Development of a Computer Model for Polycrystalline Thin-Film CuInSe₂ and CdTe Solar Cells

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NUMERICAL MODELING OF CuInSe₂ and CdTe SOLAR CELLS

1. INTRODUCTION	1
2. CuInSe ₂ SOLAR CELLS	4
2.1. CIS Solar Cell Fabrication Methods.....	4
2.2. Literature Survey	6
2.2.1. Material Parameters	6
2.2.2. Solar Cell Performance.....	8
2.2.3. Absorption Coefficients	11
2.3. Self - Doping of CuInSe ₂ Films	12
2.4. Effect of Cu-poor CIS Layer on ZnO/thin CdS/CIS Solar Cells.....	13
3. CdTe SOLAR CELLS.....	19
3.1. Literature Survey	19
3.1.1. Parameter Study.....	19
3.1.2. CdTe Solar Cell Performance.....	25
3.1.3. CdTe Absorption Parameters	29
3.2. Detailed Study of Some Limiting Factors of CdS/CdTe Solar Cells	30
4. WORK IN PROGRESS	33
4.1. Interdiffusion Between CdS and CdTe	33
4.2. Grain Boundary Recombination	34
4.2.1. Physics of the Grain Boundary and Some Analytical Models	34
4.2.2. Numerical Modeling of the Grain Boundary.....	38
5. FUTURE WORK.....	41
APPENDIX A. ABSORPTION MODEL	42
A.1. Absorption Properties of Semiconductors	42
A.2. ADEPT Absorption Model Description.....	43
A.3. Absorption Parameters for CuInSe ₂	47
A.4. Absorption Parameters for CdTe.....	48
APPENDIX B. MULTIPLY IONIZED IMPURITIES AND RECOMBINATION	49
B.1. Multiply Ionized Impurities	49
B.2. Numerical Modeling of Multiply Ionized Impurities.....	49
REFERENCES.....	53

1. INTRODUCTION

Solar cells operate by converting the radiation power from sun light into electrical power through photon absorption by semiconductor materials. The elemental and compound material systems widely used in photovoltaic applications can be produced in a variety of crystalline and non-crystalline forms. Although the crystalline group of materials have exhibited high conversion efficiencies, their production cost are substantially high. Several candidates in the poly- and micro-crystalline family of materials have recently gained much attention due to their potential for low cost manufacturability, stability, reliability and good performance. Among those materials, CuInSe₂ and CdTe are considered to be the best choices for production of thin film solar cells because of the good optical properties and almost ideal band gap energies [1][2]. Considerable progress was made with respect to cell performance and low cost manufacturing processes. Recently conversion efficiencies of 14.1 and 14.6% have been reported for CuInSe₂ and CdTe based solar cells respectively [3][4]. Even though the efficiencies of these cells continue to improve, they are not fully understood materials and there lies an uncertainty in their electrical properties and possible attainable performances.

The best way to understand the details of current transport mechanisms and recombinations is to model the solar cells numerically. By numerical modeling, the processes which limit the cell performance can be sought and therefore, the most desirable designs for solar cells utilizing these materials as absorbers can be predicted. The problems with numerically modeling CuInSe₂ and CdTe solar cells are that reported values of the pertinent material parameters vary over a wide range, and some quantities such as carrier concentration are not explicitly controlled. In order to solve these problems the first step was taken to gather the values of material parameters from a numerous published literatures and perform numerical modeling to determine a set of material parameters consistent with measured cell performance.

The purpose of this research is to predict the achievable performance for CuInSe₂ and CdTe based solar cells and to present the optimized design for these devices and develop a tool for analysis. Presently it has been successful to model the cells with the highest efficiencies and point out how they can be improved. However, it is not clear why most cells have lower efficiencies. One of the possible reasons is that the design of these devices is not optimized. It is also possible that there is a degradation of cell performance depending on the fabrication process used. For CdS/CdTe solar cells, some researchers report that the poor cell performance is caused by interdiffusion between CdS and CdTe [5][6]. More information about the interdiffusion will be gathered and numerically modeled. By doing this, the most efficient device design along with the

best window material for CdTe solar cells can be found. Unlike single crystals, polycrystalline material consists of grains. The recombination at the grain boundaries leads to the reduction in material parameter values like mobilities and carrier lifetimes. A few researchers have modeled the effect of grain boundary recombinations by using effective mobilities which are dependent on the grain boundary potential barrier throughout the whole material. The result of this modeling agreed well with experimental data for polycrystalline silicon [7][8]. However, not much work has been done on CuInSe₂ or CdTe. A numerical grain boundary recombination model will be developed. This model will be a useful tool to simulate polycrystalline thin film solar cells and find the best geometry for the devices.

Computer simulation of solar cells is carried out by simultaneously solving the three fundamental equations of semiconductor devices, the Poisson and current continuity equations. ADEPT (A Device Emulation Program & Tool) finds the solution to these differential equations using finite difference approximation method.

$$\nabla \cdot D = q (p - n + N_D^+ - N_A^-)$$

$$\nabla \cdot J_n = q (R - G)$$

$$\nabla \cdot J_p = q (G - R)$$

From this solution, the terminal characteristics of the solar cell can be computed. In ADEPT, the conduction and valence bands are modeled as parabolic and are characterized by effective densities of state N_C and N_V .

Some new models which were developed especially for simulation of CuInSe₂ and CdTe based solar cells were incorporated into ADEPT. The physics and numerical models for absorption process and multiply ionized impurities which can act as recombination centers as well as dopants are described in appendix A and B respectively.

Chapter 2 and 3 present preliminary results of literature survey and numerical modeling of CuInSe₂ and CdTe solar cells respectively. The results of numerical modeling in these two chapters merely suggest how some of these devices operate and are not complete. Therefore, they cannot be used to be predictive for all devices yet. The work in progress currently is described in detail in chapter 4. Chapter 5 outlines some topics for future consideration.

It is important for the reader to understand that the modeling of CIS and CdTe solar cells through the use of numerical simulation is still being developed. Material parameters and even the detailed physical mechanisms controlling device performance are not yet fully understood. The diverse fabrication methods, cell structures, and material quality all complicate the interpretation of the numerical analyses. At this point, we can make no claim that the numerical models we have

developed are precise, in that they can fully predict all device performance. Rather, the models should be used to test intuition and to examine the effects of proposed transport and recombination mechanisms, as well as influence of specific material parameters. In this way, we can develop a better understanding of these devices and continue to improve the numerical models.

2. CuInSe₂ SOLAR CELLS

2.1. CIS Solar Cell Fabrication Methods

CuInSe₂ (also called CIS) polycrystalline material belongs to I-III-VI ternary semiconductor compounds. It can be doped n and p type so that homojunction devices are possible, but the most efficient solar cells use a heterojunction with n-type wide band gap semiconductor as a window to admit light to the underlying heterojunction with p-type CuInSe₂. The conversion efficiencies of CuInSe₂ polycrystalline thin film solar cells have shown remarkable progress during last few years. Generally n-type CdS was used as a window for CuInSe₂ based solar cells [9][10][11]. Recently CuInSe₂ based solar cells using ZnO layer followed by very thin CdS as a window have shown higher efficiencies [12][3].

Various techniques have been used to obtain polycrystalline thin films of CuInSe₂. However, so far only elemental co-evaporation and two-stage processes have yielded films that could be used for fabrication of high efficiency solar cells [13]. Some common methods of producing thin film polycrystalline CuInSe₂ are listed.

Coevaporation

This method, also known as Boeing technique, coevaporates Se, Cu and In onto a heated substrate. Although some high efficient cells were fabricated [14], this technique is costly and requires elaborate control precision of the evaporant atomic beams to achieve the desired stoichiometry.

Selenization

Selenization involves growing two separate processing stages. The first step is to fabricate precursor structure containing Cu and In. Then these precursors are chemically reacted with H₂Se, thus forming CIS. The control of stoichiometry and uniform deposition of CIS films are the two critical factors that determine the performance of CIS solar cells. These factors can be brought under good control by using this method [15].

Electrodeposition

This method involves electrodeposition of Cu and In, followed by heating in hydrogen selenide gas [16].

Sputtering

Other current methods include reactive magnetron sputtering, i.e. sputtering Cu and In in an H_2Se plus Ar atmosphere [17]. Sputtering directly from CIS target has also been used with r.f. [18] and d.c. [19] in an effort to explore methods suited to large-scale production.

Vapor Transport

Another technique of interest is close-space vapor transport [20]. Using a hot CIS slice, a heated substrate is placed about 1 mm distant. When corrosive HI vapor is introduced, a thin film is deposited from the CIS slice. This process is relatively simple and gives good crystallinity.

Spray Pyrolysis

This is a potentially low-cost method of depositing thin films [21]. It is possible to deposit the chalcopyrite form of CIS on films of 1 to 2 microns with controlled resistivity, good mobility and significant (112) orientation. A remaining problem is the presence of shorting paths, believed to be pinholes.

Electrophoretic Deposition

This method involves producing CIS as a fine powder and suspending it in a mixture of organic liquids [22]. It requires extremely fine particle size to prevent the powder falling to the bottom of the solution.

