

DISSERTATION

EXPERIMENTAL AND THEORETICAL INVESTIGATIONS OF SELENIUM GRADED
CADMIUM TELLURIDE-BASED SOLAR CELLS

Submitted by

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In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

Spring 2022

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ABSTRACT

EXPERIMENTAL AND THEORETICAL INVESTIGATIONS OF SELENIUM GRADED CADMIUM TELLURIDE-BASED SOLAR CELLS

In the past few years, cadmium telluride (CdTe) based solar cells have emerged as an important photovoltaic (PV) technology for electricity generation. The optimal bandgap of the absorber material and high throughput manufacturing methods make CdTe PV a leading cost-competitive alternative to silicon solar cells. However, the performance of CdTe PV-devices strongly depends on the processing of the absorber layer. This work uses experiments in conjunction with two-probe atomistic models based on density functional theory (DFT) to understand the processing effects on the electronic properties of heterostructures in CdTe PV-devices and improve the efficiencies of CdTe solar cells.

Various processing conditions such as cadmium chloride (CdCl_2) treatment and selenium (Se) alloying of CdTe absorber layer were found to improve the PV-device efficiencies (from 0.22% to 18.3%). Atomistic simulation models utilized DFT coupled with Green's function to investigate the electronic properties of thin film surfaces, grain boundaries and interfaces within the CdSeTe/CdTe PV-device configuration. Structural and electronic properties of bulk $\text{CdSe}_x\text{Te}_{1-x}$ and $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surfaces were calculated and compared with the experimental and theoretical literature to establish the modeling parameters. The results from the elemental characterization done on the CdCl_2 treated CdSeTe/CdTe films formed the basis of respective CdSeTe/CdTe interface and grain-boundary atomistic models. The electronic properties calculated for Se-graded CdSeTe/CdTe interfaces showed a pick up in the conduction band (CB) energy level (creating electron reflector effect) and was verified experimentally by Ultraviolet Photoelectron Spectroscopy (UPS). DFT models also suggested that higher p-doping is required in CdSeTe-only absorber to achieve similar electron reflector effect at the CdSeTe/Te interface. The grain-boundary models

further showed that presence of Se and Cl at the CdTe grain-boundary passivates the critical acceptor defect states and leads to n-type inversion at the grain-boundary. The band engineering and defect state passivation in the Cl and Se-alloyed CdTe solar cells efficiently extracted the charge carriers, thereby producing high-performing CdSeTe/CdTe PV-devices (19.4%).

In comparison to unalloyed CdTe absorbers, Se alloying passivated the defect states in CdTe grain boundaries. It has also been observed that Alumina/CdSeTe/Alumina double heterostructures showed higher minority carrier lifetime indicating better passivation in the bulk and the oxide/absorber interface. The electronic properties calculated via DFT suggested Te/O interface formation at the CdSeTe/Alumina interface led to reduction in the interfacial defect states. This combination of lower density of defect states at the CdSeTe grain boundaries and CdSeTe/oxide interface produces high lifetime (430 ns) in the oxide/CdSeTe double heterostructures. Following this, TeO_x was also used as the back passivation layer of unalloyed CdSeTe/CdTe bilayer to produce 19% efficient CdTe PV-devices. The introduction of TeO_x as the potential passivation layer eliminates the requirement of copper doping in the CdTe PV-devices, thereby increasing the longevity of CdTe solar panels in the field.

ACKNOWLEDGEMENTS

I would like to take this opportunity to thank my advisors, Dr. W.S. Sampath and Dr. Christopher R. Weinberger, for his guidance and patience. I would also like to thank my committee members, Dr. James Sites and Dr. Umberto Martinez, for their time and commitment. I would like to thank the funding organization NSF I/UCRC (Industry University Cooperative Research Program) for funding this study.

My special thanks to my mentor Dr. Amit Munshi, Dr. Ramesh Pandey, Dr. Anthony Nicholson, Dr. Aanand Thiagarajan and my colleague Zach Lustig for their kind support at all important junctures. I am also thankful to our undergraduate staff Blake Hill for his help with SEM-EDS measurements. I cannot thank enough Dr. John Walls, Tom Fiducia, and Dr. Ali Abbas for doing some of the characterization at the Loughborough University, UK.

I am highly grateful to my friends and my entire family who inspired me throughout my academic career. My father Pramod K. Agarwal and mother Priya Agarwal has supported me throughout my academic carrier which has allowed me to emerge as a student I am today. I cannot thank my brother Ajay Shah enough for his support and encouragement throughout my life. Also, I show my gratitude to my paternal grandparents Late Shri Madan L. Agarwal, Late Smt. Parvati Devi, and maternal grandparents Shri Ram K. Bagaria, and Smt. Chandrakala Devi, whose blessings and confidence in my ability played a crucial role in carving my career and life. Last but not the least; I would also like to thank my sadhguru Pujya Shri Avdheshanand Giriiji Maharaj whose spiritual blessings has helped me to stay focused in achieving my life goals.

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Chapter 1

Introduction

Life on the planet earth can be conceptualized as a form of energy manipulation. From using flint stones for generating sparks to using solar panels for electricity, mankind has come a long way in their quest to achieve an efficient form of energy manipulation. In today's world, electricity is perhaps the most versatile form of energy as it can be converted to various other forms such as heat energy, mechanical work etc.

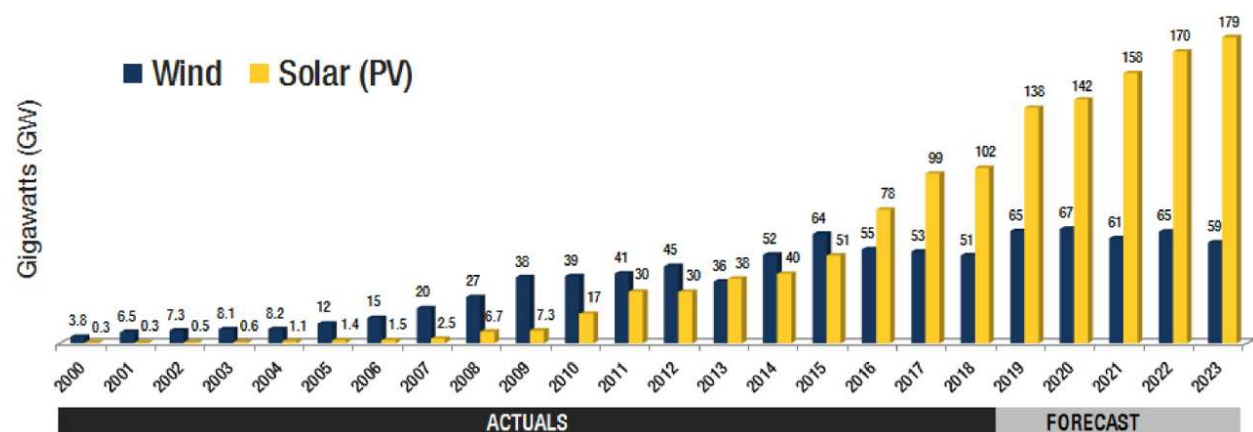


Figure 1.1: Comparison of the newly added wind and solar electricity generation capacity. The bar-graph chart compares the actual and projected forecasts of the new electricity generation capacity between the wind and solar (PV) energies. (image taken from [2])

The 20th century has seen the development of non-renewable and renewable forms of energy for the electricity generation. Non-renewable energy such as coal and petroleum technologies have been used for electricity generation for decades. But the ever rising global energy demand and limited availability of the non-renewable energy sources has challenged the society to look into the possible sustainable energy options. In past few years, amongst the renewable energy sources, solar and wind energy has emerged as an economical, and sustainable option for the electricity generation. Despite observing an initial pickup in the 1990s, the wind energy market has seen a sluggish growth in recent years owing to factors such as increased size of wind turbines, availability

of space, and inconsistency in the power output. On the other hand, the increasing efficiencies of the solar modules has allowed small scale rooftop installations of the solar panels. As a result, solar Photo-Voltaic (PV) energy have seen a higher annual new capacity addition than wind energy and is forecast to grow at a faster rate as shown in Figure 1.1.

The United States Energy Information Administration (EIA) estimated a thousand fold increase in the electricity generation (from 76 million KWh in 2009 to 69 billion KWh in 2019) from the utility scale Photo-Voltaic (PV) power plants in the last decade [9]. The substantial growth in the PV installation has been aided by a significant decrease in the cost of electricity generated by solar modules. Figure 1.2 shows the exponential decline in the utility scale solar price with increasing solar installation across the globe.

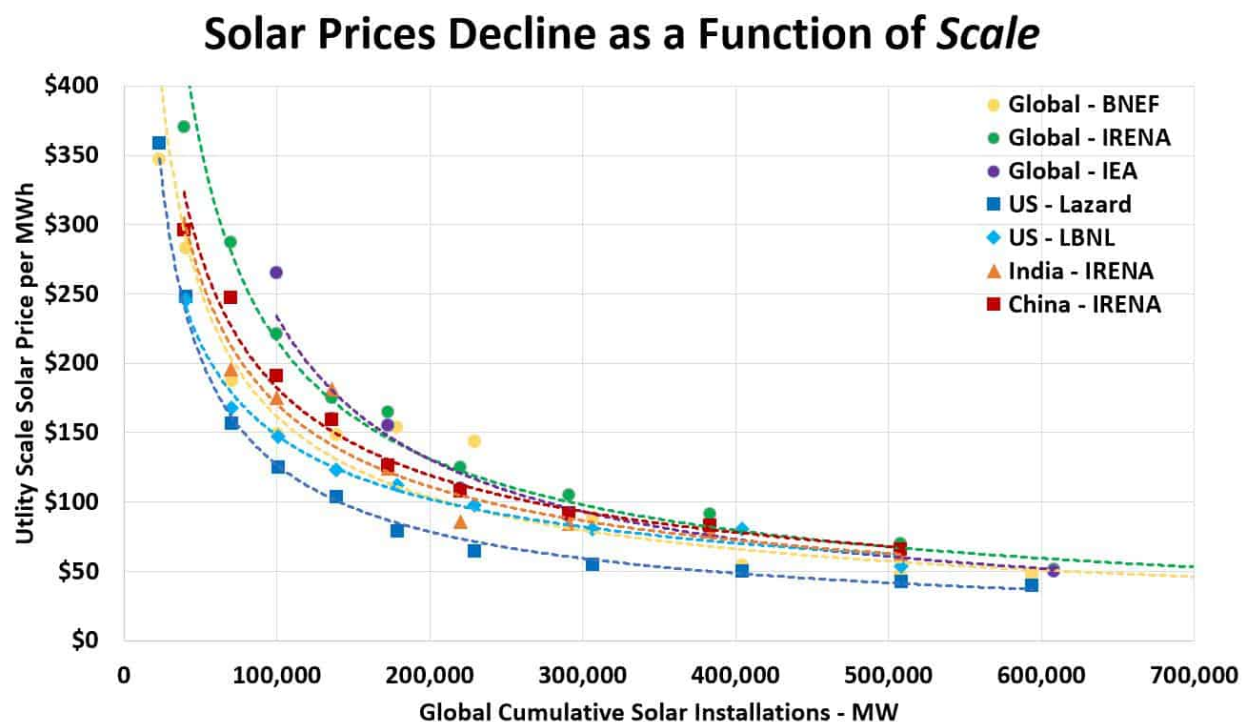


Figure 1.2: Graph depicting fall in the solar prices as a function of global cumulative solar installation for different countries.(image taken from [3])

The steep decline in the cost of PV system has made them competitive with other forms of electricity generation. The falling prices of the solar panels has also led to an increase in the

installations of residential solar panels. The growing investment in the industrial manufacturing of the PV modules has resulted in the creation of thousands of jobs in the solar industry. The increased installation of PV modules has also led to several environmental and health benefits [10]. According to a report from National Renewable Energy Laboratory (NREL), carbon footprint due to the electricity generated from the PV technologies is 25 times less than that of the coal technology [11]. The abundance of the energy source, environmental and economic benefits shown by PV technologies indicate a bright future for the solar industry. One of the PV technology currently used in the utility-scale size is cadmium telluride (CdTe) based thin film PV. The aim of this work is to understand the characteristics of the CdTe thin film PV-devices that will further enable manufacturing of highly efficient CdTe solar panels.

1.1 Cadmium Telluride Photovoltaics

Cadmium telluride solar cells over the past few years have emerged as a prominent PV technology for electricity generation. CdTe being a direct bandgap semiconductor have a high absorption coefficient and absorbs 92% of visible light in $1\mu\text{m}$ film thickness [12]. CdTe PV modules are manufactured in an inline process where glass enters into the factory and comes out as finished solar panels in two hours. The above advantages has enabled the CdTe PV technology with low capital investment and reduced energy expenditure [13].

The research community has demonstrated a steady increase in the CdTe device efficiencies over the past four decades. Figure 1.3 shows the best research cell efficiencies for various CdTe PV technologies achieved over the years. The optimization of process steps, replacement of CdS with high resistance transparent buffer layers, annealing devices in cadmium chloride (CdCl_2), doping CdTe material with copper (Cu), alloying selenium (Se) with the CdTe absorber layer, and adopting back contacts such as zinc telluride (ZnTe) has allowed the researchers to significantly increase the CdTe device efficiencies from 10% in 1980 to 22.1% in 2016 [13–20]. For polycrystalline CdTe solar cell, CdCl_2 treatment of CdTe absorber layer is considered to be a crucial step in obtaining high efficiency devices. Apart, from CdCl_2 treatment step, alloying Se to CdTe film is another

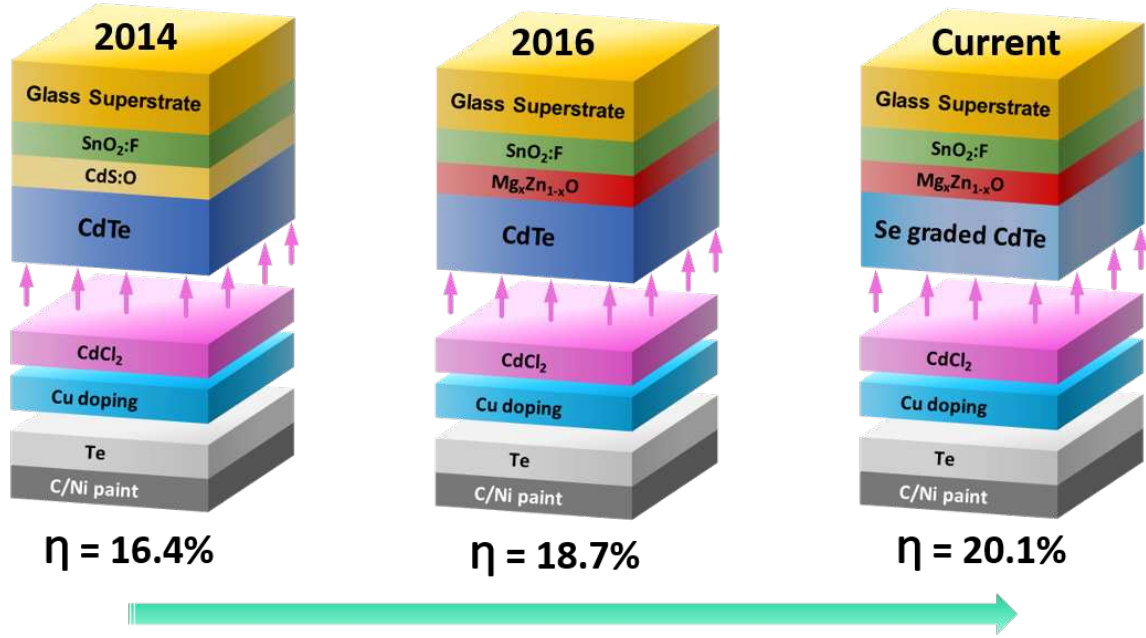


Figure 1.3: Progress in research scale device efficiencies at Colorado State University

critical step in achieving 22.1% efficiency in CdTe solar cell [21]. It is thought of that both CdCl₂ treatment and Se alloying of CdTe leads to passivation of defects in the polycrystalline absorber layer [21, 22]. The following section outlays the effect of the CdCl₂ treatment and Se alloying of CdTe absorber films on the polycrystalline (px) CdTe device efficiencies.

1.1.1 CdCl₂ treatment of px-CdTe absorber

CdCl₂ treatment is considered to be a key step for drastic enhancement in the performance of px-CdTe solar cell and has been known to the research community since 1976 [23]. It has been shown that CdCl₂ treatment of px-CdTe solar cells leads to a better device performance in comparison to single crystal CdTe based solar cells [24]. Thus, it could be inferred that Cl interaction with CdTe grain boundaries is necessary to obtain high efficiencies in px-CdTe based solar cells.

Several mechanisms using experiments and theoretical calculations have been proposed over the years, to understand the role of CdCl₂ treatment in improving the CdTe device performance. *Li et. al* in the recent report using electron energy loss spectroscopy (EELS) and density functional theory (DFT) calculations showed that Cl substitution of the tellurium (Te) sites leads to n-type

inversion at the CdTe grain-boundary [22]. The p-type grain interior when inverted to n-type at grain-boundary forms a local p-n junction and contributes in separation of electron-hole pair charge carriers. Numerous research articles suggests that high temperature CdCl₂ treatment causes the CdTe grains to recrystallize and grow in the (111) orientation [25–27]. Some of the published literature have also revealed enhancement in the charge carrier lifetime and passivation of the deep defect levels as an explanation of the improved device performance after CdTe is treated with CdCl₂ [18, 28, 29].

1.1.2 Alloying Selenium with CdTe absorber

Alloying CdTe with Se leads to formation of a ternary alloy material called cadmium selenium telluride (CdSe_xTe_{1-x}). CdSe_xTe_{1-x} like CdTe is a direct bandgap semiconductor material whose bandgap value can be adjusted by varying the Se content (x). As pointed before, the highest efficiency of 22.1% achieved in the research scale CdTe device was realized by alloying Se to CdTe absorber layer [17].

Depending on the Se content (x), CdSe_xTe_{1-x} exists either in Zinc-blende or wurtzite phase [7]. *Munshi et. al* recently demonstrated device efficiencies over 19% by using CdSe_xTe_{1-x} (x = 0.20)/CdTe absorber layer [14]. The bandgap of the as deposited CdSe_xTe_{1-x} film in the same study was measured to be 1.41 eV which is lower in comparison to the CdTe-only absorber layer (1.50 eV). The presence of lower bandgap absorber material enables high wavelength light absorption and increases the device short circuit current eventually leading to high efficiency devices. In another study with the same device structure, it was also observed that CdCl₂ treatment of CdSe_xTe_{1-x}/CdTe absorber layer leads to Se grading into the CdTe layer through the grain boundaries [30]. *Fiducia et. al* using cathodoluminescence and secondary ion mass spectroscopy further showed that presence of Se in the CdTe material passivates the critical defect in the bulk absorber layer [21]. Similar research done by *Guo et. al* utilizing structural and optical characterizations in combination with first principles calculations revealed that Se and Cl together improves the minority carrier lifetime by reducing the absorber midgap defect states [31]. Overall, the published

literature points out the importance of Se alloying and CdCl_2 treatment of CdTe absorber layer as the key steps to fabricate highly efficient solar cells.

1.2 CdTe PV: Life-cycle assessment and Environmental impact

Cadmium (Cd) in elemental form is a group 2B carcinogen and is mainly a byproduct availed during smelting of minerals such as zinc and lead ores. Therefore, it becomes necessary to utilize the Cd for useful purpose at its produced rate for Cd not to be stockpiled, cemented or buried in landfills [32]. It has been established that CdTe is more stable than elemental cadmium. *Alsema et. al* showed that thin-film CdTe panels has lowest greenhouse gas and life cycle cadmium emissions among all the energy technologies [33].

Amongst the present solar technologies, CdTe PV technology has been rated most eco-friendly technology that generates electricity power at low costs. A study done by *Raugei et. al* showed that CdTe has the smallest carbon footprint of 18g CO_2 eq/KWh and lowest water input (0.27 kg/KWh) giving it edge over other solar and conventional energy sources [34]. The fast payback time of under one year and large scale deployment of CdTe solar panels makes the CdTe PV a cost-efficient and sustainable PV technology. It has also been shown earlier that CdTe solar panels perform better in hot and humid climatic conditions in comparison to silicon solar panels [35]. In summary it can be inferred that CdTe PV technology has lower Cd emissions, is cost-effective, sustainable and eco-friendly form of PV technology which could perform better than its contemporary counterpart in harsh climatic conditions.

1.3 Research at Colorado State University

The current world record for demonstrating the highest efficiency of 22.1% in CdTe device is held by First Solar Inc. [17]. However, at Colorado State University (CSU) the best efficiency in CdTe device achieved to date is 20.14% and is highest among any other university or national labs. The $\text{CdSe}_x\text{Te}_{1-x}$ /CdTe solar cells at CSU are fabricated using multiple closed space sublimation (CSS) process in a single vacuum chamber known as Advanced Research Deposition System

(ARDS) [36]. Figure 1.4 shows a schematic illustration of the typical $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ absorber based solar cell fabricated at Colorado State University.

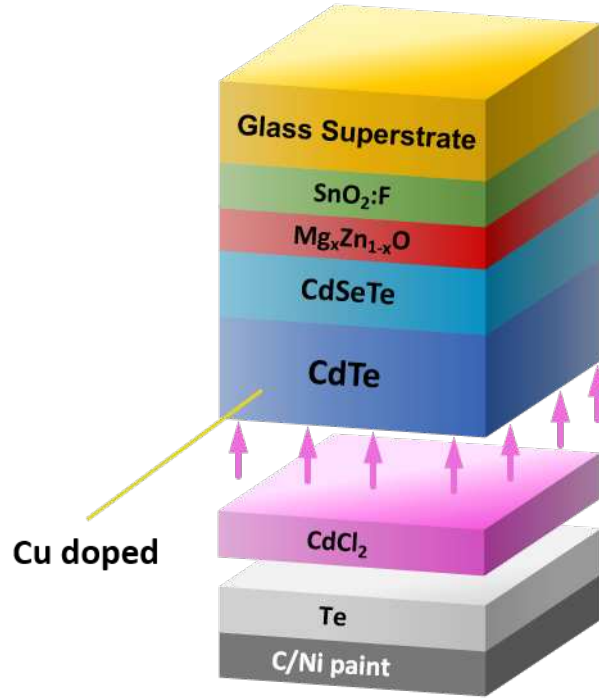


Figure 1.4: Schematic showing a typical $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ PV-device in superstrate configuration (not to scale)

The devices are fabricated on glass coated with an n-type transparent conducting oxide (TCO, mostly $\text{SnO}_2:\text{F}$). The n-type TCO is deposited by the manufacturer. The glass is cleaned in ultrasonic heated cleaner using commercially available micro-90 detergent and then dried in isopropyl alcohol/nitrogen atmosphere. Magnesium zinc oxide ($\text{Mg}_x\text{Zn}_{1-x}\text{O}$) is then deposited by RF sputtering using a single $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ target. Thereafter, the substrate is transferred to ARDS for absorber deposition and high temperature CdCl_2 treatment of the absorber layer. After CdCl_2 passivation the substrate is rinsed with water to clean residual CdCl_2 on the absorber surface. The substrate is then transferred to another vacuum chamber containing copper chloride for p-type doping of the absorber layer. Following this the film is moved to Te evaporator, where a p^* Te contact layer is deposited. The substrate is then painted with carbon and nickel paint in polymer binder and devices

are delineated using abrasive glass media for final electrical measurements. The above process describes the fabrication of a single junction CdTe PV-device. The Shockley-Queisser limit of the single junction CdTe PV-device is $\sim 33\%$ [37]. However, as mentioned before the highest efficiency achieved hitherto, for single junction CdTe device is 22.1%. Therefore, it is crucial to come up with new research initiatives and find ways to enhance the CdTe PV efficiencies.

In 2018, Department of Energy's Office of Energy Efficiency and Renewable Energy reported multiple technical challenges such as absorbers, defects, passivation of surfaces and interfaces, that needs to be addressed within the CdTe PV research community [38]. As can be seen from figure 1.4, the single junction CdTe PV-device has multiple interface. The presence of interfaces can easily influence the CdTe device efficiency. Moreover, the presence of grain boundaries and their passivation in the polycrystalline absorbers is expected to play greater role in attaining efficiencies over 25%. Therefore, it is important to comprehend the electronic properties of the interfaces and grain boundaries. For gaining a better understanding of the PV surface and interface properties, the DOE survey has categorized several key computational techniques. One such key but under-utilized computational technique suggested in the DOE report is high fidelity atomistic modeling based on quantum mechanical equations. Atomistic modeling based on quantum mechanics provides an accurate description of electronic properties such as defect states, energy band alignment for the surfaces and interfaces. It is important to understand the energy band alignment and defect characteristics at the interfaces for further enhancing the efficiencies of the CdTe PV-devices. Therefore, this research proposal entails the experimental findings corroborated with atomistic modeling to understand the bulk and interface electronic properties of the polycrystalline $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ absorber based solar cells.

Chapter 2

Energy band alignment for heterojunctions

2.1 Heterojunction

A famous quote by the noble laureate Dr Herbert Kroemer, "*The interface is the device*" [39] forms the basis of modern semiconductor industry. An interface is a heterojunction that occurs between two dissimilar semiconductor materials. In recent times, use of heterostructures (structures containing multiple heterojunctions) in fabricating the semiconductor devices have garnered lot of attention. The design of devices using heterojunction layers has led to improvement in device performance [40]. The use of heterojunctions has guided the semiconductor industry to fabricate devices with variety of new structures that could not have been realized using homojunction technology [40]. The main advantage of using heterojunctions as opposed to homojunctions, is exploiting the electronic property, such as bandgaps of different semiconductor materials across the junction. This allows to engineer the energy bands in many solid state devices, including solar cells which in turn leads to better device performance. Engineering energy bands is important in such solid state devices as the device performance is dictated by charge transport mechanism which depends on these energy band alignments.

In past researchers, have explained charge transport mechanisms (across the heterojunction) based on energy band alignments by both theoretical and experimental means. Fritzsche et. al [5] using X-ray Photoelectron spectroscopy experimentally calculated the energy band alignments for CdS/CdTe and CdTe/Te interfaces used in CdTe solar cells. This was recently verified theoretically using Density Functional theory (DFT) by Nicholson et. al [6]. Another research by Kephart et. al [41] showed that replacing CdS with $\text{Mg}_{0.23}\text{Zn}_{0.77}\text{O}$ (MZO) in CdTe solar cells leads to improvement in performance. Kephart et. al [41] used SCAPS (based on Anderson's model) for modelling MZO/CdTe interface and described a spike in conduction band at the MZO/CdTe heterojunction. This spike feature, aids e- transport in a better manner in MZO/CdTe heterojunction

and increases the efficiency of the CdTe solar cells. There have been other efforts by researchers to try and engineer the energy band alignment to get better performance from solid state devices [41]. Thus, it becomes imperative to understand the theoretical band alignment models. This chapter briefly review the effects of various band alignment model on the charge transport mechanism in heterojunctions formulated hitherto.

2.2 Common terminologies

Before learning the construction of band alignment across heterojunctions, it is important understand the physical concepts encompassing the band alignment construction. Solid state physics states that, due to the interactions of atoms their discrete energy levels eventually splits into allowed (Conduction band and Valence band) and forbidden energy bands (band-gap region) obeying the Pauli's exclusion principle [42].

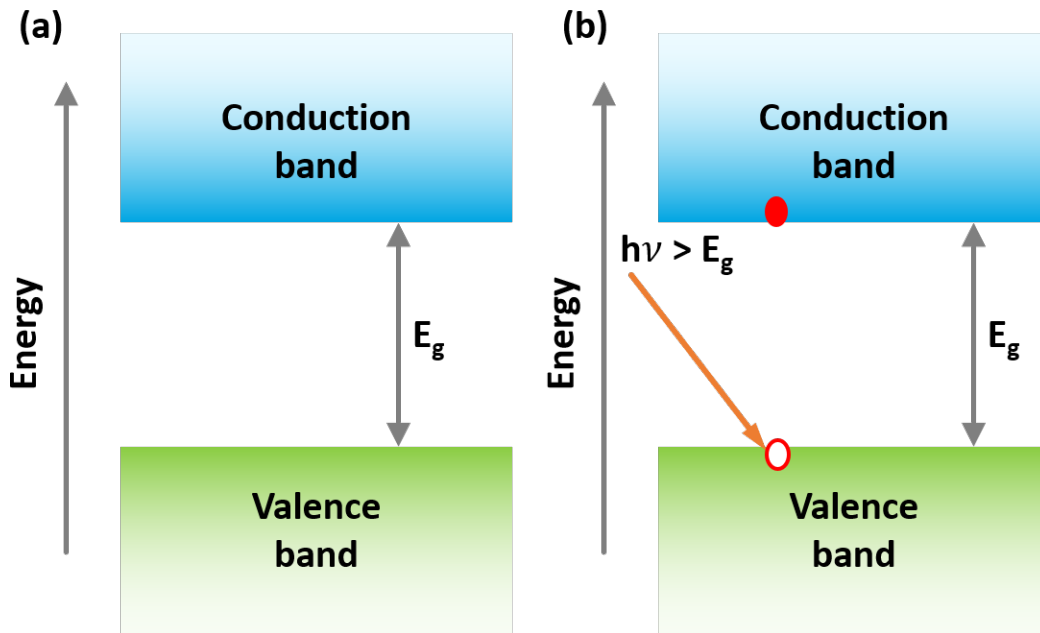


Figure 2.1: Schematic showing the (a) valence band, conduction band and bandgap region E_g in a semiconductor at $T=0K$ (b) excitation of electron from valence band to conduction band when light of energy $h\nu > E_g$ strikes the semiconductor. This leads to formation of electron-hole charge carriers.

Assuming an intrinsic semiconductor, Bandgap is the region where no electronic states exists after band splitting. It also separates valence band and conduction band. The valence band represents the highest level of energy state that are occupied by the valence electrons at $T=0K$. The conduction band represents the lowest level of energy states unoccupied by the electrons at $T=0K$. Figure 2.1 (a) shows the Valence band, Conduction band and the bandgap region in a semiconductor at $T=0K$. The electrons from valence band can be excited into the allowed levels of conduction band, if the exciting energy for electron is greater than the bandgap (E_g) of the intrinsic semiconductor. The excitation of electrons leads to formation of another type of charge carriers called holes in the valence band. Figure 2.1 (b) shows the formation of electron-hole pairs when the electrons are excited. The separation of these charge carriers constitutes current and is the principle of working of the solar cells. Sometimes the generated electron-hole pairs can recombine and emit energy in form of light which forms the principle of working of LEDs.

