June 2015

Drift Mobility Measurements and Electrical Characterization in Thin Film Cadmium Telluride Solar Cells

Qi Long
Syracuse University

Follow this and additional works at: https://surface.syr.edu/etd

Part of the Physical Sciences and Mathematics Commons

Recommended Citation
https://surface.syr.edu/etd/270

This Dissertation is brought to you for free and open access by the SURFACE at SURFACE. It has been accepted for inclusion in Dissertations - ALL by an authorized administrator of SURFACE. For more information, please contact surface@syr.edu.
ABSTRACT

Thin film CdTe solar cells are leading the production in the thin film photovoltaic industry for the recent few years. The electric properties and mechanism for fabrication of high efficiency solar cells are still not well established. In this thesis, I'll report electron and hole drift mobilities measurements in thin film CdTe solar cells based on two characterization methods: time-of-flight and photocapacitance. For a deposition process similar to that used for high-efficiency cells, the electron drift mobilities are in the range $10^{-1} - 10^0$ cm$^2$/Vs, and holes are in the range $10^0 - 10^1$ cm$^2$/Vs. The electron drift mobilities are three orders of magnitude smaller than those measured in single crystal CdTe, the hole mobilities are about ten times smaller. Cells were examined before and after a vapor phase treatment with CdCl$_2$; treatment had little effect on the hole drift mobility, but decreased the electron mobility. The electron mobility shows an interesting inverse correlation with the open-circuit voltage for the CdTe coupons with and without the CdCl$_2$ treatment. We speculate that this correlation is due to the diffusion limited recombination. We also discuss the mechanisms reducing the mobilities from the single crystal values. In this thesis, we are able to exclude bandtail trapping and dispersion as a mechanism for the small drift mobilities in thin film CdTe. Other mechanisms like classic scattering, grain boundaries effect, and also polaron interaction will also be discussed in this thesis. All mechanisms mentioned above show little evidence on the influence to the mobility value. The true reason for such a huge change of the drift mobility from its single crystal values still need more interpretations.
Drift Mobility Measurements and Electrical Characterization in Thin Film Cadmium Telluride Solar Cells

By

Qi Long

B.S., Wuhan University, 2008

Dissertation
Submitted in partial fulfillment of requirement for the Degree of Doctor of Philosophy in Physics
Syracuse University
June, 2015
ACKNOWLEDGEMENTS

I would have never been able to finish my dissertation without the help from great many people.

First, I would like to express my deepest gratitude to my advisor, Prof. Eric A. Schiff, for his great guidance, support, caring, and patience to make this a thoughtful and rewarding journey. And I would like to thank all my committee members Prasanta Ghosh, Edward Lipson, Tomasz Skwarnicki, Liviu Movileanu and Jennifer Schwarz for their valuable advices to my dissertation.

I would like to thank for the support from our collaborators Jeremy Theil, Ming Yu, and Gang Xiong from First Solar, Inc. They provided nearly all the samples that we measured in this work. I would like to thank my lab mates Steluta Dinca, Hui Zhao and Brian Maynard with their help and suggestions to my researches.

Also, I would like to thank my parents for their great support and encouragement throughout my graduate studies in a foreign country.

Finally, I would like to thank my wife Wenjun Cai, and my son Evan Long. They bring the joy and power to everyday of my life.

This research was partly supported by the National Science Foundation (CBET-1336147).
TABLE OF CONTENTS

Abstract...........................................................................................................................................i

Acknowledgements.................................................................................................................iv

List of figures..........................................................................................................................vii

List of tables ....................................................................................................................................xiii

1 Introduction ...................................................................................................................................1

1.1 What is a thin-film solar cell? ...............................................................................................1

1.2 What is a thin-film CdTe solar cell .....................................................................................5

1.3 How important is the drift mobility in CdTe? ...................................................................7

1.4 Synopsis .................................................................................................................................12

2 Characterization methods for CdTe ......................................................................................16

2.1 Coupon details .......................................................................................................................16

2.2 $I-V$ measurement ..............................................................................................................18

2.3 Quantum efficiency measurement .....................................................................................21

2.4 Capacitance measurements ...............................................................................................28

2.5 Recombination lifetime measurement ...............................................................................32

3 Transport characterization for CdTe ......................................................................................38

3.1 Transport characterization introduction .............................................................................38
3.2 Time of Flight technique ........................................................................... 39
3.3 Time-of-flight experiment setup ................................................................. 41
3.4 Surface illumination ...................................................................................... 42
3.5 Uniform illumination ...................................................................................... 54
3.6 Temperature-dependent time-of-flight ......................................................... 59
3.7 Time-of-flight results ..................................................................................... 61
3.8 Photocapacitance technique ......................................................................... 62
3.9 Photocapacitance results ............................................................................... 68
3.10 Time-of-flight and photocapacitance comparison .................................... 70
3.11 Discussion I - mobility $V_{oc}$ correlation ................................................ 74
3.12 Discussion II – lifetime measurement ....................................................... 76
3.13 Discussion III – transport mechanism ...................................................... 79
Vita ..................................................................................................................... 89
LIST OF FIGURES

Fig. 1-1 The annual cumulative capacity vs module prices for the PV industry...2

Fig. 1-2. Schematic density of states distribution for amorphous silicon solar cell
with the band tail structure.................................................................4

Fig. 1-3. Three types of recombination mechanisms for the photogenerated carriers.
.........................................................................................................11

Fig. 2-1. Superstrate configuration for thin-film CdTe coupon. The coupon is
illuminated from the front glass side and electron and hole pairs are generated inside
the CdTe absorption layer. .................................................................18

Fig. 2-2. The left graph shows the simplified circuit model for CdTe solar cells.
The right side of the graph shows the basic experiment setup for I-V measurements.19

Fig. 2-3. The left side of the figure shows the dark and light I-V measurements for
coupon with large series resistance and the right side of the figure shows the dark and
light I-V measurements for the normal CdTe coupon.................................20

Fig. 2-4. Experimental setup for quantum efficiency measurement.............23

Fig. 2-5. Quantum efficiency measurements for bifacial coupons. The left side
graph is for treated coupon 6 and the right side graph is for untreated coupon 5. The
coupon details can be found in Table 1 of chapter 3. The black lines at the top are for
the quantum efficiency measurement through the front side (glass side) of the coupon
at several bias voltages. The light grey lines (bottom sets) are for the measurement
through the back contact. The stronger grey lines have been normalized to correct for
the non-unity transmittance of the back contact based using the data from 850 nm...26
Fig. 2-6. Experiment setup for capacitance measurement. The capacitance is measured in the dark condition. The light source is only needed for the photocapacitance measurements. .................................................................29

Fig. 2-7. Capacitance measurement on CdTe coupon at room temperature with different bias voltages. The dashed line represents the fitting using Schottky analysis. The intercept gives the value for offset potential $V_0$. .................................................................30

Fig. 2-8. The cumulative percentage of a) offset potentials $V_0$ b) the depletion width $W_d$ at 0 V and c) the acceptor doping level $N_A$ for all measurable cells obtained from a standard Schottky analysis of dark C-V. The black open dots is the cells before light soaking; grey dots shows the cells after 3.5 hours light soaking and the light grey open dots is for the cells after 24 hours light soaking. .................................................................31

Fig. 2-9. Frequency dependence of modulated photovoltage for both real and imaginary part. .................................................................34

Fig. 2-10. The modulated photovoltage shown in the complex plane. The dash line is the fitting using the classical IMVS model. .................................................................34

Fig. 2-11. The modulated photovoltage components plotted in the complex plane for the untreated bifacial coupon. The lifetime corresponding to the top of the arc is around 3.5 µs........................................................................................................35

Fig. 3-1. Experiment setup for time-of-flight method. ..............................................42

Fig. 3-2. Example of drift mobility measurement. The slope of the transit time curve gives the value for drift mobility. .................................................................44

Fig. 3-3. Time-of-flight measurement at 293K on a cell from untreated bifacial
coupon 5. (a) Photocharge transients $Q(t)$ for front illumination (through the glass substrate) using a 4 ns laser pulse (660 nm wavelength). Results are shown for four separate reverse bias voltages. (b) Photocharge transients along with the electronic risetime $t_{RC}$ (vertical gray line). The solid lines show the constant drift-velocity model predictions corresponding to the transit times $t_T$ calculated for each transient. (c) Photocharge collected in 1 µs as a function of bias voltage with front and back illumination (holes and electrons). The solid lines are fits to the Hecht formula for deep-trapping. (d) Drift mobilities for holes from untreated coupon 5 and electrons for the treated bifacial coupon 2 calculated from the transit times at different bias voltages. The dash lines show the prediction of a dispersion model $\alpha = 0.75$ for the hole mobility of untreated coupon and $\alpha = 0.70$ for electron mobility of treated coupon.

Fig. 3-4. Transient photocurrent at 0V on coupon 5. The dash line represent the photocurrent dispersive behavior after transit time, the slope gives the value for $\alpha$. ..50

Fig. 3-5. Transient photocharge for untreated coupon at 1.0V. The straight line shows the fitting for non-dispersive model and the curved line shows the fitting for dispersion model with $\alpha = 0.75$...

Fig. 3-6. Dark capacitance measurements ($10^3$ Hz) on cells from all six coupons. Coupon 1 and 5 are untreated, the remaining coupons received post deposition treatments. We illustrate the Schottky model fits for the cells from coupons 4 and 6. The corresponding depletion widths and acceptor densities are 2.87 µm, $8.97 \times 10^{13}$ cm$^{-3}$ and 2.8 µm, $1.79 \times 10^{14}$ cm$^{-3}$ respectively.

Fig. 3-7. Time-of-flight measurement on the treated coupon 6. Panel (a) shows the
$Q(t)$ for the surface illumination is using 4ns pulsed laser diode with a wavelength of 660nm. And panel (b) shows the $Q(t)$ for the uniform illumination is using 850nm 10ns pulsed laser diode. The voltage dependent normalized photocharge graph in the panel (c) is showing both illumination together. The surface illumination with 660nm laser diode is showing in the top part of the graph and the uniform illumination we divide the $Q(V)$ by $2Q_0$. Panel (d) shows the mobility fitting for two different illumination. The uniform and surface illumination from the glass side intercept in the same point on x-axis which is indicate the built-in potential for the coupon. ..........................57

Fig. 3-8. Temperature dependent drift mobility for both electron and hole on coupon 5 and coupon 6. The solid dots are the measurements for electrons and the open dots are the measurements for holes. And the squares are for the untreated sample, the circles are for the treated sample. .............................................................58

Fig. 3-9. Temperature dependence of hole drift mobilities in different samples. Solid lines are taken by other groups (Plaiseau03 and Stuttgart91). Open data are taken from UniSolar, and solid ones are measurements on BP solar samples. ......................60

Fig. 3-10. Correlation of the electron and hole drift mobilities in single crystals as well as a summary of the present measurements on bifacial thin-film CdTe coupons. For the thin-film samples, the drift mobilities correspond to a displacement/field ratio $L/E = 5 \times 10^{-8}$ cm$^2$/V. The different symbols indicate different coupons; solid symbols are for untreated coupons. The gray-filled hexagon symbols are for single crystals of CdTe..........................................................61

Fig. 3-11. Photocapacitance effects at short-circuit for a thin film CdTe cell
photocurrents \( i_p \) are generated by white light of varying intensity, and measured at -1.0 V. \( C_p \) is the slope of \( \partial C / \partial i_p \) at \( i_p = 0 \).

Fig. 3-12. Illustration for photocapacitance technique. The experiment setup is the same as capacitance measurement discussed on the previous chapter.

Fig. 3-13. Capacitance and photocapacitance measurements for a bifacial thin film CdTe solar cell. (a) \( 1/Cd^2 \) and photocurrent \( i_p \) as a function of voltage. The dashed line represents Schottky behavior, and yields the offset potential \( V_0=0.26 \)V. (b) Voltage dependence of the normalized photocapacitance for three types of laser illumination at the indicated wavelengths. 550 nm illumination is strongly absorbed, and eq. (16) can be used. The corresponding electron and hole drift mobilities for this cell are 0.01 cm\(^2\)/Vs and 0.03 cm\(^2\)/Vs, respectively.

Fig. 3-14. Correlation of electron and hole drift mobility for the CdTe coupon with non-transparent back contact using photocapacitance method.

Fig. 3-15. Comparison of drift-mobilities for thin-film CdTe and CIGS based on TOF and low-frequency photocapacitance measurements. The hexagons are for the CIGS measurements, the circles are measurements for ordinary CdTe coupons, and squares are measurements for special bifacial CdTe coupons.

Fig. 3-16. Calculated electron displacement/field ratio \( l/E \) with deep trapping. The parameters are \( \mu_{TOF} = 0.5 \) cm\(^2\)/Vs, \( \mu_{PC} = 0.01 \) cm\(^2\)/Vs, and \( \mu_{T} = 2 \times 10^{-7} \) cm\(^2\)/V. \( \tau_{PL} \) is the photoluminescence lifetime, \( \tau_{T} \) is the trapping time, and \( \tau_{E} \) is the trap emission time.

Fig. 3-17. \( V_{OC} \) correlation with hole drift mobility measured by the photocapacitance method.
coupons. ........................................................................................................74

Fig. 3-18. Correlation of the electron and hole mobilities vs open circuit voltage under solar simulator illumination for bifacial coupons using time-of-flight technique. The different symbols indicate different coupons. The solid symbols represent measurements on untreated coupons; the open symbols are for coupons following treatment. ........................................................................................................76

Fig. 3-19. Calculated electron displacement/field ratio $l/E$ with deep trapping. The parameters are $\mu_{TOF} = 0.5 \text{ cm}^2/\text{Vs}$, $\mu_{PC} = 0.01 \text{ cm}^2/\text{Vs}$, and $\mu \tau_t = 2 \times 10^{-7} \text{ cm}^2/\text{V}$. $\tau_{PL}$ is the photoluminescence lifetime, $\tau_t$ is the trapping time, and $\tau_E$ is the trap emission time. 78

Fig. 3-20. The Ioffe-Regel limit calculation for CdTe. The black line is the calculation for electron mobilities and grey line is the calculation for hole mobilities. The temperature dependence electron and hole mobilities from time-of-flight experiments for both single crystal and thin film CdTe are also shown in the graph. The solid dots represent for the electron mobilities and the grey dots are for the hole mobilities........................................................................................................80
LIST OF TABLES

Table 3-1: Coupon details for all six coupons ................................................................. 43
1 INTRODUCTION

1.1 WHAT IS A THIN-FILM SOLAR CELL?

Photovoltaic (PV) technology directly converts the energy from sunlight to electrical power using semiconductor modules which are illuminated by the photons. For semiconductor materials, there is an energy gap between the valence band which is filled with electrons, and a nearly empty conduction band. When the energy of an incident photon exceeds the energy of the band gap, the photons can excite the bonded electrons from the valence band to the conduction band where they can move freely. In this way, it forms an electric current in the semiconductor material.

