

Development of High-Efficiency CdTe Solar Cells

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1. INTRODUCTION

Polycrystalline thin film CdTe solar cells are one of the leading candidates for terrestrial photovoltaic applications. Theoretical calculations project an efficiency of 27% for CdTe cells, while the practically achievable efficiency for polycrystalline CdTe cells is 18-20% (1). Recently, an efficiency of 15.8% has been reported on CdTe films grown by the closed space sublimation technique (2). In order to attain the full potential of CdTe, many design modifications such as the replacement of the CdS window layer by higher bandgap material (eg. CdZnS), and the replacement of SnO₂ by ZnO have been suggested. However, a simultaneous effort to increase the fundamental understanding of carrier loss and transport mechanisms at the CdTe/CdS heterojunction is also crucial for bridging the gap between current and practically achievable CdTe cell efficiencies. In current CdTe/CdS solar cells, interface states play a major role in limiting the open circuit voltage (3,4). Cells made by different groups show a significant variation in short circuit currents and open circuit voltages. A lot of effort, especially in the industry, has been devoted to finding empirical solutions to the problems rather than first identifying and then removing the source of the problems. Consequently, the configuration and the behavior of the efficiency limiting defects have not been revealed, understood and quantified to any degree of satisfaction. It is important to know which process step needs to be modified first and why, in order to expedite and improve the cell performance intelligently. It may be necessary to develop new tools and models, and apply existing tools more prudently, in order to reveal and quantify loss mechanisms in CdTe solar cells.

Therefore, the overall goal of this program is to improve the basic understanding of the loss mechanisms in thin film CdS/CdTe solar cells and to improve their efficiency by characterizing the properties of the films as well as the finished devices. In order to accomplish this goal, solar cells were fabricated on glass/SnO₂/CdS substrates by MOCVD growth of CdTe films and evaporation of Cu/Au contacts. The substrates were provided by Solarex Corporation, and recently the CdS films have been grown in-house on glass/SnO₂ substrates using solution growth. The Cd/Te mole ratio in the MOCVD growth ambient was varied in an attempt to control the native defect concentration and to analyze

its impact on the cell performance. The films were characterized by Auger electron spectroscopy (AES) and photoluminescence studies, and the solar cells were studied with light and dark I-V-T, DLTS and bias dependent spectral response measurements. The electrical measurements were used to test some models in order to identify and quantify dominant carrier transport and loss mechanisms. This know-how was applied to modify the process sequence in order to enhance the cell performance.

Rapid thermal processing (RTP), which is still a relatively new technology with growing applications in the semiconductor industry, is being investigated in this program as an alternative to the conventional post-growth furnace anneal of the CdS/CdTe films. The RTP system allows annealing of the films for short durations at temperatures that are higher than those that can be used with the conventional furnace. This provides a tool to control inter-diffusion and defect formation at the CdS/CdTe interface.

Consistent with the long term goals of cost-effective large scale terrestrial applications of photovoltaics, we have also made some preliminary investigation of a solution growth technique for depositing CdTe films. This simple and inexpensive technique deserves further investigation.

2. TECHNICAL PROGRESS

2.1 Fabrication of high efficiency CdTe solar cells

CdS films were deposited on textured SnO₂/glass substrates, supplied by Solarex Corporation, using solution growth starting from cadmium chloride, thiourea, ammonium chloride and ammonia. A reaction temperature of 80°C-85°C was used and CdS films about 3000 Å in thickness were produced with two consecutive runs on each substrate. The CdS/SnO₂/glass substrates were treated with CdCl₂ solution and annealed in a furnace at 450°C in N₂ ambient.

Prior to the CdTe deposition by MOCVD, the substrates were again annealed inside the reactor, this time in hydrogen atmosphere at a temperature of 450°C for eight to ten minutes. The surface modification of CdS after this heat treatment has been studied using Auger electron spectroscopy and has been reported earlier (5). CdTe films were deposited on the annealed CdS/SnO₂/glass substrates at a temperature of 400°C. Dimethylcadmium and diisopropyl tellurium were used as Cd and Te sources. The relative amounts of cadmium and tellurium in the growth ambient were changed by controlling the temperature of the bottles that contain the metallorganic precursors and the flow rate of the hydrogen which was used as the carrier gas. A series of experiments were performed in which the Te/Cd mole ratio in the growth ambient was varied from about 0.02 to 6.

Front wall n-p solar cells, with the structure comprising glass/SnO₂/CdS/CdTe/Cu-Au, were fabricated by sequential evaporation of about 100 Å Cu and 400 Å Au after the CdS and CdTe depositions. Light and voltage biased quantum efficiency (QE), Auger depth profile, I-V-T and photoluminescence measurements were performed to characterize the defects, material properties and carrier transport in the finished devices.

Prior to starting the in-house growth of CdS films at Georgia Tech, we were using glass/SnO₂/CdS substrates provided to us by Solarex Corporation. Since the growth of CdS films on SnO₂/glass substrates was not a routine part of the project at Solarex, we decided to grow CdS films at Georgia Tech. Moreover, the high sensitivity of the CdS film quality,

the CdS film thickness, and the cell performance to the growth conditions warranted careful control of the CdS growth process. The solution growth of CdS is described in detail in Section 2.2. With the in-house CdS film growth we have recently achieved 11.0% to 12.0% efficient n-p CdTe cells (Table 1) as opposed to 6.0% to 10.5% efficient cells before (Table 2). Careful control of CdS growth parameters has not only improved the cell efficiencies, but also the yield. Our best NREL verified cell efficiency is 11.2% (Cell ID# 110492-4-2).

Table 1: CdS/CdTe cells with in-house grown CdS films tested at Georgia Tech

Cell ID#	V_{oc} (volts)	J_{sc} (mA/cm ²)	FF	η
A13-3-7	0.76	24.6	0.64	11.9%
A17-11-1	0.75	23.2	0.64	11.2%
A18-7-6	0.75	24.5	0.62	11.5%
A18-8-3	0.76	24.2	0.63	11.6%
A21-1-2	0.77	23.0	0.62	11.0%
A25-2-6	0.75	24.0	0.63	11.4%
A27-3-4	0.74	23.5	0.64	11.3%
A27-4-2	0.75	24.5	0.66	12.0%
A27-4-4	0.75	24.0	0.65	11.7%
A30-11-3	0.74	23.6	0.66	11.7%

Table 2: CdS/CdTe cell performance prior to in-house growth of CdS films

Cell ID#	V_{∞} (volts)	J_{sc} (mA/cm ²)	FF	η
0910-10-2	0.70	20.4	0.56	8.1%
0910-10-6	0.68	17.7	0.54	6.5%
0917-7-5	0.71	23.9	0.56	9.5%
0917-8-2	0.70	23.6	0.57	9.5%
0917-8-4	0.66	22.9	0.43	6.5%
0923-1-2	0.73	22.0	0.56	8.9%
0923-1-5	0.68	22.0	0.44	6.6%

Figure 1 shows the I-V curve for an NREL measured 11.1% efficient cell. The quantum efficiency (QE) spectrum and the dark I-V curve for the same cell are shown in Figures 2 & 3 respectively. The cell had a V_{∞} of 758 mV, a J_{sc} of 22.5 mA/cm² and a fill factor of 0.65. Notice that our V_{∞} is still well below the best reported V_{∞} values in the range of 810 mV to 850 mV (6). This triggered the research on the fundamental understanding of interface defects which is reported in Sections 2.3 and 2.4.