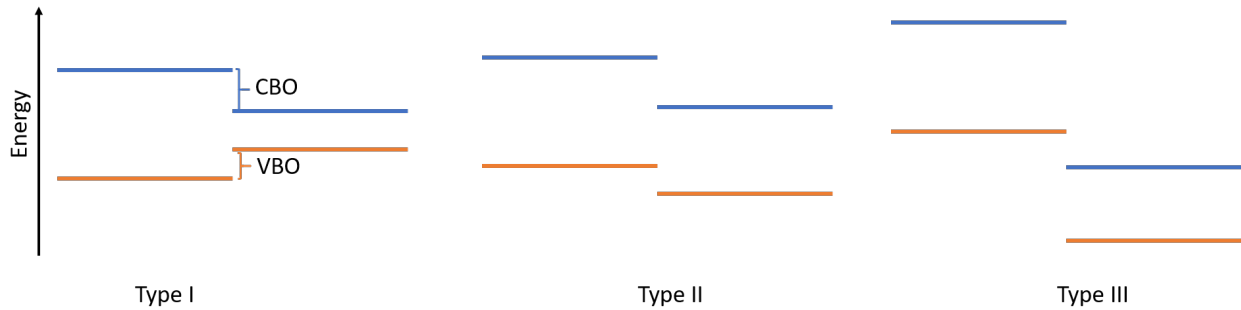


Figure 2.2: Schematic showing three different types of heterojunctions. The blue line refers to conduction band and the orange line refers to valence band. Conduction band offset (CBO) and Valence band offset (VBO) is shown only for Type I.

In heterojunctions, when two dissimilar materials forms the interface, the conduction band and valence band does not align. Based on their energy band alignments, these interfaces are broadly classified into three types of heterojunctions. They are called Straddling gap (Type I), Staggered gap (Type II) and broken gap (Type III). Figure 2.2 shows the different band alignment for heterojunctions. Another important physical parameter for heterojunction is the band offset. Band offsets are defined as the difference of the energy of conduction band (Conduction band

offset) and valence band (Valence band offset) of the dissimilar materials across the heterojunction. Band offset depends on how the energy bands line up and the bandgap of the material. The charge carrier transport and hence the quality of the devices formed using heterostructures depends on the band offsets. This is discussed in detail in next section.

2.3 Charge transport in heterojunctions

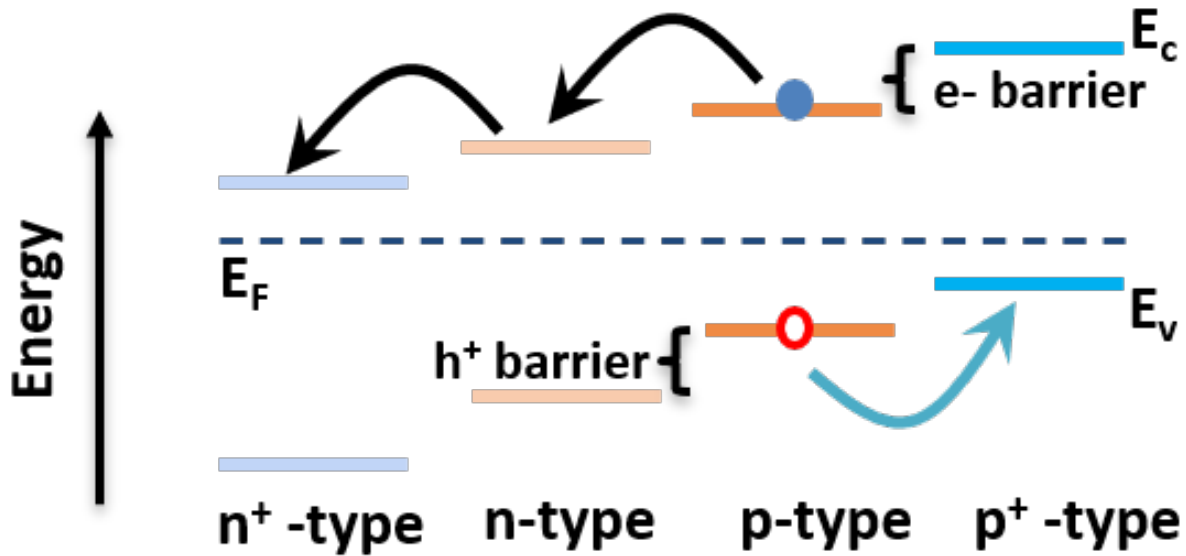


Figure 2.3: Schematic showing the conduction band and Valence band alignment in the heterojunction solar cell. The band alignment diagram shows the movement of electrons to lower conduction energy band to achieve a lower energy configuration.

As discussed before, the band offsets govern the charge transport mechanisms. The rule of the nature states that if given a chance, a particle always travels from high energy area to a lower energy point (unless forced otherwise). Figure 2.3 shows the same concept can be applied to the charge carriers, that is electrons and holes. The electrons when excited to the conduction band state would move to a lower energy state if available in the conduction band. This is where the heterojunction becomes more effective. Kumar et al. has shown that by creating a series of steps

of lower energy in the conduction band, the electrons can be extracted from the semiconductor material [43].

Holes are visualized as the charge carriers created due to absence of electrons or the deficiency of negative charge. It is not a positive charge but can be treated like a positive charge particle. Since electrons are actual particles whose energy decreases while moving down the conduction band, holes can be treated as the particles whose motion is exactly opposite of electrons. So, holes move up the valence band to achieve a lower energy state [43]. The movement of the charge carriers is therefore critical and band offsets play an important role in determining the charge transport across the heterojunction.

2.4 Band alignment construction in heterojunctions

The charge transport mechanisms discussed in the previous section (depending on the type of heterojunction) will determine the device performance. For a novel heterojunction, one would like to have a simple yet effective method to determine the band offsets. To be of use of quantitative description and in designing a device the band offset values should be accurate to ± 0.1 eV [40]. This section starts with the experimental method used in constructing the band alignment and then reviews the theoretical models formulated to determine the band offsets of heterojunctions.

2.4.1 Experiment: Photoemission Spectroscopy

Assuming two compounds X and Y forming an interface, the valence band offset $\Delta E_v(X/Y)$ at the interface is given by

$$\Delta E_v(X/Y) = \Delta E_{VBM,C}^X - \Delta E_{VBM,C8}^Y + \Delta E_{C,C8} \quad (2.1)$$

Here, $\Delta E_{VBM,C}^X = E_{VBM}^X - E_C^X$ is the energy separation between core level and the maximum of the valence energy band. Also, $\Delta E_{C,C8} = E_C^X - E_{C8}^Y$ is the difference between core level binding energy between X and Y on either side of the interface. The first two terms are calculated from

photoemission spectroscopy data for the isolated compounds X and Y, that is before forming the interface. Photoelectron spectroscopy is then done on the interface X/Y and $\Delta E_{C,C8}$ is calculated.

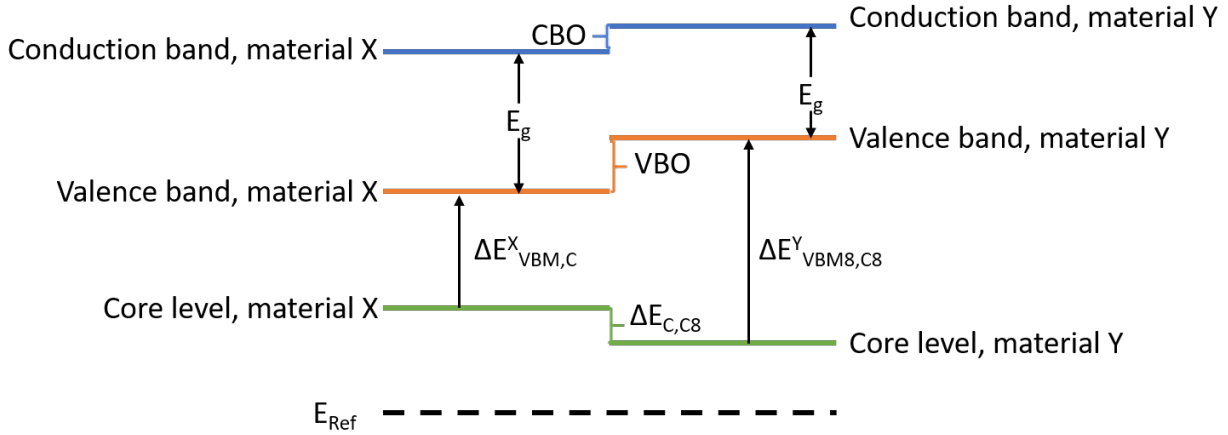


Figure 2.4: Schematic showing the calculation of band offsets value from Photoemission spectroscopy data for an interface X/Y. Core Binding energy and maximum of the valence energy band is calculated from spectroscopy and conduction band is calculated by adding the individual bandgaps.

The conduction band is then calculated by adding the respective optical bandgap to the valence bands of X and Y. The conduction band offset is then calculated by taking the difference between the conduction band levels at the interface. Figure 2.4 depicts the pictorial understanding of the above calculation to obtain the Valence and conduction band offset.

2.4.2 Theoretical models

Anderson's model/ Electron affinity rule

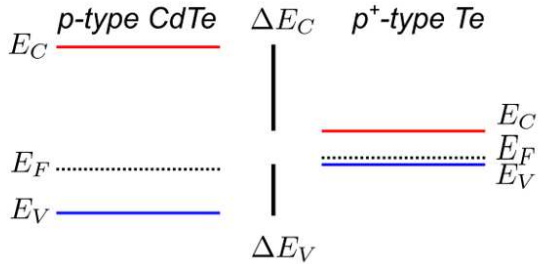
Anderson's model or the electron affinity rule is the most widely used theoretical band alignment construction model [44]. The Anderson's rule obeys the following equation to construct the band alignment model across the interface:

$$\Delta E_g = \Delta E_v(X/Y) + \Delta E_c(X/Y) \quad (2.2)$$

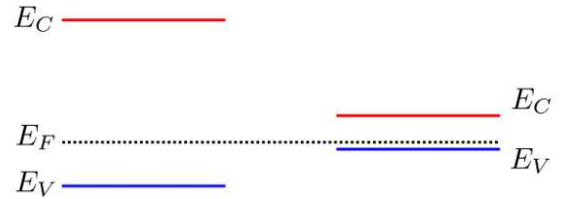
where $\Delta E_g, \Delta E_v, \Delta E_c$ are the differences in the bandgap of compound X and Y ($\Delta E_g = \Delta E_g^X - \Delta E_g^Y$), Valence band offset and conduction band offset respectively. Additionally, Anderson's model also utilizes the Fermi level (E_F) of both the semiconductor materials (X and Y) for the band alignment construction. This fermi level (or chemical potential) for each material is calculated depending on their doping and defect levels.

After obtaining all the important values the band alignment is then constructed in four steps using Anderson's rule [45]: 1) Before equilibration the Valence band, conduction band and Fermi energy levels are placed with respect to a common vacuum level, 2) A common flat fermi level is created between the two materials. This denotes the equilibrium condition, 3) The band offset values are then adjusted, and 4) the band edges of both the materials are then connected starting with the majority carrier. Figure illustrates the step by step schematic format for band alignment adapted from [45].

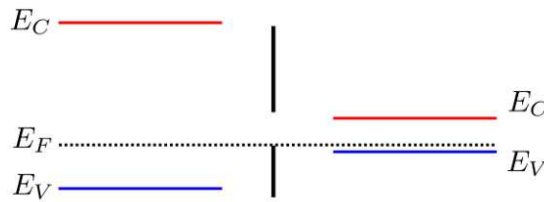
1) Obtain parameters



2) Align Fermi levels



3) Account for band offsets



4) Draw band diagram

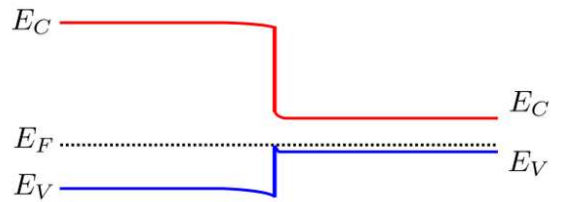


Figure 2.5: Illustrated four step example of band alignment of a p-type CdTe absorber layer with a p⁺- type Te back contact layer (image taken from Research proposal by Anthony et al. [4])

However, due to the simplistic assumptions within the Anderson's model, there are some major drawbacks associated to the model. The Anderson model fails to account for the defects such as

grain boundaries at the interface. The other limitations includes the chemical intermixing at interface, ignoring effects of plane orientation and surface terminations on the band alignment. These limitations of Anderson's model has made researchers to look towards first-principle approach such as Density Functional Theory to construct the accurate energy band alignments [4].

Density Functional Theory

Density Functional Theory (DFT) is used as a high-fidelity simulation method in the semiconductor industry. DFT is a first principle quantum theory based method and is used to calculate the electronic properties of materials. DFT allows researchers to explore the systems from an atomistic point of view and is derived from time independent many-body Schrodinger equation [46].

$$(2.3) \quad \left[-\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{\mathbf{r}_i - \mathbf{r}_j} + \frac{1}{2} \sum_{I \neq J} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{\mathbf{R}_I - \mathbf{R}_J} - \sum_{i,I} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{\mathbf{r}_i - \mathbf{R}_I} \right] \Psi = E_{tot} \Psi$$

where the respective terms in the equation are electron kinetic energy, nuclei kinetic energy, electron-electron interaction, nuclei-nuclei interaction and electron-nuclei interaction. The E_{tot} is the eigenvalue energy for the system and Ψ is total wavefunction of all the electrons present in the system. The physical constants have their usual meaning. Due to the complexity of the eigenvalue problem, it becomes almost impossible to computationally solve of the many-body wavefunction. In order to resolve this issue, some approximations such as independent electron approximation, mean field approximation needs to be applied to solve for Ψ . These simplifications made to many-body Schrodinger equation allow one to arrive at well known single particle wavefunction equation known as Kohn-Sham (KS) equation:

$$\left[-\frac{1}{2} \nabla^2 + V_n(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \Phi_i(\mathbf{r}) = E_i \Phi_i(\mathbf{r}) \quad (2.4)$$

where $V_n(\mathbf{r})$, $V_H(\mathbf{r})$ and $V_{XC}(\mathbf{r})$ are the respective nuclei, Hartree, and exchange-correlation potentials at position $\mathbf{r}$, Φ_i is the single-particle wavefunction, and E_i is the ground-state energy for i th particle. The KS equation is then solved iteratively and electron density is derived from the single particle wavefunction Φ_i . This electron density then forms the basis for the major property calculations such as bandgap, energy etc.

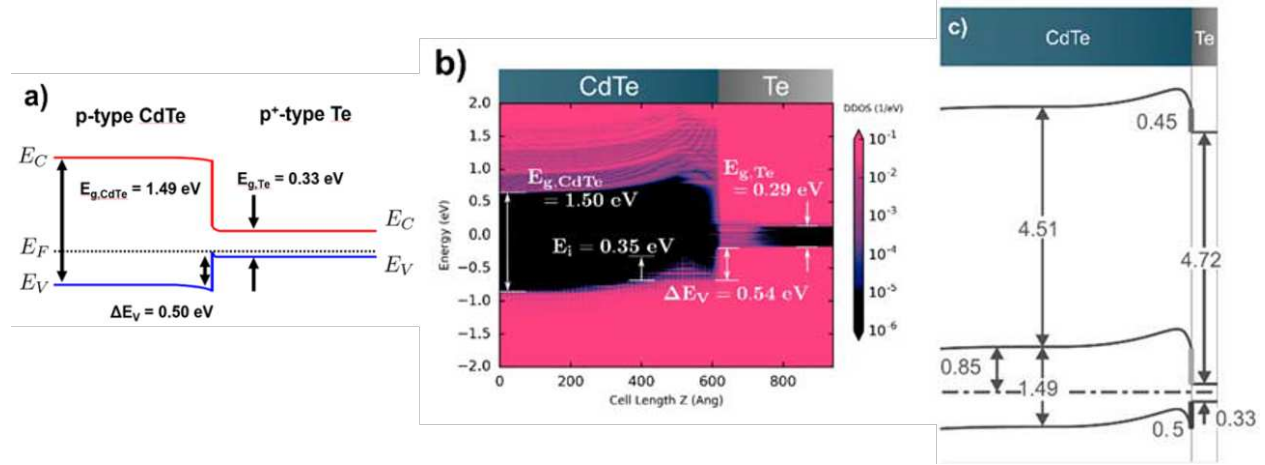


Figure 2.6: Comparison of CdTe/Te interface energy band alignment determined from a) Anderson's rule, b) DFT atomistic modelling, and c) experimental measurements from photoelectron spectroscopy (image adapted from Fritsche et al. [5] and Nicholson et al. [6])

DFT has been used by researchers to study the interfaces, calculate the density of states, defect energy levels, band alignment models etc. [47] Nicholson et al. and Thiagarajan et. al. using Linear combination of Atomic Orbitals (LCAO) basis sets with DFT constructed the Cd terminated CdTe/Te and O-Te terminated MZO/CdTe band alignment model [6, 48]. This DFT based model matched with experimentally obtained results for CdTe/Te [5] interface and is illustrated in Figure 2.6. Li et al. and Feng et al. used Plane wave basis sets with DFT to study the effects of Chlorine [22] and Oxygen [49] at the grain-boundary respectively. Based on the results Chen Li et al. constructed the band alignment diagrams with Chlorine at the CdTe grain boundaries [22]. Other researchers [50] too have used DFT to understand the band alignment models for the heterojunction interface.

DFT has thus proved to be the best model hitherto to understand the behavior of bands at the interface. Several advantages of DFT includes modelling from atomistic point, incorporating defects at interfaces, consideration of plane orientations, effect of surface termination in band alignment, and intermixing of elements or compounds at the interface. However, some of the drawbacks with DFT modelling is that it is computationally very expensive. For calculation of electronic properties such as bandgap DFT alone might not give correct results and therefore a correction parameter such Hubbard U [6] or DFT-1/2 method is needed. Also, the choice of exchange-correlation functionals (V_{xc}) sometimes may impact the results.

Other models

Apart, from the ones discussed above, some other models have also been proposed to predict the band alignment. Like Anderson's rule where band alignment is predicted based on vacuum energy level (or vacuum-electron affinity), there is another model known as Common anion model. The common anion rule suggests that as anionic states contribution to the valence band is highest, materials forming heterojunctions (CdTe/ZnTe) with common anions should have very small valence band offset. However Wei et al. [47] with his DFT calculations showed that this might not be always correct. Tersoff et al. [51] proposed gap state model based on metal semiconductor junctions. The model includes a dipole layer at the interface which leads to induction of mid gap states at the interface. The transport of electrons occurs through tunneling from the conduction of one material to the induced states of another material. The gap state model have seemed to work well with the systems having close lattice parameters (GaAs/AlAs).

Researchers sometimes also use other models like 60:40 rule, Pseudopotential theory of Frenseley and Kroemer, LCAO theory of Harrison etc [40]. Each of them have their own theory and therefore work well with particular systems. However, to date every band alignment construction model has some limitations and thus cannot be applied to every system.

2.5 Conclusion

The use of heterojunctions in solid state devices has increased over years. The performance of a solid state device depends on movement and extraction of the charge carriers across the interface. Therefore, it becomes imperative to understand the charge transport properties across the heterojunctions. Valence band offset and conduction band offset are the two important parameters for doing band alignment construction. Experiments such as X-ray Photoelectron spectroscopy have been used by researchers to determine the band offset values. These band offset values are then used in theoretical model for band alignment construction. One of the most simple but widely used model is Anderson's model or Electron Affinity rule. It helps in constructing the band alignment by accounting for electron affinity of the material. Some other common models are gap state model, 60:40 rule, common anion model etc. However, all these model are system specific and hence can not be applied to all the hterojunction system.

First principles approach such as density functional theory therefore stands a common ground where all the heterojunction can be evaluated. This is so because DFT starts from very basic equation, that is, many body schrodinger equation. However, DFT has it own limitations of high computing costs and choice of exchange correlational functionals. With combined upcoming theories like using LCAO basis sets with DFT, it is believed that computational expense will significantly reduce and will provide a better understanding of charge transport across the interface.

Chapter 3

Density Functional Theory

Density Functional Theory can be described as a computational modeling method that utilizes quantum mechanical equations to predict the electronic properties of materials. The material properties calculated using DFT is based on the variational principle of quantum theory [52] which minimizes the total energy of the system. From understanding the chemical kinetics involved in synthesis of various chemicals (such as Ammonia) to calculating materials properties for modeling planetary formations, DFT calculations has been used as a modeling tool in diverse range of scientific fields [53]. Various researchers in past have also used DFT to probe the semiconductor properties at the atomic-scale [4,8,22,47,54,55]. Literature reports also suggest that DFT has been used to understand the physical, chemical and electronic properties of surfaces and interfaces in various systems [4,55,56]. With the miniaturization of the semiconductor devices, such an understanding of the surface and interface properties at the atomistic level will lead to incubation of low cost-high performance semiconductor devices.

3.1 Kohn-Sham equation

DFT is based on the single particle Kohn-Sham equation derived from the time-independent many-body Schrödinger equation [53]:

$$\left[\underbrace{-\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2}_{e^- \text{ kinetic energy}} - \underbrace{\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2}_{nuclei \text{ kinetic energy}} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{e^- - e^- \text{ interaction}} + \underbrace{\frac{1}{2} \sum_{I \neq J} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}}_{nuclei \text{ interaction}} - \underbrace{\sum_{i,I} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}}_{e^- - nuclei \text{ interaction}} \right] \Psi = E_{tot} \Psi \quad (3.1)$$

The labels on each term of the equation 3.1 describes the energy contributed to the total ground-state energy of the system. Out of the five terms in equation 3.1, calculation of the potential

energy involving e^-e^- interaction is computationally expensive [46]. Therefore, the many-body Schrödinger equation in its current form is computationally difficult to solve for most of the multiple e^- systems (other than one electron system such as hydrogen or helium cation, He^+).

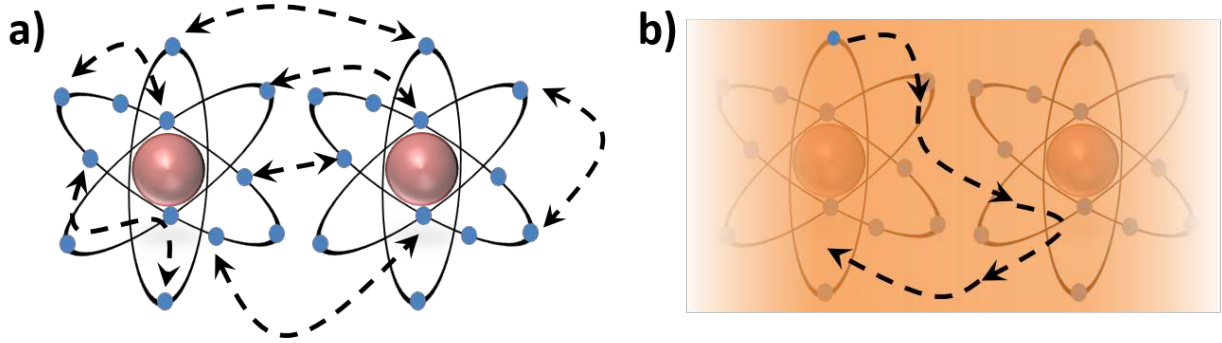


Figure 3.1: Schematic showing the (a) interaction between electrons in the many-body electron system, and (b) a single-particle representation of the many-body system where each particle interacts with an effective potential resulting from the interactions between different species of the system.

In order to apply equation 3.1 to multiple e^- system, researchers in past have developed several approximations to simplify the many-body Schrödinger equation. These approximations while maintaining the accuracy is computationally less expensive and allows one to study materials at atomistic level. These approximations are as follows:

- *Born-Oppenhemier approximation:* Electron moves faster than nucleus due to their smaller weight (in comparison to nucleus). Further since atoms in solids are held at fixed position, nuclei are considered to be immobile or clamped with respect to the electrons. Thus, the kinetic energy of nuclei can be neglected and nuclei-nuclei potential energy could be simplified to a constant value.
- *Independent electron approximation:* Due to the complexity of the eigenvalue problem, it becomes computationally difficult to solve the many-body wavefunction (Figure 3.1 (a)). Independent electron approximation redefines the many-body wavefunction to be a product of single particle wavefunction. This implies that the interaction between electrons are

dissolved and the individual electronic wavefunctions are considered to solve many-body Schrödinger equation.

- *Mean-field approximation:* Mean-field approximation is applied to restore the classical electron interaction within the many-body system. This approximation applies an averaged electrostatic potential, known as "Hartree Potential" ($V_H(\mathbf{r})$) calculated through Poisson's equation (see Figure 3.1 (b)).
- *Hartree-Fock equation:* The mean-field approximation reintroduces the electron interaction via classical electrostatic potential. Since electrons are quantum particles, the quantum effects cannot be ignored. Hartree-Fock equation consider electrons as fermions and introduces Exchange Potential ($V_X(\mathbf{r}, \mathbf{r}')$). Exchange potential unlike Hartree Potential is a non-local potential. The physical meaning of V_X relates to Pauli's exclusion principle which prevents two electrons from occupying the same quantum state.
- *Kohn-Sham equation:* It is intuitive to think that the probability of finding two electrons close to each other is very low (Coulomb repulsion). In simple words, it could be stated that there is a correlation between the existence electrons. This gives rise to correlation potential V_C . Finally, the single particle Kohn-Sham equation is arrived by assembling all the components defined through the approximations:

$$\left[-\frac{1}{2}\nabla^2 + V_n(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \Phi_i(\mathbf{r}) = E_i \Phi_i(\mathbf{r}) \quad (3.2)$$

The term " V_{XC} " in equation 3.2 combines exchange and correlation potential together and is known as exchange-correlation potential. The Kohn-Sham formulation defines the electronic system as a single particle wavefunction (Φ_i) in vicinity of non-interacting electron gas that exists within an effective potential comprising of classical e^-e^- interactions V_H , electron-ion interactions V_n , and quantum exchange-correlation potential V_{XC} (see figure 3.1 (b)). E_i in equation 3.2 is further defined as the ground state energy of i^{th} particle. The total ground-state energy of the

system, E_{GS} is obtained by summation of the ground state eigenenergies E_i . Furthermore, the single particle eigenfunction Φ_i is used to calculate the electron density throughout the system via a simple expression, $n(\mathbf{r}) = \sum_i |\Phi_i|^2$. As per the Hohenberg-Kohn theorem, the ground-state energy E_{GS} of a many-electron system can be expressed as a functional of electron density $n(\mathbf{r})$ [46]. This forms the foundation of the density functional theory as the ground-state energy can be formally described as functional of electron density of the system. The ground-state energy E_{GS} in terms of functional of electron density $n(\mathbf{r})$ can further be described as:

$$-\sum_i \int d\mathbf{r} \Phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \Phi_i(\mathbf{r}) + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d\mathbf{r} n(\mathbf{r}) V_n(\mathbf{r}) + E_{XC}[n] = E_{GS} \quad (3.3)$$

where the first three terms represents energy contribution from electron kinetic energy, electron-electron interaction, and electron-nuclei interactions. The final term $E_{XC}[n]$ denotes the exchange-correlation energy and is discussed in details in section 3.4.

3.2 Basis sets

A set of functions representing the one particle electronic wavefunctions in the Kohn-Sham equation (equation 3.2) are known as Basis sets. Basis sets can comprise of either atomic orbitals or plane waves electronic wavefunctions. This section further describes the plane wave and atomic orbital basis sets and their relevant use in different types of atomistic modelling domain.

3.2.1 Plane-wave basis sets

The plane-wave representaion of electronic structure has a long tradition in the computational study of periodic bulk systems. The following equation describes the plane wave function:

$$\Psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \quad (3.4)$$

The key advantage of plane-wave basis sets is related to its smooth convergence in a monotonic manner with respect to the target electronic wavefunction. Some of the other advantages of using Plane-wave basis sets are as follows:

- The single particle electronic wavefunction can be described accurately by simply increasing the number of plane waves included in the calculation.
- The total energy expressions and hamiltonians are easy to implement.
- A user choice based cutoff energy decides the basis sets to be used in Plane wave calculation.
- Since the functions in the Plane-wave basis sets are mutually orthogonal, they do not exhibit basis set superposition error.

3.2.2 Linear Combination of Atomic Orbitals (LCAO) basis sets

Atomic orbitals are solution to the Schrödinger's equation for the electrons and are bounded to the atom by nucleus's electric field. In other words, these orbitals are centered around the atoms and therefore are localized. Atomic orbitals, in its index form is defined as:

$$\Phi_{j,nlm} = R_{j,nl}(|\mathbf{r}_j|)Y_{lm}(\hat{\mathbf{r}}_j) \quad (3.5)$$

where $R_{j,nl}(|\mathbf{r}_j|)$ and $Y_{lm}(\hat{\mathbf{r}}_j)$ describes the respective radial and spherical harmonics part of the atomic orbitals. The subscripts n, l , and m refers to the principle, angular, and magnetic quantum number of the j^{th} electron respectively. The basis function $\Phi_{j,nlm}$ is then summed over all the atoms within the simulation model domain to form basis set, Φ_i :

$$\Phi_i = \sum_j c_j \Phi_j(\mathbf{r}) \quad (3.6)$$

The above equation describes the expansion of the atomic orbitals over the simulation domain through the Linear Combination of Atomic Orbitals (LCAO). The research community developing the LCAO have optimized the basis functions for all the elements in the periodic table. The prop-

erties of the atomic orbitals can be controlled based on the size, shape and diffusivity of the basis functions. Therefore, the optimization of LCAO basis functions includes consideration of the three main features viz. size, shape, and range. The size of the basis orbitals is governed by predefined radial functions (single ζ , double ζ). The angular direction of the orbitals are controlled by the polarization functions. Thus, the predefined radial and polarization functions controls the size of the atomic orbitals. The term single and double in predefined radial functions refers to number of basis functions utilized for a particular orbital. The use of more basis functions is motivated by a desire to provide additional variational flexibility, so that the LCAO process can account for variable diffusiveness with the varying local electro-negativity of the system. The spatial extension of the atomic orbitals is defined as its range and is controlled by cutoff radius (r_{cutoff}). The accuracy and computational efficacy of the calculation depends on the r_{cutoff} value, and is therefore a crucial parameter in achieving the convergence. The shape of these basis functions is accounted by the Pseudopotential and will be discussed in details in section 3.3.

3.2.3 Advantages of LCAO over Plane-wave basis sets

The key advantages of using LCAO basis sets over the Plane-wave basis sets are as follows [54]:

- *Convergence:* Due to the localized nature of basis functions, the orbitals are confined to region of interaction. This helps LCAO basis sets to converge quickly.
- *Number of basis sets:* The strictly localized atomic orbitals provides numerical stability over the plane-wave basis sets (plane-wave basis sets presents numerical instabilities at shorter range). This reduces the number of LCAO basis functions (in comparison to plane-wave basis sets) required to describe a simulation domain.
- *Non-periodic systems:* When coupled with Green's Function formalism, LCAO basis sets are well suited to simulate non-periodic surfaces and interfaces [4, 54, 55].
- *Modeling domain size:* Since plane-wave basis sets are limited to periodic systems, a large modeling domain perpendicular to the surface/ interface is needed to sufficiently converge

the calculation. This is not the case with LCAO basis sets. The LCAO basis sets can be used for non-periodic systems.