Liquid Phase Epitaxy

The LPE method requires a liquid solvent from which the CIS can be deposited from solution onto a substrate with similar lattice constants [23].

Flash Evaporation

It consists of dropping very small particles onto a hot surface so that the whole particle is evaporated in full so that stoichiometry is preserved on a receptor surface [24]. In principle, the method is inexpensive, free from use of troublesome or poisonous vapors, fast and single-step.

Laser-Induced Synthesis

The individual element layers are deposited sequentially in a multiple sandwich structure in approximately stoichiometric proportions and then subject this to sudden intense heat [25]. The laser-induced temperature was estimated as below the melting point of Cu (1356K).

Molecular Beam Epitaxy

Although CIS can be fabricated by MBE, this method is far too costly for solar conversion devices.

2.2. Literature Survey

2.2.1. Material Parameters

In order to numerically model the CuInSe₂ based solar cells, the variables in the semiconductor transport equations should be correctly given. These parameters such as band gap energy, effective density of states, dielectric constants, etc., are the properties of the material. Unlike silicon whose properties are extensively investigated and standardized, the reported values of CuInSe₂ material parameters vary in a wide range.

Table 2.1 shows the gathered data of CuInSe₂ material parameters and the basic set used in modeling.

Table 2.1 CuInSe₂ Material Parameters

	values	reference	values used
E _g [eV]	0.95- 1.01 1.04 1.94 -1.06 1.0 1.01 - 1.03 1.15 1.1 1.02 1.02 ± 0.02	[26][27] [28] [29] [30] [31] [32] [33] [21][34][35][36] [37]	1.02
electron affinity [eV]	5.48 4.3	[28] [31][38]	4.3
dielectric constant	ε _o =13.6 ε _a =8.1 ε _o =15.2 ε _a =8.5 ε _o =16.0 ε _a =9.5	[29] [39] [40]	13.5
refraction index	2.90 2.79	[41] [42]	

Table 2.1 continued

	values	reference	values used
mobility μ [$\text{cm}^2/\text{V/s}$]	63 - 485 > 500 $\mu_n = 90 - 900$ $\mu_p = 15 - 50$ 10 - 27 5 - 150 $\mu_n = 180 - 800$ $\mu_p = 3 - 18$ 20 (hole) 920 2 (p-type) 4 (n-type) $\mu_n = 140-700$ $\mu_p = 4 - 60$	[29] [43] [38] [44] [45] [46] [47] [34] [37]	$\mu_n = 50$ $\mu_p = 5$
reflection coefficient	0.257	[42]	
N_c [cm^3]	6.6e17 5.0e18	[42] [44]	6.6e17
N_v [cm^3]	1.5e19 1.0e19	[42] [44]	1.5e19
carrier life time [nsec]	2.2 10 - 190	[48] [38]	4.4
lattice constant [Å]	$a = 5.782$ $c = 11.62$ $a = 5.789$ $c = 11.612$ $a = 5.785$ $c/a = 2$	[28] [49] [50]	
effective mass	$m_n^* = 0.09 m_0$ $m_n^* = 0.09 m_0$ $m_h^* = 0.73 m_0$ $m_{hh} = 0.71 m_0$ $m_{lh} = 0.092 m_0$	[37][43] [51] [38]	

Unlike elemental semiconductors such as Ge and Si for which large production capacities have been developed, with an intense study of the techniques of producing large high quality single crystals possessing very low densities of impurities and defects, bulk specimens are prepared in a relatively small number of research laboratories and in small amounts for CuInSe₂. Hence, many measured parameters refer to particular specimens from one lab and may not be closely applicable to others. Thus, it is not surprising that the reported values for mobilities and carrier life times which depend highly on the densities of impurities and defects are scattered in wide ranges.

To get a basic set of material parameters to be used in the modeling, informations about material parameters, device performance parameters and cell structures had to be collected from published literatures. First most frequently reported values were taken and solar cell simulation results were compared with experimental results. Each material parameters were varied within the reported range until the simulation results agreed reasonably.

The accepted values of CuInSe₂ energy band gap of 1.02 eV with effective density of states for conduction band and valence band of 6.6×10^{17} and $1.5 \times 10^{19} \text{ cm}^{-3}$ presently give a reasonable open circuit voltage. Although there is very little information about electron affinity and surveyed values differ very much, numerical simulations showed that the conduction band discontinuity in either direction had little effect on the CdS/CuInSe₂ solar cell performance [48].

2.2.2. Solar Cell Performance

The surveyed solar cell performance parameters are summarized in table 2.2. The solar cells with same window materials were grouped together. When there were a number of cells in one literature, data for only a couple of cells whose efficiencies were highest were collected. Next to the cell performance parameters, the growth method of CuInSe₂ for the base of the cell are noted.

In the beginning of making CuInSe₂ solar cells, CdS was considered to be the best choice as a window material since it had considerably larger band gap energy (2.4 eV) and was easy to match the lattices. Since then, variety of other materials have been tried. As it can be seen in table 2.2, cells with single CdS window layer have relatively low open circuit voltage and low short circuit current due to recombination and absorption of light in CdS. So far cells with ZnO followed by a very thin layer (about 500 Å) as a window have achieved maximum V_{oc} , J_{sc} and efficiencies.

There has been significant improvement in fill factor as the technique of producing better quality CuInSe₂ has got better. Although the evaporation method of growing the thin film of CuInSe₂ still dominates, there have been much effort to minimize the density of impurities in these films by after treatments like annealing [52][53].

It should be noted that the spectrums under which the solar cell were measured differ. Careful consideration should be given when comparing the short circuit current of each cell. However, in general, the J_{sc} continue to improve as better technology allows the production of very thin window layer. Simulation results also support that thin window layers are critical for better performance [54].

Table 2.2 Survey of Measured CuInSe₂ Cells

window	Voc [V]	Jsc [mA/cm ²]	FF	Efficiency. [%]	Illumination	Growth method	Ref.
CdS	0.396	35	0.64	8.72 (no AR coating)	AM1 101.5 mW/cm ²	evaporation	[55]
	0.396	39	0.63	9.53* (10.01**)			
	0.3482	32.92	0.5509	7.22	87.5 mW/cm ²	hybrid sputtering & evaporation	[56]
	0.3	34	0.44	6.9	ELH 60 mW/cm ²	sintering	[57]
	0.470	30.50	0.715	10.26* (10.8**)		selenization	[15]
	~ 0.43	~ 32	~0.67		AM1	evaporation	[58]
	0.42	35 - 40	0.66				[59]
	0.370	35	0.64	8.5		vacuum evaporation	[27]
	0.395	38	0.67	10.1			
	0.278	36	0.55	5.5			
single-layer	0.35	31.7	0.38	4.2	100 mW/cm ² AM1.5	?	[60]
(CdZn)S	0.430	37.0	0.675	12.3	ELH	thermal evaporation	[61]
	0.433	35.2	0.66	11.5	87.5 mW/cm ²		
	0.43 [#]	39			ELH 87.5mW/cm ²	vacuum evaporation.	[62]
	0.4	32.5	0.647	9.64	87.5 mW/cm ²	physical vapor deposition	[63]
	0.392 [#]	38.3	0.667	10.0	ELH 87.5mW/cm ²	selenization	[64]

Table 2.2 continued

window	Voc [V]	Jsc [mA/cm ²]	FF	Efficiency. [%]	Illumination	Growth method	Ref.
ZnO	0.22 [#]	39.8	0.47	4.0	ELH 87.5 mW/cm ²		[65]
	0.463	26.52	0.666	8.18* (10.89**)		evaporation	[15]
(CdZn)S:In /ITO	0.418 [#]	36.6	0.689	10.5	ELH 87.5mW/cm ²		[65]
	0.425 [#]	35.9	0.685	10.4	AM1.5		
(CdZn)S /ITO	0.404	36.1	0.677	9.9	ELH normalized to AM1.5	e-beam evaporation, selenization	[66]
ZnCdS	0.4314	38.96	0.6309	10.6	ELH 100 mW/cm ²	evaporation	[14]
ZnO/thin- CdS	0.487	32.85	0.7	11.2* (12.5**)	AM1.5 global 100 mW/cm ²	?	[67]
	0.455	40.6	0.661	12.2	100 mW/cm ² AM1.5 global	?	[68]
	0.453	41	0.69	12.8	AM1.5 global 100mW/cm ² ELH	evaporation by 15 steps	[69]
	0.4832	35.6	0.6665	11.5 (12.4**)	AM1.5 global	e-beam evaporation, selenization	[70]
	0.4271	37.41	0.641	10.23	AM1.5 global	EDCF	[71]
	0.44	35.6	0.62	9.7	100 mW/cm ² , AM 1.5 global	?	[60]
	0.445	34.7	0.596	9.19	100 mW/cm ² AM 1.5 global	? (as deposited)	[72]
	0.508	41.0	0.677	14.1**	100 mW/cm ² AM1.5	?	[73] [3]

** Efficiencies with ** are the active area efficiencies.

* Efficiencies with * are the total efficiencies.

All the others do not specify which efficiency they were measuring.

Jsc normalized to 100 mW/cm².