GIT, CdS/CdTe/Glass,Global

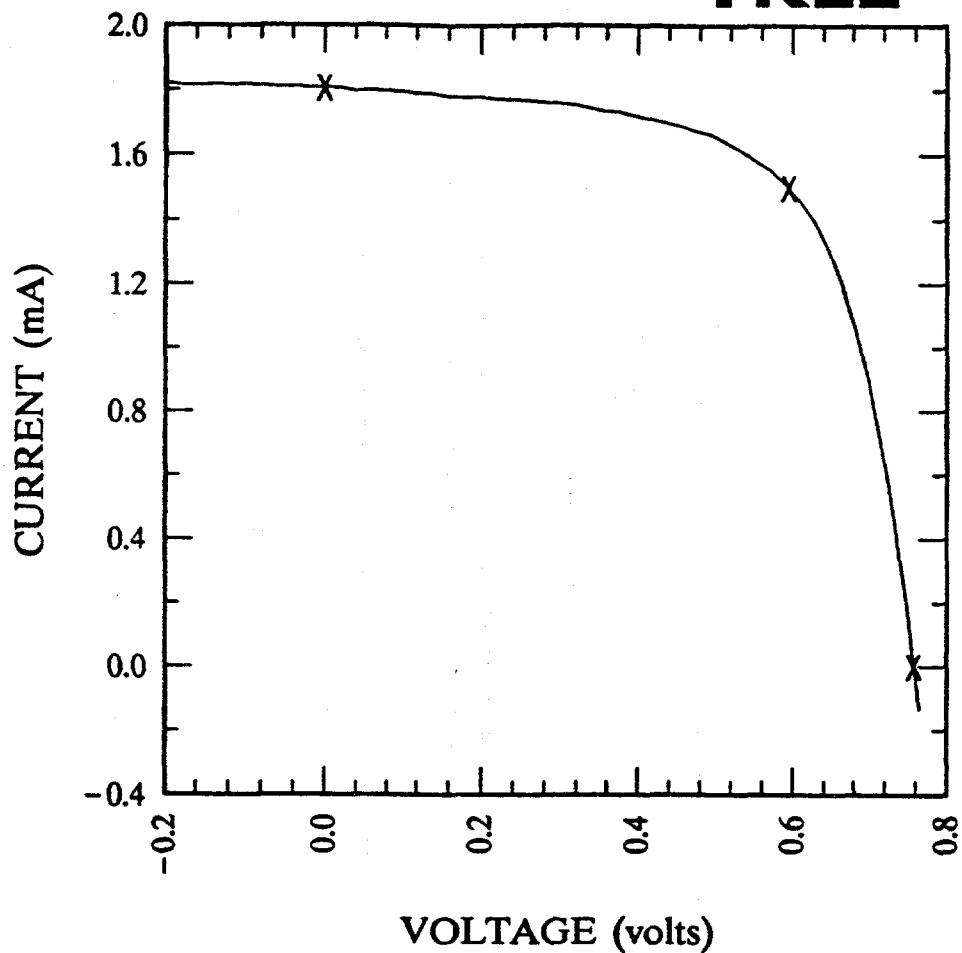
Sample:110492-4-4

Temperature = 25.0°C

Nov. 12, 1992 4:43 pm

Area = 0.0802 cm²

NREL



$V_{oc} = 0.7586$ volts

$I_{sc} = 1.806$ mA

$J_{sc} = 22.52$ mA/cm²

$P_{max} = 0.892$ mW

Fill factor = 65.10 %

$I_{max} = 1.498$ mA

Efficiency = 11.1%

$V_{max} = 0.5951$ V

Figure 1: NREL measured I-V curve for 11.1% efficient cell

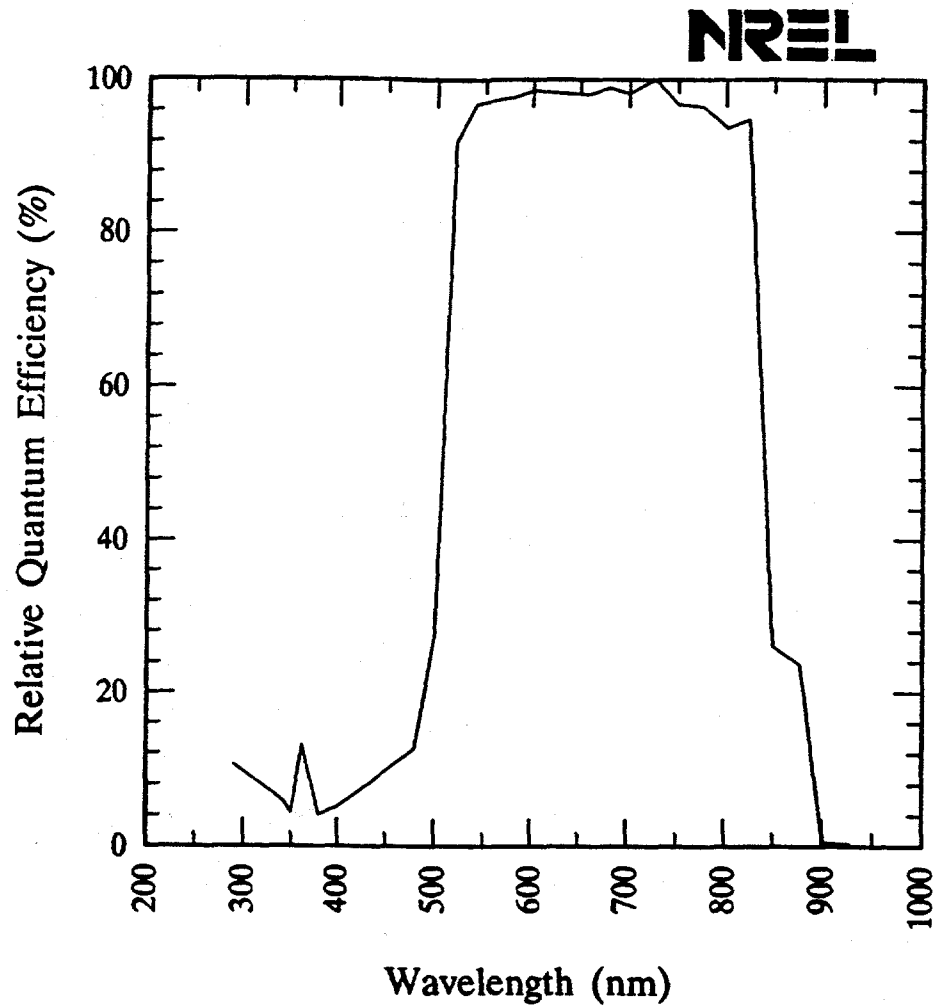
GIT, CdS/CdTe/Glass

Sample: 110492-4-4

Temperature = 25.0°C

Nov. 12, 1992 3:44 pm

Area used = 0.0797 cm²



Light bias = 1.00 mA

Zero voltage bias

Figure 2: NREL measured QE data for 11.1% efficient cell

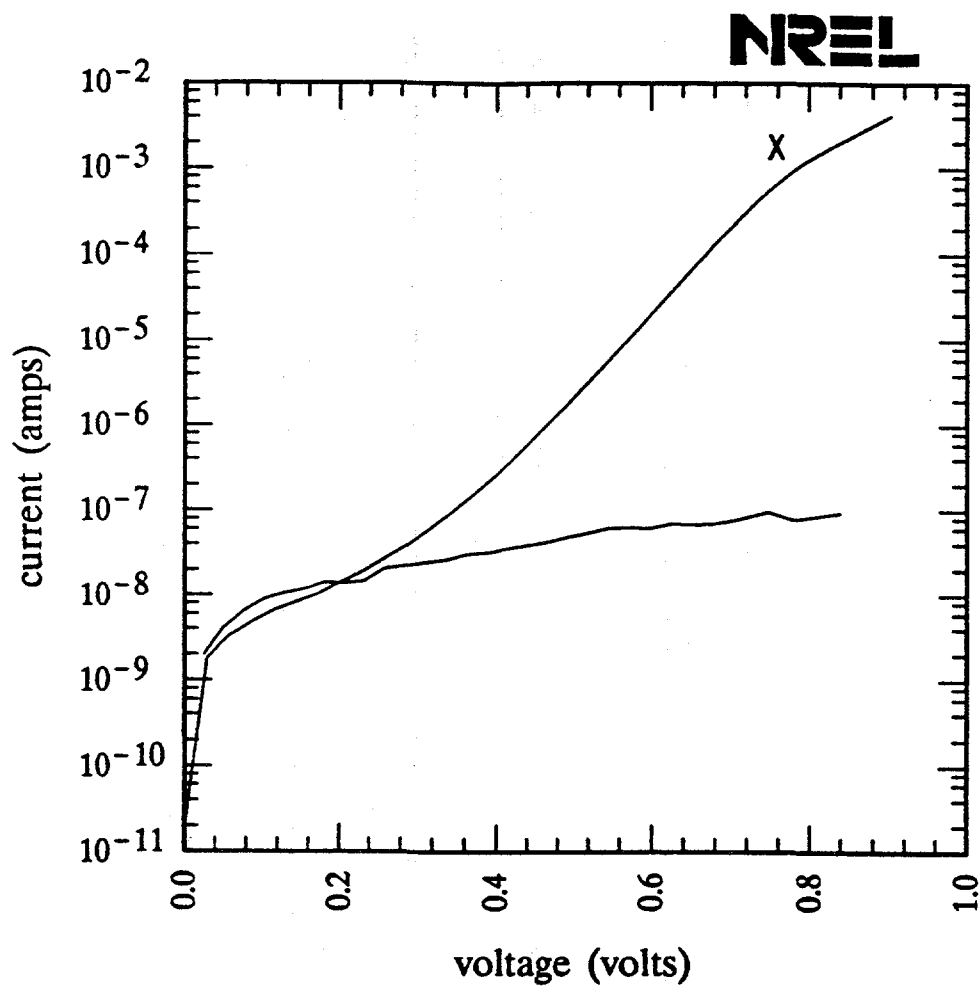
GIT, CdS/CdTe/Glass

Sample: 110492-4-4

Temperature = 25.0°C

Nov. 12, 1992 4:45 pm

Area = 0.0802 cm²



$R_{\text{shunt}} = 8.53 \times 10^3$ Kohms

$R_{\text{series}} = 45.1$ ohms

Equivalent $R_s = 42.3$ ohms

Figure 3: NREL measured dark I-V curve for 11.1% efficient cell

2.2 Solution Growth of CdS Films

In recent years a lot of interest has been generated in the Solution Growth Process for making CdS films as window layers in thin film polycrystalline solar cells. The process has been studied by various investigators, and different approaches have been employed to monitor the reaction process (7,8). A very delicate balance between the various experimental parameters such as concentration of reactants, pH of the solution, and the reaction temperature and time are required in order to obtain CdS films of high conductivity and smooth morphology.

Mechanism of reaction: The concentrations of the free ions, Cd^{2+} and S^{2-} , that are responsible for the growth of CdS films are strong functions of pH and temperature. The source of Cd^{2+} can be any cadmium salt such as chloride or acetate, and the source of S^{2-} is thiourea. An ammonium salt is added to produce a tetramine complex of Cd, and the extent of this complex formation is a key factor influencing the growth rate. Also, ammonia is added to the solution to promote the hydrolysis of thiourea to yield S^{2-} ions.

The solution growth of CdS is a self limiting process. The first 500-1000 Å film is generally adherent, smooth and of interest for devices. This step is controlled by heterogenous nucleation which results in the formation of CdS at the substrate by an ion by ion condensation reaction. The reaction then moves to the next phase which is wasteful since large particles of CdS are formed throughout the solution. It is desirable to suppress this homogenous reaction since it leads to pin holes and shunting paths in the films.

The following procedure was used for the growth of CdS films on SnO_2 -coated glass substrates:

- 1) A stock solution containing 0.025 M $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ & 0.05 M NH_4Cl , and another containing 0.04 M thiourea were prepared. The thiourea solution was filtered using Whatman filter papers #4 and #5.
- 2) The 3" x 3" substrates were cleaned with a soap solution and clean room wiper to remove some of the dirt and stains, and then cleaned ultrasonically with TCE, methanol and deionized water.

3) 200 ml of the mixed chloride solution, and 1470 ml of deionized water were added to a 4 liter beaker.

4) The beaker was then placed on a hot plate equipped with a magnetic stirrer, heated to about 82°C. Two substrates were clamped together with the conducting coatings on the outside, mounted vertically on a teflon holder and lowered into the beaker. This was done to avoid deposition of CdS on the glass sides of the substrates.

5) 150 ml of 30% ammonia were added to the beaker. After allowing sufficient time for the reaction mixture to attain a steady temperature of 82°C, 200 ml of the thiourea solution were finally added to begin the film growth. The beaker was covered with a pyrex plate to minimize evaporation of water and ammonia.

With the procedure described above, the reaction mixture turns faint yellow in color after 2 to 3 minutes, and orange in 4 or 5 minutes. CdS film thickness of 800-1000 Å is achieved in 10 minutes. The substrate is pulled out of the solution at the end of 10 minutes, and thoroughly rinsed in deionized water. To obtain a thicker CdS film the entire process is repeated with the same substrate. Typically, two consecutive runs result in a thickness of 2200 to 3000 Å on the inner substrate which faces the center of the beaker. The CdS thickness of the film on the outer substrate is a couple of hundred angstroms less, possibly because the stirring is not very effective close to the wall of the beaker.

It is worth noting that the filtration of the thiourea solution to remove suspended particles is crucial. Increased homogenous precipitation during the reaction was observed when unfiltered solution was used, and the corresponding solar cells had extremely poor efficiencies. Proper cleaning of the substrates was found to be equally important. Certain other variations in the growth parameters were made to observe their effects on film growth. For example, reducing the thiourea concentration by a factor of 5, reduced the growth rate by a factor of 3. No significant difference in cell parameters was observed when the cadmium chloride solution was substituted by cadmium acetate solution (Table 3).

Table 3: Comparison of cell parameters with use of cadmium chloride and cadmium acetate

	Cadmium chloride (#A-32)	Cadmium acetate run (#A-34)
V_{oc} (volt)	0.68	0.69
J_{sc} (mA/cm ²)	21.4	22.3
Fill Factor	0.58	0.55
Efficiency	8.6%	8.6%

In selected instances, the textured SnO₂-coated glass substrates from Solarex were replaced by Nippon un-textured substrates. Table 4 gives a comparison of cell data with the two sources.

Table 4: Comparison of cell parameters with use of Solarex and Nippon substrates

	Solarex textured coating (#S1)	Nippon un-textured coating (#A-2)
V_{oc} (volt)	0.73	0.69
J_{sc} (mA/cm ²)	23.7	20.5
Fill Factor	0.61	0.56
Efficiency	10.7%	8.0%

It appears that the characteristics of the SnO₂ coating also have a marked effect on the CdS growth, and therefore on the cell parameters. However, this effect has not been well characterized and understood. We are making an attempt to do so.

The purity of ammonia also had a marked effect on cell performance. The 30% ammonia (A.R. Grade) supplied by J.T. Baker & Co. typically gave better results compared

to those that were obtained with the use of ammonia from Fisher Scientific (Table 5). We also found that it was important not to expose the CdS films to any HCl vapors when the acid is used to clean the teflon holders and the glassware in preparation of the experiments. In one instance, when an attempt was made to remove the CdS coating on the glass side of a substrate using a Q-tip and dilute HCl, the CdS coating on the SnO₂ side was also affected, resulting in poor cell parameters.

Table 5: Comparison of cell parameters with use of Fisher Scientific & J.T. Baker ammonia

	Fisher Scientific ammonia (A-32)	J.T. Baker ammonia (A-27)
V _{oc} (volt)	0.68	0.73
J _{sc} (mA/cm ²)	21.4	24.2
Fill Factor	0.59	0.60
Efficiency	8.6%	10.7%

The CdS films were treated with CdCl₂-methanol solution and annealed at 450°C for 90 minutes in N₂ ambient prior to loading in the MOCVD chamber. The concentration of the CdCl₂-methanol solution was varied to observe the effect on cell performance (Table 6). The effect, if any, was not very clear.

Table 6: Comparison of cell parameters with different CdCl₂ concentration used for post-growth treatment of CdS films

CdCl ₂ concentration (g/100 ml)	0.25	0.40	0.80
V _{oc}	0.75	0.75	0.73
J _{sc}	23.5	22.9	23.6
Fill factor	0.62	0.62	0.61
Efficiency	11.1%	10.6%	10.7%

In conclusion, we are quite surprised to note how sensitive the quality of the solution grown films is to the growth parameters and the purity of raw materials. The technique is otherwise very simple and inexpensive, and holds tremendous promise for commercialization. Extensive research is in progress to further improve the CdS film quality, because we believe that this could have a significant impact on the cell performance.

2.3 Effect of Te/Cd mole ratio in MOCVD growth ambient on the carrier transport mechanism and cell performance

The relative mole fractions of tellurium and cadmium present in the MOCVD growth ambient were varied by controlling the temperatures of the bottles that contain the metallorganic precursors diisopropyltelluride ($(C_3H_7)_2Te$) and dimethylcadmium ($(CH_3)_2Cd$), and by controlling the flow rate of the carrier gas H_2 through the two bottles. The Te/Cd mole ratio calculations were based on the H_2 flow rates and the temperature dependent partial vapor pressures of the metallorganic precursors. For diisopropyltelluride,

$$\log P = 8.125 - 2250/T$$

and for dimethylcadmium

$$\log P = 7.764 - 1850/T$$

where P is the partial pressure in mm Hg, and T is in Kelvin.

A series of experiments were performed in which the Te/Cd mole ratio was varied from 0.02 to 6. Some sample calculations are presented in Table 7. The ambient conditions were found to have a marked effect on the cell parameters. A thorough characterization of the films grown under different conditions was done using a variety of electrical and optical measurements. The results have been discussed in the following subsections.

Table 7: Te/Cd ambient mole ratio during MOCVD growth

Sr. #	Partial pressure, P (mm Hg)	H ₂ flow rate (ml/min)	Effective Te/Cd mole ratio
1	P _{Te} at 20°C = 2.8 mm	90	0.02
	P _{Cd} at 37°C = 62.6 mm	180	
2	P _{Te} at 20°C = 2.8 mm	360	0.09
	P _{Cd} at 37°C = 62.6 mm	180	
3	P _{Te} at 20°C = 2.8 mm	400	5.8
	P _{Cd} at 0°C = 9.7 mm	20	

2.31 Auger spectroscopy: Auger spectroscopy was performed on the CdS/CdTe films to analyze the effect of Te/Cd mole ratio in the MOCVD growth ambient during CdTe deposition. The sputtering rate of the CdTe film with argon ion bombardment was adjusted to about 0.1 $\mu\text{m}/\text{minute}$. The sensitivity of AES ($\sim 1\%$ atomic) was not sufficient to resolve the differences, if any, in the Te/Cd atomic ratio in the bulk of the CdTe films. However, it can be clearly seen in Figure 4 that the Auger signal of atomic Te dropped from the bulk CdTe value to the background level ($\sim 5\%$) over a relatively large width for the film that was grown with $\text{Te}/\text{Cd} \approx 6$. This result indicates that the atomic inter-diffusion at the CdS/CdTe interface is maximum when the MOCVD growth is done in tellurium rich conditions ($\text{Te}/\text{Cd} \approx 6$). Moreover, it was also found that the post-growth CdCl_2 treatment and 400°C anneal had no detectable effect on the atomic composition at the interface. As suggested in the literature (9), some inter-diffusion and the formation of solid solutions of $\text{CdS}_{1-x}\text{Te}_x$ during annealing are possible. However, our results suggest that the compositional differences in the MOCVD grown films primarily stem from the differences in the growth ambient.

2.32 Electrical measurements and carrier transport analysis: Consistent with the change in inter-diffusion at the interface, the CdTe growth ambient had a significant effect on J_{sc} as well as on V_{oc} . As shown in Figure 5, J_{sc} is minimum at Te/Cd ratio of ~ 0.1 , and increases on both sides of this value, giving rise to a "U" shape profile. In contrast to J_{sc} , V_{oc} increases monotonically with Te-rich growth conditions and is lower for the Cd-rich conditions (Figure 6). The higher V_{oc} under Te-rich conditions could be due to a reduction in interface states resulting from reduced lattice mismatch due to the higher inter-diffusion. Our results endorse the merit of using Te-rich growth ambient for making high efficiency cells (See Figure 7).