3.3 Pseudopotential

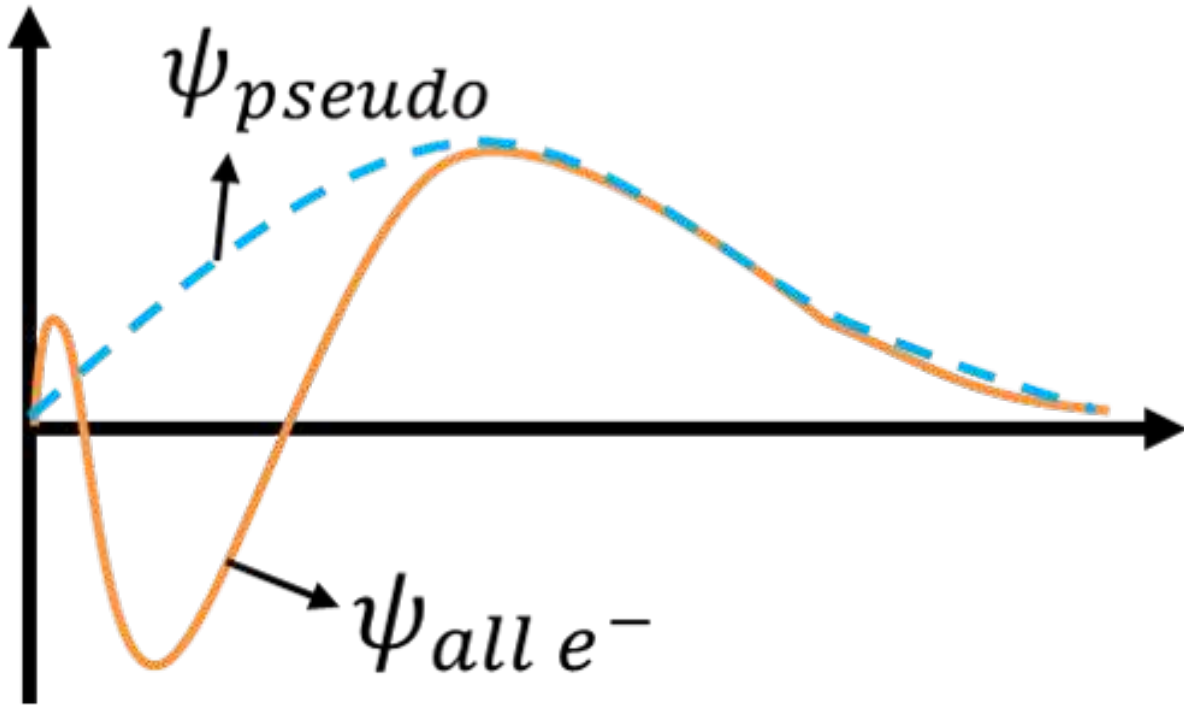


Figure 3.2: Schematic showing the oscillations in the all electron wavefunction (solid line) and the smoothed approximated electron wavefunction after pseudopotential approximation (dashed line).

The electrons in an atom could be divided into core and valence electrons. Core electrons are the ones closer to atom's nucleus and are therefore tightly bounded in atoms. Since the core electrons are closely bounded, the electronic wavefunction oscillates on short length scale near nucleus (see figure 3.2). However, as the material properties such as chemical bonding, mechanical and electrical properties are dominated by less tightly bound valence electrons, potentials and oscillations in wavefunction due to core electrons can be approximated to improve the computational efficacy of the simulation. Therefore, a weaker effective potential described as pseudopotential is used to replace the coulomb potential accounting for the core electron interaction with the nucleus.

However, it must be ensured that with the constructed pseudopotential the resulting valence pseudo basis is identical with the electronic wavefunction calculated by an all electron method. Since the oscillated core electron wavefunction is replaced by a smoothed pseudo-wavefunction, use of pseudopotentials leads to less computationally expensive calculations by reducing the number of basis sets required to fully describe the system.

3.4 Exchange-Correlation Functional

As discussed before, Exchange-Correlation potential restores the quantum mechanical effects for electron-electron interaction. The Exchange-Correlation functionals primarily accounts for the self-interaction correction and the avoidance criteria for electrons as they move throughout the electron density. The exchange part relates to the Pauli exclusion principle while the correlation part captures electron-electron repulsion due to the coulombic forces.

In order to solve the Kohn-Sham single particle equations (equation 3.2), one needs to have a defined exchange-correlation potential. However, the existence of exact exchange-correlation functional for different systems is yet unknown [53]. Fortunately, researchers over the years in the DFT community have worked out some predefined exchange-correlation (XC) functionals which can be utilized to calculate the properties of different system. Some of the XC functionals are Local Density Approximation (LDA), General Gradient Approximation (GGA), meta-GGA, Hybrid functionals etc. The simplest of all is the local density approximation (LDA), which is expressed as follows:

$$E_X^{LDA}C[n] = \int d^3r n(\mathbf{r}) \epsilon_{XC}^{unif}(n(\mathbf{r})) \quad (3.7)$$

where ϵ_{XC}^{unif} represents the XC energy per electron of a gas with uniform electron density. The above equation 3.7 is valid for the slow variation of electron density over the space [57]. Despite of its simplistic assumption of uniform electron gas, LDA is quite accurate in predicting the material properties in most of the systems. The current work utilizes the LDA XC functional for all the

calculations. Although, XC functionals accurately estimates the material properties, some of its shortcomings are:

- *Self-interaction error*: The electron is formally allowed to interact with itself within the average electron density $n(\mathbf{r})$. This prevents the electron from localizing in its proper orbital.
- *Excited states*: The poor description of the conduction band energy levels by XC functionals leads underprediction of the band-gap energy in semiconductors and insulators.

To overcome the above short-comings, semi-empirical Hubbard-U or DFT-1/2 correction methods are applied to estimate the accurate electronic properties of semiconductor materials. This work utilizes DFT-1/2 correction method and is discussed in details in the next section.

3.5 DFT-1/2 Correction

The DFT calculation has been known to underestimate the band-gaps of the semiconductors and insulators. It has been reported in the literature that the main cause of this discrepancy is related to the delocalization of valence electrons [4, 58]. In order to get the correct band-gap of a semiconductor material, researchers in past have used a semi-empirical DFT-1/2 correction method [58]. The current study also utilizes DFT-1/2 method to obtain the correct band-gap values of the investigated compound semiconductors.

In principle, the DFT-1/2 method corrects Kohn-Sham eigenvalues around the top of the valence band and bottom of the conduction band [58]. Figure 3.3 shows the comparison of the CdTe band-structure calculated via DFT (LDA) and DFT-1/2 (LDA-1/2) methods. A band-gap of 0.57 eV was calculated with DFT which increased to 1.51 eV with DFT-1/2 method. The DFT-1/2 calculated band-gap value is in good agreement with the existing experimental literature [7, 47, 55]. Further, it can be observed from the band-structure diagram that DFT-1/2 changes the bottom of the conduction band and top of the valence band to arrive to a correct CdTe band-gap value.

As has been discussed before, the XC energy in the Kohn-Sham potential includes the self interaction error. The self interaction leads to the delocalization of the charge carriers preventing

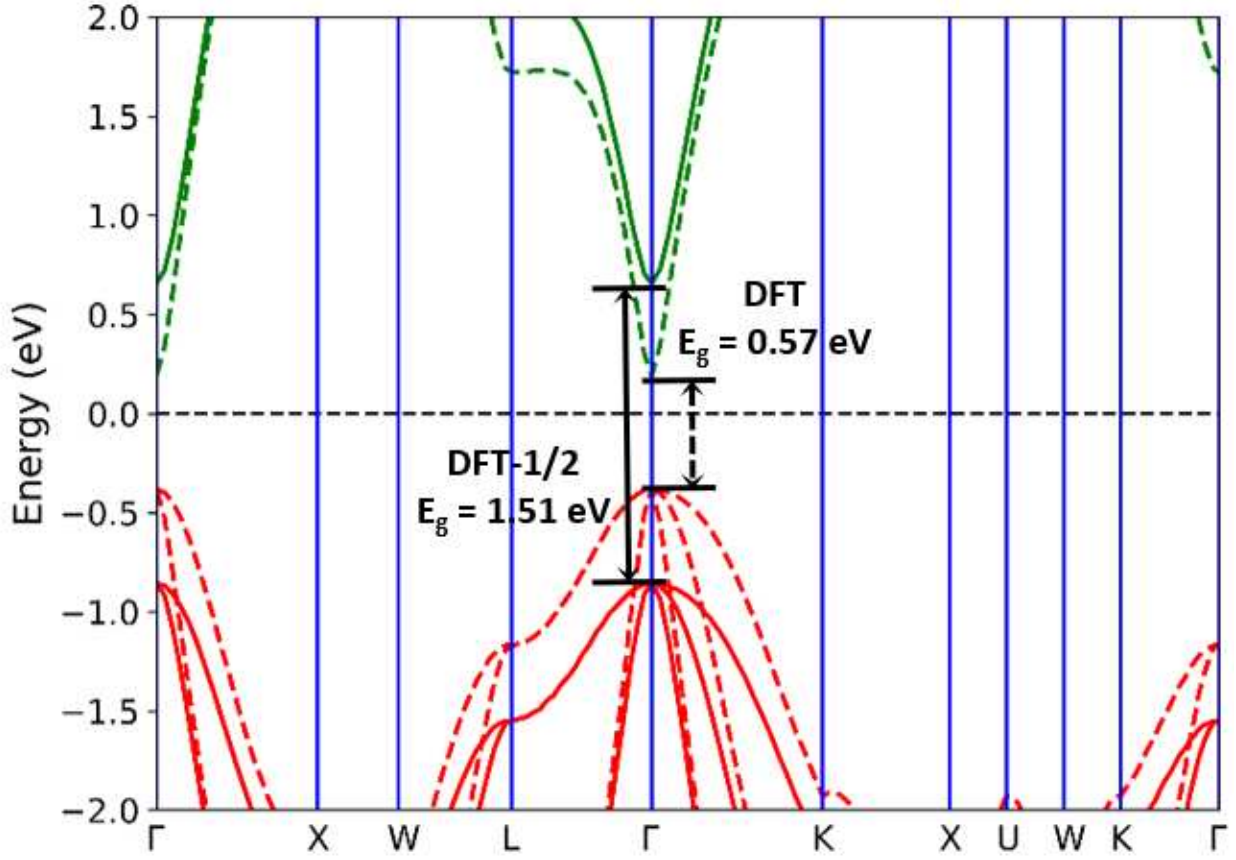


Figure 3.3: band-structure diagram of CdTe comparing the band-gaps calculated using DFT (dashed lines) and DFT-1/2 (solid lines) methods. $E = 0$ refers to the Fermi energy level. The green lines denote the conduction bands while the red line denotes the valence bands.

them from occupying the correct orbitals. The DFT-1/2 method accounts for this self-interaction potential ($V_S(\mathbf{r})$) and modify the Kohn-Sham potential by subtracting the $V_S(\mathbf{r})$ from original Kohn-Sham potential:

$$V_{mod,KS}(\mathbf{r}) = V_{KS}(\mathbf{r}) - V_S(\mathbf{r}) \quad (3.8)$$

The LDA self-interaction error $V_S(\mathbf{r})$ potential is calculated for the atoms using the Slater half occupation scheme (reason for suffix "-1/2 in DFT-1/2"). The self-interaction error $V_S(\mathbf{r})$ potential is then multiplied by a trimming function and is transferred to the crystals:

$$\Theta(\mathbf{r}) = A \left[1 - \left(\frac{r}{r_{cut}} \right)^n \right]^3, r < r_{cut} \quad (3.9)$$

$$\Theta(\mathbf{r}) = 0, r > r_{cut} \quad (3.10)$$

where r_{cut} is determined variationally, $n = 8$ and $A = 1$. The $r_{cut} = 0$ corresponds to the normal DFT calculation (without any correction). The optimum value of r_{cut} along with the self-interaction potential helps to localize the electronic wavefunctions in the valence band. The optimum value of r_{cut} also depends on the element in the periodic table.

Chapter 4

Research questions

4.1 Motivation

As discussed before, alloying Se with the CdTe absorber layer has aided the CdTe research community to fabricate the highly efficient PV-devices. The chlorine treatment of the $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ film leads to formation of Se-graded CdTe absorber layer [31]. It is thought of that Se and Cl together passivates the absorber defects [21], but the mechanism of copassivation effect of Se and Cl is still unknown. The published literature also indicates importance of understanding electronic properties of surfaces and interfaces [4, 18]. However, the surface and interface electronic properties of ternary $\text{CdSe}_x\text{Te}_{1-x}$ alloys from atomic scale perspective has not been explored hitherto. Moreover, the understanding of the interfacial and surface defect properties at heterojunctions will further advance the fabrication of CdTe PV cells.

As proposed in the DOE Sunshot initiative, the atomistic modeling computational technique should be applied to PV research to comprehend the atomic scale features in thin film devices. The oversimplified Electron-Affinity/Anderson's rule does not provide full understanding of the electronic features such as energy band alignments, defect properties etc. Therefore, the current research work employs the experimental methods to understand the structural properties of the Se-graded $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ device at atomic level and then calculate the electronic properties at surfaces and interfaces using first principles atomistic simulations.

4.2 Key Questions and hypothesis

The current research work adopts a systematic approach to first verify the existing results available in the literature and then ascertain the effect of Se alloying of CdTe on the surface and interface electronic properties. The atomistic models designed on the basis of the experiments will not only help to decode the primary mechanisms that guides the energy band alignment results, but will

also provide new details to enhance the CdTe PV-device performance. The following questions in a structured manner has been undertaken to ascertain the surface and interface properties of $\text{CdSe}_x\text{Te}_{1-x}$ /CdTe based solar cells:

- **Q 1: How do structural and electronic features in bulk $\text{CdSe}_x\text{Te}_{1-x}$ alloys modeled using LCAO basis set compares with those modeled using plane wave basis sets?**

Hypothesis: The bulk properties of CdTe binary alloy modeled using LCAO basis sets have matched well with the existing experimental and theoretical results. Therefore, the structural and electronic properties of bulk $\text{CdSe}_x\text{Te}_{1-x}$ ternary alloy modeled using LCAO basis sets should also be in good agreement with the properties modeled using Plane wave basis sets.

- **Q 2: Are structural and electronic features of $\text{CdSe}_x\text{Te}_{1-x}$ surfaces like those of the CdTe surface?**

Hypothesis: The structural and electronic properties of CdTe surfaces have been shown to depend on the surface polarity and the termination layer. The surface relaxation of Cd-terminated CdTe(100) surface have shown the formation of surface Cd-dimers [4]. Similarly, a non-polar CdTe(110) shows an atomic chain tilt at the surface [59]. Also, the polar CdTe(111) plane orientation indicates that a (2×2) reconstruction of the CdTe(111) surface will be energetically favorable [4]. Previous DFT simulations done for unreconstructed polar CdTe(100) and (111) surfaces by Nicholson et. al. shows the presence of cusp feature in the surface VBM [4]. Since, $\text{CdSe}_x\text{Te}_{1-x}$ like CdTe is also a II-VI compound alloy, its surface structural properties in various orientations is expected to match to those of CdTe surfaces. With regards to the electronic properties, the polar $\text{CdSe}_x\text{Te}_{1-x}$ (111) and $\text{CdSe}_x\text{Te}_{1-x}$ (100) unreconstructed and reconstructed surfaces is expected to have a presence of hole charge transport aiding cusp-feature in the VBM as observed in CdTe polar surfaces. The non-polar $\text{CdSe}_x\text{Te}_{1-x}$ (110) surface is expected to give a flat energy band alignment diagram.

- **Q 3: How does Se grading in CdTe absorber lead to an improved device performance?**

Hypothesis: Se is graded into the CdTe film from $\text{CdSe}_x\text{Te}_{1-x}$ due to the CdCl_2 treatment of the absorber layer [14]. Literature reports by *Fiducia et al.* and *Guo et al.* suggests that Se and Cl passivates the defect levels in the polycrystalline CdTe [31,60]. DFT analysis by *Li et al.* has revealed that chlorine occupies the Te sites at grain boundaries and causes an inversion from p-type absorber grain interior to n-type grain boundaries [22]. Such an inversion leads to electrostatic field between the grain and grain-boundary and helps in better extraction of the charge carriers. *Mhirech et al.* made similar observation, where a p-type absorber was inverted to n-type at the absorber/oxide interface [61]. It is thought of that the presence of high density of donor states at an interface will cause such an inversion [61, 62]. However, the mechanism elucidating the cause of inversion at the CdTe grain boundaries have not been identified yet. In this study, it is hypothesized that the Se alloying and Cl passivation of CdTe will lead to high density of donor states at the CdTe grain-boundary. The presence of high donor density should be the major cause of p-n type inversion at grain boundaries (as found in other published literature [61, 62]). Moreover, Se-alloyed, Cl-passivated CdTe grain-boundary should depict higher density of donor states (leading to higher p-n inversion) in comparison to Cl-passivated CdTe grain-boundary. The higher p-n inversion caused by alloying Se and Cl at the CdTe grain boundaries could be the main reason for high efficiencies observed in the Se-graded CdTe PV-devices.

- **Q 4: Why does a polycrystalline $\text{CdSe}_x\text{Te}_{1-x}$ absorber-based double heterostructure have a higher minority charge carrier lifetime than polycrystalline CdTe based heterostructure?**

Hypothesis: Characterization techniques such as Time-Resolved Photoluminescence (TRPL) has been used to report that CdCl_2 -treated polycrystalline $\text{CdSe}_x\text{Te}_{1-x}$ absorber/Alumina based double heterostructure has higher carrier lifetime in comparison to the CdTe absorber/Alumina based double heterostructure [21,63]. A higher minority charge carrier lifetime would imply less carrier recombination in the bulk $\text{CdSe}_x\text{Te}_{1-x}$ and $\text{CdSe}_x\text{Te}_{1-x}$ /Alumina interface than its CdTe counterpart. It could be theorized that Se alloying of CdTe would

lead to defect passivation in the $\text{CdSe}_x\text{Te}_{1-x}$ grain boundaries, making $\text{CdSe}_x\text{Te}_{1-x}$ a better bulk material than CdTe. Furthermore, the insights gained from the double heterostructure results could also be thought of as less defect state assisted charge carrier recombination should occur at the $\text{CdSe}_x\text{Te}_{1-x}$ /Alumina interface in comparison to CdTe/Alumina interface.

- **Q 5: How does the $\text{CdSe}_x\text{Te}_{1-x}$ /Te-interface energy band alignment compare to that of the CdTe/Te interface?**

Hypothesis: It has been observed experimentally that $\text{CdSe}_x\text{Te}_{1-x}$ -only absorber based PV-devices shows lower performance than CdTe-only solar cells [55]. Nicholson et. al have previously reported the presence of hole charge carrier transport aiding cusp feature in CdTe surfaces and CdTe/Te interface [4]. Based on the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface energy band alignment obtained to answer Q2 and work done by *Nicholson et al.*, it could hypothesized that the absence of cusp of feature in the VBM of $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface will translate to $\text{CdSe}_{0.25}\text{Te}_{0.75}$ /Te interface. A higher density of defect states is also expected at the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ /Te interface leading to high charge carrier recombination and therefore overall lower PV-device performance in $\text{CdSe}_x\text{Te}_{1-x}$ -only absorber based PV-devices.

4.3 Methodology

The proposed research topic utilizes first-principles techniques in conjunction with experiments to understand the surface and interface electronic properties of the $\text{CdSe}_x\text{Te}_{1-x}$ /CdTe based absorber layer. The PV-devices and absorber films for characterisation are fabricated in what is known as the Advanced Research Deposition System at Colorado State University [36]. The device-fabrication parameters have been described in detail in the upcoming chapters. The characterisation of absorber films has been carried out in collaboration with researchers at Loughborough University, United Kingdom.

The atomistic models based on DFT coupled with Green's Function will be used to understand the structural and electronic properties of $\text{CdSe}_x\text{Te}_{1-x}$ based surface and interfaces. To perform all the DFT calculations, QuantumATK has been chosen as the *ab initio* modeling package. The Quan-

tumATK software package has been developed by Synopsys Denmark and is specifically designed to provide state-of-the-art and high-fidelity atomistic modeling techniques with a user-friendly graphical user interface. The enhanced software capabilities allows the user to investigate various surface and interface models suitable for PV-device and other semiconductor technologies [56]. The complexity of atomistic models based on the given problems has required efficient hardware capabilities to undertake the tasks described above. Therefore, the DFT+GF surface and interface models has been simulated on the high-performance Rocky Mountain Advanced Computing Consortium (RMAcc) Summit cluster. To maintain the computational efficacy of the models, the simulations have been executed by parallelizing the processors within the QuantumATK platform.

Density functional theory is based on quantum mechanical equations. Chapter 3 described the concepts involved within the DFT calculations to establish a fundamental background in quantum-based atomistic modeling. Chapter 5 discusses the converged DFT results for the structural and electronic properties of the bulk $\text{CdSe}_x\text{Te}_{1-x}$ in relation to the question 1 outlined in section 4.2. The chapter also establishes the modeling parameters by comparing the bulk results obtained in this work with the published literature. Chapter 6 studies the $\text{CdSe}_x\text{Te}_{1-x}$ surface-electronic-properties in different orientations to account for the polycrystalline nature of the absorber layer. The surface-electronic-properties comparison between CdTe and $\text{CdSe}_x\text{Te}_{1-x}$ is also included in this chapter in order to verify the hypothesis presented for question 2.

Chapter 7 verifies hypothesis 3 and starts with the experimental findings describing the device performance, microstructure, and atomic distribution of Se and Cl in $\text{CdSe}_x\text{Te}_{1-x}$ /CdTe absorber based PV-devices. Based on EBSD result and other published literature, a (110)/(100) CdTe tilt grain-boundary has been investigated to understand the effect of grading Se and Cl in the CdTe absorber. This chapter also outlays the method for understanding the role of Se and Cl atoms in passivating the grain-boundary defect states. Chapter 8 investigates hypothesis 4 by studying the energy band alignments of CdSeTe grain boundaries and CdSeTe/Alumina interface. This chapter establishes passivation mechanism that forms the basis of understanding high carrier lifetime observed in CdSeTe double heterostructures. Further, the learning gained from DFT simulations

were utilized in fabricating the high efficiency undoped CdSeTe/CdTe bilayer devices. Chapter 9 explores hypothesis 5 by studying the CdSeTe/Te and CdSeTe/CdTe atomistic models. Using various experimental methods in conjunction with the results from atomistic models, chapter 9 lays out a method that utilizes different processing conditions to fabricate CdSeTe-only absorber solar cells. The above findings in various chapters suggest that to further improve the efficiency of CdTe solar cells, different processing conditions need to be explored for CdSeTe-only absorber based PV-devices. Chapter 10 summarizes the results obtained to date and lays out a brief description of the mechanisms through which $\text{CdSe}_x\text{Te}_{1-x}$ absorber enhances the CdTe PV-device performance.

The current work combines the experimental findings with the theoretical models and advances the understanding of the how different alloying atoms, surfaces and interfaces can influence PV-device performance. It is our reckoning that this research work enabled by quantum-based computational methods will further contribute to the development of CdTe-based PV technology.

Chapter 5

Modeling bulk Cadmium selenium telluride¹

5.1 Introduction

Over the recent years, II-VI compound semiconductors have found enormous potential for applications in area of photovoltaics, nonlinear optics, optical communications and other improved solid state laser systems. Quantum dots of cadmium selenium telluride ($\text{CdSe}_x\text{Te}_{1-x}$) with tunable florescence emission have been used as biolables [64]. Shenouda et al showed that electrodeposited CdSe and CdTe grains could be used to enhance the efficiencies of Photo-Electrochemical cells (PEC) [65]. In CdTe solar cells, $\text{CdSe}_x\text{Te}_{1-x}$ alloy have been used as lower bandgap absorber material to achieve higher device efficiencies [14]. Swanson et al. further showed that bandgap of the ternary $\text{CdSe}_x\text{Te}_{1-x}$ alloy can be tuned based on the Se concentration (x) [7].

Many researchers in past have used plane wave basis sets based DFT models to investigate the structural, optical, thermodynamical and electronic features of $\text{CdSe}_x\text{Te}_{1-x}$ alloy [1,47]. As stated before Linear Combination of Atomic Orbitals (LCAO) basis scheme has certain computational advantage over the traditional plane-wave basis sets and could be applied extensively to model the interfaces. However, before modeling $\text{CdSe}_x\text{Te}_{1-x}$ interfaces, it is important to validate the bulk properties of the ternary $\text{CdSe}_x\text{Te}_{1-x}$ alloy with the existing experimental and theoretical literature.

¹This chapter has been modified from a peer-reviewed journal article: A. Shah, A. H. Munshi, A. P. Nicholson, A. Thiagarajan, U.M. Pozzoni, and W. S. Sampath (2021). Atomistic modeling of energy band alignment in CdSeTe surfaces. Applied Surface Science, 544:148762.

Akash Shah: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization.

Amit H. Munshi: Cell fabrication, Writing - review editing.

Anthony P. Nicholson: Software, Formal analysis, Data curation, Writing - review editing.

Aanand Thiagarajan: Software, Formal analysis, Writing - review editing.

Umberto M. Pozzoni: Software, Supervision.

Walajabad S. Sampath: Conceptualization, Resources, Project administration, Funding acquisition

This chapter probes the structural and electronic properties bulk $\text{CdSe}_x\text{Te}_{1-x}$ alloy using LCAO basis set along with DFT-1/2 correction scheme.

5.2 Computational details

The DFT $\text{CdSe}_x\text{Te}_{1-x}$ bulk and surface models have been simulated using the QuantumATK P-2019.03 software tool [66]. The single particle Kohn-Sham eigenvalue problem is solved using electronic wavefunctions represented by the Linear Combination of Atomic Orbitals (LCAO) basis scheme. The FHI pseudopotential basis sets for Cd and Se atoms in combination with OpenMX Low (s2p2d1) basis sets [67, 68] for Te atoms have been used in all the calculations. The Perdew-Zunger [69] form of the Local Density Approximation (LDA) exchange correlation functional is utilized in the relaxation of the bulk supercells and the surfaces. However, it is well known that DFT underestimates the bandgap values for semiconductors and therefore the semi empirical correction DFT-1/2 method [58] is applied to obtain the appropriate bulk $\text{CdSe}_x\text{Te}_{1-x}$ bandgap.

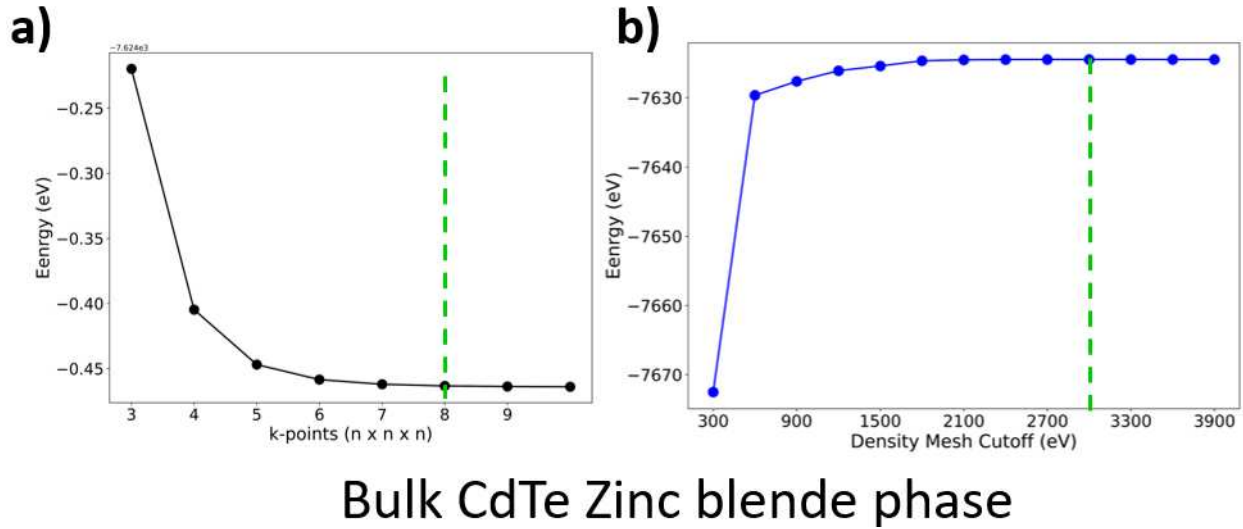


Figure 5.1: Convergence testing for Zinc-blende CdTe with respect to a) varied k-point density at $E_{\text{mesh}} = 3600$ eV and b) varied density mesh cutoff E_{mesh} at $11 \times 11 \times 11$ k points. The green line marks the 1 meV/cell threshold for the absolute difference in total energy. The CdTe bulk primitive cell with a fixed lattice constant of 6.480 Å is utilized for all calculations.

An energy convergence test simulation have been performed on the bulk Zinc-blende phase of CdTe and wurtzite phase of CdSe to estimate the optimum density mesh cutoff and k point sampling values. Figure 5.1 and 5.2 shows the results from energy convergence test for bulk CdTe and CdSe. Based on the results of energy convergence test, a Monkhorst-Pack grid with $8 \times 8 \times 8$ k-point sampling was employed for the bulk $\text{CdSe}_x\text{Te}_{1-x}$ calculations and the density mesh cutoff value was set to 3000 eV.