2.2.3. Absorption Coefficients

Depending on the composition of CuInSe_2 , the absorption properties are slightly different. The absorption coefficients for different compositions of CuInSe_2 were obtained [27] and curve fitting were carried out to determine the absorption parameters needed for ADEPT (see appendix A).

Figure 2.1 shows absorption coefficients for different compositions of CuInSe_2 . Curve (d) represents the absorption coefficients for almost stoichiometric CuInSe_2 , while curve (b) and (c) represent In-poor and Cu-poor CuInSe_2 respectively. It is clear that CuInSe_2 with ideal stoichiometry has the highest absorption coefficients and therefore is best suited for the base of solar cells. As it deviates from the ideal composition of 1:1:2, the absorption property gets a lot worse as shown in curve (a). For In-poor CuInSe_2 , there is a significant sub-band gap absorption. Although the nature of this sub-band gap absorption is not clearly understood, some researchers suggest that it is due to valence band tailing and/or the presence of secondary phase [41]. If the sub-band gap absorption is caused by the secondary phase, Cu_{2-8}Se , the absorption is of a free carrier nature in the semi-metallic Cu_{2-8}Se and therefore will not produce photo-generated carriers.

Figure 2.1 Absorption coefficients vs energy for different compositions of CuInSe_2 .

2.3. Self - Doping of CuInSe₂ Films

The electrical, optical and structural properties of CuInSe₂ are dominated by intrinsic defects and defect compensation. Without any intentional doping, CuInSe₂ can be made n-type or p-type conducting with carrier concentrations varying over several orders of magnitudes. It has been suggested by many authors that the point defects like vacancies, interstitials and antisite defects are the main electrically active species. Twelve possible intrinsic defects may exist in CuInSe₂, including three vacancies and three interstitials of three elements copper, indium and selenium, in addition to six anti-sites.

For stoichiometric CIS, a number of attempts have been made to identify the most prevalent point defects. Lange, et al. [74], assigned the energy position of Se-vacancy (donor), In-vacancy (acceptor), and Cu_{In} antisite to 70 meV below the conduction band edge and 80 meV and 40 meV above the valence edge respectively from the photoluminescence study.

Neumann and Tomlinson [43] reported that p-type conductivity is due to a shallow acceptor with an ionization energy in the range from 20 - 30 meV for samples with [Cu]/[In] > 1 and due to a second deeper acceptor between 78 and 90 meV above the valence edge in samples with [Cu]/[In] < 1. They predicted the deeper acceptor to be copper vacancies and possible candidates for the shallow acceptor to be Cu_{In} antisite defect and the indium vacancy.

Haba, et al., [21] reported that two distinct acceptor levels were measured at 20 and 110 meV above the valence band and a deep donor level was located 220 meV below the conduction band. They assigned these defects to be copper vacancies, selenium vacancies and indium interstitials, respectively.

Tanda, et al. [36] carried out photoluminescence study on CuInSe₂ thin films and identified the selenium vacancy (donor) level below the conduction band, and the acceptor levels, copper vacancy and copper on antisite at indium at 85 and 40 meV above the valence band edge, for stoichiometric CIS. For indium-rich CIS, they identified Se-vacancy (70 meV vs CB, donor) and Cu-vacancy (40 meV vs VB, acceptor) to be the most prevalent defect levels.

In order to investigate the auto-doping of stoichiometric CIS material, the dependence of hole concentration on the density of defects was examined for different defect models. It was assumed that the density of each defect were equal for every defect type. Figure 2.2 is the plot of hole concentration vs defect density for different models. It is clear that all the models give approximately the same results. Since Tanda et. al. proposed models for not just stoichiometric CIS but as well as Cu-rich and In-rich CIS, those models were used for ADEPT simulations [75].

Figure 2.2 Plot of hole concentration vs density of each defects resulting from different defect models. The CuInSe₂ was not intentionally doped.

2.4. Effect of Cu-poor CIS Layer on ZnO/thin CdS/CIS Solar Cells

Since a large improvement in CuInSe₂ solar cell efficiency was achieved by bi-layer technique a few years ago, there has been much debate whether the Cu-poor layer is actually necessary for better performance [14][11]. The Cu-poor CuInSe₂ layer sandwiched between the window layer and stoichiometric CuInSe₂ is generally believed to have poor electrical properties, like less carriers and lower mobilities. Based on this fact, some groups have processed CIS cells without using the bi-layer technique and obtained cells with comparable efficiencies.

The main difference between stoichiometric and Cu-poor CIS is the point defects which control the carrier concentration. By using a proposed defect model, the auto doping of p-type CIS material was simulated and the role of the thickness of the Cu-poor CIS layer was examined. The defect model proposed by Tanda, et.al. is shown in figure 2.3 for both Cu-poor and stoichiometric CIS. As mentioned before, other researchers identify the defects differently. However, in the numerical modeling, the “name” of these defects do not matter at all. The importance of these defect levels in this case is that they are either acceptor-like or donor-like and provide the carriers

necessary for electrical transportation. In this preliminary study, the defect densities are chosen to be the same for each defect type. A density of $8.0 \times 10^{16} \text{cm}^{-3}$ was used as it gives a reasonable majority hole concentration in the stoichiometric CIS material. It should be pointed out that above models are not necessarily correct for all CIS materials, but they represent some of the CIS materials whose characteristics are p-type when stoichiometric and almost intrinsic when Cu-poor. As the content of Cu deviates from the stoichiometry, it has been observed experimentally that there is a sharp change in the carrier concentration of the material as it changes from p- to n-type. Therefore, the characteristics of Cu-poor CIS layer cannot be summarized for all cells but differ for individual cell. The simulation results presented in this section are for the case in which the CIS layer adjacent to CdS is very slightly Cu-poor so that this layer is almost intrinsic but not quite n-type. If the experimentally obtained layer is strongly lacking Cu and becomes n-type, the simulation results given here might not agree with the experimental results.

In stoichiometric material, the donor-like defect near the conduction band edge compensated one of the acceptor-like state near the valence band, leaving only one active acceptor state. In Cu-poor CIS, the material was nearly intrinsic due to compensation of the two defect levels.

The solar cell modeled was ZnO/thin-CdS/CIS [75]. The cell with highest efficiency had this structure. The quantum efficiency and the cell performance parameters were obtained from published literatures [73][68]. Figure 2.4 shows the structure of modeled solar cell. The basic structure was taken from the literature, with the added assumption of a Cu-poor region near the CdS. The only difference between Cu-poor and stoichiometric CIS was assumed to be the defects. This enabled to simulate an experimental illuminated I-V and a quantum efficiency measurement only adjusting the lifetime in CIS, the thickness of Cu-poor CIS layer and the series resistance. Using a life time of 4.4 ns in CIS material, a series resistance of $0.27 \Omega\text{-cm}^2$ which is consistent with measured values, and 0.5 μm of Cu-poor layer, a good fit was obtained. Simulated and reported solar cell performance parameters under 100 mW/cm² AM1.5 global condition are summarized in the table 2.4. The experimental and simulated quantum efficiency is also shown in figure 2.5.

Figure 2.3 The defect models used for unintentional doping of both Cu-poor and stoichiometric CuInSe₂.

Figure 2.4 Structure of modeled ZnO/thin-CdS/CuInSe₂ Solar Cell.

Table 2.3 Comparison of experimental and simulated cell performance.

	Experimental Values	Simulation Results	
		with $R_s = 0$	with $R_s = 0.27 \Omega\text{-cm}^2$
Voc [mV]	508	508	508
Jsc [mA/cm ²]	41	40.9	40.9
fill factor	0.677	0.694	0.678
Efficiency [%]	14.1	14.8	14.1

Figure 2.5 Quantum efficiency of ZnO/thin-CdS/CIS solar cell : The solid line is experimentally obtained quantum efficiency and the dots represent a simulated result using 4.4 nsec carrier lifetime.

Figure 2.6 shows a family of illuminated I-V curves for a variety of Cu-poor layer thickness. Since Cu-poor layer is almost intrinsic, its thickness is almost the same as the thickness of the depletion width. Therefore for cells with thicker Cu-poor layer, the collecting field of the depletion region extends further, resulting in higher short circuit current. However, for thick Cu-poor layers, much of the recombination under open-circuit conditions occurs in the depletion region. The space charge recombination dominates, causing the open circuit voltage to drop (figure 2.7). In other words, the low carrier concentration near the window layer forces the electrical junction to extend further into the CIS, thus causing low open circuit voltages.

Compromising between the short circuit current and the open circuit voltage, the efficiency reaches an optimum value of 17% with 0.07 μm thick Cu-poor CIS layer and 0.27 $\Omega\text{-cm}^2$ series resistance. The dependence of efficiency on the Cu-poor layer thickness is shown in figure 2.8. It is predicted that CIS solar cell efficiency higher than 17% can be achieved by precise control of the Cu-poor CIS layer thickness and reduction in the series resistance.

Figure 2.6 Predicted I-V characteristics for cells with different thickness of Cu-poor CIS layer with no series resistance.

Figure 2.7 For the cell with Cu-poor layer, most of the recombination occurs in the depletion region under open circuit condition. The dominating depletion region recombination reduces the open circuit voltage.