I-V-T measurements (Figure 8) were performed to study the carrier transport in these solar cells and to make a detailed transport analysis. The diode quality factor A for cells grown in Cd-rich ambient ($\text{Te}/\text{Cd} \approx 0.1$ and 0.02) were found to be temperature dependent (See Tables 8 & 9). These results can be explained by the tunneling/interface recombina-

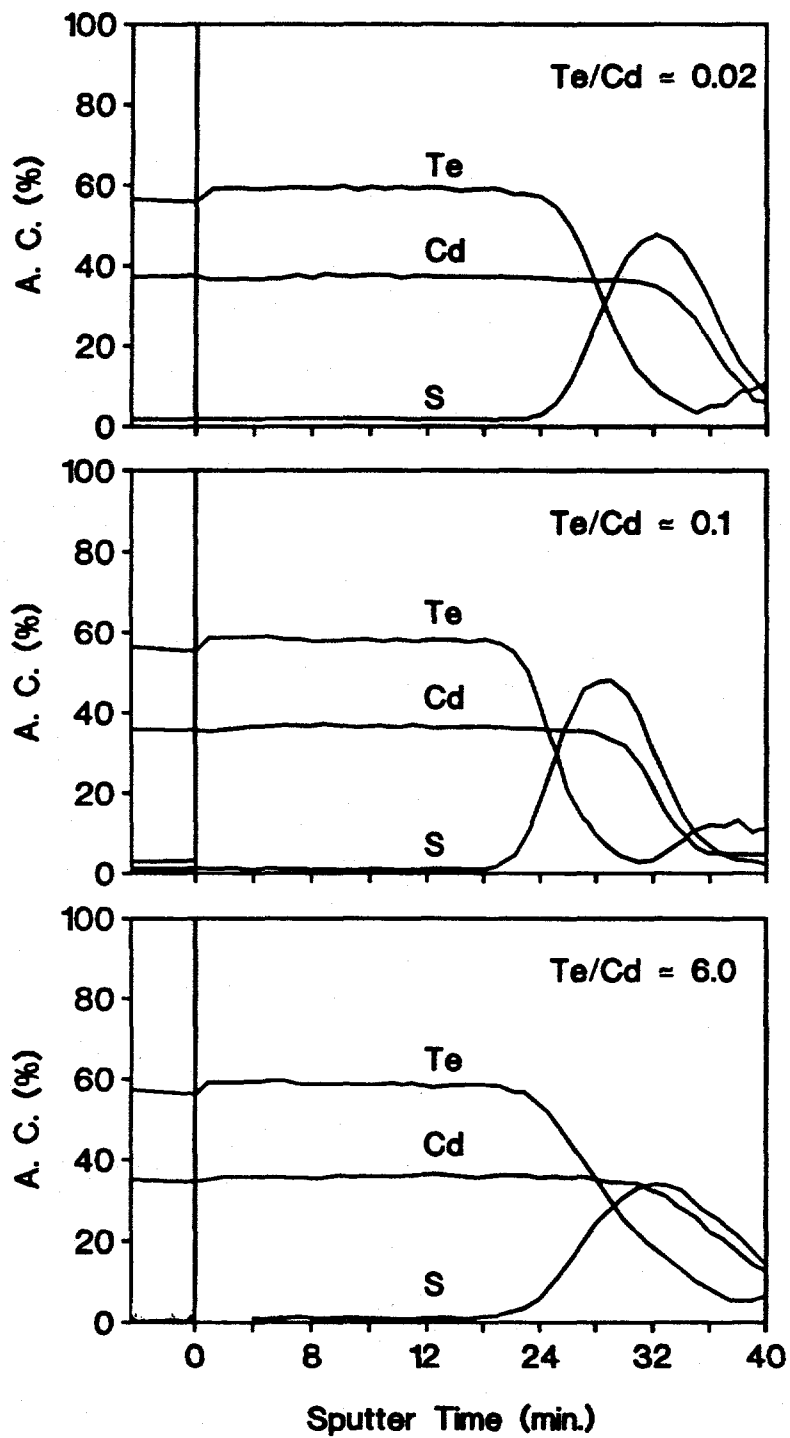


Figure 4: Auger data showing that inter-diffusion at the CdS/CdTe interface is maximum when the MOCVD growth ambient is Te-rich

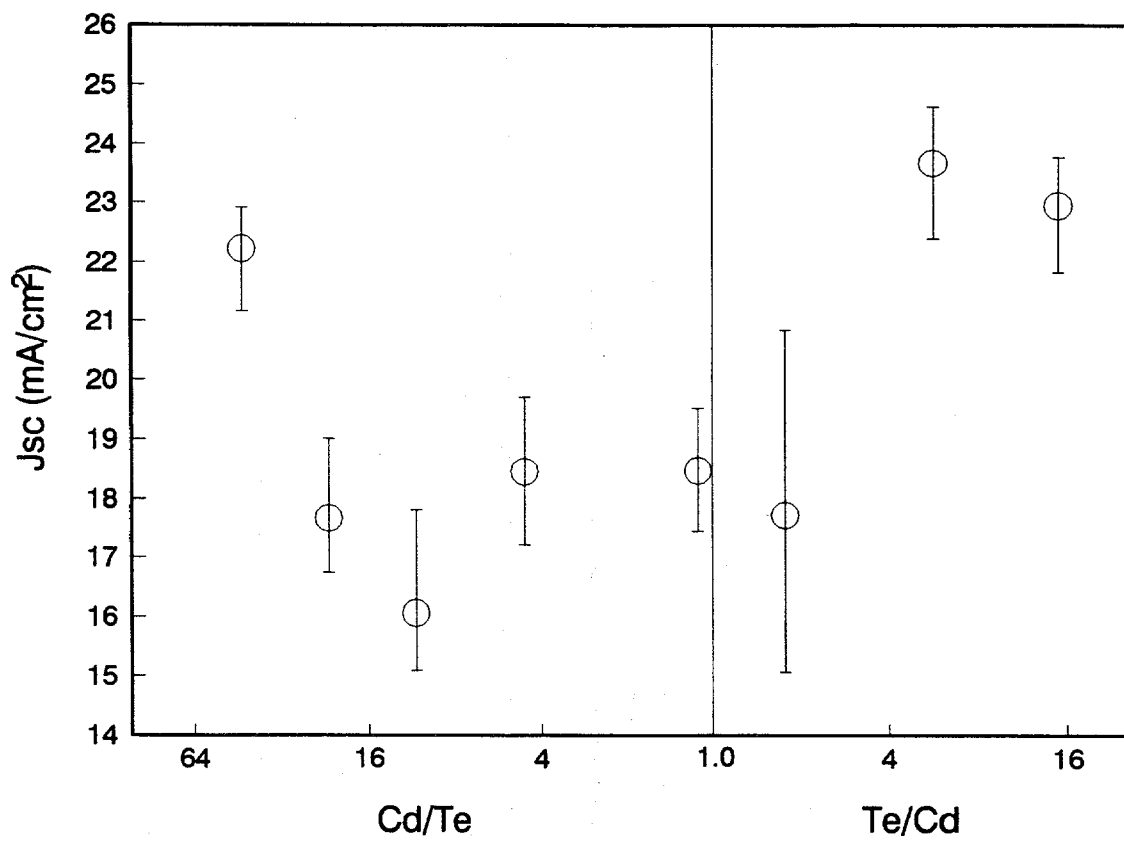


Figure 5: Short circuit current as a function of MOCVD Te/Cd mole ratio

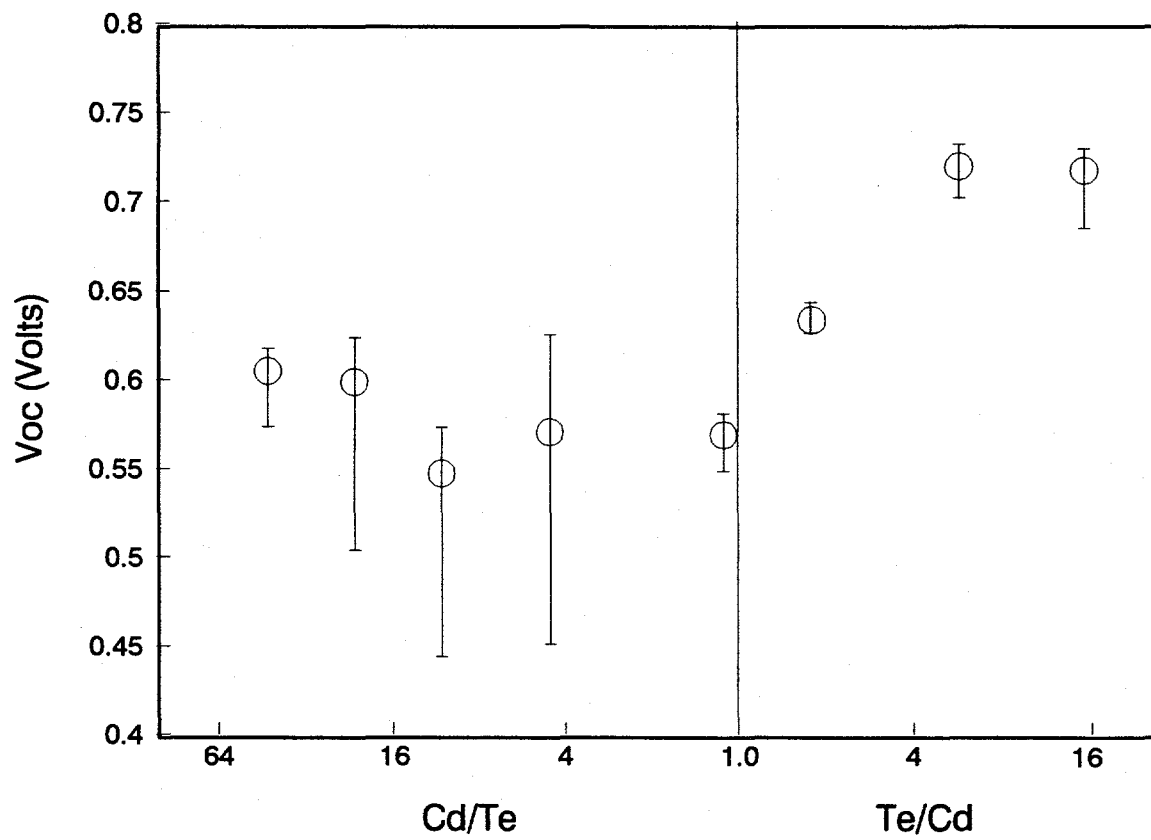


Figure 6: Open circuit voltage as a function of MOCVD Te/Cd mole ratio

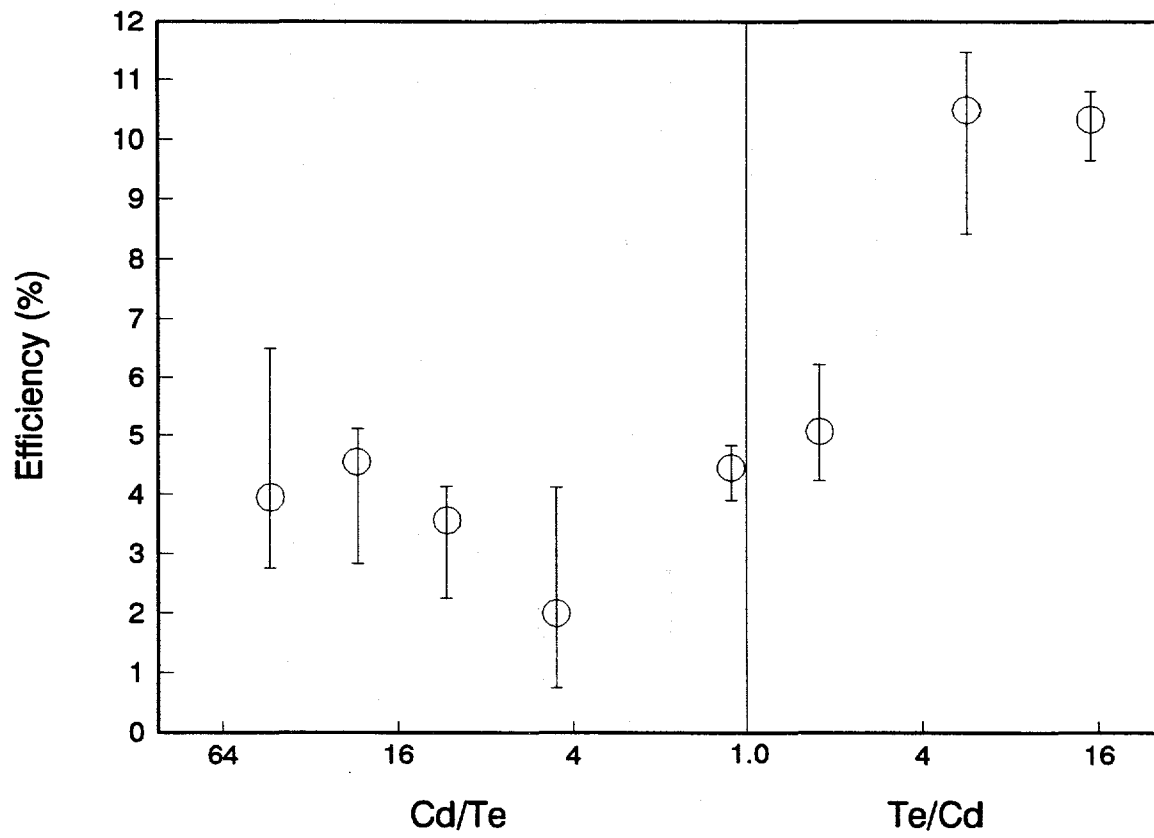


Figure 7: Cell efficiencies as a function of MOCVD Te/Cd mole ratio

tion (T/IR) transport model (10) which approximates the thermally assisted tunneling process by a series combination of direct tunneling and pure interface recombination. According to this model,

$$I = I_0[\exp\{C(V-JR_s)\}-1] + (V-JR_s)/R_{sh}$$

with $I_0 = I_{00}\exp(-\Delta E/kT)$,

and $C = q/AkT = (1-f)B + f/(\xi kT)$

where ΔE is the thermal activation energy, C is the slope of the $\ln J$ vs V plot, B is a temperature-independent tunneling parameter, and ξ represents the voltage division between the CdTe and CdS. The value of the parameter f quantifies the degree of tunneling in the observed I-V behavior with $f=1$ representing pure interface recombination and $f=0$ representing direct tunneling. By plotting the experimentally determined value of C ($=q/AkT$) vs $1000/T$, the values of $(1-f)B$ and f/ξ were determined to be 19.2 volt^{-1} and 0.254 for the cell in which the MOCVD growth ambient had a Te/Cd mole ratio of ~ 0.1 (Figure 9) and 20.6 volt^{-1} and 0.135 for the case in which the ratio was ~ 0.02 (Figure 10). The above analysis shows that the current transport in the cells grown in Cd-rich ambient is limited by both interface recombination and tunneling.

The cells grown with Te-rich ambient ($\text{Te/Cd} \approx 6$) had an ideality factor which was more or less temperature independent ($A \approx 1.87$, see Table 10). Moreover, the slope of $\ln (J_0 T^{2.5})$ vs $1000/T$ plot yields an activation energy of 0.77 eV which is approximately equal to half of the CdTe bandgap energy (Figure 11). This result is expected when depletion region recombination dominates current transport (11,12). It appears that because of the presence of fewer interface defects in films grown under Te-rich ambient, the transport mechanism is no longer dominated by the interface. Instead, defects in the depletion region become more important.

