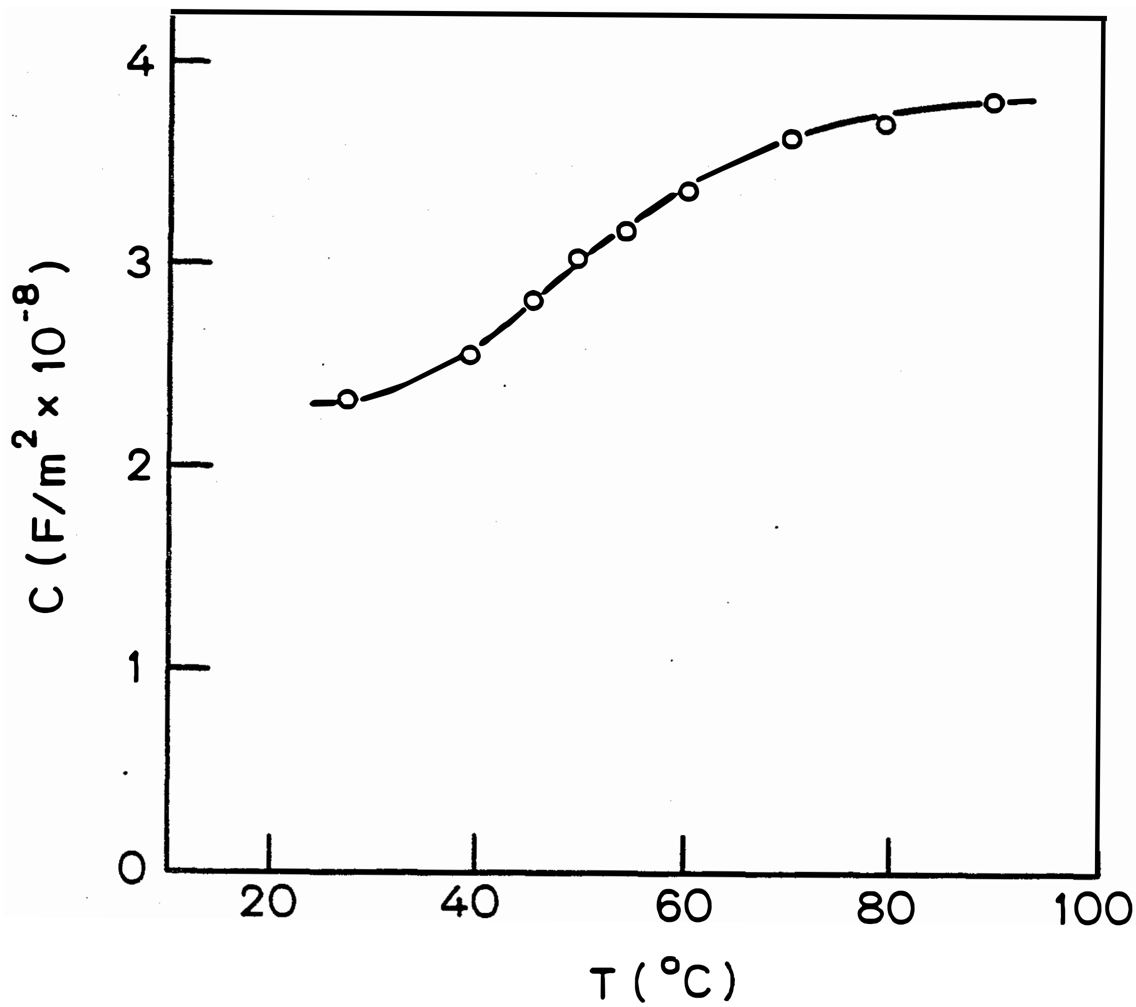

Figure 9. Capacitance per unit area vs temperature for grain boundary sample 10-52b-M-GB3.