Figure 2.8 Efficiency vs Cu-poor layer thickness. It clearly shows that there is an optimum value for the Cu-poor layer thickness

3. CdTe SOLAR CELLS

CdTe is considered to be a good material to be used as a base of a solar cell. CdTe solar cells are inexpensive and have achieved relatively high efficiencies. In order to evaluate and realize the potential of these cells, it is necessary to understand the processes which limit the device performance.

In this chapter, the results of CdTe material parameter study are presented, as well as absorption coefficients. Then the preliminary results of numerical modeling of the CdS/CdTe solar cell which has the best efficiency reported so far, are summarized.

3.1. Literature Survey

3.1.1. Parameter Study

An extensive review of the literature has been performed to tabulate both measured cell performances and material parameters [76]. Table 3.1 lists CdTe material parameters as reported in the literatures. Table 3.2 lists the measured performance characteristics of CdTe based solar cells as reported in the literatures.

Table 3.1 CdTe Material Parameters

parameter	values	references	parameter	values	references
Eg [eV]	1.51 (n - type)	[77]	a _o [nm]	0.647	[78]
	1.46 (p - type)			0.648 ± 0.002	[79]
	1.5	[80][81][82][83] [84]	m _n [*]	0.1 m _o	[85][86]
	1.45	[87][88][89][90] [91][92]		(0.11±0.01)m _o	[93]
	1.58	[94]	m _h [*]	0.35 m _o	[95]
	1.44	[96][97][79][98] [99]		0.12 m _o	[100]
	1.46	[101]		0.4 m _o	[85][86]

Table 3.1 continued

parameter	values	references	parameter	values	references
μ [cm ² V ⁻¹ s ⁻¹]	60-250 (n-type)	[102]	n_i [/cm ³]	1.0e7	[98]
	5 - 10 (n- type)	[103]	N_c [/cm ³]	8.65e17	[79]
	40-45 (p - type)	[80]	N_v [/cm ³]	1.27e19	[104]
	65	[81]	dielectric constant	7.21	[97]
	1200 at 170 K	[93]		10.31 (static)	[93]
				7.6 (optical)	
	159 (p - type)	[101]		9.6	[79]
	800	[79]	electron affinity [eV]	4.28	[98][105]
	$\mu_p=60$ $\mu_n= 600$	[106]	t [nsec]	6.7	[81]
	$\mu_n=68$ (doped), 70 (undoped)	[95]		for calculations, $t_n=160$ $t_p=0.8$	
	1130	[107]		5 (longest)	[109]
	60 - 250	[108]		100	[110]
	40 - 60 (Hall)	[110]		0.06	[112]
	50 (Hall)	[111]		0.1	[113]
	4 (at junction)	[85]			
	$\mu_n = 4$	[114]	S_I [cm/sec]	2.0e6	[112][104]

Intrinsic Carrier Concentration

The simulation carried out using cited values of effective density of states predicted unrealistically high open circuit voltage. These values of effective density of states also lead to a significantly smaller value of n_i than that listed in table 3.1.

In order to bring the simulated cell performance near the experimental results, the effective density of states of conduction band had to be raised. It was found that N_c should be at least $9.0e18$ cm⁻³. In fact, this agrees well with the value of N_c determined from the ratio of effective masses. i.e.,

$$\frac{N_c}{N_v} = \frac{N_c}{1.27e19} = \left(\frac{m_n^*}{m_p^*}\right)^{\frac{3}{2}}$$

$$m_n^* = 0.1 m_0$$

$$m_p^* = 0.12 m_0$$

The value of N_c from above equation was $9.96e18 \text{ cm}^{-3}$. The effect of N_c , and hence n_i on the open circuit voltage is shown in figure 3.1.

Figure 3.1 Dependence of open circuit voltage on the effective density of conduction band states.

Conduction Band Offset

The electron affinity, χ , of CdTe is generally taken to be slightly smaller than that of CdS (4.3 eV). Its exact value can have an influence on predicted cell performance. A number of simulations were performed changing only the electron affinity of the CdTe. The results show that the open circuit voltage decreased slightly with increasing electron affinity of CdTe until the conduction bands of the two layers line up, then there is no change as the CdTe electron affinity increases further, since the Fermi energy pins at the conduction band edge. The band offset controls the spatial extent of the depletion region.

When $\chi_{\text{CdTe}} < \chi_{\text{CdS}}$, the depletion width into the CdTe is smaller than when $\chi_{\text{CdTe}} > \chi_{\text{CdS}}$. This can be seen in figure 3.2 and 3.3. Recombination in the depletion width has a strong influence on the open circuit voltage. Figure 3.4 shows the recombination rate in the CdTe for the two cases depicted in figure 3.2 and 3.3 at open circuit.

Figure 3.2 The electron affinity of CdTe is assumed to be 3.9 eV while that of CdS is set to be 4.3 eV. As the χ of CdTe approaches 4.3 eV, the recombination in the depletion width increases resulting in slightly lower open circuit voltage.

Figure 3.3 While keeping the χ of CdS at 4.3 eV, the electron affinity of CdTe is increased to 4.7 eV. Although this creates a potential barrier at the interface, it does not have a strong influence on the cell performance.

Figure 3.4 Recombination Rate vs position for different values of electron affinity of CdTe. The χ of CdS was kept at 4.3 eV. Once χ of CdTe gets larger than 4.3 eV, there is hardly any change in the depletion region width.

Interface Recombination Velocity

Although it is typically thought that recombination at the window layer/CdTe have a major influence on cell performance, the simulations do not substantiate this assumption. When CdS/CdTe solar cell was modeled with no recombination and $S=2.0 \times 10^6$ cm/s at the interface, almost no difference in performance is predicted. This is due to the fact band bending at the heteroface shifts the collecting junction away from the interface into CdTe (figure 3.5). Since most of the excess carriers are created in the CdTe, they need only to reach the collecting junction before they recombine. Thus, the heteroface is effectively screened out and cell performance is nearly unaffected.

Figure 3.5 This energy band diagram explains why the interface recombination density has little effect on the cell performance. The electrical junction where most of the carriers are collected is away from the interface of CdS and CdTe.

Carrier Mobility and the Back Contact

Figure 3.6 shows the effect of CdTe minority carrier mobility and back surface effective recombination velocity on the short circuit current. The back surface has little effect on the short circuit current except for the highest simulated mobilities. This is because most of the carriers are created within the CdTe depletion region and are collected by the drift field. This also decreases the sensitivity of the cell to the mobility value. The short circuit current varies by only about 10% for mobilities ranging from 10 to 650 $\text{cm}^2/\text{V}\cdot\text{s}$.

Figure 3.6 The effect the value of minority carrier mobility has on the short circuit current is strongly influenced by the back surface effective recombination velocity.

Carrier Lifetime

Larger values of carrier lifetime significantly improves all open circuit voltage, short circuit current, fill factor leading to a sharp increase in the efficiency of the cell. Although some of the reported values of the carrier lifetime of cadmium telluride are in a high range, there can be a large variance depending on whether the material is a single crystal, or poly-crystalline thin film. The poly-crystalline thin film CdTe is usually used for solar cells because of the low manufacturing cost. Deducing from the simulated solar cell runs, the carrier life time of CdTe is thought to be around 10 nsec.

3.1.2. CdTe Solar Cell Performance

The energy band gap of CdTe which is 1.45 eV is an ideal value for operation of solar cells since most of the solar spectrum power is spread around that energy. As shown in table 3.2, the values of open circuit voltage are a lot higher than those of CuInSe₂ solar cells with energy band gap of 1.02 eV.

Table 3.2 Survey of Measured CdTe Cells

window	Voc [V]	Jsc [mA/cm ²]	FF	Effi. [%]	Illumination	Growth method	Ref.
CdS	0.725	21.23	0.67	10.31	AM1.5 100 mW/cm ²	electrodeposition	[115]
	0.7484	22.21	0.6339	10.5	AM1.5	CSS	[116]
	0.75	17	0.62	10.5	AM2 75 mW/cm ²	CSS	[117]
	0.72	27	0.65	12.6		electrodeposition	[118]
	0.785	19.38	0.674	8.1* (10.1**)	AM1.5 global 100 mW/cm ²	Writing method	[119]
	0.807	23.8	0.66	12.7**	AM1.5 global, 100 mW/cm ²	electrodeposition	[120]
	0.819	23.5	0.74	14.2**	ELH		
	0.754	27.9	0.61	12.8**	AM1.5 100 mW/cm ²	screen-printing	[121]
	0.612	20.5	0.605	8.7	ELH 87.5 mW/cm ²	Evaporation	[80]
	0.7	23.9	0.7	11	global 100 mW/cm ²		[122]
	0.78	22.5	0.58	11.6	87.3 mW/cm ²	sintering	[123]
	0.83	22.57	0.6	11.3	global 100 mW/cm ²	CSS	[124]
	0.759	18.6	0.57	8.8	ELH white light		[125]
	0.747	21.69	0.657	10.6	AM1.5 global	CSS	[126]
	0.747	17.3	0.67	8.7		?	[114]
	0.77	18.5	0.69	9.8	AM1.5 global 100 mW/cm ²	?	[127]
	0.745	22.1	0.6603	10.9		MOCVD and	[6]
	0.713	24.19	0.5976	10.3		MBE	
	0.72	27.9	0.65	13.1	AM1 1000 W/m ²	electrodeposition	[128]
	0.804	18.9	0.7	10.6	100 mW/cm ²	?	[129]
	0.68	20.5	0.56	7.9		MOCVD	[130]
	0.813	19.6	0.62	9.9	100 mW/cm ²	MOCVD	[131]
	0.8496	24.41	70.35	14.6	100 mW/cm ²	CSS	[131]
	0.786	19.0	0.616	8.7	100 mW/cm ²	rf sputtering	[132]
	0.783	24.98	0.627	12.3	AM1.5 global	?	[133]

