Role of Polycrystallinity in CdTe and CuInSe₂ Photovoltaic Cells

**Annual Subcontract Report
1 April 1992 – 31 March 1993**

J. R. Sites
*Colorado State University
Fort Collins, Colorado*

NREL technical monitor: B. von Roedern

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
A national laboratory of the U.S. Department of Energy
Operated by Midwest Research Institute
for the U.S. Department of Energy
under contract No. DE-AC02-83CH10093

Prepared under Subcontract No. XC-0-10046-1

February 1994

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

This publication was reproduced from the best available camera-ready copy submitted by the subcontractor and received no editorial review at NREL.

NOTICE

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Printed in the United States of America
Available from:

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Microfiche A01
Printed Copy A03

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issue of the following publications which are generally available in most libraries: *Energy Research Abstracts (ERA)*; *Government Reports Announcements and Index (GRA and I)*; *Scientific and Technical Abstract Reports (STAR)*; and publication NTIS-PR-360 available from NTIS at the above address.

Printed on recycled paper

DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.

SUMMARY

Several investigations of thin-film polycrystalline solar cells were completed: (1) An analysis of high-efficiency solar cells fabricated at the University of South Florida showed significant reduction in forward recombination current, and the cells were stable over a three-month test period. (2) Transient voltage effects have now been documented in a large number of polycrystalline cells and attributed to long-lived trapping states sensitive to voltage changes near one-half V_{oc} . (3) Collection efficiency and its voltage dependence have been carefully calculated. The typical effect on photocurrent at operating voltages is about 2% for $CuInSe_2$, less for other cells.

TABLE OF CONTENTS

	SUMMARY	ii
1.	INTRODUCTION	1
2.	PRESENT STATUS	1
3.	HIGH-EFFICIENCY CdTe ANALYSIS	3
4.	VOLTAGE TRANSIENTS	12
5.	COLLECTION EFFICIENCY	21
6.	RECOMMENDATIONS	29
7.	COMMUNICATIONS	29
7.1	<u>Publications</u>	29
7.2	<u>Submissions</u>	29
7.3	<u>Talks</u>	30
7.4	<u>Specific Cell Reports</u>	30
8.	REFERENCES	30

FIGURES

2-1.	Maximum-current comparison	2
2.2	Maximum-voltage comparison	2
2-3.	Maximum fill factor comparison	4
2-4.	Maximum efficiency comparison	4
3-1.	I-V curves for high-efficiency CdTe cells	5
3-2.	Forward current for some cells	6
3-3.	Photon losses for high-efficiency CdTe cells	7
3-4.	Variations of CdTe parameters with intensity	8
3-5.	Variations of CdTe parameters with temperature	10
3-6.	Three-month CdTe parameter tracking	11
4-1.	Transient-voltage measurement apparatus	13
4-2.	Typical V_{oc} transients	15
4-3.	Relaxation of transient-voltage states	16
4-4.	ΔV_{oc} variation with pre-bias	18
4-5.	Dark vs. light transient voltage	19
4-6.	Transient voltage using three techniques	20
5-1.	Calculated quantum efficiencies	22
5-2.	Variation of collection efficiency with depletion width	23
5-3.	Voltage-dependent photocurrents for four cell-types	24
5-4.	CuInSe ₂ photocurrent reduction at maximum power	25
5-5.	Effect of photocurrent reduction on forward-current analysis	26
5-6.	Calculated magnitude of photocurrent reduction	27

TABLES

4-1.	V_{oc} transients for several polycrystalline cells	12
4-2.	Listing of transient-voltage measurements	14

1. INTRODUCTION

The objective of the Colorado State program is the evaluation of individual loss mechanisms in thin-film polycrystalline solar cells. Loss comparisons are done in the context of (1) ideal cells of the same bandgap, (2) high-quality crystalline cells, and (3) hypothetical target cells representing realistic goals for the next few years. During the past year, primary emphasis has been on (1) high-efficiency CdTe cells fabricated at the University of South Florida, (2) transient-voltage behavior found in a large number of polycrystalline cells, and (3) analysis of collection efficiency, including predictions of its voltage dependence.

Three research students, Rick Sasala, Xiaoxiang Liu, and Ingrid Eisgruber were responsible in large part for the experimental and analytical studies that follow. The high-efficiency CdTe cells discussed were fabricated at the University of South Florida. Cells used in the other sections were made by Siemens Solar, ISET, IEC, NREL, and Boeing. Two colleagues, Chris Ferekides at USF and Keith Emery at NREL, were particularly helpful in discussions of the results presented here.

2. PRESENT STATUS

The series of four figures on the next pages graphically illustrate the present status of the thin-film polycrystalline solar-cell community. In Fig. 2-1, the solid line shows the maximum photocurrent available from a standard AM1.5 solar spectrum as a function of absorber bandgap. Maximum current densities achieved by polycrystalline CuInSe₂ and CdTe are compared to those achieved by crystalline Si and GaAs cells. The labels indicate the percentage of the theoretical maximum that has been seen to date. The polycrystalline currents are a modest 5% lower than the crystalline currents. The difference is due to three fairly small effects: red collection limited by diffusion length, blue collection hampered by the window layer, and somewhat less effective AR coatings.