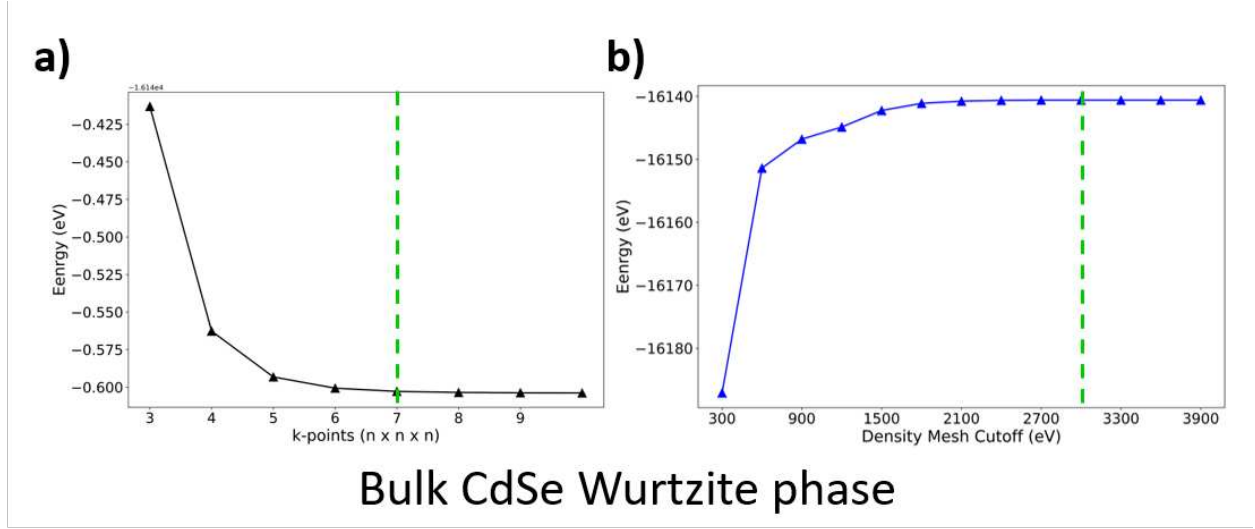


Figure 5.2: Convergence testing for wurtzite CdSe with respect to a) varied k-point density at $E_{\text{mesh}} = 3600$ eV and b) varied density mesh cutoff E_{mesh} at $11 \times 11 \times 11$ k points. The green line marks the 1 meV/cell threshold for the absolute difference in total energy.

Depending on the selenium concentration, cadmium selenium telluride can exist either in the Zinc-blende or wurtzite phases [7]. The published experimental literature shows a phase transition of $\text{CdSe}_x\text{Te}_{1-x}$ ($0 < x < 1$) from Zinc-blende to wurtzite phase between $x = 0.6$ and 0.7 [70]. Therefore, the structural and electronic properties of the bulk $\text{CdSe}_x\text{Te}_{1-x}$ have been investigated using a 16 atom Zinc-blende and wurtzite supercells (illustrated in fig.5.3 a) and fig.5.3 b)) for the $x = 0$, 0.25 , 0.50 , and 0.75 , 1.0 concentrations respectively. Depending on the relative Se atomic distance, the ground-state total energy of the above four Se concentrations were calculated for the 16 configurations in total and the lowest energy configuration for each of the concentration was chosen for the further analysis. Three more concentrations of Se $x = 0.11$, 0.125 Zinc-blende and a 16

atom wurtzite supercell for $x = 0.875$ were included to verify the credibility of the DFT modeling parameters used in simulation. Se is found to have a high probability for random distribution as a $\text{CdSe}_x\text{Te}_{1-x}$ alloy [47]. To accommodate for the random distribution, the bulk simulations use the special quasirandom structure (SQS) for each of the above described Se concentrations. To generate confidence in the DFT modeling parameters with the SQS generated structures, Se concentration of $x = 0.11$ had a 54 atom supercell while $x = 0.125$ were calculated with 16, 32, and 128 atom Zinc-blende supercells. It is to be noted that the structural and electronic bandgap values for all the $x = 0.125$ supercell were close, however the closest match to the literature is reported which came from 128 atom supercell.

5.3 Structural properties

The lattice constants computed for the relaxed $\text{CdSe}_x\text{Te}_{1-x}$ Zinc-blende and wurtzite phase are tabulated in Table 5.1. The calculated lattice constants in this study were in good agreement with other theoretical and experimental literature values reported earlier [1, 7]. It was observed that the lattice constant value decreases with an increase in the Se concentration. A good linear fit of the lattice parameters (see fig. 5.3 c)) indicate that both phases of $\text{CdSe}_x\text{Te}_{1-x}$ alloy follow Vegard's law [7, 71].

5.4 Electronic properties

For the electronic properties, DFT calculations typically underestimate the band-gap values of the CdTe compounds [4]. Therefore, the DFT-1/2 correction scheme [58] was applied to the relaxed $\text{CdSe}_x\text{Te}_{1-x}$ structures to compute the band-gap (E_g) values of the Zinc-blende and the wurtzite phase. Fig.5.4 shows the band-structure plot of $\text{CdSe}_x\text{Te}_{1-x}$ alloy for various Se content. For the cubic Zinc-blende structure the bandgap value decreases with the increase in the Se content. However after transitioning to the wurtzite structure the bandgap value again increases with the Se content. The band-structure plots confirms that $\text{CdSe}_x\text{Te}_{1-x}$ alloys are direct bandgap semiconductor as the conduction band minimum and valence band maximum are located at the center

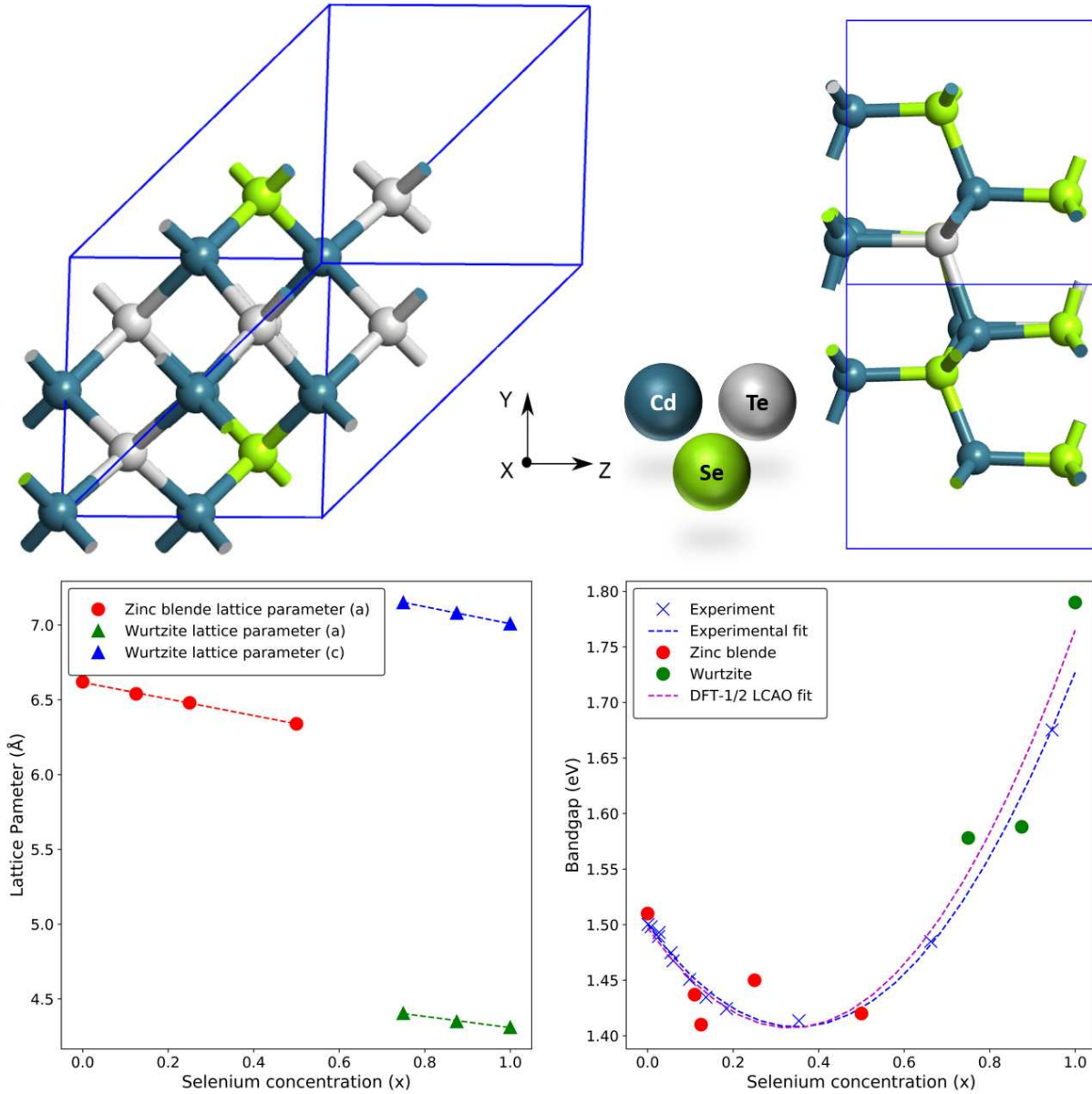


Figure 5.3: Illustration of a) $\text{CdSe}_{0.25}\text{Te}_{0.75}$ Zinc-blende phase and b) $\text{CdSe}_{0.75}\text{Te}_{0.25}$ wurtzite phase. c) Calculated lattice parameter of the Zinc-blende (a) and wurtzite phase (a & c) with respective Se concentration. The linear fit of the lattice parameters indicate the $\text{CdSe}_x\text{Te}_{1-x}$ alloy follow Vegard's law. d) Calculated band-gaps vs selenium concentration curve shows the typical bowing feature in $\text{CdSe}_x\text{Te}_{1-x}$ alloy which matches well with the experimental band-gap [7]

of the Brillouin zone (Γ point). The band-structure plots also shows a shift of the conduction band towards the fermi level with increasing Se concentration in the Zinc-blende phase. However, opposite observations were made with the wurtzite phase, where the conduction band maxima shifts away from the fermi level. But irrespective of Se concentration or phase the valence band maxima

Table 5.1: Lattice constant comparison between DFT LCAO model values calculated in this work, experimental (Exp.) values and other reported theoretical (Theo.) values for respective Se concentrations. The supercell used for $x=0.75$ in reference [1] is double the size of the supercell used in this study) along the c -direction.

Se conc.(x)	Phase	a(Å)	c(Å)	a(Å) Exp.	c(Å) Exp.	a(Å) Theo.	c(Å) Theo.
0	Zinc-blende	6.62	-	6.48 ^a , 6.54 ^b	-	6.62 ^c , 6.63 ^d	-
0.125	Zinc-blende	6.54	-	-	-	-	-
0.25	Zinc-blende	6.48	-	-	-	6.32 ^c	-
0.5	Zinc-blende	6.34	-	-	-	6.41 ^c	-
0.75	Wurtzite	4.41	7.23	-	-	4.43 ^c	14.89 ^c
0.875	Wurtzite	4.35	7.08	-	-	-	-
1.0	Wurtzite	4.31	7.01	4.3 ^e	7.01 ^e	4.34 ^c	7.27 ^c

^aRef. [72]

^bRef. [73]

^cRef. [1]

^dRef. [74]

^eRef. [75]

Table 5.2: band-gaps comparison between DFT-only, DFT-1/2 LCAO model values calculated in this work, experimental (Exp.) values and other reported theoretical (Theo.) values for respective Se concentrations.

Se conc.(x)	Phase	E _g (eV) DFT	E _g (eV) DFT-1/2	E _g Exp. (eV)	E _g Theo. (eV)
0	Zinc-blende	0.57	1.51	1.50 ^a	1.31 ^b
0.11	Zinc-blende	0.46	1.44	-	-
0.125	Zinc-blende	0.41	1.41	-	-
0.25	Zinc-blende	0.36	1.45	-	1.44 ^b
0.5	Zinc-blende	0	1.38	1.48 ^c	1.56 ^b
0.75	Wurtzite	0	1.58	1.425 ^d	1.55 ^b
0.875	Wurtzite	0	1.59	-	-
1.0	Wurtzite	0.32	1.79	1.82 ^e	1.60 ^b

^aRef. [7]

^bRef. [1]

^cRef. [76]

^dRef. [77]

^eRef. [72]

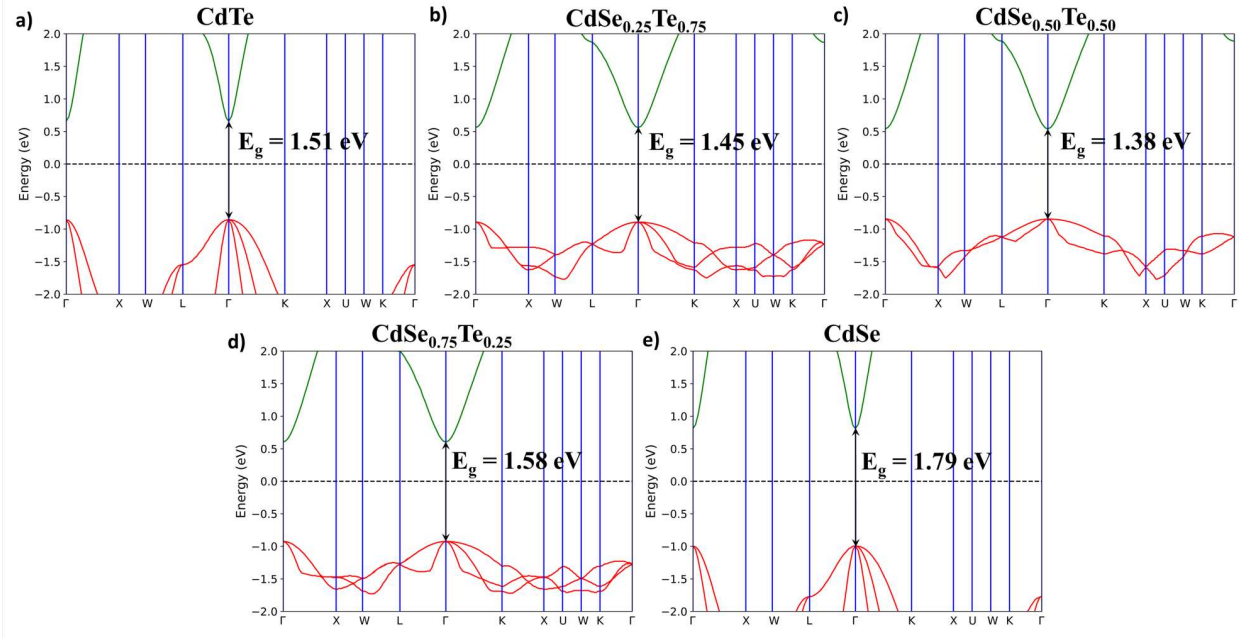


Figure 5.4: The calculated band-structure of the Zinc-blende phase of $\text{CdSe}_x\text{Te}_{1-x}$ for $x=0, 0.25$, and 0.50 and wurtzite phase of the $\text{CdSe}_x\text{Te}_{1-x}$ for $x=0.75, 1.0$. The green line indicates the conduction band minima while the red line depicts the valence band maxima. The dashed line indicates the Fermi level position. The band-structure calculation was performed using DFT-1/2 correction scheme.

was found to remain fixed. Similar observations were made by Reshak et. al while calculating the band-structure diagrams for $\text{CdSe}_x\text{Te}_{1-x}$ structures using plane wave based DFT codes [1]. The calculated band-gap values for varying Se composition are compiled in Table 5.2 for comparison with the previously reported literature values. The typical band-gap bowing feature observed in Se-alloyed CdTe compounds was confirmed in fig. 5.3 d) for the calculated theoretical band-gap values. It has been shown previously that the band-gap of $\text{CdSe}_x\text{Te}_{1-x}$ alloys could be fitted to a bowing formula [78]:

$$E_g(x) = (1 - x)E_g(\text{CdX}) + xE_g(\text{CdY}) - bx(1 - x), \quad (5.1)$$

where b is the "optical bowing coefficient," E_g is the band-gap of the alloy at composition x , and $E_g(\text{CdX})$ and $E_g(\text{CdY})$ are the band-gap of the binary constituents. A second degree polynomial curve fitting of the experimental and theoretical bandgap values has been employed to obtain the

optical bowing coefficient. The computed bowing parameter $b_{\text{theo}} \sim 0.806$ agrees well with the experimental bowing parameter $b_{\text{exp}} \sim 0.754$ and the published literature [47] values $b_{\text{lit}} \sim 0.80$.

Overall, the structural and electronic properties of the bulk $\text{CdSe}_x\text{Te}_{1-x}$ structures modeled using LCAO basis sets in conjugation with DFT-1/2 correction scheme is in good agreement with the existing literature. The modeling parameters worked out from simulating bulk $\text{CdSe}_x\text{Te}_{1-x}$ structures will be further used for surface and interface calculations.

Chapter 6

Modeling $\text{CdSe}_x\text{Te}_{1-x}$ surfaces¹

6.1 Introduction

In the case of CdTe-only absorber based solar cell, research studies suggest that CdTe surface characteristics govern the minority carrier lifetime that determines the CdTe device performance [79]. The non-polar and polar low index CdTe surface facets have been extensively investigated using theoretical and experimental techniques to understand the relaxation and reconstruction of the CdTe surfaces [59, 80, 81]. Theoretical analyses based on Density Functional Theory (DFT) have also been used to probe the surface energy band alignment of the unreconstructed and reconstructed CdTe surfaces [4]. *Nicholson et al.* in different DFT studies further observed that a cusp feature developed in CdTe(111) surface energy band alignment is retained for the CdTe/Te interface and attributed that cusp feature as an additional mechanism for hole charge transport towards the back electrode [4, 6]. The above observations imply the importance of understanding the surface behavior for predicting the interface properties in heterojunction solar cells.

However, the surface structural and electronic behavior of $\text{CdSe}_x\text{Te}_{1-x}$ ternary alloys have not been explored hitherto. It has been observed experimentally that the CdTe-only absorber based solar cell is a low performing device in comparison to $\text{CdSe}_x\text{Te}_{1-x}$ /CdTe absorber based solar cells [14, 21, 31]. This shows that $\text{CdSe}_x\text{Te}_{1-x}$ surface forming distinct interface would influence the

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Akash Shah: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization.

Amit H. Munshi: Cell fabrication, Writing - review editing.

Anthony P. Nicholson: Software, Formal analysis, Data curation, Writing - review editing.

Aanand Thiagarajan: Software, Formal analysis, Writing - review editing.

Umberto M. Pozzoni: Software, Supervision.

Walajabad S. Sampath: Conceptualization, Resources, Project administration, Funding acquisition

electronic properties in the solar cell device performance. A comprehensive understanding of the electronic properties of $\text{CdSe}_x\text{Te}_{1-x}$ surface is therefore essential for further improvement in the device performance.

This chapter covers atomistic modeling based on DFT coupled with surface Green's function to study the structural and electronic features of polar Cd-terminated low index $\text{CdSe}_x\text{Te}_{1-x}(100)$, (111) , and non-polar $\text{CdSe}_x\text{Te}_{1-x}(110)$ surfaces. Since $\text{CdSe}_x\text{Te}_{1-x}$ is a group II-VI based compound alloy, similar reconstruction effects on $\text{CdSe}_x\text{Te}_{1-x}$ surface are expected as observed in CdTe surface experimentally. Thus both the unreconstructed and reconstructed $\text{CdSe}_x\text{Te}_{1-x}$ surfaces have been simulated to evaluate the energy band alignment characteristics for each case. The experimental device performance of $\text{CdSe}_x\text{Te}_{1-x}$ -only and CdTe-only devices fabricated under identical conditions is also reported. The energy band alignment diagrams for the $\text{CdSe}_x\text{Te}_{1-x}$ and CdTe surface comparison at equilibrium have been plotted to understand the charge transport within $\text{CdSe}_x\text{Te}_{1-x}$ -only and CdTe-only absorber based solar cells. The comparison also give insights into the potential reason for (but not limited to) the lower performance of $\text{CdSe}_x\text{Te}_{1-x}$ -only absorber based solar cells.

6.2 Experimental details

6.2.1 PV-device fabrication

Photovoltaic devices with two p-type absorbers were fabricated using similar processing conditions and optimized for high device performance. The devices were fabricated on NSG Pilkington TEC10 soda lime glass that had a layer of fluorine doped tin oxide deposited by the manufacturer as the n-type transparent conducting oxide. Both the substrates had a 100 nm layer of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ($x=11$ at.%) (MZO) deposited by RF sputter deposition using a single $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ target. Thereafter, the absorber deposition and CdCl_2 passivation treatment were performed using an in-line sublimation system with 9 processing stations designed and optimized for fabrication of CdTe-based thin-film PV-devices. This system is extensively described by Swanson et al [7]. The first substrate was heated to a temperature of about 530°C and the substrate was then transferred to the

CdTe sublimation station using a computer controlled magnetic transfer mechanism. About 3 μm of CdTe was deposited on the preheated substrate over 150 seconds following which the substrate was transferred to CdCl_2 sublimation station for 200 seconds. The substrate was then moved to an annealing station for 200 seconds. CdCl_2 was deposited at 442°C and annealing station operated at 400°C . Thereafter the substrate was transferred to a cooling station within the vacuum chamber for 300 seconds before it was removed from the vacuum chamber and the residual CdCl_2 film from the surface was rinsed off using deionized water and dried using pressurized ultrahigh purity nitrogen gas.

For the $\text{CdSe}_x\text{Te}_{1-x}$ device, the same fabrication system was used. However, the processing conditions were slightly different as they were optimized for deposition of a lower band-gap material with a deposition rate different from the CdTe. The substrate with 100 nm of MZO was preheated to a temperature of about 538°C after which the substrate was transferred to the station containing a $\text{CdSe}_x\text{Te}_{1-x}$ ($x=20$) source charge. A 3.3 μm film was deposited over 360 seconds with the $\text{CdSe}_x\text{Te}_{1-x}$ sublimation source operating at 575°C . Following the deposition of the film, the substrate was transferred to the CdCl_2 passivation treatment station where the film was exposed to CdCl_2 vapor for 900 seconds from a CdCl_2 sublimation source operating at a temperature of 450°C . Thereafter, the substrate was cooled in the vacuum chamber for 180 seconds. The substrate was removed and like the earlier CdTe film, the residual CdCl_2 layer was rinsed off using deionized water and dried using a pressurized ultrahigh purity nitrogen gas. The high purity CdTe, $\text{CdSe}_x\text{Te}_{1-x}$ and CdCl_2 materials used in this study were provided by 5N Plus Inc.

Following this the films were moved to an evaporator where 30 nm of pure Te was vapor deposited. The substrates were then painted with graphite and nickel paint in polymer binder manufactured by Henkel Chemicals Company that formed the back electrodes. The films were masked and delineated into square area devices (area $\sim 0.65\text{ cm}^2$) using a plastic abrasion medium sprayed using pressurized gas. 25 small area research devices were fabricated for substrate with CdTe film while 10 devices were fabricated on the substrate with $\text{CdSe}_x\text{Te}_{1-x}$ film. It must be noted that the substrates used for both the device structures were identical. However, half of the

$\text{CdSe}_x\text{Te}_{1-x}$ substrate did not receive the 30 nm Te layer and therefore only the films with Te back-contact layer are eligible for comparison with the CdTe devices that are discussed here.

Electrical measurements were performed with a Model 10600 solar simulator from ABET Technologies using a high-pressure xenon arc lamp with an AM1.5 filter. Current density vs voltage curves were generated based on electrical measurements performed using Keithley 2420 SourceMeter controlled via LabView. Current-density and device area for each set of measurement were calibrated to cells measured by National Renewable Energy Laboratory (NREL). Device areas were measured using a webcam that took an image of a backlit solar cell and counted the pixels below a certain brightness.

6.2.2 Device performance results

The box plot (see Fig. 6.1) shows the % efficiency and % Fill Factor comparison for the CdTe-only and $\text{CdSe}_x\text{Te}_{1-x}$ -only absorber based solar cell devices. CdTe-only devices consistently showed higher efficiencies and the fill factor values with a tight spread in comparison to the $\text{CdSe}_x\text{Te}_{1-x}$ -only devices. The larger spread in the $\text{CdSe}_x\text{Te}_{1-x}$ -only devices could be attributed to the variation in thickness during the $\text{CdSe}_x\text{Te}_{1-x}$ film deposition. Out of several devices, Fig. 6.1(c) shows the current density vs voltage curve for the highest performing device from each experiment set. The lower performance seen in $\text{CdSe}_x\text{Te}_{1-x}$ -only devices is explained further using DFT-based atomistic modeling.

6.3 Computational details

For bulk $\text{CdSe}_x\text{Te}_{1-x}$ alloy, the electronic properties computed using the DFT LCAO basis set scheme and DFT-1/2 correction method were in good agreement with experimental and other theoretical published literature. Therefore the same modeling parameters were used further to study the energy band alignment features of non-polar $\text{CdSe}_x\text{Te}_{1-x}(110)$ as well as polar $\text{CdSe}_x\text{Te}_{1-x}(100)$ and (111) surface facets. A one-probe DFT + SGF modeling domain (Fig 6.2) was setup with the $\text{CdSe}_x\text{Te}_{1-x}$ bulk electrode region adopting the Dirichlet boundary condition and the surface region

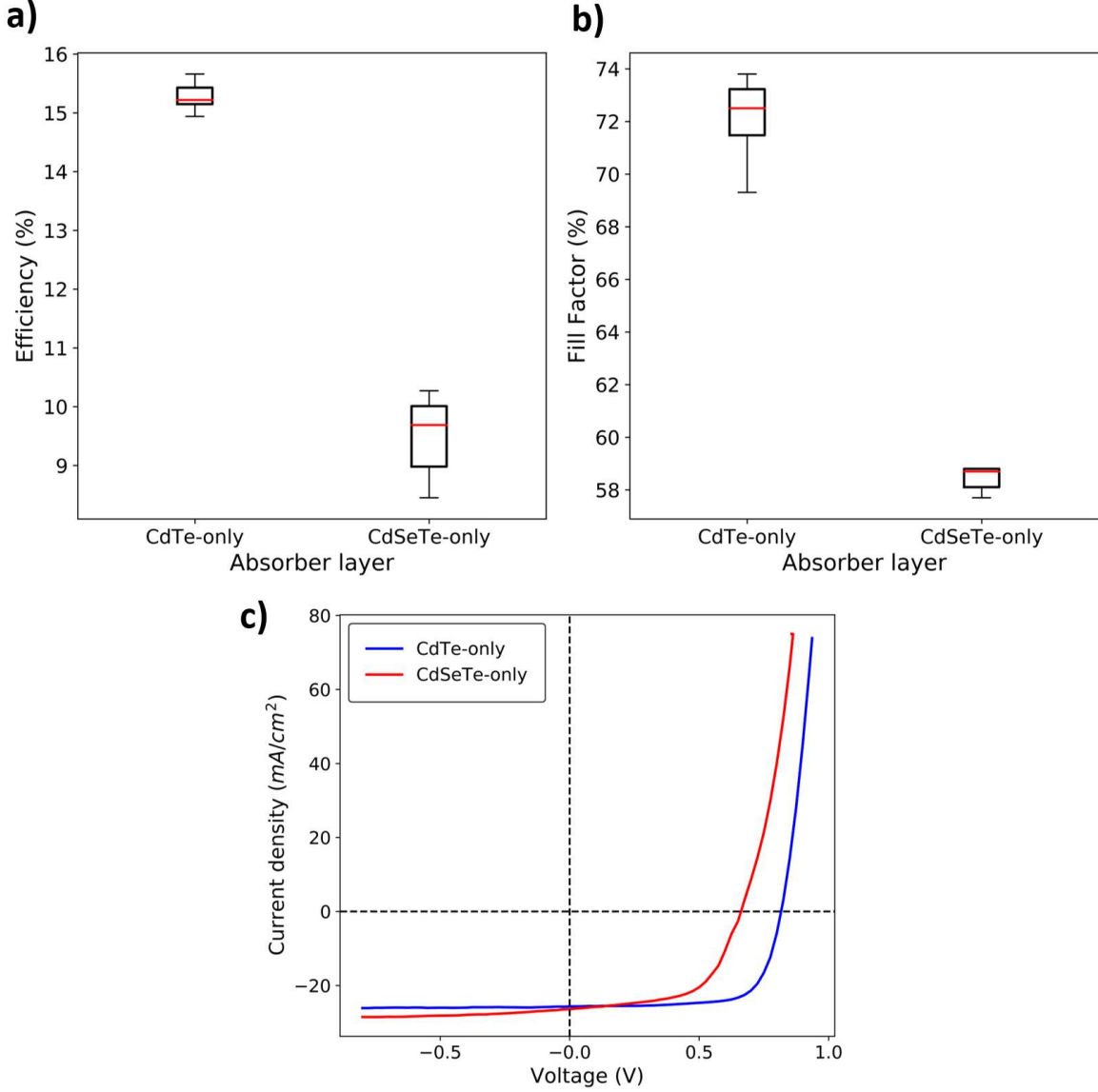


Figure 6.1: Box plot comparing the (a) % Efficiency and (b) % Fill Factor between CdTe-only and CdSe_xTe_{1-x}-only absorber based solar cells. (c) compares the device performance between CdTe-only and CdSe_xTe_{1-x}-only solar cell. The CdTe-only absorber based solar cells produced always produced higher efficiency device than the CdSe_xTe_{1-x}-only absorber device.

adopting Neumann boundary condition for the reasons described by *Nicholson et al.* [4]. All the low index surface facets were cleaved from bulk CdSe_{0.25}Te_{0.75} (Se at.% = 12.5%) model to closely follow the at. % concentrations (11 at. %) reported in previous studies [21,31]. A $6 \times 6 \times 150$ Monkhorst-Pack grid distribution of k-points was setup for computing the electronic properties of CdSe_{0.25}Te_{0.75} surface facets.

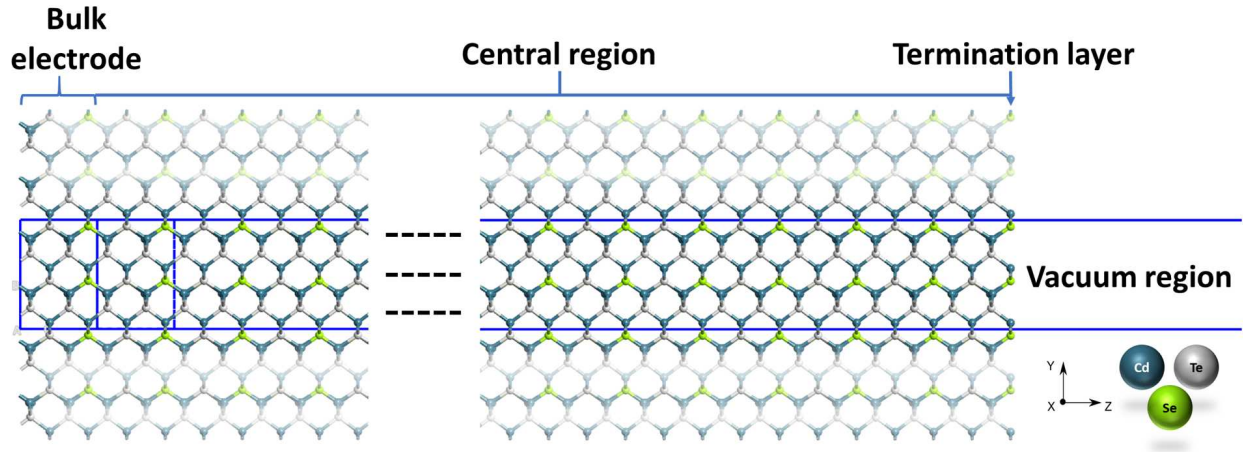


Figure 6.2: Schematic diagram showing $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface one-probe modeling domain.