Table 3.2 Continued

window	Voc	Jsc	FF	Effi.	Illumination	Growth Method	Ref.
CdS	0.84	21.9	0.726	13.4	global 100 mW/cm ²	CSS	[134]
	0.79	26.2	0.615	12.7	global 100 mW/cm ²		[102]
	0.81	19.5	0.73	11.5	global 100 mW/cm ²		[102]
	0.745	22.1	0.66	10.9	global 100 mW/cm ²	MOCVD	[135]
	0.8245	18.16	0.623	9.3	global 100 mW/cm	vapor deposition	[136]
	0.797	21.1	0.672	11.3	AM1.5 100 mW/cm ²	screen printing	[137]
ITO	0.81	20	0.55	10.5	85 mW/cm ²	single crystal	[138]
	0.892	20.1	0.745	13.4* (14.4**)	AM1.5 100 mW/cm ²	single crystal	[139]
TO	0.663	28.1	0.563	10.5	AM1.5 global 100 mW/cm ²	CSS	[12]
	0.82	21		10.7	AM1 106 mW/cm ²	CSS	[140]
	0.723	12	0.63	6	AM1	vapor phase epitaxy	[141]
ZnO	0.45	18	0.41	4.8		single crystal	[142]
	0.53	12.5		3.7	60.5 mW/cm ²	co-evaporation	
	0.54	19.5		7.6	100 mW/cm ²		[143]
	0.54	19.5		8.8**	AM1 100 mW/cm ²	single crystal	[144]
Au	0.807	20.9	0.67	15.1	AM2	electrodeposition	[145]
Zn _{0.3} Cd _{0.7} S	0.78	23.4	0.594	10.84	ELH AM1	CSS	[105]

** Efficiencies with ** are the active area efficiencies.

* Efficiencies with * are the total efficiencies.

All the others do not specify which efficiency they were measuring.

The most popular window material for CdTe is CdS. CdS/CdTe solar cells have reasonably high open circuit voltage as well as high short circuit current and can be fabricated by a number of different methods. The cell with maximum efficiency of 14.6 % under 1.5 AM global spectrum of 100 mW/cm² is produced by close-spaced vapor transport method. Some of the fabrication methods of CdTe thin films for solar cells are:

Electrodeposition

The cathodic deposition of CdTe films from aqueous electrolytes was demonstrated in 1978. CdTe plating electrolytes typically contain an excess amount of Cd^{2+} and 30 -40 ppm of HTeO_2^+ [120].

Screen Printing

In this approach a paste consisting of a mixture of 91 wt% CdS power, 9 wt% CdCl_2 and an appropriate amount of propylene glycol is first screen printed on a borosilicate glass substrate. After drying, the film is sintered at 690 °C for 90 minutes in a N_2 atmosphere. A paste consisting of a stoichiometric mixture of 99.5 wt% Cd and Te powders, 0.5 wt% CdCl_2 and propylene glycol is then screen printed on the CdS layer. After drying the whole structure is annealed in N_2 atmosphere to form the CdTe film and the CdTe/CdS junction [137].

Close Spaced Sublimation (CSS)

In the CSS approach, first a CdS film then a CdTe layer are deposited on an ITO coated glass substrate temperature of 550 and 600 °C, respectively. Cells fabricated by this method have shown very high efficiencies [134]. Figure 3.7 is the schematic diagram of the apparatus.

Figure 3.7 Schematic of the apparatus for the deposition of CdTe films by the CSS technique.

Spraying

An aqueous solution of CdCl_2 and thiourea was first sprayed onto a heated ITO/glass substrate, forming a thin-CdS layer. A CdTe layer is then grown over the CdS layer by spraying a

solution containing Cd and Te species. High efficiency CdTe/CdS solar cell fabrication by the spraying technique involve high temperature annealing steps for grain growth and film formation [146].

Other methods used for fabrication of CdTe solar cells are sputtering [113], evaporation [147], MOCVD [96] and atomic layer epitaxy.

3.1.3. CdTe Absorption Parameters

The absorption coefficients of p-type CdTe are different from those of n-type CdTe. Although p-type CdTe is used for heterojunction solar cells for the reason that accompanying transparent semiconductors to be used as window materials are only available as n-type, both n-type and p-type CdTe absorption parameters for ADEPT were found and listed in appendix A. Figure 3.8 shows the absorption coefficients as a function of wavelength. It is possible to make homojunction CdTe solar cells. Generally, for the homojunction CdTe solar cells, p-type CdTe is used as a base layer since its absorption coefficients are higher than those of n-type CdTe. However, homojunction CdTe solar cells have exhibited poorer performance than heterojunction solar cells have.

Figure 3.8 CdTe absorption coefficients vs wavelength in microns. The experimental absorption coefficients were obtained from [77]

3.2. Detailed Study of Some Limiting Factors of CdS/CdTe Solar Cells

At the time of this work, the best CdS/CdTe solar cell had an conversion efficiency of 13.4% with open circuit voltage of 0.84 V, short circuit current of 21.9 mA/cm² and 72.6% fill factor [134]. This cell was prepared from CdS deposited from an aqueous solution, a low temperature, low cost technique, and CdTe deposited by close-spaced sublimation. Although it has very high V_{oc} and fill factor compared to other cells, it has relatively low short circuit current. It can be said that in this case the limiting factor of the cell efficiency is the short circuit current. One of the possible explanations why this cell has a low short circuit current is that the reflection of the CdS window layer in the short wavelength region is significant.

A number of numerical modeling of this cell were carried out. The modeled cell was 4 μm thick p-CdTe with CdS window layer of 0.1 μm in thickness. For all simulations, everything was kept the same except for the optical transmission of CdS window layer. With a constant value of reflection of CdS window (up to 15%), the predicted value of short circuit current was always higher than the reported value. A very close prediction was made only when wavelength dependent transmittance of CdS window layer was used. Figure 3.9 is the experimental and simulated I-V characteristics under different conditions. The loss of short circuit current is evident in figure 3.10 which shows the CdS transmittance and normalized AM1.5 global spectrum. (The only reason for normalization was to show it with CdS transmission spectrum in the same graph.) Although the CdS layer reflectance is smaller than 5% for long wavelength, the incident power in the energy range larger than 2.4 eV is transmitted only about 20%. This loss is rather large since the power in this range makes up about a third of total available power. Therefore it is essential to improve the CdS layer to transmit more in the short wavelength range. The reason why the simulated CdS/CdTe solar cell gives a slightly smaller value for the short circuit current is probably due to the fact the reflectance of CdS was pinned to 4.6% for energies less than 1.58 eV since this was the last point available from the published data [148].

The numerical modeling of CdS/CdTe results show that the reason why this cell with the best efficiency so far does not have the highest short circuit current is that there is a considerable loss of available photons due to the reflectance of CdS window layer. It is predicted that by improving the transmittance of CdS layer over lower wavelength range, it would be possible to have much higher short circuit current. Another option would be to use a wider band gap material such as ZnO.

Figure 3.9 Experimental and simulated I-V characteristics of CdS/CdTe solar cells under AM1.5 global conditions.

Figure 3.10 (a) Normalized AM 1.5 global spectrum and CdS reflectance as a function of energy.

Figure 3.10 (b)

Same as figure 3.10 (a) except that only the energy range in which the solar spectrum power is strongest is shown.

4. WORK IN PROGRESS

In the last chapter, the limiting factor of short circuit current of CdS/CdTe solar cell was discussed. Even though some CdTe based solar cells achieved open circuit voltages higher than 800 mV, most cells have lower open circuit voltages. It has been suggested that interdiffusion between CdS and CdTe is the main cause of degraded performance [5][6].

For both CuInSe₂ and CdTe based cells, series resistance significantly reduces the fill factor, thus leading to lower efficiency. The series resistance could be both internal and external. The internal series resistance which could be arising from grain boundary recombination cannot be avoided.

First section of this chapter describes the studies that will be done on the interdiffusion between CdS and CdTe. The second section shows the general physics of grain boundary recombination and then describes the numerical modeling of grain boundary recombination that will be carried out. These results will show what is limiting the solar cell performance and how the cell could be improved. From these understandings, it will be possible to present the optimum designs for CdTe and CuInSe₂ solar cells.