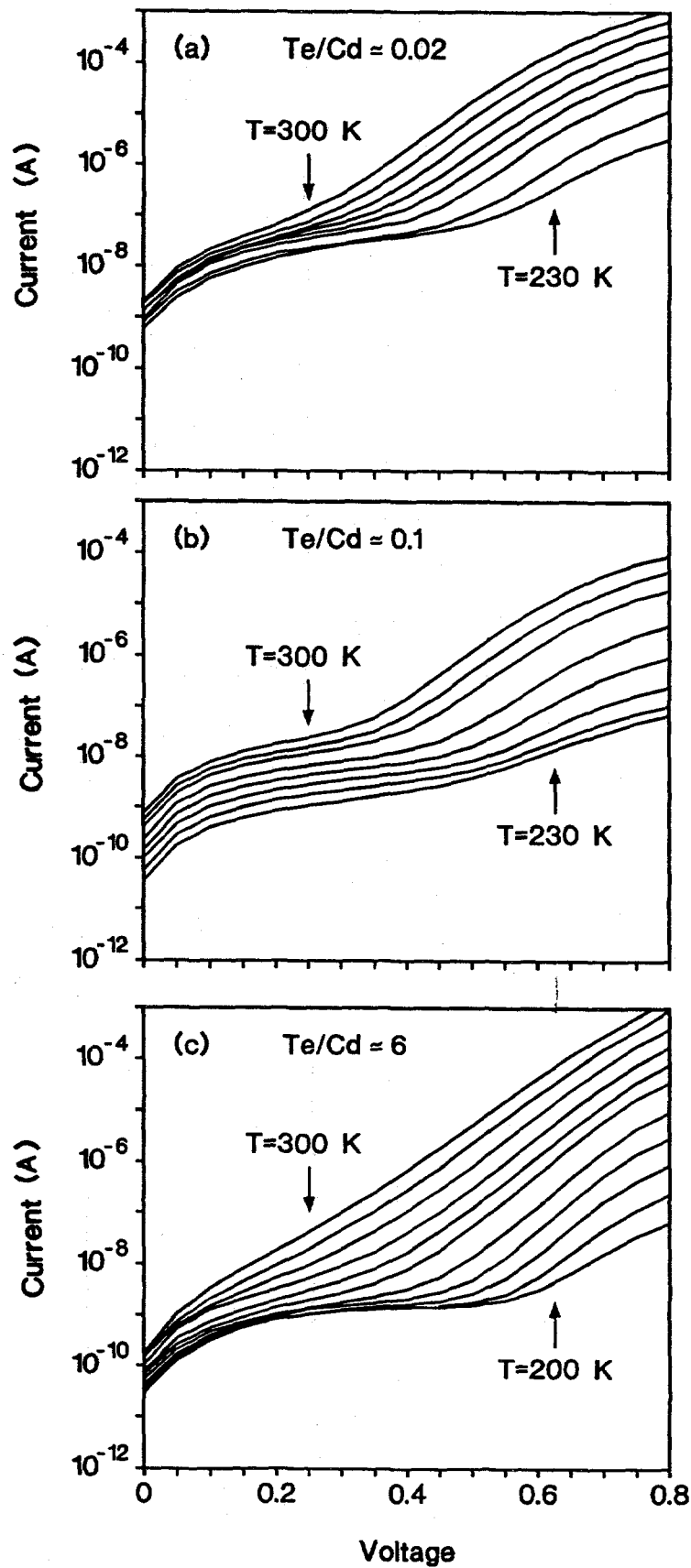


Figure 8: I-V-T plots for cells grown with different Te/Cd mole ratios

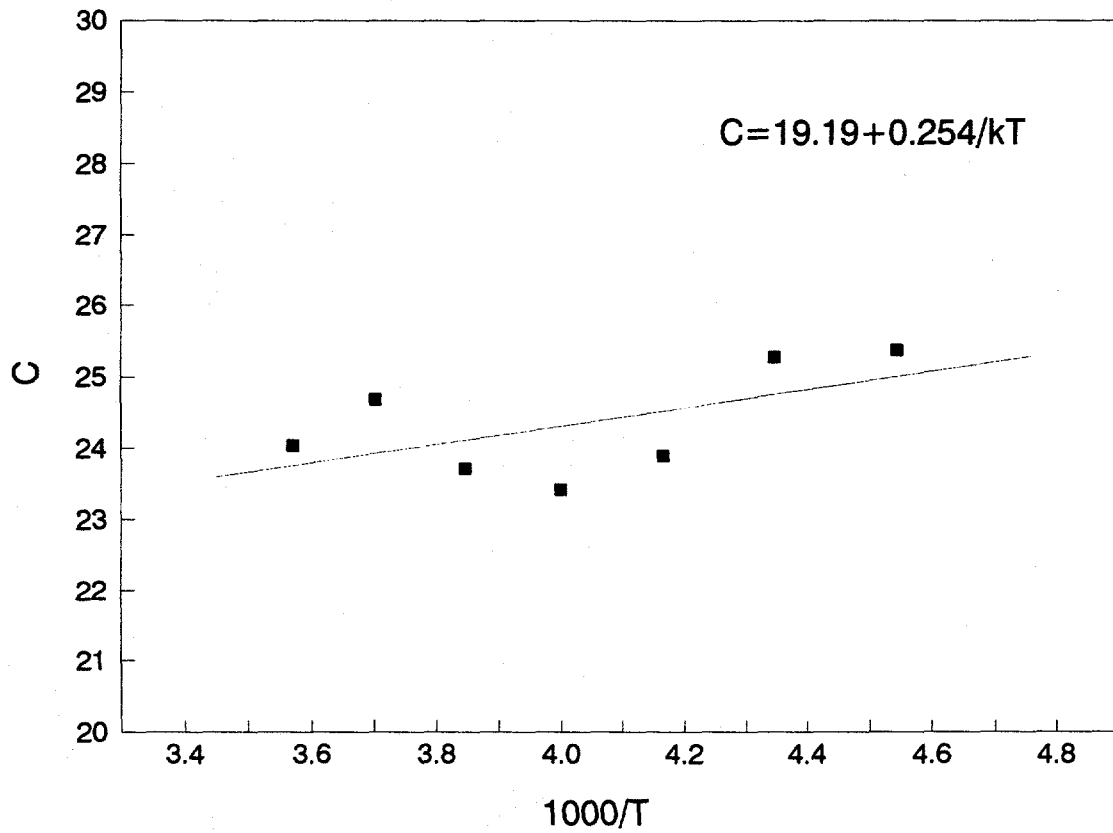


Figure 9: Plot of C-factor vs 1000/T indicating both interface recombination and tunneling limited behavior for cell corresponding to Te/Cd mole ratio ≈ 0.1

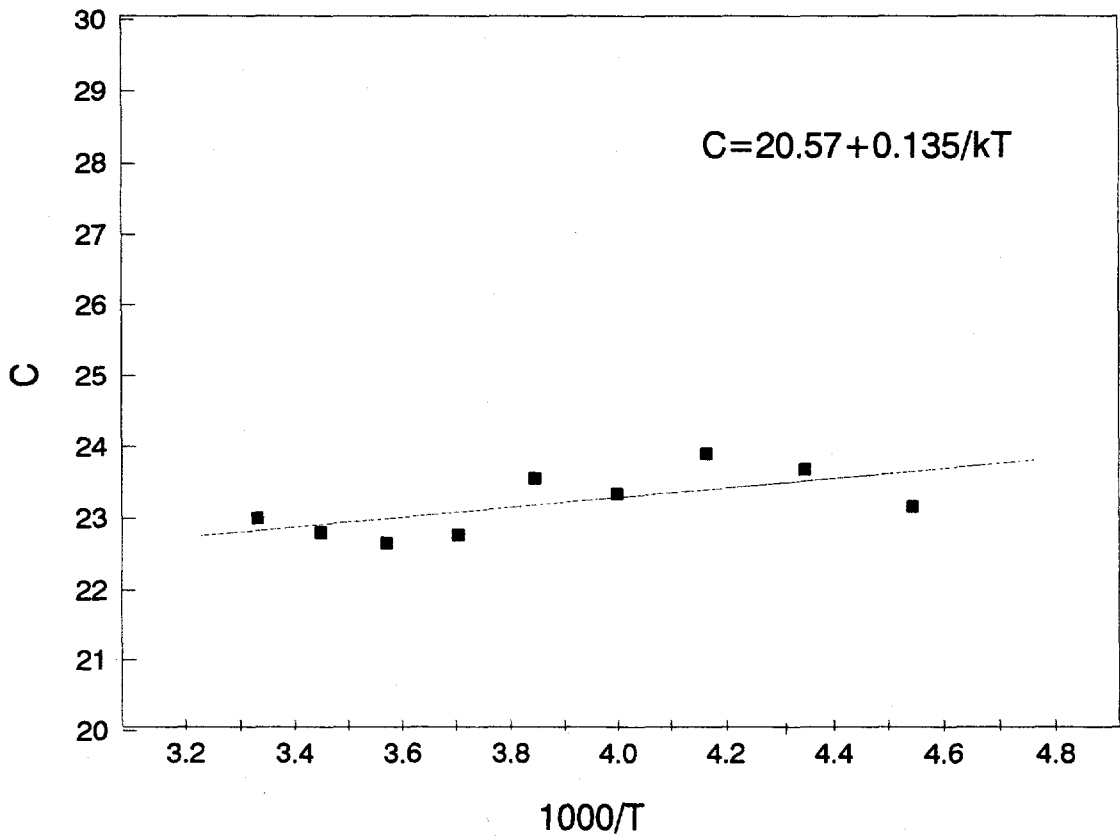


Figure 10: Plot of C-factor vs 1000/T indicating both interface recombination and tunneling limited behavior for cell corresponding to Te/Cd mole ratio = 0.02

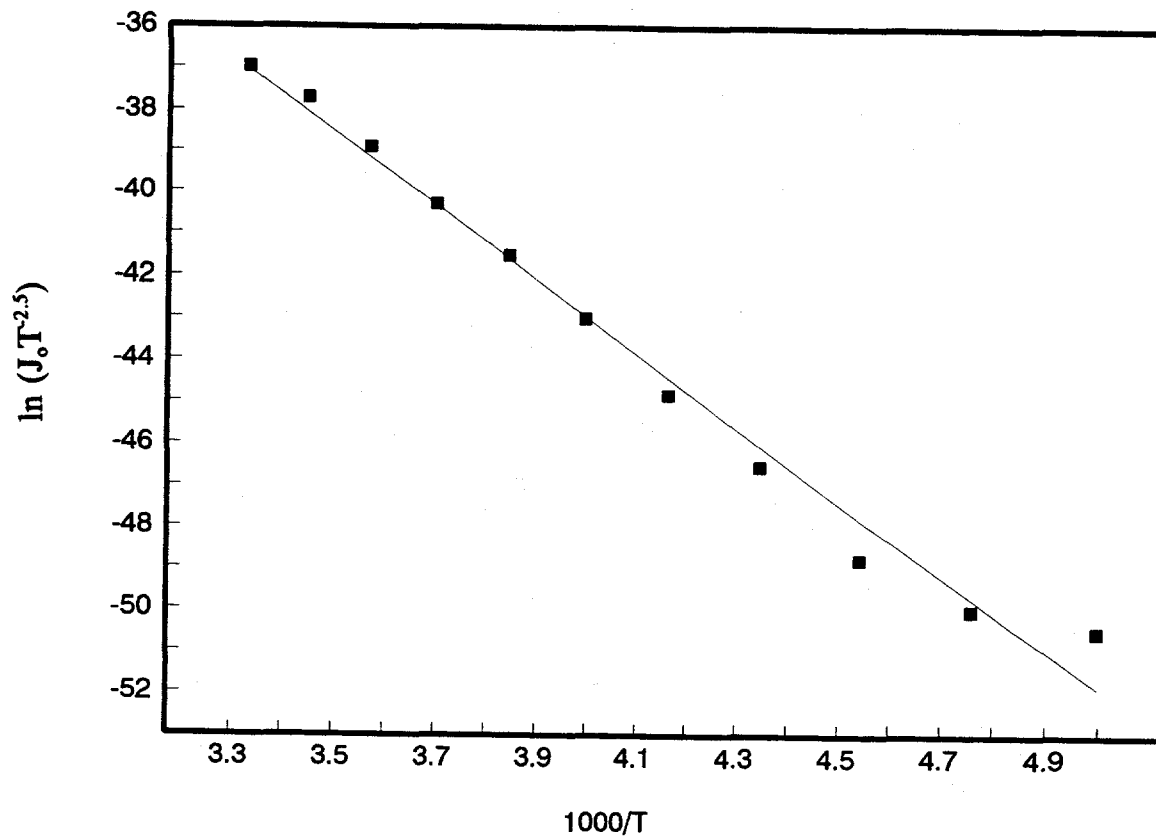


Figure 11: Plot of $\ln (J_0 T^{2.5})$ vs $1000/T$ for the cell corresponding to $\text{Te}/\text{Cd} \approx 6$. The slope yields an activation energy of 0.77 eV, which is approximately equal to half of the CdTe bandgap, suggesting depletion region recombination dominates current transport.

Table 8: I-V-T data for cell with MOCVD Te/Cd mole ratio of 0.02

Temperature (K)	J_0 (A/cm ²)	A
220	7.4×10^{-13}	2.28
230	1.7×10^{-12}	2.13
240	4.8×10^{-12}	2.02
250	3.1×10^{-11}	1.99
260	7.4×10^{-11}	1.89
270	2.2×10^{-10}	1.88
280	5.5×10^{-10}	1.83
290	1.1×10^{-9}	1.75
300	2.3×10^{-9}	1.68

Table 9: I-V-T data for cell with MOCVD Te/Cd mole ratio of 0.1

Temperature (K)	J_0 (A/cm ²)	A
220	8.6×10^{-14}	2.08
230	2.8×10^{-13}	2.00
240	2.4×10^{-12}	2.02
250	1.9×10^{-11}	1.98
260	4.3×10^{-11}	1.88
270	7.2×10^{-11}	1.74
280	2.8×10^{-10}	1.72

Table 10: I-V-T data for cell with MOCVD Te/Cd mole ratio of 6.0

Temperature (K)	J_0 (A/cm ²)	A
220	5.9×10^{-15}	1.84
230	6.2×10^{-14}	1.88
240	3.8×10^{-13}	1.87
250	2.6×10^{-12}	1.86
260	1.3×10^{-11}	1.89
270	4.8×10^{-11}	1.88
280	2.1×10^{-10}	1.89
290	7.6×10^{-10}	1.87
300	1.7×10^{-9}	1.81

Capacitance-voltage measurements were made on both type of cells - cells that were not treated with CdCl₂-methanol solution (Figure 12) and cells that were treated with CdCl₂-methanol solution (Figure 13) prior to the conventional 400°C furnace anneal. The C-V plots indicate that the capacitance of the untreated cells is not voltage dependent, except for the Te/Cd ≈ 6 case, and that the CdCl₂ treatment alters the C-V plots for the cells with Te/Cd mole ratios of 0.1 and 0.02. This behavior, and the QE data discussed below, are consistent with what is expected if the Cd-rich MOCVD ambient produces n-type CdTe and an n-p homojunction near the back copper contact.