Fig. 2-2 shows the open-circuit voltage comparison. The maximum value assumes thermionic emission, and the range denotes parameter variation among common semiconductors. The difference between the crystalline and polycrystalline values achieved is more pronounced. The difference here is about 15%. It is due to forward currents that are 2 to 3 orders of magnitude larger in the polycrystalline cells. These forward currents, the largest single problem with polycrystalline cells, are the result of significant numbers of recombination traps in the depletion region. Considerable progress, in reducing these trap densities has, in fact, been made in the

Fig. 2-1. Largest current densities achieved to date for four common cell materials. Theoretical maximum for 100 mW/cm² AM1.5 spectrum shown for reference.

Fig. 2-2. Highest voltages achieved to date.

past few years through a combination of planned and fortuitous fabrication improvements.

In Fig. 2-3, the highest fill factors are compared to the theoretical values. The differential between polycrystalline and single crystals cells here is about 10%. The primary difference is the diode quality factor, which tends to be near 1.5 for CuInSe_2 cells, 2 for CdTe , but close to 1 for crystalline cells. Polycrystalline cells also tend to have higher values of series resistance and more significant leakage than crystalline cells. They also have slightly lower fill factors since their voltages are a smaller fraction of their bandgap.

Finally, Fig. 2-4 shows the maximum efficiency comparison. When the three factors are combined, the best thin-film polycrystalline cells have achieved efficiencies about two-thirds as large as the best crystalline cells. This may not be an unreasonable price to pay given the massive economies of scale offered by thin-film fabrication techniques. Furthermore, the polycrystalline cells have the potential for additional improvements. There are a variety of individual losses that can be lowered small amounts even without major breakthroughs. Thus, it is a reasonable expectation that the efficiency gap between thin-film polycrystalline and crystalline cells will continue to narrow a small amount each year.

3. HIGH-EFFICIENCY CdTe ANALYSIS

Current-voltage characteristics of several high-efficiency ($\sim 15\%$) CdTe cells, fabricated at the University of South Florida (USF), were measured at room temperature in the dark and under 100 mW/cm^2 illumination. Fig. 3-1 shows the light current-voltage characteristic for the 15% cell which showed the best junction characteristics. A USF CdTe cell from one year earlier with 14.6 efficiency [1], and the highest efficiency (15.8%) USF cell [2] are included for comparison. Also shown in this figure is a hypothetical 18% target cell ($J_L = 26 \text{ mA/cm}^2$, $V_{OC} = 875 \text{ mV}$, $A = 2.0$, $R_s = 0$, $R_{SH} = \infty$, and resulting $FF \approx 79\%$).

Fig. 3-2 shows the forward diode current extracted from the cell data of Fig. 3-1. Solid points were taken in the dark, and open ones in the light. The dashed lines are fits with series and shunt resistance effects removed ($R_s \rightarrow 0$, $R_{SH} \rightarrow \infty$). The solid line is the fit for the hypothetical 18% target cell. The fit for the 15% efficient cell, which has a high open-circuit voltage (860 mV), but relatively modest photocurrent (23 mA/cm^2), is approaching the target curve.

Fig. 2-3. Largest fill-factors achieved.

Fig. 2-4. Highest efficiencies to date for four solar cell materials. CdTe composite value, combining parameters from two cells, is significantly higher; others are not.

Fig. 3-1. Current-voltage curves for highest-efficiency 1991 USF cell (11-4-8A, 14.6%), highest-efficiency 1992 cell (6-1B-6B), 15.8%), best-junction cell (5-1A-12B, 15.0%), and target cell (18%).

At any selected voltage, its forward current under illumination is smaller than the other two CdTe cells. Its dark forward current (also shown) is in fact less than the target value. Thus the junction behavior is significantly improved in this cell compared to the best cell from the previous year, and even to the highest efficiency cell.

Quantum efficiency measurements were used to quantitatively separate the individual photocurrent loss mechanisms [3]. Fig. 3-3 shows the lost photon fraction, one minus the measured quantum efficiency, as a function of wavelength for the three USF cells discussed in Fig. 3-1, as well as the highest-current Photon Energy CdTe cell [4]. The individual losses are calculated by attributing a loss mechanism to each lost-photon area, multiplying by the solar spectrum in photon current units [5], and integrating over wavelength. Window absorption (the

Fig. 3-2. Comparison of forward diode currents for same CdTe cells.

loss at short wavelengths due to absorption in the window layer of the cell) for the 15% cell is high (4 mA/cm^2) compared to the highest efficiency USF cell ($2\frac{1}{2} \text{ mA/cm}^2$) and the earlier USF cell (1 mA/cm^2). In the 1992 cells all photon losses are accounted for by the window absorption, reflection (nearly wavelength independent), and deep penetration (at long wavelengths). The 1991 cell, however, had an unexplained mid-wavelength loss of $2\frac{1}{2} \text{ mA/cm}^2$. If the photocurrent losses of the best-junction USF cell were equal to those of the highest efficiency cell, its efficiency would be 16.3%. If they equalled the highest-current Photon Energy cell, the efficiency would be 17%.

The current-voltage characteristics of the best-junction cell were measured at twelve different light intensities from dark to 100 mW/cm^2 using ELH illumination. Open-circuit voltage and efficiency increase nearly logarithmically with increasing light intensity. Fig. 3-4 shows the

Fig. 3-3. Comparison at photocurrent losses in three USF cells and the highest-current Photon Energy CdTe cell (12.4%).

effects of intensity variations on other key cell parameters. Short-circuit current is quite linear with light intensity. The series and shunt resistances decrease continuously with intensity, but most of their decrease is in the first 10 mW/cm². The A-factor increases gradually with intensity between 0 and 100 mW/cm². These variations are qualitatively similar to those seen in other CdTe and CuInSe₂ cells.

