2012

Studies of sputtered CdTe and CdSe solar cells

Dohyoung Kwon
The University of Toledo

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A Dissertation

entitled

Studies of Sputtered CdTe and CdSe Solar Cells

by

Dohyoung Kwon

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Doctor of Philosophy Degree in Physics

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December 2012
CdTe has recently become the most commercially successful polycrystalline thin-film solar module material. Its low cost, large-area solar module is reshaping the silicon-dominated solar panel market; however, CdTe has much room to improve and thus more fundamental understanding is needed. Current thin film solar cell research is focused on two areas: One is identifying loss mechanisms and understanding the polycrystalline nature of single junction device to improve device performance. Another is searching for new materials and fabricating tandem solar cells. In this study, along with other people’s work to improve the efficiency of CdTe solar module, I studied loss mechanism and growth mode of CdTe solar cells to have fundamental understanding of polycrystalline films. In addition to that, in an effort to make tandem solar cells, I fabricated and characterized CdSe solar cells, which is considered as an ideal candidate for the top cell with its band gap of 1.7 eV.

This dissertation is designed to show similarities and differences between CdTe and CdSe solar cells, side by side. After the introduction (Chapter 1), I will review the physical properties of CdTe and CdSe solar cells (Chapter 2). Two primary tools to study
defects and surface morphology were photoluminescence (PL) and atomic force microscopy (AFM). PL showed information on the crystallinity and defects of CdTe and CdSe films before and after annealing. (Chapter 3). AFM measurements and their analysis using scaling theory revealed information on the growth modes of CdTe and CdSe films. (Chapter 4).

With the goal of exploring suitability for tandem structures with ~1.7 eV top cell and ~1.1 eV bottom cell, I fabricated and characterized single-junction CdSe devices. (Chapter 5) In addition, for the bottom cell I fabricated HgCdTe cells with Eg~1.1 eV. Single junction HgCdTe and two-terminal CdTe/HgCdTe tandem solar cells were fabricated and characterized. (Chapter 5)
Acknowledgements

I would like to thank Dr. Compaan for his financial supports and teaching physics to me for six years. I am thankful to my committee members, Dr. Amar, Dr. Karpov, Dr. Kvale, and Dr. Giolando for their review and comments on my dissertation. I would like to thank Dr. Shim for teaching me the scaling theory and numerous discussions related with that. I am also thankful to Dr. William Ingler for trouble shooting the AFM machine. I would like to thank Dr. Shvydka for her advice on interference fringes in my PL data.

I would like to thank CdTe group members for their help: Dr. Wieland, Dr. Walker, Dr. Liu, Dr. Plotnikov, Dr. Parikh, Dr. Vasko, Dr. Paudel, Dr. Nawarange, Hasitha Mahabaduge, Sankeerth Rajalingam, and Ryan Zeller. I also appreciate the work of all the staffs in Physics and Astronomy, especially, Terry Kahle, Bob Lingohr, Dr. Irving, Mike Brown, and Shan Ambalanath for their help to my experiments. I am also thankful to the Dr. Ellingson, Dr. Carmen Cioc and Neale Haugen for TRPL measurements and Dr. Collins, Prakash Koirala for ellipsometry measurements. I also want to thank the staffs and collaborators outside the department: Dr. Pannee Burckel, Steven Moder in chemistry; Dr. Joseph Lawrence in engineering; Dr. Kai Sun and Dr. Carl Henderson in EMAL of University of Michigan.

Lastly, but not least, I am thankful to my parents and sister for their support and constant encouragements.
# Table of Contents

Abstract ............................................................................................................................. iii

Acknowledgements ............................................................................................................ v

Table of Contents ............................................................................................................. vi

List of Tables ................................................................................................................... x

List of Figures .................................................................................................................. xii

1 Introduction .............................................................................................................. 1
   1.1 Current energy status .............................................................................................. 1
   1.2 History of solar cells .............................................................................................. 5
   1.3 How solar cell works .............................................................................................. 7
       1.3.1 Solar spectrum .......................................................................................... 7
       1.3.2 Solar cell diode model ............................................................................. 9
       1.3.3 Performance parameters ....................................................................... 11
       1.3.4 Bandgap and efficiency ........................................................................ 14
   1.4 Conclusion of chapter 1 ...................................................................................... 17

2 CdTe and CdSe Solar Cells ....................................................................................... 19
   2.1 RF-Sputtering deposition .................................................................................... 19
   2.2 Physical properties .............................................................................................. 23
   2.3 History of CdTe and CdSe solar cell ................................................................... 27
2.4 Advantages and issues of CdTe solar cell........................................................28
2.5 Advantages and issues of CdSe solar cell........................................................30
2.6 Motivations and topics of my study.................................................................32

3 Photoluminescence (PL) study of CdTe and CdSe Solar Cells .....34
3.1 Review of PL processes...................................................................................34
3.2 PL of CdTe.......................................................................................................38
   3.2.1 CdTe Sample preparation ........................................................................38
   3.2.2 PL experimental setup ............................................................................41
   3.2.3 PL of as-deposited films .........................................................................43
   3.2.4 PL of CdCl₂ treated films .......................................................................45
   3.2.5 Power dependent PL ...............................................................................47
   3.2.6 Temperature dependent PL .....................................................................51
   3.2.7 Conclusion of CdTe PL ..........................................................................54

3.3 PL of CdSe.......................................................................................................55
   3.3.1 Background of the CdSe study ................................................................55
   3.3.2 Sample preparation ..................................................................................57
   3.3.3 PL of CdSe single crystal .......................................................................58
   3.3.4 PL of undoped CdSe sputtered film .........................................................59
   3.3.5 PL of As-doped CdSe film ......................................................................60
   3.3.6 PL of Ag doped CdSe film ......................................................................61
   3.3.7 PL of GaCl₃ doped CdSe film ..................................................................62
4 AFM Study of CdTe and CdSe Solar Cells and Films .................. 65

4.1 Working principles of the Atomic Force Microscope (AFM) ............ 65

4.2 Surface analysis theory ........................................................................ 68

4.3 Surface analysis of CdTe ........................................................................ 79

4.3.1 Background of CdTe surface study ................................................. 79

4.3.2 Experimental details ........................................................................... 79

4.3.3 Roughness exponent of CdTe ........................................................... 82

4.3.4 Growth exponent of CdTe ................................................................. 87

4.3.5 Grain size distribution of CdTe.......................................................... 89

4.3.6 Conclusion of CdTe surface analysis ................................................ 93

4.4 Surface analysis of CdSe ......................................................................... 93

4.4.1 Background of CdSe surface study ............................................... 93

4.4.2 Experimental details .......................................................................... 94

4.4.3 Roughness exponent of CdSe ........................................................... 95

4.4.4 Growth exponent of CdSe ................................................................. 99

4.4.5 Conclusion of CdSe surface analysis .............................................. 101

5 Studies of Polycrystalline Tandem Device ........................................ 103

5.1 Background of tandem solar cell ......................................................... 103
5.2 CdSe top cell .................................................................105
  5.2.1 Metal-insulator-semiconductor (MIS) solar cell .............106
  5.2.2 ZnSe film optimization .................................................107
  5.2.3 CdSe film optimization ...................................................110
  5.2.4 MIS device on Cr contact ..............................................110
  5.2.5 CdSe solar cell on AZO contact .....................................119
  5.2.6 Conclusion of CdSe top cell ...........................................127

5.3 HgCdTe bottom cell .........................................................127
  5.3.1 Single junction HgCdTe device .....................................127
  5.3.2 Two-terminal tandem HgCdTe .......................................133
  5.3.3 Conclusion of HgCdTe study .........................................135

5.4 Prospect of tandem solar cell ............................................135

6 Conclusions ........................................................................137

References ..............................................................................142

A Interference fringes in PL signal ..........................................149
B Strain of CdS/CdTe films calculated from XRD .......................158
List of Tables

2.1 Basic physical properties of CdS/CdTe and CdSe/ZnSe films..............................23
2.2 Brief history of CdTe solar cell. ............................................................................27
2.3 Brief history of CdSe solar cell..............................................................................27
3.1 Sample list for various CdTe deposition pressure. ................................................40
3.2 Summary of power exponent k ..............................................................................49
3.3 Summary of binding energy calculated by one-exponential fitting of temperature
dependent PL from CdCl$_2$ treated samples ....................................................................52
3.4 Summary of the CdSe deposition parameters...........................................................55
3.5 Summary of the hot-probe measurements on CdSe films ......................................57
4.1 Width with varying scales of observation (width from 120 min CdTe film). ......75
4.2 Summary of the key definitions.............................................................................77
4.3 Correlation length summary of CdTe. .................................................................86
4.4 Structure factor’s slope (−γ) of CdTe.................................................................87
4.5 Correlation length summary of CdSe. .................................................................99
4.6 Structure factor’s slope (−γ) of CdSe.................................................................100
5.1 Various ZnSe deposition condition and light and dark resistivity....................107
5.2 MIS solar cell deposition parameters.................................................................111
5.3 MIS solar cell layer thickness .............................................................................112
5.4 MIS solar cell performance result.......................................................................114
5.5 Maximum efficiency of the cells in various test conditions...............................122
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.6</td>
<td>Ast316 structure and annealing conditions and efficiency</td>
<td>123</td>
</tr>
<tr>
<td>5.7</td>
<td>Ast318 structure and annealing conditions</td>
<td>126</td>
</tr>
<tr>
<td>5.8</td>
<td>CdS and CdTe buffer layer thickness</td>
<td>130</td>
</tr>
<tr>
<td>A.1</td>
<td>Thicknesses measured by Dektak profilometer</td>
<td>149</td>
</tr>
<tr>
<td>A.2</td>
<td>Thickness calculated from PL using interference condition (Film-side PL of</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>as-deposited film)</td>
<td></td>
</tr>
<tr>
<td>A.3</td>
<td>Thickness calculated from PL using interference condition (Junction-side PL</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>of as-deposited film)</td>
<td></td>
</tr>
<tr>
<td>A.4</td>
<td>Thicknesses calculated from the simulated reflectance of a single-layer film</td>
<td>153</td>
</tr>
<tr>
<td>A.5</td>
<td>Thicknesses calculated from the simulated reflectance of three-layer films</td>
<td>155</td>
</tr>
<tr>
<td>B.1</td>
<td>(111) peak positions of the CdS/CdTe films in θ values</td>
<td>158</td>
</tr>
</tbody>
</table>
List of Figures

1-1 Total energy consumption by source in U.S. in 2010.................................1
1-2 Bell solar battery...........................................................................................5
1-3 Solar spectrum (AM0 is the sunlight outside the atmosphere, AM1.5G is sunlight on earth tilted in 48° from normal including diffused light).........................8
1-4 Solar cell band diagram and diode model, where $W =$ depletion width, $R_s =$ Series Resistance, $R_{sh} =$ Shunt Resistance, $R_L =$ Load resistance, $V_{bi} =$ Built-in potential, $I_{PH} =$ Photogenerated current, $I_D =$ Diode current....................................................9
1-5 JV curve of a CdTe solar cell (An arrow indicates the maximum power point) ...11
1-6 QE of CdTe solar cell ....................................................................................13
1-7 (a) PN junction from narrow bandgap (Low voltage) .....................................15
1-7 (b) Solar spectrum with narrow bandgap (~1.1 eV) device (High current)....15
1-8 (a) PN junction from wide bandgap (High voltage) .......................................16
1-8 (b) Solar spectrum with wide bandgap (~1.7 eV) device (Low current)........16
1-9 Optimum bandgap from various solar cell materials......................................17
2-1 DC sputtering system diagram.....................................................................20
2-2 RF-magnetron sputtering chamber (Classic chamber system) .....................21
2-3 Cross sectional diagram of magnetron sputtering gun...............................22
2-4 Crystal structure of Zinc-Blende (CdTe, ZnSe) and Wurtzite (CdS, CdSe)......23
2-5 (a) XRD of CdTe ...........................................................................................24
2-5 (b) XRD of CdSe .................................................................24

2-6 (a) Phase diagram of CdTe ....................................................25

2-6 (b) Phase diagram of CdSe ....................................................25

2-7 (a) Bandgap of CdTe and CdSe ...............................................26

2-7 (b) QE of CdTe and CdSe.......................................................26


3-2 DAP diagram (x-axis indicates spatial distance) .........................................................36

3-3 Efficiency of three devices from various pressures and CdCl$_2$ treatment times; for each pressure; CdCl$_2$ activation times were 20, 30, 40 min (left to right)..........40

3-4 Low temperature PL setup diagram.........................................................41

3-5 (a) Film-side PL of as-deposited film (10K).............................................43

3-5 (b) Junction-side PL of as-deposited films (10K).................................43

3-6 (a) PL of CdCl$_2$ treated films from film-side (10 K) .................................45

3-6 (b) PL of CdCl$_2$ treated films from junction-side (10 K)........................45

3-7 Excitation power dependent PL of CdTe deposited at 18 mTorr, 30 min CdCl$_2$ treated film (film-side, 10K) Dotted line indicates the peak of the PL at 1.437 eV .................................47

3-8 Power dependence PL for 1.59 eV peak ..............................................48

3-9 Power dependence PL for 1.53 eV peak ..............................................48

3-10 Power dependence PL for the 1.43 eV peak for various CdCl$_2$ activation times and deposition pressures .................................................................49

3-11 PL of deep defect states near 1 eV from 30 min CdCl$_2$ treated 30 mTorr sample.50
3-12 A typical temperature dependence PL from 30 min CdCl$_2$ treated 18 mTorr sample .................................................................51

3-13 Temperature dependent PL at 1.43 eV (10, 18, 30 mTorr data were shifted to right by 0.01 in 1/T axis for clarity) ..................................................................................52

3-14 Temperature dependent PL of samples grown at different pressure.........................53

3-15 Hot-probe measurements (a) setup diagram (b) selected results (ITO=Indium doped tin-oxide, AZO=Aluminum doped zinc-oxide, Tec15HRT=HRT coated fluorine doped tin-oxide) ........................................................................................................56

3-16 PL of CdSe single crystal ..........................................................................................58

3-17 PL of undoped CdSe sputtered film before and after heat annealing .......................59

3-18 PL of As-doped CdSe film before and after heat annealing ..................................60

3-19 PL of Ag-doped CdSe film before and after heat annealing ................................61

3-20 PL of GaCl$_3$ doped film before and after heat annealing ...................................62

3-21 PL of Cu-doped films before and after thermal annealing ....................................63

4-1 Schematic diagram of AFM scanner .........................................................................65

4-2 SEM image of AFM tip (Nanosensor) ....................................................................65

4-3 Zones of interaction in AFM ..................................................................................67

4-4 Rescaling a self-affine function, in the case of DNA walk. Only if two unequal magnification factors $M_l$ and $M_h$, by which the $l$ and $h$ directions are rescaled, are selected correctly will the enlarged portion have the same statistical properties as the original ..................................................................................................................69
4-5 Growth of the interface, where \( w = \text{width}, w_s = \text{saturated width}, t = \text{deposition time}, t_x = \text{crossover time}, \alpha = \text{roughness exponent}, \beta = \text{growth exponent}, L = \text{length scale of observation} \) .............................................................................................................70

4-6 Scaling of \( w \) and \( t \) axis to calculate growth exponent \( \beta \) ........................................72

4-7 Average height and width for different length scale of observation (a) narrow
\( (L=1000 \text{ nm}) \) (b) wide \( (L=5000 \text{ nm}) \) .................................................................73

4-8 Width analysis by different length scale ........................................................................74

4-9 Scaling of \( w \) and \( l \) axis to calculate roughness exponent \( \alpha \) ..............................75

4-10 AFM images of surfaces with various deposition times (The time indicates the
CdTe deposition time. i.e., 7.5 min = Tec15/HRT/CdS(60 nm)/CdTe(7.5 min). \( (x = 5000 \text{ nm}, y = 5000 \text{ nm}, z = 500 \text{ nm scale}) \) .......................................................................................82

4-11 SEM images of Tec15/HRT, CdS and CdTe films with various growth times \( (x =
4000 \text{ nm}, y = 3200 \text{ nm}) \) ........................................................................................................83

4-12 The RMS roughness of CdTe films deposited with various deposition times......84

4-13 Anomalous scaling width versus \([\ln(\text{thickness})]^{1/2}\) for different scan sizes........85

4-14 Scan size vs. average width (Slope shows the roughness exponent \( \alpha \)) ..............86

4-15 Structure factor (power spectrum) of the CdTe films (Multiplied by 10 for clarity
for each growth time interval)......................................................................................87

4-16 Growth exponent \( \beta \) from deposition time vs. width fitting \( (\beta = 0.26) \) .............88

4-17 Grain size distribution (the mean grain size is indicated by arrows and given as
numbers) .........................................................................................................................89

4-18 Thickness versus grain size ......................................................................................90

4-19 Average grain size versus (roughness) width ..........................................................91
4-20 Grain growth shapes ...........................................................................................................92
4-21 AFM images of CdSe films grown at different temperatures. (x = 10 \mu m, y = 10 \mu m, z = 200 nm scale). (Thickness of all the samples = 1.21 \pm 0.03 \mu m) ...........95
4-22 SEM images of CdSe films (x = 4000 nm, y = 3200 nm) ...........................................96
4-23 (a) SEM and (b) AFM images of the same sample (310 °C) in the same scale.
(SEM image x = 4 \mu m, AFM image x = 10 \mu m) ..........................................................97
4-24 The RMS roughness of CdSe films deposited at different substrate temperatures
as function of scan length l ........................................................................................................98
4-25 Scan size vs. Average width (Slope shows the roughness exponent \alpha) .............98
4-26 Structure factor (power spectrum) of the CdSe films (Multiplied by 10 for each
interval) ....................................................................................................................................99
4-27 Band gap calculation from line of sight transmission from CdSe films deposited at
different substrate temperatures. Estimated band gaps are shown in arrows and
written with the temperature in the legend. ..............................................................................100
4-28 XRD of CdSe films deposited at different substrate temperatures ......................101

5-1 MIS band diagram........................................................................................................106
5-2 MIS structure diagram ...............................................................................................106
5-3 XRD of various ZnSe depositions ............................................................................108
5-4 SEM of various ZnSe films ......................................................................................109
5-5 Slow deposition rate at the beginning of ZnSe deposition ..................................113
5-6 JV of CdSe MIS-type solar cell ...............................................................................115
5-7 Best CdSe solar cell on Cr contact ............................................................................116
5-8 JV of the best CdSe top cell on Cr.................................................................117
5-9 QE of the best CdSe top cell on Cr .................................................................118
5-10 Tube furnace (a) system, (b) furnace, (c) graphite block..............................120
5-11 Temperature profile of the tube furnace (400 °C set point)...........................121
5-12 Efficiency, $J_{sc}$ and $V_{oc}$ of Ast316 (18 ~ 20 dot cells of 0.062 cm$^2$ area for each sample).................................................................................................................123
5-13 Fill factor, series and shunt resistances of Ast316........................................124
5-14 Performance of Ast318 (Dry CdCl$_2$ treated samples, A: N$_2$, B: Dry air) ....126
5-15 Structure of HgCdTe single junction device..................................................128
5-16 CdCl$_2$ treatment temperature optimization..................................................128
5-17 HgCdTe thickness optimization (CdS 0.2 μm, No CdTe layer, CdCl$_2$ treated at 420°C for 2 min)...................................................................................................................129
5-18 JV results of various CdS/CdTe thickness (Efficiency, $V_{oc}$, $J_{sc}$) ...............130
5-19 JV results of various CdS/CdTe thickness (Fill factor, $R_s$, $R_{sh}$. Each sample has 45~50 dot cells).................................................................................................................131
5-20 JV result of the best single junction HgCdTe ..................................................132
5-21 QE of HgCdTe solar cell....................................................................................132
5-22 2-terminal tandem solar cell (JV of dot 25 is shown in Figure 5-23) ..........133
5-23 JV of 2-terminal tandem solar cell (dot 25)....................................................134
A-1 Single layer interference model ....................................................................150
A-2 Reflectance due to a single-layer thin film interferences ($t_1 = 2.2$ μm) (CdTe index of refraction $n_1$ varies by wavelength, all other index of refractions are fixed.) .............................................................................................................153
A-3 Multiple layer interference model.................................................................154

A-4 Reflectance due to three layers of thin-film interferences ($t_1 = 2.2 \, \mu m$) (CdTe index of refraction $n_1$ varies by wavelength, all other index of refractions are fixed.) .................................................................................................................155

A-5 A model of light propagation for PL................................................................156

B-1 Schematic diagram of x-ray diffraction in CdTe films on glass substrate (In-plane compressive strain increases atomic spacing $d$).......................................................159

B-2 Strains of the as-deposited and CdCl$_2$ treated films deposited in various Ar pressures.................................................................................................................................160
Chapter 1

Introduction

In this chapter, I will review why solar cells are the most practical solution to our current energy and environmental issues. Then, I will briefly review the history and types of solar cells. I will conclude the chapter by reviewing how solar cells work and discussing the meaning of solar cell performance parameters.

1.1 Current energy status

![Figure 1-1. Total energy consumption by source in U.S. in 2010 [1-1]](image)

- **Transportation**
- **Heating and mechanical power**
- **Electricity generation**

Fossil Fuels (Coal and Petroleum) (83%)

Nuclear (9%)

Hydro

Renewable (8%)

Solar/PV (0.1%)
Energy is an indispensable element of modern civilization. The issue of current energy status is that we are heavily dependent on fossil fuels. In 2010, 83% of energy in the United States comes from fossil fuels such as coal, petroleum, and natural gas; 9% comes from nuclear power; and 8% comes from renewable energy such as hydro power, wind and solar.[1-1] Depletion of fossil fuel is one issue, however, this is not the main problem. The reality and consequence of climate change is a clear threat, although the degree may be debatable to a certain extent. For example, in 2008, the government of Netherlands formed a special committee to prepare for sea level rise. The report recommended to spend more than €100 billion until 2100 to prepare for the 0.65 ~ 1.3 m sea level rise.[1-2] Major costal cities around the world will lose inhabitable area significantly because of melting of icebergs and water volume expansion, caused by CO$_2$ emission from fossil fuels.

Besides, nuclear accidents in Japan or Russia gave serious wake-up calls that nuclear power has enormous hidden costs. Therefore, alternative energy sources like wind, solar, biomass, geothermal, tidal power generation and hydro power are regaining people's attention more than ever. These alternative energy sources are also called renewable energy because they can be used again, unlike fossil fuels. In the United States, among all renewable energy, about one third comes from hydro power, one fifth comes from wind and the rest is biomass, geothermal and solar energy. In 2010, both solar thermal and photovoltaic (PV) solar cells contribute only 0.1% of the total US energy consumption. When we say solar energy, it includes both solar thermal, which uses the heat of the sun light and solar cells or photovoltaic cells, which convert the sun light into electricity. Increased investment and efforts were poured into solar energy research in
recent several years, but the outcome is slow. To replace 83% of fossil fuels with solar thermal or solar cells alone, we would need to install 800 times as many solar thermal devices or solar cells than have been installed up to now. That will be a huge task, and it will take time and dedication.

Then, why do I study solar cells? Why are companies and scientists eager to do research on solar cells despite the current small contribution to the total energy? The answer is in solar energy’s potential capacity. Solar energy that we receive on earth in a year is approximately 12000 times larger than the total energy consumption of the whole world in a year. In comparison, the wind has the capacity of approximately 7 times larger than the total energy consumption. Furthermore, hydro power is out of consideration because there are no more major rivers to build new dams. Biomass has some issues with large scale implementation due to the requirement of large land use. For example, some argue that even if all the corn grown in the U.S. is used to produce bio-diesel, it is not sufficient to power all the vehicles in the U.S.[1-3] Additionally, biomass energy from algae depends on a very costly and inefficient extraction process.[1-4]. Nuclear fusion, which promised to solve our energy problem 50 years ago, needs another 50 years or more to reach practical implementation. [1-5] Geothermal is available only in remote areas usually far from the urban end users. Wind turbines are also restricted by the geographic location where strong wind is readily available. However, solar cells can be installed right next to the end user, which will reduce the transmission loss, and it doesn’t have restriction of location as long as sun light reaches there. In fact, all the energies of wind, hydro, and biomass, even fossil fuels originated from solar energy. Then, why not use solar energy directly to generate electricity having minimal impact on environment?
The reason why I study solar cells over solar thermal devices is because electricity is a more valuable form of energy. In Figure 1-1, more than one third of total energy is consumed to generate electricity because there is a 60~70% conversion loss. In other word, if we generate electricity directly from solar energy, then it will reduce the fossil fuel usage more effectively.