Six different $\text{CdSe}_x\text{Te}_{1-x}$ surfaces were studied to understand the surface properties in various plane orientations. Previous studies have demonstrated the prevalence of (1×1) unreconstructed polar $\text{CdTe}(100)$ and $\text{CdTe}(111)$ surfaces under certain experimental conditions. Various other DFT studies and films grown under epitaxial conditions have shown that $c(2 \times 2)$ and (2×2) reconstructions in the respective Cd terminated $\text{CdTe}(100)$ and $\text{CdTe}(111)$ generate thermodynamically stable surface structures [4, 80–83]. Thus, the four surface configurations described above were evaluated for polar Cd terminated $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface facets. The $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ and (2×2) $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ reconstructed surfaces were constructed as per the method described by *Nicholson et al.* [4]. For the non-polar $\text{CdTe}(110)$ surface, earlier DFT studies show that relaxation of the $\text{CdTe}(110)$ surface causes atomic chains to tilt [59]. That is why for the $\text{CdSe}_x\text{Te}_{1-x}(110)$ surface, structural and electronic properties were compared between non-relaxed and relaxed geometries.

All the unreconstructed and reconstructed $\text{CdSe}_{0.25}\text{Te}_{0.75}$ facets were structurally relaxed in the central region extending 5-6 nm from the termination surface. A force threshold of $0.05 \text{ eV/\AA}$ was used in all the surface relaxations [58]. For describing the structural features of the relaxed surface, the movement of atoms into and out of the plane of surface atoms with respect to the unrelaxed surface configuration are denoted by " $\leftarrow$ " and " $\rightarrow$ " symbols respectively. The electronic properties of the unreconstructed and reconstructed surfaces were compared to gain insight on how

reconstructions affect the surface band alignment. Further comparison of the $\text{CdSe}_x\text{Te}_{1-x}$ and CdTe surface energy band alignments were performed to understand one of the potential reason for lower performance observed in $\text{CdSe}_x\text{Te}_{1-x}$ -only devices.

6.4 Results and Discussion

Cleavage energy γ_c for the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surfaces were calculated to verify the stability of the polar and non-polar surfaces. The cleavage energy from the DFT + SGF method was calculated as follows [54]:

$$\gamma_c = \frac{2E_2 - E_1}{2A} \quad (6.1)$$

where E_2 is the one-probe total energy of the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface, E_1 is the total energy of the two-probe representation of the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ bulk along a given orientation, and A is the cross sectional area of the given simulation domain. The cleavage energy values, γ_c for $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$, (110) , and (111) surfaces were 1.76, 1.05, and 1.37 J/m² respectively. The cleavage energy calculation indicated that non-polar $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface had higher stability than polar $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ followed by $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface and were in qualitatively good agreement with other published literature values [4, 84].

Pertinent electronic features of the low index $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface models were studied to understand the effects of atomic relaxation and surface reconstruction on the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface energy band alignment. Local density of states were computed and projected along the z-direction to generate the energy band alignment plot for all the six surface configurations described earlier. Macroscopically averaged curve fits of valence band maximum (VBM) and conduction band minimum (CBM) were obtained using gaussian kernel method described by *Nicholson et al.* [4]. In accordance with the labels provided in Fig. 6.3 e), the band-gap energy, $E_{\text{CdSe}_{0.25}\text{Te}_{0.75}}^g$ was determined from the energy differences of the VBM and CBM at positions located to closest bulk-like $\text{CdSe}_{0.25}\text{Te}_{0.75}$ structure. The dip observed in the valence band is defined as the surface potential E_{surf} , and was calculated by taking the difference between the curve fit VBM value (labeled point

2) near the surface and the curve fit VBM value of the bulk-like $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (labeled point 1).

Table 6.1 summarizes all the electronic features for the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surfaces described earlier.

Table 6.1: Salient electronic features of the low indexed $\text{Cd}_{0.25}\text{Te}_{0.75}$ surfaces. $L_{z,\text{bulk}}$ (Å) and $L_{z,\text{surf}}$ (Å) denotes the bulk electrode and the surface region length respectively. N_{atoms} represents the number of atoms within the surface region.

$\text{CdSe}_{0.25}\text{Te}_{0.75}$ Surface	$E_{\text{CdSe}_{0.25}\text{Te}_{0.75}}^g$ (eV)	E_{surf} (eV)	$L_{z,\text{bulk}}$ (Å)	$L_{z,\text{surf}}$ (Å)	N_{atoms}
(1×1) (100)	1.37	-0.25	12.10	245.48	607
$c(2 \times 2)$ (100)	1.37	-0.02	12.10	244.20	605
Unrelaxed (110)	1.36	-0.02	17.25	145.55	511
Relaxed (110)	1.36	-0.04	17.25	177.38	607
(1×1) (111)	1.39	-0.38	9.67	191.05	407
(2×2) (111)	1.37	-0.06	9.67	184.83	398

6.4.1 $\text{CdSe}_x\text{Te}_{1-x}$ (100) surface

Fig. 6.3 shows the structural and energy band alignment features of the relaxed Cd terminated (1×1) and $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface. The $c(2 \times 2)$ surface was implemented using the (1×1) periodic unit cell in the transverse direction but required the removal of two Cd atoms from the original surface unit cell. The relaxation of (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (100) surface led to the Cd-dimer formation on the surface. Using the atomic positions of an unrelaxed (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (100) as a reference, it was found that the two surface Cd atoms moved towards each other by 1.866Å to form the surface Cd-dimer (Fig. 6.3 (c)). Similar phenomena of surface Cd-dimer formation has been reported for the (1×1) CdTe(100) surface [4].

The relaxation of $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (100) surface led to the flattening of the surface (Fig. 6.3 (b)). Again, using the atomic positions of an unrelaxed $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (100) as a reference, it was noted that surface Cd atoms move into the surface plane by 1.374Å, while the anionic (Te/Se) layer beneath it moved out of the surface plane by 0.329Å in the [100] direction.

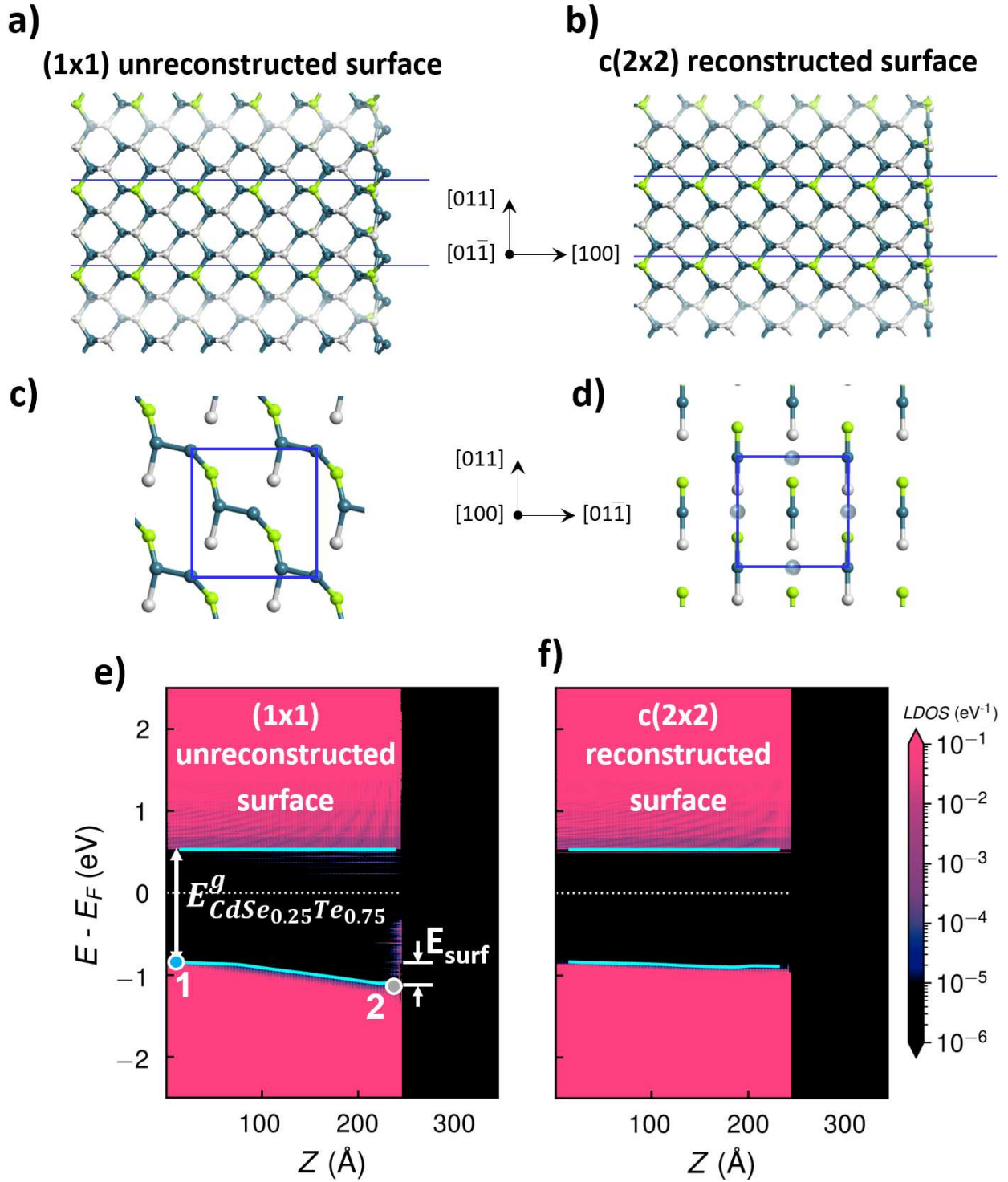


Figure 6.3: Side view and the top view of the respective relaxed atomic configurations of (a,c) the (1×1) unreconstructed and (b,d) the $c(2 \times 2)$ reconstructed $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surfaces. (e) and (f) shows the energy band alignment diagram of the respective relaxed atomic configurations of the (1×1) unreconstructed and the $c(2 \times 2)$ reconstructed $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surfaces.

Such movement of cationic and anionic layer results in a flattened surface and has been reported in earlier CdTe(100) DFT studies [4, 81].

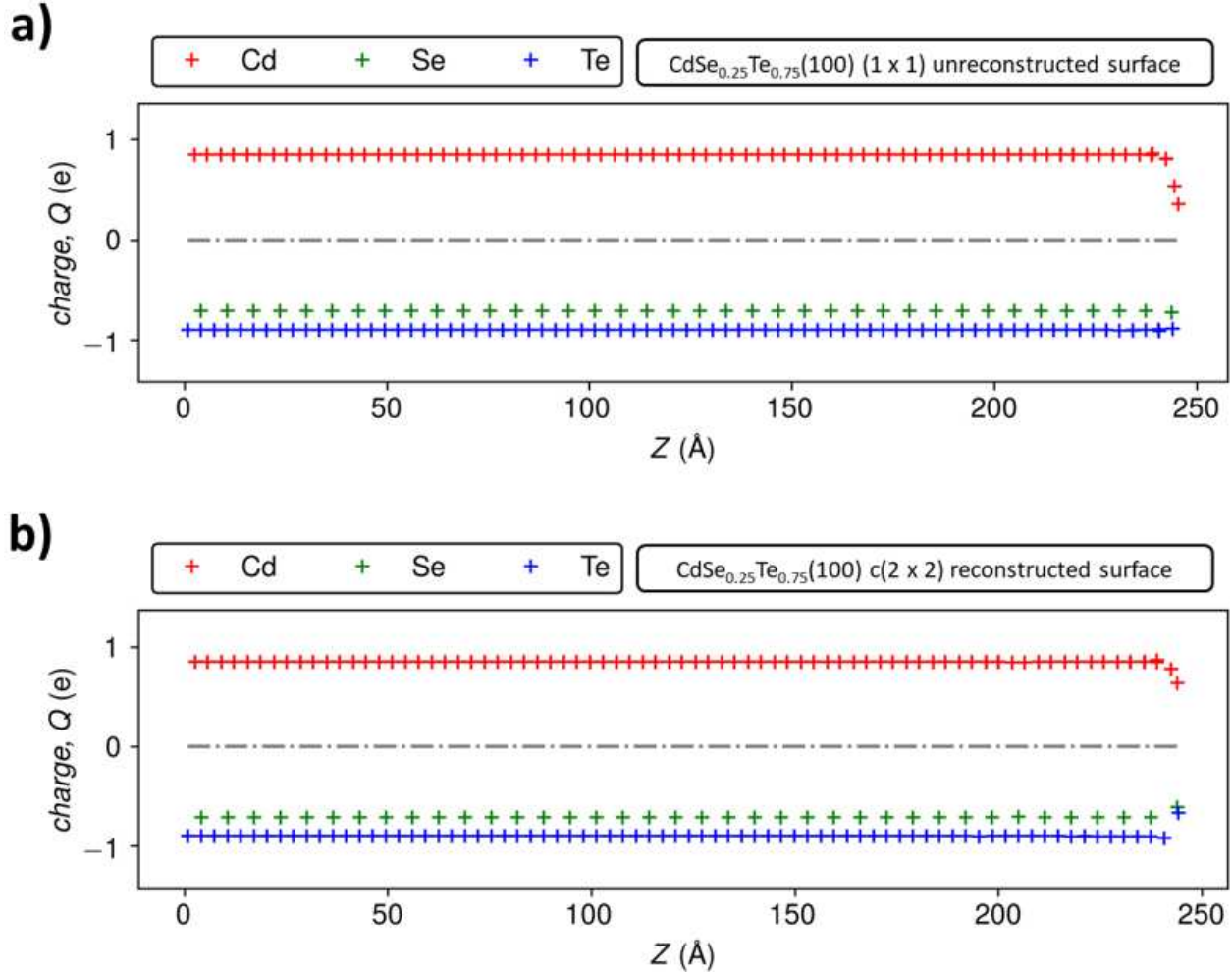


Figure 6.4: Mulliken population analysis showing the atomic charge distribution for (a) (1×1) CdSe_{0.25}Te_{0.75}(100) surface and (b) $c(2 \times 2)$ CdSe_{0.25}Te_{0.75}(100) surface.

A Mulliken population analysis was performed on the relaxed Cd terminated (1×1) and $c(2 \times 2)$ CdSe_{0.25}Te_{0.75}(100) surface to estimate the partial atomic charges on the atoms [85]. Fig. 6.4 shows the partial charge distribution on the Cd, Se, and Te atoms (in terms of the electronic charge(e)) along the transverse z-direction. A positive electronic charge indicates cationic behavior, while the negative electronic charge shows anionic behavior of the atoms. A smooth and homogeneous charge distribution was observed for both the surfaces in the bulk-like region far away from the

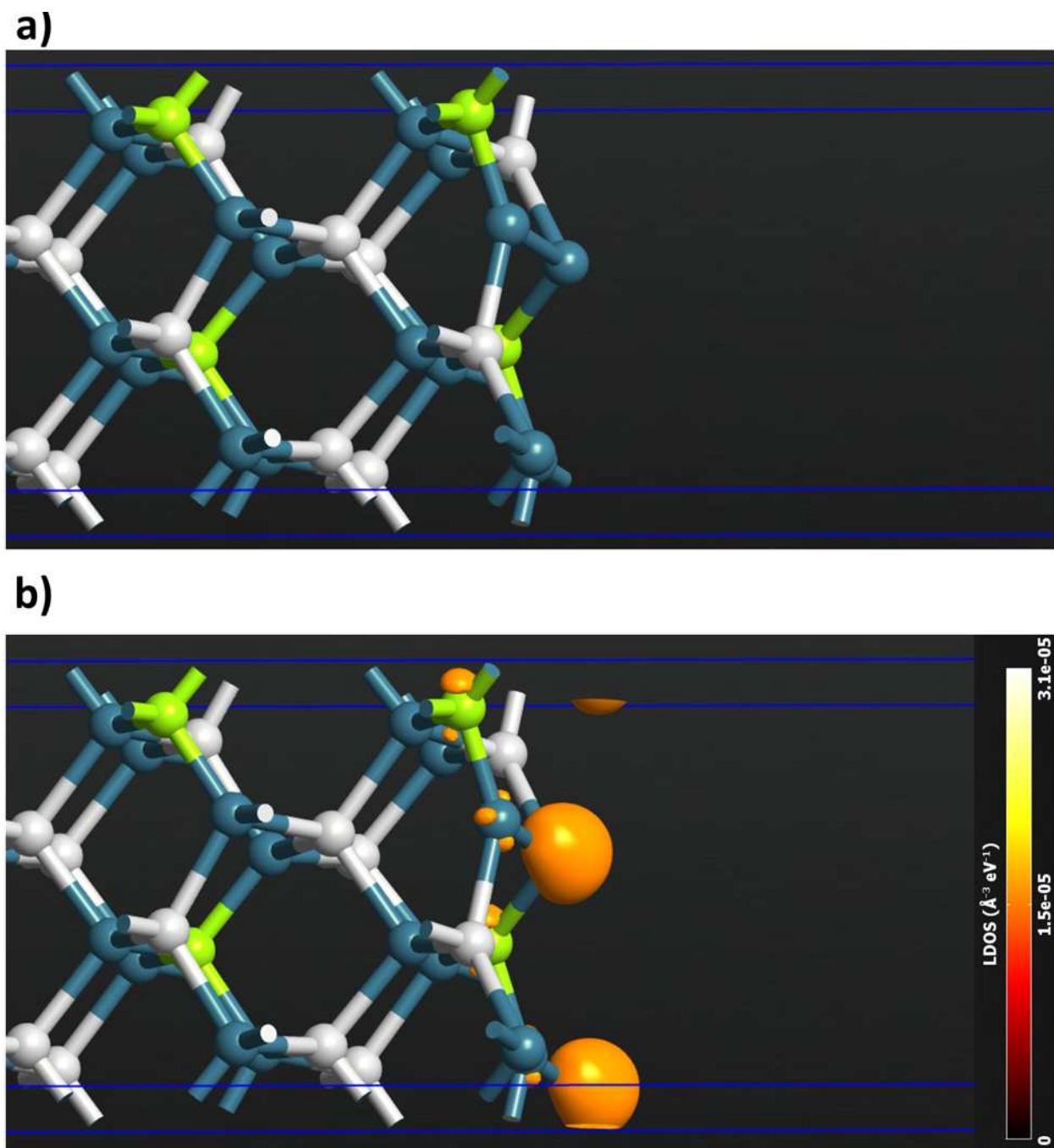


Figure 6.5: Relaxed atomic configuration showing (a) Cd-Cd dimer formation in Cd terminated CdSe_{0.25}Te_{0.75}(100) surface and (b) Local density of states (LDOS) around Cd atom involved in the dimer formation. This LDOS was calculated for one of the prominent surface state observed in the energy band alignment diagram of unreconstructed CdSe_{0.25}Te_{0.75}(100) surface at $E = -0.61$ eV.

surface as the cations and anions periodically arranged with no perturbation in the electrostatic potential. However, the lower energy configuration of atoms during relaxation causes the surface

atoms to deviate from the ordered cationic/anionic arrangement. The deviation from a periodic atomic arrangement would induce a perturbation in the electrostatic potential and affect the charges on the atoms. Similar observations were made for the (1×1) and $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface. Using Fig. 6.4 (a), a net charge of $+1.786e$ was found to reside on the two Cd atoms forming dimers at the surface. However, for the $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface, the net surface charge added only $+0.008e$ (Fig. 6.4 (b)). This small amount of charge on the reconstructed surface revealed that the cationic moving into the plane ($\leftarrow$) and anionic layer moving out of the plane ($\rightarrow$), happened to redistribute the charge. The redistributed charges with flat surface structure satisfy the Electron Counting Rule (ECR) [86] as the number of empty cation (Cd) dangling bonds become equal to the filled anionic (Te/Se) dangling bonds [4].

It is expected that the charges present on the surface influence the surface band bending. A positively charged surface is known to repel the majority hole charge carrier by bending the VBM down. Similar observations were made in the surface energy band alignment results shown in Fig. 6.3 (e), (f). Fig. 6.3 (e) shows that the (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface has a negative surface potential value of -0.25 eV (Table 6.1) with a high density of surface states near the valence band. A local density of state analysis done on one of the most prominent surface state at $E = -0.61$ eV (see fig. 6.5) further suggests that the occurrence of such surface state is due to the Cd dimer formation in the unreconstructed $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface. However, the $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface resulted in flat bands ($E_{\text{surf}} = -0.02$ eV) with minimal density of surface states (Fig. 6.3 (f)). Such contrasts in the VBM bending can be attributed to the different surface charging effect observed in Mulliken population plot. A higher net surface charge of $+1.786e$ produces a larger VBM bending ($E_{\text{surf}} = -0.25$ eV) in the (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface whereas a lower surface charge of $+0.008e$ induces a smaller VBM bending ($E_{\text{surf}} = -0.02$ eV) in the $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface. In terms of charge transport, while the $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface with flat bands does not obstruct or enhance the charge carrier flow, the presence of a larger downward bend in the VBM seen in (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface would induce a barrier for hole charge carrier transport towards the back electrode of the solar cell.

6.4.2 $\text{CdSe}_x\text{Te}_{1-x}(110)$ surface

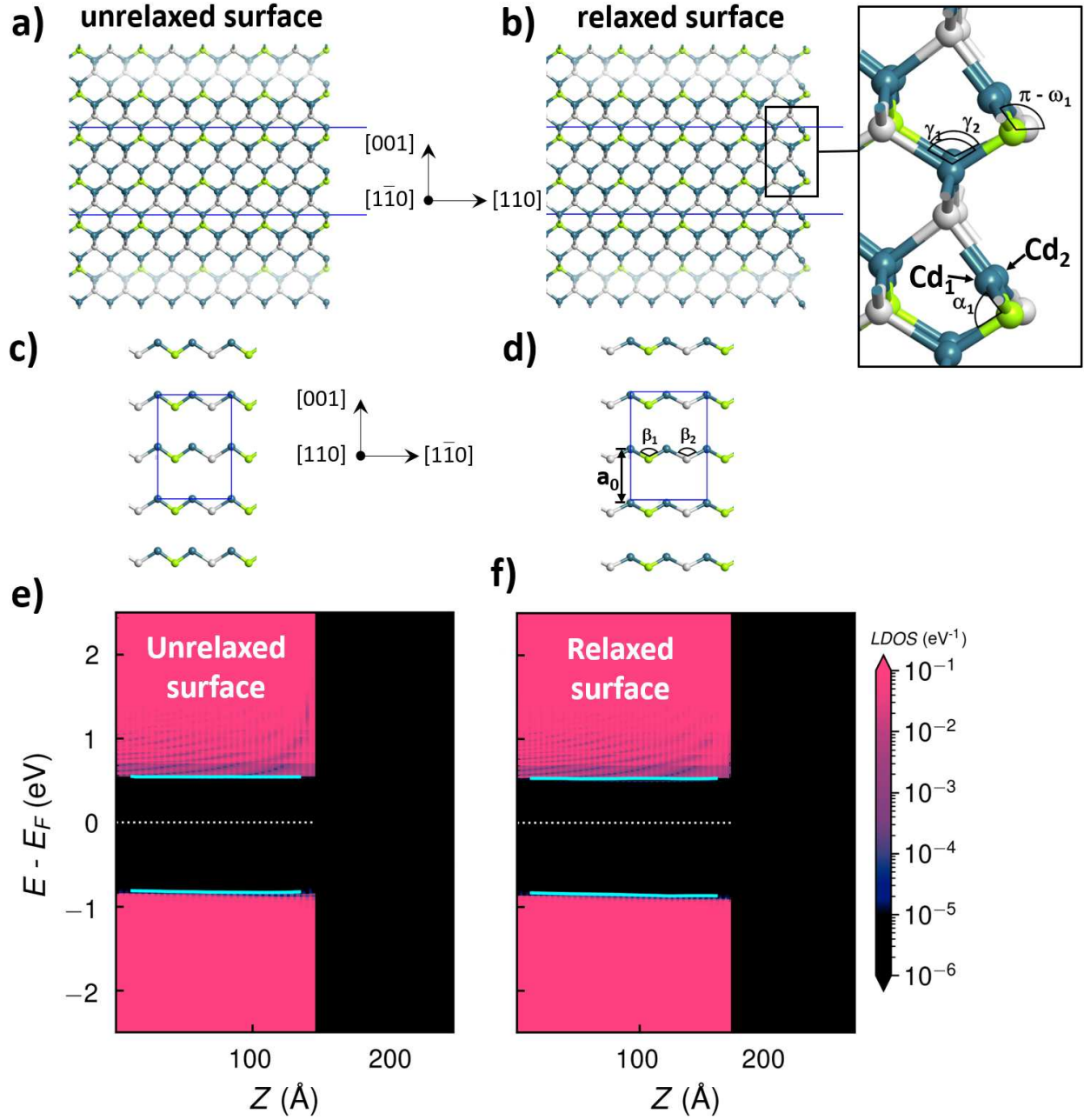


Figure 6.6: Side view and the top view of the respective atomic configurations of (a,c) the unrelaxed and (b,d) the relaxed $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface. The top view shows the last two atomic layers of the surface for clarity. The side view is shown along the transport direction. The subfigure in (b) shows the tilt angle and the bond angles measured for cations and anions. In (d), parameter $a_0 = 6.48 \text{ \AA}$ measures the lattice constant of the bulk $\text{CdSe}_{0.25}\text{Te}_{0.75}$. (e) and (f) shows the energy band alignment diagram of the respective atomic configurations of the unrelaxed and the relaxed $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface.

The $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface is non-polar since the (110) plane contains equal numbers of cations and anions. As discussed earlier, the (110) plane has the lowest cleavage energy as it inherently satisfies the ECR. Previous literature studies for III-V(110) surface have reported about 28° - 32° atomic chain tilt on the top (110) surface layer [86]. Similar atomic chain tilt features with a tilt angle(ω) of 30° have been observed experimentally for the $\text{CdTe}(110)$ surface [87]. Another *Ab-initio* study using DFT has reported 30.2° and 27.1° tilt angle for the respective $\text{CdTe}(110)$ and $\text{CdSe}(110)$ surfaces [59].

Fig. 6.6 shows the structural and electronic features of an unrelaxed and relaxed $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface. The structural comparison between the unrelaxed and relaxed $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface showed the classic atomic chain tilt observed in other III-V(110) and II-VI(110) surfaces. It can be seen that the surface relaxes with surface anions (Te/Se) moving out (vertical buckling($\Delta_{\perp,1}$)) of the (110) plane and surface cations moving inwards. Previous studies with binary alloys have reported only a single vertical buckling parameter for the cation and anion [59,86]. However, with the ternary $\text{CdSe}_{0.25}\text{Te}_{0.75}$ alloy, it was observed that the vertical buckling of Cd atom (labeled in Fig. 6.6 (b) subfigure) was dependent on the anion atom (Te or Se) lying directly beneath it. Similarly, the vertical buckling of the Te and Se anions differed and has been summarized in Table 6.2. The difference in the electronegativity of the Se and Te atoms causes variation in vertical buckling values for anions and is consequently reflected in the corresponding Cd atom attached to either of the anions. *Watari et al.* made similar observations where the more electronegative Se anion has less vertical buckling than the Te anion [59].

Table 6.2: Vertical buckling values of the surface Cd, Se and Te atom. The $\leftarrow$ and $\rightarrow$ symbols indicate respective atoms moving inward and outward of the (110) surface plane.

Atoms	Cd ₁	Cd ₂	Se	Te
$\Delta_{\perp,1}$	$\leftarrow 0.528 \text{ \AA}$	$\leftarrow 0.536 \text{ \AA}$	$\rightarrow 0.135 \text{ \AA}$	$\rightarrow 0.323 \text{ \AA}$

Fig. 6.6 (b) and (d) shows the *pyramidal angle* α at the anion, the *in-plane angle* β and the *planar angle* γ at the cation. Due to the difference in relaxation of the Se and Te anion, each of the above listed angles measured different values. The *pyramidal* and *in-plane angles* measured for Se anions were labeled as α_1 and β_1 respectively, while for the Te anions they were designated as α_2 and β_2 . Similarly, the *planar angles* at the cation were labeled as γ_1 and γ_2 for the Te-Cd-Se and Se-Cd-Te measurements respectively (shown in Fig. 6.6 (b) subfigure). In addition to the difference between the above angles, the *tilt angle* ω_1 computed for the plane containing Cd₁ and Se atom differed from the *tilt angle* ω_2 calculated for the plane containing Cd₂ and Te atom. All the angles with their respective values obtained in this calculation are summarized in Table 6.3.

The trend of *pyramidal angle* α being closer to 90° and decreasing from 92.5° for Se to 85.5° for Te atom is in agreement with the binary CdTe and CdSe alloy. The *planar angle* γ at the cation is close to 120° as the surface cation atoms prefer sp^2 -like hybridization. The *in-plane angle* β is lower than γ and is closer to the tetrahedral bond angle of 109.47° as the anions prefer sp^3 -like hybridisation with their three cation neighbors. The *tilt angle* ω also lies close to the expected 30° mark but its exact value needs to be verified experimentally. In general, all the angles calculated for relaxed CdSe_{0.25}Te_{0.75}(110) surface in this study are in qualitative agreement with the published literature values [59].

Table 6.3: Calculated tilt angle and bond angle values for anions and cations.