PV energy is a very clean energy and usually the solar cell module can work for decades. The whole PV industry has grown nearly exponentially in the recent 30 years. As illustrated in Fig. 1-1, the accumulated photovoltaic capacity worldwide has increased almost 5 orders of magnitude from 0.3 megawatts (MW) in 1976 to 90 gigawatts (GW) in 2012; here one watt refers to the output of a solar module under standard noontime conditions. The cost of the module has dropped nearly 2 orders of magnitude from 70 $/watt to 0.7 $/watt. The power-law form of Fig. 1-1 is typical of growing industries, and is referred to as an “experience curve”. From the experience curve we can get the progress ratio of 79% which means that the price of the module is reduced by 21% every time the cumulative production is doubled.

With such a promising future for the PV industry, the technology for the solar cell modules has also developed rapidly. Currently, there are three types of solar cell
modules dominating the PV industry: single-crystal silicon solar cells, polycrystalline silicon solar cells, and thin film solar cells. Single crystal cells are typically made from wafers sliced from large boules of nearly perfect crystalline silicon; polycrystalline cells are made from less expensive polycrystalline boules. Thin film solar cells are usually grown by depositing the thin film using a vacuum technology such as evaporation or sublimation. In 2013, the Si-wafer based PV technology (single and polycrystalline silicon) occupied almost 90% of the total production, and thin film solar cells was about 10% of the total production.  

Although the Si-wafer based technology is dominating in the current PV industry, the thin film solar cell has its own advantages. The advantage of using thin film solar cells including the reduction of the cost per watt, the flexibility, and also less weight (for a-Si or CIGS deposited on the stainless steel substrate) compared with Si-wafer based solar cells. There are three main types of thin film solar cells currently dominating in thin film inorganic solar cell industry: CdTe, Cu(In,Ga)(Se,S)₂ (CIGS), and

---

**Fig. 1-1** The annual cumulative capacity vs module prices for the PV industry.
hydrogenated amorphous silicon (a-Si:H).

The development of thin film solar cells started with the doping of the hydrogenated amorphous silicon. The deposited thin film amorphous silicon films are less than a micrometer thick, which should be compared with Si-wafers which are typically a few hundreds of micrometers thick. The first hydrogenated amorphous silicon film was made around 1965 by Sterling et al. using a silane (SiH₄) glow discharge to deposit a film onto a substrate. Following the work from Sterling, Chittick et al. manufactured the first intrinsic amorphous silicon with acceptable quality; the glow discharge technique is now usually called plasma enhanced chemical vapor deposition (PECVD).

Amorphous silicon thin film solar cells were largely developed in the 1980s. a-Si:H based alloys were also developed in the purpose of gaining higher efficiency. Silicon-carbon alloys (a-SiC:H) were developed as a low absorption top layer, since these alloys have a larger bandgap than a-Si:H. Similarly, a-SiGe:H was developed as a lower bandgap material that is typically used as a strongly absorbing bottom layer. The annual production capacity for amorphous silicon solar cell reached 15 MWp at the end of the 1980s, and grew to several hundred megawatts by 2010. CdTe thin film solar cells were commercialized somewhat later, but have now overtaken a-Si:H. The capacity for thin film solar cells reached 3 GWp in 2013.

Differing from single crystal solar cells, the main absorbing layer in thin film solar cells is usually made with materials that contain a large density of defects, which brings the problems of localized defects as the dangling bonds or the grain boundaries in
such kind of materials. The increasing level of disorder in thin film solar cells would affect the solar cell properties in many ways.

For amorphous silicon, the localized defects including dangling bonds would soften the band edge between the conduction band and valence band, this is called the band tail in amorphous silicon. Different than the crystalline silicon which has a sharp band edge between conduction and valence band, the density of states in amorphous silicon is broadened to extend into the forbidden gap region. This can be seen in Fig. 1-2, the density of the states graph show the band tail structure for amorphous silicon. The band tail structure in amorphous silicon is very important since it would affect the optical, photocarriers transport and recombination properties of the solar cell. The photocarriers would be trapped and thermally reemitted later in the localized defects and this would decrease the photocarriers drift mobility and would also lengthen the recombination time for the photocarriers. Since the photocarriers emit from these traps
thermally, the drift mobility for amorphous silicon would be temperature dependent in this case.

The studies of disorder properties in amorphous silicon also led to research in other thin film solar cells. A band tail structure has also been claimed in CIGS and CdTe.\textsuperscript{8,9} We would thus expect differences in optical, transport and recombination properties of the thin film CdTe and CIGS compared with their single-crystal properties. Although the mechanism of the carriers’ transportation and recombination for thin film CdTe and CIGS would not be similar with amorphous silicon, the large scale of disorder in thin film materials might be the reason for the discrepancy between solar cell properties of thin film solar cells and their single crystal properties.

1.2 WHAT IS A THIN FILM CdTe SOLAR CELL

Polycrystalline thin film solar cells have become one of the leading solar cell modules in the thin film industry. In 2004, the annual PV capacity of CdTe was just 1% of the total PV production. In 2013, the percentage for the CdTe in the whole PV production reached 5% and it occupied 54% of the total thin film PV production.\textsuperscript{1} The development of thin film CdTe solar cells started with the announcement of first thin film polycrystalline CdTe solar cells made with the evaporated CdTe layer on top of the CdS/SnO\textsubscript{2}/glass substrate from Adirovich, \textit{et al.}\textsuperscript{10} in 1969. This type of structure is known as a “heterojunction”. The classical p-n diode is typically a homojunction created by a boundary between two types of chemical doping in a single semiconductor. For silicon, a typical “p-type” dopant is boron, which leaves mobile “holes” in the valence band. A typical “n-type” dopant is phosphorus, which leaves mobile electrons
in the conduction band. CdTe/CdS is also a p-n junction structure with two types of doping on CdTe and CdS respectively. CdTe is naturally p-type, even without intentional chemical doping. The natively occurring defects act similarly to p-type dopants. CdS is naturally n-type. The first ever thin film CdTe solar cell had an efficiency of 2%.\textsuperscript{11} The use of molybdenum (Mo) as the front contact later on in the 1972 publication by Bonnet and Rabenhorst improved the efficiency to 5-6%.\textsuperscript{12}

The efficiency of the thin film CdTe solar cell was greatly improved after 1980s. The two main factors that were crucial to the high efficiency solar cells were the adoption of a “superstrate” structure and a high-temperature treatment with CdCl\textsubscript{2}. Thin film CdTe is deposited in two different configurations: superstrate and substrate. The superstrate configuration starts with a glass substrate topped with a transparent conducting oxide (TCO) layer such as indium tin oxide (ITO). Light enters the structure through the glass superstrate. A thin layer of n-type CdS is deposited onto the TCO, and p-type CdTe is then deposited on top of the CdS layer. The last step is to deposit a thin metal contact layer, which forms the back contact. This configuration differs from the substrate configuration that typically uses stainless steel as the substrate and back contact. This is followed by the sequence of layers CdTe/CdS/TCO. Starting from 1980s, thin film CdTe solar cells have been always fabricated with the superstrate configuration.

Besides the superstrate configuration, other conditions in the deposition process like the deposition temperature, the post deposition heat treatment, and especially the post deposition CdCl\textsubscript{2} treatment are also crucial to high efficiency solar cells. Among
all the processing techniques, the post-deposition CdCl$_2$ treatment, which refers to the post-deposition exposure to a chlorine containing species such as CdCl$_2$ combined with high temperature (usually around 380-450 °C), is the most important step to bring tremendous improvements to the solar cell properties of thin film CdTe. The efficiency of thin film CdTe solar cells passed 20% in 2014.\textsuperscript{13}

1.3 HOW IMPORTANT IS THE DRIFT MOBILITY IN CdTe?

Single crystal silicon solar cells reached a solar conversion efficiency above 20% in the early 1990s, at which time none of the thin film solar cells had exceeded 10%.\textsuperscript{14} Thus the energy conversion efficiency has been a major issue for thin film photovoltaics. Taking CdTe as an example, the theoretical maximum value (Shockley-Queisser limit) of the efficiency for CdTe is about 30% - which is about the same as for crystalline silicon. With such a large gap between the theoretical value and the experimental one, researchers have been looking in every direction to make efficiency higher. Right now, the world record for thin film CdTe has risen to just over 21%.\textsuperscript{15} This is truly remarkable progress, but there is little understanding of the mechanisms which have limited this efficiency in the past, or that could lead to still higher values in the future.

Solar cell conversion efficiencies are determined by several processes. The most fundamental is recombination of electrons and holes after their photogeneration by sunlight. The absolute minimum rate of recombination is “radiative”, which means that an electron and hole recombine by emitting a photon to carry away the excess energy. A detailed balance argument shows that radiative recombination is proportional to the optical absorption coefficient; it is this argument that leads to the fundamental
Shockley-Queisser limit for the efficiency of a solar cell.\textsuperscript{16} Real solar cells have additional non-radiative recombination mechanisms that are generally determined by structural defects. In addition, the Shockley-Queisser calculation assumes that the drift and diffusion of the electrons and holes proceeds rapidly. Again, real photocarriers may diffuse and drift slowly enough to affect conversion efficiencies.

This thesis is primarily concerned with the drift of photocarriers in thin film CdTe, which is characterized by a “drift mobility”. This mobility is the proportionality factor between the drift speed of a carrier and the local electric field. It is written:

\[ v = \mu E \]  

(1-1)

where \( v \) is the photocarrier’s drift speed under the influence of the electric field \( E \) and \( \mu \) is the photocarrier’s drift mobility. The conventional units for mobility are cm\(^2\)/Vs.

The drift mobility will be hugely affected by the formation of defects in the intrinsic layer of the semiconductor material. For the single crystal structure, the drift mobility is usually a very large number. For the polycrystalline or amorphous structure, the largely increasing disorders in the material would lower the drift mobility value by several orders of magnitude. To take crystalline and amorphous silicon as an example: the electron mobility for single crystal Si is around 1500 cm\(^2\)/Vs and for the hole it is around 500 cm\(^2\)/Vs.\textsuperscript{17} However, for amorphous silicon, both electron and hole mobilities are several orders of magnitude lower than the single crystal values. The room temperature electron mobility is around 1 cm\(^2\)/Vs and the hole mobility is around 0.01 cm\(^2\)/Vs.\textsuperscript{18} The disorder in a-Si:H thus reduces the hole mobility by more than 10\(^4\) at room temperature, and by much more at lower temperatures.
It is surprising that the drift mobilities in thin film CdTe have not been carefully studied. The values in single crystals are well established. Electrons have a mobility of about $10^3$ cm$^2$/Vs at room temperature, and holes are around $10^2$ cm$^2$/Vs.\textsuperscript{19} For thin films there is a single preliminary report from the Hall effect which gave a value for electrons around 200 cm$^2$/Vs.\textsuperscript{20}

One explanation for the neglect of thin film measurements of the drift mobilities is that crystal values seem consistent with recombination lifetimes as inferred from radiative recombination (photoluminescence) measurements. The measured luminescence decays last for nanoseconds at longest.\textsuperscript{21} Similar values have been reported by many groups and dozens of materials, and the identification of the luminescence decay time with recombination is widely accepted. Solar cell modeling that assumes these lifetimes are the actual recombination lifetimes then require mobilities similar to crystal values.\textsuperscript{22}

In this thesis I report direct measurements of the photocarrier drift mobilities in a wide range of thin film CdTe solar cells. I use the best tested measurement method, which is the time-of-flight method. The range of drift mobilities we got for both types of carrier is 0.1 – 1 cm$^2$/Vs, which is at least two orders of magnitude below the values assumed by most previous workers. The result implies that the photoluminescence decays occur faster than true electron-hole recombination. One alternative explanation for the luminescence decays is that they correspond to the time for a photogenerated electron-hole pair (essentially an exciton) to dissociate.

As I discuss later, the bandtail mechanism used to describe the low mobilities in a-
Si:H does not account in detail for the mobilities in thin film CdTe, and we do not yet have a satisfactory theoretical understanding. Even without such an understanding, the mobilities offer some interesting insights into thin film CdTe.

The main step that researchers follow in making high efficiency thin film CdTe is a post-deposition CdCl$_2$ treatment. In particular, a CdCl$_2$ treatment increases the open circuit voltage $V_{OC}$ of the solar cell, which is the voltage measured across an illuminated cell with an ordinary voltmeter. The open circuit voltage is a fairly direct indicator of the recombination rate for photocarriers, and the Shockley-Queisser value is the largest one that is possible for a given material. For the real solar cells, besides the radiative recombination which defined the Shockley-Queisser limit of the open-circuit voltage, the recombination process also involves the non-radiative recombination which would lower the true open-circuit voltage of the cell. The non-radiative recombination usually consists two main mechanisms: the Auger recombination which the excess energy from the recombination of the electron-hole pair would excite a third charge carrier (electron or hole) which would thermalize quickly by emitting phonons. Auger recombination is usually the dominating recombination mechanism for high quality single crystal silicon solar cells. For the thin film solar cells like CdTe, the defects level is much higher. So the other non-radiative recombination process would dominate in this case. This is called Shockley-Read-Hall recombination, or the trap-assist recombination. The recombination process would via the defect states in the forbidden gap. The illustration of these three types of recombination could be seen in Fig. 1-3.
For the SRH recombination, the simplest model to calculate the recombination time assumes that the capture cross section of electrons and holes to be the same. Then the recombination time of SRH model could be simply expressed as:

$$\tau = \left( \nu_{th} \sigma N_T \right)^{-1}$$

(1-2)

where \(\tau\) is the recombination time of the charge carriers, \(\nu_{th}\) is the thermal attempt to escape frequency, \(\sigma\) is the capture cross section and \(N_T\) is the defect density of states. In this simple model, we can see that there is no correlation between the carrier’s drift mobility and the recombination time which is the indicator for the open-circuit voltage of the cell.