2.33 Quantum efficiency (QE) measurements: Figures 14 (a) (b) & (c) show the QE data from cells with CdTe films grown under different ambient conditions. These cells have not undergone the conventional post-growth CdCl₂ treatment. The data

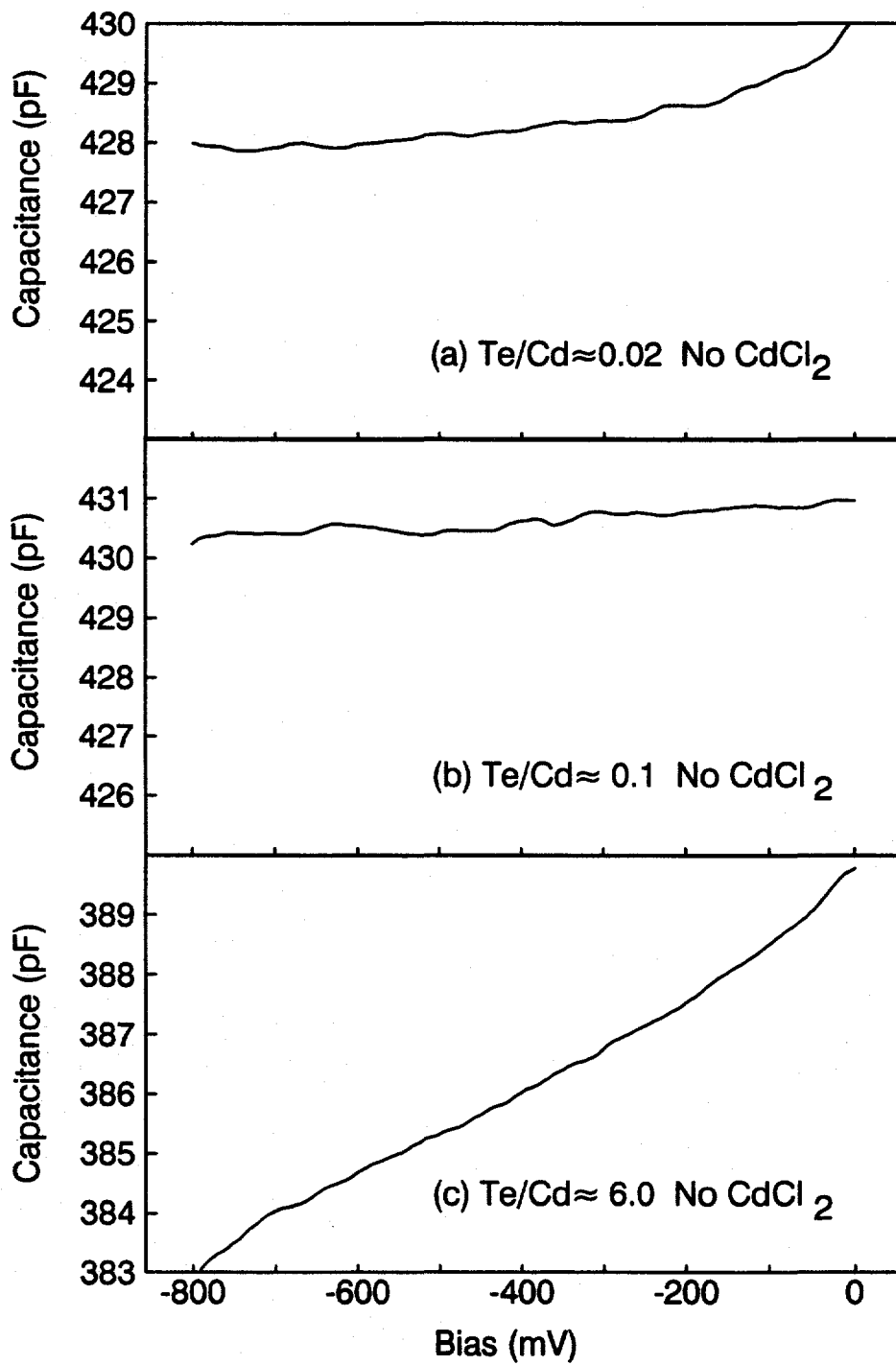


Figure 12: C-V plots for cells that were not treated with CdCl₂-methanol solution

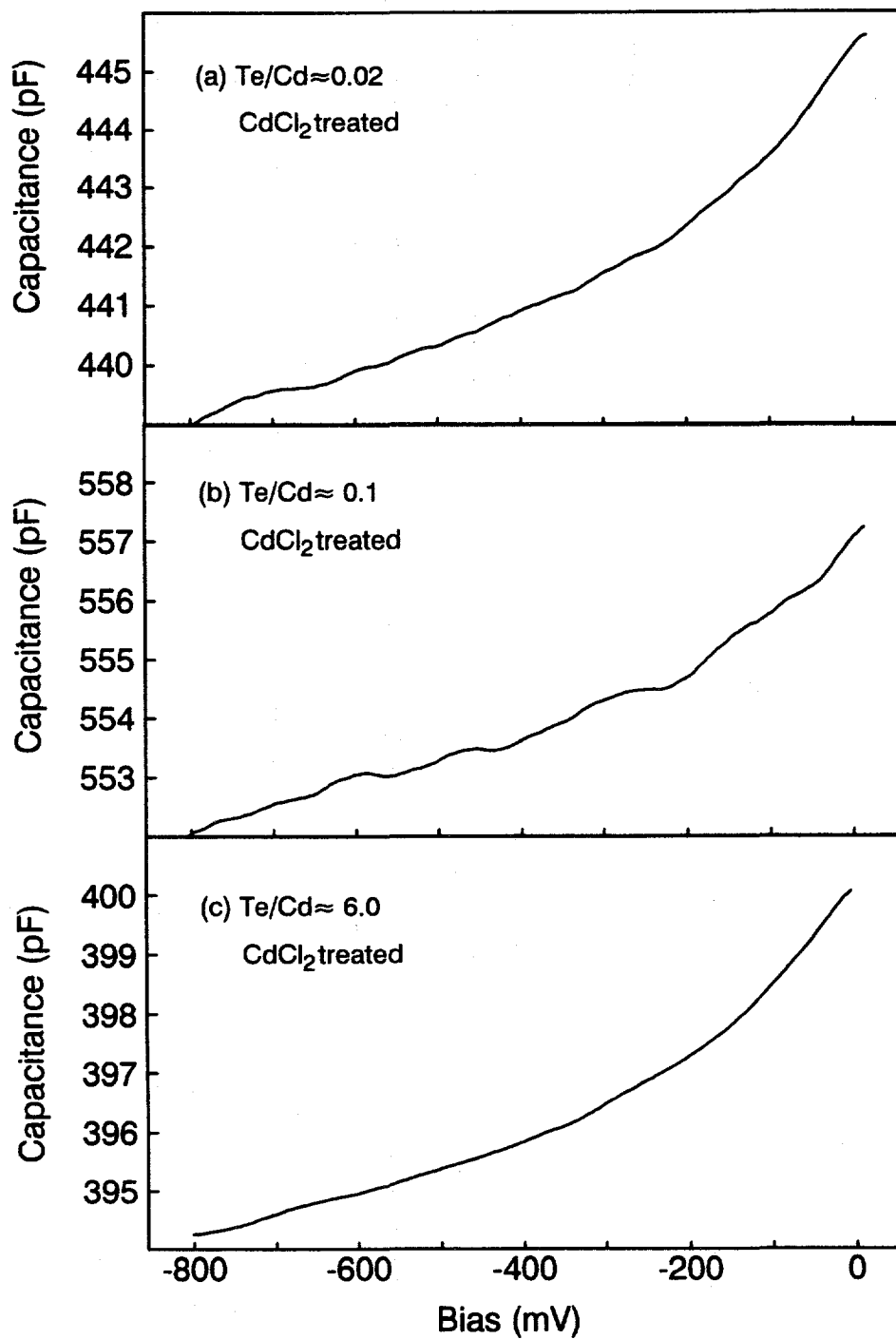
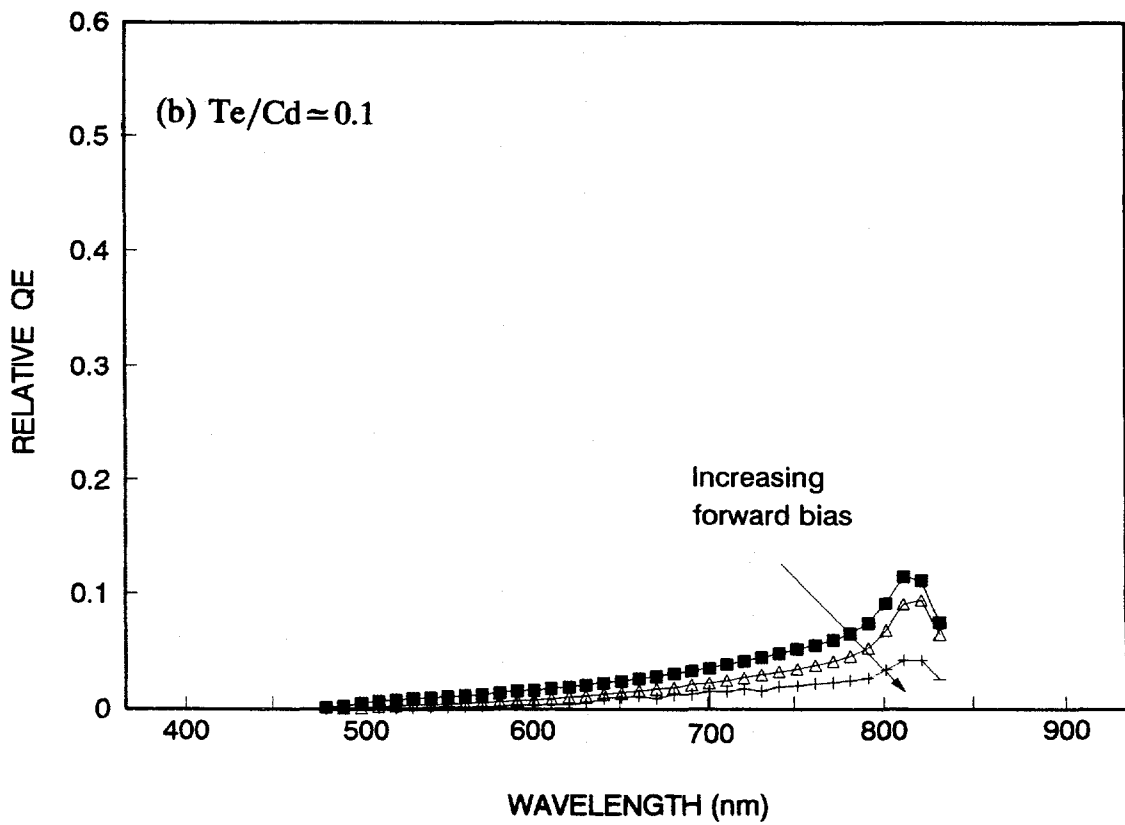
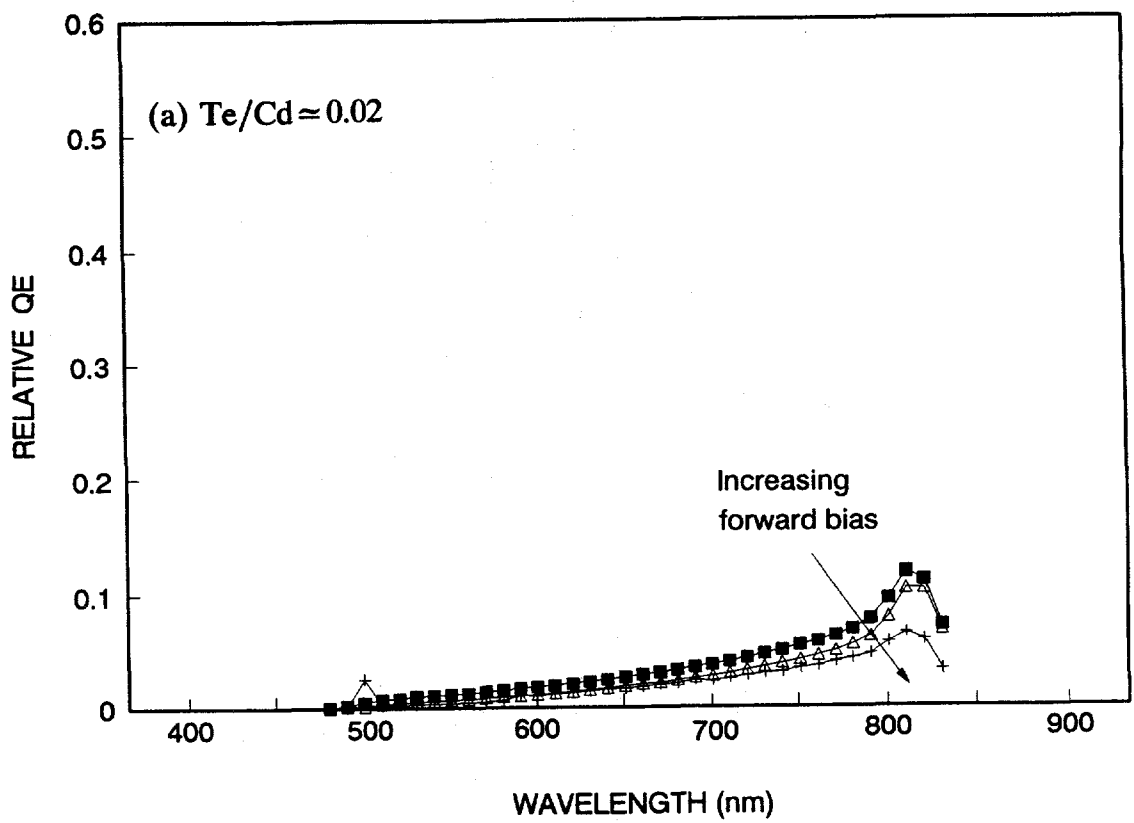


Figure 13: C-V plots for cells that were treated with CdCl₂-methanol solution

again indicate that the effect of Te-rich ambient is to create p-type CdTe and a p-n junction at the CdTe/CdS interface. It appears that the absence of excess Te in the ambient creates a homojunction in the CdTe films which results in low QE values at short wavelengths. In these films, the blue response is larger when the cell is illuminated from the Cu/Au contact side instead of the CdS side, and the red response is larger from the CdS side (Figure 15).