Many people in this field anticipate that solar energy will be a dominant renewable energy source in next few decades. However, solar cells are not a panacea for all energy problems. Solar cells have a few major disadvantages. First, solar cells cannot function at night. That means either it needs energy storage or it should be connected to the electricity grid. Solar-cell technology cannot go alone; it needs improvements in battery or in other energy storage technology. Second, solar cells are made out of semiconductors. They are either expensive or the manufacturing process needs lots of energy. Thus, current researches in solar cells are focused on making solar cell cheaper, and reliable for long time use. This is why increasing solar cell production in a short time period of time is difficult. One study anticipated that it would take 50 years to replace fossil fuels with solar cells.[1-6] Third, solar cells are not suitable to replace transportation fuel which requires high energy density. Again, this means improvements should be made in other technologies such as batteries, hydrogen fuel cells or use of bio-diesel or natural gas.
1.2 History of solar cells

The first commercial solar cell started from the needs of remote power source. The telephone company, Bell, had many signal amplification stations around the U.S. They developed silicon (Si) solar cells to supply power for their equipment in remote location. Single crystalline Si solar cells are called 1st generation, and still occupy 80% of solar cell markets at present. However, Si has a major drawback. Its low absorption coefficient requires very thick (~200 µm) layer of Si to fully absorb sunlight. Furthermore, high purity Si ingots can be produced only with high electricity use. Although Si solar cells are very stable and have high efficiency (module efficiency of 22.9% in 2011) [1-8], the energy payback time (EPBT) is low. EPBT is defined as the ratio of how much energy is used to make a solar cell to how much energy can be produced throughout the lifetime of that solar cell.

Those drawbacks of Si prompted research on thin film polycrystalline solar cells, which we call 2nd generation. Amorphous Si (a-Si), copper indium gallium diselenide
(CIGS), cadmium telluride (CdTe) are the three commercially available solar cells of the 2\textsuperscript{nd} generation. Unlike Si single crystal solar cells, polycrystalline solar cells have lower efficiencies, but they have higher absorption coefficients, thus only a few-µm-thick-layer of thin film semiconductor is used in a low-cost process, rather than expensive single crystal Si growth. Currently, CdTe solar cell is leading the 2\textsuperscript{nd} generation solar cells by reaching lower than 1$/peak watt goal, which is a milestone for competiveness with fossil fuel generated electricity.[1-9]

There are solar cells which do not belong to 1\textsuperscript{st} and 2\textsuperscript{nd} generation solar cells. Scientists are trying to overcome low efficiency using new concepts or tailoring material properties with nanostructures or quantum dots. These are called the 3\textsuperscript{rd} generation solar cell. These are actively studied in many laboratories, but commercialization has not yet been successful due to stability [1-10] and efficiency issues.

Another area of solar cells is multijunction solar cells using GaAs, which is the product of space research project. They require epitaxial growth to make multiple junction solar cells, which makes the highest efficiency possible (cell efficiency of 43.5\% in 2011, under 418 suns)[1-8], at the expense of high manufacturing cost. Their use was limited in satellites and spacecrafts, but recently, they are installed in Concentrated Solar Power (CSP) to maximize the utilization of expensive active material. However, CSP requires sun tracking system and high direct normal irradiance (DNI), which restricts the possible installation sites to desert -like conditions.
1.3 How a solar cell works

1.3.1 Solar spectrum

Solar cells convert sunlight directly into electricity. In other words, a solar cell generates current and voltage when the sun shines on it. Outside the atmosphere sunlight has a power density of 1353 W/m². However, sunlight attenuates when it passes through the atmosphere by Rayleigh scattering or scattering by molecules, dust particles, and absorption by atmosphere and gases such as oxygen, ozone, water vapor and carbon dioxide.[1-11] The degree of attenuation is highly variable, but the most important parameter determining the total incident power under clear condition is the length of the light path through the atmosphere. To standardize solar cell testing, a standard solar spectrum was defined by the air mass (AM) concept. AM is defined by \(1/\cos \theta\), where \(\theta\) is the angle between the sun and normal direction of the earth under the standard amount of elements of scattering and absorption. For example, AM1 is defined when sun is directly overhead and incident normal to the earth’s surface for a standard amount of water vapor, dust, etc.
Figure 1-3 shows AM1.5G, which is the most generally used standard solar spectrum for terrestrial application (just a convenient average morning to evening and seasonal) Note that there are several big dips in AM1.5G spectrum due to water absorption. G stands for global, meaning it includes both direct sunlight and diffused light, which usually makes up 20% of the direct sun light. The raw data of AM1.5G is integrated to 963 W/m². However, for convenience, spectrum is normalized to 1000 W/m² and used for the input power for the solar cell testing. Solar cells are normally tested under xenon lamps. Intensity of the lamp is fixed to maintain 1000 W/m² output power using calibrated Si detector.
1.3.2 Solar cell diode model

Figure 1-4. Solar cell band diagram and diode model, where $W$ = depletion width, $R_s$ = Series Resistance, $R_{sh}$ = Shunt Resistance, $R_L$ = Load resistance, $V_{bi}$ = Built-in potential, $I_{PH}$ = Photogenerated current, $I_D$ = Diode current
Figure 1-4 (a) is the diagram of the CdS/CdTe solar cell. Figure 1-4 (b) is the energy band diagram of the same cell. Before CdS and CdTe come into contact the n-type CdS layer has its Fermi level close to conduction band, and the p-type CdTe layer has its Fermi level close to the valence band. After the contact, negative free carriers (electrons) in CdS diffuse into the CdTe layer and positive free carriers (holes) in CdTe diffuse into CdS layer. This makes an area where no free carriers are exist. This is called the depletion region (W in Figure 1-4 (a)). Fixed positive ions in CdS and negative ions in CdTe make the electric field which prevents further diffusion of free carriers. As a result of the migration of free carriers, the PN junction comes to have one Fermi level in thermal equilibrium. When the PN junction get one Fermi level, energy bands need to bend as shown in Figure 1-4 (b).

Figure 1-4 (a) shows electron-hole pair generation due to absorbed sunlight. Most of the light with energy higher than the band gap energy of the solar cell will be absorbed in a 2 µm thick CdTe film. Longer wavelength light, depicted by the red arrow can arrive deep into the film due to high penetration depth. Then, electron in CdTe will diffuse into the depletion region because of electron density gradients and drift to the CdS layer by the built-in electric field. After that, electrons will be collected through the transparent conductive oxide (TCO) layer and flow through the wire, and resistive load $R_L$. The electron finally arrives at the back contact side to recombine with a hole. Electrons and holes generated by high energy light (blue arrow) and medium energy light (green arrow) will be collected mainly by drift because they are mostly generated in the depletion region.
Figure 1-4 (c) shows the equivalent diode model of the solar cell. Under darkness, the solar cell can be described by one diode. Current $I_D$ can flow from p-CdTe to n-CdS and cannot flow in the opposite direction. However, with light illumination, a current source is added to flow $I_{PH}$ to opposite direction of $I_D$. When solar cell is connected to the resistive load $R_L$, because of voltage difference across $R_L$, the p-CdTe side has a higher voltage and the n-CdS has a lower voltage. This forward biasing lowers the built-in voltage and induces more current flow. Series resistance ($R_s$) is an in-line resistance to hinder current collection, and shunt resistance ($R_{sh}$) is the resistance across the thickness of the solar cell. Higher shunt resistance and lower series resistance are important for good solar cell performance. Typically, a good CdTe solar cell with 12.6 % efficiency has a series resistance ($R_s$) of ~5 Ohm⋅cm$^2$ and a shunt resistance of ~1 kOhm⋅cm$^2$.

1.3.3 Performance parameters

![JV curve of a CdTe solar cell](image)

$J_{sc} = 22.24 \text{ mA/cm}^2$

$V_{oc} = 0.82 \text{ V}$

FF = 69.2 %

Eff = 12.6 %

**Figure 1-5.** JV curve of a CdTe solar cell (An arrow indicates the maximum power point)
There are four primary performance parameters for solar cells: *Efficiency*, open circuit voltage (*V*<sub>oc</sub>), short circuit current (*J*<sub>sc</sub>), and fill factor (FF). These can be characterized by a current density-voltage (JV) measurement. Figure 1-5 shows the JV results of one CdTe solar cell. One particular operating point (*V*<sub>Max</sub>, *J*<sub>Max</sub>) will produce maximum power. However, *V*<sub>Max</sub> and *J*<sub>Max</sub> are not easily observable in the JV graph. Instead, *V*<sub>oc</sub> and *J*<sub>sc</sub> are easily noticeable because they are cross-points with x and y axis.

The efficiency of the solar cell is defined as the ratio of input power in light form and output power in electricity form.

\[
Efficiency = \frac{Output_{electric\_power}}{Input_{optical\_power}} = \frac{V_{max} J_{max}}{100 mW/cm^2} = \frac{V_{oc} J_{sc} FF}{100 mW/cm^2}
\]

where, 
\[
FF = \frac{V_{max} J_{max}}{V_{oc} J_{sc}}
\]

FF is the ratio of dotted and solid squares or the squareness of the JV curve. (i.e., if JV curve is close to square, FF becomes close to 1) In Figure 1-5, the efficiency is:

\[
V_{oc} * FF = 22.24 \text{ mA/cm}^2 \times 0.82 \text{ V} \times 69.2 \% / (100 \text{ mW/cm}^2) = 12.6 \%
\]
Figure 1-6. QE of CdTe solar cell [from Ref. 1-14]

Quantum efficiency (QE) is the response of a solar cell with varying wavelength of input light. If one incoming photon generates one electron and one hole at a given wavelength, and current is collected successfully, then it has 100 % QE at that wavelength. However, in a real solar cell, it has lower than 100 % QE due to reflection of the light at the surface of the glass or solar cell; the absorption; or many different loss mechanisms. Thus, QE can tell optical and electrical loss of the device. Figure 1-6 shows various reasons of losses. Optically, glass has approximately 8 % reflection (4% per interface) and some absorption in the visible and near-infrared (NIR) regions. TCO (SnO$_2$) has absorption, and CdS has absorption below 520 nm. Longer than 830 nm, IR is not fully absorbed by a thin CdTe layer (deep penetration loss). Under AM1.5G
spectrum normalized to 100 mW/cm², the sum of the losses is the difference between the measured and maximum current density [1-14]

1.3.4 Bandgap and efficiency

When P and N type semiconductors make are connected, the energy bands bend to align the Fermi level (E_f). Due to the differences in work function, there is a built-in potential energy(eV_{bi}). Narrow bandgap solar cells have lower output voltage (V_{oc}) than wider band gap solar cells. Let’s review why band gap affects V_{oc}:

The built-in voltage can be expressed in Eq.(1). It is a function of the absorber band gap E_{gp} (in this case, p-type CdTe) and electron affinities and relative location of the Fermi energy relative to the conduction or valence bands.

\[ V_{bi} = E_{gp} + \Delta E_c - \delta_n - \delta_p \] (1) [1-15]

where, \( E_{gp} \) = Energy band gap of p-type material, \( \Delta E_c = \chi_p - \chi_n \), \( \delta_n \) = displacement of Fermi level from conduction band minimum, \( \delta_p \) = displacement of Fermi level from valence band maximum.

Therefore, the changes in built-in voltage (V_{bi}) is proportional to the energy band gap (E_{gp}), if electron affinity and \( \delta_n \), \( \delta_p \) don’t change.

\[ J_0 = J_{\infty} \exp\left(-\frac{qV_{bi}}{kT}\right) \] (2)[1-15]
Eq. (2) shows the relationship between built-in voltage ($V_{bi}$) and saturation current ($J_o$). If the built-in voltage or electric field is high, then it will reduce the recombination caused by diffusion. The diode saturation current decreases if the built-in voltage increases. As a result of reduced $J_0$, the output voltage ($V_{oc}$) increases as shown in Eq. (3)

$$V_{oc} = \frac{kT}{q} \ln\left(\frac{J_{PH}}{J_0} + 1\right)$$

(3)[1-11]

where $J_{PH} = $ light current, $J_0 = $ diode saturation current

This is why $V_{oc}$ is proportional to the energy band gap.

**Figure 1-7.** (a) PN junction from narrow bandgap (Low voltage)  
**Figure 1-7.** (b) Solar spectrum with narrow bandgap (~1.1 eV) device (High current)

Figure 1-7 (a) shows the energy diagram of a PN junction solar cell with a narrow band gap. In here, red arrow represents low photon energy light, blue arrow high energy, and green arrow medium level of energy. Any light with energy higher than the bandgap can contribute to the current generation. Therefore, a large portion of the solar spectrum (shaded area in Figure 1-7 (b) is for a cell with approximate band gap of 1.1 eV) can generate current. However, excess energy of the green and blue light will be lost as heat.
Thus, lower than optimum bandgap solar cells will generate higher current and lower voltage, which yields less than optimum power.

Figure 1-8. (a) PN junction from wide bandgap (High voltage)

Figure 1-8. (b) Solar spectrum with wide bandgap (~1.7 eV) device (Low current)

Figure 1-8 depicts a solar cell with a wide bandgap (~1.7 eV). Only high energy (blue) light (i.e., small spectrum of sun light) can generate current. Light with $h\nu$ lower than the bandgap cannot excite the electrons in the semiconductor. Therefore, in this case, the solar cell may have higher voltage, but it will have lower current and the product also will be less than optimum.

Optimally, the most efficient solar cell should generate the maximum power, (i.e. multiplication of current and voltage) and there is an optimum band gap for a single junction cell which maximizes output power. It is summarized in Figure 1-9. CdTe has a near optimum bandgap which has theoretical efficiency of about 28 %, next to GaAs. But, the highest experimental result is only about 17.5%. Researchers are trying to understand the cause of the low efficiency for polycrystalline thin film CdTe cells and improve it.
1.4 Conclusion of chapter 1

Our heavy dependence on fossil fuels has been creating pollution and environmental disasters. Among many alternative energy sources, direct conversion of sunlight into electricity is the most practical and effective way to replace fossil fuels.

1st generation solar cell started from single crystal silicon (Si) in the 1950’s. The single crystal Si solar module can have very high efficiency (22.9 % in 2011), but they have long energy payback time (EPBT). That triggered extensive research on low-cost
2nd generation solar cells. They are thin-film solar cells such as amorphous silicon, polycrystalline CdTe, and polycrystalline copper indium gallium diselenide (CIGS). 2nd generation solar modules have relatively low efficiencies compared to single crystal Si solar modules; however, they are gaining market share because they have short EPBT and large-area, low-cost mass production capability. Nanostructure or quantum dot solar cells are called 3rd generation solar cells. They have not been commercialized yet due to stability and efficiency issues. GaAs multi-junction solar cells have very high efficiency (43.5% in 2011, under 418 suns), but for cost-effective use they require a sun tracking system, a concentrator and very strong sunlight which limits the geographic range of installation sites.

A standard solar spectrum AM1.5G is usually used for terrestrial solar cell testing. Most of the solar cells are made by stacking p and n-type semiconductors. A solar cell has four primary performance parameters. They are: open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill-factor (FF), and efficiency. The efficiencies of these PN-junction solar cells are affected by the energy band gap of the absorbing semiconductor layer. GaAs has the optimum band gap for power generation used in single junction solar cells, and CdTe has near optimum value.
Chapter 2

CdTe and CdSe solar cells

This chapter will start with the discussion of RF-sputtering technology, which was used to fabricate most of the thin films used in the dissertation. Then, it will review the physical properties, advantages and disadvantages of CdTe and CdSe solar cells. The chapter will conclude with a summary of how the fundamental issues of CdTe and CdSe solar cells motivated my research.

2.1 RF-Sputtering deposition

To fabricate CdTe thin film, there are various deposition techniques such as close space sublimation (CSS), vapor transport deposition (VTD), electrodeposition, metal organic chemical vapor deposition (MOCVD), spray deposition, screen print deposition and sputtering. Sputtering has several advantages. It has better control of uniformity and grain size by changing sputtering parameters such as Ar pressure, power, and substrate temperature. In this section, I will review the basic principles of RF-sputtering.

Sputtering is a technique to use the kinetic energy of heavy ions to break the bonds of the compound and deposit the atoms on the substrates. The most frequently used heavy ion is Ar⁺. However, because Ar is neutral in normal condition, electrons are
accelerated by electric field to collide with Ar. As a result, neutral Ar becomes Ar\(^+\) ion and gets kinetic energy from electrons. The simplest sputtering is DC sputtering.

![DC Sputtering System Diagram](image)

**Figure 2-1.** DC sputtering system diagram

However, for an insulating target, positive charge builds up on the target surface and will repel the Ar\(^+\) ions because the target is biased by negative voltage. To solve this problem, radio frequency (RF) sputtering has been developed. It replaces the DC with an RF power supply and adds an RF matching network to match the impedance for an efficient power transfer. In addition to that, it is known that a magnetic field can trap electrons close to target. Therefore, permanent magnets are added below the sputter target and the electrons follow helical paths around the magnetic field lines undergoing more ionizing collisions with Ar. This enhances the ionization of the plasma near the target leading to a higher sputter rate. It also allows the plasma to be maintained at lower pressures. This is called RF magnetron sputtering. Magnets can be arranged in a many different ways. Two extremes are highly unbalanced and balanced. It is also known that
unbalanced magnetron system can make higher density plasma and higher energy and flux of ion bombardment.[2-1] The CdTe and CdSe films used in my experiments were fabricated by unbalanced RF magnetron sputtering system.

**Figure 2-2.** RF-magnetron sputtering chamber (Classic chamber system)

Figure 2-2 shows the schematic diagram of one CdTe deposition system used in our lab. After a cleaned glass substrate is loaded in the substrate holder, the chamber is pumped down to the $10^{-6}$ Torr high vacuum range by mechanical and turbo pumps. During pumping down of the chamber, the substrate is heated radiatively by a hot tantalum wire. The substrate holder is electrically isolated from the chamber wall and has floating potential. Then, Ar gas is flowed into the chamber; the gate valve is closed to increase the Ar pressure in the chamber. Then, with turning on the RF power supply [the
DC bias is developed spontaneously] and RF power is applied. RF oscillation of electric field supplies the kinetic energy to the electrons in the chamber, which start to collide with neutral Ar gas. Then, Ar becomes ionized to $\text{Ar}^+$ and is attracted to the target which develops a negatively bias spontaneously. The $\text{Ar}^+$ ion bombardment breaks the bonds of the CdTe compound and neutral or charged Cd and Te elements came out and travel to all directions. Some of the Cd and Te atoms arrive on the heated glass substrate and diffuse until they make new bonds with other atoms.

Figure 2-3. Cross sectional diagram of magnetron sputtering gun [from Ref. 2-2]

The magnets under the target make the B-field to produce cycloidal orbits for electron shown in Figure 2-3. That induces more ion bombardment of the area, which will make a race track shape erosion pattern. The matching network helps transfer RF-power to the target by minimizing impedance difference.
2.2 Physical properties

Table 2.1. Basic physical properties of CdS/CdTe and CdSe/ZnSe films [2-3]

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>CdS</th>
<th>CdTe</th>
<th>CdSe</th>
<th>ZnSe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Wurtzite</td>
<td>Zincblende</td>
<td>Wurtzite</td>
<td>Zincblende</td>
</tr>
<tr>
<td>Lattice constant a (Å)</td>
<td>4.137</td>
<td>6.482</td>
<td>4.299</td>
<td>5.669</td>
</tr>
<tr>
<td>Lattice constant c (Å)</td>
<td>6.716</td>
<td>7.015</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>4.82</td>
<td>5.86</td>
<td>5.68</td>
<td>5.27</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1475</td>
<td>1092</td>
<td>1239</td>
<td>1515</td>
</tr>
<tr>
<td>Thermal conductivity (W/cmK)</td>
<td>0.3</td>
<td>0.075</td>
<td>0.09</td>
<td>0.19</td>
</tr>
<tr>
<td>Dielectric constant (ε∥c)</td>
<td>10.3</td>
<td>10.3</td>
<td>10.7</td>
<td>9.1</td>
</tr>
<tr>
<td>Dielectric constant (ε⊥c)</td>
<td>9.4</td>
<td>9.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.67</td>
<td>2.91</td>
<td>2.64</td>
<td>2.61</td>
</tr>
<tr>
<td>Bandgap at room temperature (eV)</td>
<td>2.38</td>
<td>1.52</td>
<td>1.74</td>
<td>2.71</td>
</tr>
<tr>
<td>Optical transition type</td>
<td>Direct</td>
<td>Direct</td>
<td>Direct</td>
<td>Direct</td>
</tr>
<tr>
<td>Electron mobility (cm²/Vsec)</td>
<td>350</td>
<td>1200</td>
<td>650</td>
<td>530</td>
</tr>
<tr>
<td>Hole mobility (cm²/Vsec)</td>
<td>15</td>
<td>100</td>
<td>50</td>
<td>28</td>
</tr>
<tr>
<td>Electron affinity (eV)</td>
<td>4.79</td>
<td>4.28</td>
<td>4.95</td>
<td>4.09</td>
</tr>
</tbody>
</table>

Figure 2-4. Crystal structure of Zinc-Blende (CdTe, ZnSe) and Wurtzite (CdS, CdSe) [from Ref. 2-5]

Compound semiconductors which consist of various elements have widely ranging physical properties. By selecting appropriate compound semiconductor materials,
It becomes possible to realize various devices which cannot be achieved using an elemental semiconductor material such as Si.\[2-3\] Semiconducting materials typically have tetrahedral bonding, and therefore typically form cubic or hexagonal structures. Zincblende is two face-centered-cubic lattices with a displacement between them of \((1/4,1/4,1/4)\). (Figure 2-4 (a)). Wurtzite is a modification of the zincblende structure. In this structure A atoms form a hexagonal lattice and B atoms form another hexagonal structure with the \((3/8)c\). (Figure 2-4 (b)). CdTe has zincblende structure and it can be easily seen in XRD data. In Figure 2-5 (a), an as-deposited film has a strong \((111)\) peak, which is a signature of the zincblende structure. After CdCl\(_2\) treatment other peaks start to show up.

![Figure 2-5. (a) XRD of CdTe](image1)

![Figure 2-5. (b) XRD of CdSe](image2)

In Figure 2-5 (b) for CdSe, the hexagonal wurtzite structure can be identified by the characteristic \((002)\) peak. Low temperature depositions have strong \((002)\) orientation and it becomes weaker as the deposition temperature goes up and it disappears in the film deposited at 310 °C.
CdTe and CdSe are materials for which stoichiometry is easily maintained. In Figure 2-6, showing the phase diagrams note that the highest melting points in CdTe and CdSe are at 50/50% composition. If CdTe is off stoichiometry, then it melts in low temperature, and when CdTe is formed in 1:1 stoichiometry, that can survive high temperature up to 1092 °C. Single-phase CdTe only exists very near the 50/50% stoichiometric composition. Another important fact is that CdTe has congruent sublimation. When CdTe is heated the rate of evaporation of 2Cd and Te$_2$ gas is roughly the same. They condense onto a cooler surface, with the same rate, too. These two similar processes makes it possible for a lump of stoichiometric CdTe to become a film of nearly stoichiometric CdTe.[2-6]

![Figure 2-6](a) Phase diagram of CdTe [from Ref. 2-7]

![Figure 2-6](b) Phase diagram of CdSe [from Ref. 2-3]

Note that CdSe has higher melting point than CdTe due to a smaller ionic radius and stronger bond.
From the transmission and reflection data one can calculate the bandgap of the films. Figure 2-7(a) shows the square of the absorption coefficient of CdTe and CdSe films deposited in our sputtering system. The CdTe film has approximately 1.49 eV bandgap in room temperature and 1.71 eV for CdSe. The bandgap directly affects the quantum efficiency of a solar cell as can be seen in Figure 2-7 (b). The red curve is the QE data of a CdSe/ZnSe MIS solar cell from the Battelle group [2-7] and the blue curve is the QE of one of our sputtered CdS/CdTe solar cells. Note that the high QE of the CdTe lies in 500 to 850 nm region of the spectrum. The QE of the CdSe solar cell lies in the wavelength of the 300 to 700 nm region of the solar spectrum. The falloff at 730nm matches well with CdSe bandgap of ~1.7 eV. This shorter wavelength falloff will give more light to a bottom cell in a tandem configuration. This is why the higher bandgap CdSe is good as a top cell.
### 2.3 History of CdTe and CdSe solar cells

#### Table 2.2. Brief history of CdTe solar cell [2-9]

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1960</td>
<td>Homojunction cell with ~4% efficiency: Vodakov</td>
<td></td>
</tr>
<tr>
<td>1963</td>
<td>First thin film solar cell (n-CdTe/ p-CuxTe. ~6%): Cusano</td>
<td></td>
</tr>
<tr>
<td>1967</td>
<td>First thin film module (84 cells, area: 2168 cm(^2)): Hanson</td>
<td></td>
</tr>
<tr>
<td>1968</td>
<td>Au/CdS/CdTe/Te heterojunction diode: Dutton and Muller</td>
<td></td>
</tr>
<tr>
<td>1972</td>
<td>Mo/CdTe/CdS substrate solar cell: Bonnet and Rabenhorst</td>
<td></td>
</tr>
<tr>
<td>1982's</td>
<td>Development of various methods (screen printing, plating) and Cl, oxygen treatments, back contacts</td>
<td></td>
</tr>
<tr>
<td>1993</td>
<td>CSS optimization and 15% cell: Britt et al.</td>
<td></td>
</tr>
<tr>
<td>2001</td>
<td>World record efficiency on borosilicate glass and highly transparent TCO: Wu et al.</td>
<td></td>
</tr>
<tr>
<td>Late 2000’s</td>
<td>Large scale manufacturing: First solar</td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td>First solar cell efficiency 17.3 % [2-10]</td>
<td></td>
</tr>
</tbody>
</table>

CdTe solar cell has been studied for nearly half a century. The transfer of the laboratory devices in the late 80’s to mass production took almost 15 years. The polycrystalline nature of the CdTe thin film requires more fundamental understanding to achieve further breakthroughs in current efficiency.