Angles	α_1	α_2	β_1	β_2	γ_1	γ_2	ω_1	ω_2
Values	92.5°	85.5°	114.4°	116.6°	118.5°	126.5°	33.73°	31.33°

The net charge on each surface estimated using the Mulliken population analysis for the unrelaxed and relaxed CdSe_{0.25}Te_{0.75}(110) surface was found to be ~ 0 . This net surface zero charge implies a neutral surface and was expected as the (110) maintains stoichiometry. However, a decrease in the positive cationic and negative anionic electronic charge was observed for the relaxed

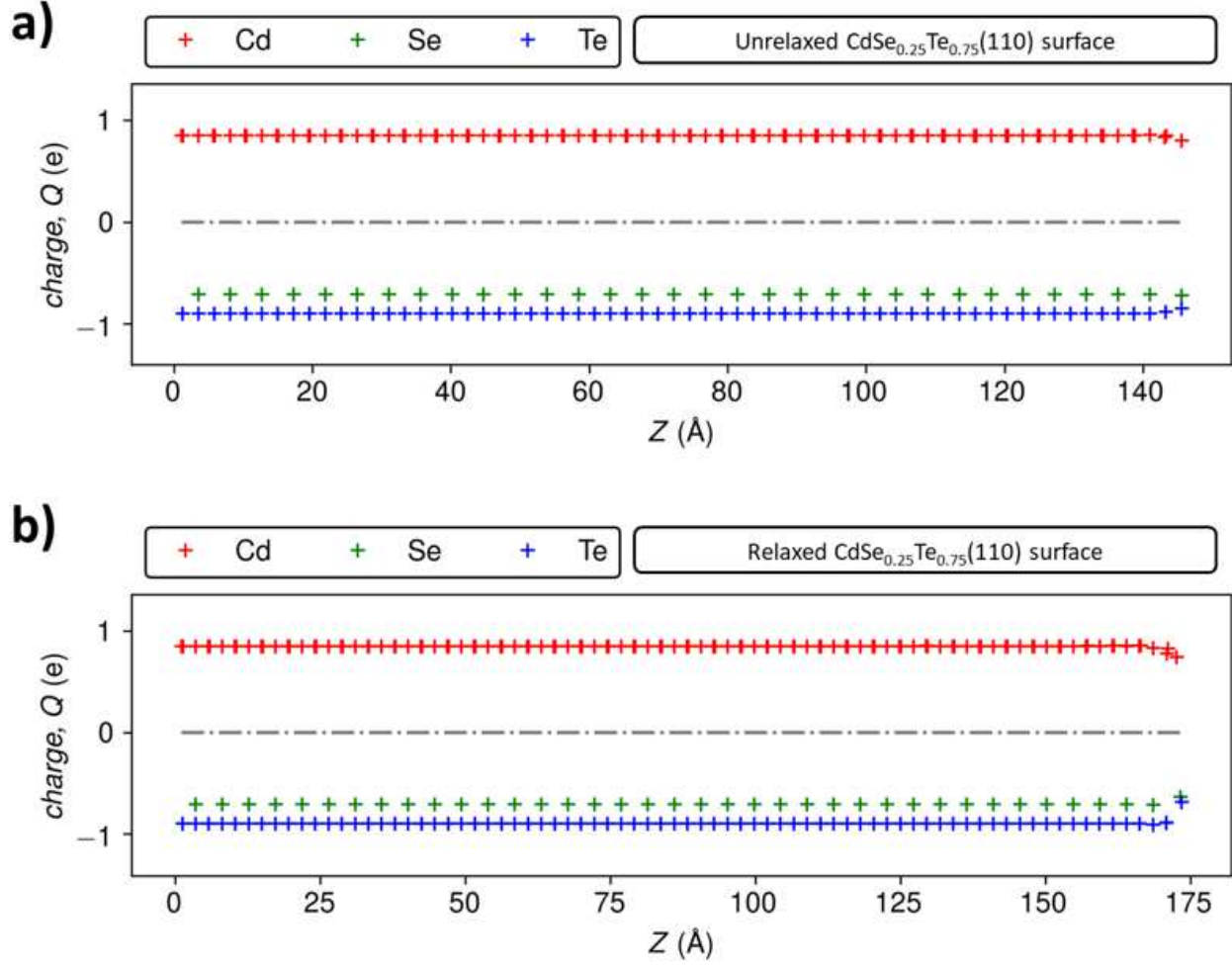


Figure 6.7: Mulliken population analysis showing the atomic charge distribution for (a) unrelaxed $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface and (b) relaxed $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface.

$\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface when compared to the unrelaxed case. Such changes in the partial charges before and after surface relaxation suggest a charge transfer from the anionic Se/Te to cationic Cd atoms. A net 0.158 e charge transfer from the anions (Se and Te combined) to the surface Cd cations was determined using the data points from Fig. 6.7 (a) and (b). It is hypothesized that this charge transfer between the cations and anions occurs due to the tilting of the (110) surface. A similar charge transfer of 0.75 e from the cation to anion has been reported earlier due to the tilting of III-V(110) binary alloy surface [86].

The energy band alignment diagrams shown in Fig. 6.6 (e) and (f) for the respective unrelaxed and relaxed $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surfaces results in flat bands. The cleavage along the (110) plane

creates a clean electronic surface as no surface states are observed in the energy band alignment diagrams. The flat bands were anticipated for the non-polar (110) surface as no surface charging effect was observed in the partial atomic charge distribution. As discussed previously, the presence of such flat bands would neither enhance nor obstruct the charge carrier transport towards the back electrode of the solar cell device.

6.4.3 $\text{CdSe}_x\text{Te}_{1-x}(111)$ surface

Regarding Cd terminated $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ surface, Fig. 6.8 shows the structural and electronic features of the (1×1) unreconstructed and (2×2) reconstructed surface. The relaxed (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ surface in Fig. 6.8 (a) clearly demonstrates that the (2×2) reconstructed surface would be an energetically favorable facet. This is verified by the fact that after the relaxation of the (1×1) unreconstructed surface, a surface Cd atom is displaced in the $[111]$ direction by $1.549 \text{ \AA}$ from its original position in the unrelaxed surface. It was also noted that the atomic rearrangement of the surface atoms due to the relaxation of $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ surface generated a flat surface. Using the positions of the unrelaxed (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ surface as a reference, the Cd terminating layer moved into the surface plane by $0.926 \text{ \AA}$ and the Te and Se atoms beneath it moves out of the surface plane by $0.107 \text{ \AA}$ and $0.123 \text{ \AA}$ respectively. A Similar surface flattening was observed in the relaxed (2×2) $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ surface. Again, using the unrelaxed (2×2) case as a reference, it was found that surface Cd terminating layer move into the surface plane by $0.808 \text{ \AA}$, while the Te and Se atoms beneath it move out of the surface plane by $0.169 \text{ \AA}$ and $0.099 \text{ \AA}$ respectively. Such flattening of the surface observed for the (2×2) $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ model was in agreement with the other calculations done for (2×2) $\text{CdTe}(111)$ and III-V(111) surface [4, 86].

The partial atomic charge distribution plotted using Mulliken population analysis, showed surface charging effect in (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ surface. Using Fig. 6.9 (a), it was estimated that the displaced Cd atom in (1×1) surface had an extra $+0.289e$ charge, while the reconstructed (2×2) surface was found charge neutral (Fig. 6.9 (b)). It was thus inferred that the charge neu-

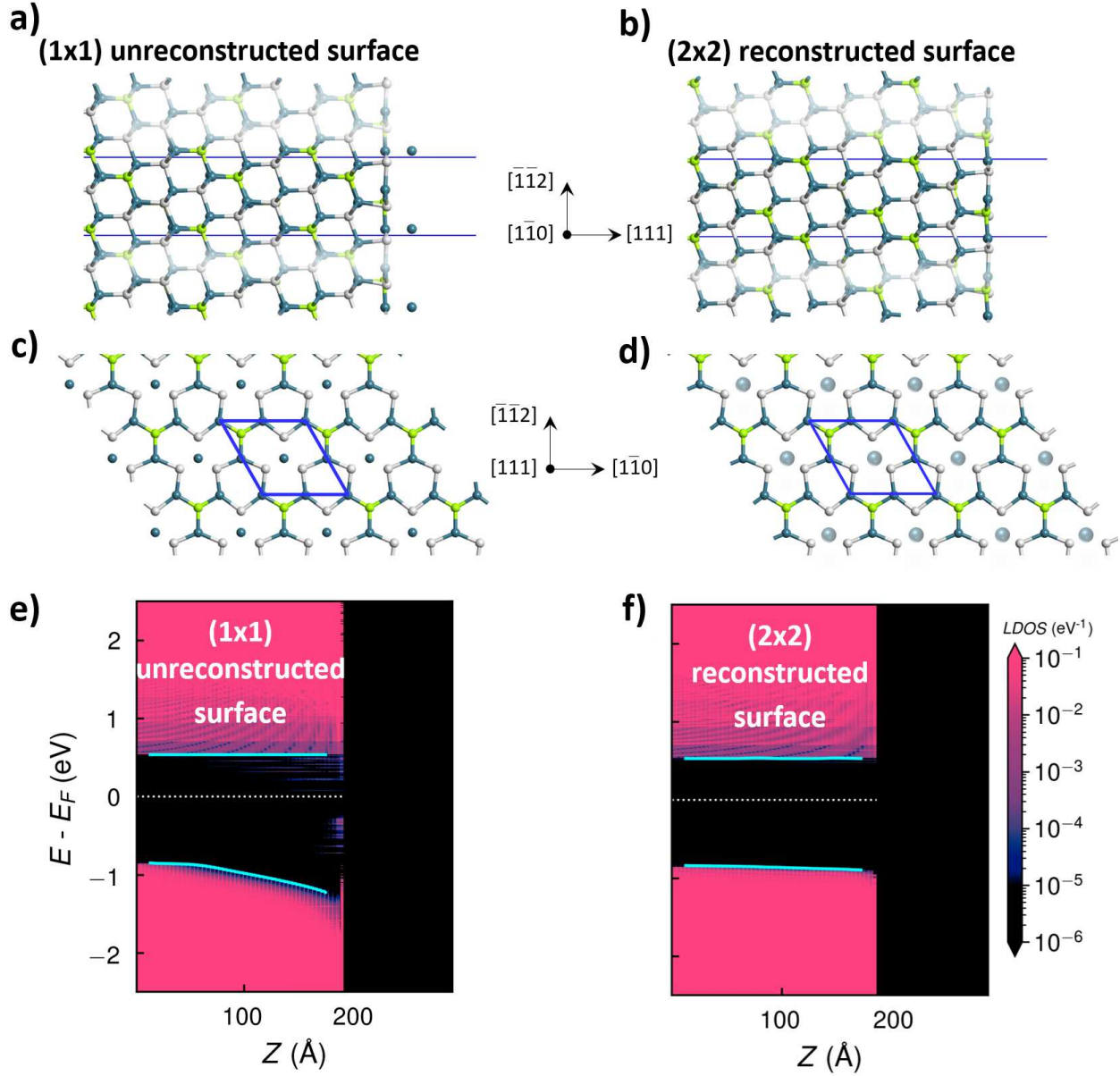


Figure 6.8: Side view and the top view of the respective relaxed atomic configurations of (a,c) the (1×1) unreconstructed and (b,d) the (2×2) reconstructed CdSe_{0.25}Te_{0.75}(111) surfaces. The top view shows the last two atomic layers of the surface for clarity. The side view is shown along the transport direction. The blue translucent spheres in (d) represent the missing Cd atom in (2×2) reconstructed surface. (e) and (f) shows the energy band alignment diagram of the respective relaxed atomic configurations of the (1×1) unreconstructed and the (2×2) reconstructed CdSe_{0.25}Te_{0.75}(111) surfaces.

trality in reconstructed (2×2) surface was due to the missing surface Cd atom. The flattening of surface also played a role in achieving a neutral surface. Previous DFT studies for CdTe(111) had attributed flattening of (2×2) reconstructed surface as a means of satisfying ECR [4]. This was

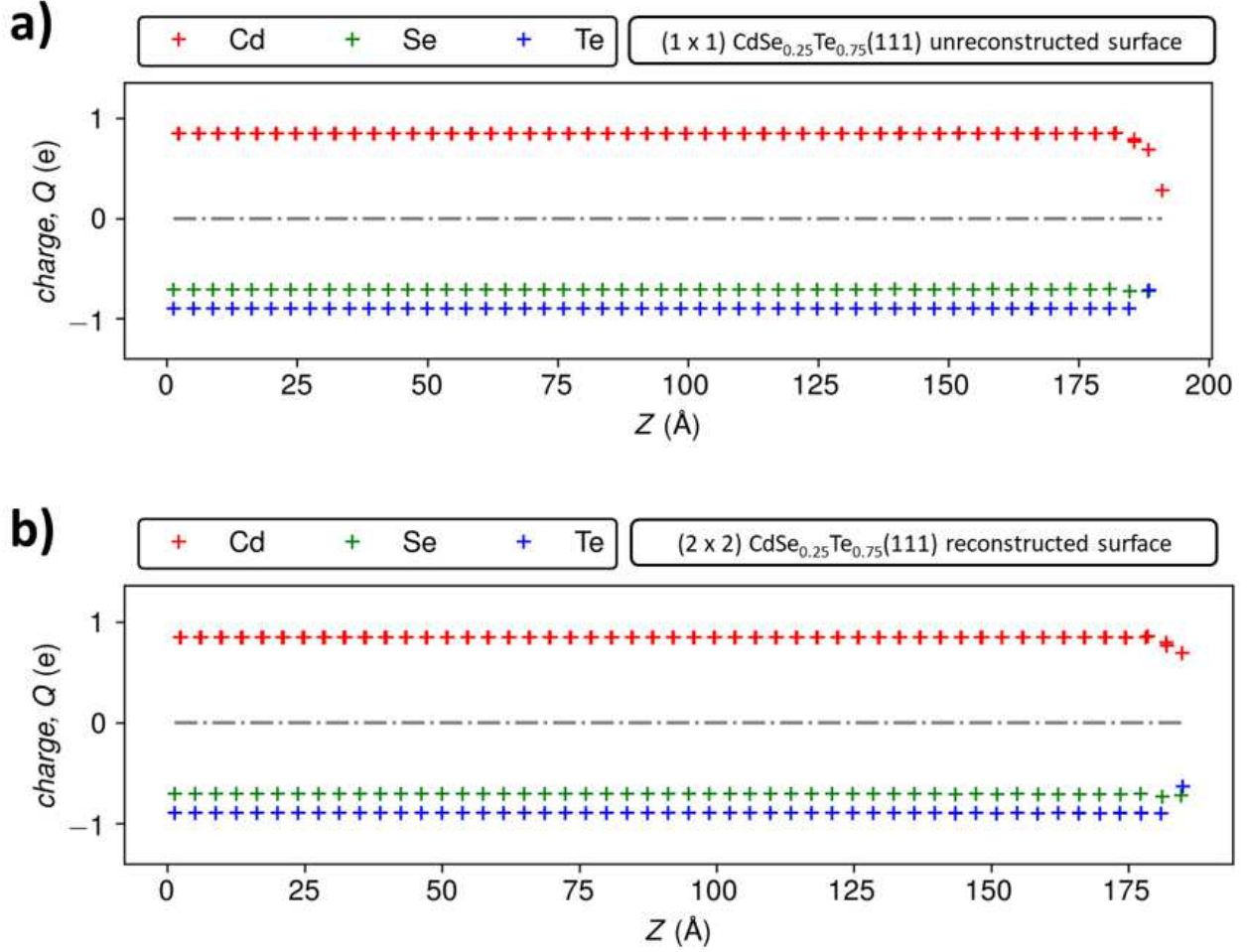


Figure 6.9: Mulliken population analysis showing the atomic charge distribution for (a) (1×1) CdSe_{0.25}Te_{0.75}(111) surface and (b) (2×2) CdSe_{0.25}Te_{0.75}(111) surface.

again validated for (2×2) CdSe_{0.25}Te_{0.75}(111) surface with the above reasoning. As discussed earlier for (100) surface, the effects of surface charging on the energy band alignment was observed in (1×1) (111) surface. The positive charge at the surface bent the VBM down (Fig. 6.8 (e)). High density of the surface states also resulted from the displaced surface Cd atom showing that the (1×1) CdSe_{0.25}Te_{0.75}(111) surface is not clean. The local density of states (LDOS) calculation (see supplementary Fig. 6.10) at $E = -0.35$ eV for one of the prominent surface state further verifies the fact that the displaced Cd atom contributes to the high density of surface state in the (1×1) CdSe_{0.25}Te_{0.75}(111) surface. However, due to surface charge neutrality no band bending was seen in the reconstructed (2×2) surface (Fig. 6.8 (f)). The presence of a hole barrier in

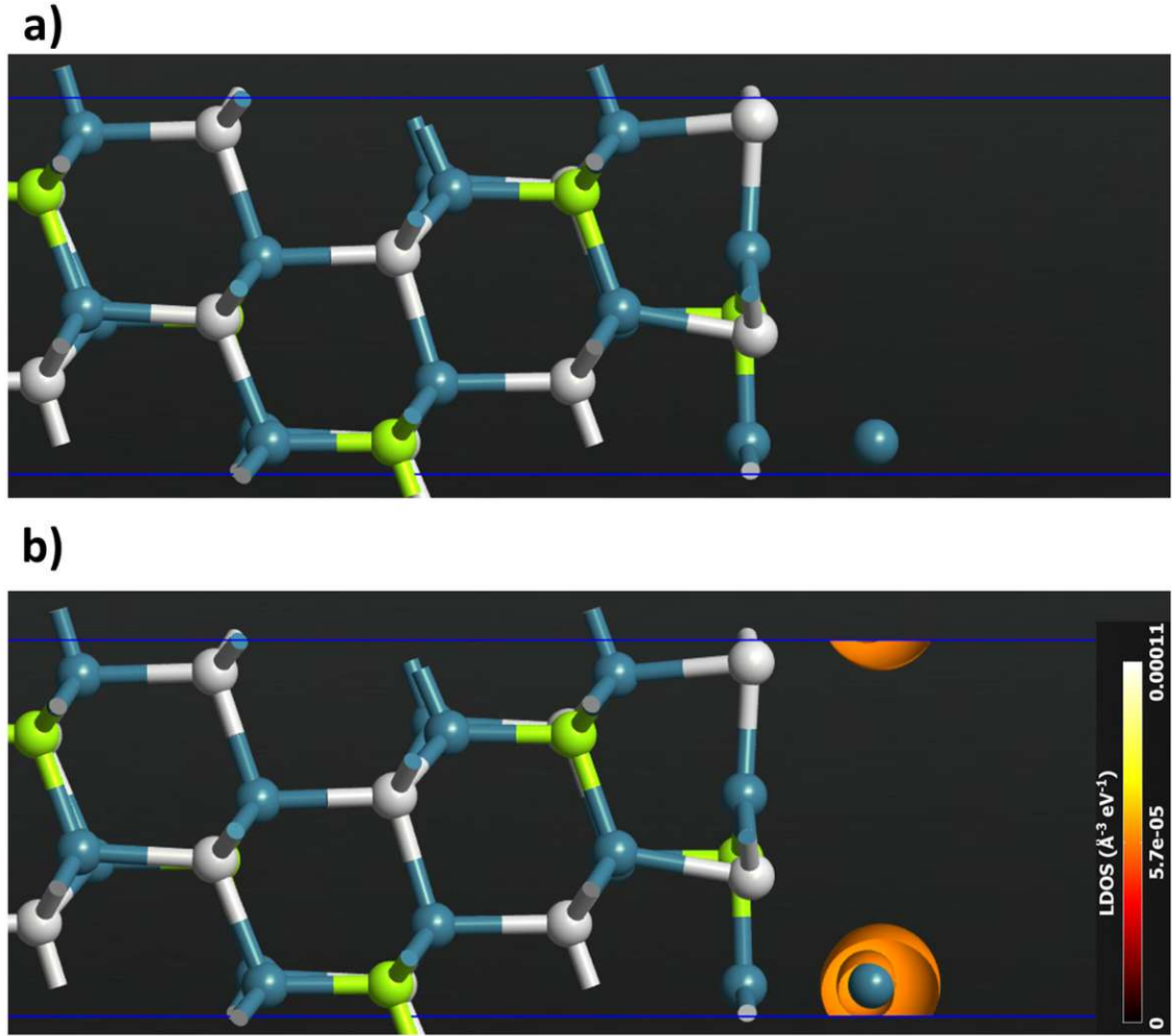


Figure 6.10: Relaxed atomic configuration showing (a) Cd terminated CdSe_{0.25}Te_{0.75}(111) surface and (b) Local density of states (LDOS) around one of the Cd atom. This LDOS was calculated for one of the prominent surface state observed in the energy band alignment diagram of unreconstructed CdSe_{0.25}Te_{0.75}(111) surface at $E = -0.35$ eV.

(1×1) surface would impede the majority hole carrier (for p-doped CdSe_xTe_{1-x} absorber) transport in unreconstructed surface in comparison to the reconstructed (2×2) surface.

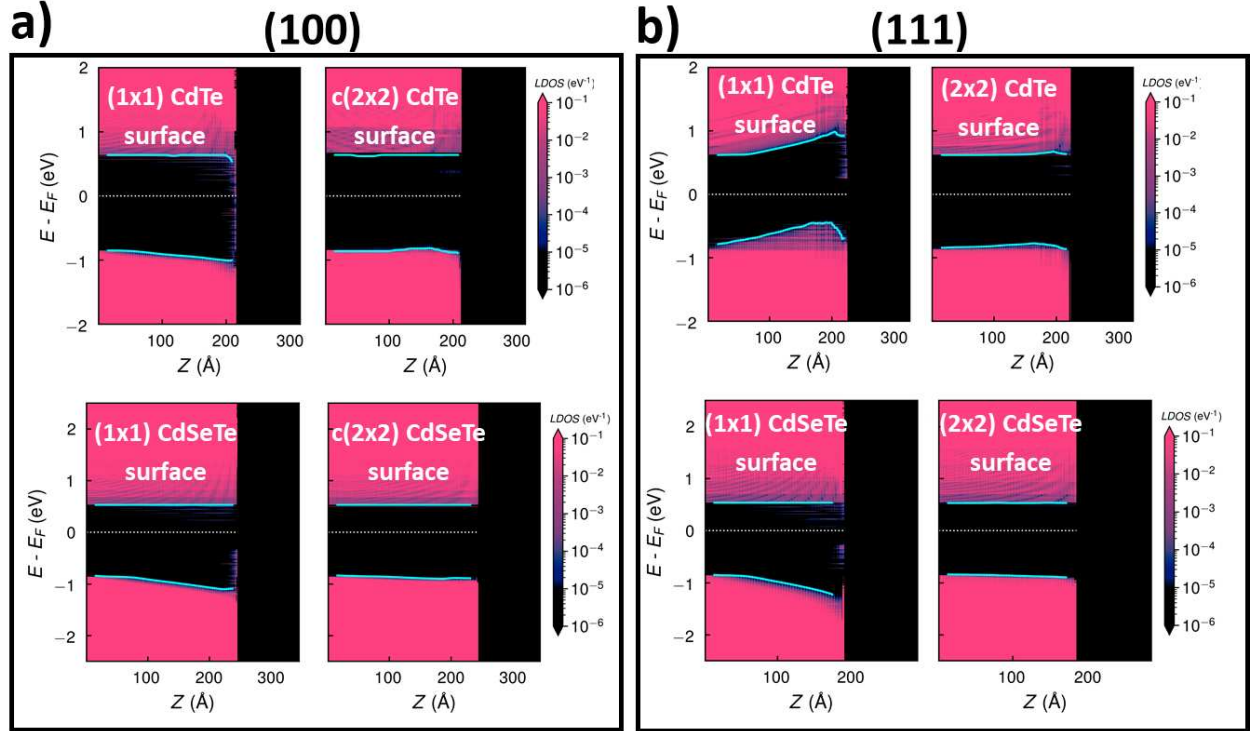


Figure 6.11: Energy band alignment comparison of unreconstructed and reconstructed CdTe and CdSe_{0.25}Te_{0.75} (a) (100), (b) (111) surface facets. The CdTe surface energy band alignment results were adapted from *Nicholson et al.* [4], with permission.

6.5 CdTe vs CdSe_{0.25}Te_{0.75} : Surface energy band alignment comparison

Fig. 6.11 (a) and (b) compares the surface energy band alignment of the polar (100) and (111) facets of CdTe and CdSe_{0.25}Te_{0.75} alloy. This comparison was done to explain one of the potential reasons (but not limited to) for lower performance of CdSe_xTe_{1-x}-only devices in contrast to CdTe-only devices. Fig. 6.1 (c) shows the current density vs voltage measurement comparison for one of the high performing CdSe_xTe_{1-x}-only and CdTe-only devices. It was noted that CdSe_xTe_{1-x}-only device was 10.27% efficient whereas an efficiency of about 15.4% was recorded with the CdTe-only device. Table 6.4 summarizes the measurements performed on both the device.

While the CdSe_xTe_{1-x}-only device showed a relatively higher short circuit current (J_{SC}) value than CdTe-only device (CdSe_xTe_{1-x} being a lower bandgap material than CdTe), other parameters such as open circuit voltage (V_{OC}) and the Fill Factor (%FF) were notably smaller. The lower

Table 6.4: J-V measurement comparison of the performance of $\text{CdSe}_x\text{Te}_{1-x}$ -only and CdTe-only solar cells.

Absorber layer	J_{SC} (mA/cm ²)	V_{OC} (mV)	%FF	% η
$\text{CdSe}_x\text{Te}_{1-x}$	26.4	662	58.7	10.27
CdTe	25.7	817	72.7	15.24

performance of $\text{CdSe}_x\text{Te}_{1-x}$ -only absorber based solar cell device indicates a higher recombination and an inferior charge transport when compared to CdTe-only absorber based device. The comparison of the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ and CdTe surface energy band alignment diagrams calculated using DFT gave further insights into the features affecting the charge transport in CdTe and $\text{CdSe}_{0.25}\text{Te}_{0.75}$ layers. *Nicholson et al.* showed a cusp feature in the CdTe surface calculations and credited this feature to be beneficial for hole charge transport towards the back electrode of the device [4]. Previous theoretical and experimental studies on CdTe/Te interface have also shown the presence of a similar cusp feature as seen in the DFT CdTe surface calculations [5, 6]. While a cusp feature in the valence band has been observed in CdTe surface and interface calculations, no such feature was observed in the DFT study of $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surfaces. The absence of such feature from the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface energy band alignment diagram would be reflected in the hole charge carrier transport leading to a lower device performance when compared to CdTe-only absorber based PV-devices. Further, lower performance of $\text{CdSe}_x\text{Te}_{1-x}$ -only devices could also be due to presence of high defect density at MZO/ $\text{CdSe}_x\text{Te}_{1-x}$ and $\text{CdSe}_x\text{Te}_{1-x}$ /Te interfaces in addition to the absence of key cusp feature in $\text{CdSe}_x\text{Te}_{1-x}$ surfaces. The DFT study probing the energy band alignment diagrams of the interface is in progress and the results will be reported subsequently. As pointed before, Se tends to exhibit a random distribution in the $\text{CdSe}_x\text{Te}_{1-x}$ alloy, however the random distribution of Se using SQS presents a computational challenge (due to high number of atoms) with the current one-probe model to study the $\text{CdSe}_x\text{Te}_{1-x}$ surface. Nonetheless, at least from a first-order perspective the comparison of electronic features in $\text{CdSe}_x\text{Te}_{1-x}$ surface (Se in fixed regular lattice position) with CdTe provides useful insights into the difference in the electronic structure observed in the ternary $\text{CdSe}_x\text{Te}_{1-x}$ alloy absorber.

Chapter 7

Copassivation effect of chlorine and selenium for CdTe Grain Boundaries¹

7.1 Introduction

One of the important fabrication step that has facilitated efficiency enhancements in CdTe PV-device involves cadmium chloride (CdCl_2) treatment of the CdTe absorber layer. Published literature shows the CdCl_2 treatment of polycrystalline (px) CdTe based cells lead to superior device performance compared to the single crystal CdTe based solar cell [24]. This suggests that the chlorine (Cl) interaction with the grain boundaries is crucial to obtain high efficiencies in the px-CdTe solar cells.

Over the years, several mechanisms have been proposed to explain the success of CdCl_2 treatment in improving the CdTe device performance [18]. Numerous reports conclude that the high temperature CdCl_2 treatment of the CdTe layer leads to recrystallisation and grain growth along the close packed (111) orientation [25–27]. It has also been proposed that CdCl_2 heat treatment passivates the deep defect levels and enhances the lifetime of charge carriers [18, 28, 29]. In another report, *Li et al.* using scanning transmission electron microscopy along with density functional theory described that Cl substitution of the tellurium (Te) sites leads to n-type inversion at the

¹This chapter has been adapted from a peer-reviewed journal article: A. Shah, A. P. Nicholson, T.A.M Fiducia, A. Abbas, R. Pandey, J. Liu, C. Grovenor, J. M. Walls, W. S. Sampath, and A. H. Munshi (2021). Understanding the copassivation effect of Cl and Se for CdTe Grain Boundaries, ACS Applied Materials and Interfaces, 13 (29), 35086-35096.

A. Shah: Conceptualization, Methodology, cell fabrication, Software, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization.

A. P. Nicholson: Software, Formal analysis, Data curation, Writing - review editing.

T.A.M. Fiducia, A. Abbas, J. Liu: nano-SIMS, EBSD characterization, Writing - review editing.

R. Pandey: Cell fabrication, Writing - review editing.

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grain-boundary [22]. This establishes local p-n junction between the grain interior and the grain-boundary which assists in separation of electron-hole pair charge carriers.

Apart from the CdCl_2 treatment step, the recent device efficiency improvement to 22.1% has been realized by alloying Se within the CdTe film [17]. Published literature reveals, cadmium chloride (CdCl_2) treatment of Se-alloyed CdTe layer leads to Se grading through the CdTe grain-boundary, forming a graded $\text{CdSe}_x\text{Te}_{1-x}$ /CdTe absorber layer [21,31]. One study shows that grading Se in the CdTe film passivates the non-radiative recombination centers in the bulk material [21]. It is also thought that the improvement in minority carrier lifetime is due to the presence of Se and Cl in the CdTe grain boundaries [31]. These findings emphasize the need to understand the effects of grading Se from $\text{CdSe}_x\text{Te}_{1-x}$ to CdTe absorber layer to further improve the device performance.

However, the effects of existence of Se and Cl at the CdTe grain boundaries on the electronic structure and charge carrier transport mechanism are unknown. In this work, we report the Se, Cl atomic scale composition and electronic structure of the grain boundaries through nano SIMS and density functional theory simulations respectively. The study demonstrates that Se and Cl together at grain-boundary passivates the deep level acceptor trap states when compared to bare or only Cl at the CdTe grain-boundary. The energy band alignment result shows high density of benign donor states existing below the Fermi level. The presence of high density benign donor states inverts the boundary region from p-type to n-type establishing local p-n junction for efficient charge extraction. This understanding of the role of Se and Cl in copassivating the CdTe grain-boundary defect states provides useful details that can further contribute to higher CdTe device efficiency.

7.2 Experimental and Computational details

7.2.1 Cell fabrication and electrical measurements

Photovoltaic devices with two CdTe and one $\text{CdSe}_x\text{Te}_{1-x}$ /CdTe p-type absorbers were fabricated using similar processing conditions and optimized for high device performance. The devices were fabricated on NSG Pilkington TEC10 soda lime glass that had layer of fluorine doped tin oxide

deposited by the manufacturer as the n-type transparent conducting oxide. All the substrates had a 100 nm layer of $\text{MgZn}_{1-x}\text{O}_x$ ($x=11$ at.%) (MZO) sputtered via RF sputter deposition using a single $\text{MgZn}_{1-x}\text{O}_x$ target. Thereafter, the absorber deposition and CdCl_2 passivation treatment were performed using an in-line sublimation system described by Swanson et al [36]. Two of the substrates were first heated to a temperature of about 520°C and was then transferred to the CdTe sublimation station using a computer controlled magnetic transfer mechanism. About $3.5\text{ }\mu\text{m}$ of CdTe was deposited on the preheated substrate over 270 seconds following which the one of the substrate was transferred to CdCl_2 sublimation station for 600 seconds. The substrate was then moved to an annealing station for 180 seconds. CdCl_2 was deposited at 450°C and annealing station operated at 400°C . Thereafter the substrate was transferred to a cooling station within the vacuum chamber for 300 seconds before it was removed from the vacuum chamber and the residual CdCl_2 film from the surface was rinsed off using deionized water and dried using pressurized ultrahigh purity nitrogen gas.