4.1. Interdiffusion Between CdS and CdTe

CdTe based solar cells with low open circuit voltages but with high short circuit current are generally prepared by screen-printing, spray-process or MOCVD. It has been reported that in cells made by screen-printing and sintering technique, there is an intermixing of CdS and CdTe during growth forming a new material, CdTe_{1-y}S_y [6][5]. There is a large increase in the number of defects in the new interface layer and this leads to a narrower band gap. It has been suspected that this layer with narrower band gap is the cause for low open circuit voltage. However, some research groups argue that it is not the narrower band gap that is degrading the cell performance but the cause for lower efficiency is the large density of defects in the newly formed layer [6]. The thickness of this layer could be controlled to some extent by controlling the temperature during the film growth. When the temperature is low, there is less interdiffusion between CdS and CdTe.

Even though this unintentionally formed layer is speculated to cause the reduction in open circuit voltage, it is not known whether the band gap narrowing or the increased number of defects resulting in the increased recombination of generated carriers is limiting the efficiency. Also, it is not known exactly how much this new layer is limiting the performance of the solar cell or if it affects only V_{oc} or other parameters as well.

The interdiffusion between CdTe and CdS will be investigated. By doing a series of simulations, the exact amount of loss and how much reduction in the efficiency this loss leads to

can be known. Even with these loss mechanisms, the efficiency of cadmium telluride based solar cells can be improved by optimization of the design of the solar cells.

4.2. Grain Boundary Recombination

Polycrystalline semiconductors are different from single crystalline semiconductors due to the presence of grain boundaries. Although the grain boundaries are physically much smaller than individual grains, they greatly influence the carrier transport in the material. A grain boundary may be considered as a surface characterized by a distribution of interface states within the energy gap. At this grain boundary, there are a large number of defects due to incomplete atomic bonding. This results in the formation of trapping states. These trapping states are capable of trapping carriers and thereby immobilizing them. This reduces the number of free carriers available for electrical conduction. After trapping the mobile carriers the traps become electrically charged, creating a potential energy barrier which impedes the charge transfer [8].

Although in most cases the microscopic nature of these defects is still poorly understood, their influence on the electric properties can be addressed on a quantitative level. Their effect can be significant causing a decrease in mobility and carrier concentration of high-resistivity space-charge region surrounding the grain boundary. The grain boundaries generally have a negative influence on the photovoltaic properties of pn junctions.

In thin film solar cells, the photo-generated current has to pass across several grain boundaries. These grain boundaries can cause [149]:

- * recombination centers for minority carriers
- * interface recombination at the heterojunctions due to lattice mismatch and imperfect epitaxial growth of the window layer
- * increased series resistance due to reduced majority carrier mobility across grain boundaries in the window layer
- * shunt currents along conductive grain boundaries.

4.2.1. Physics of the Grain Boundary and Some Analytical Models

In the energy band diagram, grain boundaries leads to a formation of a double Schottky potential barrier due to the interface states. The grain boundary recombination models developed by many researchers in the past make several approximations. In the case where the barrier width is much larger than the mean free path of the carriers, the current across the grain boundary is assumed to be dominated by diffusion current while in the other case, it is essentially the

thermionic emission current over the potential barrier that is contributing to the current [150][7][151].

The Diffusion Theory

If the barrier width, w is much larger than the mean free path, l of the carriers, assuming that it is n-type semiconductor, the current is obtained from the diffusion equation [152].

$$j = qn\mu \left(-\frac{\partial V}{\partial x} \right) + qD_n \frac{\partial n}{\partial x} \quad (4.1)$$

Where V is the electrostatic potential. At the grain boundary, the charge distribution is represented by figure 4.1a. By integrating Poisson's equation for this charge distribution, the electric field, potential and current across the grain boundary can be found. Figure 4.1b shows the grain boundary potential under applied bias, V_a .

$$j = qN_D\mu \frac{E_1 E_2}{E_1 - E_2} (e^{qV_2/kT} - e^{qV_1/kT}) \quad (4.2)$$

$$V_1 = -\frac{\epsilon}{2qN_D} \left(\frac{Q}{2\epsilon} - \frac{qN_D V_a}{Q} \right)^2 \quad (4.3)$$

$$V_2 = -\frac{\epsilon}{2qN_D} \left(\frac{Q}{2\epsilon} + \frac{qN_D V_a}{Q} \right)^2 \quad (4.4)$$

$$E_1 = -\left(\frac{Q}{2\epsilon} + \frac{qN_D V_a}{Q} \right) \quad (4.5)$$

$$E_2 = +\left(\frac{Q}{2\epsilon} - \frac{qN_D V_a}{Q} \right) \quad (4.6)$$

E_1 and E_2 are electric field strength at $x=0^-$ and $x=0^+$ respectively.

Figure 4.1 (a) Charge distribution at the grain boundary at $x=0$.

Figure 4.1(b) Electrostatic potential resulting from the charge at the grain boundary.

The Thermionic Emission Theory

Again assuming n-type semiconductor, the thermionic emission current is obtained by subtracting the number of electrons going right to left from the number of electrons going from left to right [152][7].

$$j = qN_D v_{th} (e^{qV_2/kT} - e^{qV_1/kT}) \quad (4.7)$$

$$v_{th} = (8 kT/\pi m^*)^{1/2} \quad (4.8)$$

Where v_{th} is the mean thermal velocity of carriers with effective mass m^* . Above equation is equivalent to,

$$j = A^* T^2 e^{-(E_g - E_F)/kT} [e^{qV_2/kT} - e^{qV_1/kT}] \quad (4.9)$$

E_g is the energy gap of the semiconductor, E_F is the Fermi level in the bulk of the grain and $A^* = 4\pi m^* q k^2 / h^3$ is effective Richardson factor.

As it can be seen from figure 4.2, the applied voltage, V_a is given by $V_1 - V_2$. When the applied voltage is small enough, the effective mobility across the grain boundary can be calculated from the conductance.

Figure 4.2 The energy band diagram showing the potential barrier at the grain boundary.

$$j_{th} = qN_D v_{th} e^{qV_B/kT} (e^{-qV_a/kT} - 1) \approx qN_D v_{th} e^{qV_B/kT} V_a \frac{q}{kT} \quad qV_a \ll kT \quad (4.10)$$

$$\sigma = \frac{q}{kT} qN_D v_{th} e^{qV_B/kT} = qn\mu \quad (4.11)$$

So, the effective mobility is :

$$\mu_{eff} = \frac{q}{kT} V_{th} e^{qV_B/kT} \quad (4.12)$$

The above equation says that the mobility is thermally activated with an activation energy proportional to the equilibrium value of barrier height. Also, the effective mobility is dependent on the potential barrier height, V_B which is a function of the density of grain boundary states.

4.2.2. Numerical Modeling of the Grain Boundary

It should be noted that the thermionic emission theory is the simplified analytical equation for the current in the vicinity of a potential barrier, with the assumptions that only those among the carriers which possesses a kinetic energy larger than the barrier height can move across the boundary. The net current is proportional to difference of the electron fluxes, crossing the boundary from left to right and from right to left. The current flow solely depends on the barrier height and not on the shape of the potential barrier. Therefore the thermionic emission current model completely ignores the inherent space charge region present at the grain boundaries. In particular, as it is apparent from the effective mobility equation, even though the dependence of mobility of carriers on the potential barrier height hence on the trap density at the grain boundary is well understood from the thermionic emission theory, this theory does not give any insight on how the size of the grains play a role in current transport.

The current flowing across is controlled by the applied bias and the height of potential barrier. The barrier height should be determined by solving the Poisson's equation. Self-consistency is required since the band bending depends on the occupation of all trap states and the filling is determined by the position of the quasi-fermi level. By numerically solving the Poisson's equation and the current continuity equations simultaneously, the current calculated across the potential barrier at the grain boundary will have the contribution from both the diffusion and the thermionic emission current, without any simplifying assumptions.

A model which is capable of handling the grain boundary recombination will be developed. In a real polycrystalline material, the crystallites have a distribution of sizes and irregular shapes. In order to simplify the model, following assumptions are made.

- (1) The semiconductor is composed of identical crystallites with a grain size L cm as illustrated in figure 4.3.
- (2) The grain boundary thickness is d cm and this grain boundary contains N_t cm⁻² of traps located at energy E_t .

Above assumptions allow the grain and grain interface thickness to be any sizes and to have different impurities. It has been shown that the assumption of identical rectangular grains with delta functioned traps at the grain boundaries for analytical calculations agreed well with experimental results for polycrystalline silicon [7][8].

Figure 4.3 The grain boundary model that will be implemented. The grain size, grain boundary width, the trap density at the interface and the location of the trap should be specified. The direction of the bend banding will be dependent of the electrical property of the traps and bulk dopant.

Given the grain size and grain boundary interface thickness, this model will generate alternating regions of grains and grain boundaries. Depending on whether the ionized impurities at the grain boundaries are acceptor-like or donor-like, the direction of the band bending will be determined. The interface traps will be treated as SHR recombination centers.

It has been reported that mobilities are thermally activated in CuInSe_2 poly-crystals [153]. It is generally believed that the grain boundary recombination is the cause for much smaller values of carrier lifetime and mobilities compared to those of CIS single crystals. A grain boundary model for polycrystalline thin film CuInSe_2 has been proposed by Tuttle, et al [154]. According to this model, the direction of the band bending can be opposite depending on the deviation from stoichiometry. For indium-rich CuInSe_2 , the grain boundary potential barrier will impede charge transfer while charge transfer between grains proceeds unimpeded for copper-rich CuInSe_2 films (figure 4.4).