#### Table 2.3. Brief history of CdSe solar cell

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1883</td>
<td>Se/Au 1% efficiency solar cell Charles Fritts [2-11]</td>
<td></td>
</tr>
<tr>
<td>1976</td>
<td>Photoelectrochemical (PEC) solar cell using CdSe photo-electrode 9.2% efficiency A.B. Ellis et al.[2-12]</td>
<td></td>
</tr>
<tr>
<td>1980</td>
<td>CdSe/ZnSe thin film solar cell 6.6% efficiency (MIS) Richter and Bonnet [2-13]</td>
<td></td>
</tr>
<tr>
<td>1980</td>
<td>PEC solar cell using CdSe photo-electrode 12% efficiency B. Heller Miller et al. [2-14]</td>
<td></td>
</tr>
<tr>
<td>1990</td>
<td>PEC solar cell using CdSe photo-electrode 16.4% efficiency Stuart Licht et al [2-15]</td>
<td></td>
</tr>
<tr>
<td>1990</td>
<td>ZnTe/CdSe thin film solar cell ~1.3% efficiency  A. K. Pal, A Mondal et al [2-16]</td>
<td></td>
</tr>
<tr>
<td>2004</td>
<td>CdSe/ZnSe thin film solar cell ~1.9% efficiency USF. [2-17]</td>
<td></td>
</tr>
</tbody>
</table>
Se started even earlier than CdTe due to photosensitivity. However, the real research of CdSe started in late 1970 for electrode of the photoelectrochemical (PEC) solar cell. Using liquid together with a solar cell had a few practical problems such as sealing and degradation of the electrode submerged in the electrolyte. In 1980, a metal-insulator-semiconductor (MIS) type CdSe/ZnSe thin film solar cell on an opaque Cr contact was extensively studied by the Battelle group and their 6.6% under AM0 still remains as a record efficiency.

2.4 Advantages and issues of CdTe solar cell

- Advantages as individual devices:

CdTe is a direct bandgap semiconductor which doesn’t require a phonon in absorption of light; as a result, it has a high absorption coefficient ($\alpha \sim 10^5 \text{ cm}^{-1}$ at 700 nm). Therefore, the CdTe solar cell needs only very thin (~ 2 µm) semiconductor material because it absorbs light more efficiently than Si (~200 µm). CdTe also has a near optimum bandgap of 1.5 eV for maximum power generation when it is used in a single-junction device. Another benefit is that CdTe is a binary compound; therefore it is easier to maintain stoichiometry than ternary or quaternary compounds.

- Advantages in manufacturing:

The fact that there is a very small amount of material use and small amount of energy consumption in polycrystalline growth gives a short energy payback time (EPBT). EPBT is the time that the energy used to manufacture the solar panel is recuperated by the energy generated by the panel. The simple binary compound allows uniform large-area
solar panels. Together with laser scribing techniques, it greatly reduces manual labor. The simple structure also made the reproduction of reasonably good efficiency possible using various deposition techniques.

- Issues in individual device:

There is a large discrepancy between the record efficiency and theoretical efficiency of CdTe solar cells. That is because open-circuit voltage ($V_{oc}$) is lower than expected.

There are three main factors that are believed to reduce the $V_{oc}$: low carrier concentration, short minority carrier lifetime, and back diode.[2-18] First, grain-boundary states in polycrystalline films partially compensate the majority-carrier holes, maintaining low hole density.[2-19] The low hole density reduces the built-in voltage in PN junction, which increases the saturation current. As a result, $V_{oc}$ decreases. Second, excess forward recombination current of electrons and holes at trapping states in the depletion region of the diode also reduces the $V_{oc}$. Third, a metal back contact tends to form a Schottky diode opposite in direction to the main junction and reduces the $V_{oc}$.

In addition to $V_{oc}$ loss, CdTe has lower FF than GaAs, which is used as a single crystal with similar band gap because of large ideality factor and series resistance. This is again related to the polycrystalline nature of the CdTe.

Lastly, the stability of Cu, which is widely used in back-contact material, is problematic and contributes in many cases to degradation of the cell efficiency.
• Issues in manufacturing:

Translation of laboratory results of CdTe solar cells to large-scale, high-yield manufacturing of solar module is more difficult than expected. That is because limited science and engineering base is available to effectively and rapidly scale up laboratory processes. Few quantitative relationships exist among critical process parameters, film growth & properties, and device performance. Better process monitoring tools are needed. Another anticipated issue is Te supply when scaling up CdTe production. [2-20]

2.5 Advantages and issues of CdSe solar cell

• Advantages in individual device:

CdSe has very similar characteristics like CdTe. CdSe is also a direct bandgap semiconductor which has a high absorption coefficient ($\alpha \sim 10^4$ cm$^{-1}$ at 720 nm). Therefore, the CdSe solar cell needs only a very thin ($\sim 2 \mu$m) film to absorb the sunlight. CdSe has a band gap of 1.7 eV which is the best candidate for top cell of tandem solar cell, with the bottom cell of 1.1 eV such as copper indium gallium diselenide (CIGS). CdSe is also a binary compound and it has 50:50 stochiometry at the highest melting point. Therefore it is also easy to maintain the stochiometry of the film. CdSe is a very stable compound because it has stronger bond and higher melting temperature (1623 °C) than CdTe due to the smaller ionic radius.
Advantages in manufacturing:

Se is more abundant than Te.[2-21] If CdTe reaches Te shortage, CdSe solar cells could replace the CdTe production. Commercial CdSe solar panels have not been done, yet. However, if a single junction CdSe device can be commercialized, the learning curve will be shorter than the other thin-film solar cells because the knowhow of the CdTe production can be applicable to CdSe. If CdSe/CIGS tandem solar cell can be successfully made, it will have two major impacts: First, it will have the highest efficiency among thin films. Second, it will be the most reliable light-weight solar module suitable for mobile power generation because CdSe can be monolithically deposited on CIGS/stainless steel substrate and a heavy glass substrate doesn’t need.

Issues in individual devices:

CdSe has slightly lower (~ 2 % absolute) predicted theoretical efficiency than CdTe because of the higher band gap when it is used in single junctions. To find the optimum fabrication conditions for a good CdSe tandem cell will be a challenging work because polycrystalline hetero-junction tandem cell has not been successful yet.

Issues in manufacturing:

Neither CdSe single junctions, nor tandem devices have been commercialized yet. For single junction device, similar issues to those encountered in CdTe are expected. That will include losses in efficiency due to grain-boundary recombination and low doping concentration. If glass substrates are not used, it might have long term stability issues.
2.6 Motivations and topics of my study

- CdTe solar cell:

For CdTe solar cells, the purpose of my study was to improve basic understanding of CdS/CdTe film growth and acquire additional defect information so that we could overcome some of the issues stated above.

In Chapter 3, I used a standard defect characterization technique, photoluminescence (PL), to connect the relationship between growth conditions and defect states. Because the sputtering technique has a good control over grain sizes and uniformity of the films, PL of sputtered films could answer the grain boundary related recombination issues of polycrystalline CdTe films. In my study I did low-temperature, ex-situ PL experiments; however, PL could also be used as inline monitoring tool in a production line if we have enough understanding and database of the films.

In Chapter 4, I used an atomic force microscope (AFM) as a surface analysis technique to obtain the growth mode and grain growth information from the surface roughness data. This will give some insights of how thin films and grain boundaries are formed.

- CdSe solar cell:

Along with the effort to improve CdTe efficiency, a tandem solar cell was pursued as an alternative way to improve the efficiency of the thin-film solar cell. For the top cell of the tandem, a CdSe solar cell was studied. I also used PL and AFM here, but for a slightly different reason.
In Chapter 3, PL was used to check the quality of doped CdSe films. Previously, CdSe doping was studied because p-type CdSe is preferred in solar cell design, however most as-grown polycrystalline CdSe has n-type conductivity. Although the goal of p-type CdSe was not attained in my experiments, the PL results showed crystallinity of doped CdSe films.

In Chapter 4, the AFM was used to examine temperature-dependent surface morphologies. This would be useful information to fabricate two-terminal tandem solar cells, which require sequential deposition of multiple layers at different substrate temperatures.

In Chapter 5, the fabrication procedures and results of single-junction CdSe solar cells were summarized. First, they were deposited on an opaque Cr surface because of good adhesion of Cr contact. Second, they were deposited on a transparent aluminum-doped zinc oxide (AZO) contact as a top cell for the tandem application.

- HgCdTe solar cell:

In Chapter 5, in addition to the CdSe top cell, a bottom cell study using HgCdTe was also included. The results of single-junction HgCdTe solar cells and two-terminal solar cells using a CdTe top cell and a HgCdTe bottom cell is presented. Although HgCdTe solar cell might not be feasible for large scale terrestrial deployment due to concern over Hg toxicity, the knowledge and experience of fabricating the tandem cell could be applicable to solve issues in other thin-film solar cells.
Chapter 3

Photoluminescence (PL) study of CdTe and CdSe solar cells

In this chapter, I used PL to investigate defects state of polycrystalline films and solar cells based on CdTe and CdSe. The chapter starts with a brief review of PL processes. And then, from the PL of CdTe solar cells deposited in different Ar pressures, presents how PL shows the correlation between pressure and performance of the solar cells. In the last section, PL is used to show the crystallinity of doped CdSe films.

3.1 Review of PL processes

PL is luminescence from material when light illuminates it. Along with other luminescence techniques, such as electroluminescence, cathodoluminescence, thermoluminescence, and piezoluminescence, PL has become one of the standard tools to study semiconductor defects. The various recombination processes leading to light emission are sketched in Fig. 3.1 below.
When an excited electron releases its energy in a semiconductor, it could be a form of light or lattice vibration. Energy released by lattice vibration can not be optically measured, thus it is called a nonradiative transition. PL will have the same or smaller energy than band gap of the material because real semiconductors have defect states in the forbidden band, and optical transitions can happen between them. PL can be categorized in these five types:
1) **Band-to-band transitions (Figure 3-1. T1)**

These are not easily observed unless the material is a very pure crystal. These dominate at higher temperatures where $kT \geq E_{ex}$, where $E_{ex}$ is the exciton binding energy.

2) **Free-to-bound transition (Figure 3-1. T2a and T2b)**

These are conduction band to defect state or defect state to valence band transitions.

3) **Donor-acceptor pair (DAP) transitions (Figure 3-1. T3)**

Initially, when a donor is occupied with an electron and an acceptor is occupied with a hole, they are in neutral state. However, when an electron in the donor and a hole in the acceptor recombine, donor and acceptor are attracted by Coulomb force.

\[
D^0 + A^0 \rightarrow h\omega + D^+ + A^-
\] (1)

**Figure 3-2.** DAP diagram (All DAP transitions will shift to the higher energy as excitation laser power increases. However, DAP of a shorter spatial distance (b) will have a larger energy shift than longer distance DAP (c))
The PL energy of a DAP can be expressed as Eq (2).

\[ h\nu = E_g - E_A - E_D + \frac{e^2}{\epsilon r} \]  \hspace{1cm} (2)

DAP has a characteristic of giving higher energy (i.e. blue shift) PL as excitation power increases. That is because increased excitation power more rapidly cycles through nearby donors and acceptors. This arose from the higher recombination rate for nearby DAPs (Figure 3-2 (b)) compared with more distant DAPs (Figure 3-2 (c)). As a result, the average DAP distance, \( r \), of those DAPs contributing to the steady state PL gets shorter and photon energy \( h\nu \) gets higher.

Generally, the intensity of PL is described by Eq. (3),

\[ PL\_Intensity = I^k. \] \hspace{1cm} (3)

where \( I \) is the excitation laser power and \( k \) is the power exponent. DAP PL usually has PL \( k<1 \) power dependence because it is less efficient than excitonic transitions.

4) Exciton transitions include free excitons (Figure3-1. T4) and bound excitons (Figure3-1. T5a, T5b) Exciton is a particle that consists of an electron and a hole paired by Coulomb force. When the electron and the hole recombine or annihilate each other, a radiative transition happens. Strong exciton transitions generally are regarded as characteristic of a good crystal. If an exciton is free to move in the energy band, it is called a free exciton. If an exciton is captured by a shallow donor or a shallow acceptor,
then it is called a bound exciton. Excitonic transitions have an exponent k>1 for excitation power dependence PL.

5) A-center related transitions

Donors or acceptors can make complex states, and transitions can occur between them. For CdTe, a Cd vacancy is a double acceptor while a donor on a nearby Te site (e.g., Cl) usually makes V_{Cd-D_{Te}} complex. Thus, the A-center is an acceptor defect complex.

In addition to observing normal PL or power-dependent PL, temperature-dependent PL can also give the binding energy of donors or acceptors. The dependence of PL intensity on T is given by

\[
\frac{I(T)}{I(0)} = \frac{1}{1 + C_1 \exp(-\frac{E_1}{kT}) + C_2 \exp(-\frac{E_2}{kT})} \tag{4}
\]

where, E_1, and E_2 are the binding energies of the defect states involved in thermal quenching of the PL signal.

3.2 PL of CdTe

3.2.1. CdTe Sample preparation

For this study, two sets of samples were prepared with nearly identical conditions. The first set of samples was used to take the full spectrum of PL for as-deposited and CdCl_2 treated samples from both film-side and junction-side (See Figure 3-4.). For the first set of samples, the CdCl_2 treatment time was fixed at 30 minutes. To identify
possible systematic errors, a second set of samples was fabricated and cell performance, as well as power-dependent, and temperature-dependent PL were measured. In both cases, Tec15/HRT was used as the substrate. All samples have about a 60 nm thick sputtered CdS layer. A CdTe layer of 2.3 \( \mu \text{m} \) thickness was deposited by RF sputtering in various Ar pressures. (Table 3.1) The substrate temperature during deposition was kept at about 270 °C and the RF power for CdS and CdTe deposition were kept at 35 W and 20 W, respectively. Two-inch sputtering targets for CdS and CdTe depositions were purchased from Materion Corp. The depositions were done in our Classic chamber system with the substrate heated by radiative heating from a serpentine tantalum wire spaced about 5 mm interval. The base pressure of the vacuum chamber was about \( 5 \times 10^{-6} \) Torr. For sample set 2, samples were cut into 6 pieces and CdCl\(_2\) treated with three separate times (20, 30, 40 minutes) in dry air (Table 3.1). After CdCl\(_2\) treatment, Cu (3 nm)/ Au (10 nm) were evaporated through a mask and heated for 45 minutes in the oven at 150 °C in room ambient. For each sample, current-voltage (JV) measurements of 20 dot cells of 0.062 cm\(^2\) area were carried out for gathering statistically meaningful data. For each sample, the quantum efficiency (QE) of two dot cells of average or above average efficiency cells was measured, too. After that, the thicker part of the each samples was cut into approximately 5mm * 8 mm size pieces for PL measurements. PL was taken from areas between dots where Cu/Au was not evaporated.
Figure 3-3. Efficiency of three devices from various pressures and CdCl$_2$ treatment times; for each pressure; CdCl$_2$ activation times were 20, 30, 40 min (left to right)

For PL from samples deposited at 18 mTorr, a 30 min CdCl$_2$ treated sample was chosen because of the highest efficiency. For other pressures, conditions that yield statistically narrowly confined efficiencies, such as 40 min for 5 mTorr, 40 min for 10 mTorr, 30 min for 30 mTorr were chosen to avoid nonuniformity effects and acquire the data that represents the whole device. (Figure 3-3). Table 3.1 summarizes the lists of the first and second sets of samples which were used in PL measurements.

Table 3.1 Sample list for various CdTe deposition pressure.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Sample Set 1</th>
<th>Set 1 CdCl$_2$ time</th>
<th>Sample Set 2</th>
<th>Set 2 CdCl$_2$ time</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mTorr</td>
<td>Ssc305</td>
<td>30 min</td>
<td>Ssc416</td>
<td>40 min</td>
</tr>
<tr>
<td>10 mTorr</td>
<td>Ssc307</td>
<td>30 min</td>
<td>Ssc426</td>
<td>40 min</td>
</tr>
<tr>
<td>18 mTorr</td>
<td>Ssc303</td>
<td>30 min</td>
<td>Ssc415</td>
<td>30 min</td>
</tr>
<tr>
<td>30 mTorr</td>
<td>Ssc306</td>
<td>30 min</td>
<td>Ssc417</td>
<td>30 min</td>
</tr>
</tbody>
</table>

Note: CdS deposited at 18 mTorr
No Cu/Au or Cu annealing
Cu/Au and Cu annealing done
3.2.2 PL experimental setup

**Figure 3-4.** Low temperature PL setup diagram.

PL was excited with the 514.5 nm ($h\nu = 2.41$ eV) line of an argon ion laser (COHERENT INNOVA) with PL detected in a single stage spectrograph equipped with a 1024 pixel diode array InGaAs detector (Princeton Instrument OMA V:1024-1.7). A low (photon energy) pass filter (Onset at 526 nm) was used in front of the spectrograph to remove the strong elastically scattered laser light which also appears at second order near 1.2 eV.

As shown in the inset of Figure 3-4, excitation and light collection could be done either through the glass or from the back contact side between the dot cells defined by the Cu/Au dots.
Because 514.5 nm light has a penetration depth of about 100 nm, through-the-glass-side PL probes the CdS/CdTe junction, therefore it is also called junction-side PL. Back-contact-side PL is also called film-side PL because light arrives on CdTe film first, not on the glass substrates. The cryostat was cooled by Leybold closed-cycle He refrigerator, which can make the sample mount temperature as low as 10 K. A Lakeshore 321 temperature controller adjusts the temperature of the sample mount or cold finger, which is made of a block of Cu. PL samples were attached to the sample mount by homemade thermally conductive paste, which is made by mixing Apiezon N vacuum grease and Cu powder with a 2:1 volume ratio. Prior to cooling down the sample, the cryostat was pumped down by a mechanical pump and a diffusion pump to reduce the unwanted moisture and gas which may condense on the sample when it becomes cold. The laser intensity was measured between the spike filter and the 8 cm focusing lens by a power meter (Metrologic Radiometer). The Ar laser intensity was very stable after an hour of warming up and has less than 2% variation. The spot size of focused laser at the sample is approximately 200 µm. For a full spectrum, PL power density was kept at 20 W/cm² and for power dependent PL it was varied by a factor of 1000 between 30 mW/cm² and 30 W/cm². For temperature dependent PL, ~3 W/cm² of low power density was used to minimize sample heating by laser.
3.2.3. PL of as-deposited films

In Figure 3-5 (a), as-deposited, film-side PL shows that the 5 mTorr sample has weak near-band-edge PL and a series of deep defect peaks near 1 eV. These deep defects peaks have several lower energy vibronic features at intervals of about 80 meV. Initially, these peaks were thought to be lattice coupled deep defect states; however, 80 meV is much higher than known LO phonon frequency of CdTe (21 meV) and the reflectance calculations (Appendix A) from thin film interference fringes give the peak patterns with very similar intervals. Detailed explanations of the vibronic peak and interference fringes are summarized in appendix A. The trend in spectra from 10 mTorr sample and 18 mTorr sample clearly shows the reduction of the deep defect feature in comparison to the shallow defect peak around 1.4 eV as pressure increases. Note that the 18 mTorr sample,
which is the optimum pressure for best cell performance, has the highest ratio of shallow to deep defect bands. Stronger ion bombardment at 5 mTorr may explain the dominant deep defect states of the film. In sputtering, ion bombardment on the target generates the source flux of the thin film; however, Ar can also bombard the growing surface. The Ar energy is very sensitive to the deposition pressure. At a low Ar pressure, fewer collisions between Ar ions and the neutral Ar atoms make atoms be more energetic and have long mean free paths. Therefore, a strong Ar bombardment in 5 mTorr sample could have caused re-sputtering, densification of the film or implantation of Ar itself into the film, and thus resulted in more defects. This high Ar bombardment effect in lower pressure sample is consistent with the larger strains in 5 and 10 mTorr samples. (Appendix B)

The scale of the PL intensity varies from 2 ~ 60 (in arbitrary units) in as-deposited film-side PL. Sometimes, these relative intensity differences among samples are due to the sample mounting position in the cryo-chamber and focusing condition of the optics. Thus, they may not necessarily represent the degree of radiative transitions when the intensities are in the same order of magnitude.

The as-deposited, junction-side PL in Figure 3-5 (b), shows little of deep defect band but a broader, shallow defect band near 1.4 eV. Note that CdTe is grown on the 60 nm CdS layer deposited at 18 mTorr, and the junction-side PL probes this CdS/CdTe region within about 300 nm of the junction. For as-deposited junction-side, PL intensity increased in the order of 2 or 3 than that of as-deposited film-side PL.

The 1.479 eV zero-phonon peak seen strongly in the junction-side PL most likely involves the A-center acceptor complex $V_{\text{Cd}}-\text{Cl}_{\text{Te}}$. The deep defects peaks around 1 eV
may have similar origin of 1.13 eV zero-phonon deep defect peak discussed by Krustok, et al.[3-1] that they attribute to a $V_{\text{Te}}$ coupled to a Te interstitial. Based on our measurements of cell performance, strong deep-defect features are disadvantageous to good cell performance. This is reasonable because the strong PL indicates high densities of the $V_{\text{Te}}$-Te or $V_{\text{Cd}}$-Cl$_{\text{Te}}$ which serve as recombination centers. In general, defect levels in the forbidden gap create an efficient two-step recombination process whereby electrons relax from conduction-band energies to the defect level and then relax to the valence band, annihilating a hole. The recombination rate depends on the defect energy level. For example, for a shallow defect, the recombination rate is low because the electron can be trapped to the defect state and re-emitted to the conduction band while a hole moves to the same energy state from the valence band. For a deep defect, such as mid-gap defect, electron and hole can stay at the mid gap together and recombine very effectively.

### 3.2.4 PL of CdCl$_2$ treated films

![Figure 3-6](image)

**Figure 3-6 (a)** PL of CdCl$_2$ treated films from film-side (10 K)

**Figure 3-6 (b)** PL of CdCl$_2$ treated films from junction-side (10 K)
Figure 3-6 (a) shows film-side PL after CdCl$_2$ treatment, the intensity increases 5 or 6 orders of magnitude compared with as-deposited films and all vibronic features due to the interference effect are suppressed. The much stronger PL intensity of the 1.424 eV band compared with the as-deposited films, indicates that nonradiative transitions are greatly suppressed, consistent with many fewer recombination centers than in as-deposited films. Also, for film-side PL, near 1.59 eV, a weak bound exciton peak appears after CdCl$_2$ treatment (Figure 3-6 (a) Inset), which is an indicator of improved crystallinity and minority carrier lifetime.

Figure 3-6 (b) shows junction-side PL of CdCl$_2$ treated films. After CdCl$_2$ treatment, intensity of the junction-side PL increased 3 or 4 orders of magnitude. All have a peak at 1.377 eV in junction side PL which is probably related to the S alloying in CdTe near the junction. It has been widely reported that when CdS and CdTe were codeposited, the optical bandgap of CdTe-CdS solid solution alloy varies with the composition according to $E_g(x)=2.40x + 1.51(1-x)-bx(1-x)$, with the bowing parameter, $b=1.8$ and the sulfur composition $x$ [3-2]. The 18 mTorr and 30 mTorr samples have similar peaks at 1.424 eV in CdCl$_2$ treated film-side PL. The energy difference from 1.377 eV in CdCl$_2$ treated junction-side PL is 47 meV, which can be attributed to the intermixing of CdS$_x$ and CdTe$_{(1-x)}$, in this case $x=0.06$. Thus, we know that CdS and CdTe composition within 300 nm of the junction for 18 mTorr and 30 mTorr samples are close after CdCl$_2$ activation. That is also shown in the energy shift of the bound exciton peak. For example, film-side PL of 18 mTorr sample has a bound exciton at 1.582 eV (Figure 3-6 (a) blue line) and junction-side has a huge peak at 1.375 eV (Figure 3-6 (b) blue line), which is a shift of 43 meV.
3.2.5 Power dependent PL

![Power dependent PL spectrum](image)

**Figure 3-7.** Excitation power dependent PL of CdTe deposited at 18 mTorr, 30 min CdCl$_2$ treated film (film-side, 10K) Dotted line indicates the peak of the PL at 1.437 eV.