The current-voltage characteristics of the same cell were also measured as a function of temperature between 250 K to 350 K. The short-circuit current is flat within experimental error.

Fig. 3-4. Effect of light-intensity variation on selected parameters of the best-junction CdTe cell.

The open-circuit voltage decreases with temperature at about 1.8 mV/K and has zero-temperature extrapolation of approximately 1.4 V. The fill factor decreases at high temperatures because V_{OC} is dropping. It also decreases at low temperatures, primarily because series resistance shows a marked increase. The voltage difference between the translated light curve and the dark curve in the operating range, after both are corrected for resistive effects, is about 50 mV at higher temperatures and 70 mV at lower ones. This value is larger than that seen in the high-quality CuInSe₂ cells [6], but considerably lower than displayed by CdTe cells until recently [3]. It should be viewed as another indication of improvement in junction quality.

Fig. 3-5 shows effects of temperature on the cell's parameters. The dark hole density, extracted from capacitance measurements, is quite low at all temperatures ($< 2 \times 10^{14} \text{ cm}^{-3}$), as normally seen with CdTe cells. The series resistance is large at low temperatures, especially for the dark data. The diode quality factor A decreases with increasing temperature, as seen in other polycrystalline cells. The product AT is essentially constant in the dark, and increases slightly at low temperatures in the light. The fact that A is greater than 2 at low temperatures and AT is constant in the dark suggests that the current transport is not dominated by simple SRH recombination in the space-charge region with a single mid-gap trap level [7].

Cell performance over time was measured for several 1992 cells and compared to the 1991 cell used above for reference (see Fig. 3-6). Initial and final measurements were done by NREL, intermediate ones at Colorado State. No changes in photocurrent or open-circuit voltage were observed either year. Also the A -factors and shunt resistances were flat over time within experimental error in both years. The series resistance of the 1991 cell, however, showed a gradual increase from 0.4 to 2.6 $\Omega\text{-cm}^2$ over a three month period. This increase, possibly associated with contact degradation, resulted in a 40 mV decrease in V_{MP} and a corresponding fill-factor decrease from 0.725 to 0.68. In 1992, six cells were tracked, three kept in desiccant and three not. None of the parameters measured changed with time outside of experimental uncertainties. Thus, the series-resistance degradation has been effectively eliminated.

In summary, the efficiency improvements in recent USF-fabricated CdTe cells are primarily a result of success in keeping the forward recombination current well below that achieved by other groups. Not only is the dark forward current quite low, but the light-dark differential is

Fig. 3-5. Effect of temperature on best-junction CdTe cell parameters.

Univ. S. Florida CdTe Cell ($100\text{mW}/\text{cm}^2$, 25°C)

Year	1991	1992
Efficiency [%]	13.4-12.5	15
V_{oc} [mV]	840	860
J_{sc} [mA/cm^2]	22	23
fill factor	0.725-0.68	0.755
SERI/NREL	□	■
Colorado State	○	●

Fig. 3-6. Fill factor parameters of 1991 and 1992 USF cells tracked for three months.

relatively modest. The best-junction cells are in fact somewhat low in photocurrent, implying that efficiencies up to 17% should be fairly readily achievable. Furthermore, an earlier USF problem of series resistance degradation seems to have been solved, and the cells are now quite stable over at least a three-month interval.

4. VOLTAGE TRANSIENTS

When thin-film polycrystalline CdTe and CuInSe₂ solar cells are illuminated, the voltage continues to increase during the time range of 1 ms to over 10 ks. For an ideal solar cell, the voltage would stabilize in a few microseconds. The CuInSe₂ voltage increase (ΔV) was observed several years ago by the Boeing group and investigated by Ruberto and Rothwarf [8]. The voltage effect was more recently brought to our attention when efficiency shifts for CdTe modules made by Golden Photon (formerly Photon Energy) were noted at NREL [9]. Since then, careful measurements of the voltage on many polycrystalline CuInSe₂ and CdTe solar cells have been made to document the voltage effect and to understand the physical mechanism(s) responsible. Deep traps located near the metallurgical junction in the absorber material that effectively increase the barrier height V_{bi} are thought to be the primary mechanism responsible.

Table 4-1. Change in V_{oc} between 1 ms and 2000 s after the onset of illumination

Cell Type	Origin	V_{oc} (long t)	ΔV_{oc} (1ms-2ks)
Silicon		512 mV	$0 \pm 2\text{mV}$
CuInSe ₂	ISET	452	22
		460	18
	IEC	440	15
	NREL standard process variable fluxes	432	17
		424	15
	Siemens standard process no CdS	446 487	4 6
CuInSe ₂ + (high E_g)	Boeing	533	20
	Siemens	619	20
CdTe	Photon Energy	764	38
	U So Florida	858	36

Measurements have been made on samples from a variety of laboratories employing several different techniques and compositions. A summary of ΔV for the various samples is given in Table 4-1.

ΔV has been found to result from the cell being in forward bias and is not directly due to the cell being illuminated [10]. The evidence for this observation is that biasing the sample in the dark near the steady-state V_{oc} for a sufficiently long time (> 10 ks) eliminates the voltage increase when the light is turned on and the voltage measured. Further proof that ΔV occurs because of the applied bias is that the voltage increase is similar in the dark when a constant current is passed through the sample.