My collaborators at First Solar, Inc. provided us a series of samples with varying CdCl₂ treatments. The hole mobility was little affected by the treatment, although \(V_{OC}\) increased from 0.4 to 0.8 V. This increase in \(V_{OC}\) corresponds to a million times increase in the electron photocarrier density of the illuminated CdTe film. Surprisingly, the electron mobility decreased by about ten times with treatment. At first glance this seems a paradoxical result as we mentioned previously with the SRH recombination model.
As I explain later, we think this is an indicator that electron recombination in thin film CdTe may be “diffusion limited”, and is thus actually slowed when the diffusion (and mobility) of a carrier are reduced. At a given rate of photogeneration, an increase in the lifetime corresponds to an increase in the photocarrier density.

1.4 SYNOPSIS

The main results from my dissertation research are the following:

1) The electron and hole drift mobilities in thin film CdTe measured on materials of interest for solar cells are 100 to 10,000 times smaller than the values measured in crystals. The magnitudes are low enough to challenge the widespread use of photoluminescence decay times as a surrogate for direct recombination time measurements.

2) Both the time-dependence and the temperature-dependence of these drift mobilities are inconsistent with the bandtail trapping model developed for amorphous semiconductors, although the actual mobility magnitudes near room temperature are similar.

3) The CdCl$_2$ treatment that is commonly used to prepare high efficiency thin film CdTe solar cells does affect the drift mobility of electrons, but not of holes. The “anti-correlation” of the electron drift mobility and the open-circuit voltage of solar cells as CdCl$_2$ treatment progresses suggest that electron recombination in efficient solar cells may be diffusion-limited.

4) We further developed the photocapacitance technique for drift mobility measurements. This is a much faster method than time-of-flight, and can be
used on samples that are unsuitable for time-of-flight. We used it to conduct a survey of hundreds of solar cells for First Solar, and it also proved to be a convenient method for a highly sensitive “magnetomobility” measurement.

The structure of the rest of this thesis is organized as follows. In the second chapter, we will discuss mainly the basic electric characterization methods for measuring thin film CdTe. This includes the current-voltage (IV) measurements, external quantum efficiency measurements (EQE), capacitance measurements, and also lifetime measurements. Also, in the second chapter, we will compare the results for each different type of characterization method among thin film CdTe coupons with different post-deposition treatments. In the third chapter, we will mainly focus on the drift mobility measurements on thin film CdTe. We use two different methods to measure the photocarriers’ drift mobilities: the traditional time-of-flight (TOF) method, which is also used in measuring the drift mobility in single-crystal CdTe, and the fast profiling photocapacitance (PC) method. We will show the comparison between the two methods. In the last part of the chapter, other than providing the details of measuring mobility in CdTe, we also discuss the possible mechanisms behind low mobility values in thin film CdTe. We will show different approaches we made for testing different theories currently existing for low mobility explanations.
REFERENCES


7 B. McCandless, L. Moulton, R. Birkmire, Prog. Photovolt. 5, 249–C260 (1997).


15 M. A. Green, K. Emery, Y. Hishikawa, W. Warta and E. D. Dunlop, Prog. Photovolt:


24 P. Auger, J. Physique et Le Radium, 6, 205 (1925).

2 CHARACTERIZATION METHODS FOR CdTe

2.1 COUPON DETAILS

The CdTe coupons we have were made with superstrate configuration. Although different deposition methods have been applied during the fabrication process, it always follow the same superstrate structure for high efficiency solar cells. Here is the detail process of producing superstrate thin film CdTe. As shown in Fig. 2-1, the first step is to coat a thin layer of transparent conducting oxide (TCO) like SnO\textsubscript{2} or In\textsubscript{2}O\textsubscript{3}:Sn (ITO) onto the glass substrate. After the coating of conduction layer, it follows with the deposition of an ultra-thin layer of CdS using chemical bath deposition, sputter deposition or physical vapor deposition for the transmission of most blue photons. The short wavelength photons would be absorbed very close to the surface of the active layer. If the thickness of the CdS is too thick, most of these generated photons would be absorbed in the CdS layer which will not contribute to total photocurrent. However, the ultra-thin layer of CdS usually would cause a shunt current between TCO and CdTe layer. The best way to prevent this leakage current is to deposit a thin, highly resistive layer of undoped SnO\textsubscript{2} or Zn doped SnO\textsubscript{2} or In\textsubscript{2}O\textsubscript{3} between the CdS and TCO. This highly resistive transparent layer can also act as a diffusion barrier to prevent contamination of the CdS and CdTe by the impurities in the glass and also TCO. Following the n-type CdS layer, it’s the main absorbing p-type CdTe layer. Usually the sequence of depositing a CdTe layer is first the chlorine-free pre-deposition of CdTe using close space sublimation followed by the high-temperature CdCl\textsubscript{2} post deposition.
treatment. As we mentioned earlier, the CdCl$_2$ treatment is the key to achieve high efficiency CdTe solar cells. The post-deposition CdCl$_2$ treatment helps the solar cell in many ways including increasing the efficiency of the solar cell,$^1$ the grain size,$^2$ and also the minority carrier lifetime.$^3$ The last step to finish the CdTe solar is the deposition of back contact. To prevent the formation of Schottky barriers between the p-type CdTe and the metal contact, the deposition usually start with a tellurium-rich surface by chemical etching, then deposited/evaporated copper to the surface with post-anneal treatment to diffuse copper into the CdTe layer. Copper would react with Te to form Cu$_2$Te to give a p+ layer in order to lower the back-contact barriers.$^4$ The secondary contact then applied as the current-carrying conductor.

In this thesis, we will mainly discuss the influence of CdCl$_2$ treatment on the solar cell transport properties, and especially the photocarriers drift mobilities, which are barely mentioned in literatures. The detailed discussion of the drift mobility measurements will be shown in the next chapter.

Generally, for the purpose of our experiment, we have two groups of thin film CdTe coupons prepared by First Solar Inc. to test solar cell properties. The first group is the traditional thin film CdTe with the superstrate configuration (group I), and the second group (group II) is with the special bifacial preparation. For the bifacial coupons (group II), the back contact (metal contact) side is semi-transparent so the light can penetrate partially through the back of the cell. The reason for this special treatment is so that the electron and hole pairs can be generated from the opposite side. By applying a bias voltage on the coupon, we can separate two types of carriers and measure hole
mobilities and electron mobilities individually. For group II, the coupons can also be sorted into two different groups: the coupons without CdCl₂ treatment and coupons with CdCl₂ post-deposited treatment. The deposition conditions are not clear for group I coupons. In this chapter, we will discuss mainly on the electric characterization methods to extract the basic solar cell properties for thin film CdTe solar cells including short-circuit current $I_{SC}$, open-circuit voltage $V_{OC}$, quantum efficiency QE, the capacitance or the depletion width and also the recombination time of the photocarriers. For each of these parameters, we will show some results for the different types of CdTe coupons.

### 2.2 $I$-$V$ MEASUREMENT

In order to measure the basic parameters for solar cell, the current-voltage ($I$-$V$) measurement is one of the most simple and direct method to apply to the solar cell. To measure the $I$-$V$ curve for solar cells, first we need to know the voltage to current response of a solar cell. For an ideal solar cell, we can write the current response under illumination as:

$$I_{light}(V) = I_{01}\left[\exp\left(\frac{qV}{kT}\right) - 1\right] + I_{02}\left[\exp\left(\frac{qV}{2kT}\right) - 1\right] - I_{sc} \quad (2-1)$$

$I_{SC}$ is the short-circuit current, $kT/q$ is the thermal voltage and $I_{0i}$ is the dark saturation current.
current due to the recombination in the quasi-neutral regions and $I_{02}$ is the dark saturation current due to the recombination in the space-charge region. So from eq. (2-1), an ideal solar cell could be modeled by current source $I_{SC}$ in parallel with two diodes: one with ideality factor 1 and one with ideality factor 2. The ideality (quality) factor is the constant in front of the $kT$ term in eq. (2-1), and usually has a value between 1 and 2. Value 1 corresponds to recombination in the quasi-neutral region and 2 corresponds to the recombination in the space-charge or depletion region. However, for real solar cells, there are some parasitic series and shunt resistances inside the solar cell. With the existence of these resistances, we can illustrate the real solar cell as Fig. 2-2. The general current equation for this case would be modified as:

$$I(V) = I_{01} \left[ \exp \left( \frac{q(V + IR_s)}{kT} \right) - 1 \right] + I_{02} \left[ \exp \left( \frac{q(V + IR_s)}{2kT} \right) - 1 \right] + \frac{(V + IR_s)}{R_{Sh}} - J_{sc} \quad (2-2)$$

$R_s$ is the series resistance and $R_{Sh}$ is the shunt resistance. In order to make the solar cell to reach the ideal case as much as possible, the value for $R_s$ has to be as small as possible and the value for $R_{Sh}$ has to be big enough.

In Fig. 2-2, we also show the basic setup for doing $I$-$V$ measurement, the CdTe coupon is illuminated by a 150 W solar simulator (Newport Solar Simulator model: Source Meter CdTe)

Fig. 2-2. The left graph shows the simplified circuit model for CdTe solar cells. The right side of the graph shows the basic experiment setup for I-$V$ measurements.
produce a uniform, collimated, 2 inch × 2 inch output beam with the spectrum closely match to sunlight power equivalent to 1 sun. The coupon is connected through the back contact with the source meter (Keithley 2400) to provide a step voltage and measure the current signal from the front contact. The source meter is then connected to a computer using GPIB interface to record and analyze the data.

In Fig. 2-3, we show some of the results from different coupons. The right side graph gives a normal result with a coupon from group I. The coupon shows the typical diode behavior where the current for the reverse bias is almost zero. Since the physical thickness for the CdTe coupon is around 3 μm, it can easily reach the breakdown with a relatively small reverse bias voltage. The typical reverse bias range we use on the CdTe is less than 2V. For this coupon under simulator illumination, the $I_{SC}$ is around 27 mA and $V_{OC}$ is around 0.8V. The left side graph shows a result for another coupon from the group II with a large series resistance. This coupon was made with the special

Fig. 2-3. The left side of the figure shows the dark and light I-V measurements for coupon with large series resistance and the right side of the figure shows the dark and light I-V measurements for the normal CdTe coupon.
bifacial treatment, for which the back contact has a resistance of order $10^3 \, \Omega$/square. The $V_{oc}$ of this coupon is still has a normal value of 0.8 V, but the $I_{sc}$ and fill factor are largely affected by the series resistance. We can see from left side graph that the series resistance does largely affect the performance of a solar cell.

### 2.3 Quantum Efficiency Measurement

Quantum efficiency is one of the most important electrical characterization methods for determining the properties of a solar cell. For an ideal single absorption layer solar cell, the maximum power conversion is described by the Shockley-Queisser (SQ) limit. In the SQ limit, for one photon with energy larger than the band gap of the absorber material, it will generate one electron-hole pair inside the cell and the charge will be collected by the solar cell even under short circuit conditions. However, for a real solar cell, the electron-hole pair generation is not equal to unity, here we use the quantum efficiency to present the photon-electron conversion rate. The external quantum efficiency (EQE) is defined as the number of electrons collected by the circuit per incident photon on the solar cell. The unity of the EQE corresponds to the full conversion to electrons from the generated photons inside the solar cell.

Usually, the EQE depends on two basic parameters: the bias voltage across the sample and the incoming light wavelength. We usually measure the quantum efficiency under zero bias or the short circuit condition, and for most cases, the reverse bias voltage would not change the value of the EQE. For analyzing the quantum efficiency spectrum, we would also need to know the absorption spectrum corresponding to strong absorption and weak absorption.
The typical quantum efficiency setup in our lab consists of four parts:

1) Monochromator with the broad band spectrum covered from 400 nm to 1100 nm.

2) Light processing part which will split the incoming light beam into two parts. One for the testing sample and one for the reference sample.

3) Data processing part which will collect the electric currents signal from both reference and testing parts.

4) Data analysis part which will analyze the photocurrent signals from both testing and reference parts and calculate the QE for the testing sample.

In Fig. 2-4 we show the basic experiment setup for the QE experiments. The light source we use is a typical tungsten halogen lamp (300W) which has wavelength range from 400nm to 2500nm. Then follows the monochromator (model: Horiba Jobin-Yvon model H20) to provide nearly monochromatic light. The H20 monochromator is mounted with a 600 g/mm grating. The actual wavelength from the monochromator would differ by 2X of the mechanical counter reading. The angle of the grating is adjustable with a stepping motor. The motor unit is programmable through the GPIB port connecting with computer. The H20 model also provides with a set of slit inserts: 0.5 mm, 1.0 mm and 2.0 mm. Decreasing the slit width would increase the wavelength resolution by limiting the bandpass, but also limits the amount of the light that passes through the slit. For the 2mm slit width that we choose, the wavelength resolution is 2 nm.
For the halogen lamp that we use, we start to observe the higher orders of diffraction from the short wavelength beams at 800nm, so we need to put a 800 nm high pass wavelength filter right after the monochromator when we’re measuring wavelengths shorter than 800 nm.

After the monochromic light emerges from the monochromator, we need to use an optic chopper to chop the light in a certain frequency that we can read the modulated signal from the lock-in amplifier. Then for the modulated light beam, we will split the light beam into two parts. One for the reference detector and one for the sample. The reference detector that we use is a silicon photodiode (OSI optoelectronics model NO: PIN-10DP-SB) with a known spectral response (SR) from 400 nm to 1100 nm. The incident beam intensity on the silicon photodetector can be calculated using:

\[ N = \frac{I_R \lambda}{SR \times hc} \]  

(2-3)

Here \( N \) is the intensity of the light, \( I_R \) is the photocurrent from the reference detector, and SR is the (known) spectral response from the silicon photodetector. The real part of the modulated signal in the lock-in amplifier represents the current signal. Since the
real part in the lock-in amplifier is not frequency dependent for the low frequency, we usually choose 300 Hz as the modulation frequency for our measurements.

Before measuring the quantum efficiency of CdTe coupons, we also need to do some calibrations for our setup to define the ratio of the beam splitter. We can put two silicon photodetectors (PIN-10DP-SB) one in the testing sample position and one in the reference position to measure the electric current spectrum. Since the spectral response for two silicon photodetector are identical, the current ratio \( n = I_1/I_2 \) would give the beam intensity ratio for the beam splitter. After we calibrate for the ratio of the beam splitter, we can write the equation for the quantum efficiency as:

\[
EQE(\lambda) = \frac{I_S}{I_D} \frac{hc}{\lambda e} SR \times n \tag{2-4}
\]

Where \( I_S \) is the sample current and \( I_D \) is the detector current. The external quantum efficiency measures the optical loss between the incident photon flux and generated currents.