QE data from CdCl₂ treated films indicate high collection efficiency for cells grown in Te-rich and extremely Cd-rich conditions, and lower QE for cells that were grown under moderately high Cd-rich conditions (Figure 16). This suggests that the carrier lifetime in the films grown under moderately high Cd-rich condition is low (See discussion on photoluminescence below). Thus, the data is consistent with the trend observed for J_{sc} as a function of ambient mole ratio described in Figure 5. Moreover, under forward bias, QE drops less rapidly for the cell grown under Te-rich ambient (Figure 17). This is again possibly due to fewer interface states at the CdS/CdTe interface states resulting from the enhanced inter-diffusion at the interface in these films.



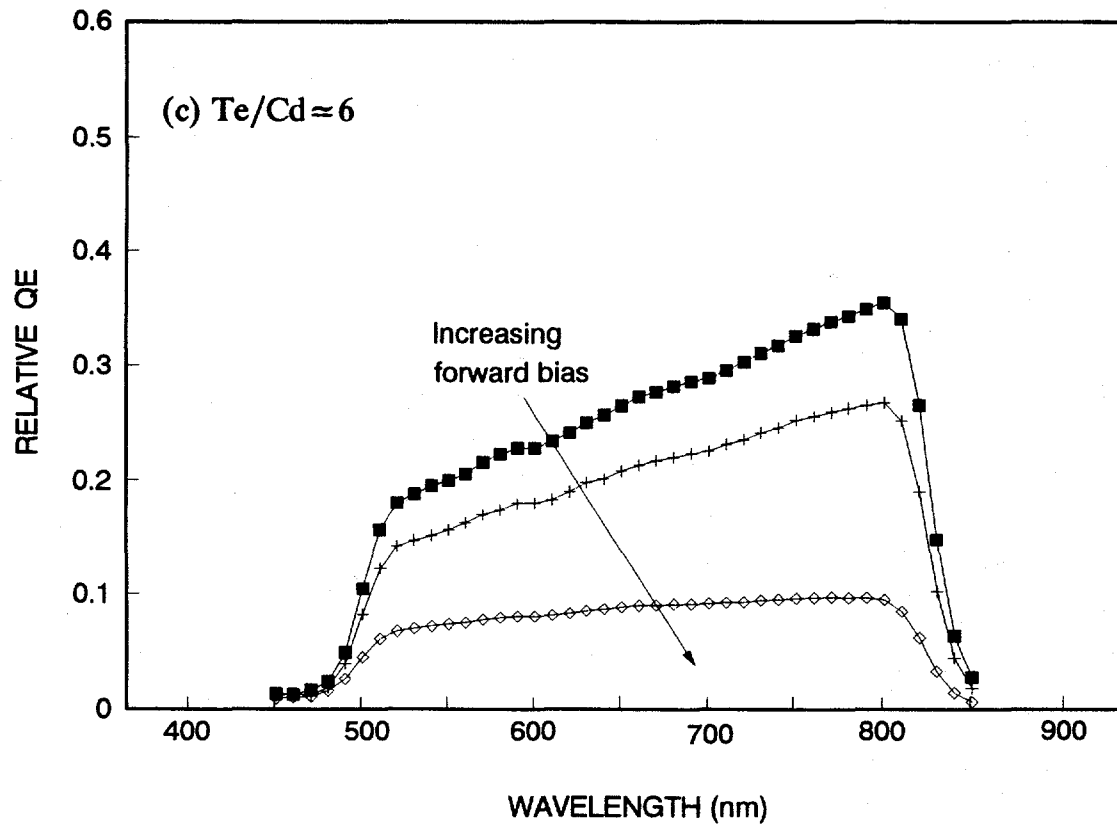


Figure 14: QE data from cells that have not been treated with CdCl_2 -methanol solution for MOCVD Te/Cd mole ratios of (a) 0.02, (b) 0.1, & (c) 6

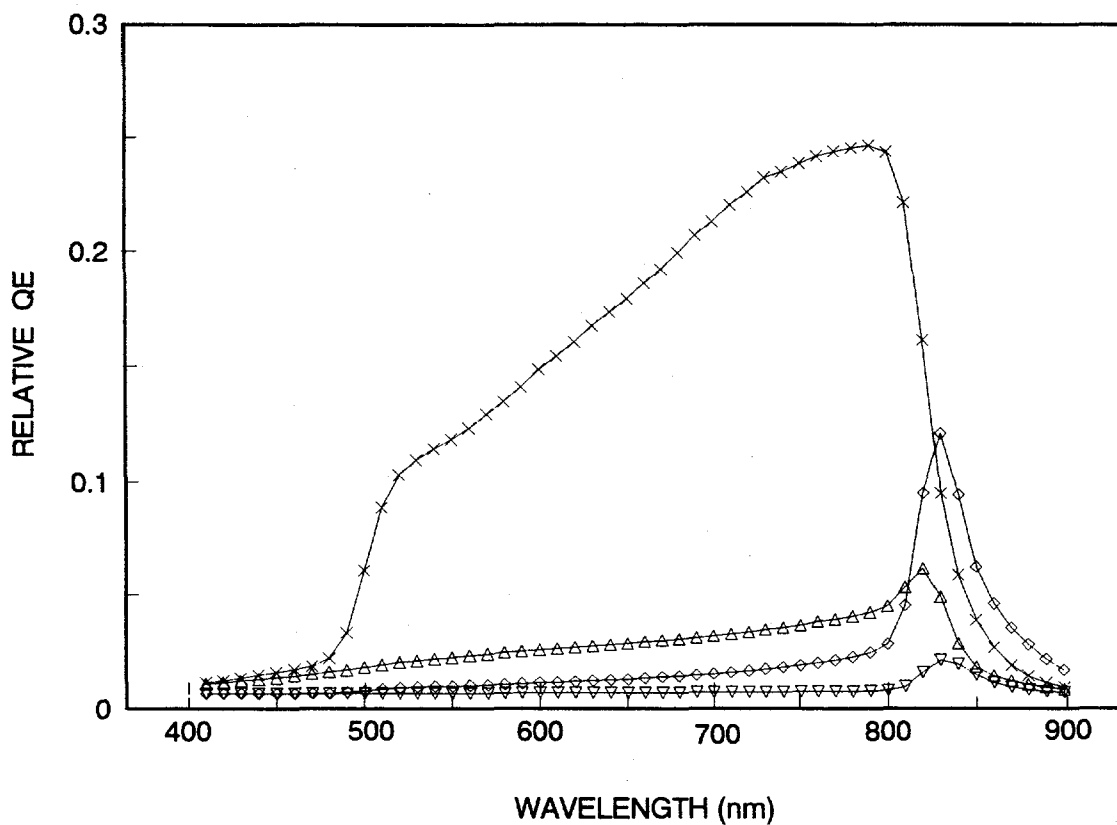


Figure 15: Comparison of QE data for illumination from front and back sides of cells for MOCVD Te/Cd mole ratio of 6:

- ◇ illumination from CdS side, not annealed
- △ illumination from Cu/Au contact side, not annealed
- × illumination from CdS side, annealed at 400°C in air
- ▽ illumination from Cu/Au contact side, annealed at 400°C in air

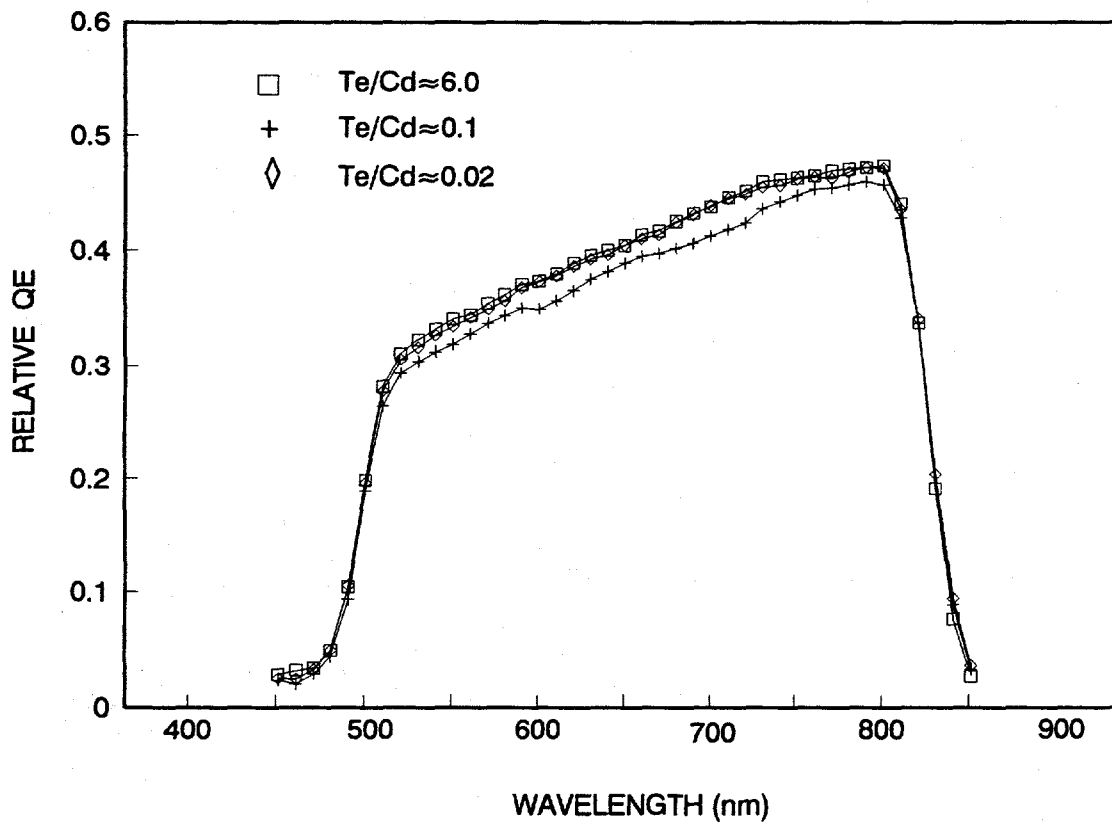


Figure 16: QE data from CdCl₂ treated cells at zero voltage bias

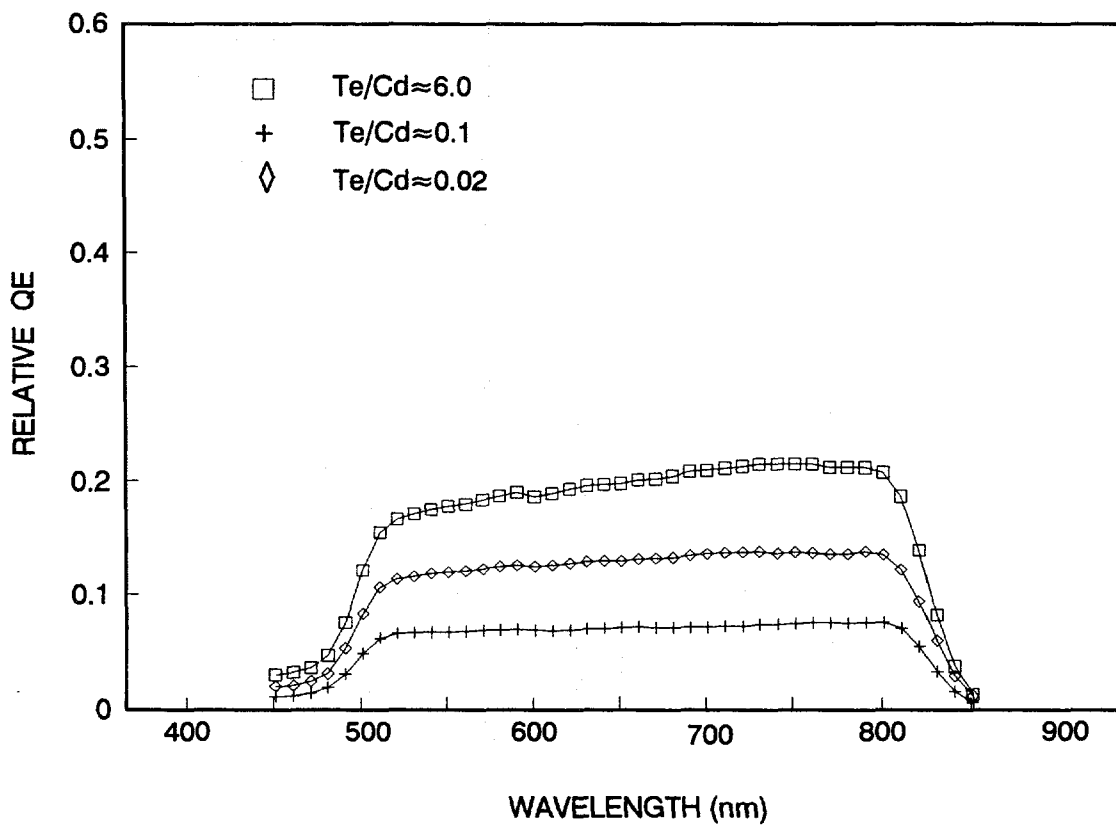


Figure 17: QE data from CdCl₂ treated cells with forward bias of 0.6 V

2.34 Photoluminescence (PL) data: PL measurements were performed at NREL on our CdTe films to study the correlation between cell parameters and effective carrier life times. The PL measurements were taken at 295 K using 600 nm radiation from a pulsed laser. A typical time-resolved PL plot is shown in Figure 18. Table 11 contains the measured lifetimes on films grown under different conditions. The data show that the post-growth CdCl₂ treatment increases the carrier lifetime, possibly due to passivation of grain boundary states. In addition, Te-rich growth ambient gives a relatively higher effective lifetimes even in the as-grown films. The data clearly indicate that a Te-rich ambient not only improves the interface quality and produces p-type CdTe, but also reduces bulk defects. Our results suggest that the difference in the parameters of CdTe cells fabricated by various investigators, who use different growth techniques, could be partly due to the differences in the ambient which in turn affect the native defect concentration.