A diagram of the apparatus used for the voltage transients is shown in Fig. 4-1. The light source is an ELC 24V light bulb powered by a DC power supply. Worst case intensity

Fig. 4-1. Schematic drawing of transient-voltage measurement apparatus

fluctuations are $\pm 1\%$. The light is collimated and then passed through a 35 mm camera which is used for its shuttering capabilities. The opening time of the shutter is under 0.5 ms. The temperature of the sample is controlled by a combination of cold N_2 gas and a heater. A regulated flow of N_2 gas cools the sample to a temperature slightly lower than desired. A temperature controller, using a thermocouple placed as close as physically possible to the sample, regulates a heater to maintain the desired temperature $\pm \frac{1}{2}^\circ\text{C}$ for many hours. Maintaining constant temperature is critical to the experiment since the measured voltage changes are often comparable to those that would result from a temperature change of a few degrees. Electrical measurements that have been performed are summarized in Table 4-2. In shutter and switch measurements the voltage is changed from 0 to V_{oc} . They both yield the same curves which suggests that the voltage increase is dependent on the voltage of the sample and not the illumination [10]. A load resistor measurement gives information about voltage changes at operating voltages. The pre-bias measurement is completed in three steps (1) the sample is held at an applied voltage V_{appl} in the dark for two hours, (2) the light is turned on and the bias off simultaneously and (3) V_{oc} is measured. The resulting ΔV_{oc} is independent of the switching from applied bias to illumination as long as the switching time is under 1 ms, which is easily achieved. Using a constant current source, voltages outside the operating range, including dark voltages, can be probed. In the final measurements, intensity is varied with a combination of an aperture in front of the light source and neutral density filters to achieve intensities from 0.02 to 100 mW/cm².

Table 4.2. Summary of electrical measurements and initial conditions

Measurement Designation	Pre-measurement Illumination	Measurement Illumination	Pre-measurement Voltage	Measurement Voltage
Shutter	0 mW/cm ²	100 mW/cm ²	0	V_{oc}
Switch	100	100	0	V_{oc}
Load Resistor	0	100	0	$V_{operating}$
Pre-bias	0	100	V_{appl}	V_{oc}
Constant Current	0 or 100	0 or 100	0	V (current)
Intensity	0-100	0-100	0	V_{oc} (intensity)

Fig. 4-2. V_{oc} transients for a typical ISET CuInSe₂ solar cell.

The voltage versus time at four temperatures for a typical ISET CuInSe_2 cell is shown in Fig. 4-2. The total voltage change diminishes somewhat as the temperature is increased above room temperature but the initial increase is independent of temperature. The room temperature voltage change is about 30 mV, most of which occurs after the region denoted pulse simulator range. A pulse simulator sweeps the I-V curve during a 1-4 ms light pulse and is commonly used to determine the efficiency of modules, since heating and non-uniform illumination are minimized. The increase in voltage for most cells measured to date is the order of 5%, leading to a corresponding rise in efficiency. No significant change in the short circuit current has been observed. Since the voltage effect is reversible, it is important to determine how the cells revert to their initial dark equilibrium condition. To date, this relaxation has only been measured indirectly by (1) monitoring the open-circuit voltage for 20 ks (≈ 6 hours), (2) shorting the sample for a specified time t_s , (3) measuring the open-circuit voltage for 2 ks, and (4) repeating the cycle using progressively longer values of t_s . If a trap is filled in the initial 20 ks measurement and has a depopulation time constant t_{relax} , the trap will remain filled as long as $t_s < t_{\text{relax}}$. The experiment was done on a sample similar to the cell measured for Fig. 4-2 and the results are shown in Fig. 4-3. The cell was shorted for 2, 5, 10, 50, and 500 s. All the

Fig. 4-3. Relaxation behavior of ISET cell following 6 hours at V_{oc} . t_s denotes time the cell was shorted prior to measurement.

measurements with $t_s < 50$ s saturate at 438 mV implying that 438 mV is the steady-state open-circuit voltage V_{oc-ss} . If t_s for each curve is compared to the time at which the curves saturate t_{sat} , it can be seen that $t_s \sim t_{sat}$. This implies that the relaxation to the dark equilibrium occurs at approximately the same rate and with the same magnitude as the voltage increase in the light. Measurements done on CdTe samples made at Golden Photon show a similar trend except that these samples relax slightly faster than the voltage increases. The probable cause of the voltage increase is electronic traps in the absorber material near the metallurgical junction. A technique is needed to determine the spatial and energy profiles of these traps. Since the voltage increase spans seven orders of magnitude of time, a fit of the data with exponential rates of trap population and depopulation would require a large number of parameters and would have a questionable relationship to reality. While it is possible that there are several discrete traps with specific time constants, it seems more plausible that the traps form a semi-continuous range of levels near mid-gap.

A qualitative picture of the trap distribution can be determined by measuring ΔV using different bias conditions. Changing the bias changes the position of the Fermi level and hence the probability that a trap at a given energy level be populated. Changing the bias also changes the depletion width, which can yield useful information about the spatial distribution. The analysis is complicated by the fact that the Fermi energy is not well defined in the depletion region other than at zero bias. Nevertheless, variations in the bias condition can give a qualitative idea of where and at what energy level the traps are located and indicate regions in energy and space where traps will not be effective.