To verify the origin of the PL peaks, power-dependent PL was measured for CdCl$_2$ treated samples deposited at different pressures. For power-dependent and temperature-dependent PL, different samples with the same growth conditions were used. Figure 3-7 shows the power-dependent PL spectra for 30 min CdCl$_2$ treated 18 mTorr sample. As excitation laser power changes, each peak responds differently. 1.43 eV peak shows a linear power dependence for relatively higher power such as 2.65 mW, but 1.53 eV and 1.59 eV peak steered away from the linearity after 1 mW, apparently showing thermal quenching of the PL intensity.

Figures 3-8 to 3-10 show the fitting of excitation power vs. PL intensity of 1.59 eV, 1.53 eV and 1.43 eV peaks in log-log scale and results are summarized in Table 3.2.
Figure 3-8. Power dependence PL for 1.59 eV peak

Figure 3-9. Power dependence PL for 1.53 eV peak
Figure 3-10. Power dependence PL for the 1.43 eV peak for various CdCl$_2$ activation times and deposition pressures.

The slopes of Figure 3-10 were fitted only up to 2.65 mW because after that most of the slopes deviated from linearity. This is especially seen in 30 mTorr sample. The reduced slope of the PL intensity at higher excitation power may indicate an increase of the nonradiative transitions, but more likely is a result of laser heating of the film.

Table 3.2 Summary of power exponent $k$

<table>
<thead>
<tr>
<th>PL peak</th>
<th>1.43 eV</th>
<th>1.53 eV</th>
<th>1.59 eV</th>
<th>1 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mTorr</td>
<td>0.71 ± 0.03</td>
<td>1.11 ± 0.05</td>
<td>1.12 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>10 mTorr</td>
<td>0.74 ± 0.01</td>
<td>0.97 ± 0.03</td>
<td>0.95 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>18 mTorr</td>
<td>0.75 ± 0.04</td>
<td>1.28 ± 0.04</td>
<td>1.32 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>30 mTorr</td>
<td>0.88 ± 0.03</td>
<td>Weak signal</td>
<td>Weak signal</td>
<td>0.82 ± 0.01</td>
</tr>
</tbody>
</table>

Table 3.2 displays the results of fitting of the power dependence curves to a power law behavior according to Eq. (3). Recall, $k$ is the power exponent of
From Table 3.2, the 1.43 eV peak has a power exponent of $k<1$.

When $k<1$, the origin of the peak can be either a Donor-Acceptor Pair (DAP) or a Free to Bound transition. However, the blue shift expected for DAP transitions was not observed in the 1.43 PL of any samples. (For example, see the dotted guide line in Figure 3-7)

Therefore, 1.43 eV peak would be assigned as Free to Bound transition rather than DAP.

The 1.59 eV peak, which is known to be a bound exciton (BE), shows $k>1$ except for the 10 mTorr sample. That may be due to a measurement error. The 1.53 eV peak also shows $k>1$, therefore it must be a BE, too. In Figure 3-11, a deep defect peak near 1 eV from 30 min CdCl$_2$ treated 30 mTorr sample also has power exponent $k<1$ and doesn’t show blue shift, thus, that must be free-to-bound transition.

**Figure 3-11.** PL of deep defect states near 1 eV from 30 min CdCl$_2$ treated 30 mTorr sample
3.2.6 Temperature dependent PL

![Graph showing temperature dependent PL intensity](image)

**Figure 3-12.** A typical temperature dependent PL from 30 min CdCl$_2$ treated 18 mTorr sample

As sample temperature increases, the intensity of PL decreases due to thermal quenching effects. Usually, thermal energy opens up a path for non-radiative transition which will compete with radiative PL transitions. Using Eq. (4), we can extract the binding energies of the defect states involved in these thermal quenching pathways. However, sometimes, complex PL mechanism gives erroneous fit values when we use two exponential decay form in Eq. (4). Another method is, using one exponential decay term, Eq. (5), to fit only the high temperature part of temperature dependent PL data (Figure 3-13).

$$\frac{I(T)}{I(0)} = \frac{1}{1 + C_1 \exp\left(-\frac{E_1}{kT}\right)} \quad (5)$$
Figure 3-13. Temperature dependent PL at 1.43 eV (10, 18, 30 mTorr data were shifted to right by 0.01 in 1/T axis for clarity)

Table 3.3 Summary of binding energies for E1 calculated by one-exponential fitting of temperature dependent PL from CdCl$_2$ treated samples.

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>E1 from 1.43 eV peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mTorr</td>
<td>(8.4 ± 9.5)*10$^{-5}$</td>
<td>149.0 ± 21.9 meV</td>
</tr>
<tr>
<td>10 mTorr</td>
<td>(6.4 ± 3.2)*10$^{-4}$</td>
<td>108.3 ± 7.0 meV</td>
</tr>
<tr>
<td>18 mTorr</td>
<td>(9.9 ± 7.2)*10$^{-4}$</td>
<td>89.6 ± 11.3 meV</td>
</tr>
<tr>
<td>30 mTorr</td>
<td>(4.0 ± 5.2)*10$^{-5}$</td>
<td>109.8 ± 19.7 meV</td>
</tr>
</tbody>
</table>

An acceptor level of 150 meV above the valence band is commonly seen in Hall measurements with p-type material and other luminescence measurements (Zanio [3-3]).

In spite of the fact that our 1.43 eV peak consists of multiple peaks and LO phonon energy of 21 meV, 1.455 eV and 1.43 eV peaks can be explained by free-to-bound (in this case, conduction band to acceptor level) transition. The 5 mTorr sample shows very
similar binding energy. 18 mTorr sample shows the lowest binding energy and that means shallower defect states than other samples.

**Figure 3-14.** Temperature dependent PL of samples grown at different pressure

Figure 3-14 shows one interesting phenomenon. Due to thermal quenching, PL intensity of all samples decreases as temperature increases, except for the 5 mTorr sample. For 5 mTorr sample, the measurement starts from 10 K and PL intensity rises from 10 K to the maximum at 20 K, then it starts to decrease. Biernacki et al (1993) [3-4] reported that the A-center luminescence zero-phonon line (ZPL) had a slight blue shift at 20 K and decreased. They explained this by thermal excitation of donor electrons to the conduction band followed by recombination. In my case, the blue shift was not observed, but it matches with their explanation that this event can occur only below 30 K due to the smallness of conduction band variation and donor and acceptor level with temperature. It is not clear whether this shallow donor level in the 5 mTorr sample exists due to a
deposition-pressure-related effect or possibly to a CdCl$_2$ over treatment, but at least it shows that 5 mTorr sample has a different defect structure than other samples.

### 3.2.7 Conclusions for CdTe PL

Sputter deposition is very sensitive to the Ar pressure because it greatly affects the energy of ion bombardment on the depositing film. In Figure 3-5 (a), PL of as-deposited low pressure (5 mTorr) sample shows dominant deep defect states due to film damage from ion bombardment. As pressure increases, shallow defect PL at 1.4 eV becomes stronger and at the optimum pressure, i.e. 18 mTorr, the PL intensity ratio of shallow defects to deep defects becomes the greatest.

During CdCl$_2$ treatment, intermixing of CdS and CdTe happens. In Figure 3-6 (a) and (b), film-side PL peak of 1.424 eV becomes 1.377 eV in junction-side PL. This 47 meV of energy shift is due to the band bowing of CdS$_x$ and CdTe$_{1-x}$ when $x = 0.06$.

The excitation power dependence of the PL showed that the 1.43 eV peak is a free-to-bound transition because it has a power exponent of $k<1$, but it didn’t show a blue shift as the excitation power increases, which is a characteristic of DAP transitions. The 1.59 eV peak is a bound exciton transition because it showed $k>1$. The origin of the 1 eV peak is a free-to-bound due to $k<1$ and no blue shift.

Temperature dependent PL of the 1.43 eV peak of CdCl$_2$ treated samples grown at different pressures shows that the 18 mTorr deposited sample has lowest binding energy or the defect. It also shows that the 5 mTorr sample has a shallow donor state that other samples do not have.
3.3 PL of CdSe

3.3.1 Background of the CdSe study

In an effort to make efficient CdSe solar cells, two goals were set. The first one was to make a good crystalline n-type CdSe film, and make a metal insulator semiconductor (MIS) type device. The MIS study was summarized in Chapter 5. The second goal was to make p-type CdSe by doping. Polycrystalline CdSe is generally n-type and it is known to be hard to dope p-type. However, most of the transparent conductive oxides (TCO) are n-type, therefore it is preferred to have p-type CdSe absorber layer. Then, one could make a PN junction solar cell. I made four doped targets. Doped and undoped films were deposited by RF-sputtering.

In this study, PL was used to see the defect states and obtain a measure of the crystallinity of the films before and after annealing.

Table 3.4 Summary of the CdSe deposition parameters.

<table>
<thead>
<tr>
<th>No</th>
<th>Sample ID</th>
<th>Target</th>
<th>Mfg</th>
<th>Substrate</th>
<th>Temp (°C)</th>
<th>Pressure (mTorr)</th>
<th>Dep Time (min)</th>
<th>Gas</th>
<th>RF power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SCMT69</td>
<td>CdSe</td>
<td>Cerac</td>
<td>SLG</td>
<td>300</td>
<td>20</td>
<td>30</td>
<td>Ar</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>SCMT86</td>
<td>CdSe:Cu 1%</td>
<td>In-House pressed</td>
<td>SLG</td>
<td>300</td>
<td>15</td>
<td>100</td>
<td>Ar</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>AST56</td>
<td>CdSe:GaCl₃ 0.38 wt %</td>
<td>In-House pressed</td>
<td>SLG</td>
<td>160</td>
<td>8</td>
<td>20</td>
<td>Ar</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>AST146</td>
<td>CdSe:Ag 1 at %</td>
<td>In-House pressed</td>
<td>ASG</td>
<td>180</td>
<td>8.5</td>
<td>30</td>
<td>Ar+N₂</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>AST176</td>
<td>CdSe:As 1 at %</td>
<td>In-House pressed</td>
<td>SLG</td>
<td>160</td>
<td>10</td>
<td>122</td>
<td>Ar</td>
<td>40</td>
</tr>
</tbody>
</table>

(*SLG and ASG stands for soda lime glass, and aluminosilicate glass)

For dopants, Cu and Ag were chosen because they have similar atomic mass and ionic radius so that they could replace Cd and dope CdSe p-type. As was also chosen because it has almost identical mass and ionic radius with Se and could dope CdSe p-type, too. For GaCl₃, Ga would be an n-type dopant; however, it was chosen because there was
a possibility that Cl could form acceptor complex with Cd vacancy to dope CdSe p-type, too.

Figure 3-15. Hot-probe measurements (a) setup diagram (b) selected results

(ITO=Indium doped tin-oxide, AZO=Aluminum doped zinc-oxide, Tec15HRT=HRT coated fluorine doped tin-oxide)

Semiconductor type was tested by hot-probe measurement shown in Figure 3-15. Hot-probe is a simple setup to measure the carrier type by monitoring the voltage difference of the heated and unheated area of the semiconductor. When a small area of semiconductor film is heated by solder iron, intrinsic carriers are released. In the setting shown in Figure 3-15 (a), if the majority carrier of semiconductor is hole, then the thermally released holes from the area under the brass rod flow into the pogo-pin and collected in the negative contact of multimeter. As a result the voltage drop will be shown in the multimeter. If the majority carrier is electron, electrons will flow into negative
contact and positive voltage will be monitored. As a reference p-type ZnTe:N film and three TCOs are tested together with CdSe films. Unfortunately, none of the CdSe films showed p-type conductivity. (Table 3.5) All TCOs are shown n-type. ZnTe:N was shown strong p-type. CdSe:GaCl₃ before annealing was shown strong n-type in Figure 3-15.

Table 3.5 Summary of the hot-probe measurements on CdSe films

<table>
<thead>
<tr>
<th>No</th>
<th>Sample ID</th>
<th>Target</th>
<th>Before anneal</th>
<th>After anneal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SCMT69</td>
<td>CdSe</td>
<td>weak n-type</td>
<td>weak n-type</td>
</tr>
<tr>
<td>2</td>
<td>SCMT86</td>
<td>CdSe:Cu 1%</td>
<td>no signal</td>
<td>no signal</td>
</tr>
<tr>
<td>3</td>
<td>AST56</td>
<td>CdSe:GaCl₃ 0.38 wt %</td>
<td>n-type</td>
<td>n-type</td>
</tr>
<tr>
<td>4</td>
<td>AST146</td>
<td>CdSe:Ag 1 at %</td>
<td>weak n-type</td>
<td>weak n-type</td>
</tr>
<tr>
<td>5</td>
<td>AST176</td>
<td>CdSe:As 1 at %</td>
<td>no signal</td>
<td>n-type</td>
</tr>
</tbody>
</table>

3.3.2 Sample preparation

Table 3.4 is the summary of the targets and deposition conditions. All films were rf-sputter deposited in vacuum chamber mostly with approximately 10 mTorr of Ar pressure. One sputtering target was commercially purchased and all doped targets were cold pressed in our lab from high purity CdSe and elemental dopant powder. For example, Ag doped CdSe target was made by cold pressing of CdSe powder mixed with 1 atomic % of Ag powder. Both powders were very fine particles (CdSe has particle size of ~10 µm 99.99% purity, and Ag was 100 mesh 99.95% purity). Therefore, they were mixed with ball miller for five minutes for uniform mixing. Then, it was pressed into a stainless steel cup and mounted in the sputtering gun.

After deposition, pieces of samples were heat annealed for 60 minutes at 400 °C in dry air ambient. PL was taken for both as-deposited and heat-annealed samples side-by-side.
3.3.3 PL of CdSe single crystal

Figure 3-16 shows the PL of a single crystal of CdSe measured at 10 K, which is presented for reference. Only two near-band-edge bound exciton peaks (1.833 eV and 1.823 eV) are evident, which means the sample is a high quality crystal. For this single crystal, red PL was bright enough to be seen by naked eyes. These exciton peaks have also been discussed in other literature such as by Jager et al. (1988) [3-5] which shows 1.821 eV exciton at 3 K from evaporated CdSe films, and Silberstein et al. (1983) [3-6] which shows 1.8226 eV exciton at 77 K from electrodeposited CdSe films.
3.3.4 PL of undoped CdSe sputtered film

![Graph showing PL intensity vs. energy for undoped CdSe films before and after heat annealing.](image)

**Figure 3-17.** PL of undoped CdSe sputtered film before and after heat annealing

Fig. 3-17 shows the PL of undoped CdSe films sputtered from a commercial target (Cerac). The as-deposited film shows weak deep DAP peaks (DDAP), however after heat annealing, this DDAP was greatly suppressed and the 1.567 eV shallow DAP peak became dominant with higher intensity. This indicates that high temperature annealing reduces the deep defect states, therefore shallow-defect-related radiative processes become dominant.
3.3.5 PL of As-doped CdSe film

![Graph showing PL intensity vs. energy for As-doped CdSe film before and after heat annealing.](image)

**Figure 3-18. PL of As-doped CdSe film before and after heat annealing**

Arsenic (As) is one of the best candidates that could dope CdSe p-type. Arsenic is a group V element and Se is a group VI. As and Se have very similar masses, 74.94, 78.96, respectively. Furthermore, they have similar ionic radii. As is 33.5 pm and Se is 28 pm. A 1 atomic % As doped target was made and depositions were done. After annealing (Figure 3-18), deep defect states were not suppressed as for the undoped film, but new shallow defect states at 1.527 eV and 1.65 eV emerged. Wavelength Dispersive Spectroscopy (WDS) was done at the Electron Microbeam Analysis Laboratory (EMAL) of the University of Michigan. It verified that As is in the film. PL intensity was weaker than other samples, which means As doping must have induced a large number of defects, therefore nonradiative transitions become more dominant than in the stoichiometric CdSe.
sample. Unfortunately, the annealed CdSe:As film exhibited n-type activity in hot probe measurements, and the as-deposited film didn’t show any distinct carrier type.

3.3.6 PL of Ag-doped CdSe film

![PL Intensity vs Energy graph](image)

**Figure 3-19.** PL of Ag-doped CdSe film before and after heat annealing

Ag dopant was chosen due to similar atomic mass to Cd, 107.87, 112.41, respectively. Thus, if Ag(+1) replaces Cd(+2), it could dope CdSe p-type. However, hot probe studies of sputtered films both as-deposited and heat annealed showed the CdSe:Ag filmsto be n-type. Before annealing only a very weak deep defect around 1 eV is shown in PL. After annealing broad peaks slightly higher than as-deposited film are shown near 1.18 eV and 1.31 eV, along with a shallow defect peak near 1.63 eV. It means that the quality of the films is not very good possibly due to the induced defects in
the doping process. Even heat annealing could not remove the dominant deep defects or nonradiative processes. The poor quality of the film may be due to the high concentration of Ag atoms in CdSe film.

### 3.3.7 PL of GaCl₃ doped CdSe film

![Graph showing PL intensity vs. energy for CdSe:GaCl₃ (0.3 wt%) before and after heat annealing.](image)

**Figure 3-20.** PL of GaCl₃ doped film before and after heat annealing

GaCl₃ doping was chosen because it could form an acceptor complex. In CdTe, Cd vacancy (V_{Cd}) is a double acceptor and forms acceptor complex with a single donor such as Cl_{Te}. I wanted to test here, whether CdSe would dope p-type in the similar way. For the as-deposited films, before annealing only very weak deep defects are shown in PL. After annealing, not only did the PL intensity of deep defects increase, but also
strong shallow defect peaks appeared. The highest energy peak is 1.63 eV, which was also observed in CdSe:As and CdSe:Ag samples.

Deep defect PL in these GaCl$_3$ doped films has vibronic features with the interval of approximately 100 meV, which is much higher than bulk LO phonon energy of 26.3 meV. Similar to the 80 meV interval peaks observed in CdS/CdTe films (Appendix A), these vibronic features are likely due to the thin film interference fringe artifacts. CdSe:GaCl$_3$ also showed n-type conductivity in the hot-probe tests.

### 3.3.8 PL of Cu-doped CdSe film

![PL of Cu-doped film before and after thermal annealing](image.png)

**Figure 3-21.** PL of Cu-doped film before and after thermal annealing
Cu was chosen as a dopant because it is group I and could replace group II (Cd) to dope CdSe p-type. PL of CdSe:Cu shows 1.82 eV and 1.76 eV peak after heat annealing in air. 1.82 eV is the bound excitation peak which is an indicator of a good crystalline film. Cu doped CdSe was the only sample that showed bound exciton peak. According to Jager et al (1988) [3-5], 1.76 eV is assigned to free to bound transition. They also found this peak after their sample was treated by all three annealing steps: heat annealing in air, chemical and photo-etching, but in my case it showed up after heat annealing in air.

3.3.9 Conclusions of the CdSe PL studies

For the CdSe study, we had two goals in the beginning. The first one was to make p-type film, however, none of our doped sample showed p-type in the hot probe measurements. The second goal was to optimize the quality of the polycrystalline film. After thermal annealing of the Cu-doped CdSe film, it showed a strong, near-band-edge bound exciton which is an indicator of reasonably good crystallinity. For undoped CdSe films, shallow defect states shown in as-deposited films are greatly suppressed after annealing and a shallow DAP peak became dominant (Figure 3-17). In addition, the sheet resistance was lowered by a factor 100 after the thermal annealing. That shows a need of high temperature (T > 400 °C) annealing of films grown at relatively low temperatures (T < 300 °C). GaCl$_3$ doped CdSe also seems to be a reasonably good polycrystalline film. After annealing, nonradiative or deep defect states were passivated and strong shallow defect states became dominant. As and Ag doped samples showed very strong deep defect states even after heat annealing and appear not to be promising candidates for p-type polycrystallinen CdSe.
Chapter 4

AFM Study of CdTe and CdSe Solar Cells and Films

Surface morphology controls many important physical and chemical properties of thin films. In this chapter, I will show findings of surface study using atomic force microscope (AFM). I will review how an AFM works, and introduce scaling theory. Then, I will analyze the AFM data of CdTe and CdSe thin films based on the scaling theory.

4.1 Working principles of the Atomic Force Microscope (AFM)

Figure 4-1. Schematic diagram of AFM scanner [4-1]  
Figure 4-2. SEM image of AFM tip (Nanosensor)
The atomic force microscope (AFM) is an instrument to observe the surface of the material in atomic resolution. Unlike a conventional microscope, it uses a tiny sharp tip to see the surface. It is very similar to the way a blind man uses a stick to see obstacles in front of him. A silicon cantilever with a sharp tip at the end made by photo lithography or FIB etching, is mounted on the stage in the AFM scanner, which can move in 3-D by the piezo crystals. Changes in surface morphology make deflection of the cantilever that is sensed by the reflected laser light from the upper side of the cantilever and mapped into 3-D images of the surface.

In general, there are two modes of operation. One is the contact mode and the other is the alternating contact (AC) mode. The AC mode is also called tapping mode or intermittent contact mode. In contact mode, the AFM tip is physically touching and rastering the surface of the sample. The contact mode gives atomic scale resolution, however, the tip will be vulnerable to damage by the rough surface. The AC mode is more suitable for rough surfaces with a compromise of the high resolution. In the AC mode, the cantilever is driven to oscillate and the tip moves through an interaction potential that includes long-range attractive and short range repulsive forces. The forces will change the amplitude, phase and resonance frequency of the oscillating cantilever. A feedback system maintains the amplitude at a set value. The topography image is the voltage applied to the piezo required to keep the oscillation amplitude constant, multiplied by the sensitivity of the piezo. The AC mode can operate in either the intermittent contact or non-contact regime. During the intermittent contact, the tip is brought close to the sample and it lightly contacts the surface causing the oscillation amplitude to drop. There are two methods to drive the cantilever oscillation: acoustic and
magnetic. The acoustic AC (AAC) mode is driven by the oscillation of the piezo crystal and the magnetic AC (MAC) mode is driven by the magnetic coil below the stage. The MAC mode requires a magnetic-material-coated cantilever and a built-in magnetic coil stage, but it has less noise than the AAC mode and is particularly beneficial when imaging in liquid.[4-1]

**Figure 4-3.** Zones of interaction in AFM [from Ref. 4-1]

I used Molecular Imaging’s PicoPlus AFM. The main controller is PicoScan 2500 picoSPM II. Data were acquired in the AC mode by the PicoScan 5.3 software.
4.2 Surface analysis theory

The importance of roughness and brief history of surface analysis theory was well summarized in Karabacak’s paper. [4-4]

“In many applications of thin films, it is often desired to have atomically flat surfaces. However, in many deposition techniques such as sputtering, chemical vapor deposition (CVD), and thermal evaporation, the surface morphology generates a growth front roughness. A conventional statistical mechanics treatment cannot be used to describe the complex phenomenon of surface mechanics morphology formation in thin film growth.

In 1985, Family and Vicsek [4-2, 4-3] introduced a dynamic scaling approach to describe the morphological evolution of a growth front. Dynamic scaling theory treats the growing surface having a fractal morphology, which can occur as a result of competition between local smoothening effects (e.g., surface diffusion) and random fluctuations during growth. Because of fractal property, it is expected that morphology of the thin-film should incorporate similar surface features when investigated at different length scales. In addition, dynamic scaling theory predicts that surface roughness can be scaled with time, which implies the dynamic invariance of surface features. Depending on the type of surface smoothening mechanism, scaling of surface morphology through space and time can be defined by a unique set of scaling exponent.”

The relativistic nature of the roughness and a need to have a better description of the surface morphology is expressed below in Barabasi and Stanley’s book [4-5]

“Surfaces can be smooth, such as the Himalayas viewed from space, but the same surface can also be rough, such as the same mountains viewed from earth. In general, the morphology depends on the length scale of observation. In fact, we shall see that the concepts like roughness are replaced by exponents that refer not to the roughness itself, but to the fashion in which the roughness changes when the observation scale itself changes. Fractal objects in nature are the same on different observation scales.

Many interfaces and surfaces are examples of self-affine objects, which are ‘intermediate’ between fractal objects and non-fractal objects in the following sense. When we make a scale change that is the same in all directions, self-affine objects change morphology. On the other hand, when we make a scale change that is different for each direction, then interfaces do not change morphology.”
Figure 4-4. Rescaling a self-affine function, in the case of DNA walk. Only if two unequal magnification factors $M_l$ and $M_h$, by which the $l$ and $h$ directions are rescaled, are selected correctly will the enlarged portion have the same statistical properties as the original.[4-5]
Figure 4-4 shows the example of self-affine surface, which can have the same pattern when it is scaled in \( l \) and \( h \) direction.