Liquid N₂ temperature photoluminescence spectra revealed bands at about 905 nm in as-grown CdTe films that were grown with Te/Cd mole ratios of 0.02 and 0.1 (See Figure

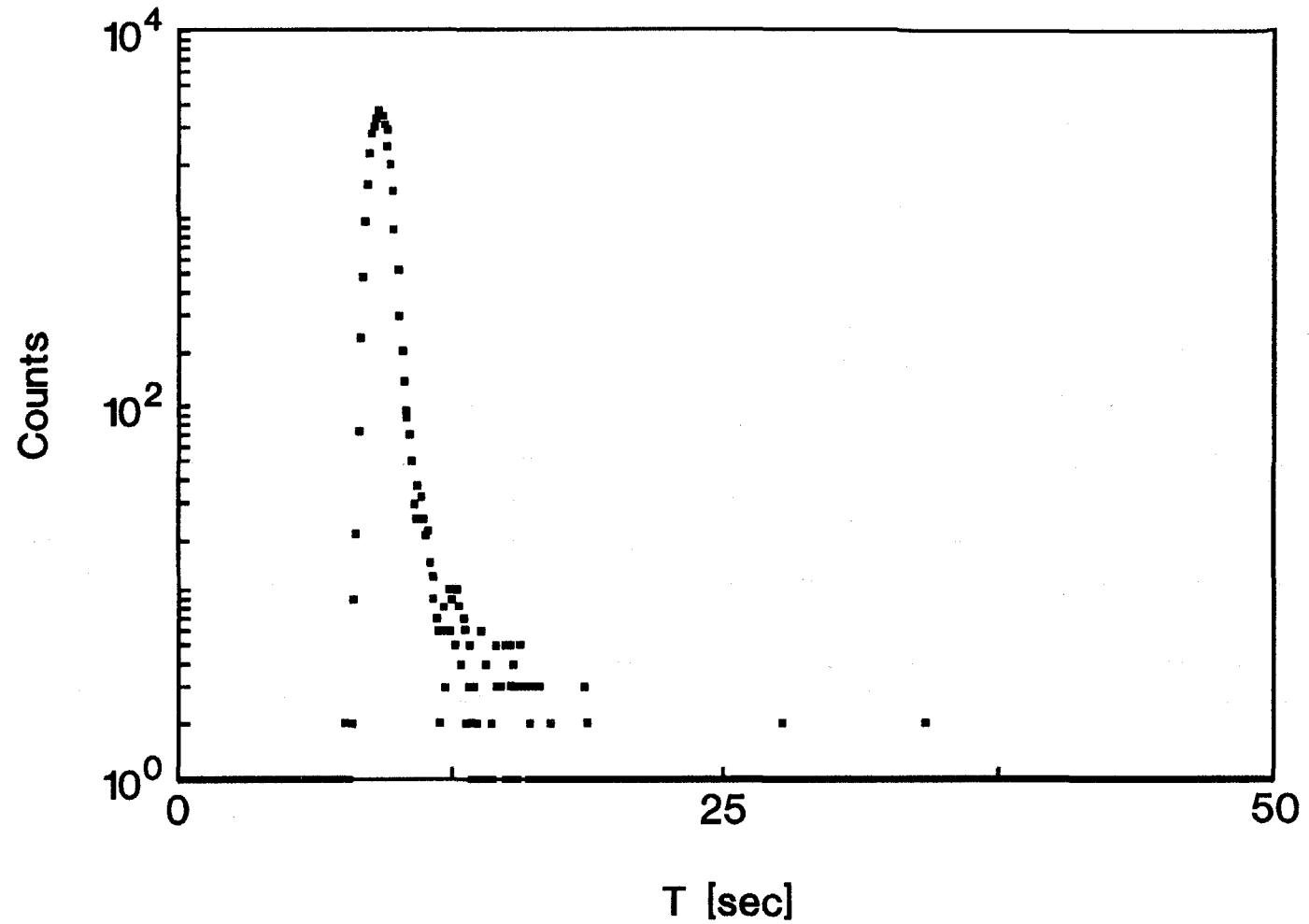


Figure 18: Time-resolved photoluminescence data for carrier lifetime measurement

Monochromator Setting	825 nm	Lifetime	2.36×10^{-10} sec
Slit Widths	500, 500 μ m	Structure	CdS/CdTe cell
Excitation Wavelength	600 nm		
Excitation Power	2.0 mW	Sample Temperature	295 K
Laser Repetition Rate	800 kHz	Collection Time	120 sec

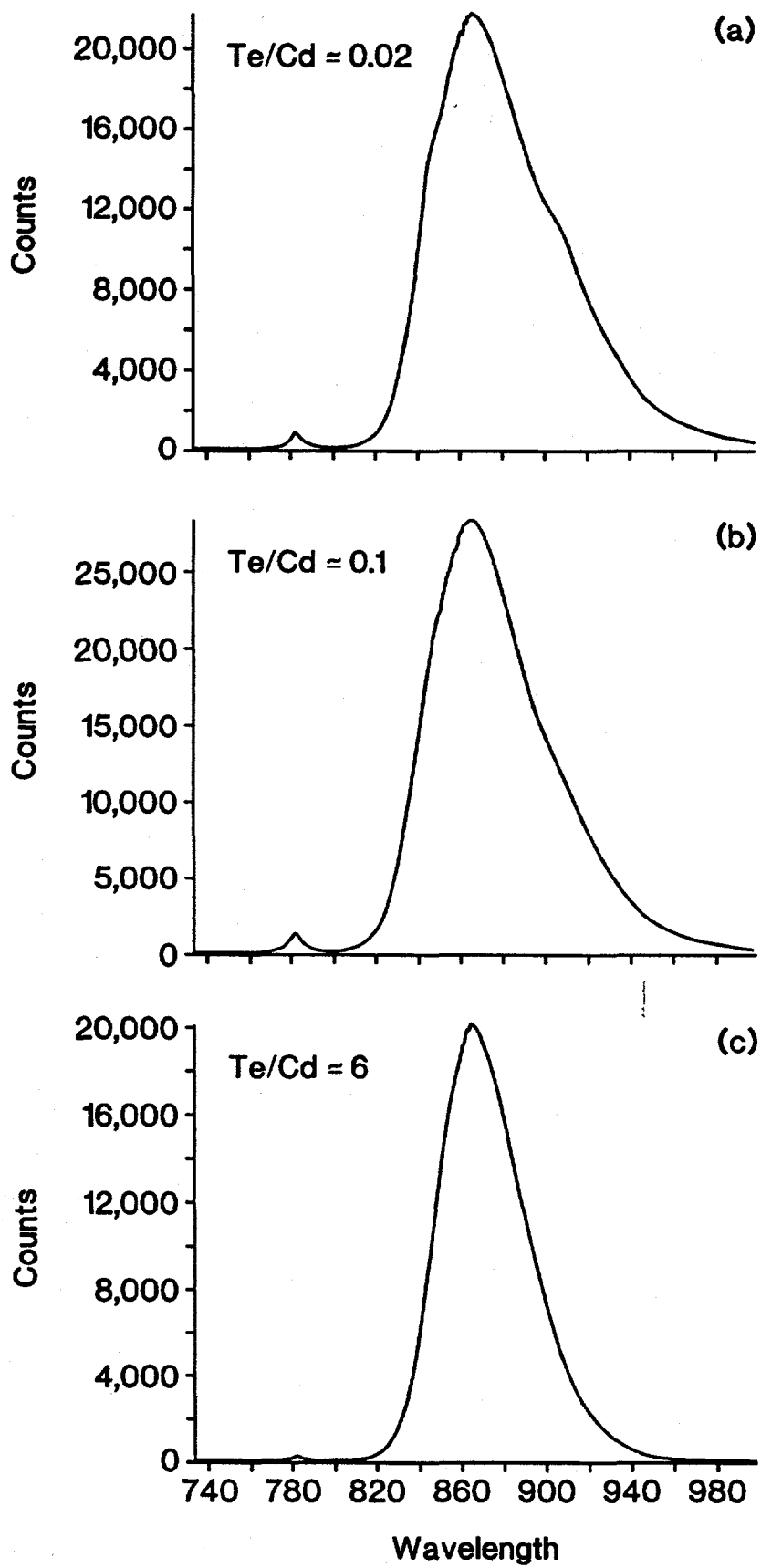


Figure 19: Photoluminescence spectra from as-grown CdTe films

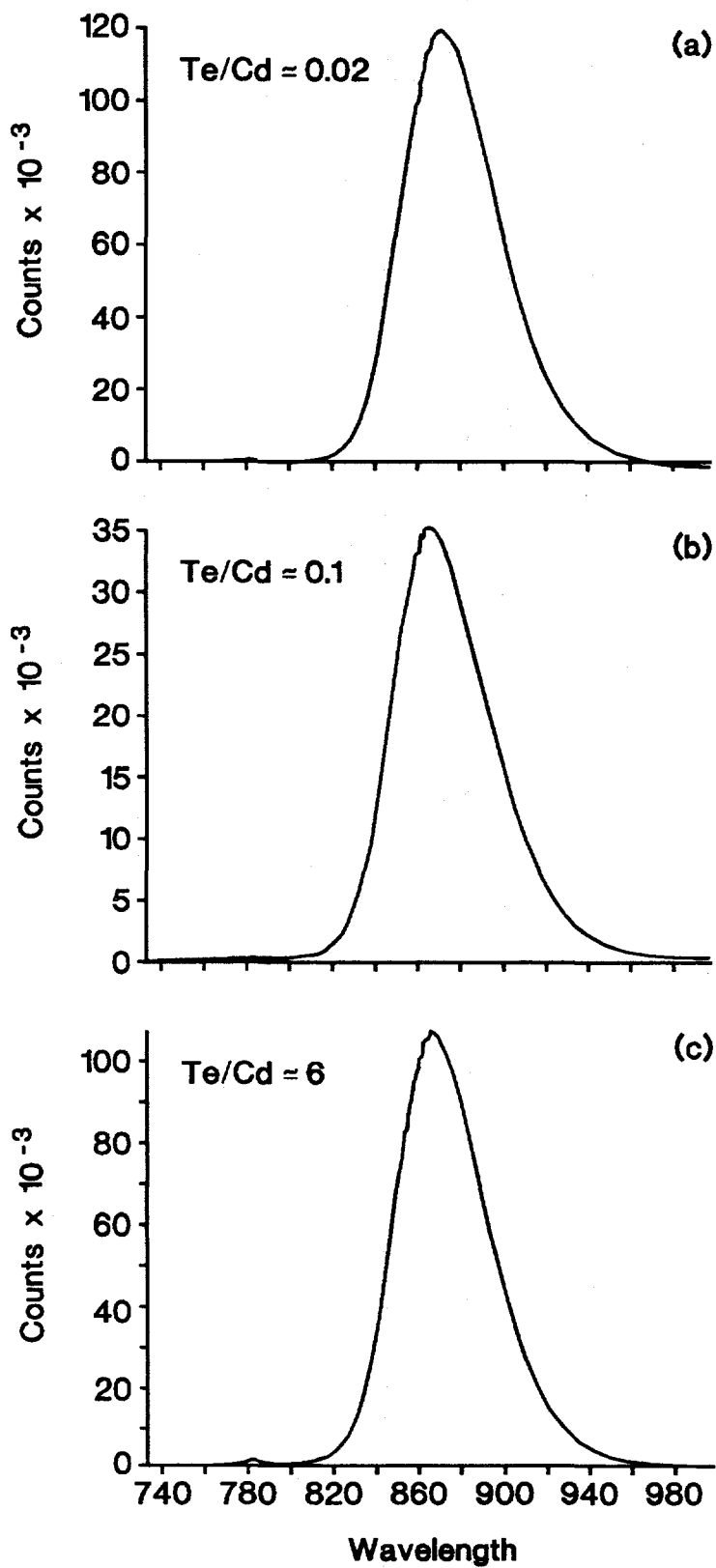


Figure 20: Photoluminescence spectra from CdCl_2 -treated and annealed CdTe films

19). This band was not observed for the $\text{Te/Cd} \approx 6$ film, and disappeared even in the Cd-rich films after the post-growth CdCl_2 treatment and the 400°C anneal (Figure 20). The band has been associated with Te vacancies or its complexes (13).

Table 11: Photoluminescence lifetimes

Te/Cd mole ratio	CdCl_2 treatment	Lifetime (nsec)
0.02	No	0.116
0.1	No	0.121
6.0	No	0.153
0.02	Yes	0.210
0.1	Yes	0.201
6.0	Yes	0.236

2.4 Rapid Thermal Processing of CdS/CdTe films

Treatment of CdS/CdTe films with saturated CdCl₂-methanol solution followed by a 30 to 50 minute anneal at 400°C in air has been routinely used by several groups to produce polycrystalline CdTe solar cells with efficiencies exceeding 10% (9,14,15). Although the post-growth CdCl₂ treatment described above is believed to enhance grain growth and significantly improve cell performance, efficiencies produced to date are below the theoretically projected value of ~18% for the polycrystalline CdTe solar cells. Amongst the possible limiting factors are: 1) defects due to the presence of an excessive amount of CdCl₂, and 2) undesirable diffusion related defects at the CdS/CdTe interface during the long annealing duration. In order to avoid these possible deleterious effects, we have explored the use of Rapid Thermal Processing (RTP) for enhancing the performance of CdTe solar cells with higher annealing temperatures and yet reduced annealing duration.

The RTP was done in an AET Addax computer-interfaced processor. The glass/SnO₂/CdS/CdTe samples were placed on a quartz disc, covered by a quartz watch glass, and radiatively heated to the desired temperature with a bank of halogen quartz lamps (See Figure 21). The film surface temperature was measured by direct thermal contact using thermocouple wires. The annealing was done in controlled O₂-N₂ or forming gas ambient. A complete list of process variables for the post-growth treatment includes:

- (1) concentration of CdCl₂-methanol solution
- (2) RTP temperature (typical range: 400°C - 750°C)
- (3) RTP time (typical range: 5 sec -100 sec)
- (4) Ambient gas composition and pressure

A typical sample of the annealing profile generated by the RTP controls is shown in Figure 22.