TABLE II

Correlation of Barrier Height with Angle of Mismatch for Grain Boundaries

Barrier Height, eV	Angle of Mismatch
0.015	2^{o}
0.38	4.3^{o}
0.43	14.7^{o}
0.46	21.5^{o}

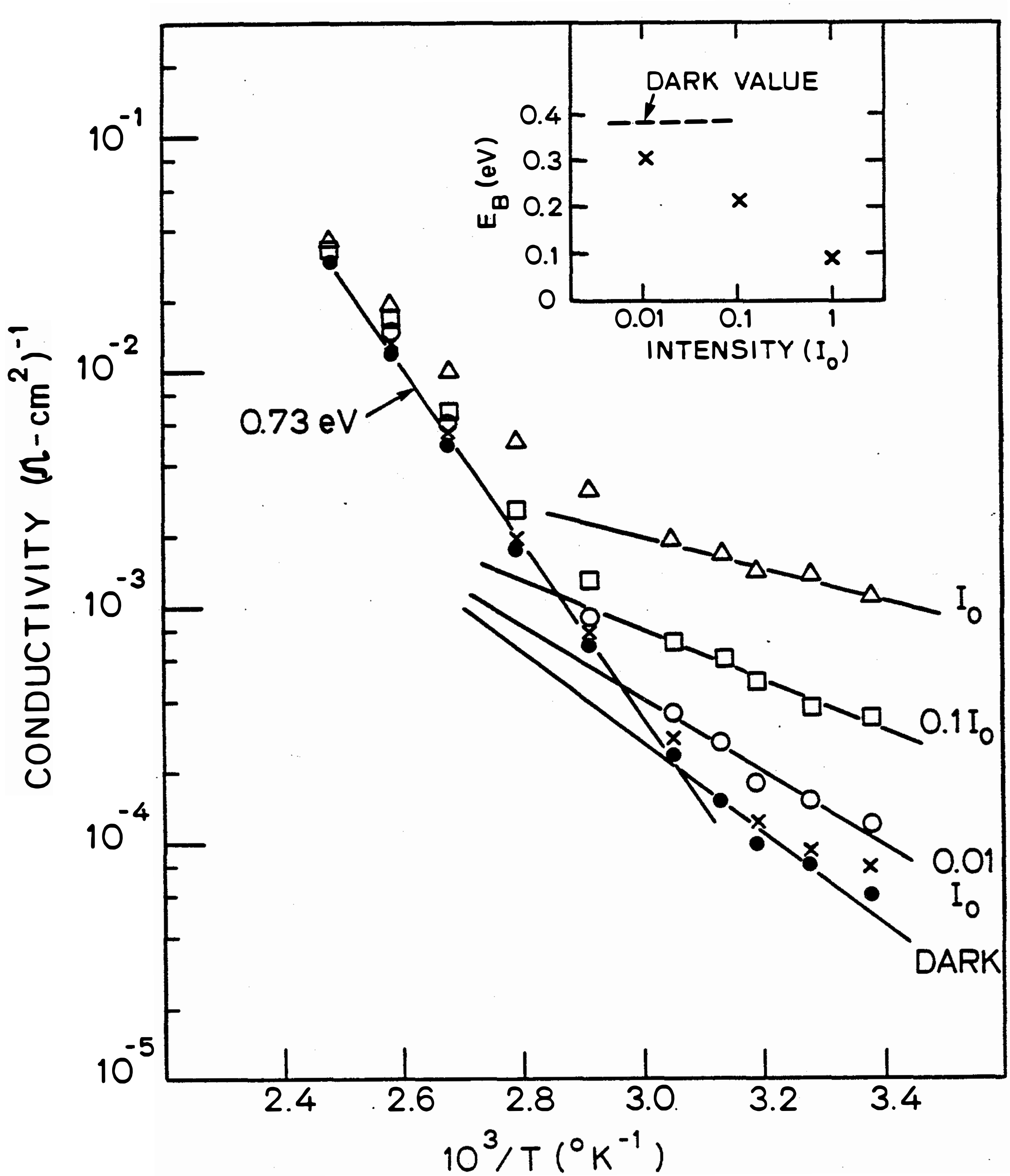

Figure 10. Grain boundary conductivity vs temperature in dark and light for sample T-41-GB1. Inset shows the apparent variation of barrier height at low temperatures with light intensity.

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