![Figure 4-4](image)

Figure 4-5. Growth of the interface, where \( w= \) width, \( w_{sat}= \) saturated width, \( t= \) deposition time, \( t_x= \) crossover time, \( \alpha= \) roughness exponent, \( \beta= \) growth exponent, \( L= \) length scale of observation) [from Ref. 4-5]

The interface width is an average fluctuation of the surface height in a given length scale \( L \).

\[
w(L, t) \equiv \sqrt{\frac{1}{L^2} \sum_{i=1}^{N} (h(i, t) - \bar{h}(t))^2}
\]  \hspace{1cm} (1)

\[
w(L, t) \sim L^\alpha f \left( \frac{t}{L^\beta} \right)
\]  \hspace{1cm} (2)

To monitor the roughening process quantitatively, I measured the width of the interface as a function of time. All the AFM measurements were taken after thin film
deposition was finished. Although the surface roughness was not measured in real time, I can analyze the temporal roughness changes of CdTe films because I made several films with varying deposition times. The interface at time zero is a straight line. And as deposition goes on, the interface gradually roughens. Suppose we deposit a thin film for infinite time, then the roughness will grow initially but will saturate after a certain time. (Figure 4-5) The time at which the extrapolated initial slope reaches the saturation value is called cross-over time, $t_x$. The saturated roughness $w_{sat}$ is $L^\alpha$, where $L$ is the length scale of observation and $\alpha$ is called the roughness exponent. Note that the saturated roughness is a function of length scale of the observation; however, the roughness exponent $\alpha$ is independent of the details of observation. A typical plot of the time evolution of the surface width has two regions separated by a ‘cross-over’ time $t_x$. Initially, the width increases as a power of time, $[4-5]$ 

$$w(L,t) \sim t^\beta \text{ for } t \ll t_x$$  

The exponent $\beta$ called the growth exponent, characterizes the time-dependent dynamics of the roughening process. The power-law increase in width does not continue indefinitely, but is followed by a saturation regime during which the width reaches a saturation value, $w_{sat}$. As system size $L$ increases, the saturation width, $w_{sat}$ increases as well, and the dependence also follows a power law,

$$w_{sat}(L) \sim L^\alpha \text{ for } t \gg t_x$$  

The exponent $\alpha$ is a second critical exponent that characterizes the roughness of the saturated interface. The crossover time $t_x$ (sometimes called saturation time) at which
the interface crosses over from the behavior of Eq.(3) to that of (4) depends on the system size $L$,

$$t_x \sim L^z$$

(5)

where $z$ is called the dynamic exponent.

This implies that $z = \frac{\alpha}{\beta}$ [4-5]

![Graph](image)

**Figure 4-6.** Scaling of $w$ and $t$ axis to calculate growth exponent $\beta$ [from Ref. 4-5]

Suppose that we have measured the saturation width for three different system sizes, $L_1$, $L_2$, $L_3$. Then, it will have three different cross-over times and three different saturated widths. If we normalize $w$ axis with each saturated width $L_1^\alpha$, $L_2^\alpha$, $L_3^\alpha$, then the $w$ axis of the graph will have the same value.(Figure 4-6 (b)). If we normalize $t$ axis with each cross-over time ($t_{1x}$, $t_{2x}$, $t_{3x}$), then all the graphs will collapse on one graph.(Figure 4-6 (c)). The slope of the graph will give growth exponent $\beta$ of the surface.
Now, let’s review how the roughness exponent $\alpha$ is calculated. Figure 4-7 shows that width (RMS roughness) varies when the scales of observation (Red dotted box) changes. Figure 4-8 illustrates how the average widths are calculated from AFM data. In my experiment, the AFM scans over a 5000 nm $\times$ 5000 nm area of the film surface. Then, the software calculates width data over the 5000 nm $\times$ 5000 nm area. Then, 4 widths data of 2500 nm $\times$ 2500 nm are calculated, and averaged. This goes on until the size becomes 10 nm $\times$ 10 nm, which is equivalent to 2 pixel $\times$ 2 pixel, then it has 262144 (=512 * 512) widths and it is averaged, too.
Figure 4-8. Width analysis by different length scale

Table 4.1 shows an example of width measurement by different length scales.

Note that after 2500 nm, the width didn’t change. This means that the width is saturated and our choice of 5000 nm is large enough to get the saturated width.
Table 4.1. Width with varying scales of observation (width from 120 min CdTe film)

<table>
<thead>
<tr>
<th>Isize</th>
<th>Length scale(nm)</th>
<th>width(nm)</th>
<th>stdev(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>9.8</td>
<td>1.2</td>
<td>0.1</td>
</tr>
<tr>
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<td>19.5</td>
<td>2.7</td>
<td>0.1</td>
</tr>
<tr>
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<td>39.1</td>
<td>5.4</td>
<td>0.3</td>
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<td>16</td>
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<td>0.5</td>
</tr>
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<td>32</td>
<td>156.3</td>
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</tr>
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<td>312.5</td>
<td>26.7</td>
<td>1.7</td>
</tr>
<tr>
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<td>625</td>
<td>35.0</td>
<td>1.0</td>
</tr>
<tr>
<td>256</td>
<td>1250</td>
<td>39.7</td>
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<td>0.1</td>
</tr>
<tr>
<td>1024</td>
<td>5000</td>
<td>41.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Instead of waiting infinite time to reach a saturated width, and measure the roughness exponent $\alpha$ shown in Figure 4-5, we can calculate $\alpha$ in a different way.

Figure 4-9 summarized the concept. In Figure 4-9 (a), each graph depicts the width data with varying length scale of the measurement. Note that each graph has a different saturated width at different $l$.

![Figure 4-9](image)

**Figure 4-9.** Scaling of $w$ and $l$ axis to calculate roughness exponent $\alpha$
We can normalize width by dividing \( w(l, t) \) by the saturated width, \( w_s \). The normalized width follows the scaling law Eq. (6)

\[
w(l, t) \sim l^\alpha f\left(\frac{t}{l^{\gamma}}\right)
\]

\[
f(u) = \text{const} \quad (u \gg 1)
\]

\[
w(l, t) \sim \text{const} \cdot l^\alpha = w_{sat} l^\alpha \quad (l^{\gamma} \ll t) \text{ or } (l \ll t^{1/\gamma} = \xi)
\]

where \( \xi \) is correlation length which defines the distance that atoms interact with each other.

\[
\frac{w(l, t)}{w_{sat}} \sim (l / \xi)^\alpha (\xi)^\alpha = (l / \xi)^\alpha (t^{1/\gamma})^\alpha
\]

\[
\frac{w(l, t)}{w_{sat}} \sim (l / \xi)^\alpha t^\beta
\]

Then, if log-log graph is drawn from Eq. (5), then the slope will be \( \alpha \). (Figure 4-9)

In addition to extracting the exponents from the width, there is another way to get information from the surface. That is called structure factor or power spectrum. The structure factor is defined as

\[
S(\vec{k}, t) = \left\langle \hat{h}(\vec{k}, t) \hat{h}(\vec{-k}, t) \right\rangle
\]

\[
\text{where } \hat{h}(\vec{k}, t) = \frac{1}{L} \sum_r [h(\vec{r}, t) - \langle h(t) \rangle] \exp(-i\vec{k} \cdot \vec{r}) \text{ and } \vec{k} \text{ is the wave vector.}
\]

The dynamic scaling hypothesis can be translated to the structure factor, with the result

\[
S(\vec{k}, t) = L^\gamma k^{-\gamma} s(tk^{\gamma})
\]
where $L$ = length scale of measurement, $\chi$ = anomalous exponent, $z$ = dynamic exponent, $t$ = time, $k$ = wave number, and $\gamma$ is an exponent having relationship of $\chi + \gamma = z$.

$s(x) = \text{const for } x>>1$  \hspace{1cm} (13)

$s(x) \sim x^{\chi/z}$ for $x<<1$ \hspace{1cm} (14)

$S(\tilde{k}, t) = \text{const} \cdot k^{-\gamma}$ for $k>>1/\xi(t)$ and $\chi = 0.$ \hspace{1cm} (15)

which gives the $\gamma$ value. $\chi + \gamma = z.$ $\chi = 0$ when there is no anomalous effect.

We can calculate the growth exponent by using $\beta = \alpha / z$ \hspace{1cm} (16)

**Table 4.2. Summary of the key definitions.**[4-5, 4-6]

| Mean height | $\bar{h}(t) = \frac{1}{L^2} \sum_{i=1}^{L^2} h(i, t)$ |
| Interface width | $w(L, t) = \sqrt{\frac{1}{L^2} \sum_{i=1}^{L^2} [h(i, t) - \bar{h}(t)]^2}$ |
| Growth exponent | $w(L, t) \sim t^\beta$ \quad $[t << t_x]$ |
| Roughness exponent | $w_{\text{sat}}(L) \sim L^\alpha$ \quad $[t >> t_x]$ |
| Dynamic exponent | $t_x \sim L^z$ |
| Scaling relation | $w(L, t) \sim L^\alpha f(t / L^z)$ |
| Scaling law | $z = \alpha / \beta$ |
| Structure factor | $S(\tilde{k}, t) = \text{const} \cdot k^{-\gamma}$ for $k>>1/\xi(t)$ and $\chi = 0$ |
| Structure factor | $\chi + \gamma = z$ |
| Correlation length | $\xi \sim t^{1/z}$ |
Sputtering deposition can be explained by the fourth-order linear Langevin equation which was initially used to describe Molecular Beam Epitaxy (MBE)

\[
\frac{\partial h}{\partial t} = -\kappa_0 \nabla^4 h + \eta(r, t)
\]  \hspace{1cm} (17) [4-7, 4-8]

A freshly deposited particle having only one nearest neighbor bond seeks a neighboring site providing more bonds than the present one and diffuses to that site. If the present site has more than one bond, then the particle becomes immobile. If there are two neighboring sites [in (1+1)D] providing more bonds regardless of the number of bonds, then the particle chooses one of them randomly and moves to the site.[4-9, 4-10] In (2+1) D Eq. (17) yields \(\alpha=1, \beta=0.25, \text{ and } z=4\). [4-5] (Note that here, I used (2+1) D notation. The first number ‘2’ means the substrate dimension, the second number ‘1’ means the dimension of growth or height. Therefore, (2+1) D describes the situation that on two dimensional substrate, one dimensional height is growing.)

From Figure 4-10, the roughness increase can be seen from CdTe deposition times of (e) 30 min, (f) 60 min, (g) 120 min films. At the same time, grain size increase is also evident from SEM images in Figure 4-11. Note that SEM images look flatter than AFM images. That’s because z (height) scale of AFM images are 10 times magnified than x-y scale. Besides, SEM images are made by the electron-material interactions. Therefore, electron beam current, voltage setting, and material property will affect the image; while AFM is using short-range force interaction, which is suitable to characterize surface morphologies.
For (a) Tec15/HRT, (b) CdS, (c) CdS/CdTe (7.5 min), (d) CdS/CdTe (15 min) deposited films, not much roughness change is identifiable by eyes. In fact, the width decreased in (c) CdS/CdTe (7.5 min). That indicates the intermixing of CdS and CdTe films, resulting smoother films.

4.3 Surface analysis of CdTe

4.3.1. Background of CdTe surface study

Although CdS/CdTe thin film solar modules are one of the fastest growing contenders in the market due to low manufacturing cost, there is a constant criticism that fundamental understanding is lacking because of apparent differences between best device efficiency and theoretical efficiency. CdTe can be deposited by various techniques, such as closed space sublimation (CSS), vapor transport deposition (VTD), evaporation and sputtering. Sputtering is an important deposition technique because of precise control of thickness, grain size, and uniformity of the film. There are several surface morphology or growth mode studies of CdTe films deposited by hot wall epitaxy (HWE) [4-11] or metalorganic chemical vapor deposition (MOCVD) [4-12]; however, a growth mode study of sputtered CdTe film using scaling theory has not yet been done. Here we perform such a study.

4.3.2. Experimental details

In this work, CdS/CdTe films were deposited on Tec15/HRT glass with various deposition times to examine how surface morphology and growth mode are affected by
growth time. Atomic force microscopy (AFM) data was used to calculate the RMS surface roughness and structure factor.

CdS/CdTe films were deposited on HRT coated Tec15 glass by RF-sputtering. Glass was thoroughly cleaned with our lab procedure. Glass was submerged in DI water with soap (Micro 90) and heated up to 90 °C and went through ultrasonic cleaning for 25 minutes. After repeated rinsing with de-ionized (DI) water, they are dried with a N₂ jet. Films were deposited by RF magnetron sputtering in a chamber made by AJA International. Only the deposition time was changed and all other conditions, such as deposition temperature, pressure, gas flow rate and RF power were kept the same. The reason why I did time varying CdTe depositions was that it will give the growth exponent \( \beta \) in two different ways. Then, the consistency of the result can be checked by them.

All films were deposited at 10 mTorr of Ar and an RF power of 50 W for the 2-inch diameter, CdS and CdTe sputtering targets, which were purchased from Materion Materials (formerly Cerac). Film thickness was measured by both a laser interference thickness monitor during deposition using a 980 nm laser diode and a Dektak thickness profiler after deposition. The substrate was heated radiatively by two tungsten lamps. The glass substrate temperature was measured indirectly by a thermocouple in contact with the heater window and deposition temperature was 270 °C. (The thermocouple temperature readouts have been validated with temperatures inferred from ellipsometry and by interference reflection techniques.)

AFM measurements were conducted on a Pico SPM II system (Molecular Imaging) with silicon cantilevers having resonance frequencies at \(~300\) kHz. Scan
resolution was 1024 × 1024 pixels which correspond to a scan area of 5 \( \mu m \times 5 \mu m \).

Using the height profile obtained from AFM measurements, surface roughness was defined as RMS surface height was calculated. The structure factor was also calculated from the height profile of the AFM scan.
4.3.3. Roughness exponent of CdTe

Figure 4-10. AFM images of surfaces with various deposition times (The time indicates the CdTe deposition time. i.e., 7.5 min = Tec15/HRT/CdS(60 nm)/CdTe(7.5 min). (x = 5000 nm, y = 5000 nm, z = 500 nm scale)
Figure 4-11. SEM images of Tec15/HRT, CdS and CdTe films with various growth times (x = 4000 nm, y = 3200 nm)
Figure 4-12. The RMS roughness of CdTe films deposited with various deposition times

The AFM images in Figure 4-10 show that the roughness of the CdTe films increases with deposition time. The large-scale, saturated RMS roughness $w_s$ increases from 19.5 nm to 41 nm with increasing deposition time (Figure 4-12, Table 4.3).

In Figure 4-12, for a given $l < \xi$, there is a systematic shift in width as deposition time increases. This is an indication of presence of anomalous scaling. [4-13, 4-14] It has been also shown [4-15] that when groove instabilities are present in surface growth, the root-mean-square local slope increases with time, $\langle (\nabla h)^2 \rangle \sim \ln(t)$, which was also confirmed experimentally in sputter-deposition polycrystalline growth of Pt on glass. [4-16] In order to test anomalous scaling behavior in this CdTe growth, I have examined the dependence of the width on time at scan size of $l = 19.53$ and 39.06 nm as suggested in [4-13, 4-14]. Indeed I have found that the width increases $(\ln(t))^{1/2}$ for such scan sizes of $l$, as shown in Figure 4-13.
Figure 4-13. Anomalous scaling width versus $[\ln(\text{thickness})]^{1/2}$ for different scan sizes

In addition, the RMS surface roughness $w(l)$ measured over a size of $l \times l$ increases with the scan size $l$ and saturates for a large $l$. This indicate the roughness exponent $\alpha \approx 1$ (Figure 4-14).¹ We note that the total scan size $L$ is large enough to get significant surface information for these films. Using the saturated value of the surface roughness $w_s(T)$ and the correlation length $\xi$, we have obtained a good scaling for the surface roughness $w(l)$, as can be seen in Figure 4-14.

¹ Calculation of $\alpha$: From the individual width versus scan size graph, saturated width ($w_s$) can be determined by drawing a parallel line connecting the highest two or three data points. After that, by connecting the lowest two or three data points we can draw a second line. The cross-section of these two lines gives saturated width ($w_s$) and correlation length ($\xi$) of the measured surface. For each sample, two AFM measurements were done and the average width and correlation length were summarized in Table 4.3. After each width and correlation length were determined, width ($w$) data of individual samples were divided by the saturated widths ($w_s$) and the scan size ($l$) data were divided by the correlation length ($\xi$) as illustrated in Figure 4-9. Then, the slope of the scaled graph is the roughness exponent ($\alpha$).
It is interesting that the correlation length and average grain size in Figure 4-17 have the same order of magnitude. The trend shown in the correlation length (Table 4.3) is that CdS, CdTe after 7.5 min, and CdTe after 15 min have the same lowest value and it increases as deposition goes on. This is very similar to the trend shown in the average grain size (shown in Figure 4-17 below). Correlation length defines the lateral size that atoms can interact with each other. This similar trend in the correlation length and grain size implies that grain boundaries are working as barriers of interactions among atoms and inhibited diffusion makes the rough surfaces inside the grain boundaries.

**Figure 4-14.** Scan size vs. average width (Slope shows the roughness exponent $\alpha$)

**Table 4.3.** Correlation length summary of CdTe

<table>
<thead>
<tr>
<th>Deposition time (min)</th>
<th>Tec15HRT</th>
<th>CdS</th>
<th>7.5</th>
<th>15</th>
<th>30</th>
<th>60</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlation length $\xi$ (nm)</td>
<td>180</td>
<td>190</td>
<td>190</td>
<td>190</td>
<td>200</td>
<td>270</td>
<td>270</td>
</tr>
<tr>
<td>Saturated width $w_s$ (nm)</td>
<td>17.6</td>
<td>23.0</td>
<td>19.5</td>
<td>20.3</td>
<td>23.3</td>
<td>32.5</td>
<td>41</td>
</tr>
</tbody>
</table>
4.3.4. Growth exponent of CdTe

![Graph showing structure factor (power spectrum) of CdTe films.](image)

Figure 4-15. Structure factor (power spectrum) of the CdTe films (Multiplied by 10 for clarity for each growth time interval)

Table 4.4. Structure factor slope (-\(\gamma\)) of CdTe

<table>
<thead>
<tr>
<th>Deposition time</th>
<th>7.5 min</th>
<th>15 min</th>
<th>30 min</th>
<th>60 min</th>
<th>120 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope (-(\gamma))</td>
<td>-4.6 ± 0.1</td>
<td>-4.6 ± 0.1</td>
<td>-4.6 ± 0.1</td>
<td>-4.3 ± 0.1</td>
<td>-4.2 ± 0.1</td>
</tr>
</tbody>
</table>

From Figure 4-14, the scaling of the interface width gave \(\alpha \approx 1\). When anomalous exponent \(\chi = 0\), then \(\gamma = z\) from \(\chi + \gamma = z\). and from Eq.(16) \(\beta = \alpha/z\). Therefore, the growth exponent \(\beta\) is from 0.24 to 0.22. In (2+1) D Eq. (17) yields \(\alpha = 1\), \(\beta = 0.25\) and \(z = 4\). But, our \(z\) is slightly larger than the expected value. It may be because polycrystalline grains hinder the interactions between atoms.

Based on Figure 4-5, if we have width \(w\) (RMS roughness) data with changing time, then, we can calculate growth exponent \(\beta\). Using five CdTe width data points with
varying deposition time, the growth exponent $\beta$ of CdTe films was calculated in Figure 4-16.

![Graph showing growth exponent $\beta$ from deposition time vs. width fitting ($\beta = 0.26 \pm 0.02$).](image)

**Figure 4-16.** Growth exponent $\beta$ from deposition time vs. width fitting ($\beta = 0.26 \sim 0.36$)

The widths are fitted by a power law and the slope was calculated on a log-log scale. This method gives $\beta = 0.26 \pm 0.02$, which is consistent with $\beta$ calculated by structure factor ($\beta = 0.22 \sim 0.24$). It also matches with the theoretical value ($\beta = 0.25$) of the linear fourth-order equation, where the roughness exponent is predicted to be $\alpha = (4-d)/2 = 1$, the growth exponent, is predicted as $\beta = (4-d)/8 = 2/8 = 0.25$, and the dynamic exponent $z = 4$ where $d = 2$ is the substrate dimension [4-5]. The error may be due to the limited number of AFM measurements. In this experiment, two spots per sample were measured. In addition to that, some error also may be due to the effect of grain boundaries, which are not included in Eq. (17).
4.3.5. Grain size distribution of CdTe

All of the above have been from AFM measurements and complementary information can be gotten from SEM images, including the grain size distribution. The grain size follows a log-normal distribution summarized in Figure 4-17.

\[
f(D)dD = \frac{1}{\sqrt{2\pi}\sigma D} \exp\left(-\frac{(\ln D - \mu)^2}{2\sigma^2}\right)dD
\]

(18) [4-17]

where \( D \) is the grain diameter, \( \sigma \) is the standard deviation of \( \ln(D) \) and \( \mu \) is the mean of \( \ln(D) \).

![Figure 4-17: Grain size distribution (the mean grain size is indicated by arrows and given as numbers)](image)

Figure 4-17. Grain size distribution (the mean grain size is indicated by arrows and given as numbers)

From the SEM images in Figure 4-11, the area of each grain was calculated by ImageJ software. Then, a grain size, \( D = \sqrt{\text{Area}} \) was calculated and summarized in
Figure 4-17. Approximately 80 to 250 grains were used for each plot. Grain size follows the log-normal distribution. The solid line is a fitting with a log-normal distribution. The average grain size, distribution width, and sigma are calculated from raw data, not from the natural log of the data. Then, they are used to do a log-normal fit to the raw data. In these fittings, a scale factor is used because x in the denominator of the fit is grain size, which is not a normalized value. The scaling factor turned out to be similar numbers between 22 ~ 24. Figure 4-17 (f) appears to deviates from the log-normal distribution due to much smaller sampling size.(~ 80)

Note that the average grain size increases as deposition time increases from 30, to 60, and 120 min. Again, CdS/CdTe(7.5 min) has a reduced average grain size, which undoubtedly indicates CdS/CdTe intermixing. The same trend is shown in the roughness.

![Graph of Thickness versus Grain Size](image)

**Figure 4-18.** Thickness versus grain size
A study of magnetron sputtered aluminum [4-18] indicates that when the surface diffusion and grain growth are competing, the thickness versus grain size has a slope of 0.25 ~ 0.5. Our slope of 0.36 is within that range. The study also showed that for thickness above 100 nm, smaller grains decay due to surface diffusion and larger grains coarsen due to grain growth. The error bar in Figure 4-18 is large because it covers minimum to maximum of grain sizes. However, the average grain size clearly shows the power law relationship between the thickness and the grain size of the films.

![Graph](image.png)

**Figure 4-19.** Average grain size versus (roughness) width

Figure 4-19 shows a strong linear relationship between average grain size and width. The linear relationship between grain size and width can be explained by the nucleation and growth model depicted in Figure 4-20.
Figure 4-20. Grain growth shapes [From Ref. 4-19]

Figure 4-20 shows how the surface roughness and grain size increase as the polycrystalline thin film gets thicker. It starts from nucleation of the atoms on the surface, pre-coalescence. When two islands touches each other coarsening starts. The bigger island got bigger and smaller one get smaller. The bigger island became a bigger grain in area and it gets thicker as deposition goes on. However, if substrate temperature is not high enough, grain becomes like a cone shape and the roughness in the grain increases because the grain boundary works as a diffusion barrier. This model explains the growth of our as-deposited CdTe films very well.
4.3.6. Conclusion of CdTe surface analysis

From the scaling of the surface roughness of the AFM data, the growth, roughness, and dynamic exponents of RF-sputtered CdS/CdTe film were calculated. (I found the roughness exponent $\alpha \approx 1$, growth exponent $\beta = 0.22 \sim 0.28$, and dynamic exponent $z = 4.2 \sim 4.6$). These values are close to the theoretical values obtained from the fourth-order linear equation. This means that the growth mode of films by rf-sputtering is very similar to that of molecular beam epitaxy (MBE). In both cases, atoms arrive on the surface and they diffuse until they meet a kink which has more than one bond. That process repeats in the next atoms until they fill in the whole substrate. The differences between MBE and sputtering are that in MBE, impurities are very low and deposition is very slow. Besides, MBE is done in much higher temperature than sputtering. Therefore, atoms have enough time and kinetic energy to diffuse and form epitaxial layer. For sputtering, the effects of Ar bombardments, impurity of the sputtering source, and higher deposition rate contribute to form polycrystalline material.