One technique is to bias the sample with a constant voltage in the dark prior to making the open-circuit voltage versus time measurement. This was done on a representative sample made at Boeing and the result is shown in Fig. 4-4. For dark pre-bias of less than 200 mV, there is no change in ΔV_{oc} . For dark pre-bias greater than 200 mV ΔV_{oc} decreases rapidly, and $\Delta V_{oc} = 0$ when $V_{appl} \approx V_{oc}$. This implies the traps are located in an energy range of about 200 mV. An implication for efficiency measurements is that a pre-measurement bias at the steady-state open-circuit voltage will yield only a slightly different efficiency from a pre-measurement bias at maximum power. Fig. 4-4 implies that voltage changes that keep the voltage below 200 mV or above 400 mV have little effect on the occupation of long-lived traps. Significant

Fig. 4-4. ΔV_{oc} following dark pre-bias for two hours.

changes in trap occupation, however, occur when the voltage change spans the 200-400 mV region. This observation has been verified with two other types of measurement:

- (1) With no light at all, dark current was switched from zero to a positive value and held constant. The subsequent transient voltage was recorded. When the dark current produced a voltage less than 200 mV, no transient voltage was seen. when the dark current was switched to a value the order of J_{sc} , however, the voltage jumped to near V_{oc} and continued to increase. This increase is quite similar (see Fig. 4-5) to the voltage response following the onset of illumination. This technique, however, fails in some CdTe cells where series resistance also appears to have a long-lived response to voltage or illumination changes.
- (2) Positive values of either pre-bias or final bias can be established using variable illumination intensity ranging from 10^{-4} to 1 sun, or greater. Since no current flows at

Fig. 4-5. Comparison of voltage increases following the turn-on of a constant dark-current and following the turn-on of illumination.

any value of V_{oc} , the resistance problem is eliminated. Here also, it is found that there is no significant transient voltage effect when the voltage is kept below 200 mV or above 400 mV. The transient effect is present, so in the other measurements, when the induced voltage jump spans the 200-400 mV region.

Fig. 4-6 compares the magnitude of the voltage transient when the voltage history is determined by fixed pre-bias, by constant current, and by the level of illumination. All three techniques yield the same value for the transient voltage increase. We conclude, therefore, that long-lived traps, whose equilibrium occupation changes in the 200-400 mV bias range are responsible for a 15 mV photovoltage variation. In other cells the magnitude of the voltage effect may be different, but the relevant bias range is the same for CuInSe_2 and its alloys, somewhat higher for CdTe.

Fig. 4-6. Magnitude of transient voltage after bias is abruptly switched from zero using three separate techniques.

5. COLLECTION EFFICIENCY

The internal collection efficiency of a solar cell is the ratio of photogenerated carriers in the external circuit to carrier pairs excited in the absorber region of the cell. For a cell to be competitive, this value should be close to unity. In general it is desirable to have a wide depletion region, or a large minority-carrier diffusion length, so that electric field and diffusion will maximize the photogenerated carriers in the junction current. Wide depletion, however, often implies lower doping density and thus a smaller junction potential barrier and lower voltage output. Additionally, since depletion width changes with voltage, collection efficiency can vary somewhat with cell voltage. Furthermore, diffusion lengths may be restricted in polycrystalline thin-film structures either by grain-boundary recombination or the physical thickness of the semiconductor.

The collection efficiency (CE) is determined by the quantum efficiency (QE) of a solar cell:

$$CE = \int_0^{\lambda_g} N_{ph}(\lambda) QE(\lambda)_{int} d\lambda / \int_0^{\lambda_g} N_{ph}(\lambda) d\lambda \quad [1],$$

where λ_g is the bandgap cut-off wavelength, $QE(\lambda)$ is the internal quantum efficiency, and $N_{ph}(\lambda)$ is the non-reflected photon flux. The quantum efficiency from depletion-region photon absorption should be

$$QE_{dr} \approx 1 - \exp(-\alpha W) \quad [2]$$

and that from bulk photon absorption followed by carrier diffusion should be

$$QE_b \approx \alpha L_{eff} \exp(-\alpha W) / (\alpha L_{eff} + 1) . \quad [3]$$

where α is the absorption coefficient for wavelength x and W is the depletion width. These equations combine for a total quantum efficiency

$$QE \approx 1 - \exp(-\alpha W) / (\alpha L_n + 1) \quad [4]$$

There are corrections for cells with effective diffusion lengths L_{eff} comparable to thickness and for small fields associated with very large depletion widths.

Quantum efficiency was calculated as a function of wavelength for four different solar cells (crystalline Si and GaAs, polycrystalline CuInSe₂ and CdTe) using published values for absorption coefficient [11-14] and typical values of the doping density and reflection. Fig. 5-1 shows the contributions from field-driven depletion-region collection and diffusion-limited bulk

collection separately as well as the total for three of these cell types. Also illustrated is the effect of variation in diffusion length on the bulk, and hence the total quantum efficiency.

For the CuInSe_2 curves, the quantum efficiency from the depletion region dominates at most of wavelengths, because this depletion region is relatively wide and the absorption coefficient is

Fig. 5-1. Comparison of calculated quantum efficiencies of CuInSe_2 , GaAs, and Si cells with typical parameters.

large. CdTe cells are even more dominated by depletion-region absorption and are not shown in Fig. 5-1. Crystalline GaAs and Si cells, however, have quantum efficiencies determined to a much greater extent by bulk-region absorption. The larger bulk contribution to the GaAs quantum efficiency is due to a typically large doping density, which results in a small depletion width. For crystalline Si cells, the large bulk contribution is due to the low absorption coefficient of the indirect-band gap material. When diffusion length is increased for any of these materials, quantum efficiency, especially at longer wavelengths, is also increased due to the small recombination loss in the bulk region.