For the $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ device, the same fabrication system was used. However, the processing conditions were slightly different as they were optimized for deposition of a lower band-gap material with a deposition rate different from the CdTe. The substrate with 100 nm of MZO was preheated to a temperature of about 520°C after which the substrate was transferred to the station containing a $\text{CdSe}_x\text{Te}_{1-x}$ ($x=20$) source charge. A 500 nm $\text{CdSe}_x\text{Te}_{1-x}$ film was deposited over 360 seconds with the $\text{CdSe}_x\text{Te}_{1-x}$ sublimation source operating at 575°C . After this the substrate was transferred to CdTe station to get about $3\text{ }\mu\text{m}$ of CdTe film on the $\text{CdSe}_x\text{Te}_{1-x}$ film. Following the deposition of the absorbers, the substrate was transferred to the CdCl_2 passivation treatment station where the film was exposed to CdCl_2 vapor for 900 seconds from a CdCl_2 sublimation source operating at a temperature of 450°C . Thereafter, the substrate was cooled in the vacuum chamber for 180 seconds. The substrate was removed and like the earlier CdTe film, the residual CdCl_2 layer was rinsed off using deionized water and dried using a pressurized ultrahigh purity nitrogen gas. The high purity CdTe, $\text{CdSe}_x\text{Te}_{1-x}$ and CdCl_2 materials used in this study were provided by 5N Plus Inc.

Following this the films were moved to an evaporator where 30 nm of pure Te was vapor deposited. The substrates were then painted with graphite and nickel paint in polymer binder manufactured by Henkel Chemicals Company that formed the back electrodes. The films were masked and delineated into square area devices (area $\sim 0.65 \text{ cm}^2$) using a plastic abrasion medium sprayed using pressurized gas. 20 small area research devices were fabricated for all the three substrates.

Electrical measurements were performed with a Model 10600 solar simulator from ABET Technologies using a high-pressure xenon arc lamp with an AM1.5 filter. Current density vs voltage curves were generated based on electrical measurements performed using Keithley 2420 SourceMeter controlled via LabView. Current-density and device area for each set of measurement were calibrated to cells measured by National Renewable Energy Laboratory (NREL). Device areas were measured using a webcam that took an image of a backlit solar cell and counted the pixels below a certain brightness.

7.2.2 Nano-SIMS characterization

To remove surface roughness and prepare the samples for SIMS measurements, a region of the back surface of the absorber layer (i.e. in the CdTe part of the absorber, near the back contact) was first polished with a Xe ion beam. NanoSIMS measurements were then performed on the polished region using a Cameca secondary ion mass spectrometer (NanoSIMS 50). During the measurement a 16 keV, 0.5 – 1 pA Cs⁺ primary beam with a nominal diameter of 60 nm was rastered over the measurement area and sputtered secondary ions analysed with a double-focused mass spectrometer. The raster size was 12 x 12 m (512 x 512 pixels) and the dwell time was 1 ms per pixel. Masses analysed were ³⁵Cl⁻ and ⁸⁰Se⁻, giving high resolution images of distributions of chlorine and selenium in the measured area. The scan was repeated 500 times giving 500 stacked images of the distributions of each element below the polished surface. Images in Figure 3 (a-c) are a sum of five stacked images from near the polished surface. The ‘auto-track’ feature in ImageJ

was used to correct a small amount of image drift before the images were summed and for the 3D renderings. The nano-SIMS characterization was done Loughborough University.

7.2.3 Computational details

CdTe(110)/(100) grain-boundary model was simulated using the QuantumATK P-2019.03 software tool [66]. The DFT calculation was performed under a Linear Combination of Atomic Orbitals (LCAO) basis scheme to solve the single particle Kohn-Sham eigenvalue problem. The pseudopotential and basis sets model parameters for Cd, Se, Te and Cl atoms were chosen from the earlier studies performed by *Shah et al.* [55, 88]. The Perdew-Zunger form of Local Density Approximation (LDA) exchange correlation functional was utilized in self-consistent calculations [69]. A Monkhorst-Pack grid for k-points was utilized with 6x6x150 k-point sampling for CdTe grain-boundary two-probe device simulations. A density mesh cut-off of 3000 eV was used in all calculations.

A two-probe DFT coupled with Green's function modeling domain was setup to represent the CdTe(110)/(100) grain-boundary. The interface strain was 0.63% for both (110) and (100) orientations of CdTe. Figure 7.4 (c) illustrates the schematic of two probe CdTe(110)/(100) grain-boundary model. The model comprises of a semi-periodic central region and semi-infinite CdTe (110) and CdTe (100) grain orientation. The interface was relaxed with a force threshold of 0.05 eV/Å, to achieve equilibrium structure at the grain-boundary. It is well known that DFT underestimates the bandgap values for semiconductors and therefore the semi empirical correction DFT-1/2 method [58] was applied to obtain the appropriate bulk-like CdTe bandgap.

7.3 CdTe and $\text{CdSe}_x\text{Te}_{1-x}$ /CdTe absorber based PV-devices

To perform the study, two CdTe (with and without Cl) and one $\text{CdSe}_x\text{Te}_{1-x}$ /CdTe absorber based solar cells were fabricated as described in the methods section. Figure 7.2 (a) shows the schematic device structure of the $\text{CdSe}_x\text{Te}_{1-x}$ /CdTe solar cell. To understand the effect of selenium and chlorine alloying elements on the device performance, the $\text{CdSe}_x\text{Te}_{1-x}$ /CdTe film and one CdTe

absorber based substrate received the CdCl_2 treatment while the other CdTe substrate was finished into device without any CdCl_2 treatment. The electrical measurements were performed on the finished devices to generate the current density vs voltage diode curves. The box plot (see Figure 7.1) depicts the Open-circuit Voltage (V_{OC}), Short-circuit current density (J_{SC}), Fill Factor (%), and Efficiency (η) comparison between the untreated CdTe, CdCl_2 -treated CdTe and CdCl_2 -treated $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ based PV-devices. Comparing the device parameters from the box plot results (see Figure 7.1), it was evident that the CdCl_2 treatment of the CdTe absorber layer plays a prominent role in bolstering the PV-device performance from $<1\%$ to $15\%+$ efficiency.

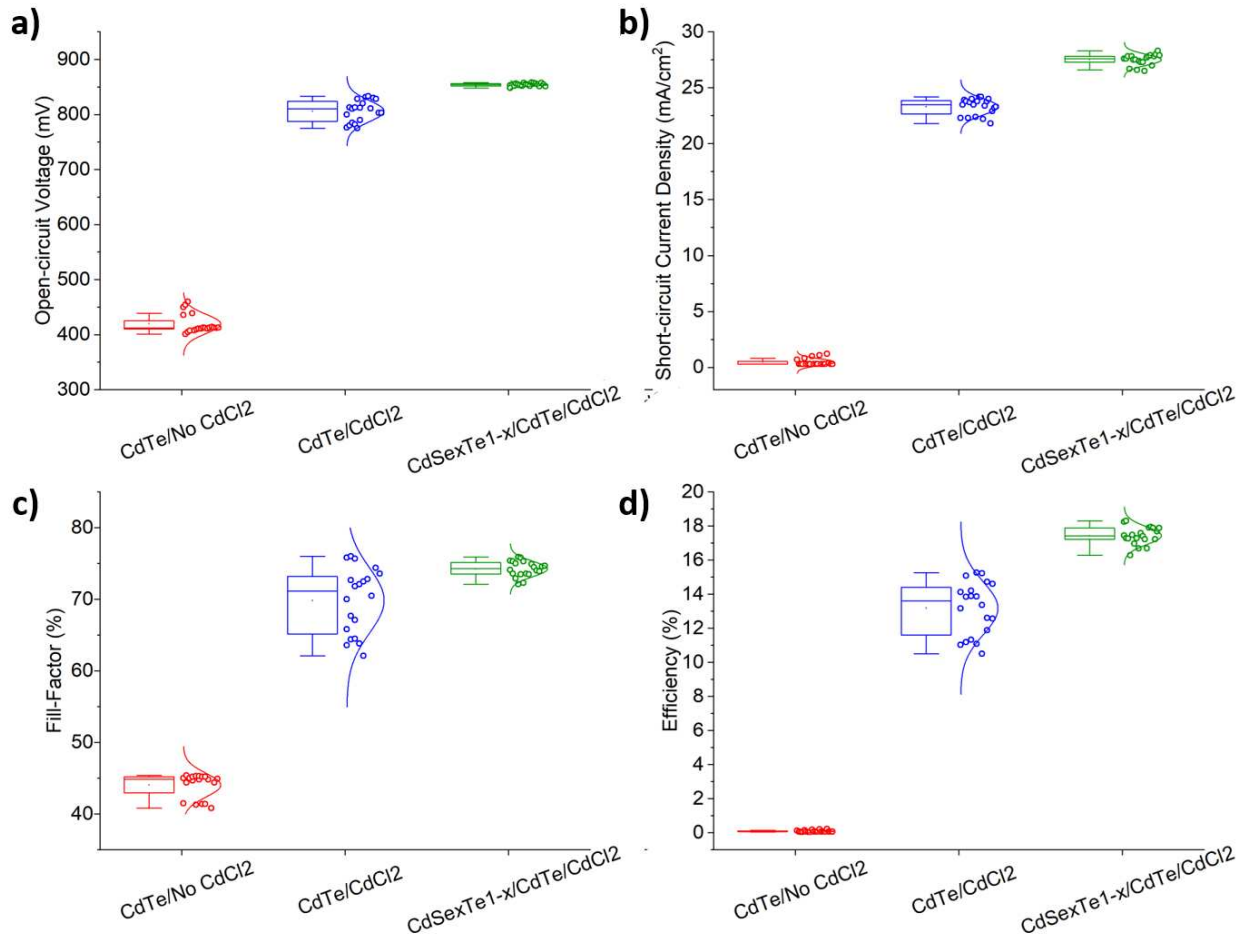


Figure 7.1: Box plot comparing the (a) Open-Circuit Voltage (V_{OC}) (b) Short-Circuit current density (J_{SC}) (c) Fill Factor (%) (d) Efficiency (η) between untreated CdTe, CdCl_2 -treated CdTe and CdCl_2 -treated $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ PV-devices. Each box plot contains device data for 20 solar cells.

For CdCl_2 -treated $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ absorber based solar cells, a notable increase in the J_{SC} was obtained due to the use of a smaller bandgap $\text{CdSe}_x\text{Te}_{1-x}$ material toward the front of the device. The small bandgap absorber material increases light absorption in the longer wavelength region of the spectrum and thus more current can be extracted from the PV-device [14, 21]. In addition to an improved short-circuit current, alloying Se in the CdTe layer also enhances the Open-Circuit Voltage values in $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ PV-devices (Figure 7.1 (a)). Such an improvement in the V_{OC} values has been credited to improved minority carrier lifetimes in the absorber [14, 21, 89]. Figure 7.2 (b) shows the current density-voltage diode curves for the best performing devices from each experiment set. The best performing untreated CdTe device gave an efficiency of 0.22%, while the CdCl_2 -treated CdTe device gave an efficiency of 15.27%. The efficiency value further increased to 18.30% for the CdCl_2 -treated $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ PV-device. Table 7.1 summarizes the measured device parameters for the above three best performing devices.

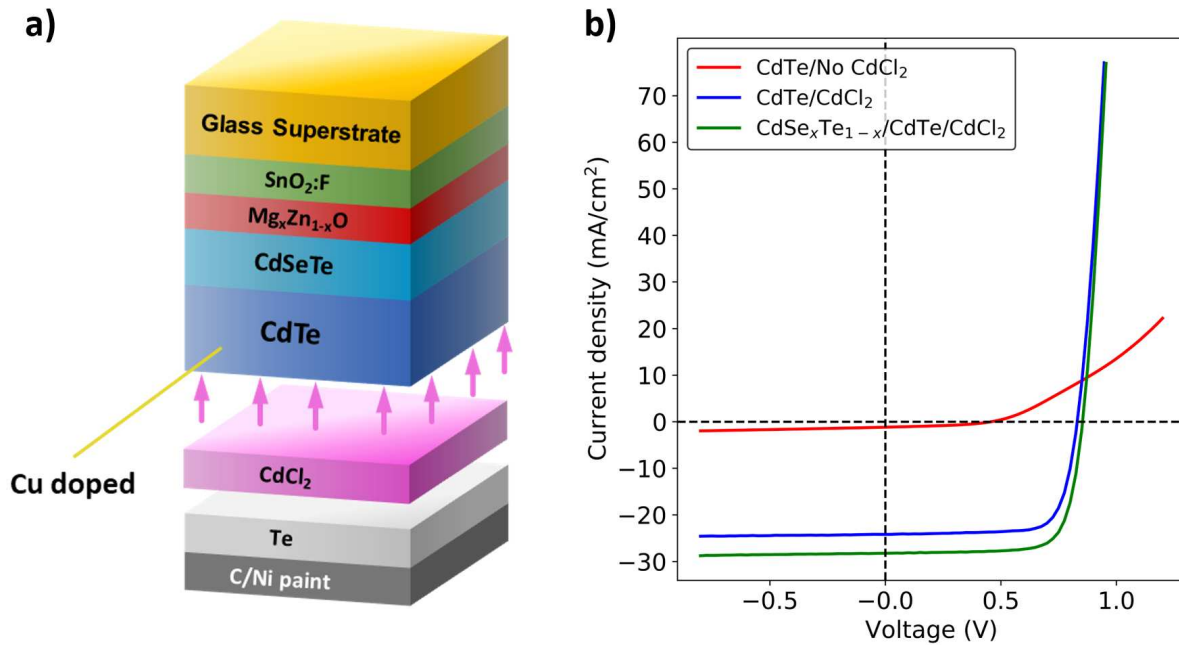


Figure 7.2: (a) Schematic showing highly efficient $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ PV-device in superstrate configuration (not to scale). (b) Comparison of the best performing untreated CdTe, CdCl_2 -treated CdTe and CdCl_2 -treated $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ PV-devices.

Table 7.1: J-V measurement comparison of the performance of CdSe_xTe_{1-x}-only and CdTe-only solar cells.

Absorber layer	JSC (mA/cm ²)	VOC (mV)	%FF	% η
CdTe/No CdCl ₂	1.2	460	40.8	0.22
CdTe/CdCl ₂	24.2	831	76.0	15.27
CdSe _x Te _{1-x} /CdTe/CdCl ₂	28.3	854	75.8	18.30

To understand the atomic distribution of Se and Cl atoms in the highly efficient CdCl₂-treated CdSe_xTe_{1-x}/CdTe PV-device, the elemental mapping was performed using the nano-SIMS technique (described in the methods section) on a similar CdCl₂-treated CdSe_xTe_{1-x}/CdTe absorber film. Figure 7.3 (a) shows a plane-view image of the chlorine signal intensity in the Se-interdiffused CdTe absorber layer. It can be seen that the strongest chlorine signal emanates from the CdTe grain-boundary regions, with small Cl hotspots located in the interior of the grains. Figure 7.3 (b) shows a plane-view image of the selenium signal intensity in the CdTe absorber. As well as being concentrated at the grain boundaries, selenium signal is also present in the outside of the CdTe grains – the grain fringes. The superimposed image of the chlorine and selenium signals in Figure 7.3 (c) further confirms that selenium diffuses into the CdTe grains while chlorine is mainly concentrated at the CdTe grain-boundary regions. This suggests that during CdCl₂ treatment of bilayer CdSe_xTe_{1-x}/CdTe absorbers Se diffuses into the CdTe grains through the grain boundaries. While analyzing the Se-graded CdSe_xTe_{1-x}/CdTe absorber based PV-devices, *Fiducia et al.* and *Guo et al.* have made similar observations in different studies [31, 60]. Figure 7.3 (f) shows a line profile of the selenium and chlorine signals across two grain boundaries in the CdTe absorber layer. As described earlier, the selenium signal was found to be further diffused into the CdTe grain interior compared to chlorine (it should be noted that the chlorine profile will be widened due to the 50-100 nm spot size of the ion beam). Figure 7.3 (d) and (e) shows 3D renderings of the chlorine and selenium signals, showing the diffusion of selenium into the CdTe grains.

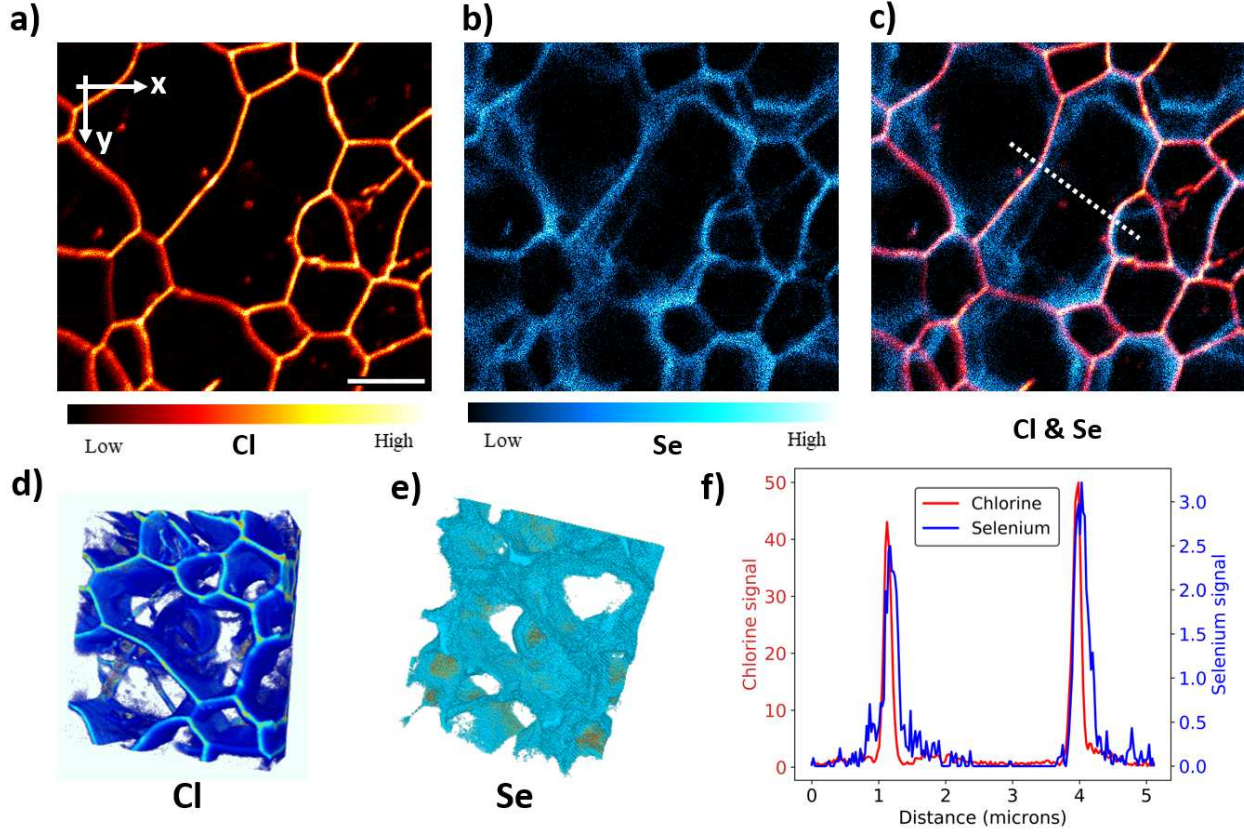


Figure 7.3: Planar nano-SIMS performed on the CdCl_2 -treated $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ absorber, near the back contact, shows (a) the distribution of Cl along the CdTe grain boundaries (b) the distribution of Se along the CdTe grain boundaries (c) combined distribution of Cl and Se in the absorber. The white dotted line indicates the position of the line profile shown in (f). (d) 3-D rendering of the chlorine distribution in the measurement volume. (e) 3-D rendering of the selenium distribution in the measurement volume. (f) Line profile of the Cl (red) and Se (blue) signal intensities across the region shown by the dashed line in (c).

7.4 Atomistic modeling of $\text{CdTe}(110)/(100)$ grain-boundary

After determining the Se and Cl distribution in CdTe absorber film, the microstructural mapping of the CdTe surface (schematic shown in Figure 7.4 (a)) was done with Electron Back Scatter Diffraction (EBSD) technique. Figure 7.4 (b) shows the inverse pole image of the CdCl_2 -treated CdTe film with different colors representing various grain orientations. As evident from Figure 7.4 (b), the CdTe grains orient themselves in random crystallographic directions forming distinct grain-boundary regions. Using the color code of CdTe grains, one random $\text{CdTe}(110)/(100)$ grain-boundary (see zoomed view of Figure 7.4 (b)) was chosen for the atomistic modeling. The basis for choosing $\text{CdTe}(110)/(100)$ grain-boundary also comes from the previous research study,

where *Sen et al.* used Density Functional Theory (DFT) to analyze the electronic properties of CdTe(110)/(100) grain-boundary [8]. The atomistic CdTe(110)/(100) model represents an idealistic case of the grain-boundary as the twist angle associated with the grain-boundary is unknown.

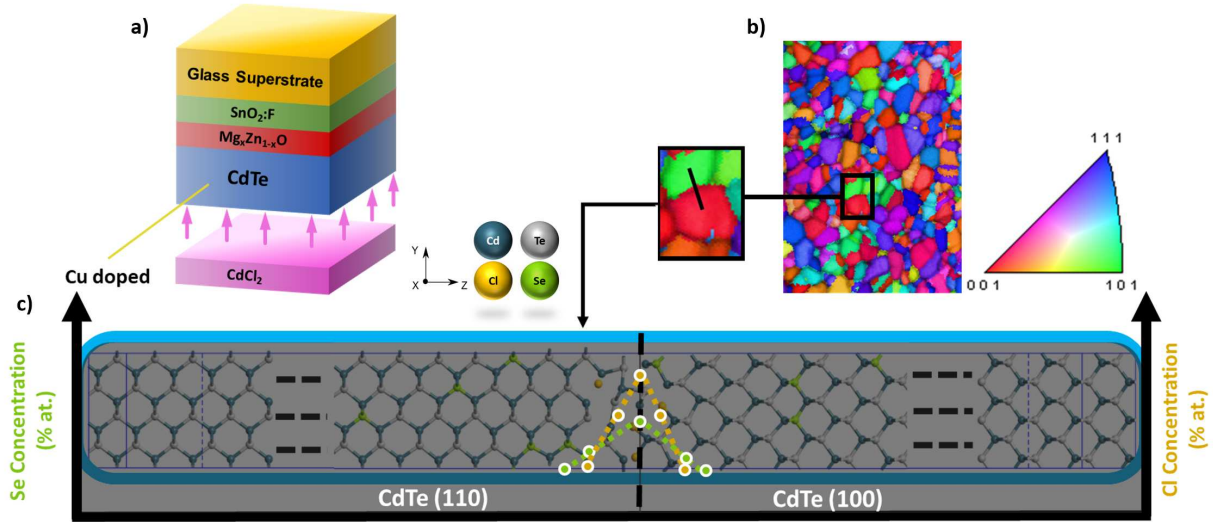


Figure 7.4: (a) Schematic of CdCl₂-treated CdTe absorber film for surface EBSD analysis (b) CdTe surface EBSD image showing various CdTe grain orientations and grain boundaries. The subFigure shows a zoomed view of (110)/(100) CdTe grain-boundary chosen for atomistic modeling. This grain-boundary orientation has been reported in other literature [8]. (c) Schematic showing a two-probe model of CdTe (110)/(100) grain-boundary. The dashed black line indicates the presence of grain-boundary. The gold and green line shows the respective Cl and Se atomic concentration distributed across the grain-boundary (Figure not drawn to scale). The modeled distribution is the first order approximation of the experimental Se and Cl atomic concentration obtained from nano-SIMS analysis (Figure 7.3 (f))

Figure 7.4 (c) shows the schematic of two probe CdTe(110)/(100) grain-boundary model. The interfacial energy per unit area, γ_{GB} was calculated from DFT as follows [88]:

$$\gamma_{GB} = \frac{1}{2A} [E^{Total} - E_{bulk,110} \times n_{110} - E_{bulk,100} \times n_{100}] \quad (7.1)$$

where E^{Total} is the total energy of the grain-boundary model, $E_{bulk,110}$ and $E_{bulk,100}$ are the bulk total energies for (110) and (100) orientations respectively, n_{110} and n_{100} are the repeating bulk equivalent unit cells in the respective (110) and (100) orientations that are required to form the central region of the two-probe model, and 'A' is the cross sectional area of the simulation do-

main. The calculated interfacial energy value came out to be 1.37 J/m^2 and is in qualitatively good agreement with other published literature values [8, 88].

It has been shown earlier by *Li et al.* that the CdCl_2 treatment of CdTe absorber leads to substitution of chlorine in the tellurium sites [22]. *Munshi et al.*, *Fiducia et al.*, and *Guo et al.* have also reported that selenium from $\text{CdSe}_x\text{Te}_{1-x}$ layer grades into the CdTe absorber by substituting the tellurium sites [14, 21, 31]. *Guo et al.* using electron energy loss spectroscopy (EELS) further analyzed a similar $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ device to arrive to the conclusion that $\sim 35 \text{ at.}\%$ Cl and $\sim 20 \text{ at.}\%$ Se substitutes the Te sites in the grain boundaries near the $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ interface [31]. Based on the atomic distribution of elemental Se and Cl atoms imaged through the nano-SIMS (Figure 7.3) technique and the literature reports described above, Se and Cl atoms were substituted randomly at the Te sites in the CdTe grain-boundary atomistic model. In line with experimental observations, Figure 7.4 (c) shows a first-order representation of the atom distribution with the green dashed line representing the diffused Se atoms (maximum concentration $\sim 20 \text{ at.}\%$) and the gold dashed line representing the concentrated Cl atoms (maximum concentration $\sim 35 \text{ at.}\%$) in the two probe $\text{CdTe}(110)/(100)$ grain-boundary model.

Pertinent electronic features of the $\text{CdTe}(110)/(100)$ atomistic model were studied to understand the copassivation mechanism of Se and Cl atoms in the CdTe grain boundaries. Local density of states were computed and projected along the z-direction to generate the energy band alignment plot for the bulk CdTe, bare CdTe grain-boundary and Se/ Cl alloyed CdTe grain-boundary. Figure 7.5 and 7.6 shows the energy band alignment diagrams with macroscopically averaged curve fit trace of the conduction band minimum (CBM) and valence band maximum (VBM) obtained using the gaussian kernel method described by *Nicholson et al.* [4]. The band-gap energy, E_{110}^g and E_{100}^g were determined from the energy differences of the VBM and CBM at positions located closest to the $\text{CdTe}(110)$ and $\text{CdTe}(100)$ bulk electrode ends respectively (Figure 7.6 (a)). The energy band alignment diagram further shows various features such as a pickup/ dip in the CBM and pickup/ dip in the VBM. In accordance with the labels provided in Figure 7.5 (b), the peak energy potential in the CBM, E_{peak} is defined as the energy difference between the peak curve fit of CBM (labeled

point 2) and the curve fit CBM value of the bulk-like CdTe(110) (labeled point 1). A positive value of E_{peak} indicates a pickup (barrier for electron charge carriers) while a negative value suggests a dip (enhancer for electron charge carriers) in the CBM at the CdTe(110)/(100) grain-boundary. Similarly, cusp energy potential E_{cusp} is simply defined as the energy difference between the peak curve fit value of VBM (labeled point 4) and the curve fit VBM value of the bulk-like CdTe(110) (labeled point 3). The dip energy potential E_{dip} is defined as the energy difference between the lowest dip curve fit value of the VBM (labeled point 5) and the curve fit VBM value of the CdTe(110) bulk-like region (labeled point 3). The presence of a dip in the VBM indicates an inversion from bulk p-type to n-type at the grain-boundary and would act as a barrier for the hole charge carrier transport across the grain-boundary. Table 7.2 summarizes all the electronic features for various grain-boundary cases described earlier. The band-gap values calculated with DFT-1/2 for the bulk-like CdTe (E_{110}^g and E_{100}^g) far away from the grain-boundary is in good agreement with the existing literature [4, 88].

Table 7.2: Salient electronic features in the energy band alignment of various CdTe(110)/(100) grain boundaries.

CdTe(110)/(100) grain-boundary	E_{110}^g (eV)	E_{100}^g (eV)	E_{peak} (eV)	E_{cusp} (eV)	E_{dip} (eV)
Bare	1.44	1.51	0.18	0.66	-0.33
Cl _{Te}	1.51	1.49	-0.64	-	-0.52
Se _{Te}	1.50	1.48	-0.05	0.30	-0.37
Se _{Te} + Cl _{Te}	1.51	1.48	-0.56	-	-0.58

7.5 Classification of the defect states

Figure 7.5 (a) and (b) shows the energy band alignment features of the bulk CdTe and bare CdTe(110)/(100) grain-boundary respectively. Figure 7.5 (c) and (d) shows the partial charge distribution (obtained by a Mulliken population analysis [85]) on the Cd and Te atoms (in terms of the electronic charge(e)) along the transverse z-direction for the respective bulk CdTe and

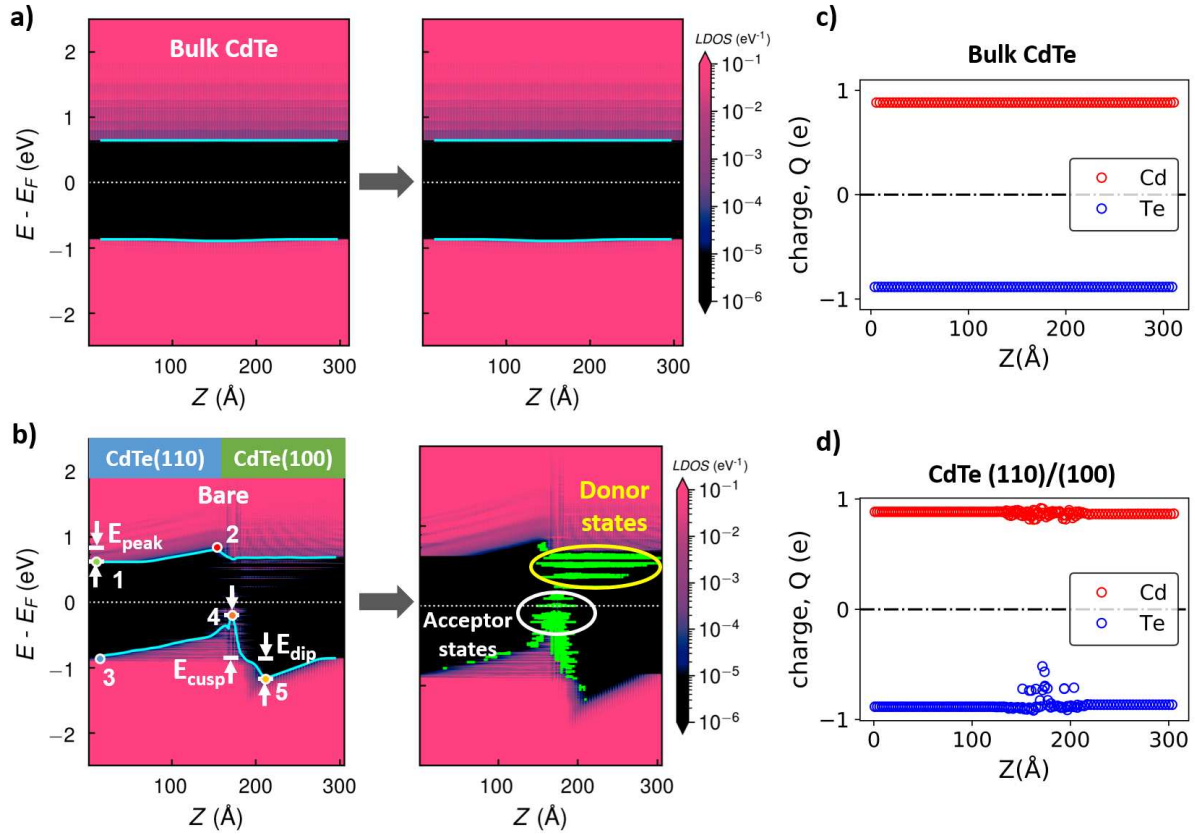


Figure 7.5: Energy band alignment diagram of the (a) bulk CdTe and (b) CdTe (110)/(100) grain-boundary. The dotted line indicates the Fermi energy level and the blue curves are the trace of the macroscopic average fits of the VBM and CBM. The second set of energy band alignment diagrams highlights the grain-boundary defect states (indicated by green lines) mapped with respect to energy and localized positions based on 10^{-5} eV Local Density of States (LDOS) cutoff value. Mulliken population analysis further shows the atomic charge distribution for (c) bulk CdTe and (d) CdTe (110)/(100) grain-boundary.