4.4 Surface analysis of CdSe

4.4.1. Background of CdSe surface study

Although CdTe solar modules are increasing their market share due to their low cost, it must still become cheaper to compete with conventional electricity generation, such as coal and nuclear. While researchers are trying to increase the efficiency of CdTe solar cells, the other approach is to make stacked solar cells with different band gap materials to improve the utilization of the solar spectrum and increase overall efficiency.
The simplest multiple junction is a tandem, which consists of a higher bandgap top cell and a lower bandgap bottom cell. One study [4-20] showed that tandem solar cells with 1.7 eV top cell and 1.1 eV bottom cell will give optimum power generation. For the bottom cell, CIGS solar cell has 1.1 eV and is commercially available. For the top cell, CdSe is best suited for that because it has a bandgap of 1.7 eV.[4-20, 4-21] CdSe was widely studied for electrodes for photoelectrochemical (PEC) solar cells[4-22], and transistors[4-23], and detectors[4-24], and there is a report of about 6 % efficiency in polycrystalline CdSe solar cell [4-25, 4-26, 4-27], but, a tandem solar cell using CdSe at the top cell has not yet been reported.

One of the difficulties comes from different optimum temperatures for each semiconductor layer.[4-20] Sometimes multiple layers need different substrate temperatures; properties of an earlier deposited layer and surface morphology are affected by the later layer. Hence, the temperature dependence of surface roughness and growth mode plays an important role in tandem device fabrication. However, not much work has been done to investigate surface morphology or growth mode of CdSe films. To address the changes in temperature-dependent surface morphology for tandem solar cell application, a single-layer of CdSe films were deposited in various substrate temperatures and surface morphology was measured by AFM, then growth mode was analyzed by scaling theory in a similar manner as it was done in CdTe solar cells.

4.4.2. Experimental details

Polycrystalline CdSe films were deposited on aluminosilicate glass by RF-sputtering. Previously, CdS/CdTe films were deposited in Tec15/HRT glass to get the
growth information of the actual solar cell structure. In the similar sense, to compare to the data of the record efficiency CdSe solar published in the literature [4-22], which was deposited on smooth microscope slides, a smooth glass was chosen as a substrate. Durability in high temperature and chemical resistance was another reason of the choice. Deposition is done at 10 mTorr of Ar environment and RF power of 50 W for 2 inch diameter, 99.995% CdSe sputtering target, which was purchased from Materion materials. Only substrate temperatures were changed and other conditions, such as deposition pressure, gas flow rate and RF power, film thickness were kept the same. Depositions were done at 25°C, 100°C, 200°C, 250°C, 310°C. One difference from CdTe deposition is that heating is done by tantalum wire and substrate was fixed during the deposition. The AFM settings were the same as described in the CdTe section except that the scan area was 10 um × 10 um.

4.4.3. Roughness exponent of CdSe

Figure 4-21. AFM images of CdSe films grown at different temperatures. (x = 10 μm, y = 10 μm, z = 200 nm scale). (Thickness of all the samples = 1.21 ± 0.03 μm)
The AFM images in Figure 4-21 show that the roughness of the CdSe films increases with substrate temperature. In particular, the large-scale, saturated width $w_s$ increases from 6.2 nm to 34 nm with increasing substrate temperature from 25°C to 310°C (Figure 4-21 and Table 4.5). In addition, the width $w(l)$ measured over a size of $l \times l$ increases with the scan size $l$ and saturates for a large $l$. This indicates the roughness exponent $\alpha \approx 1$. I note that the total scan size $L$ is large enough to get significant surface information for these films because it saturated before the size reaches 10 µm. Using the saturated value of the surface roughness $w_s(T)$ and the correlation length $\xi$, I have obtained an excellent scaling shown in Figure 4-25.

The grain size gets bigger and porosity characterized by voids between grains increases with increasing substrate temperatures. For example, the 310 °C sample has more than 10 times bigger grains than that of 100 °C sample.

![Figure 4-22. SEM images of CdSe films (x = 4000 nm, y = 3200 nm)](image)
Figure 4-23. (a) SEM and (b) AFM images of the same sample (310 °C) in the same scale. (SEM image x = 4 µm, AFM image x = 10 µm)

The AFM image captures the reality of the surface morphology very well and AFM and SEM images agree well when considering grain size and shape. The peak height of the AFM image is approximately 250 nm scale(Color bar in Figure 4-23 (b)). The average width (RMS roughness) is 51 nm.(Table 4.5) Compared with 3-D AFM images in Figure 4-21, this 310 °C sample has a much rougher and more porous surface than surfaces deposited at lower temperatures.
Figure 4-24. The RMS roughness of CdSe films deposited at different substrate temperatures as function of scan length $l$

Figure 4-25. Scan size vs. Average width (Slope shows the roughness exponent $\alpha$)
Table 4.5 Correlation length summary of CdSe

<table>
<thead>
<tr>
<th>Substrate temperature(°C)</th>
<th>25</th>
<th>100</th>
<th>200</th>
<th>250</th>
<th>310</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlation length ξ (nm)</td>
<td>110</td>
<td>150</td>
<td>170</td>
<td>280</td>
<td>310</td>
</tr>
<tr>
<td>Saturated width w_s (nm)</td>
<td>2.9</td>
<td>6.6</td>
<td>7.0</td>
<td>19.0</td>
<td>51.0</td>
</tr>
</tbody>
</table>

Figure 4-25 shows a good scaling of the width data and the roughness exponent α is close to 1. As discussed in CdTe section, the correlation length summarized in Table 4.3 increases as the grain size increases, as shown in SEM images. (Figure 4-22) For example, 310 °C sample has the biggest grain which is approximately 300 ~ 500 nm sizes. That is consistent with correlation length of 310 nm in Table 4.3 Therefore, I can reconfirm that grain boundaries define the correlation length as a result of hindering interactions among atoms.

4.4.4. Growth exponent of CdSe

![Figure 4-26](image_url)

**Figure 4-26.** Structure factor (power spectrum) of the CdSe films (Multiplied by 10 for each interval)
From Figure 4-26, the slope of the structure factor (or power spectrum) is $-\gamma$. Since the roughness exponent $\alpha = 1$ (Figure 4-24), $S(k,t) = k^{-\gamma}$. Thus, the slope in Figure 4-26 becomes $-\gamma$. We can get the growth exponent $\beta$ from Eq.(4). $\beta = \frac{\alpha}{z}$ From Eq.(5), for $k \gg 1/\xi(t)$, scaling function $s(x)$ is constant.

Table 4.6. Structure factor’s slope ($-\gamma$) of CdSe

<table>
<thead>
<tr>
<th>Substrate temperature</th>
<th>25 °C</th>
<th>100 °C</th>
<th>200 °C</th>
<th>250 °C</th>
<th>310 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope ($-\gamma$)</td>
<td>-5.2 ± 0.1</td>
<td>-5.2 ± 0.1</td>
<td>-5.2 ± 0.1</td>
<td>-5.0 ± 0.1</td>
<td>-5.1 ± 0.1</td>
</tr>
</tbody>
</table>

Figure 4-27. Band gap calculation from line of sight transmission from CdSe films deposited at different substrate temperatures. Estimated band gaps are shown in arrows and written with the temperature in the legend.

The band gap increases from 1.62 eV to 1.71 eV as substrate temperature increases. Note that the slope of the absorption edge gets sharper and interpolates to a higher energy at a high substrate temperature. This indicates that crystallinity increases as substrate temperature increases. For all temperatures, except 25 °C, the slope and changes
in bandgap with temperature are evident. For 25 °C sample, 1.62 eV may have an error due to the difficulty of finding slope from less evident curve.

![Figure 4-28. XRD of CdSe films deposited at different substrate temperatures.](image)

CdSe has a strong (002) preferential orientation in most of the substrate temperatures tested; from 100 °C to 250 °C other peaks coexist with (002) peak; however, the (002) peak disappeared at 310 °C, indicating drastic changes in the preferred orientation. That may explain the large faceted grains in the SEM image which could have different crystal orientations than the smooth films deposited at lower temperatures.

### 4.4.5. Conclusion of CdSe surface analysis

The surface roughness of the RF-sputtered polycrystalline CdSe film increases as substrate temperature increases. Therefore, although it makes highly crystalline film at 310 °C, slightly lower temperature such as 250 °C will be a better choice for smoother interface with the following layer. From the scaling of the roughness of the AFM data,
the roughness exponent ($\alpha$) is close to 1. The growth exponent ($\beta$) is 0.19 ~ 0.20. Again, this growth mode may be explained by Eq. (17), which is diffusion dominated surface growth.

From the AFM studies of sputtered CdTe and CdSe films there are a few notable findings:

First, regardless of the material and the configurations of the deposition chambers (CdTe deposition was done on rotating substrates with tilted angle with the gun, while CdSe was deposited on fixed substrates with normal incidence with the gun), they give similar exponents, which can be explained by the fourth-order linear equation in Eq. (17). This means that films deposited by sputtering processes have similarities in morphology regardless of other conditions.

Second, from the grain size distribution of CdTe films, it is interesting to note that the roughness and grain size have linear relationship. (Figure 4-19) The films get rougher as grain size increases. It is quite evident that since the average grain size $D_{av} \sim l$ with roughly $\alpha = 1$, increasing the average grain size means a linear increase in the surface roughness. Third, from the CdSe AFM, the surface roughness increases as substrate temperature increases. From the SEM images, the grain size increase with increasing temperature can be verified. (Figure 4-22) Therefore, grain sizes are defined by the dynamic process of increased diffusion due to a high substrate temperature and grain boundary barrier height. It seems that growth temperature 310 °C does not supply high enough kinetic energy to completely overcome the grain boundary barriers.
Chapter 5

Studies of Polycrystalline Tandem devices

5.1 Background of the tandem solar cell

Constructing a multiple-junction device is an alternative way to improve the efficiency of a solar cell by utilizing a larger portion of the solar spectrum. When solar cells with different bandgaps are stacked mechanically, or deposited successively with interconnecting layers, they could generate more power than a single junction solar cell. This concept has worked successfully in epitaxially grown GaAs multiple-junction and a-Si n-i-p solar cells. Although the GaAs type multiple-junction solar cell gives high efficiency, epitaxial growth is not a suitable method for mass production of terrestrial solar module due to high costs. Also, a-Si triple junction solar cells are not advantageous over other single-junction devices, such as CdTe or CIGS, due to relatively low overall efficiency.

Recently, CdTe solar module achieved a manufacturing cost target of $0.73/peak watt [5-1], however, electricity generation costs from most solar panels is still higher than that of conventional methods. For example, according to one EIA report [5-2] regarding average levelized cost of electric generating technologies entering service in 2017,
conventional coal has 97.7 (2010 $/ MWh), advanced natural gas fire plant has 63.1 (2010 $/MWh), and advanced nuclear is 111.4 (2010 $/ MWh), while solar photovoltaic (PV) is 152.7 (2010 $/MWh). That’s because solar cell has low (25 %) capacity factor due to limited operation only during day time. Another reason is that there are other costs in addition to the solar module cost such as inverter, installation, balance of system (BOS), and margins. BOS refers to the necessary system components to generate electricity from solar module such as installation material, charge controller, and batteries.[5-3] Studies show that actual cost for power generation, semiconductor material cost is approximately 10 % of average sales price (ASP) of an installed CdTe solar panel [5-4, 5-5]. Therefore, if we could increase the power generation (i.e. efficiency) even with slight increase of active semiconductor material cost, that’s the right way to pursue. A tandem structure is the simplest multiple-junction solar cell because it requires only two different bandgap solar cells. One theoretical study [5-6] from Timothy Coutts et al in NREL predicted that a maximum efficiency of 28.2 % is possible if we can properly assemble 1.74 eV top cell and 1.14 eV bottom cell. In the following sections, studies of CdSe for top cells and HgCdTe for bottom cells will be presented. CdSe was chosen because it has bandgap of 1.7 eV at room temperature, which is an ideal bandgap for a top cell. Hg$_x$Cd$_{1-x}$Te was chosen because its bandgap can be adjustable around 1.1 eV (x=0.17) by changing the Hg content.
5.2 CdSe top cell

CdSe has been studied widely for electrode for photoelectrochemical (PEC) solar cells[5-7], transistors[5-8], and detectors[5-9]. CdSe is normally an n-type semiconductor. For a PN junction device, usually a p-type absorber layer is used because most transparent conductive oxides (TCO) are n-type semiconductors. For example, in a CdTe solar cell, the actual structure is glass/n-TCO/n-CdS/p-CdTe/metal(back contact). In a CIGS solar cell, the structure is n-TCO/n-CdS/p-CIGS/Mo back contact)/stainless steel (substrate). In both cases, the sunlight comes through the n-TCO/n-CdS first and goes to the p-type absorber layer. We want the PN-junction to be as close as the incoming side of the sunlight as possible so that the generated electron-hole pairs can be separated efficiently by the strong electric field near the junction. Therefore, if we want to use n-TCO as a front contact and CdSe as the absorber layer, it would be better to a p-type, but p-type conductivity in CdSe was only reported in epitaxially grown CdSe [5-10], not polycrystalline. And p-type doping is known to be difficult.[5-11]

For a p-type/intrinsic/n-type (PIN) solar cell, we need an intrinsic semiconductor which can be doped either p-type or n-type. However, because of difficulties in p-type doping in CdSe, this is not a good option, either.

In 1980, Bonnet and Rickus at the Battelle Institute[5-12, 5-13] first made a metal-insulator-semiconductor (MIS) type CdSe solar cell. For this structure, n-type CdSe can be successfully used as an absorber layer because current collection is done through a rather different mechanism, tunneling through the very thin insulator.
5.2.1. Metal-insulator-semiconductor (MIS) solar cell

An MIS solar cell uses a Schottky barrier potential to separate the electron-hole pair by tunneling, but the photovoltaic characteristic is improved by addition of very thin insulating film (I-layer) in Figure 5-1. [5-12]. Figure 5-1 shows the energy band diagram of an MIS solar cell. In this case, the semiconductor is a 2 µm thick, n-CdSe, the insulating layer is 5 nm ZnSe. Photo-generated holes in the valence band, which are depicted as empty circles in Figure 5-1, can tunnel through this thin insulator, but electrons (filled circle in conduction band) are blocked. It is also known that doping ZnSe with Cu makes a deep acceptor level in ZnSe. Cu-doping is done by evaporating a very thin layer (0.5 nm) of Cu on ZnSe, followed by another metal layer (6 nm Au) and annealed in a N₂ environment at 150 ~ 200 °C. The doping moves the ZnSe band upward (Figure 5-1 dotted box in I-layer), causing holes to flow toward the metal and blocking the flow of energetic electrons toward the metal at the same time. The complete structure is glass\Cr\n-CdSe(1~2 µm)\ZnSe(5 nm)\Au(6 nm).
5.2.2. ZnSe film optimization

To get the best result, the ZnSe layer deposition condition was optimized. The Battelle group used evaporation to deposit individual layers. In our case, we used rf-sputtering to deposit ZnSe as well as CdSe, and evaporation for Cu and Au. Table 5.1 is the summary of ZnSe films deposited in various conditions and light and dark resistivity measurements.

Table 5.1. Various ZnSe deposition condition and light and dark resistivity

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Substrate</th>
<th>Deposition pressure (mTorr)</th>
<th>Gas</th>
<th>Temp.-erature (°C)</th>
<th>RF power (W)</th>
<th>Dep.-osition time(min)</th>
<th>Thickness by Dektak (nm)</th>
<th>Growth rate (nm/min)</th>
<th>Light Resistivity (Ohm-cm)</th>
<th>Dark Resistivity (Ohm-cm)</th>
<th>Light/Dark Resistivity Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ast231</td>
<td>ASG</td>
<td>10</td>
<td>Ar+N₂(4.1 sccm)</td>
<td>25</td>
<td>50</td>
<td>98</td>
<td>740</td>
<td>7.6</td>
<td>Noise</td>
<td>Noise</td>
<td></td>
</tr>
<tr>
<td>Ast232</td>
<td>ASG</td>
<td>10</td>
<td>Ar</td>
<td>210</td>
<td>50</td>
<td>128</td>
<td>650</td>
<td>5.1</td>
<td>9.7E+10</td>
<td>1.3E+13</td>
<td>130</td>
</tr>
<tr>
<td>Ast230</td>
<td>MS</td>
<td>10</td>
<td>Ar</td>
<td>25</td>
<td>50</td>
<td>100</td>
<td>700</td>
<td>7.0</td>
<td>2.3E+10</td>
<td>2.3E+10</td>
<td>1</td>
</tr>
<tr>
<td>Ast160</td>
<td>MS</td>
<td>10</td>
<td>Ar</td>
<td>200</td>
<td>50</td>
<td>96</td>
<td>440</td>
<td>4.6</td>
<td>7.2E+09</td>
<td>7.2E+09</td>
<td>1</td>
</tr>
<tr>
<td>Ast171</td>
<td>ASG</td>
<td>10</td>
<td>Ar</td>
<td>240</td>
<td>60</td>
<td>170</td>
<td>1060</td>
<td>6.2</td>
<td>6.9E+09</td>
<td>2.8E+12</td>
<td>400</td>
</tr>
<tr>
<td>Ast234</td>
<td>ASG</td>
<td>10</td>
<td>Ar</td>
<td>310</td>
<td>50</td>
<td>289</td>
<td>610</td>
<td>2.1</td>
<td>7.9E+08</td>
<td>3.2E+11</td>
<td>400</td>
</tr>
</tbody>
</table>

(*MS and ASG stands for microscope slides and aluminosilicate glass, respectively.)

From Table 5.1, all the ZnSe films give high light and dark resistivity of more than 10^9 Ohm*cm, except for the deposition done at 310 °C, which has light resistivity of 8*10^8 Ohm*cm. Compared with light and dark resistivity of CdSe, ~10^6 Ohm*cm, most of the films have three orders of magnitude higher light and dark resistivity values, which is suitable for the insulating layer. Three samples (Ast232, 171, 234) on ASG showed strong photo-resistivity, but two samples (Ast230, 160) on MS did not. It is not clear whether this is substrate related issue or other parameters caused this, but at least we could see that ZnSe is a photosensitive material and it could reduce resistivity by 130 ~ 400 times when light shines on it. This could be an issue if we need high resistive
insulator layer for MIS solar cell. Ultimately, the highest light resistivity film (Ast232) would work best for the insulator layer.

![XRD of various ZnSe depositions](image)

**Figure 5-3.** XRD of various ZnSe depositions

The ZnSe film grown at 310 °C (ast234) doesn’t show preferential orientation in XRD and it shows very rough surface with crescent shaped grains in SEM (Figure 5-4 (d)). It seems that 310 °C is too high to make smooth film with high resistivity. The film grown at room temperature (ast230) shows a relatively weak (111) preferential orientation and a porous surface in SEM images (Figure 5-4 (a)). The film grown with Ar+N₂ didn’t show any peak, which indicates the amorphous nature of the film due to reactive sputtering with N₂.
ZnSe can have either cubic or hexagonal structure. Ast171 and ast234 show the hexagonal (102), (103) peaks, which do not appear in the cubic structure. Ast160, ast230 have approximately 0.8% of in-plane tensile strain based on the strongest peak at 27.71° (2θ) and cubic (111) peak position at 27.48° (2θ) from XRD database (01-080-0021).

Ast232, which was the first heated deposition after cryo-pump regeneration, gives the highest XRD intensity and the least in-plane tensile strain (0.19%) and smooth film. This implies that lower base pressure after cryo-pump regeneration is one important factor to fabricate a highly crystalline film, but also substrate temperature is important, too.

Because room temperature deposition (Ast230) has weaker XRD intensity and higher strain than film deposited at 200 °C (Ast232).

Figure 5-4. SEM of various ZnSe films
5.2.3. CdSe film optimization

My temperature dependent CdSe deposition study is summarized in Chapter 4, Section 2. It showed that the surface gets rougher as deposition temperature increases. Therefore, for smooth junctions needed for a good Schottky junction, it would be better to do the deposition below 310 °C.

Different post deposition treatments were evaluated using photoluminescence (PL) in Chapter 3, Section 3. It showed that all as-deposited samples give very weak PL and air annealing gives strong band edge PL, however, strong midgap PL exists with them. In general, midgap states have detrimental effects in solar cells because they work as recombination centers to hinder current collection.

5.2.4. MIS device on Cr contact

The structure of an MIS solar cell is shown in Figure 5-2. Table 5.2 summarizes the deposition parameters of the Battle group and mine. The Battelle group made a CdSe evaporation source using high purity (6N) elemental Cd and Se powder. They used evaporation for CdSe and ZnSe depositions, while I used RF-sputtering for CdSe and ZnSe depositions from a commercial sputter target (4N). This may be an important factor in high quality thin film fabrication because Battelle group also had some issues in using commercial CdSe compound, initially. After they made CdSe compound with 6N high purity elemental Cd and Se powder, they got the good result.[5-13]
### Table 5.2. MIS solar cell deposition parameters.

<table>
<thead>
<tr>
<th></th>
<th>Dieter Bonnet/Battelle papers</th>
<th>Our samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Microscope slides</td>
<td>Microscope slides or Tec7</td>
</tr>
<tr>
<td>Cr</td>
<td>100 nm RF or DC sputtering</td>
<td></td>
</tr>
<tr>
<td>CdSe</td>
<td>2 µm (Evaporation at 425 °C)</td>
<td>~ 1 µm (RF sputtering at ~ 220 °C)</td>
</tr>
<tr>
<td>ZnSe</td>
<td>5 nm</td>
<td>~ 7 nm (RF sputtering at ~ 220 °C)</td>
</tr>
<tr>
<td>Cu</td>
<td>0.5 nm</td>
<td>0.5 ~ 2 nm</td>
</tr>
<tr>
<td>Au</td>
<td>6 nm (Area: ~ 1 cm²)</td>
<td>6 ~ 20 nm (Area: 0.031 ~ 0.062 cm²)</td>
</tr>
<tr>
<td>Annealing</td>
<td>30 min with N₂ flow at 200 °C</td>
<td>30 min with N₂ flow at 200 °C</td>
</tr>
<tr>
<td>Grid (Au)</td>
<td>Not used</td>
<td>Not used</td>
</tr>
<tr>
<td>Anti-reflection</td>
<td>5.5 nm ZnS</td>
<td>Not used</td>
</tr>
</tbody>
</table>

Chromium (Cr) was used as a back contact because it is one of the "glue" or "binder" layers that works well in providing adhesion on glass due to the fact that chromium is oxygen active and reacts chemically with the oxide surface.[5-14]

CdSe was chosen for an active absorber layer because it is a direct semiconductor with a high (1.7 eV) band gap suitable for a top cell of the tandem device. According to Rickus, [5-13] CdSe is very stable material that they showed was insensitive to humidity.

ZnSe was chosen for an insulator layer based on the study of Bonnet and Rickus [5-13] that among 12 different insulator materials, only ZnSe and Sb₂Se₃ resulted in good photovoltaic properties. Other materials such as ZnS, Sb₂S₃, SiO, LiF showed either low \( J_{sc} \) or \( V_{oc} \).

Au was chosen for a front contact because it gave the second highest \( V_{oc} \) among metals such as indium (In), titanium (Ti), antimony (Sb), aluminum (Al), silver (Ag), copper (Cu), tellurium (Te), palladium (Pd), platinum (Pt) before annealing. And it gave the highest \( V_{oc} \) after annealing from the study of Rickus and Bonnet.[5-15]
Table 5.3. MIS solar cell layer thickness

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Condition</th>
<th>Layer thickness. (MS stands for Microscope slide)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AST164A</td>
<td>Without annealing</td>
<td>MS/Cr/CdSe(~1µm)/ZnSe(6.7nm)/Au(6nm)</td>
</tr>
<tr>
<td>AST164A2</td>
<td>After anneal with N₂ 30 min at 200°C</td>
<td>MS/Cr/CdSe(~1µm)/ZnSe(6.7nm)/Au(6nm)</td>
</tr>
<tr>
<td>AST166A2</td>
<td>Tec7 without Cr</td>
<td>Tec7/CdSe(~1µm)/ZnSe(6.7nm)/Au(20nm)</td>
</tr>
<tr>
<td>AST168B1</td>
<td>0.5 nm Cu added</td>
<td>MS/Cr/CdSe(~1µm)/ZnSe(6.7nm)/Cu(0.5nm)/Au(6nm)</td>
</tr>
<tr>
<td>AST168C1</td>
<td>Smaller Area Cell</td>
<td>MS/Cr/CdSe(~1µm)/ZnSe(6.7nm)/Cu(0.5nm)/Au(6nm)</td>
</tr>
<tr>
<td>AST172B1</td>
<td>Tec7/thin Cr(20nm)</td>
<td>Tec7/Cr(20nm)/CdSe(~1µm)/ZnSe(6.7nm)/Cu(0.5nm)/Au(6nm)</td>
</tr>
</tbody>
</table>

Controlling the thickness of a very thin ZnSe layer was one of the challenges. Although, an in-situ thickness monitor using laser interference fringes was used, the required thickness was less than one fringe, which is hard to track accurately. Therefore, a 330 nm thick ZnSe deposition was made first for 90 minutes and the estimated time (1min 50sec) was used to make 6.7 nm thick deposition. Another issue was that even after shutter was opened, actual deposition might not have started right away. Laser interference fringe measurements in reflection generate a sinusoidal intensity (current) response from the silicon detector. Normally, after opening the shutter, the film starts to be deposited on the substrate and sinusoidal intensity change of the Si detector’s current signal can be monitored. However, sometimes it had very slow rate of deposition in the beginning of the deposition. This is probably related to the dependence of growth nucleation on the details of the surface preparation.
**Figure 5-5.** Slow deposition rate at the beginning of ZnSe deposition

Figure 5-5 shows an example of slow deposition rate in the beginning. The average deposition rate was approximately 6 nm/min for this one. But, for initial 13 minutes, deposition rate was 0.04 nm/min. The conditions of the two depositions were not exactly the same. For example, this was ZnSe deposited on microscope glass without CdSe and the substrate temperature was lower than that of the MIS device (200 °C in MIS, this one was 140 °C). However, if a similar event like this had happened to ZnSe layer in MIS device, the thickness of ZnSe insulator layer would be very thinner than we had estimated by the deposition time.