Figure 4.4 A model of thin film CuInSe_2 grain boundary for copper-poor and copper-rich film compositions.

The influence of the grain boundary recombination and the effect of grain size on the performance of solar cells will be investigated in detail. The proposed polycrystalline thin film CuInSe_2 grain boundary model will be verified numerically to see how the deviation from stoichiometry affects the material parameters like mobilities. Comparisons between the results of numerical modeling of grain boundary recombination and other analytical models will be made.

5. FUTURE WORK

The measured data of various characteristics of CIS and CdTe solar cells will be gathered and numerically modeled in order to understand these devices better. The numerical modeling will especially focus on the temperature and light dependence of these cells. It is well known that some of CIS based solar cells IV characteristics do not obey the super imposition law under illumination, while some cells do. In general solar cells perform better in lower temperature. Both CIS and CdTe solar cells have shown increased performance with decreased temperature but they also showed that there was a change in diode quality factors with temperature. Understanding the physics of these phenomena with the aid of numerical modeling will be beneficial in the effort of improving these solar cells.

Also the effect of the processing steps on the physics of devices could be sought by the numerical modeling. After treatments like annealing have significantly increased the performance of these solar cells.

The outcome of these studies could eventually lead to producing higher performing solar cells with full use of their potentials.

APPENDIX A. ABSORPTION MODEL

A.1. Absorption Properties of Semiconductors

The absorption properties of a semiconductor play the most important role in photovoltaic devices since these devices generate electric energy by absorbing the sun light. Light absorption can occur by the excitation of transitions between the allowed bands in a semiconductor and energy levels introduced in to the forbidden gap by impurities.

Fundamental absorption refers to the annihilation of absorption of photons by the excitation of an electron from the valence band up into the conduction band, leaving a hole in the valence band. Both energy and momentum must be conserved in such a transition. A photon has quite a large energy but a small momentum. Figure A.1 shows the absorption process for a direct-band-gap semiconductor. The energy difference between the initial and final state is equal to the energy of the original photon:

$$E_f - E_i = hf \quad (A.1)$$

Where h is the Plank constant and f is the frequency of the photon. Therefore, it is easily seen that the fundamental absorption occurs when the energy of the photon is larger than the fundamental optical band gap, E_g . As the photon energy hf increases, so does the value of the crystal momentum at which the transition occurs as shown in the figure. The energy away from the band edge of both the initial and final states also increases. The probability of absorption depends on the density of electrons at the energy corresponding to the initial state as well as the density of empty states at the final energy. Since both of these quantities increase with energy away from the band edge, the absorption coefficient increases rapidly with increasing photon energy above E_g .

Transitions can occur at lower energies by a two-step process involving not only photons and electrons but also a third particle, a phonon. As opposed to photon, phonons have low energy but relatively high momentum. A carrier can be excited to a higher energy across the direct band gap by a photon with the emission or absorption of a phonon. This process is relatively weak but is strongest at long wavelength when carrier concentrations are large. However, it should be noted that this absorption process does not generate an electron-hole pair, thus does not contribute to the operation of the solar cells.

Figure A.1 Energy - crystal momentum diagram showing the absorption of a photon by the excitation of an electron from the valence band and two-step photon absorption process.

Polycrystalline thin films are a set of grains joined by grain boundaries with carrier traps that cause a depletion region inside the grains, a built in electric field and band bending. The near band-edge absorption spectrum of such films can be typically separated in three different regions.

1. Band to band absorption beyond the fundamental threshold energy band gap.
2. Defect and impurity absorption below this.
3. In the upper part of the band gap, an excess of absorption is caused by phonon-assisted tunneling (Franz-Keldysh effect arising from built-in electric field) in a small range below E_g .

A.2. ADEPT Absorption Model Description

Very accurate absorption coefficients can be generated in ADEPT by reading various coefficients from the input data. Almost all the known equations for different kinds of absorption are existent in the code. ADEPT is capable of handling allowed direct transitions, forbidden direct

transitions as well as phonon assisted transitions. Basically the absorption model is divided into two regions, above the band gap energy and below the band gap energy.

Band Gap Absorption

In some materials, it is possible to have more than one optical band gap energy.[1] Up to three optical band gap energies can be selected in the code. The fundamental optical band gap energy can be the same as electrical band gap energy. If this is the case, by setting EG.OPT= -1, EG.OPT defaults to electrical band gap energy, Eg. The equation for the absorption coefficient is,

$$\alpha = \beta_0 + \beta_1*(E-Eg)^{0.5} + \beta_2/E*(E-Eg)^{1.5} + \beta_3/E*(E-Eg)^2 + \beta_4*E*(E-Eg)^2 + \alpha_1/E*(E-Eg)^{0.5} + \alpha_2/E*(E-Eg2)^{1.5} + \alpha_3/E*(E-Eg3)^{1.5} \quad (A.2)$$

where E is the energy, Eg is the fundamental optical band gap energy, Eg2 is the second and Eg3 is the third optical band gap energies.

Sub-Band Gap Absorption

In some cases, absorption below the fundamental band gap energy is significant. As mentioned before, if the sub-band gap absorption is due to the phonon assisted process, it would not create electron-hole pair. However, it is possible that two step photon absorption can occur via some defects inside the band gap. In this case, the absorption of the photon will generate electron-hole pairs. There are two choices for handling these situations. One can select either TAIL.OPT or PHONON.OPT.

When TAIL.OPT is chosen, the code assumes that absorption is exponentially decaying below Eg (see figure A.2). Therefore α_c and ζ , which determine how strongly and quickly the absorption is decaying should be present in the input deck.

$$\alpha_{tail} = \alpha_c * \exp[-\zeta * (\lambda - \lambda_c)] \quad (A.3)$$

λ_c is the cutoff wavelength.

It should be noted that there is no relation between absorption coefficients for above and below the band gap energy. Each energy region is dealt separately. Therefore, when sub-band gap absorption occurs, it is possible to have absorption coefficient calculated from the equation for the energies above the band gap is smaller than the absorption coefficient obtained by using the above equation at Eg. In this case, in order to smooth out the absorption coefficient curve, cut-off energy for sub-band gap absorption is automatically found in the code by bisectional method.

Figure A.2 TAIL.OPT --- Residual absorption below the band gap energy is exponentially decaying.

It is wise to choose PHONON.OPT when the absorption coefficient varies significantly with the energy. This models phonon assisted transitions with up to 2 different phonon energies. The absorption coefficient due to phonon - assisted transition is given by

$$\alpha = \frac{B(h\nu - E_g + E_p)^2}{\exp(E_p/kT) - 1} \quad (A.4)$$

where B is a constant independent of phonon energy, E_p is the phonon energy and kT the thermal energy.

It has been reported that by extrapolating $\alpha^{1/2}$ vs energy curve to 0, regions of energies separated by intervals of phonon energies which are close to optical phonon wave number values were found [30]. Based on this fact, the code was modified to handle up to 5 sub regions below the band gap energy. These sub regions are separated by phonon energies (see figure A.3). The user should enter the values of phonon energies, E_{p1} and E_{p2} and the absorption coefficients at the edge of each sub region, $\alpha[i]$. Inside each sub region, the absorption coefficient is generated assuming the residual absorption mechanism is due to phonon-assisted transitions.

In the i-th region, the absorption coefficient is calculated according to the following equation.

$$\alpha = \alpha[i] + \frac{b[i] \times (e - E_g + e[i])^2}{\exp(e[i]/kT) - 1} \quad (\text{A.5})$$

where $\alpha[i]$: known value (experimental value) of absorption coefficient at $(E_g - e[1+i])$

$$\begin{aligned} e[1] &= E_{p1} \\ e[2] &= E_{p1} + E_{p2} \\ e[3] &= E_{p1} + E_{p2} + E_{p1} \end{aligned} \quad (\text{A.6})$$

Only E_{p1} , E_{p2} and $\alpha[i]$ need to be defined by the user.

Figure A.3 PHONON.OPT --- The sub-band gap absorption is due to phonon-assisted transitions.