Different RTP conditions were studied to relate the effect of some of the parameters listed above to the solar cell efficiency. A 700°C, 5 second anneal in an O₂-N₂ gas mixture gave an efficiency of ~8.2% without any CdCl₂ treatment on the CdTe film. This result is radically different from the conventional anneal result, where the omission of CdCl₂

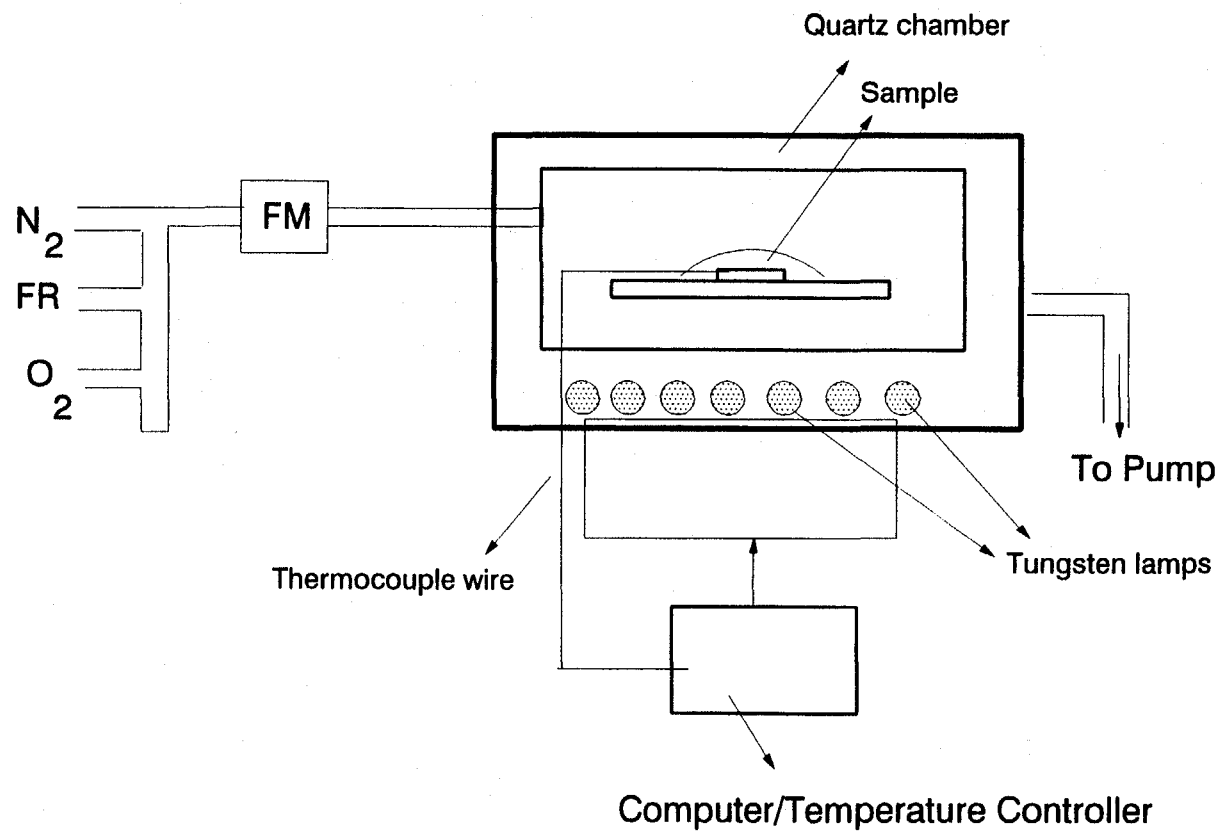


Figure 21: AET ADDAX Rapid Thermal Processor

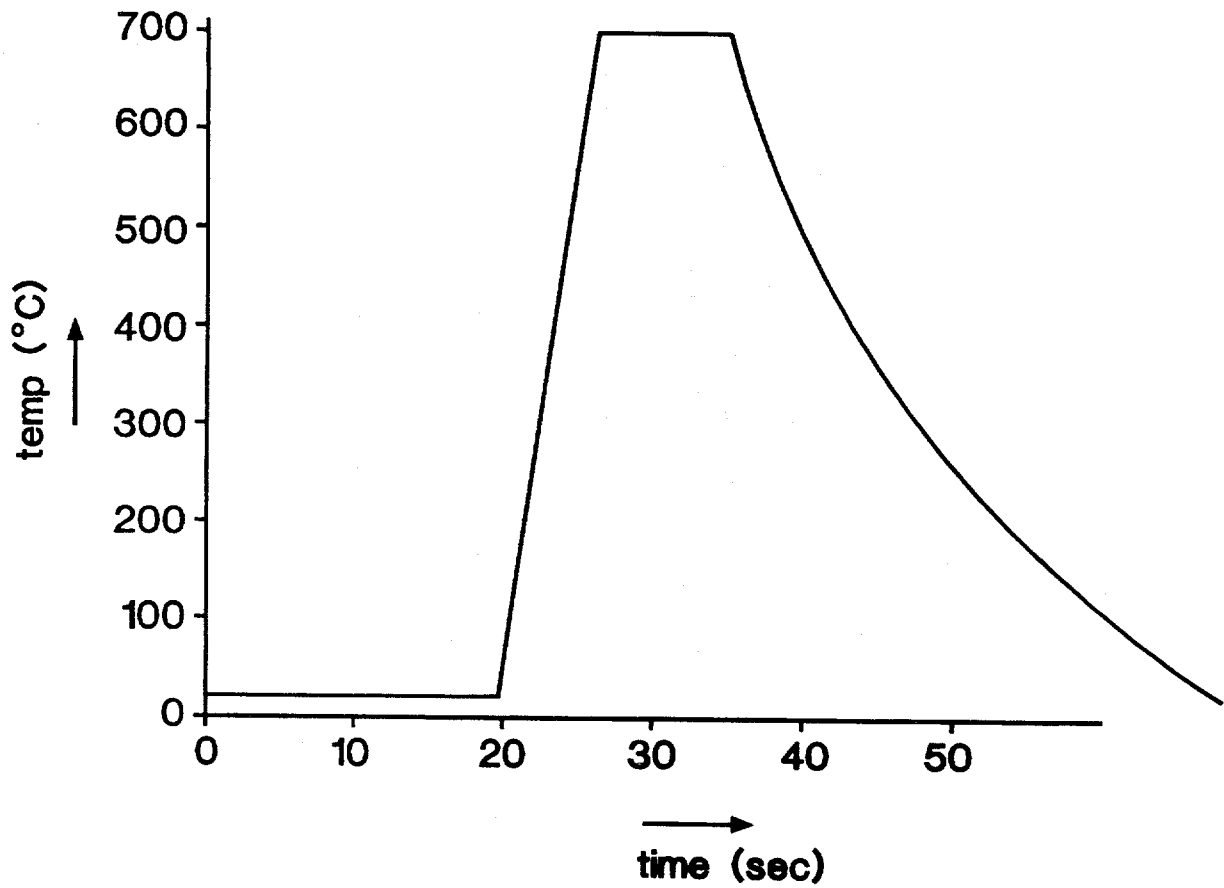


Figure 22: Typical annealing profile generated by RTP control

treatment only gives 3%-5% efficient cells. It was also found that the oxygen content in the ambient was very critical. According to Hsu et al (16), the presence of oxygen in CdTe gives rise to p-type conductivity. Moreover, according to these authors carrier activation due to oxygen is limited, and an excessive incorporation of oxygen can also lead to reduced mobility. Increasing the ambient oxygen content during RTP above a certain value (while leaving the other parameters unchanged) resulted in reduced short circuit current (Table 12), and our results appear to be consistent with the observation made by Hsu et al.

Table 12: Effect of ambient O₂ content during RTP on J_{sc}

O ₂ content	J _{sc} (mA/cm ²)
low	16.5
optimum	19.4
high	17.5
higher	15.4
highest	13.4

Table 13 gives a summary of results obtained with different post-growth treatments. Conventional furnace anneal at 400°C for 30 minutes without CdCl₂ treatment typically gives less than 3% efficient cells with our MOCVD grown films. In the usual CdCl₂ treatment, a few drops of 50% CdCl₂ solution are placed on the sample and allowed to dry for a few minutes. A 400°C conventional furnace anneal with the usual CdCl₂ treatment typically gives an 11% cell. However, RTP at 600°C with the same CdCl₂ treatment gave less than 1% efficient cells, suggesting a need to reduce the CdCl₂ concentration or the amount of solution used in conjunction with RTP. The effective amount of CdCl₂ solution used was reduced by simply using a 7 second dip in the 50% solution, followed by a quick blow dry. RTP at 600°C in an O₂-N₂ mixture with this modified CdCl₂ treatment gave a respectable 7.7% efficient cell. Eliminating the CdCl₂ treatment completely and simultaneously

increasing the RTP temperature from 600°C to 700°C gave an efficiency of 8.2%.

Table 13: Dependence of cell efficiency on post-growth treatment

Annealing condition		V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	Efficiency
Furnace (air)	CdCl ₂ + 400°C	745	22.10	66.0	10.9%
RTP (N ₂ + H ₂)	CdCl ₂ + 600°C	547	7.09	47.8	1.9%
	CdCl ₂ + 600°C	690	20.76	53.9	7.7%
RTP (N ₂ + O ₂)	No CdCl ₂ , 600°C	704	18.51	53.5	7.0%
	No CdCl ₂ , 700°C	711	19.40	59.5	8.2%

It is reasonable to expect that the high temperatures attainable by RTP for short durations will enhance grain regrowth while minimizing re-evaporation of CdTe from the surface. The observations described above also suggest that higher temperatures achieved using RTP should allow grain regrowth in the presence of a lower concentration of CdCl₂, and thus reduce the chlorine related defects. The RTP equipment was temporarily shut down due to ceratin problems in the electronic circuitry. A more complete investigation of the process parameters will be continued once the equipment is back on line.

2.5 Solution growth of CdTe

A low cost solution growth technique for making CdTe thin films is currently being investigated in our laboratory. R.W. Buckley (17) reported on using solution growth to fabricate CdS/CdTe solar cells at the recently held 11th European Photovoltaic Conference and Exhibition in Montreux, Switzerland. Solution growth of CdTe has been reported earlier by Padam and Malhotra (18).

The deposition is based on the reaction between the triethanolamine complex of Cd^{2+} ions and TeO_2 in basic medium. 45 ml of 0.05 M cadmium chloride solution was taken in a 500 ml beaker and to it 45 ml 3.0 M triethanolamine (TEA), 150 ml of ammonia solution, and 150 ml of de-ionized water were added. The solution was stirred with a magnetic stirrer and filtered. CdS/ SnO_2 /glass substrates and SnO_2 /glass substrates were mounted vertically in the beaker and the beaker was placed in a water bath kept at $\sim 90^\circ\text{C}$. 7.5 ml of hydrazine hydrate and 0.1 g of TeO_2 powder were added to the reaction mixture and the solution was continued to be stirred. CdTe precipitates and some deposition were observed after several minutes. The deposition was not uniform and the CdTe films were not adherent. Also, there is some concern regarding the use of the highly toxic hydrazine in the process. It is desirable to substitute hydrazine by another reducing agent which is more benign and yet equally effective. Keeping in mind the low cost of the technique and the promising results reported by Padam et al and by Buckley ($\eta=9.8\%$), we plan to continue with our study of the process.

SUMMARY

An attempt has been made to improve the fundamental understanding of the efficiency limiting defects and mechanisms in order to reduce the gap between current and practically achievable efficiency of polycrystalline thin film CdS/CdTe solar cells. In this study, CdTe/CdS solar cells were fabricated by depositing CdTe films on glass/SnO₂/CdS substrates by MOCVD in different growth ambients with varying Te/Cd mole ratios in the range of 0.02 to 6. The short circuit current density (J_{sc}) showed a minimum at a Te/Cd ratio of about 0.1. The J_{sc} increased on both sides of the minimum giving rise to a "U" shaped curve. However, unlike the J_{sc} , open circuit voltage (V_{oc}) was highest for the extremely Te-rich growth ambient and lower as the Cd content in the ambient was increased. The best cell efficiencies in the range of 11.5% to 12.0% were obtained with the Te/Cd ratio of about six. Detailed measurements and analysis revealed a high degree of atomic inter-diffusion at the interface when the CdTe films were grown in the Te-rich ambient. The current transport in the cells grown in Cd-rich ambient was found to be controlled by the tunneling/interface recombination mechanism, and the detailed transport analysis showed that the depletion region recombination became dominant in the "Te-rich" cells. This suggests that the enhanced inter-diffusion reduces interface states which not only switches the transport mechanism but also explains why the forward biased quantum efficiency (QE) decreases relatively rapidly for the Cd-rich CdTe cell. The hypothesis about reduced defect density in the films grown in the Te-rich conditions is further supported by the time-resolved photoluminescence and light biased QE measurements which gave higher bulk effective lifetimes in the Te-rich films.

Rapid thermal processing (RTP) has been investigated as an alternative to the conventional post-growth furnace anneal of the CdS/CdTe films. A 700°C, 5 second anneal in an O₂-N₂ gas mixture gave an efficiency of ~8.2% without any CdCl₂ treatment of the CdTe film. This is radically different from the conventional 400°C/30 minute anneal result, where the omission of CdCl₂ treatment only gives 3%-5% efficient cells. We believe that the high temperatures achieved using RTP will allow grain regrowth in the presence of a

lower concentration of CdCl_2 , and thus reduce chlorine related defects.

In-house solution growth of CdS at Georgia Tech has increased the cell efficiencies from 9%-10% range to 11%-12% range. Close control of the process parameters has also improved the yield of high efficiency cells. An NREL tested cell has a V_{oc} of 748 mV, J_{sc} of 23.08 mA/cm², fill factor of 0.647, and an efficiency of 11.2%.

A solution growth process for CdTe films which is similar to the solution growth process for CdS films is currently under study.

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16. Abstract (Limit: 200 words) This report describes work to improve the basic understanding of the loss mechanisms in thin-film CdS/CdTe solar cells and to improve their efficiency by characterizing the properties of the films as well as the finished devices. To accomplish this, solar cells were fabricated on glass/SnO ₂ /CdS substrates by metal-organic chemical vapor deposition (MOCVD) growth of CdTe films and evaporation of Cu/Au contacts. The substrates were provided by Solarex Corporation and were recently grown in house on glass/SnO ₂ substrates using solution growth. Rapid thermal processing (RTP), still a relatively new technology with growing applications in the semiconductor industry, is being investigated in this program as an alternative to the conventional post-growth furnace annealing of the CdS/CdTe films. Consistent with the long-term goals of cost-effective, large-scale terrestrial applications of photovoltaics, we also made some preliminary investigations of a solution growth technique for depositing CdTe films.			
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