The optical loss can be further broken down into the losses due to the reflection of light and the parasitic absorption within the device; we ignore the possibility of transmission of light through the cell’s back reflector. If we exclude the loss due to the reflection, than we can measure the quantum efficiency corresponding to the ratio of collected electrons and the number of photons absorbed by the solar cell. This is called internal quantum efficiency (IQE). The relation between EQE and IQE can be expressed as:

\[
IQE(\lambda) = \frac{EQE(\lambda)}{1-R} \tag{2-5}
\]

\( R \) is the reflectance of the solar cell. For the current section, we will mainly show the
data from EQE measurements.

In Fig. 2-5, we show our experiment results for the quantum efficiency measurements on the thin film CdTe coupons from group II. The coupons we use to measure EQE are the special bifacial coupons. The coupon can be illuminated on both sides. In this way, we can measure the EQE from both front and back contacts. From the front side the transmittance is almost 100% and from the back semi-transparent contact the transmittance is only around 30%. We show the comparison between front and back illumination EQE in Fig. 2-5. We also applied a series of bias voltages to the sample. The left side is the result for the untreated bifacial coupon and the right side shows the result for the bifacial coupon with post-deposition CdCl$_2$ treatment.

We can see from the graph the front side results for both coupons are very similar throughout all applied voltages. It begins with a region at shorter wavelengths where the EQE increases sharply. Since for the short wavelength (blue) illumination, the photocarriers are mainly generated near the CdS/CdTe interface or in the CdS layer. Generation of a photocurrent requires that holes generated in the CdS diffuse out and pass the interface, which is very unlikely in CdS due to a very short diffusion length in the n-type material.

For the range of 450-800 nm, the EQE remains at a very high value; nearly all incident photons contribute to the photocurrent. The other decreasing region after 800 nm is due to the weak absorption of the longer wavelength light by CdTe, which has a bandgap of 1.51 eV.

However, for the back illumination the EQE for two coupons shows very different
results. In Fig. 2-5, we also show the lines for the back EQE which we excluded the effect of 30% transmittance. We can see that after correcting for the optical loss by the semitransparent film, the EQE data from the back illumination is still much lower than the front illumination. Also, we can see from Fig. 2-5, the quantum efficiency measured from back illumination for treated sample shows a strong voltage dependence. However, the EQE from the back for the untreated coupon remains almost the same for different bias voltages. The voltage dependence of the back illumination on the treated coupon can be explained by the special sample properties of the treated coupon.

The depletion width for the treated coupon 6 in the short circuit condition is thinner than the physical thickness of the CdTe layer. We will show this result later on the thesis. The treated coupon 6 shows a linear increase of the depletion width with the reverse
bias voltages, which means with higher bias voltage the deeper the depletion width. So, in this case, the CdTe layer is divided into two regions: the depletion region which the carriers move under the influence of the electric field and the diffusion region where the carriers diffuse along the gradient of the carriers’ concentration. If the photocarriers are generated near the front side, then holes would first move across the depletion region and diffuse through the diffusion region to the back contact. Eventually, all the carriers would be collected in the measuring time. However, for the back illumination where the photocarriers are generated near the back side, the photocarriers would be generated inside the diffusion region. In this case, carriers could diffuse in two directions – to the front side and also to the back side. For the electrons which diffuse to the back contact side would contribute as the negative current in this case. If the diffusion length is very long, then carriers would take more time to move to the depletion region, in this way, more carriers would be collected by the back contact side, then this would result a lower QE value. This is the reason why we see a voltage dependent QE for the back illumination on the coupon which is not fully depleted.

As for the untreated coupon 5, since the coupon is not treated with Cu deposition, the back diffusion effect is much lower. However, some of the carriers for the back illumination still will be generated outside the depletion region of the CdTe layer. So, we expect a competition between the diffusion of the electrons to the back and the drift of the electrons to the front. Still, some of the carriers would be lost during this process. So, the back EQE will be smaller compare with the front QE. There are also other groups showed the simulation of the quantum efficiency due to the diffusion transport.
which has the similar behavior compared with our back illumination data.\textsuperscript{7}

\section{2.4 Capacitance Measurements}

Capacitance experiments for thin film solar cells are a very important approach to measure the depletion width and also a quick way to probe the space charge distribution inside sample. For the simple solar cell structure (Fig.\textsuperscript{2-2}), the sample could be treated as a RC circuit in the AC signal modulated condition. In this case, we measure the capacitance as the differential capacitance or a small signal capacitance. Comparing with the large signal capacitance where the value of the capacitance is defined as the ratio of $Q/(V - V_{bi})$, the small signal capacitance measures the charge response to a small voltage change. The small signal capacitance could be expressed as $\delta Q/\delta V$. Usually these two measurement converge to the same number. The basic principle of measuring the small signal capacitance is similar with analyzing the RC circuit. When a small AC signal applied on the sample, the response current will consist of two parts: the in phase part which is related to the response from the resistance and the out of phase part which is related to the response of the capacitance:

$$I = V(R + i\omega C)^{-1}$$  \hspace{1cm} (2-6)

In this way, we can measure the capacitance signal using the lock-in amplifier. The out of phase or the imaginary part value would be related to the small signal capacitance. The in phase or the real part value is related to the series resistance of the solar cell. If the series resistance value is too large, the RC circuit would act as a low pass filter which the output on the Y channel of the lock-in amplifier is no longer an accurate value for the capacitance. The criteria we choose for our capacitance measurement is that the
The capacitance measurement setup is the configuration shown in FIG.2-6. The back contact of the CdTe coupon is connected with the function generator (Aglient 33210A). The function generator provides a modulated sinusoidal AC signal on the DC bias to the back side of the CdTe coupon. The front contact is then connected to a trans-impedance amplifier (current to voltage preamplifier). The magnified voltage signal would then transfer to the lock-in amplifier (Stanford Research System SR830). The voltage signal on the Y channel would convert into the capacitance using:

\[ V_Y = \frac{I}{S} = \frac{V_m}{2\pi f c S} \]  (2-7)

where \( S \) is the gain from the trans-impedance amplifier, \( f \) is the modulated frequency, \( V_m \) is the average voltage of the AC signal.

We showed the room-temperature capacitance measurement for one of the CdTe coupons in Fig. 2-7. For all the capacitance measurements, we use the modulation
frequency of 1 KHz, with an AC signal of 100 mV amplitude. We also fit the dark capacitance measurement data for the CdTe coupon at room temperature in Fig. 2-7 using the form suggested by the Schottky analysis:\(^8\):

\[
\left(\frac{1}{C^2}\right)^2 = \frac{2(V_0 - V)}{e\varepsilon_0 N_A},
\]

(2-8)

where \(N_A\) is the acceptor doping level, \(\varepsilon\) is the relative dielectric constant, and \(V_0\) is an offset potential. The offset potential from our measurements is related to the built-in electric field throughout the depletion width. However, it is not necessarily the true built-in potential of the cell since the electric field is not uniform throughout the whole depletion region under the external applied bias. It actually represents the electric field near the region where the photocarriers are generated. In Fig. 2-7, we can extract the value of \(N_A\) and also the offset potential \(V_0\) from the fitting. Moreover, we can get the information for the depletion width of the cell directly from the capacitance measurement:

Fig. 2-7. Capacitance measurement on CdTe coupon at room temperature with different bias voltages. The dashed line represents the fitting using Schottky analysis. The intercept gives the value for offset potential \(V_0\).
The capacitance measurements could be a simple tool to help us find out the correlation of the different solar cell properties with the different post-treatments on CdTe coupons. For instance, we also studied the comparison between groups of

\[ W_d = \frac{eA}{C} \]  

(2-9)

Fig. 2-8. The cumulative percentage of a) offset potentials \( V_0 \) b) the depletion width \( W_d \) at 0 V and c) the acceptor doping level \( N_A \) for all measurable cells obtained from a standard Schottky analysis of dark \( C-V \), The black open dots is the cells before light soaking; grey dots shows the cells after 3.5 hours light soaking and the light grey open dots is for the cells after 24 hours light soaking.
coupons from group I before and after different light soaking conditions, and we show the results from the capacitance measurements for the groups before and after light soaking in Fig. 2-8. From the dark C-V measurements, the most important effect that we find after the light soaking is the offset potential for both groups (3.5 hours and 24 hours) got increased. From Fig.2-8 (a), we can see that $V_0$ for the cells before light soaking is around 0.2 V. And after 3.5 hours light soaking, the $V_0$ for most of measurable cells are scattering around 0.3 to 0.4 V. And for the cells after 24 hours light soaking, $V_0$ scatters in an even wider range, from 0.25 to 0.6 V. For both groups, we observe an increase of $V_0$ after light soaking. And the longer length of light soaking has brought a stronger effect to the offset potential or we can say that the built-in electric field in the depletion region becomes unstable after longer time light soaking. As for the depletion width, in Fig.2-8 (b), $W_d$ shows only a small change for both 3.5 and 24 hours light soaking. The light soaking does not change the depletion width of the CdTe sample. We also can get the acceptor doping level from the slope of the dark C-V measurements. In Fig 2-8 (c), we can see that the light soaking has increased the $N_A$ value and also broadened the scattering range of the doping level. For the difference between the different lengths of light soaking, we can only observe a small change from Fig. 2-8 (c).

2.5 RECOMBINATION LIFETIME MEASUREMENT

We measured the minority carrier lifetime for thin film CdTe using intensity modulated photovoltage spectroscopy (IMVS). This is a common method for measuring carrier lifetime mainly in dye-sensitized solar cells and also some amorphous silicon solar cells\textsuperscript{9,10}. IMVS measures the photovoltage modulation under open-circuit
conditions in response to the modulation of the illumination intensity. The carrier lifetime information can be extracted from the modulated response signals.

During the measurement of IMVS, the solar cell is illuminated with a modulated light using a small sinusoidal ac bias voltage (10% smaller than the DC bias). The periodic illumination function can be written as:

\[ I(t) = I_0 \left[ 1 + (\delta e^{i \omega t}) \right] \]  

(2-10)

where \( \omega \) is the modulated frequency and \( \delta I_0 \) is the AC component of the incident photon flux. Then the photovoltage response is measured as the amplitude and phase shift with respect to eq. 2-10. It can also be presented in the IMVS complex plane plot.

The analytical solution of this amplitude and phase shift would give an expression as\(^{11}\):

\[
\begin{align*}
\text{re}(\Delta V_{oc}) &= \frac{-M}{1 + \omega^2 \tau^2} \\
\text{im}(\Delta V_{oc}) &= \frac{-M \omega \tau}{1 + \omega^2 \tau^2}
\end{align*}
\]  

(2-11)

where M is the scale factor and \( \tau \) is the carrier lifetime. In this case, we can directly measure the lifetime of the photocarriers from the response to the modulated incident light.

The experimental setup is very similar to the capacitance setup\(^{12}\). We measure the real and imaginary part of the phase shift of the photovoltage directly from the lock-in amplifier under different modulated frequencies. The only difference compared with ordinary capacitance measurement, is that we use an intensity modulated laser diode to illuminate CdTe coupon. We used the 525 nm laser diode with a modulation signal 5% of the laser intensity and the open circuit voltage measured under this condition is around 0.2V. The \( V_{OC} \) measured under the full sunlight using solar simulator is around
0.75 V and the electron drift mobility for this particular coupon is around 3.5 cm²/Vs using photocapacitance method¹³.

Fig. 2-9. shows the frequency dependence for both real and imaginary part of the modulated photovoltage signal. Using IMVS method, we plot the real and imaginary part of the signal in Fig. 2-10, the frequency which the imaginary part reaches the

Fig. 2-10. The modulated photovoltage shown in the complex plane. The dash line is the fitting using the classical IMVS model.
maximum (top point on the semicircle) corresponding to the minority carrier lifetime
\( \tau = \frac{1}{2\pi f} \). Applying the fitting from eq. 2-11 we can get the minority lifetime corresponding to this particular thin film CdTe coupon is around 1.6 \( \mu \)s. We also did another lifetime measurement on one of the untreated bifacial CdTe coupon. The measured average mobility for the untreated coupon is lower compared with the ordinary thin film CdTe coupon which we did the lifetime measurements on. If we think the recombination is diffusion limited, than we would have a longer recombination time

\[
\tau = 3.5 \, \mu s
\]

Fig. 2-11. The modulated photovoltage components plotted in the complex plane for the untreated bifacial coupon. The lifetime corresponding to the top of the arc is around 3.5 \( \mu \)s.

for the lower mobility cells. In Fig. 2-11, we showed the IMVS measurement on one of the cells for this untreated bifacial coupon. The lifetime we get for this cell is around 3.5 \( \mu \)s, which is longer than the previous measurement.

**REFERENCES**


2 McCandless BE, Birkmire RW. *Proceedings of the 16th European Photovoltaic Solar*
Energy Conference and Exhibition, Glasgow; 349 (2000).


3 TRANSPORT CHARACTERIZATION FOR CdTe

3.1 TRANSPORT CHARACTERIZATION INTRODUCTION

In this chapter, we will discuss the characterizations for the electric transport properties, especially the drift mobility of photocarriers in the solar cells. After the electron-hole pairs are photogenerated inside the solar cells, they will move separately into the two opposite sides of the solar cells by both the internal electric field and the external applied electric field. The transport properties of these photocarriers are often described in terms of mobilities. The definition for the mobility \( \mu \) is the ratio of the drift velocity of the photocarriers \( v \) and electric field \( E \), which can be written as:

\[
v = \mu E
\]  

(3-1)

The mobility is an important parameter to connect with other properties of the solar cell like conductivity, photocarriers’ lifetime, and defect properties. There are several ways to measure the mobility in solar cells:

The first type of mobility measures the steady-state conductivity of the sample like the photoconductivity experiment. This mobility value is called conductivity mobility which is the photocarriers’ velocity per unit electric field. And the conductivity (steady-state) mobility measures the free photocarriers’ (electrons and holes) movement in the conduction band or the valence band.

The second type of mobility is determined by the Hall Effect. In the Hall Effect experiments, the photocarriers which contribute to the measurement are still the free electrons
or holes moving in the conduction and valence band. In most single crystals, the conductivity mobility is commonly the same as the Hall mobility.

The third type of mobility is called drift mobility. The drift mobility measures the movement of generated photocarriers moving across the sample under the influence of external electric field. The measurement of drift mobility can be very different comparing with above two types of mobility measurements. The capture and emission of the photocarriers from the defects’ states (traps) in the band tail region of the disordered material would largely reduce the mean velocity of the photocarriers. The drift mobility involving the multiple trapping in the band tail region would be orders of magnitude lower than the conductivity mobility which measures the free carriers movement in the band edge. In this thesis, we will discuss the result for only the drift mobility measurements since it represents the transversal movement of the carriers through the solar cell and also represents the photocarriers moving in the band tail of the disordered material.