In the code, above parameters are equivalent to the following:

equation	ADEPT	equation	ADEPT
b0	BO.OPT	Eg	EG.OPT
b1	B1.OPT	Eg2	EG2.OPT
b2	B2.OPT	Eg3	EG3.OPT
b3	B3.OPT	α_c	ALFC.OPT
b4	B4.OPT	ζ	ZETA.OPT
a1	A1.OPT	Ep1	EP1.OPT
a2	A2.OPT	Ep2	EP2.OPT
a3	A3.OPT	$\alpha[i]$	ALF.OPT[i]

A.3. Absorption Parameters for CuInSe₂

ADEPT	(a)	(b)	(c)	(d)
A1.OPT	2.641932e4	4.280328e4	4.640943e4	3.903080e4
A2.OPT	7.415209e4	5.487097e4	5.535324e4	8.040365e4
A3.OPT	.	.	.	3.375030e5
ALF.OPT[1]	1.825084e+06	1.875890e+06	5.834784e+06	3.151848e+06
ALF.OPT[2]	3.191912e+06	6.894068e+06	9.665732e+06	8.818179e+06
ALF.OPT[3]	1.768182e+07	1.096972e+07	3.111858e+07	4.732103e+06
ALF.OPT[4]	6.498228e+07	2.593351e+07	.	7.669954e+06
ALF.OPT[5]	.	4.018558e+07	.	1.490329e+07
ALF.OPT[6]	.	2.449951e+09	.	5.927302e+08
EG.OPT	1.00	0.945	1.00	0.95
EG2.OPT	1.10	1.18	1.10	1.10
EG3.OPT	.	.	.	2.10
EP1.OPT	0.019			
EP2.OPT	0.031			

at. % Cu/In/Se

a)17.3/27.9/54.8 b)25.7/23.9/50.4

c)22.0/26.8/51.2 d)24.2/25.0/50.8

A.4. Absorption Parameters for CdTe

ADEPT	p - CdTe	n - CdTe
EG.OPT	1.533	1.588
BO.OPT	0.8788e4	0.5898e4
B1.OPT	5.6555e4	6.0955e4
B2.OPT	-9.1585e4	-9.1585e4
B3.OPT	4.9434e4	4.9434e4
B4.OPT	1.4176e4	1.4176e4
ALFC.OPT	1.14e4	1.204e4
ZETA.OPT	33	26.557

APPENDIX B. MULTIPLY IONIZED IMPURITIES AND RECOMBINATION

B.1. Multiply Ionized Impurities

In compound semiconductors like CuInSe₂ and CdTe, a deviation from stoichiometry generates donors or acceptors depending on whether it is the cation or the anion which is in excess. Therefore, even when the semiconductors are not intentionally doped, they can still be p- or n-type by the self-doping mechanism. When an impurity atom can contribute more than one extra carrier (electron or hole), it becomes a multiple donor or multiple acceptor. The multiple impurity has a state for each carrier it can contribute. Thus it is likely that the multiple impurity has some significant effect in the self-doping mechanism.

In order to have an insight on how the self-doping mechanisms are carried out, a model which is capable of handling a number of singly ionized SHR recombination centers as well as multiply ionized impurities has been developed. The multiply ionized traps can have any charge state. For example if the trap has two electrons when it is neutral but cannot capture any more, there will be three different charge states for this trap. When it releases one electron, it will become singly ionized donor and when it releases the other electron as well, it will become doubly ionized donor. If a multiple trap has an electron when it is neutral and capable of capturing another electron, this trap can be singly positively charged or singly negatively charged. When the trap is multiply ionized, the corresponding binding energy is thought to be much higher than singly ionized state. Therefore the energy level at which the trap is located could be dependent on the charge state of the trap.

B.2. Numerical Modeling of Multiply Ionized Impurities

The mathematical derivation of the multiply ionized recombination center follows the multiple energy level impurity center model from reference [155]. Suppose an impurity center which is at (s)th charge state can release r electrons and capture t electrons. The impurity center can be charged to (s+1) charge state by capturing an electron or to (s-1) charge state by capturing a hole. For the (s)th charge state, there are N_s centers per unit volume and the rate of change of this concentration comes from the eight emission and capture processes illustrated in figure B.1.

There are four transition processes related to a given charge state. Let the notation $E_{s+1/2}$ refers to the effective energy level involved in the capture and emission of electrons and holes related to both the initial charge state, s and the final charge state, s+1. c_{ns} (e_{ns}) is the probability coefficient of electron capture (emission) by a center initially in (s)th charge state.

The rates of the four transition processes involving the energy level $E_{s+1/2}$ are :

a) Rate of electron capture by a center initially in (s)th charge state to s+1 state :

$$c_{ns}N_s n \quad (B.1)$$

b) Rate of electron emission with change of charge state s+1 to s :

$$e_{ns+1}N_{s+1} \quad (B.2)$$

b) Rate of hole capture with change of charge state s+1 to s :

$$c_{ps+1}N_{s+1}p \quad (B.3)$$

b) Rate of hole emission with change of charge state s to s+1 :

$$e_{ps}N_s \quad (B.4)$$

The net electron capture rate is (a) - (b), given by

$$r_{cn}(s+1/2) = c_{ns}N_s n - e_{ns+1}N_{s+1} \quad s \rightarrow s+1 \quad (B.5)$$

and the net hole capture rate is (c) - (d), given by

$$r_{cp}(s+1/2) = c_{ps+1}N_{s+1}p - e_{ps}N_s \quad s+1 \rightarrow s \quad (B.6)$$

At equilibrium, detailed balance requires fundamental processes to self-balance. Therefore, r_{cn} and r_{cp} must equal to zero under equilibrium conditions. Under the assumption that the emission and capture coefficients all remain approximately equal to their equilibrium values under non-equilibrium conditions the emission coefficients can be eliminated from above equations.

$$r_{cn}(s+1/2) = c_{ns} (N_s n - N_{s+1} n_{s+1/2}) \quad (B.7)$$

$$r_{cp}(s+1/2) = c_{ps+1} (N_{s+1} p - N_s p_{s+1/2}) \quad (B.8)$$

To facilitate the computations of $n_{s+1/2}$ and $p_{s+1/2}$, note that

$$\begin{aligned} n_{s+1/2} &= (N_{s,o} / N_{s+1,o}) n_o = \exp((E_{s+1/2} - E_f)/kT) n_i \exp((E_f - E_i)/kT) \\ &= n_i \exp((E_{s+1/2} - E_i)/kT) \end{aligned} \quad (B.9)$$

$$p_{s+1/2} = n_i \exp((E_i - E_{s+1/2})/kT) \quad (B.10)$$

The rate of change of a charge state density is given by :

$$dN_s/dt = r_{cn}(s-1/2) - r_{cp}(s-1/2) - [r_{cn}(s+1/2) - r_{cp}(s+1/2)] \quad -r < s < t \quad (B.11)$$

$$dN_s/dt = -[r_{cn}(-r+1/2) - r_{cp}(-r+1/2)] \quad s = -r \quad (B.12)$$

$$dN_s/dt = r_{cn}(t-1/2) - r_{cp}(t-1/2) \quad s = t \quad (B.13)$$

Under steady - state condition, there can be no net transfer of the center from a charge state s to a neighboring charge state s+1. In other words,

$$r_{cn}(s+1/2) = r_{cp}(s+1/2) \quad (B.14)$$

$$c_{ns}N_s n + e_{ps}N_s = e_{ns+1}N_{s+1} + c_{ps+1}N_{s+1}p \quad (B.15)$$

which gives,

$$N_{s+1}/N_s = (c_{ns}n + e_{ps})/(e_{ns+1} + c_{ps+1}p) \quad (\text{B.16})$$

The total steady-state recombination rate of electrons or holes at the impurity centers is obtained from the sum of the steady-state recombination rate at each level.

$$R_{ss} = \sum_{s=-r}^{t-1} r_{cn(s+1/2)} = \sum_{s=-r}^{t-1} r_{cp(s+1/2)} \quad (\text{B.17})$$

Now, the total charge per unit volume can be expressed as

$$\rho = (p - n + N_D - N_A - \sum_{s=-r}^t s N_s) \quad (\text{B.18})$$

The total density of recombination centers, N_{tt} is sum of the densities of each charged state, N_s .

$$\begin{aligned} N_{tt} &= \sum_{s=-r}^t N_s = N_{-r} + N_{-r} \left(\frac{N_{-r+1}}{N_{-r}} \right) + N_{-r} \left(\frac{N_{-r+1}}{N_{-r}} \right) \left(\frac{N_{-r+2}}{N_{-r+1}} \right) + \dots \\ &= N_{-r} \left[1 + \sum_{\alpha=-r}^{t-1} \prod_{s=-r}^{\alpha} \frac{N_{s+1}}{N_s} \right] \end{aligned} \quad (\text{B.19})$$

Therefore once the total density of the impurity center, N_{tt} and the number of the electrons this center can capture and release, t and r respectively are entered in to the code, each charge state density N_s is calculated automatically as a function of the charge state position in the band gap.

Figure B.1 Carrier capture and emission processes for the transitions $s-1 \leftrightarrow s$, $s \leftrightarrow s+1$. The kinetic coefficients have two subscripts. The first subscript shows whether the involved carrier is hole or electron, and the second subscript stands for the initial charge state. The transitions between (s-1)th and (s)th charge states are shown in real lines and the transitions between (s)th and (s+1)th charge states are shown in dashed lines.

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16. Abstract (Limit: 200 words) This report describes research to predict the achievable performance for CuInSe ₂ - and CdTe-based solar cells and to present the optimized design for these devices and develop a tool for analysis. Presently, it has been successful to model the cells with the highest efficiencies and point out how they can be improved. However, it is not clear why most cells have lower efficiencies. It is possible that the design of these devices is not optimized or that there is a degradation of cell performance depending on the fabrication process used. For CdS/CdTe cells, some researchers report that poor cell performance is caused by interdiffusion between CdS and CdTe. This report presents preliminary results of a literature survey and the numerical modeling of CuInSe ₂ and CdTe solar cells, work currently in progress, and topics for future consideration.			
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