In an MIS type device, the insulator (ZnSe) thickness is critical. If it is less than 3 nm, it may have too many pinholes and short the junction. If it is too thick, tunneling can not happen efficiently. [5-16] Table 5.4 summarizes the of JV result of JV MIS type solar cells.
**Table 5.4. MIS solar cell performance result**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Condition</th>
<th>(V_{oc}(V))</th>
<th>(J_{sc}(mA/cm^2))</th>
<th>FF (%)</th>
<th>Eff (%)</th>
<th>(R_s(\text{Ohm cm}^2))</th>
<th>(R_{sh}(\text{Ohm cm}^2))</th>
<th>Area (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AST164A</td>
<td>Without annealing</td>
<td>0.18</td>
<td>0.70</td>
<td>31.3</td>
<td>0.04</td>
<td>158</td>
<td>367</td>
<td>0.062</td>
</tr>
<tr>
<td>AST164A2</td>
<td>Annealed with (N_2) 30 min at 200 °C</td>
<td>0.45</td>
<td>1.03</td>
<td>30.0</td>
<td>0.14</td>
<td>260</td>
<td>628</td>
<td>0.062</td>
</tr>
<tr>
<td>AST166A2</td>
<td>Tec7 without Cr</td>
<td>0.19</td>
<td>0.87</td>
<td>31.4</td>
<td>0.05</td>
<td>99</td>
<td>317</td>
<td>0.062</td>
</tr>
<tr>
<td>AST168B1</td>
<td>0.5 nm Cu added</td>
<td>0.57</td>
<td>1.07</td>
<td>31.5</td>
<td>0.19</td>
<td>418</td>
<td>800</td>
<td>0.062</td>
</tr>
<tr>
<td>AST168C1</td>
<td>Smaller Area Cell</td>
<td>0.59</td>
<td>0.85</td>
<td>27.8</td>
<td>0.14</td>
<td>565</td>
<td>897</td>
<td>0.031</td>
</tr>
<tr>
<td>AST172B1</td>
<td>Tec7/Thin Cr(20nm)</td>
<td>0.15</td>
<td>1.12</td>
<td>26.5</td>
<td>0.05</td>
<td>94</td>
<td>153</td>
<td>0.062</td>
</tr>
<tr>
<td>AST172B1 _Bar</td>
<td>AST172B1 measured in superstrate configuration.</td>
<td>0.00</td>
<td>0.05</td>
<td>0</td>
<td>0</td>
<td>40</td>
<td>40</td>
<td>0.062</td>
</tr>
</tbody>
</table>

Many devices showed decent \(V_{oc}\), but poor \(J_{sc}\). I suspect that this might be related to the poor control of very thin ZnSe thickness. The results indicate a few things. First, \(N_2\) annealing improved \(V_{oc}\). Second, Cu doping improved \(V_{oc}\) even more. Third, Tec7 glass does not give good \(V_{oc}\) regardless of starting the device with and without the Cr adhesion layer. It maybe due to the rough surface of Tec glass might have shadowy area which was not covered by thin ZnSe resulting in a poor tunneling junction.
Figure 5-6. JV of CdSe MIS-type solar cell

Figure 5-6 is the JV graph of the best MIS-type solar cell. It shows a high $V_{oc}$ (650 mV), but small FF and very weak $J_{sc}$. It also shows a rollover in the first quadrant. The JV is quite different from the ideal JV of the one-diode model. It seems that more than two diodes are combined in this device. I suspect that this is due to non-uniformity of the tunneling junction, which shows different response to the applied voltage.

To overcome this issue, a device with very thick ZnSe (90 nm) was fabricated. For this device, after ZnSe, 0.5 nm Cu was also evaporated and diffused during the annealing. In this case, the device should function as a PN-junction device between n-CdSe and Cu-doped p-ZnSe because of the low possibility of tunneling through thick
ZnSe layer. Figure 5-7 shows the picture of the device on a microscope slide and a sketch of the cell structure of it.

![Microscope slide](image1)

**Figure 5-7.** Best CdSe solar cell on Cr contact

The Cr layer was DC-sputtered on a clean microscope slide with 90W of power at room temperature in Ar. Then, it was moved to the CdSe/ZnSe deposition chamber. CdSe and ZnSe were RF-sputtered at the substrate temperature of 300°C without breaking the vacuum. Both RF powers were set to 50W, deposition pressure was 10 mTorr in Ar. Then, the device was heat annealed under N$_2$ flow up to 400 °C for 30 minutes. After that, 0.5 nm Cu, 20 nm Au were evaporated through a mask. Finally, the device was annealed at 150°C under room air for Cu diffusion. A razor blade was used to make mechanical scribing around the cell and indium was soldered around to make good contact to the Cr layer. Figure 5-6 (c) shows the Cr layer on a microscope slide. Cr layer had very good adhesion to the glass and very hard to remove by a razor blade. Then, JV and QE measurements were done.
**Figure 5-8.** JV of the best CdSe top cell on Cr

The efficiency of the device was still very low; however, it shows a better efficiency than the previous one shown in Figure 5-6. It also shows a very nice JV curve (no rollover and smooth rectification pattern of one diode). This is definitely not an MIS-type device because it has a very thick (90 nm) ZnSe layer, too thick for the tunneling.
Figure 5-9. QE of the best CdSe top cell on Cr

Figure 5-9 is the quantum efficiency (QE) of the CdSe device on Cr shown in Figure 5-7 and 5-8. The wavelength cut-off near 730 nm matches well with CdSe band gap of 1.7 eV. The cell has 20 nm thick Au layer for front contact which sunlight has to pass through. However, if thinner Au layer and anti-reflection coating had been used, they may have increased the QE. In this experiment, because this was the first trial of the CdSe solar cell in our lab, relatively thick (20 nm) Au was used to eliminate the possibility of the measurement error due to pogo pin scratch. An anti-reflection coating was not used either because it would not make big difference. However, the overall shape looks reasonable as a top cell. Transmission for $\lambda > 700$ nm will supply enough light for a lower bandgap bottom cell to operate. For two-terminal tandem, it is usually estimated that 2/3 of the power should come from the top cell, and rest is from the bottom cell.[5-6]
That means top CdSe device should have at least 12–13 % efficiency to compete with 17.5 % single junction CdTe or 20 % CIGS device. Although this device works, there is clearly much work needed to reach higher efficiencies.

5.2.5. CdSe solar cell on AZO contact

One issue of using Cr as back contact is its opacity. For a tandem solar cell, all layers of the top cell should be transparent so that bottom cell gets maximum sunlight to operate. Therefore, I fabricated a CdSe device on a transparent aluminum doped zinc oxide (AZO) contact. Until the previous experiment, the CdCl$_2$ treatment system for CdTe solar cells was shared for CdSe device heat annealing. Every effort was made to avoid cross contamination from CdTe or CdCl$_2$ residue in the system. For example, I used a new graphite block for CdSe treatment only. I also baked out graphite block before the treatment to remove the moisture in the block. The system was purged with N$_2$ more than 5 minutes before actual annealing.
However, starting with this experiment, I set up the tube furnace system for CdSe film use only. Figure 5-10 shows the picture of the system. It is consisted of a top and bottom heating unit connected with a hinge. The heating units are powered by a Variac. Samples are enclosed by top and bottom graphite blocks and positioned at the center of the 1.2 inch diameter pyrex glass tube. Both ends of the tube are closed by the rubber stopper which has gas line and thermocouple line. Temperature is controlled by PID controller and recorded by Labview program. Dry air or N\textsubscript{2} gas can flow during the annealing and the flow rate can be set and monitored by a flow meter. One disadvantage of tube furnace is slow heating up and cooling down compared to CdCl\textsubscript{2} treatment system. However, the temperature recording showed a reliable heating and cooling profile for consistent heat annealing as shown in Figure 5-10.
This experiment was prepared to explore the effect of the substrate, conductive layer, high resistivity transparent (HRT) layer, and effects of annealing such as N\textsubscript{2}, dry air, and wet CdCl\textsubscript{2} treatment.

I used three different substrates: Tec15/HRT; aluminosilicate glass (ASG); microscope slide (MS). And three different conductive layers: SnO\textsubscript{2} in Tec15/HRT; aluminum doped zinc oxide (AZO); Cr. Finally, three different annealing conditions were
used: N₂ annealing was done for 20 min at 400 °C; air annealing was done for 20 min at 400 °C; wet CdCl₂ treatment was done for 20 min at 400 °C with dry air flow.

Table 5.5. Maximum efficiency of the cells in various test conditions

<table>
<thead>
<tr>
<th>Substrate/Conductor/HRT</th>
<th>Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N₂</td>
</tr>
<tr>
<td>Tec15/HRT w. HRT</td>
<td>(a) 0.11 %</td>
</tr>
<tr>
<td>Tec15/HRT w/o. HRT</td>
<td>(d) 0.09 %</td>
</tr>
<tr>
<td>ASG/AZO w. HRT</td>
<td>(g) 0.15 %</td>
</tr>
<tr>
<td>ASG/AZO w/o. HRT</td>
<td>(j) 0.24 %</td>
</tr>
<tr>
<td>MS/Cr w/HRT</td>
<td>(m) 0.00 %</td>
</tr>
<tr>
<td>ASG/Cr w/o. HRT</td>
<td>(q) 0.00 %</td>
</tr>
</tbody>
</table>

(Tec15/HRT=HRT coated Tec15 glass, ASG=Aluminosilicate glass, MS=microscope slide, HRT = high resistivity transparent layer (ZnO), AZO=aluminum doped zinc oxide, w.=with, w/o.=without)

Below is the summary of the findings.

**Finding 1.** N₂ annealing has better efficiency than CdCl₂ activation.

**Finding 2.** HRT doesn’t improve the cell efficiency. (j) has higher efficiency than (g).

**Finding 3.** Wet CdCl₂ treatment damages the junction. They have lower efficiency than N₂ annealed or even untreated sample, (p). Visually, N₂ annealing left smooth surfaces; however, air annealing and wet CdCl₂ left rough surface.

**Finding 4.** Dry air annealing made a short circuit in junction.

---

2 Wet CdCl₂ treatment means that CdCl₂ + methanol saturated solution is dropped directly to the sample. After methanol evaporates, it is heated up in a tube furnace at 400 °C for 20 minutes enclosed by graphite blocks under dry air flow. After cooled down, the sample is rinsed with methanol to remove the residual CdCl₂ powder and dried with N₂ jet.
Finding 5. Tec glass didn’t have better results than AZO on ASG.

Because Tec15/HRT didn’t have good result and Cr is not a preferred contact for CdSe solar cell and used temporarily for initial optimizing, below only the results of Ast316 are presented in detail to get meanings of the results clearly.

Table 5.6. Ast316 structure and annealing conditions and efficiency

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Structure</th>
<th>Post deposition treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ast316A</td>
<td>AZO/ZnO/CdSe/ZnSe</td>
<td>N₂ anneal</td>
</tr>
<tr>
<td>Ast316B</td>
<td>AZO/CdSe/ZnSe</td>
<td>N₂ anneal</td>
</tr>
<tr>
<td>Ast316C</td>
<td>AZO/ZnO/CdSe/ZnSe</td>
<td>Wet CdCl₂ treated in dry air</td>
</tr>
<tr>
<td>Ast316D</td>
<td>AZO/CdSe/ZnSe</td>
<td>Wet CdCl₂ treated in dry air</td>
</tr>
<tr>
<td>Ast316E</td>
<td>AZO/ZnO/CdSe/ZnSe</td>
<td>Dry air annealed</td>
</tr>
<tr>
<td>Ast316F</td>
<td>AZO/CdSe/ZnSe</td>
<td>Dry air annealed</td>
</tr>
</tbody>
</table>

(For Ast316, substrate was ASG, front contact was Cu (5 Å)/Au (100 Å))

Figure 5-12. Efficiency, Jₜₛᶜ and V₀ᶜ of Ast316 (18 ~ 20 dot cells of 0.062 cm² area for each sample)
**Finding 1.** N₂ annealed A, B samples have better efficiencies than CdCl₂ treated C, D or dry-air annealed E, F. It is primarily because of high $V_{oc}$ (Figure 5-12 (b)) and high shunt resistance (Figure 5-13 (c)). That means the PN-junction is in good condition.

**Finding 2.** A ZnO HRT layer didn’t improve the performance of the devices. Sample A has a ZnO layer and B does not. A has higher fill factor (Figure 5-13 (a)), but the $J_{sc}$ is lower, and resulted in lower efficiency than B. The HRT layer usually helps the efficiency for CdS/CdTe devices, perhaps because it is superstrate configuration and the PN-junction is closer to the glass, which is usually less than 100 nm, which is more vulnerable to the diffusion of impurities from the glass. However, for this CdSe/ZnSe solar cell, the junction is near the back contact, thus it seems to be not affected much by the existence of the HRT layer which is 1 µm below the PN-junction.

**Finding 3.** CdCl₂ treated cells C and D have the lowest shunt resistances (Figure 5-13 (c)), although they have the highest $J_{sc}$ (Figure 5-12 (c)). That means that either the
PN-junction is damaged or the front and back contacts are short circuited by pin holes. For CdS/CdTe devices, the wet CdCl$_2$ treatment procedure probably doesn’t cause any damage because the PN-junction is near the TCO and hidden from direct surface contacts where surface gets rougher, and gets alternately wet and dry, and experiences physical force from the N$_2$ jet. For CdSe/ZnSe devices, it seems that CdCl$_2$ treatment is beneficial to increase the current generation, but at the same time, it damages the PN-junction and blocks the current collection.

**Finding 4.** Air is doing detrimental effect to CdSe/ZnSe devices. Sample E and F were heat annealed with dry air and both have almost zero $V_{oc}$ and $J_{sc}$.(Figure 5-12 (b), (c))

In summary, a standard CdCl$_2$ treatment improves the $J_{sc}$ and produces the lowest series resistance; however, it seems to damage the PN junction giving low shunt resistance. Visually, the surface of CdCl$_2$ treated sample becomes rough or shows signs of delamination. N$_2$ annealing gives a smoother surface than air, and it gives a better efficiency than air annealing, too. Therefore, I did another experiment to test dry CdCl$_2$ treatment$^3$ and N$_2$ flow, instead of air.

---

$^3$ Dry CdCl$_2$ treatment uses a source plate to contain CdCl$_2$ powder. A sand blasted ASG with several drops of CdCl$_2$ saturated methanol solution is used as a source plate. The sample and source plates are facing each other but separated by a 1 mm thick glass pieces. The advantage of dry CdCl$_2$ treatment is that there are no CdCl$_2$ residue on the surface of the sample and no need to be rinsed with methanol and dried with N$_2$ jet, which could physically damage the surface of the thin film.
Table 5.7. Ast318 structure and annealing conditions.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Structure</th>
<th>Post deposition treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ast318A</td>
<td>ASG/AZO/CdSe/ZnSe</td>
<td>Dry CdCl$_2$ with N$_2$</td>
</tr>
<tr>
<td>Ast318B</td>
<td>ASG/AZO/CdSe/ZnSe</td>
<td>Dry CdCl$_2$ with dry airs</td>
</tr>
</tbody>
</table>

![Graphs](image)

(a) Efficiency    (b) $V_{oc}$    (c) $J_{sc}$    (d) Fill factor    (e) $R_s$    (f) $R_{sh}$

Figure 5-14. Performance of Ast318 (Dry CdCl$_2$ treated samples, A: N$_2$, B: Dry air)

One noticeable thing in dry CdCl$_2$ treatment is that $J_{sc}$ goes up to 6 mA/cm$^2$ for CdCl$_2$ treated with dry air. This is a promising sign that $J_{sc}$ can be improved with proper passivation of recombination centers. Dry CdCl$_2$ treatment in N$_2$ environment gave almost zero $V_{oc}$ and FF.
5.2.6. Conclusion of CdSe top cell

My initial goal of CdSe top cell was to repeat the 6% efficiency of the Battelle Institute’s result done in 1980 [5-13]. I got 0.5% on my Cr layer CdSe solar cell. Although the $V_{oc}$ was comparable to their result, but $J_{sc}$ and FF were much lower than theirs. University of South Florida (USF) had 1.9% CdSe device [5-17], but they reported higher $J_{sc}$ (14 mA/cm$^2$). From my last experiment, $J_{sc}$ was 6 mA/cm$^2$ which is twice the value of other cells that I made. I think there is still possibility of optimization.

5.3 HgCdTe bottom cell

HgCdTe study had two purposes. The first one is to make high efficiency single junction device and the second one is to make monolithically integrated (two-terminal) tandem device.

5.3.1. Single junction HgCdTe device

Cells were deposited on Tec7 glass. I had three stages of optimization. First, I optimized CdCl$_2$ treatment time (Figure 5-16). Second, HgCdTe thickness (Figure 5-17). Third, CdS and CdTe buffer layer thicknesses were optimized. (Table 5.8 and Figure 5-18 and 5-19)

Figure 5-15 shows the structure of a HgCdTe solar cell. During the first two stages of optimization, a CdTe buffer layer was not used. Instead, a thicker CdS (0.2 µm) was used, compared with 0.1 µm CdS.
Figure 5-15. Structure of HgCdTe single junction device

Figure 5-16. CdCl$_2$ treatment temperature optimization
The results of CdCl$_2$ optimization are shown in Figure 5-17 as a function of annealing temperature. Wet CdCl$_2$ treatment was applied here and time was fixed at 2 min. The reason that I chose very short (2 min) annealing time is because HgCdTe could not survive the longer annealing due to low melting point.

Without CdCl$_2$ treatment, the device efficiency is very low (~0.2 %), but uniform. The efficiency is maximum at 420 °C, and reduces at lower and higher temperatures, which indicates under and over-treatment. The variations in efficiency become larger from 400 °C or above. The CdCl$_2$ treatment time was fixed at 2 min. The heat annealing was done in the tube furnace without graphite blocks, however, the temperature profile should be similar to Figure 5-10. The samples used in Figure 5-15 did not have the CdTe buffer layer that was used later.

**Figure 5-17.** HgCdTe thickness optimization (CdS 0.2 μm, No CdTe layer, CdCl$_2$ treated at 420°C for 2 min)
Figure 5-17 shows that as HgCdTe thickness increases the efficiency decreases. It can be explained that longer diffusion length with the increasing thickness leads to a higher possibility of recombination during diffusion. That loss exceeds the increase of electron-hole pair generation due to thicker HgCdTe layer.

Thin CdTe buffer layer improved overall efficiency because it reduces the lattice mismatch between CdS and HgCdTe. Four different samples with varying CdS/CdTe thickness were fabricated, while the HgCdTe thickness was fixed at 1.5 µm. (Table 5.8)

**Table 5.8.** CdS and CdTe buffer layer thickness.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CdS (µm)</th>
<th>CdTe(µm)</th>
<th>HgCdTe(µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (mct83)</td>
<td>0.1</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>B (mct84)</td>
<td>0.2</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>C (mct85)</td>
<td>0.2</td>
<td>0.2</td>
<td>1.5</td>
</tr>
<tr>
<td>D (mct86)</td>
<td>0.1</td>
<td>0.2</td>
<td>1.5</td>
</tr>
</tbody>
</table>

**Figure 5-18.** JV results of various CdS/CdTe thickness (Efficiency, \(V_{oc}\), \(J_{sc}\))
Figure 5-19. JV results of various CdS/CdTe thickness (Fill factor, $R_s$, $R_{sh}$. Each sample has 45~50 dot cells)

Figure 5-18 (a) shows that sample C and D which have CdS/CdTe thickness of (0.2/0.2 µm) and (0.1/0.2 µm) give better efficiency than A and B which has a thinner (0.1 µm) CdTe layer with 0.1 or 0.2 µm CdS. Especially, D (0.1/0.2 µm) gives the best $J_{sc}$ with smallest variation. (Figure 5-18 (c)).

Figure 5-18 (b) shows that thick (0.2 µm) CdS (B, C) gives higher $V_{oc}$ and D which has thinner CdS with a thick (0.2 µm) CdTe buffer layer has a better $J_{sc}$. That must be related to the short wavelength absorption loss in CdS. Thicker CdTe layer than 0.2 µm was not tried because it will increase the absorption in higher portion of solar spectrum, which would not be used in bottom cell configuration.
Figure 5-20. JV result of the best single junction HgCdTe

Figure 5-20 shows JV results of the best device with CdTe buffer layer. It has CdS (0.1 µm), CdTe (0.2 µm), and HgCdTe (1.5 µm).

Figure 5-21. QE of HgCdTe solar cell
Figure 5-21 shows the QE of the best HgCdTe solar cell. Note that QE extends over to 1100 nm in the IR region, so that it clearly shows the effect of the Hg alloying and shows potential to operate as a bottom cell.

5.3.2. Two-terminal tandem HgCdTe

![2-terminal tandem Cell (Dot 25)](image)

**Figure 5-22.** 2-terminal tandem solar cell (JV of dot 25 is shown in Figure 5-23)

Optimization information of CdTe top cell was already known in our lab. Now that I have information of optimum thickness of single junction HgCdTe absorber layer, CdTe buffer layer, and CdCl$_2$ treatment condition, I moved on to fabricate two-terminal tandem solar cells using a HgCdTe device as a bottom cell.

Figure 5-22 shows a two-terminal tandem device using HgCdTe as a bottom cell. The structure of the cell is T15 HRT/ CdS (0.1 µm)/ CdTe (0.7 µm)/ ZnTe:N (0.1 µm)/ ZnO:Al (0.1 µm)/ CdS (0.1 µm)/ CdTe (0.2 µm)/ HgCdTe (1.5 µm).
First, CdS and CdTe layers were fabricated in AJA vacuum chamber without
breaking the vacuum. Then, dry CdCl\textsubscript{2} treatment was done. After that, ZnTe was
deposited with N\textsubscript{2} + Ar ambient. The sample was taken out from the AJA chamber and
moved to another chamber for ZnO:Al deposition. Then, the sample was brought to the
AJA chamber again for CdS/CdTe layer depositions. After that, it was moved to HgCdTe
deposition system and 1.5 µm of HgCdTe was deposited. Then, it was CdCl\textsubscript{2} treated for 2
minutes in tube furnace. Finally, Cu/Au was evaporated on the sample and heat annealed
in air for 15 minutes at 150 °C for Cu diffusion.

Nitrogen doped ZnTe (ZnTe:N) and aluminum doped zinc oxide (AZO) layers
were used as an interconnect junction. For a two terminal tandem cell, current matching
is the most important requirement of a good device.

![Figure 5-23. JV of 2-terminal tandem solar cell (dot 25)](image)

\begin{align*}
\text{Voc} &= 921 \text{ mV} \\
\text{Jsc} &= 0.13 \text{ mA/cm}^2 \\
\text{FF} &= 35.7 \% \\
\text{Eff.} &= 0.04 \% \\
\text{Area} &= 0.031 \text{ cm}^2
\end{align*}
Figure 5-23 shows the JV data the tandem device. However, QE data could not be taken due to low short circuit current. It has 921 mV of $V_{oc}$ which is the evidence of two working PN junctions because the highest $V_{oc}$ of single CdTe junction is approximately 840 mV. Perhaps, low $J_{sc}$ was due to the issues in interconnect junction. Because this device went through several heatings and annealings of the sample, the quality of the earlier deposited layers could have been degraded at the end of device fabrication.