Approximate collection efficiency shown in Fig. 5-2 for direct-gap cells is calculated from plots similar to Fig. 5-1 for a range of depletion widths using Eq. 4. As depletion width is increased, the dashed line in the inset graph is pushed to the right increasing the fraction of photoelectrons collected by the junction field. At a given depletion width, the collection efficiency increases with diffusion length. For hole densities above 10^{16} cm^{-2} , typical of CuInSe₂ and GaAs, the reduction in collection efficiency can be significant. When hole density is below 10^{15} cm^{-3} ,

Fig. 5-2. Collection efficiency of typical direct gap cells as a function of depletion width, or hole density.

typical of today's CdTe cells, essentially all absorption takes place in the field-driven region, and the collection efficiency should be close to unity. At very wide depletion and small diffusion length, the field may not be strong enough to sweep out all carriers before recombination. If we assume the correction results only from the recombination effect, which can be approximately written as $[1 - \exp(-t/\tau)]$ (t and τ are transition time and lifetime respectively), the collection efficiency will be reduced somewhat as seen with the $0.5 \mu\text{m}$ curve in Fig. 5-2. For indirect gap silicon, carrier densities are mid-range, and the large αL_{eff} product should keep the collection efficiency relatively high.

If a positive voltage is applied to a solar cell, the depletion width, and hence the collection efficiency will decrease, but only by a small amount. Integration of the quantum efficiency curves, weighted by a standard solar spectrum [15], yield the voltage-dependent light-generated currents shown in Fig. 5-3 for four types of cell with typical parameters. The largest variation

Fig. 5-3. Voltage-dependent photocurrents for four types of solar cell with typical doping densities. Curves are terminated at open-circuit voltage.

occurs for the polycrystalline thin-film CuInSe_2 , which has a photocurrent difference between zero voltage and open-circuit voltage (~ 0.5 V) of about 3%. The expanded-scale inset shows that the photocurrent vs. voltage plot has considerable curvature, and hence need not be misidentified as a linear shunting effect. For the crystalline Si cell, with its very large minority-carrier diffusion length (over 100 times that of the polycrystalline CuInSe_2 cell), the variation is essentially zero.

Fig. 5-4 illustrates how the voltage-dependent photocurrent effect near the maximum power voltage ($V_{MP} \approx 0.5V_{bi}$) varies with hole density p for CuInSe_2 cells. At low hole densities (10^{15} cm^{-3} range), $\Delta J_L/J_L(0)$ is small, but increases with increasing p . For densities above 10^{16} cm^{-3} , it saturates and remains nearly constant. Thus an accurate determination of carrier density is most important for analysis of cells with intermediate-range carrier density. At high carrier densities, the large influence of diffusion length requires the diffusion length to be determined as accurately as possible.

Fig. 5-4. Variation of the reduction in CuInSe_2 maximum-power photocurrent with hole density and diffusion length.

For many years, it has been observed experimentally that the apparent quantum efficiency of a solar cell decreases with increasing voltage. The magnitude of the observed decrease near open-circuit voltage, however, is generally much larger than that one expected from the photocurrent variations shown in Fig. 5-3 and 5-4. The reason for the discrepancy is that the large decreases in apparent quantum efficiency are due to the electrical resistance of the cell and the circuit [16, 17], and should not be interpreted as a true variation in collection efficiency.

The effect of voltage-dependent photocurrent $J_L(V)$ on the forward-current curve for a high-efficiency (14.1%) ARCO CuInSe_2 cell [18] is shown in Fig. 5-5. The top curve assumes J_L is constant with voltage, and the bottom curve uses a voltage-dependent $J_L(V)$, calculated with reasonable parameter estimates. The difference between these two curves is small in the region between maximum power voltage V_{MP} and open-circuit voltage V_{OC} (filled points), which is the

Fig. 5-5. Comparison of forward current for high-efficiency CuInSe_2 cell, assuming (1) photocurrent is constant, and (2) photocurrent is voltage dependent. Inset shows effect on apparent shunt resistance.

region generally used to calculate diode quality factor A and series resistance R_S . The apparent diode quality factor and series resistance are thus nearly unaffected by the variation of light-generated current with voltage. The apparent shunt resistance R_{SH} , however, is determined from voltage region and changes from $500 \Omega\text{cm}_2$ when J_L is assumed constant to $1700 \Omega\text{cm}_2$ when its variation is calculated (see inset graph). Thus, a major consequence of ignoring the voltage variation in photocurrent is an underestimate of the shunt resistance, and the excess loss observed in fill factor is likely to be misinterpreted as excessive shunting. For this particular CuInSe_2 cell, the fill factor and hence efficiency, is decreased by approximately $2\frac{1}{2}\%$ due to the voltage-dependence of the photocurrent. The upper limit of such a decrease should be about 3%. Also seen in Fig. 5-5, the incorporation of a voltage-dependent photocurrent extends the exponential portion of the curves to lower voltages and allows a more accurate calculation of

Fig. 5-6. Calculated magnitude of photocurrent reduction with voltage. Solid curves are for $V = 0.7V_{bi}$, which should be near V_{oc} ; dashed curves are for $V = 0.5V_{bi}$, which is generally near V_{mp} .