3.2 TIME OF FLIGHT TECHNIQUE

The traditional way of measuring the drift mobility is using the time-of-flight technique. The basic idea of the time-of flight method is to measure the electric current signal (displacement current) generated from the moving photocarriers inside the material. Assuming the sample thickness is \(d\), we use a pulsed laser to illuminate one side of the sample in order to generate a thin sheet of electrons and holes near the illuminated side of the sample. After the generation of photocarriers, the photocarriers would then drift across the solar cell under the
influence of the internal or external electric field $E$. In simple cases, the photocarriers would move across the sample with a constant drift speed. This movement of the photocarriers would produce a constant current displacement in the external circuit that will immediately drop to zero once the carriers reach the other side of the sample. The first use of the method is often attributed to Haynes and Shockley in 1949.\textsuperscript{2}

We define the time where the mean position of the photocarriers reaches the middle of the sample as the transit time $t_T$, where at this time half of the generated photocharge would have been collected by the external circuit. This constant displacement current in the external circuit is normal transport that is not affected by trapping and emission from the defects. We will discuss the more general case of dispersive transport later in this chapter.

For the normal transport where the displacement current remains constant during the carriers’ movement, we can use the simple model to express the drift mobility. The definition of the mobility is in eq. (3-1). Assuming a constant electric field $E$, the drift mobility could be expressed as\textsuperscript{3}:

$$\mu = \frac{L}{Et_T}, \quad (3-2)$$

$\mu$ is the drift mobility, $L$ is the distance the photocarriers traveled, and $t_T$ is the time for the mean position of the photocarrier distribution to move by $L$. As noted earlier, we typically select $L = d/2$, where $d$ is the sample thickness, and measure the corresponding transit time. Note that the electric field generated by the photocarriers themselves has to be very small compared with the electric field inside the sample. Typically, the applied electric field is larger
than the built-in field inside the sample. In general, the criteria we usually use is the total injected photocharge $Q_0$ needs to be smaller than 10% of total charge ($CV$) on the cell’s electrodes when viewed as a simple capacitor. In this way, the electric field of the sample is almost the same as the applied field, which is $E = V/d$, $d$ is the thickness of the depletion region of the cell, and the drift mobility could be expressed as:

$$\mu = \frac{d^2}{2V(V-V_0)t_T} \quad (3-3)$$

where $V_0$ is the offset potential. If we plot $d^2/2t_T$ vs the bias voltage, the intercept would be the offset potential and the slope is the drift mobility.

### 3.3 TIME-OF-FLIGHT EXPERIMENT SETUP

The setup for our time-of-flight experiment is illustrated in Fig. 3-1. The sample is located in the center of Fig. 3-1. We use a monochromatic laser diode as the light source. The laser diode is pulsed by a fast pulse generator (Avtech AVO-9L-C) in order to achieve a short pulse width. The typical pulse width we set for our experiment is 4 ns. We use a set of laser diodes with different wavelengths to illuminate the sample. The photocarriers are generated with different distributions inside sample at different illumination wavelengths corresponding to the absorption coefficient spectrum of the sample. The front side of the sample (glass side) is then connected to a second pulse generator (Avtech AV-1015-B) through the CH2 of the oscilloscope to provide a near constant bias voltage. The typical pulse width we use in the time-of-flight experiment is 10 ms. Since the recombination for the photocarriers in thin film CdTe we measured in the previous happens around $\mu$s, we can treat the pulse width of the bias voltage
as DC voltage. We also need to set a delay time after the RC rise time of the cell before the generation of the photocarriers to make sure the electric field is constant inside the sample. The back side of the sample (metal contact) is connected to the CH1 of the oscilloscope. We read the response current signal from CH1 of the oscilloscope (Lecroy 9350CM) which is then connected to a computer through a GPIB interface.

### 3.4 SURFACE ILLUMINATION

For the time-of-flight measurement, we did our measurements mainly on the bifacial coupons. The details of these bifacial samples are presented in Table. 3-1. For our thin film CdTe measurements, we use a pulsed diode laser to illuminate the sample. We choose fast pulsed laser diode with a pulse width lower than 10 ns to minimize the influence from the illumination duration times. The laser wavelength we use for generating a thin sheet of photocarriers near one side of the sample is around 660 nm. The physical thickness of all CdTe coupons we tested is around 2.8 μm. The absorption coefficient $\alpha$ at 660 nm is around $4 \times 10^4$ cm$^{-1}$ correspond to an absorption depth of 0.25μm.$^4$ The photocarriers generated at this wavelength would be close to the surface of the illumination side. If we need to measure both

Fig. 3-1. Experiment setup for time-of-flight method.
type of carriers (electrons and holes) separately, we cannot just change the sign of bias voltage from + to – from just one side. CdTe solar cell is a typical p-n junction diode, it can be fully depleted only under reverse bias. So, if we need to measure the transport of both carriers separately, we need to generate the photocarriers on the opposite side of the sample. The special bifacial coupons made by First Solar are ideal for measuring both electrons and holes’ drift mobilities. We can separate the movement of electron and hole photocarriers by illuminating the sample on each side. For measuring the hole drift mobility, we illuminate the sample from the glass side so only the holes would move across the sample from CdS/CdTe interface to the back of the sample under the reverse bias voltage. The electrons in this case would be collected rapidly on the glass side. As for measuring the electron mobility, we illuminated the sample from the back contact side. Only the electrons would drift from the back contact to CdS/CdTe interface. In Fig. 3-2, we show an example of TOF data for illuminations on both sides of one

<table>
<thead>
<tr>
<th>Coupon</th>
<th>Treat</th>
<th>$V_{oc}$ (V)</th>
<th>$\mu_h$ (cm$^2$/Vs)</th>
<th>$\mu_{\tau_{h,t}}$ (cm$^2$/V)</th>
<th>$\mu_e$ (cm$^2$/Vs)</th>
<th>$\mu_{\tau_{e,t}}$ (cm$^2$/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No</td>
<td>0.48</td>
<td>0.6</td>
<td>$3.0 \times 10^{-7}$</td>
<td>1.3</td>
<td>$3.9 \times 10^{-7}$</td>
</tr>
<tr>
<td>2</td>
<td>Yes</td>
<td>0.69</td>
<td>1.4</td>
<td>$2.5 \times 10^{-6}$</td>
<td>0.9</td>
<td>$2.2 \times 10^{-7}$</td>
</tr>
<tr>
<td>3</td>
<td>Yes</td>
<td>0.75</td>
<td>1.4</td>
<td>$2.6 \times 10^{-7}$</td>
<td>0.1</td>
<td>$2.1 \times 10^{-7}$</td>
</tr>
<tr>
<td>4</td>
<td>Yes</td>
<td>0.73</td>
<td>0.8</td>
<td>$1.2 \times 10^{-6}$</td>
<td>0.7</td>
<td>$2.2 \times 10^{-7}$</td>
</tr>
<tr>
<td>5</td>
<td>No</td>
<td>0.54</td>
<td>1.4</td>
<td>$5.8 \times 10^{-7}$</td>
<td>2.6</td>
<td>$1.1 \times 10^{-6}$</td>
</tr>
<tr>
<td>6</td>
<td>Yes</td>
<td>0.80</td>
<td>1.5</td>
<td>$3.8 \times 10^{-6}$</td>
<td>0.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3-1: Coupon details for all six coupons
bifacial coupon. This is one of the coupons which follows the normal transport behavior so that we can use the simple model to extract the information of drift mobility. The drift mobilities for both electrons and holes can be derived from the slope of the transient graph. Also, we can get the offset voltage from the interception on x-axis. In theory, the offset voltage for both illumination should be identical. However, we observe a mismatch for the offset voltages on this coupon for illuminations on both side. This mismatch of the offset voltage is indicating a non-uniform distribution of the electric field inside the sample. The electric field near back contact side is relatively higher than the electric field near the CdS/CdTe interface side.

Next, we will move to the details for transient photocharge measurements. The typical laser pulse width we use is 4 ns. The main limitation to the time resolution of the photocurrent measurement was not the optical pulse width, but rather the product $RC$ rise time of the cell’s capacitance $C$ and the series resistance $R$, which includes the 50 ohm electronics. The typical
area for a cell in the thin film CdTe coupon is around 1 cm$^2$, and the capacitance for that area is around 4 nF. For the bifacial coupons we mainly used for the time-of-flight experiment, it
contains a series resistance around 1000 Ω for the semitransparent back contact. So the total RC time for one cell is around 4 μs which is larger than the rise time of the photocarriers. In order to minimize the influence of the RC rise time to the experiment, we decrease the capacitance of the cell by scribing a small area in one cell. The typical scribing area is around 1 mm². And we measured the rise time $t_{RC}$ for a 50% charge response to a fast electronic step, which was about 40 ns for the small scribed area. In this way, we have enough resolution to measure the transit time for the photocarriers.

Fig. 3-3 presents the procedures we follow for analyzing time-of-flight experiments. The graphs are for a cell from one of the bifacial untreated coupon for which the electric field under reverse bias was fairly uniform across the CdTe film. This can be seen from the capacitance measurement from the previous chapter where the capacitance for some of the bifacial coupons shows almost constant value under reverse bias. The applied field $E=V/d_W$ on the sample would be almost constant since the depletion width $d_W$ for the sample under reverse bias is nearly constant.

Fig. 3-3(a) shows the photocharge transients $Q(t)$ at four voltages for 0.1, -0.2, -0.4 and -1.0 V using front surface illumination (660nm on glass side); the transients are thus dominated by hole motion. The photocurrent transient $i(t)$ was recorded and subsequently integrated to obtain photocharge $Q(t)$. As we mentioned earlier, the voltage pulses we set on this coupon were 1.0 ms long, and were applied 50 μs before the laser pulse to retain a constant applied field on the sample. With a voltage of -1.0 V, the photocharge collected in 1.0 μs is about 5.1
pC, which we equate to the total charge $Q_0$ of holes photogenerated in the CdTe film by the laser pulse. For a smaller bias voltage like -0.2 V, we can see from the graph that the charge collection in the 1.0 µs is smaller than the higher bias voltage value. This behavior is common in time-of-flight measurements, and is attributed to deep trapping which the carriers are trapped without emitting from the defect states during the normal measuring procedure.\(^5\) In Fig. 3-3(a), we can find the total collection of the photocharges by the reading the flat part of the higher voltages. Once we determine the total charge $Q_0$, we can read the rise time $t_R$ for each voltages from the graph where $Q_0/2$ are collected.

Fig. 3-3(b) shows the analysis of the transient photocharge for two bias voltages 0V and -1.0V. We use the “half collection” to obtain a transit time $t_T$ for the photocarriers to drift halfway across the sample. This “half collection” definition of $t_T$ is unusual in single crystal work, but is common in less ordered materials. We start with the measured rise time $t_R$ for the transient to reach 50% of its ultimate charge. Since the $RC$ time for the bifacial coupons is comparable with the rise time of the photocharge, we cannot simply assume the transit time $t_T$ is the same as the rise time $t_R$. To obtain the corresponding transit time $t_T$, we correct for the measured electrical response time $t_{RC}$ using the approximation:\(^6\)

$$t_T^2 = t_R^2 - t_{RC}^2 \quad (3-3)$$

This approximation is strictly true if the photocurrent signal and the electronic response function are both Gaussian functions of time, when the convolution of separate rise times could give a total rise time like eq.(3-3). In practice it’s a convenient, if rough, approximation.
vertical dashed lines in Fig. 3-3(b) indicate the measured value of the cell RC time $t_{RC} = 40$ ns.

For the two voltages, we also show solid lines for calculations of charge transients corresponding to these transit times $t_T$. If we use the assumption that the initial photocharge distribution moves at a constant drift-velocity after photogeneration at time $t = 0$, the photocharge expression is just:

$$Q(t) = Q_0 \left( \frac{t}{2t_T} \right) \left[ 1 - \exp \left( -\frac{t}{\tau_t} \right) \right] \quad t \leq 2t_T$$

where $d$ is the layer thickness and $\tau_t$ is a deep-trapping lifetime. As we mentioned earlier, the deep trapping happens when some photocarriers are trapped in the defect states while other photocharges get collected by the other side of the cell. The data taken at -1.0 V are not affected significantly by deep-trapping ($\tau_t \gg t_T$), and they show clearly that the photocharge was collected more slowly than predicted by the constant drift mobility model. The same conclusion applies at 0 V, although it is obscured somewhat by deep-trapping. We measured similar effects for both electrons and holes in all cells studied. This is commonly seen in the amorphous silicon carriers’ transport which involves dispersive transport. We will discuss the details for dispersion as well as the modeling for the photocharge behavior later in this section. Right now, we move on to the third part which we use the Hecht equation to get the information of deep trapping and offset voltage of the cell.

Followed by the transient photocharge analysis, we usually would like to see the total collection of the photocharge regarding different bias voltages. Since for the lower voltages, some of the photocarriers are still in the deep level of traps without emitting, the total
photocarriers which we collect during the transient are less than the generated photocharges. By graphing the $Q$ at different bias voltages would give us the information of the deep trapping. In Fig. 3-3(c), the solid circles show the total hole photocharge $Q(V)$ collected at 1 µs as a function of the bias voltage $V$. The charge measurements are normalized by the photocharge value at -1.0 V, which we set to be the total generation photocharges $Q_0$. As the reverse bias voltage decreases, and the magnitude of the electric field diminishes, the total photocharge $Q(V)$ at 1 µs falls. We attribute this effect to “deep trapping” of the holes carriers. The solid lines are fits to the Hecht equation:\(^7\)

$$\frac{Q(V)}{Q_0} = \frac{\mu \tau_t (V-V_0)}{d^2} \left[ 1 - \exp \left( -\frac{d^2}{\mu \tau_t (V-V_0)} \right) \right], \quad (3-5)$$

where $d$ is the thickness of the CdTe layer. $\mu \tau_t$ is a mobility-lifetime product for deep-trapping; it is not a recombination $\mu \tau$ product. $V_0$ is offset voltage related to the built-in electric field, but is not the true built-in potential of the cell. We also show the $Q(V)$ for electron photocarriers’ transit using illumination from the semi-transparent metal contact side. We show the result for electron data using grey squares. From the fittings, the $\mu \tau_t$ product for the holes in this cell is $5.8 \times 10^{-7} \text{ cm}^2/\text{V}$, and for electrons it’s $1.1 \times 10^{-6} \text{ cm}^2/\text{V}$.