5.3.3. Conclusion of HgCdTe study

Single junction HgCdTe solar cells was fabricated with the maximum efficiency of 6.6%. Two-terminal tandem solar cells which consisted of CdS/CdTe top cells and CdS/HgCdTe bottom cells were fabricated with the maximum efficiency of 0.04%. Although the efficiency was low, the $V_{oc}$ of 921 mV indicates that it has two working tandem solar-cell junctions. It is challenging to have a good interconnection junction and maintain the quality of multiple thin film layers throughout various depositions and post-deposition processes.

5.4 Prospect of tandem solar cell

Fabricating polycrystalline hetero-junction tandem solar cells is not an easy task, but still it is worth doing. For mechanically stacked tandems, the priority should be on getting high efficiency single junction top cell on TCO contact. Unfortunately, the 6% record efficiency of CdSe device was made on an opaque Cr contact. Even though our 0.5% efficiency is too low, I think it is a matter of time to repeat and exceed 6% efficiency.
CdSe solar cell is important because it can be mechanically assembled with CIGS solar cell and can improve the overall efficiency or lower the $/watt cost. Another reason that CdSe device is advantageous is because Se is more abundant than Te. The Te supply is a potential Achilles tendon in CdTe solar cell technology. When the CdTe solar cell industry faces a Te procurement problem, they can switch to even single junction CdSe and knowhow of CdTe can be similarly applied to it.

The best HgCdTe solar cell reported in the literature had record efficiency of 10.6% [5-18], which is higher than our 6.7%. However, the toxicity of Hg will be an issue in mass production of terrestrial solar cell. Besides, now that CIGS solar cell is commercially available, there is not much reason to pursue HgCdTe solar cell.

Monolithically integrated tandem (i.e., two terminal tandem) will be a real challenge in polycrystalline thin film solar cell. If we review the best two-terminal polycrystalline device up to now, no device has ever exceeded the efficiency of the single junction device. More study on interfaces of the solar cell, improvements in interconnect-junction, and careful selection of growth and post-deposition parameters will be required to achieve this. However, this will be a real tandem that can be suitable for mass production and accelerate cost reduction.
Chapter 6

Conclusions

Solar cells are the most practical ways to replace fossil fuels. Although Si solar cells have a higher market share, polycrystalline thin film solar cells are rapidly growing in recent years because of their short energy payback time (EPBT) and low manufacturing cost. CdTe solar cells have recently become the most commercially successful thin film solar module due to the low cost at large-area solar CdS/CdTe modules.

The low cost of CdTe solar modules is possible because CdTe is a direct band gap semiconductor with a high absorption coefficient, which requires only very thin (2 µm) film to absorb most of the sunlight higher than its band gap. Its band gap of 1.5 eV is a near optimum band gap for maximum power generation used as a single junction. However, the theoretical efficiency of single junction CdTe was limited because it could not use almost one third of the solar spectrum which has photon energy lower than its band gap. Moreover, actual solar cells and modules have a large discrepancy with theoretical efficiency due to low carrier concentrations, short carrier life times and recombination losses from grain boundaries.

To address these issues, researchers are taking two approaches: One is to understand defect states, loss mechanisms, and improve fundamental knowledge to raise
efficiencies of single junction CdTe devices. Another approach is to search for different materials and make tandem devices to utilize the solar spectrum better than single junction CdTe. Ultimately, both approaches have the same goals, namely achieving high efficiency solar modules. My PL and AFM study of CdTe was done in the context of the former one and the PL and AFM of CdSe was done in the context of the latter one.

My PL study of RF-sputtered as-deposited CdTe solar cells shows that the film-side PL intensity ratio of the shallow defect near 1.4 eV to the deep defects in the 0.8 ~ 1.2 eV region is the highest at 18 mTorr, which is known to be the optimum pressure for the best cell performance of the deposition chamber. This means that PL can show correlation among deposition parameters, defects and performance. The repeated peaks of ~80 meV intervals in as-deposited film-side and junction-side PL are most likely due to thin film interference artifacts.

After CdCl$_2$ treatment, the PL intensity increases 3 to 6 orders of magnitude compared with as-deposited films and all vibronic features are suppressed. Much stronger PL of the near band edge peak at 1.42 eV compared with the as-deposited films, indicates that nonradiative transitions are greatly suppressed. Film-side (or contact-side) PL shows a weak bound exciton near 1.59 eV, which is an indicator of improved crystallinity and minority carrier lifetime. Comparing the film-side peak at 1.424 eV and junction-side peak at 1.377 eV, the shift of 47 meV indicates a Cd$_x$S$_{1-x}$ and CdTe$_{1-x}$ intermixing ratio of $x=0.06$. From power dependent PL, peaks at 1.43 eV and 1 eV are shown to be free-to-bound (FB) transitions because power exponents are smaller than 1 and there is no blue shift of the peak which would be an indicator of donor-acceptor-pair (DAP) transitions. Also, peaks at 1.53 eV and 1.59 eV are bound-exciton (BE) because they have the power
exponent of larger than 1. Temperature-dependent PL showed that the binding energy of
the defect involved in the free-to-bound peak at 1.43 eV in the 18 mTorr sample has the
lowest binding energy of ~90 meV. One interesting phenomenon observed in temperature
dependent PL was that the intensity of 1.43 eV peak of 5 mTorr sample has the maximum
at 20 K, while all other samples’ PL decreases monotonically as temperature increases.
Biernacki et al observed similar phenomenon and explained that the thermal expansion
coefficient of CdTe varies with temperature and affect the energy band. They discussed
that the lowest thermal expansion coefficient of CdTe around 25 K is related to the
maximum energy of the luminescence ZPL at about 20 K. The fact that only 5 mTorr
sample shows this phenomena indicates that it has different defect mechanism than other
samples. However, at this point, it is not clear whether this difference comes from low
pressure ion bombardment or CdCl$_2$ over treatment.

In an effort to make p-type CdSe film, four doped targets were made and
crystallinity was tested by PL. Although p-type conductivity was not attained, PL showed
good crystallinity of the doped films. For CdSe PL, after annealing at 400 °C in air, the
Cu-doped CdSe film showed a strong, near-band-edge bound excitation which is an
indicator of reasonably good crystallinity. The GaCl$_3$ doped CdSe also showed strong PL
after annealing, an indicator of good crystallinity. However, As and Ag doped samples
showed very strong deep defect states even after annealing and appear not to be a
promising candidates for p-type polycrystalline CdSe.

From the AFM data and scaling analysis, the growth mode of sputtered CdTe has
the roughness exponent of $\alpha = 1$, a growth exponent of $\beta = 0.22 \sim 0.28$, and dynamic
exponent of $z = 4.2 \sim 4.6$. These values are close to the theoretical value of the linear
fourth order equation model. It means growth mode of molecular beam epitaxy (MBE) and sputtering have similarities. In both cases, the film grows by deposition and diffusion of atoms around the surface until they find most energetically favorable position. However, MBE is performed at a much higher substrate temperature, slow growth rate and very low base pressure, which can make epitaxial growth possible. While sputtering has a shorter diffusion length due to a lower substrate temperature, Ar bombardment effect, and relatively impure sputtering source make polycrystalline film. CdTe grain size follows log-normal distribution and average grain size and surface roughness has a linear relationship, which indicate that grain boundaries are diffusion barriers of the polycrystalline films.

The AFM study of sputtered CdSe films grown at different substrate temperatures showed that the surface gets rougher as substrate temperature increases. And the roughness exponent ($\alpha$) is close to 1. The growth exponent ($\beta$) is 0.19 ~ 0.20. Again, this growth mode can be explained by the linear fourth order equation.

A CdSe top cell on Cr was made to explore the metal-insulator-semiconductor (MIS) solar cell results from the Battelle group, but the efficiency of my initial devices was very low. I believe this is related to the difficulties in controlling the very thin(~7 nm) insulator layer (ZnSe) thickness which is critically important to the MIS device. For the 2nd trial, much thicker(~80 nm) ZnSe gave a better (0.5%) efficiency, in this case the solar cell worked as a PN-junction. My MIS device has a higher $V_{oc}$ and low $J_{sc}$, while CdCl$_2$ treated PN-junction device yields low $V_{oc}$ and relatively higher $J_{sc}$. For MIS type, making very thin pin-hole free ZnSe layer will be the most important factor for reaching high efficiency. To do that, we need to find optimal CdSe deposition conditions to make
smooth surface with the fewest defects. And also, we need to find a way to monitor and control the thickness of very thin ZnSe layer. For our PN junction device, the low $V_{oc}$ seems to be caused by the rough surface and damaged PN-junction after CdCl$_2$ treatment. Therefore, empirical optimization of a CdCl$_2$ activation treatment that passivates the defects at the same time as maintaining undamaged PN-junction would be needed.

If a CdSe top cell can be successfully made on a TCO contact on glass, a 4-terminal device would be easily made with further optimization of the top cell condition which would give the optimum efficiency of the device and transmission of light to the bottom cell.

However, for a two-terminal tandem device, we still need to make p-type CdSe or find a novel way to make a two-terminal device. Because MIS or PN-junction in n-CdSe/p-ZnSe top cell and n-CdS/p-CIGS bottom cell would be two diodes in opposite directions, current could not add up. Other challenges for a monolithic tandem device include: multiple layers with different processing parameters, fabricating a good interconnection junction, and reaching current matching conditions in the top and bottom cells will increase the difficulties in device fabrication.
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Appendix A

Interference fringes in PL signal

In chapter 3, I observed PL of as-deposited CdS/CdTe films. One question was the origin of series of peaks observed in 0.8 ~ 1.2 eV in Figure 3-5 (a) and 1.1 ~ 1.4 eV in Figure 3-5 (b) with approximately 80 meV intervals. Initially, these repeated peaks were considered as phonon replicas of the zero-phonon peak, but 80 meV is too large to be explained by known CdTe phonon frequency of 21 meV. During my defense, a question was raised whether these peaks are due to the interference of the thin films.

In here, I calculated the thickness of the films from the interval of the PL peaks using a simple thin film interference condition. And also, the thicknesses from PL data are compared with the thickness of the thin film reflectance simulation as well as actual thickness measured by Dektak profilometer.

Table A.1. Thicknesses measured by Dektak profilometer

<table>
<thead>
<tr>
<th>Deposition pressure</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.20</td>
</tr>
<tr>
<td>10</td>
<td>2.27</td>
</tr>
<tr>
<td>18</td>
<td>2.24</td>
</tr>
<tr>
<td>30</td>
<td>2.20</td>
</tr>
</tbody>
</table>
The simplest condition for destructive interference is Eq. (A-1)

\[ 2nt = m\lambda \]  \hspace{1cm} (A-1) [A-1]

If we consider the different index of refraction for the different wavelength, it can be rewritten as Eq. (A-3), where \( \delta_j \) is the phase shift of the light.

\[ \delta_j = \frac{2\pi}{\lambda_j} 2nt = 2m\pi \] \hspace{1cm} (A-2)

\[ \delta_j = 2\pi \cdot 2t\left(\frac{n_j}{\lambda_j}\right) = 2\pi \cdot m \]

\[ \delta_1 - \delta_2 = 2\pi \cdot 2t\left(\frac{n_1}{\lambda_1} - \frac{n_2}{\lambda_2}\right) = 2\pi \cdot [(m + 1) - m] \]

\[ t = \frac{1}{2\left(\frac{n_1}{\lambda_1} - \frac{n_2}{\lambda_2}\right)} \] \hspace{1cm} (A-3) [A-1]
Wavelength dependent index of refraction is calculated from Schubert’s reflection measurements in room temperature on MBE grown CdMn$_x$Te$_{1-x}$ thin films.[A-2] When Eq. (A-3) was applied to the peak interval of my PL data, the thickness was approximately 2.4 ~ 2.8 µm range in film-side (Table A.2) and 1.9 ~ 2.4 µm range in junction-side (Table A.3)

**Table A.2.** Thickness calculated from PL using interference condition (Film-side PL of as-deposited film)

<table>
<thead>
<tr>
<th>PL (film-side) wavelength(nm)</th>
<th>Energy(eV)</th>
<th>Delta E(meV)</th>
<th>n</th>
<th>Thickness(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mTorr</td>
<td>1,091</td>
<td>1.1369</td>
<td>81.9</td>
<td>2.77</td>
</tr>
<tr>
<td></td>
<td>1,175</td>
<td>1.055</td>
<td>82.3</td>
<td>2.76</td>
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<tr>
<td></td>
<td>1,275</td>
<td>0.9727</td>
<td>85.9</td>
<td>2.75</td>
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<td></td>
<td>1,398</td>
<td>0.8968</td>
<td>2.74</td>
<td></td>
</tr>
<tr>
<td>10 mTorr</td>
<td>1,069</td>
<td>1.1595</td>
<td>77.3</td>
<td>2.78</td>
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<td></td>
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<td>1,234</td>
<td>1.0046</td>
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<td></td>
<td>1,339</td>
<td>0.9262</td>
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<td></td>
<td>1,467</td>
<td>0.8454</td>
<td>2.74</td>
<td></td>
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<tr>
<td>18 mTorr</td>
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<td>1.148</td>
<td>79.1</td>
<td>2.77</td>
</tr>
<tr>
<td></td>
<td>1,160</td>
<td>1.0689</td>
<td>80.9</td>
<td>2.76</td>
</tr>
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<td></td>
<td>1,255</td>
<td>0.988</td>
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<td>2.75</td>
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<td></td>
<td>1,376</td>
<td>0.9012</td>
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<td></td>
<td>1,526</td>
<td>0.8127</td>
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<td>30 mTorr</td>
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<td>86.1</td>
<td>2.75</td>
</tr>
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<td>1,368</td>
<td>0.9067</td>
<td>92.4</td>
<td>2.75</td>
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<td></td>
<td>1,523</td>
<td>0.8143</td>
<td>2.74</td>
<td></td>
</tr>
</tbody>
</table>

**Table A.3.** Thickness calculated from PL using interference condition (Junction-side PL of as-deposited film)

<table>
<thead>
<tr>
<th>PL (junction-side) wavelength(nm)</th>
<th>Energy(eV)</th>
<th>Delta E(meV)</th>
<th>n</th>
<th>thickness(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mTorr</td>
<td>839</td>
<td>1.4783</td>
<td>75.6</td>
<td>2.94</td>
</tr>
<tr>
<td></td>
<td>884</td>
<td>1.4027</td>
<td>81.3</td>
<td>2.87</td>
</tr>
<tr>
<td></td>
<td>938</td>
<td>1.3214</td>
<td>89.2</td>
<td>2.82</td>
</tr>
<tr>
<td></td>
<td>1,006</td>
<td>1.2322</td>
<td>84.6</td>
<td>2.79</td>
</tr>
<tr>
<td></td>
<td>1,081</td>
<td>1.1476</td>
<td>2.77</td>
<td></td>
</tr>
<tr>
<td>10 mTorr</td>
<td>825</td>
<td>1.5031</td>
<td>67.2</td>
<td>2.99</td>
</tr>
<tr>
<td></td>
<td>864</td>
<td>1.4359</td>
<td>78.1</td>
<td>2.89</td>
</tr>
<tr>
<td></td>
<td>913</td>
<td>1.3578</td>
<td>79.6</td>
<td>2.84</td>
</tr>
<tr>
<td></td>
<td>970</td>
<td>1.2782</td>
<td>88.2</td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td>1,042</td>
<td>1.19</td>
<td>2.78</td>
<td></td>
</tr>
</tbody>
</table>
These thickness ranges are close to dektak thickness of 2.3 µm, but there are approximately 0.5 µm gap that between the actual thicknesses and the calculation. To explain these differences I wrote a computer code to calculate the reflectance of the film. According to Nussbaum [A-3], thin film layer can be described by a simple 2*2 matrix in Eq.(A-4). Here, phase shift Eq.(A-5) is defined by a half of the Eq.(A-2).

\[
M_j = \begin{pmatrix}
\cos \delta_j & \frac{i \sin \delta_j}{n_j} \\
\frac{i n_j \sin \delta_j}{\cos \delta_j} & \cos \delta_j \\
\end{pmatrix}
\] (A-4)

\[
\delta_j = \frac{2\pi}{\lambda} n_j t_j \cos \theta_j
\] (A-5)

\[
\begin{pmatrix}
a \\
b
\end{pmatrix} = \begin{pmatrix}
n_0 \\
n_0
\end{pmatrix} - 1 \begin{pmatrix}
\cos \delta_j \\
\frac{i \sin \delta_j}{n_j}
\end{pmatrix} \begin{pmatrix}
1 \\
\frac{n_j}{n_f}
\end{pmatrix}
\] (A-6)

\[
R = \left| \frac{a}{b} \right|^2
\] (A-7)

Then, the reflectance of the multilayer films can be calculated by the matrix product of each thin film layers. First, equations (A-4) to (A-7) are applied to a single layer thin film model in Figure A-1. The reflectance graph was drawn in Figure A-2. After this, based on the intervals of the peaks in Figure A-2, the thickness of the films are calculated by using Eq. (A-3) and the results are summarized in
Figure A-2. Reflectance due to a single-layer thin film interferences (t_1 = 2.2 µm)
(CdTe index of refraction n_1 varies by wavelength, all other index of
refractions are fixed.)

Table A.4. Thicknesses calculated from the simulated reflectance of a single-layer film.

<table>
<thead>
<tr>
<th>wavelength(nm)</th>
<th>Energy(eV)</th>
<th>Delta E(meV)</th>
<th>n</th>
<th>thickness(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.116</td>
<td>1.111</td>
<td>96.4</td>
<td>2.77</td>
<td></td>
</tr>
<tr>
<td>1.222</td>
<td>1.015</td>
<td>97.5</td>
<td>2.76</td>
<td>2,234</td>
</tr>
<tr>
<td>1.352</td>
<td>0.917</td>
<td>98.2</td>
<td>2.75</td>
<td>2,250</td>
</tr>
<tr>
<td>1.514</td>
<td>0.819</td>
<td>96.9</td>
<td>2.74</td>
<td>2,305</td>
</tr>
<tr>
<td>1.717</td>
<td>0.722</td>
<td>96.8</td>
<td>2.73</td>
<td>2,319</td>
</tr>
<tr>
<td>1.983</td>
<td>0.625</td>
<td></td>
<td>2.73</td>
<td></td>
</tr>
</tbody>
</table>

The thickness is not exactly 2.2 µm. It may be due to the errors of manually
selecting the peak intervals.
Figure A-3. Multiple layer interference model

However, actual thin film layers are much complex than a single CdTe layer interference. Therefore, more realistically, reflectance due to three layers is simulated below. Figure A-3 shows multiple layers of thin films, assuming the substrate is Tec7 glass. In three layer reflectance simulation, only CdTe (2200 nm), CdS (60 nm), SnO$_2$:F (470 nm) thin film layers, glass substrates and vacuum are taken into consideration.
Figure A-4. Reflectance due to three layers of thin-film interferences ($t_1 = 2.2 \, \mu m$) (CdTe index of refraction $n_1$ varies by wavelength, all other index of refractions are fixed.)

Table A.5. Thicknesses calculated from the simulated reflectance of three-layer films.

<table>
<thead>
<tr>
<th>wavelength(nm)</th>
<th>Energy(eV)</th>
<th>Delta E(meV)</th>
<th>n</th>
<th>thickness(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,082</td>
<td>1.146</td>
<td></td>
<td>2.77</td>
<td>2,136</td>
</tr>
<tr>
<td>1,184</td>
<td>1.047</td>
<td>103.6</td>
<td>2.76</td>
<td>2,096</td>
</tr>
<tr>
<td>1,314</td>
<td>0.9434</td>
<td>97.9</td>
<td>2.75</td>
<td>2,249</td>
</tr>
<tr>
<td>1,467</td>
<td>0.8455</td>
<td>97.2</td>
<td>2.74</td>
<td>2,289</td>
</tr>
<tr>
<td>1,657</td>
<td>0.7483</td>
<td>96.7</td>
<td>2.74</td>
<td>2,321</td>
</tr>
<tr>
<td>1,903</td>
<td>0.6516</td>
<td></td>
<td>2.73</td>
<td></td>
</tr>
</tbody>
</table>

The thickness is in the range of 2.1 ~ 2.3 \, \mu m. The error is still due to the difficulties in finding exact intervals, especially around 1.1 eV where an envelope of a large interference pattern originated from CdS distorts the peak patterns. In this case, the centers of the peaks were selected by the middle point of the full width of the peaks, not from the top of the peaks.
The differences in calculated thicknesses from reflectance simulations of a single layer film and three layer-films are minimal. Therefore, consideration of multiple layer would not explain the gap between the actual thickness and the calculated thickness from PL data.

Figure A-5. A model of light propagation for PL

One difference of reflection of light and PL phenomena is that the PL is generated over the region (CdTe has ~0.3 μm of penetration depth in 514.5 nm laser) of the films and they can propagate in all direction, while reflected and transmitted light can propagate only normal direction. Therefore, actual optical path length can be different from normal propagation. This might explain why the calculated thickness based on PL is different (usually thicker) than that of reflectance simulation.
Conclusion of appendix A

Based on the thicknesses calculated by the interference condition of the thin films, it is highly likely that the vibronic features recorded in the PL data are thin film interference artifacts. Further PL study with various thickness samples will confirm the validity of this conclusion.


Appendix B

Strain of CdS/CdTe films calculated from XRD

From the PL study (Figure 3-5 (a) and discussions in p44) of as-deposited CdS/CdTe films, we found that lower Ar pressure samples such as 5 mTorr and 10 mTorr have higher deep defects PL (~ 1 eV) to shallow defect (~1.4 eV) PL intensity ratio than that of 18 mTorr sample. The deep defect states near mid-gap of the CdTe are detrimental to the solar cell performance due to higher recombination rate than the shallow defect states. When solar cells are empirically optimized with varying CdCl$_2$ treatment times, those lower pressure (5 and 10 mTorr) samples with stronger deep defects do not give high performance. (Figure 3-3) However, 18 mTorr sample which shows the smallest deep defects to shallow defects ratio in PL has the highest performance.

The strains of the films (sample set 2 in Table 3.1) used in the PL experiments are calculated from the x-ray diffraction (XRD) in Bragg-Brentano configuration. Measured 2θ values of (111) peaks are summarized in Table B.1

<table>
<thead>
<tr>
<th>2θ value</th>
<th>5mTorr</th>
<th>10mTorr</th>
<th>18mTorr</th>
<th>30mTorr</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-dep</td>
<td>23.654</td>
<td>23.667</td>
<td>23.729</td>
<td>23.744</td>
</tr>
<tr>
<td>CdCl$_2$</td>
<td>23.777</td>
<td>23.765</td>
<td>23.769</td>
<td>23.797</td>
</tr>
<tr>
<td>Powder Ref</td>
<td>23.773</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
When x-ray comes in to the array of CdTe atoms there will be path length difference and the constructive interference can be made with the condition of Eq. (B-1)

$$2d \sin \theta = m\lambda$$  \hspace{1cm} (B-1)

where $d =$ the spacing between adjacent atomic layers, $\theta =$ the angle between incident x-ray and the surface of the sample, and $\lambda = 1.5405 \text{ Å}$ (the wavelength of the copper K$_\alpha$)

By comparing the angle $\theta$ of the (111) peaks between powder (strain-free) and the films, we will see whether the spacing of the atomic layer, $d$ has changed or not. Here, powder database of (03-065-0890) was used. From Table B.1, we see that angles of all as-deposited films are smaller than that of the powder. That means spacing $d$ has increased by the in-plane compressive strain. Strain (%) is calculated by the Eq. (B-2)
Strain (%) = \frac{(2\theta_{\text{obs}} - 2\theta_{\text{ref}})}{(2\theta_{\text{ref}})} \times 100 \quad \text{(B-2)}

where $2\theta_{\text{ref}} = 23.773^\circ$

Especially, 5 mTorr and 10 mTorr sample has much larger strains than 18 mTorr and 30 mTorr samples. After CdCl$_2$ treatment, the strains of the most samples were released except 30 mTorr sample shown in Figure B-2.

![Figure B-2](image)

**Figure B-2.** Strains of the as-deposited and CdCl$_2$ treated films deposited in various Ar pressures.

In my opinion, ion bombardments in lower pressure sample induce more defects and strains in the films than optimum 18 mTorr sample. And, the release of the strain after CdCl$_2$ treatment does not fully restore the quality of the films to the level of 18 mTorr film which had smaller strain. However, actual phenomena could be more complex because the lower performance of 30 mTorr sample could not be explained only by the strain.
Conclusion of appendix B

RF-sputtered films in lower Ar pressures (5 and 10 mTorr) have a larger strain and a larger ratio of the deep (~ 1eV) defects to the shallow (~1.4 eV) defects in PL intensity. And also, they have lower efficiencies than optimum 18 mTorr sample, which has the smaller strain and the smaller ratio of the deep defects to the shallow defect in PL. This could be due to the ion bombardment damages on lower pressure deposited films.