diode quality factor and series resistance. A general summary of the magnitude of the predicted variation in photocurrent with voltage is shown in Fig. 5-6. Here W_0 is depletion width at zero voltage and $\langle \alpha \rangle$ is an average absorption coefficient, which corresponds to absorption near the maximum intensity of the solar spectrum. Two different minority-carrier diffusion lengths and two voltages are shown. For polycrystalline thin-film cells, $V/V_{bi}=0.5$ is generally near the maximum-power voltage. For good crystalline cells, the ratios of these voltages to the built-in potential may be slightly higher. Fig. 5-6 shows that larger voltages and smaller diffusion lengths correspond to larger changes in photocurrent. It also shows that the greatest effect occurs when the most light is absorbed in the spatial region that changes from depletion to bulk with increasing voltage, or more mathematically, when the product [19] of absorption coefficient and depletion width is close to one.

The conclusions from Fig. 5-6 are equivalent to the curves shown earlier in Fig. 5-3. For good-quality CuInSe₂ cells, $\langle \alpha \rangle W_0$ is often not far from unity so that the reduction in photocurrent may be significant (3½ % at V_{oc} near 500 mV and $L_{eff} = 1 \mu\text{m}$). CdTe cells, in contrast, tend to have larger depletion regions, which can be determined directly through capacitance measurements [4]. In many cases the entire CdTe layer ($\sim 2 \mu\text{m}$) is depleted, and the cell basically has a p-i-n structure. Thus, the CdTe photocurrent effect corresponds to a region farther to the right in Fig. 5-6. The larger doping densities, and hence small depletion widths, typical of GaAs predict smaller photocurrent variations. Crystalline GaAs will also have a larger diffusion length and slightly larger voltage relative to V_{bi} than the polycrystalline cells, but these two effects roughly compensate each other in terms of photocurrent-voltage dependence. For crystalline Si cells, the variations in photocurrent with voltage can be ignored, because the large minority-carrier diffusion length and small absorption coefficient correspond to the region at the lower left of Fig. 5-6.

Experimentally, Fardig and Phillips [19, 20] have successfully used two techniques to determine $J(V)$ in reverse bias. These are (1) the analysis of the voltage dependence of spectral response, and (2) the separation of linear and non-linear J vs. V components. Their work on CdTe cells predicts ΔJ_L magnitudes similar to those deduced above. However, both these techniques experience increasing uncertainties in forward bias and may not easily extrapolate to give reliable values of ΔJ_L at operating voltages.

6. RECOMMENDATIONS

The general recommendation is to continue to refine analysis techniques so that the loss mechanisms in individual thin-film polycrystalline cells can be reliably and quantitatively separated. This type of analysis is becoming even more useful as cell-fabrication groups are increasingly making a series of test cells on a common substrate with a systematic variation in a single fabrication parameter.

A specific problem that needs additional attention is the extension of well-controlled studies of time-dependent effects in CdTe and CuInSe₂ cells to modules. Critical issues are the unambiguous identification of effects as reversible or irreversible, whether array of cells introduce problems not seen in individual cells, what can be done about such problems, and whether current confidence at the research level can be transferred to the market level. Experiments with modules are somewhat more difficult since it is harder to maintain steady illumination and junction temperature for larger-area structures. An effective approach to detailed module characterization will also require coordination between manufactures, researchers, and NREL test facilities.

7. COMMUNICATIONS

7.1 Publications

1. R.A. Sasala,, X.X. Liu, and J.R. Sites, "Comparitive Analysis of Recent High-Efficiency CdTe Solar Cells," Int. J. Solar Energy **12**, 17 (1992).
2. R.A. Sasala and J.R. Sites, "Transient Voltage of Thin-Film Polycrystalline Solar Cells," AIP Conf. Proc. **268**, 218 (1992).

7.2 Submissions

1. "Variation of Solar-Cell Collection Efficiency with Depletion Width," X.X. Liu and J.R. Sites. Journal of Applied Physics Letters.
2. "Analysis of Losses High-Efficiency CdTe Cells," X.X. Liu, I.L. Eisgruber, and J.R. Sites. PVSC-23.
3. "Time Dependant Voltage in CuInSe₂ and CdTe Solar Cells," R.A. Sasala and J.R. Sites. PVSC-23.
4. "Trade-off Between Collection Efficiency and Open-Circuit Voltage," X.X. Liu and J.R. Sites. PVSC-23.

7.3 Talks

1.	PVAR&D-11 (Sites)	May, 1992
2.	Performance and Reliability Workshop (Sites)	September, 1992
3.	Spring MRS (Sasala)	April, 1993
4.	PVSC-23, Louisville (Sites)	May, 1993

7.4 Specific Cell Reports

<u>DATE</u>	<u>SENT TO</u>	<u>CELLS</u>
4/29/92	(Tuttle)	NREL CIS S193-3 #1
6/10/92	(vonRoedern)	GIT CdTe 1-1, 2-4
6/10/92	(Zweibel)	USF CdTe 4-23A-14#C, -1#A
6/30/92	(Ullal)	USF CdTe 4-23A-14#C, -1#B
7/10/92	(vonRoedern)	USF CdTe 5-1A-12ABC 5-19B-19ABC 6-1B-1-B
7/17/92	(vonRoedern)	USF CdTe (same as above)
7/27/92	(Ullal)	NREL CdtE S45-11-2#2 Battelle CdTe S86a EUROCIS CIS 63#2, 69#5
9/2/92	(Basol)	ISET CIS R297B (4 cells)
10/21/92	(Zweibel)	USF CdTe 5-16-8-1
11/16/92	(Ullal)	U. Toledo CdTe SC75\75-11
12/11/92	(von Roedern)	USF CdTe 5-19B-10A
2/18/93	(vonRoedern)	NREL CIGS S319-4-5
4/12/93	(von Roedern)	NREL CIS S339-4 (6 cells)