We used the values of $V_0$ from the Hecht analysis to calculate drift-mobilities for the electrons and holes using the expression:

$$\mu_d = \frac{d^2}{2(V_0-V)(\tau_t \tau_f)} \quad (3-6)$$

In Fig. 3-3(d) we present these drift-mobility estimates as a function of the half-collection transit time, which varies with the electric field across the CdTe layer. We show the hole results
for this untreated coupon and also the electron results from another bifacial coupon with post-deposition CdCl₂ treatment.

Differing from Fig. 3-2, which shows the traditional way of getting drift mobility without dispersion, we used a slightly different expression for drift mobilities to analyze the dispersion model in this case. We now return to the distribution of transit times that’s apparent in Fig. 3-3(b). “Dispersion”⁸, which is commonly used to interpret drift-mobility measurements in non-crystalline semiconductors, is one of the possible explanations for such dispersive transport behavior⁹. In hydrogenated amorphous silicon and related materials, dispersion results from multiple-trapping in an exponential bandtail of localized electronic states lying just beyond the band edges. And the multiple-trapping for the photocarriers in the band tail region would cause the photocarriers to not move with constant velocity. This would result in a dispersive behavior of the photocharges. For the ordinary, nondispersive transport, the photocharge behave like eq.

Fig. 3-4. Transient photocurrent at 0V on coupon 5. The dash line represent the photocurrent dispersive behavior after transit time, the slope gives the value for α.
From Fig. 3-3(b), we can see that the typical nondispersive model cannot explain the measurement of the photocharge compared to the theory line. Thus, we try to explain this behavior using the dispersion model. For the dispersive case, the photocurrent transient is written:

\[
i(t) = \begin{cases} 
    i_0 \left(\frac{t}{t_T}\right)^{-1+\alpha}, & t < t_T \\
    i_0 \left(\frac{t}{t_T}\right)^{-1-\alpha}, & t > t_T 
\end{cases}
\]  

(3-7)

where \( \alpha \) is the dispersion parameter and \( t_T \) is the transit time where the power law for the photocurrent decay changes. We can get \( \alpha \) from the shape of the photocurrent curve. In Fig. 3-4, we show the fitting for post transient photocurrent. The slope of the post transient photocurrent in the log-log graph would give the value of \( \alpha \), which in our case is close to 0.75.

The current prefactor \( i_0 = \alpha Q_0/(2t_T) \), where \( Q_0 \) is defined as the photocharge collected at long times by integration of the photocurrent. After integration of the transient current, the corresponding photocharge transient would be written as:
\[ Q(t) = \begin{cases} \frac{1}{2} Q_0 (t/t_T)^\alpha, & t < t_T \\ Q_0 \left( 1 - \frac{1}{2} (t/t_T)^{-\alpha} \right), & t > t_T \end{cases} \] (3-8)

The curved line in Fig. 3-5 compares this form to a CdTe hole transient (front illumination) using \( \alpha = 0.75 \). Note that the measured data are slowed somewhat by an electronic risetime of about 40 ns. The fitting gives a reasonable account for the photocharge transient. So, does this indeed imply a dispersive transport for CdTe?

An important feature of dispersive transport is that the drift mobility depends upon the transit time. The drift mobility \( \mu_D \) is:

\[ \mu_D \equiv \frac{d^2}{2VT} = \mu_0 \alpha^{-1} (\nu t_T)^{\alpha^{-1}}, \] (3-9)

where \( d \) is the thickness of the sample, \( V \) is the voltage across the sample, \( \mu_0 \) is the mobility for the free carrier moving on the band edge (untrapped) which is usually around 1 cm\(^2\)/Vs, and \( \nu \) is the attempt to escape frequency describing the thermal emitting frequency for the photo carriers from the traps. Eq. (9) was used to calculate the dispersive curves used in Fig. 3-3(d).

We emphasize that dispersion does not imply a nonlinear field-dependence to the photocurrents; prior to transit, the average displacement of a photocarrier distribution photogenerated at time \( t = 0 \) remains proportional to the electric field. \( \mu_0 \) and \( \nu \) are parameters whose physical significance depends upon the microscopic mechanism underlying the dispersion. Thus in the exponential bandtail multiple-trapping model, they are the band mobility and the trap attempt-to-escape frequency, respectively. The hallmark of this multiple-trapping model is the relationship \( \alpha = kT/\Delta E \), where \( kT \) is the thermal energy and \( \Delta E \) is the width of the exponential bandtail.
We can clearly see from Fig 3-3.(d) that the dispersion model which is suitable for fitting the non-linear behavior of the photocharge could not explain the mobility value which is derived from different field dependent transit time. The mobility shows a very constant value with different transit times compared with the theoretical value from eq. 3-9 which is using dispersion model. This is a strong evidence that the dispersion model does not apply for the non-linear behavior of the photocharge in the room temperature. Thus, we seek other explanations for this softened behavior. One possible reason could be that lateral variation of the drift mobility especially from one grain to the other, is the reason for the spread of transit times. This mechanism is broadly consistent with previous work on micro-uniformity of CdTe cells and films, which shows significant lateral variation in quantum efficiency and photoluminescence lifetime.\textsuperscript{10,11}

Since here we only shown the mobility in room temperature, and there is little evidence of the dispersive transport at room temperature. Usually strong evidence for dispersive transport is the strong-temperature dependence of the carriers’ drift mobility. Since dispersion model involves the trapping and thermal emission from the shallow traps in the band tail region, we expect the carriers’ transport would be temperature dependent as well. To further exclude the dispersion as one mechanism to explain the low mobility, we also did the temperature dependent TOF measurements on CdTe bifacial coupons. The results will be presented in a separate section.
3.5 UNIFORM ILLUMINATION

However, for the bifacial CdTe coupons that we have, the surface illumination method could only applied to the coupons which are fully depleted. To measure the depletion width for all the bifacial coupons, we used the capacitance measurements discussed in chapter 2. For all coupons we measured the room-temperature capacitance at 1 kHz. We have graphed results for all six coupons at room temperature in Fig. 3-6 using the Schottky analysis:

\[
\left( \frac{A}{C} \right)^2 = \frac{2(V_0 - V)}{\varepsilon \varepsilon_0 N_A},
\]

where \( N_A \) is the acceptor doping level, \( \varepsilon \) is the relative dielectric constant, and \( V_0 \) is the offset potential. The capacitance for the untreated coupons shows only a small change with the reverse bias, which indicates nearly full depletion even at short circuit. For the cell from 3 treated coupon 2, 3 and 4, we only see a small decrease for the depletion width, so we can also assume these coupons are almost depleted for the reverse bias condition. We also show the geometrical capacitance expected from a profilometer measurement, which agrees well with the capacitance measurements under -2 V of reverse bias. However, for treated coupon 6, we can see voltage dependence of the capacitance measurement with different bias voltages. Thus, we cannot get a full depletion under reverse bias condition for this coupon.

For the treated coupon 6 which is not fully depleted, the absorption layer contains both the depletion region and diffusion region. Since the direction of diffusion is along the gradient of the density of states for the generated photocarriers, some of the electron carriers that generated near the back would diffuse backwards into the metal contact side as well as slowly diffuse into
the deplete region and get collected by the glass side. So, we could not get a full charge collection for the lower voltages if we generate photocarriers near the back contact side. This could also be seen from the previous quantum efficiency data where the treated coupon shows a voltage dependent QE for the back illumination. The voltage dependent QE from the back illumination indicates that the charge cannot be fully collected. Thus, an alternative method is introduced for this case. We illuminate the coupon from the front side using weakly absorbed light. In this case, the photocarriers are generated inside absorption layer uniformly. Under the bias voltages, hole carriers would move towards the back contact and electrons would move towards the front contact. If the mobilities for these two type of carriers are not too close to each other, we can use this method to separate the two types of carriers.

For the treated CdTe coupon 6, we use 850nm laser diode to illuminate the sample. From
the absorption spectrum, all the photocarriers are generated uniformly inside the sample with 850nm illumination. So, we can treat the photocarriers as they are generated from their mean position and still using the formula: $\mu = L/Et_T$. Since the carriers are uniformly generated inside the sample, the initial mean position for the generated carriers is in the middle of the absorption width. So, in this case, $L$ corresponding to half collection of the ultimate photocharge would be equal to about $d/4$. So we can write the drift mobility expression as:

$$\mu = \frac{d^2}{4V(V-V_0)t_T}. \quad (3-11)$$

This is a rough estimation. A careful calculation yields a slightly different value for non-dispersive transport, which gives the factor $1 - \frac{\sqrt{2}}{2}$ instead of $\frac{1}{4}$. For dispersive transport I’ve used the $\frac{1}{4}$ prefactor because the 15% error seemed small compared to other inaccuracies. To separate two different carriers from the uniform illumination, we make the initial assumption that one type of carrier is moving faster than the other. Thus the faster one would be collected prior to the slower one. If we use the assumption that the first half of the total charge is due to the contribution of the faster carriers and the second half of the charge is due to the contribution of the slower carriers, then we can separated the two carriers by measuring the transit time equal to $1/4Q_0$ and $3/4Q_0$.

In Fig.3-7, for one of the cells in the treated coupon which is not fully depleted, we use uniform illumination method to measure both carriers. Panel (a) shows the photocharge collection of hole carriers for different bias voltages under surface illumination using 660 nm laser diode. We can see that the charges are collected for the high bias voltages and the rise
time is very fast. In panel (b), we show the collection of the photocarriers for uniform illumination through the front side using a 850 nm laser diode. In this way, the total collection of the photocharge involves both electron and hole photocarriers. We can see from Fig. 3-5 (b)
that the photocharge takes longer time to rise up for the lower bias voltages compared to the surface illumination in Fig. 3-5 (a). From these two graphs, we can see that the holes for this coupon are moving faster than the electrons. In panel (c), we show the $Q-V$ correlation for both illuminations. The uniform illumination data is normalized by half of the photocharge reading from highest bias voltage $Q_0/2$ and the surface illumination data is normalized by $Q_0$. In panel (d), we show the transit time for both illuminations. We read the transit time for the uniform illumination at $\frac{1}{4} Q_0$ is collected. The slope would give us the mobility for both cases. Since the holes are moving faster than electrons, the fitting for uniform illumination would be the drift mobility for electrons. And we can see from the data that the hole mobility is three times larger than the fitting for electrons. In this way, we can measure drift mobilities for both type of carriers from illuminations on one side if the cell is not fully depleted. However, if the drift

Fig. 3-8. Temperature dependent drift mobility for both electron and hole on coupon 5 and coupon 6. The solid dots are the measurements for electrons and the open dots are the measurements for holes. And the squares are for the untreated sample, the circles are for the treated sample.
mobility for two type of carriers are very close to each other, we cannot use eq. 3-3 to find out the transit time for slower moving carriers. For most of our bifacial coupons, we used surface illumination from both sides to get electron and hole mobility separately. Some of the coupons indeed show very similar numbers for electron and hole mobilities. This method was originally used in amorphous silicon material for which the mobilities for two types of carriers are very different.\textsuperscript{13}

3.6 TEMPERATURE-DEPENDENT TIME-OF-FLIGHT

We now move on to the temperature dependence time-of-flight experiments. As we mentioned earlier, the dispersion parameter $\alpha$ ($\alpha = kT/\Delta E$) has a strong relation with temperature. With a lower temperature, $\alpha$ becomes smaller, and the transport of the photocarriers becomes more dispersive. This could result in a decrease of the drift mobility. Thus, if we observe a strong increase of the photocharge collection time, we still can prove the existence of dispersion in CdTe for lower temperatures even we didn’t see a strong dispersion relation for room temperature TOF experiment.

To set up the temperature dependent experiment, we cut the whole coupon into small squares. Each square would only contain one cell. We transfer the small cut square into the cryostat that connects with a vacuum system ($1 \times 10^{-5}$ torr) to perform the temperature dependent experiment. The rest of the setup is the same as room temperature time-of-flight. The cell is illuminated by the laser diode through the window of the cryostat. And we use the liquid nitrogen to cool down the temperature inside the cryostat. The cryostat is also connected to a
temperature controller (Lakeshore 321) to monitor and adjust the sample temperature. The typical range that we use for temperature dependent is around 150 K-350 K. In Fig.3-8, we can see the temperature dependent drift mobility for holes and electrons on coupon #5 and coupon #6. It shows only a slight dependence of the temperature for the lower range of the temperature (150 K to 250 K). The rest of the temperature range shows a very constant drift mobility. We also showed the result for temperature dependent data from amorphous silicon using the same setup in the separate Fig. 3-9. The solid circles are the measurements from BP solar sample, and the open squares are measurements from a United Solar sample. Different than the CdTe measurements, both amorphous silicon samples showed very strong dependence on temperature. We know transport of the photocarriers inside a-Si is dispersive,\textsuperscript{14} and we can see this strong T-dependence behavior for hole drift mobility in amorphous silicon. This comparison could be the evidence to exclude the dispersive transport as one mechanism for

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Temperature dependence of hole drift mobilities in different samples. Solid lines are taken by other groups (Plaiseau03 and Stuttgart91). Open data are taken from UniSolar, and solid ones are measurements on BP solar samples.}
\end{figure}
For the time-of-flight experiment, we report the photocarrier drift mobilities for both electrons and holes in thin film CdTe solar cells prepared at First Solar with bifacial configuration. The experimental results for six bifacial coupons are summarized in Table 3-1. The photocarrier transit times across the cells were as large as hundreds of nanoseconds. For cells with higher open-circuit voltages \( V_{OC} \), the electron drift mobilities range from \( 10^{-1} - 10^{0} \) \( \text{cm}^2/\text{Vs} \), and the hole mobilities range from \( 10^{0} - 10^{1} \) \( \text{cm}^2/\text{Vs} \). For reference, we note that typical hole mobilities reported in single crystals are around \( 10^{2} \) \( \text{cm}^2/\text{Vs} \). These results are summarized in Fig. 3-10, where we show the correlation of electron and hole drift mobilities.

**Fig. 3-10. Correlation of the electron and hole drift mobilities in single crystals as well as a summary of the present measurements on bifacial thin-film CdTe coupons.**

The different symbols indicate different coupons; solid symbols are for untreated coupons. The gray-filled hexagon symbols are for single crystals of CdTe.

3.7 **TIME-OF-FLIGHT RESULTS**

For the time-of-flight experiment, we report the photocarrier drift mobilities for both electrons and holes in thin film CdTe solar cells prepared at First Solar with bifacial configuration. The experimental results for six bifacial coupons are summarized in Table 3-1. The different symbols indicate different coupons; solid symbols are for untreated coupons. The gray-filled hexagon symbols are for single crystals of CdTe.
for the thin film CdTe cells we have measured and also for single crystals. In this figure, the solid black symbols represent thin-film cells that did not receive a vapor phase CdCl\(_2\) treatment, and thus had markedly lower open-circuit voltages. These cells have larger electron drift mobilities than the treated cells, which is an unexpected finding. The photocarrier transit times reported here are much longer than photoluminescence lifetimes in thin-film CdTe solar cells, which are less than a few nanoseconds.\(^{20,21}\) This difference in time scales appears inconsistent with the common interpretation of the photoluminescence lifetimes as identical with the fundamental photocarrier recombination process. We will return to this issue in the discussion section.

### 3.8 PHOTOCAPACITANCE TECHNIQUE

The principle behind the photocapacitance effect is that the space charge of the moving photocarriers inside the sample increases with the illumination intensity.\(^{22}\) These space charges
which are left in the depletion region would cause a change of photocharge collected at two ends. For low mobility cells, the extra space charges built up in the depletion region would be very large. If the built up space charges are comparable with the external charge produced by the bias voltage, then the electric field would not be constant throughout the whole depletion width. In order to accurately measure the mobility using the photocapacitance method, the first important condition is that the cell must be under weak illumination. This can be seen in Fig. 3-11, which is the same graph we showed in chapter one. Here we want to expand a little bit more on this figure.

In Fig. 3-11, we show the capacitance measurement under the short circuit condition for different light intensities. We use the photocurrent read at -1 V bias as our x-axis. The depletion region of this cell extends through the entire thickness of the CdTe film, and the dark capacitance is close to the geometrical capacitance of the layer. Under illumination, we can see a clear linear relation for photocurrents lower than about 2 mA/cm². In this region, the photocurrent is small enough so the generated space charge in the depletion region is very small compare with the charge produced by the bias voltages. In this way, we can continue to think of the electric field as almost constant in the cell. For the photocurrent higher than 2 mA, since it involves a large number of space charge in the depletion region, it will affect maximum collection width of the cell, and the capacitance will start to increase superlinearly.

The principle of this photocapacitance measurement is illustrated in Fig. 3-12. If light is absorbed near one side of the cell, the drifting of photocarriers will generate a space charge
region which depends upon intensity and the electric field inside the cell. Larger fields correspond to smaller transit times of the carriers, and hence a smaller space charge would be left over in the depletion region. If we illuminate the sample from the front (glass) side, all the photocarriers are generated near the CdS/CdTe interface, holes are the drifting photocarriers in this case. In the low illumination intensity condition, the electric field is nearly uniform, the space charge induced charge $Q_p$ on the front electrode is negative, with the magnitude:\textsuperscript{23}

$$Q_p = -i_p t_T = -\frac{1}{2} i_p \left( \frac{d^2}{\mu_h (V_0 - V)} \right)$$

(3-12)

where $i_p$ is the photocurrent under reverse bias condition, $t_T$ is the hole transit time (half charge collection time), $d$ is the depletion width of the sample, $\mu_h$ is the hole drift mobility, and $V_0$ is offset voltage we got from the fitting of dark capacitance Schottky eq. 2-6 which is related to the built-in potential for the sample. We are here using the conventional diode voltage polarity, reverse bias would be negative voltage in this case. The photocapacitance is then:

$$C_p = -\frac{\partial Q_p}{\partial V} = -\frac{\partial}{\partial V} \frac{1}{2} i_p \left( \frac{d^2}{\mu_h (V_0 - V)} \right) = \frac{1}{2} i_p \left( \frac{d^2}{\mu_h (V_0 - V)^2} \right)$$

(3-13)

The addition of a positive voltage decreases the magnitude of the field, and thus increases the
space charge in the thin film. Defining \( C'_p = C_p/i_p \), we have:

\[
\mu_h = \frac{d^2}{2C_p(V_0-V)^2} \tag{3-14}
\]

For thin film CdTe cells with strongly absorbed front illumination, the photocapacitance is due to hole drift, and we can use eq. 3-14 to find the hole drift mobility. For the bifacial coupons we have, rear illumination will yield a similar photocapacitance from which the electron drift mobility can be calculated. One advantage of using photocapacitance measurement is the possibility of measuring both electron and hole carriers from just one side of illumination. We use weakly absorbed light to illuminate the cell which will generate electron and hole photocarriers uniformly across the sample. Since the electron and hole space charge will induce positive and negative charge on the back and front contact separately, the total induced charges would be the combination of \( Q_p \) and \( Q_h \). The general formula for uniform illumination photocapacitance would be similar with eq. 3-14:

\[
C'_p = \frac{1}{3} \left( \frac{1}{\mu_h} + \frac{1}{\mu_e} \right) \frac{d^2}{(V_0-V)^2} \tag{3-15}
\]

Using the hole mobility we get from surface illumination in the front side, we can fit the photocapacitance measured with weakly absorbed illumination to extract the electron mobility. This way, by doing surface and uniform illumination from front side, we can get mobilities for electrons and holes separately.

The photocapacitance setup is the same as the capacitance setup. The only difference is instead of only measuring the capacitance in the dark condition, we measured the photocapacitance from the cells illuminated using solar simulator (Newport Solar Simulator
model: 91159). The low light condition is achieved by putting series of neutral filters between the solar simulator and the cell. In order to generate photocarriers near the surface or uniformly distributed in the cell, we need to use a band pass filter combine with neutral filters. The typical band pass filter we choose for surface illumination is the narrow band filter with ±5 nm band pass at 550 nm. For uniform illumination we use 830 nm long pass filter. Before measuring the photocapacitance of the cell, we need to measure the photocurrent under reverse bias \( i_p \) of the cell corresponding to a certain illumination light intensity. We use the IV setup mentioned in chapter 2 to measure the \( i_p \) of the cell. After recording the value for \( i_p \), we connect the two sides of the coupon to the capacitance setup (Fig. 2-3-6). By sweeping the voltage in the reverse bias, we measure the corresponding capacitance in both dark and light condition. We can calculate the value for photocapacitance \( C_p' = \frac{C_{\text{light}} - C_{\text{dark}}}{i_p} \). By fitting the voltage dependent photocapacitance \( C_p' \), we can get the information of drift mobility for the moving carriers. In eq. 3-14 there are two fitting parameters – mobility and offset voltage. The offset voltage we can get from the dark capacitance Schottky eq. 2-6. In Fig. 3-13, we show the data for photocapacitance measurement on one treated bifacial coupon 2. In panel (a), we showed dark capacitance Schottky analysis. The interception of \( 1/C_2 \) curve on the voltage axis would give the values for offset voltage. The slope of the linear fitting for the lower voltages would give us the information for the acceptor doping level. In panel (a), we also show the photocurrent \( i_p \) versus bias voltages. We can see that for the reverse bias range, \( i_p \) is almost constant. Panel (b) shows the typical photocapacitance data. The open circles represent the photocapacitance for
surface illumination from the front side. By fitting the data using eq. (16), we can get the
mobility for holes which is around 0.03 cm$^2$/Vs for this cell. The solid circles show the
photocapacitance data for uniform illumination through the front side. We use eq. (17) with the
hole mobility from the fitting of surface illumination to fit the curve and get the electron

![Graph showing capacitance and photocapacitance measurements for a bifacial thin film CdTe solar cell.](image)

Fig. 3-13. Capacitance and photocapacitance measurements for a bifacial thin film CdTe solar cell. (a) $1/Cd^2$ and photocurrent $i_p$ as a function of voltage. The dashed line represents Schottky behavior, and yields the offset potential $V_0=0.26V$. (b) Voltage dependence of the normalized photocapacitance for three types of laser illumination at the indicated wavelengths. 550 nm illumination is strongly absorbed, and eq. (16) can be used. The corresponding electron and hole drift mobilities for this cell are 0.01 cm$^2$/Vs and 0.03 cm$^2$/Vs, respectively.
mobility around 0.01 cm$^2$/Vs. By testing the uniform illumination photocapacitance theory, we use the same electron mobility fitting parameter from uniform illumination through the front side to fit the data of the surface illumination through the back side (semi-transparent metal contact side). Since the surface illumination from the back side would give the electron drift mobility value, we can see that using the electron drift mobility value from the uniform illumination fitting shows a good consistence with the back side strong absorption photocapacitance data.

3.9 PHOTOCAPACITANCE RESULTS

We used photocapacitance method to measure drift mobilities on two sets of coupons. The first set of coupons is with the ordinary superstrate configuration. The second set of coupons is with the special bifacial configuration. Each coupon has total of 18 cells with the superstrate structure glass/TCO/CdS/CdTe/MC (TCO-transparent conducting oxide, MC-metal contact). For the bifacial coupons, the cells had special semitransparent metal contacts and correspondingly increased series resistance.

We only measured the bifacial coupons as a test to verify the weakly absorbing light (uniform illumination) method. For the ordinary superstrate CdTe solar cells, we couldn’t illuminate the sample from the back metal contact side. So, the uniform illumination method is essential for measuring both carriers from the front glass side. The advantage of using photocapacitance method is the fast sweeping ability for mobility measurements. It usually take about five to ten minutes to measure both carriers on one cell, while traditional time-of-
flight method takes about two hours to finish measuring both carriers. So, the photocapacitance method could be a way to fast profiling the mobility values for all the cells on the coupon. In this section, we will mainly show our measurement results for the first set of coupons with ordinary superstrate configuration. We summarized our photocapacitance measurements for the first set of coupons in Fig. 3-14. In Fig. 3-14, we showed the correlation for electron and hole drift mobilities for the ordinary non-transparent back contact CdTe coupons using photocapacitance method. From the graph, we can see the mobility values for both types of carriers vary with three orders of magnitude. We will show the correlation of this large variation for both types of carriers’ mobilities with the open-circuit voltage of the cell in the separate section in this chapter. Here we can see that electron and hole drift mobilities in thin film CdTe are very close to each other. Comparing with the drift mobility values in single crystal CdTe.
which the electrons are around 1000 cm$^2$/Vs and holes around 500 cm$^2$/Vs, the drift mobility values for single crystal CdTe is very large and the two type of carriers also show a clear difference. The electron mobility is always larger than hole mobility in single crystal CdTe material which can be explained using effective mass theory.\textsuperscript{2425} Here in thin film polycrystalline CdTe, unlike the mobilities in single crystal CdTe, the boundary between electron and hole drift mobilities is not so clear. And also the drift mobilities for thin film varies a lot from cell to cell in one coupon and also from coupons to coupons. This is indicating another mechanism other than using classical effective mass theory to explain the movement of carriers in the material. The detail discussion of possible explanations will be carried out in the last part of this chapter.

3.10 TIME-OF-FLIGHT AND PHOTOCAPACITANCE COMPARISON

After introducing the two methods we used to measure the drift mobilities in CdTe, we now want to show the comparison between these two methods. Most researchers have used photocarrier time-of-flight methods for measuring drift mobilities in thin film semiconductors. The photocapacitance method provides an interesting alternative way which is more efficient compared with the traditional time-of-flight method. For some cells we have done both standard time-of-flight measurements as well as the photocapacitance measurements, and show the comparison between the time-of-flight mobility $\mu_{TOF}$ and the photocapacitance mobility $\mu_{PC}$ in Fig. 3-15. In the same graph, we also show this comparison for electron photocarriers’ mobility for photocapacitance and TOF measurements in a number of CIGS cells; all the CIGS
mobility data were taken by Steluta Dinca, and the time-of-flight measurements of these CIGS samples were reported previously.\textsuperscript{6,26} In Fig. 3-15, we can see a good correlation for the CIGS cells and about half of the CdTe cells between the two methods. However, for some of CdTe cells especially from bifacial coupons the photocapacitance method gives substantially lower mobilities for both types of carriers.

The time of flight measurement is a more accurate approach to get the carriers’ drift mobility since it directly reflects the photocarriers’ transient behavior. The photocapacitance method, however, could misinterpret the mobility values by the effects of deep trapping. To explain this in details, in Fig. 3-16, we show how photocarriers’ displacement $x(t)$ depends on time for the cell that illustrated in Fig. 3-13. Since this displacement is proportional to the electric field, we actually show the displacement field ratio $x(t)/E$. To show the theoretical

---

Fig. 3-15. Comparison of drift-mobilities for thin-film CdTe and CIGS based on TOF and low-frequency photocapacitance measurements. The hexagons are for the CIGS measurements, the circles are measurements for ordinary CdTe coupons, and squares are measurements for special bifacial CdTe coupons.
representation for $x(t)/E$ using trapping and re-emission model, we start with the expression for the photogenerated current. The photocurrent for the generated carriers $i(t)$ can be written as $i(t) = en_f(t)\mu_0(EA)$, where $n_f(t)$ is the free carriers’ density created by impulse illumination, $\mu_0$ is the free carriers’ band mobility, $E$ is the electric field and $A$ is the area. A trapping/reemission model for this free carriers density of states could be written as:

$$\frac{n_f(t)}{n_0} = \exp\left(-\frac{t}{\tau_T}\right) + \frac{\tau_T}{\tau_E}$$

where $n_0$ is the total carrier density, $\tau_T$ is the trapping time and $\tau_E$ is the emission time. Now, we can write $i(t)$ using eq. 3-16:

$$i(t) = \exp\left(-\frac{t}{\tau_T}\right) + \frac{\tau_T}{\tau_E} \frac{Q_0 V \mu_0}{d^2}$$

After we integrate the photocurrent, we get the expression for $Q(t)$

$$Q(t) = \left[-\tau_T \exp\left(-\frac{t}{\tau_T}\right) + \frac{\tau_T}{\tau_E} t + \tau_T\right] \frac{Q_0 V \mu_0}{d^2}.$$  

And the displacement field ratio $x(t)/E$ is equivalent with the normalized photocharge $\frac{Q(t)d^2}{Q_0V}$. So, the straightforward trapping and re-emission model would yields:

$$x(t)/E = \mu \left[\left\{1 - \exp\left(-\frac{t}{\tau_t}\right)\right\} \frac{\tau_t}{\tau_T} t + \tau_T\right].$$

This equation applies if $\tau_E \gg \tau_t$; when the emission time $\tau_E$ of the trapping photocarriers happens much longer than the trapping time of these carriers, it can be neglected. In Fig. 3-16, we have graphed eq.3-19 for the same cell showed in Fig. 3-13 using parameters taken from the electron time-of-flight measurements on the cell: $\mu = 0.5$ cm$^2$/Vs and $\tau_t = 4 \times 10^{-7}$ s. Until the trapping time $\tau_t$, $l/E \cong \mu t$. After $\tau_t$, there is little discernible displacement until the emission time $\tau_E$, after which displacement proceeds with a substantially reduced mobility.
This mobility, which is the one inferred from long time measurements (such as photocapacitance), is $\mu_{PC} = (\tau_t/\tau_E)\mu$, from which we infer an emission time $\tau_E = 20 \mu s$.