8. REFERENCES

1. C. Ferekides, J. Britt, and Xixian Ma, "High Efficiency CdTe Solar Cells by Close Spaced Sublimation," *Proc. 23rd IEEE Photovoltaic Specialists Conf., Louisville, (1993).*
2. T.L. Chu, S.S. Chu, J. Britt, G. Chen, C. Ferekides, N. Schultz, C. Wang, and C.Q. Wu, "High Efficiency Thin Film Cadmium Telluride Solar Cells," *AIP Conf. Proc. 268, 88 (1992).*
3. H. Tavakolian, and J.R. Sites, "Individual Losses in Thin-Film CdTe Solar Cells," *Proc. 21st IEEE Photovoltaic Specialist Conf., Florida, 556, (1990).*

4. R.A. Sasala, X.X. Liu, and J.R. Sites, "Comparative Analysis of Recent High-Efficiency CdTe Solar Cells," *Int. J. Solar Energy* **12**, 17 (1992)
5. R. Hustrom, R. Bird, and C. Riordan, "Spectral Solar Irradiance Data Sets for Selected Terrestrial Conditions," *Solar Cells* **15**, 365 (1985)
6. X.X. Liu, R.A. Sasala, and J.R. Sites, "Junction Analysis of Selenized CuInSe₂ Solar Cells," *Proc. 22nd IEEE Photovoltaic Specialists Conf., Las Vegas*, (1991), 930.
7. C.T. Sah, R.N. Noyce, and W. Shockley, "Carrier Generation and Recombination in P-N Junctions and P-N Junction Characteristics," *Proc. IRE* **45**, 1228 (1957).
8. M. Ruberto and A. Rothwarf, *J. Appl Phys.*, **61**, 4662 (1987).
9. K. Emery and K. Zweibel, private communication.
10. R. Sasala and J. Sites, *AIP Conf. Proc.* **268**, 218 (1992).
11. J. Tuttle, D. Albin, J. Goral, C. Kennedy, and R. Noufi, *Solar Cells*, **24** 67 (1988).
12. K. Rajkanan, R. Singh, and J. Shewchun, *Solid-State Electronics*, **22**, 793 (1979).
13. T.S. Moss and T.D.F. Hawkins, *Infrared Physics* **1**, 111 (1961).
14. S.S. Ou and O.M. Stafsudd, *J. Appl. Phys.* **55**, 3769 (1984).
15. R. Hulstrom, R. Bird and C. Riordan, *Solar Cells* **15**, 365 (1985).
16. J.E. Phillips and M. Roy, *Proc. 20th IEEE Photovoltaic Specialists Conf.*, 1614 (1988) 1614.
17. J.R. Sites, H. Tavakolian, and R.A. Sasala, *Solar Cells* **29**, 39 (1989).
18. K.W. Mitchell, C. Eberspacher, J. Ermer, and D. Pier, *Proc. 20th IEEE Photovoltaic Specialists Conf.*, 1384 (1988), 1384.
19. D.A. Fardig, "Characterization of CdTe/CdS Solar Cells", M.S. Thesis, University of Delaware, June 1991 (unpublished).
20. D.A. Fardig and J.E. Phillips, *Proc. 22nd IEEE Photovoltaic Specialists Conf.*, (1991), 1146.

Document Control Page	1. NREL Report No. NREL/TP-451-6215	2. NTIS Accession No. DE94000293	3. Recipient's Accession No.
4. Title and Subtitle Role of Polycrystallinity in CdTe and CuInSe ₂ Photovoltaic Cells			5. Publication Date February 1994
			6.
7. Author(s) J. R. Sites			8. Performing Organization Rept. No.
9. Performing Organization Name and Address Colorado State University Department of Physics Fort Collins, CO 80523			10. Project/Task/Work Unit No. PV431101
			11. Contract (C) or Grant (G) No. (C) XC-0-10046-1 (G)
12. Sponsoring Organization Name and Address National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393			13. Type of Report & Period Covered Technical Report 1 April 1992 - 31 March 1993
			14.
15. Supplementary Notes NREL technical monitor: B. von Roedern			
16. Abstract (Limit: 200 words) This report describes work to conduct several investigations of thin-film polycrystalline solar cells. (1) An analysis of high-efficiency solar cells fabricated at the University of South Florida showed significant reduction in forward recombination current, and the cells were stable over a 3-month test period. (2) Transient voltage effects were documented in a large number of polycrystalline cells and were attributed to long-lived trapping states sensitive to voltage changes near one-half open-circuit voltage. (3) Collection efficiency and its voltage dependence were carefully calculated. The typical effect on photocurrent at operating voltages is about 2% for CuInSe ₂ , and less for other cells.			
17. Document Analysis a. Descriptors thin film ; polycrystalline ; high efficiency ; cadmium telluride ; copper indium diselenide ; photovoltaics ; solar cells b. Identifiers/Open-Ended Terms c. UC Categories 273			
18. Availability Statement National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161			19. No. of Pages 38
			20. Price A03