This emission time is directly measurable in experiments with other materials, like amorphous silicon germanium (a-SiGe:H) thin film solar cells.$^{28}$

From Fig. 3-16, we can clearly see the two separate mobility values because of the short re-emission time. Since for the photocapacitance measurement we use 1 kHz as our modulated frequency, it correspond to 160 ms of collection time. The time-of-flight measures the photocurrent transient around 1 $\mu$s which gives the mobility value of 0.5 cm$^2$/Vs and the photocapacitance measure the space charge in the coupon for up to 160 ms which will translate as a mobility of 0.01 cm$^2$/Vs from Fig. 3-16. So, we can see from Fig. 3-16, if deep trapping involves in the carriers’ transportation, usually the photocapacitance would measure a lower value compared with the true drift mobility measured by time-of-flight. If the deep trapping
problem in the cell is not so obvious, usually these two measurements would give similar mobilities.

3.11 DISCUSSION I - MOBILITY $V_{OC}$ CORRELATION

In Fig. 3-17 we summarize the photocapacitance measured mobilities for holes and their open-circuit voltages $V_{OC}$ on series individual cells for eight different ordinary (without semitransparent back contact) thin film CdTe coupons. The open circles show all coupons without any bifacial treatment, which can only be illuminated through the front (glass) side of the coupon. The $V_{OC}$ for these set of coupons varies from 0.5 V to 0.8 V due to different post-deposition treatment. About half the cells show a fairly linear trend between $V_{OC}$ and $\log(\mu_{PC})$ for holes. However, for the high $V_{OC}$ cells with $V_{OC} \approx 0.8$ V, there is a wide range of mobilities and little correlation. The correlation can be interpreted if we presume that there is a hole trap with widely varying density that converts to a recombination center under solar illumination.

Fig. 3-17. $V_{OC}$ correlation with hole drift mobility measured by the photocapacitance method. The solid circles are for the time-of-flight method on bifacial coupons.
conditions and forward voltage bias. Also we show in the same graph with the measurements done on the bifacial coupons using time-of-flight technique. The solid dots represent for this group of measurements. The absence of correlation for the second group of samples suggests a trap that does not convert to a recombination center. It’s conceivable that the distinction is related to Fermi level positions in different cells, but we cannot offer a more specific mechanism at present. We also showed the hole mobility measured by photocapacitance on the bifacial coupons using the solid circles in Fig. 3-17. The hole mobility for the bifacial coupons does not show a correlation with the $V_{OC}$. The deep trapping effect we analyze earlier might be the reason for not giving an accurate drift mobility value in bifacial coupons using photocapacitance technique. For the bifacial coupons, we will show the correlation for both electron and hole carriers with $V_{OC}$ on the bifacial coupons using time-of-flight technique in the following paragraph.

In Fig. 3-18. we show the correlation of the solar cell open-circuit voltages $V_{OC}$ with the hole and electron drift mobilities using TOF measurements on the bifacial coupons. While there is no clear relationship of the hole drift mobility to $V_{OC}$ for these set of coupons, for the electron drift mobility there is a negative correlation: untreated cells with lower $V_{OC}$ correspond to larger values of the electron drift mobility than do the treated, higher $V_{OC}$ cells.

We speculate that the change in the electron drift mobility with treatment reflects a change in the conduction band edge, which is consistent with previously reported effects of post-deposition treatments on the interband absorption spectrum in thin films of CdTe. Presumably
treatment has relatively little effect on the valence bandedge. $V_{OC}$ is mainly influenced by electron-hole recombination processes, which are greatly suppressed by CdCl$_2$ treatment.

While mobilities are not expected to affect $V_{OC}$ directly, it is worth noting that recombination may be diffusion-limited, in which case lower mobilities do increase average recombination lifetimes.$^{30}$

### 3.12 DISCUSSION II – LIFETIME MEASUREMENT

As we mentioned earlier the photoluminescence (PL) measurements reported by other...
groups give the minority carrier lifetime of around a few nanoseconds, at most.\textsuperscript{20,21} In this session, we will try to relate this recombination time measured by PL with the transient behavior of the photocarriers. The lifetimes measured by photoluminescence also show a fair correlation with open-circuit voltages. Cells with good open-circuit voltages $V_{OC} \geq 0.8$V have photoluminescence lifetimes $\tau_{PL}$ that are around 1 ns. This interpretation of the photoluminescence lifetime appears to be inconsistent with the drift mobility measurements from both photocapacitance and time-of-flight. Transit times measured directly in time-of-flight experiments are hundreds of nanoseconds; implicit transit times calculated from photocapacitance are at least this long. These results apply even when the cell has uniform photogeneration of electrons and holes, so that recombination will occur through the bulk material not only near the interface of CdS/CdTe. Thus we conclude that photocarrier recombination is negligible on the scale of nanoseconds. So the photoluminescence is not measuring the true recombination time of the photogenerated carriers.

What about the possibility that $\tau_{PL}$ is actually an electron trapping event, so that time-of-flight is measuring a trap-limited mobility? We already used a related argument to explain why some cells show much lower mobilities with photocapacitance than with time-of-flight. Now, we use the treated bifacial coupon 2 we tested earlier with both TOF and photocapacitance methods to illustrate the correlation. Recall with previous Fig. 3-16, now we extended the time region a little bit and show in Fig. 3-18. We indicate a corresponding lifetime for a cell with $V_{OC} \approx 0.8$ V measured by PL in Fig. 3-18. The measured correlation of the lifetime with $V_{OC}$
suggests that \( \tau_{PL} \) be identified with the recombination lifetime \( \tau_r \). To explain micron scale diffusion lengths \( L_D \),\(^{31,32} \) the product \( \mu_e \tau_r = L_D^2 / (2k_B T/e) \) must be about \( 2 \times 10^{-7} \) cm\(^2\)/V, where \( k_B T/e \) is the thermal voltage of about 25 mV. This requires an electron mobility of at least 200 cm\(^2\)/Vs, which is consistent with some parameter sets proposed for device modeling, and also is comparable with the single crystal values.\(^{33} \) Our measured displacement/field ratios at 40 ns are about \( 2 \times 10^{-8} \) cm\(^2\)/V for this cell. This is then the upper limit to a short-time mobility-lifetime product; with a 1 ns lifetime, we infer a maximum subnanosecond mobility of 10 cm\(^2\)/Vs instead of 200 cm\(^2\)/Vs. So, even if the \( \tau_{PL} \) is measuring the electron trapping events, the mobility that is related with this trapping time would be much smaller than the number used by device modeling.

Our measurements are thus inconsistent with crystal-like electron drift mobilities in our thin film CdTe cells even at subnanosecond times. There is a great deal of disorder in thin-film
CdTe, as evidenced by the necessity for using vapor-phase post treatments with CdCl₂ to achieve satisfactory open-circuit voltages. We speculate that one of the mechanisms that determine fundamental mobilities in non-crystalline semiconductors may also be involved in lowering electron mobilities in thin film, but polycrystalline, CdTe. We will discuss the possible mechanisms for lowering the value of mobilities inside thin film CdTe in the following section.

3.13 DISCUSSION III – TRANSPORT MECHANISM

The traditional classical explanation for disorder charge transportation involves the Boltzmann quasiclassical theory³⁴ which is built on the picture that the free electrons are scattered by the ions occupied by the impurities and diffuse through the solid. According to this theory, the electronic conductivity of the material would be proportional to the mean free path, which is the average distance between each scattering. With this model, we can predict, with larger disorders in the system, the mean free path would be smaller and also the conductivity of the material will be lower. The lower conductivity indicates a lower mobility of the photocarriers. Also, for the classical theory, the carrier conduction is related to the effective mass of the charge carrier. Large value of effective mass would result in the low value for conductivity as well as mobility. So, for using the classical scattering model to explain the low value of mobility, the small mean free path and large effective mass are the two main factors.

The general expression for the mobility could be written as:

$$\mu = e l \sqrt{\frac{1}{m^* 3kT}}$$ (3-20)

where \( l \) is the mean free path of the photocarrier, \( m^* \) is the effective mass of the photocarrier.
This theory is only valid for a system where the mean free path is much smaller than the linear size of the system or the lattice constant. This criterion is called the Ioffe-Regel criteria. For a system where these two values are close, or the mean free path is larger than the lattice constant, the quasiclassical Drude model would not be able to explain the conductivity influenced by the disorder in the system. For the thin film CdTe, we used the classical scattering model (eq. 3-10) to calculate the mobility value for Ioffe-Regel limit. The assumption we made is to choose the electron mean free path comparable with the lattice constant. For CdTe which is cubic zincblende (sphalerite) structure, the lattice constant is 2.806 Å. We show the Ioffe-Regel limit result for CdTe using the classical scattering model along with the mobility measurements in single crystal and thin film CdTe in Fig. (3-20). We can see the electron mobilities for single crystal CdTe are much higher than the Ioffe-Regel limit while for the thin
film CdTe the measured mobilities are lower than the limit. The electron and hole mobilities, therefore, cannot use the classical scattering model for the explanation of small mobility values compare with the single crystal ones in thin film CdTe. Anderson introduced the localization states to explain for the disordered system in the case where the Ioffe-Regel limit is invalid.\footnote{Anderson} In Anderson localization theory, photocarriers, instead of scattering from the impurities, are trapped inside the defect states, and these defect states are called the localization states. The localization behavior is commonly seen in the amorphous type of materials where they define the band tail structure for the amorphous semiconductors.\footnote{It is expected for these localized states on the band tail to have no contribution to the conduction at the zero temperature. However, the conduction for among the localized states can happen though the tunneling effect if the temperature arises. So, we should see a strong temperature dependence for the Anderson localization model. And the mobility itself would also strongly depend on temperature. Also we can see from Fig. 3-20, we didn’t observe a strong temperature dependence for both electron and hole drift mobilities. In this case, the localization or the dispersion model to explain the low value of mobility wouldn’t apply for thin film CdTe. Thus, we move on to the next possible theory to explain the low mobility. The poly-crystalline thin film CdTe contains a lot of small crystal grains inside. Grains are separated by the grain boundaries, and the conduction or the charge mobility in these grain boundary are extremely low. Some of the recent findings even show a p-n-p junction between two grains formed from the Cl treated CdTe samples between two grains.\footnote{They proposed the n type inversion happens for the grain boundaries in CdTe}
samples with Cl treatment. This would provide evidence for the carrier transport behavior in CdTe layer. The low value of the mobility might be due to the transverse transport of the carriers among several grains. This could also be an evidence to show the transit behavior of our time-of-flight measurement. In TOF measurement, in Fig. 3-3 panel (b), the photocharge show a slow collection compared to the theory curve. We speculate that the slow mobility collection compare with the theoretical data is due to the lateral variation of the mobility. And the transverse transport of the photocarriers would result in the lateral variation for the mobility measurement. However, the grain size for the poly-crystalline CdTe usually is around the order of few micro meters which is comparable with the thickness of the CdTe layer. So, for the vertical transportation, the carriers mainly move inside the grains. Other groups have measured conductivity for the charge carriers inside the grain and the mobility value corresponding to the conductivity is around 300 cm$^2$/Vs,$^{40}$ which is much larger than our current measurement value. So, the grain boundary model could not fully explain why the mobility in poly-crystalline CdTe would be much lower than the single-crystal value. We need another innovative idea to explain the mechanism. Another possible explanation is similar with the current theory in thin film organic solar cells, which is using the polaron interaction to explain the transportation inside organic solar cells.$^{41}$ The transportation for the photocarriers relies on the polaron hopping from site to site. Since the transportation for the carriers is localized to the polaron interaction, the mobility of the photocarriers would be greatly reduced. The polaron effect can be observed using applied magnetic field dependence experiment. This magnetic
field effect (MFE) is very common in organic solar cells. If we could observe a photocurrent or a photocapacitance change with the existing of the external magnetic field using the photocapacitance technique, we could explain the low value of mobility in thin film CdTe using polaron model where the photogenerated electron and hole pairs are interacting with the ions. We did the preliminary measurement on the magnetic field dependence on the thin film CdTe coupon. The idea of performing magnetic field dependent experiment is similar with our photocapacitance measurement.

The photocapacitance measurement as I mentioned earlier in the thesis is a technique for detecting the space charge left by the generated photocarriers. If the moving of the photocarriers is affected by the magnetic field, it would be observed by the photocapacitance experiment since it has a relatively high sensitivity. We used the same setup as the photocapacitance and tested the signal influence due to the present of the magnetic field. The result on both treated and untreated coupons did not have any significant change larger than 0.2% under 0.5 Tesla of magnetic field. Although further experiment might be needed to give a complete conclusion, right now, we did not have any solid evidence for polaron effects in thin film CdTe.

We tried to explain the low value of photocarriers mobility in thin film CdTe coupon using four mechanisms. None of them gives a satisfactory explanation for what’s really happening inside CdTe. The grain boundaries currently seems to the most plausible reason we have since we observe a lateral variation for the mobility which might be correlated to the transverse
movement of the photocarriers along the p-n-p junction between grains. However, this could only provide a weak evidence for the small mobilities since the size of the grains is comparable with the physical thickness of the sample. Currently, we are still looking for another innovative idea which can give a complete explanation for the transport mechanism inside thin film CdTe.
REFERENCES


7 K. Hecht, Zeits, *Phys.*, **77**, 235 (1932)


13 S. A. Dinca, E. A. Schiff, S. Guha, B. Yan, and J. Yang, in *Amorphous and Polycrystalline* 85


36 International Committee for Diffraction Data, Card Number 15–770.


VITA

NAME OF THE AUTHOR: Qi Long

PLACE OF BIRTH: Wuhan, China

DATE OF BIRTH: November 27, 1985

GRADUATE AND UNDERGRADUATE SCHOOLS ATTENDED:
Syracuse University, Syracuse, New York
Wuhan University, Wuhan, China

DEGREE AWARDED:
B.S. in Physics, 2008, Wuhan University

AWARDS AND HONORS:
Graduate Teaching/Research Assistantship, Syracuse University, 2008-2015
Tuition Scholarship, Syracuse University, 2008-2015

PROFESSIONAL EXPERIENCE:
Research Assistant, Syracuse University, 2009-2015
Teaching Assistant, Syracuse University, 2008-2015