CdTe(110)/(100) grain-boundary models. A positive electronic charge indicates cationic behavior, while a negative electronic charge depicts anionic behavior of the atoms. Figure 7.5 (c) shows a smooth and homogeneous charge distribution for the bulk CdTe, as the cations and anions periodically arrange with no perturbation in the electrostatic potential. This unperturbed electrostatic potential manifests itself into a defect state free flat energy band alignment diagram with energy bandgap value of ~ 1.51 eV throughout the bulk CdTe model.

However, the atoms at the CdTe(110)/(100) grain-boundary deviates from the ordered cationic/anionic arrangement. The deviation from a periodic atomic arrangement induces a perturbation in

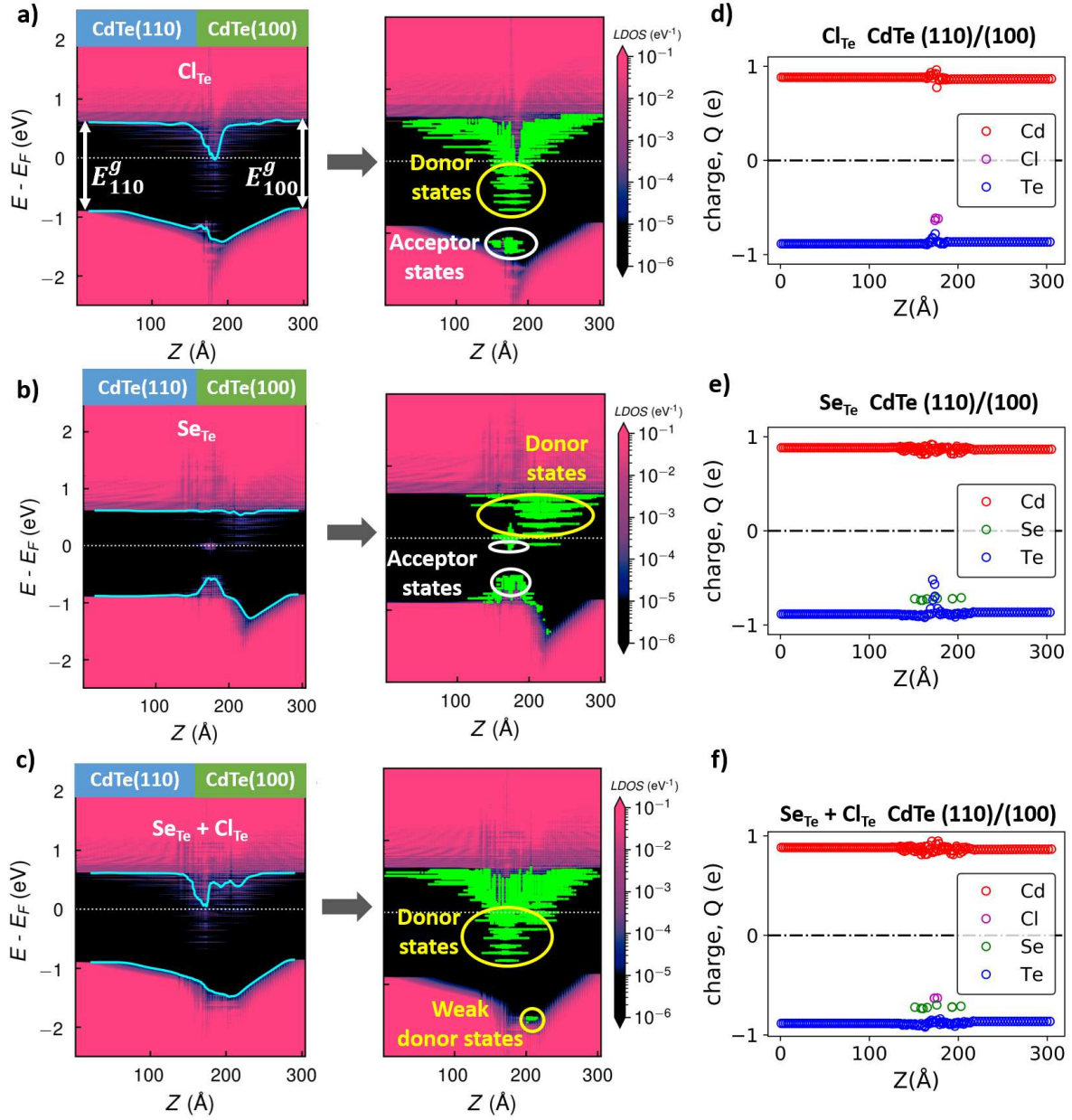


Figure 7.6: Energy band alignment diagram of the (a) Cl_{Te} CdTe (110)/(100) grain-boundary (b) Se_{Te} CdTe (110)/(100) grain-boundary and (c) $\text{Se}_{\text{Te}} + \text{Cl}_{\text{Te}}$ CdTe (110)/(100) grain-boundary along with their respective mapped defect states based on $10^{-5}/\text{eV}$ LDOS cutoff value. Mulliken population analysis further shows the atomic charge distribution for (d) Cl_{Te} CdTe (110)/(100) grain-boundary (e) Se_{Te} CdTe (110)/(100) grain-boundary and (f) $\text{Se}_{\text{Te}} + \text{Cl}_{\text{Te}}$ CdTe (110)/(100) grain-boundary.

the electrostatic potential and affect the charges on the atoms (see Figure 7.5 (d)) near the grain-boundary region. Such a disordered arrangement of atoms with varying degree of charge near the

grain-boundary creates electronic defect states in the bandgap region. These defects states can be further classified into donor or acceptor states. A donor defect state is defined as the state which donates electrons to the CBM and in turn becomes positively charged while the acceptor states accepts electrons from the VBM, thereby becoming negatively charged states. The presence of the defect states (shallow or deep levels) bend the bands depending on whether they are acceptor or donor defect states. Therefore, it is impertinent to understand the character of the defect states to comprehend the various electronic features observed in the energy band alignment diagram of bare/alloyed CdTe(110)/(100) grain boundaries. Based on $10^{-5}/\text{eV}$ LDOS cutoff value, existing defect states (indicated by green lines in Figure 7.5 (b)) were algorithmically determined with respect to energy and localized position (in transverse z-direction) in the energy band alignment diagrams. Since the origin of these sub bandgap defect states is due to variation in the atomic charges, it was theorized that the characteristics of these defect states could be directly determined by summing the charges on the atoms contributing to the existence of these defect states. If the net charge on atoms contributing to a particular defect state was found to be positive/negative, that state would be classified as a donor/acceptor state.

In regards to this, clusters of the defect states existing near different energy band alignment features were identified and the ones having highest LDOS value were analyzed to determine their respective character. For example, for the bare CdTe(110)/(100) grain-boundary in Figure 7.5 (b), two groups of defect states near the E_{cusp} and E_{dip} energy potentials were identified. From the defect state group near the E_{cusp} energy potential, two defect states with highest LDOS values at $E_{\text{defect1}} = -0.118 \text{ eV}$ (LDOS = 0.17136 eV^{-1}) and $E_{\text{defect2}} = 0 \text{ eV}$ (LDOS = 0.02385 eV^{-1}) were selected for further analysis. Using the data generated after mapping the localized positions of the defect states, E_{defect1} extended from $z_{\text{start}} = 144.11 \text{ \AA}$ to $z_{\text{end}} = 187.92 \text{ \AA}$ in the transverse z-direction. Using the Mulliken population plot in Figure 7.5 (d), it was found that a total of 74 atoms with a net -1.27 electronic charge was associated with E_{defect1} across the specified spatial range. Likewise, defect state 2 ($E_{\text{defect2}} = 0 \text{ eV}$) was located from $z_{\text{start}} = 148.80 \text{ \AA}$ to $z_{\text{end}} = 196.21 \text{ \AA}$ with a total of 88 atoms having a net -1.26 electronic charge contributing to its existence. Since, the net electronic

charge on the atoms contributing to the defect state 1 and defect state 2 were negative, both of these defect states were classified as acceptor states.

Similarly, from the other group of defect states above the E_{dip} energy potential, two defect states with highest LDOS value at $E_{\text{defect}3} = 0.362$ eV (LDOS = 0.05402 eV^{-1}) and $E_{\text{defect}4} = 0.531$ eV (LDOS = 0.69080 eV^{-1}) were analyzed. Defect state 3 ($E_{\text{defect}3} = 0.362$ eV) was located from $z_{\text{start}} = 155.83 \text{ \AA}$ to $z_{\text{end}} = 255.86 \text{ \AA}$ with a total of 180 atoms having a net +0.45 electronic charge. Likewise, defect state 4 ($E_{\text{defect}4} = 0.531$ eV) was located from $z_{\text{start}} = 148.80 \text{ \AA}$ to $z_{\text{end}} = 298.94 \text{ \AA}$ with a total of 272 atoms having a net +1.33 electronic charge. Since, the net electronic charge on the atoms contributing to the defect state 3 and defect state 4 were positive, these defect states were classified as donor states. Table 7.3 summarizes the analysis of various defect states for bare CdTe(110)/(100) grain-boundary. Based on the above analysis, it could be deduced that the cluster of defect states above the E_{cusp} energy potential would be acceptor states (labeled with white circle in Figure 7.5 (b)) and the ones above the E_{dip} energy potential would be donor states (labeled with yellow circle in Figure 7.5 (b)). Furthermore, these donor and acceptor states were classified as deep level defect states as they were found in the mid bandgap region for the bare CdTe grain-boundary model.

To understand the effect of alloying elements on the defect states, similar analyses were performed on the Se and Cl alloyed CdTe(110)/(100) grain-boundary models. It was observed that alloying the grain-boundary with Cl_{Te} leads to emergence of high density of deep level donor states (see Figure 7.6 (a)) below the Fermi level. However, acceptor type defect states were found near the VBM indicating the presence of shallow level acceptor states. This implies that passivating the grain boundaries with Cl_{Te} eliminates the deep level acceptor defect states (found in the bare grain-boundary) but introduces high density of deep level donor states.

The defect state analysis for Se_{Te} alloyed CdTe grain-boundary indicated a lower deep level acceptor state density (see Figure 7.6 (b)) than the bare CdTe grain-boundary case. In addition to that, the high density of both shallow and deep level donor states were found to exist above the Fermi level. However, alloying the grain-boundary with $\text{Se}_{\text{Te}} + \text{Cl}_{\text{Te}}$ revealed the exclusive presence

of donor defect states. The model indicates that $\text{Se}_{\text{Te}} + \text{Cl}_{\text{Te}}$ completely passivates the acceptor defects present in either of the bare, Cl_{Te} or Se_{Te} alloyed CdTe grain boundaries (see Figure 7.6 (c)). Table 7.3 summarizes the analysis of various defect states for the alloyed CdTe(110)/(100) grain-boundary.

Table 7.3: Summary of the analysis of defect states for the bare and alloyed CdTe(110)/(100) grain-boundary.

Alloy	E_{defect} (eV)	LDOS (eV^{-1})	z_{start} (Å)	z_{end} (Å)	N_{atoms}	M.P. charge (e-)	Defect State
Bare	-0.118	0.17136	144.11	187.92	74	-1.27	Acceptor
	0	0.02385	148.80	196.21	88	-1.26	Acceptor
	+0.362	0.05402	155.83	255.86	180	+0.45	Donor
	+0.531	0.69080	148.80	298.94	272	+1.33	Donor
Cl_{Te}	-1.25	0.01599	167.82	187.69	25	-0.38	Acceptor
	-1.23	0.12646	169.60	194.32	45	-0.40	Acceptor
	-1.11	0.14756	146.46	191.00	80	-1.26	Acceptor
	-0.293	0.32214	148.80	205.91	103	+1.32	Donor
Se_{Te}	-0.768	0.23196	137.16	205.32	120	-1.24	Acceptor
	-0.056	0.03154	162.52	186.99	45	-2.21	Acceptor
	+0.037	0.21187	151.17	245.50	171	+1.38	Donor
	+0.55	1.40320	185.32	262.07	140	+2.59	Donor
$\text{Se}_{\text{Te}} + \text{Cl}_{\text{Te}}$	-1.46	0.00033	201.66	214.99	23	+0.009	Weak Donor
	-0.356	0.37712	141.76	202.98	108	+0.556	Donor
	-0.068	0.01023	148.88	189.75	73	+1.41	Donor
	+0.181	1.57267	137.16	228.24	164	+0.44	Donor

7.6 Effect of defect states on the energy band alignment diagram

As described before, the presence of defect states have certain implications on the energy band alignment diagrams. Previous literature reports have shown that high density of donor/acceptor states creates a dip/cusp energy potential in the VBM [61, 62]. Similar effects were observed in the bare and alloyed CdTe grain boundaries. It was consistently found that the presence of donor defect states begins near the CBM and extends down toward the mid bandgap region. This would facilitate the donation of minority electron charge carriers to the CBM by the donor states and would make them positively charged. The presence of positively charged donor defect states in the bandgap region would further cause a repulsive field for hole charge carriers and create a barrier

(dip energy potential) in the VBM. This further explains the existence of donor defect states above the E_{dip} energy potential in the bare and alloyed CdTe grain boundaries (Figure 7.5 and 7.6).

Similarly, the acceptor states begin near the VBM and extend into the bandgap region. The shallower acceptor states would gain an electron from the VBM and create hole charge carriers. This would generate an attractive electric field and bends the VBM up toward the acceptor defect states leading to formation of cusp electric potentials (E_{cusp}) in the VBM. Such a trend was observed in all the grain-boundary cases where acceptor states were found to exist above the VBM (see Figure 7.5 (b) and 7.6 (b)). For the Cl alloyed CdTe grain-boundary (Figure 7.6 (a)), since the density of acceptor was not high, a small cusp like feature in the VBM near the acceptor states was observed instead of a high energy cusp potential. This further confirms the fact that, however small but VBM always bends up in the vicinity of the acceptor states and bends down in vicinity of the donor states. A similar conclusion is found for how donor/ acceptor states influence the band bending direction in the CBM. Such an approach of understanding the impact of defect states on the energy band alignment behavior reinforces the Mulliken population analysis results that were used to characterize the defect states.

7.7 Discussion

The atomistic modeling of the bare and alloyed CdTe(110)/(100) grain-boundary gives insight into the effect of the selenium and chlorine alloyed on the grain-boundary electronic properties. The electronic properties of the bare, Cl_{Te} alloyed, and $\text{Se}_{\text{Te}} + \text{Cl}_{\text{Te}}$ alloyed CdTe grain-boundary models could be respectively related to the performance of the untreated CdTe, CdCl_2 -treated CdTe, and CdCl_2 -treated $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ PV-devices. It is a known fact that occupation probability of a defect state depends on its energy position (E_{def}) relative to the Fermi level (E_f). It has been shown previously that the occupation probability of a defect state ($P(E_{\text{def}} - E_f)$) could be determined as [61]:

$$P(E_{\text{def}} - E_f) = 1, E_{\text{def}} < E_f \quad (7.2)$$

$$P(E_{\text{def}} - E_f) = 0, E_{\text{def}} > E_f \quad (7.3)$$

In regards to the defect states, equation 7.2 and equation 7.3 states that donor(acceptor) state above(below) the Fermi level contain positive(negative) charge [62]. As has been discussed before, for the bare CdTe grain-boundary case (Figure 7.5 (b)), the donor states above the Fermi level will be positively charged while the acceptor states will be negatively charged. Moreover, these states are in the close vicinity and therefore have a high probability of charge carrier recombination. Apart from that, a positive E_{peak} value (see table 7.2) in the CBM creates an electron reflector type effect and E_{dip} (see table 7.2) energy potential in the VBM creates a barrier for hole charge carriers. The high probability of charge recombination at the grain-boundary and transport barrier of the minority electron charge carriers (assuming p-type CdTe absorber) at the grain-boundary limits the untreated CdTe PV-device performance producing efficiencies $< 1\%$ (see Figure 7.1).

However, as described before, the Cl_{Te} alloying of the CdTe grain-boundary passivates the deep level acceptor states but induces high density of donor states. In one of the literature report, *Mhirech et al.* showed that the existence of high density donor states leads to an inversion at the interface and is beneficial for extracting the minority charge carriers [61]. Similar effects were observed for the Cl_{Te} alloyed CdTe grain-boundary in this study. The presence of high density of donor states leads to a negative E_{peak} energy potential in the CBM and a high E_{dip} energy potential in the VBM (see table 7.2). This implies that both the CBM and VBM bend downwards causing an n-type inversion (from a p-type grain interior) at the grain-boundary. Due to this inversion, minority electron charge carriers would be attracted toward the grain-boundary while majority charge carriers would be repelled, leading to better charge carrier extraction. Moreover, the presence of shallower acceptor defect states further reduces the recombination in the Cl_{Te} alloyed CdTe grain-boundary. Such low recombination and a better minority charge carrier collection in the CdCl_2 -treated CdTe PV-devices improves the open circuit voltage and short-circuit current density leading to device efficiencies over 15% (see Figure 7.1).

7.8 Conclusion

The $\text{Se}_{\text{Te}} + \text{Cl}_{\text{Te}}$ alloying of CdTe grain-boundary passivates both the deep and shallow level acceptor states found in the respective bare and Cl_{Te} alloyed of CdTe grain-boundary. The high density of donor states maintains the inversion at the grain-boundary, again allowing for a better minority electron charge carrier collection. This would further reduce the charge recombination (compared to the Cl_{Te} alloyed CdTe grain-boundary) and increase the minority charge carrier lifetime for $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ PV-devices [31,89]. The low charge carrier recombination and improved minority charge carrier lifetime further promotes higher open circuit voltages in CdCl_2 -treated $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ PV-devices (see Figure 7.1 (a)). The presence of the lower bandgap $\text{CdSe}_x\text{Te}_{1-x}$ material also leads to higher short-circuit current values (see Figure 7.1 (b)), thereby improving the PV-device efficiencies beyond 18%.

Chapter 8

High carrier lifetimes in CdSeTe double heterostructure

8.1 Introduction

The selenium diffusion into the unalloyed CdTe absorber during the CdCl₂ treatment process has shown to passivate the acceptor states and cause p-n inversion at the CdTe grain-boundary region. *Kuciauskas et. al.* and *Kephart et. al.* in past have also shown higher minority carrier lifetimes in Al₂O₃/CdSeTe/Al₂O₃ double heterostructures (DHs) in comparison to Al₂O₃/CdTe/Al₂O₃ DHs [16, 63]. Higher carrier lifetime in the CdSeTe DHs suggest that Se alloying of the CdTe absorber leads to better passivation in the bulk absorber and the oxide/absorber interface.

Kuciauskas et. al. in another work calculated the interface recombination velocity to be less than 100 cm/s at alumina/CdSeTe interface [89]. Using second harmonic generation microscopy, it has also been theorized that field-effect passivation reduces the interface recombination at Al₂O₃/CdSeTe interface and therefore improves the carrier lifetime [89]. However, the passivation mechanism enabling high carrier lifetime in the oxide/absorber DHs are still unknown.

This work involves first-principle atomistic modeling of bare CdSe_{0.25}Te_{0.75} grain-boundary, chlorine at CdSe_{0.25}Te_{0.75} grain-boundary, and CdSe_{0.25}Te_{0.75}/Al₂O₃ interface. The comparison of bare and Cl at the CdSe_{0.25}Te_{0.75} grain-boundary with its respective CdTe grain-boundary indicated lower density of trap states in CdSe_{0.25}Te_{0.75} grain boundaries. The comparison of CdSe_{0.25}Te_{0.75}/Al₂O₃ and CdTe/Al₂O₃ interface indicated high density of defect states at the interface. However, literature suggests the formation of thin TeO_x layer at the CdSe_{0.25}Te_{0.75}/Al₂O₃ interface [90]. Therefore, a thin TeO_x layer was included in between the CdSe_{0.25}Te_{0.75} and Al₂O₃ layer in the two probe atomistic model (CdSe_{0.25}Te_{0.75}/TeO_x/Al₂O₃). The electronic properties calculated with thin TeO_x layer showed much lower density of defect states indicating that it's the formation of TeO_x

layer that passivates the CdSeTe surface and gives high carrier lifetime in CdSeTe DHs. Based on above results, TeO_x was incorporated as a back passivation layer (on the undoped CdSeTe/CdTe absorber) and compared with the usual copper doped CdSeTe/CdTe baseline cells. It was found that the undoped TeO_x passivated devices were 19% efficient and were comparable to high performing copper doped CdSeTe/CdTe PV-devices.

8.2 Computational and Experimental details

8.2.1 Computational details

Various $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{Al}_2\text{O}_3$ interface were simulated using the QuantumATK P-2019.03 software tool. The DFT parameters for all the atoms were chosen from the earlier studies [55, 88]. To understand the higher bulk lifetimes in CdSeTe absorber, $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)/(100)$ atomistic grain-boundary model were simulated with and without Cl_{Te} at the grain-boundary. The chlorine distribution in the $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)/(100)$ grain-boundary (see figure 8.1 (a)) was done in the similar way as has been reported for CdTe(110)/(100) grain-boundary in an earlier chapter. This was done to understand the electronic property comparison of the CdSeTe and CdTe grain boundaries.

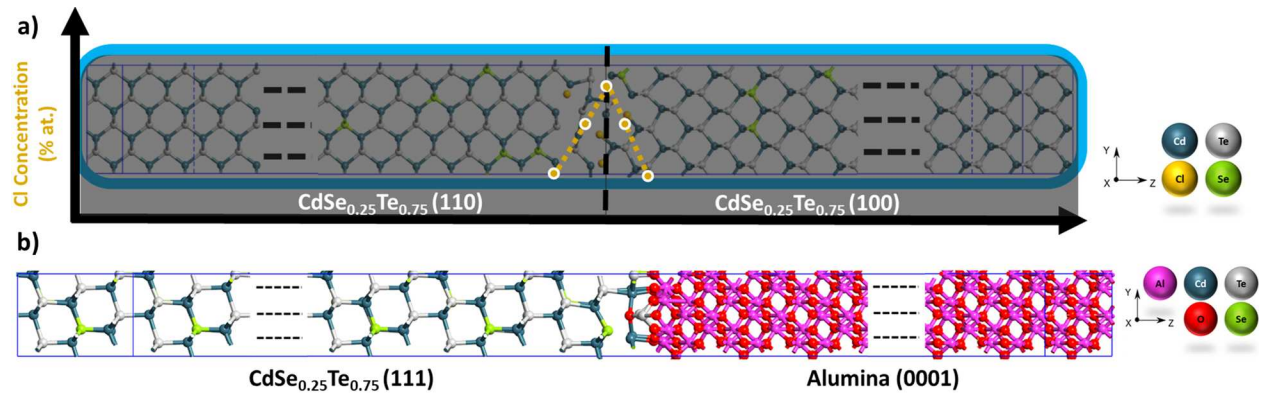


Figure 8.1: (a) Schematic showing a two-probe model of $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (110)/(100) grain-boundary. The dashed black line indicates the presence of grain-boundary. The gold shows the respective Cl atomic concentration distributed across the grain-boundary (Figure not drawn to scale). The modeled distribution is the first order approximation of the experimental Cl atomic concentration obtained from nano-SIMS analysis (Figure 7.3 (f)). (b) Schematic showing a two probe model of $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{Al}_2\text{O}_3$ interface.

Two unique $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{Al}_2\text{O}_3$ interfaces were modeled using Pristine-Interface (P-I) and Surface-Interface (S-I) two probe atomistic model as described before by *Shah et al.* [91]. The P-I model as opposed to S-I model does not have any surface relaxation before the interface formation and is a more common way of making an atomistic models. The $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{TeO}_x/\text{Al}_2\text{O}_3$ interface was modeled by using the $(\bar{1}\bar{1}\bar{1})$ orientation of the $\text{CdSe}_{0.25}\text{Te}_{0.75}$. The $(\bar{1}\bar{1}\bar{1})$ terminated $\text{CdSe}_{0.25}\text{Te}_{0.75}$ with Te/Se atoms and subsequently Al_2O_3 layer was built on the top of $\text{CdSe}_{0.25}\text{Te}_{0.75}$ with oxygen termination at the interface. This allowed the formation of thin monolayer of TeO_x and the structure was then relaxed with the force threshold of $0.05 \text{ eV/\AA}$ (see figure 8.1 (b)). The electronic properties were then calculated using the methods described in above chapters.

8.2.2 Experimental details

PV-devices with $\text{MZO}/\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ baseline structures with various back contact conditions were fabricated using the close space sublimation method described by *Shah et al.* [88]. All the devices had absorber thickness of $4\mu\text{m}$. Based on the DFT results, 4-5 nm of Al_2O_3 and TeO_x back contact were deposited via RF magnetron sputtering technique. No copper doping was done on the Al_2O_3 and TeO_x back contact substrates. The devices with Al_2O_3 and TeO_x back contact conditions were then compared to high performing copper doped $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ solar cells. All the electrical measurements were performed with Keithley 2420 SourceMeter controlled via LabView.

8.3 Results and Discussion

8.3.1 $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)/(100)$ grain-boundary

In one of his earlier works, for a $\text{CdSeTe}/\text{CdTe}$ bilayer absorber stack, *Fiducia et. al.* reported higher cathodoluminescence (CL) intensity and longer diffusion length in CdSeTe layer as compared to CdTe layer [21]. The higher CL intensity in the CdSeTe suggested that Se passivates the defect states in the bulk of the CdSeTe absorber. To understand the mechanism of defect passivation

in CdSeTe grain boundaries, energy band alignment of CdSe_{0.25}Te_{0.75}(110)/(100) grain-boundary was calculated by projecting the local density of states along the z-direction.

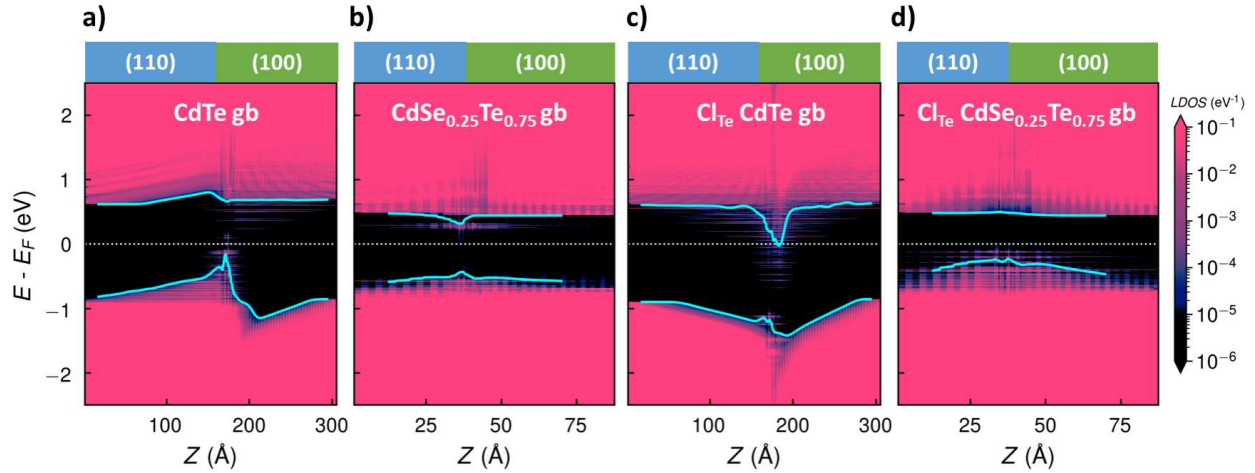


Figure 8.2: Energy band alignment diagram comparison of (a) bare CdTe (110)/(100) grain-boundary (gb), (b) bare CdSe_{0.25}Te_{0.75} (110)/(100) grain-boundary, (c) Cl_{Te} CdTe (110)/(100) grain-boundary (gb), and (d) Cl_{Te} CdSe_{0.25}Te_{0.75} (110)/(100) grain-boundary

Figure 8.2 shows the energy band alignment comparison of the bare and Cl_{Te} CdTe (110)/(100) with its respective CdSe_{0.25}Te_{0.75}(110)/(100) grain-boundary. Various electronic features such as pickup/ dip in the valence band maximum (VBM) and conduction band minimum (CBM), band-gap values for bulk like structure have been defined in chapter 7 and were calculated as per the labels provided in figure 7.5 (b). Table 8.1 summarizes all the electronic features for respective grain boundaries shown in figure 8.2. The lower values of E_{110}^g and E_{100}^g in CdSe_{0.25}Te_{0.75} (110)/(100) suggested that a larger model is required to achieve bulk-like bandgap far away from the grain-boundary. However, this model had 640 atoms and it was computationally limiting to further expand the model. Figure 8.3 further compares the grain-boundary defect states and their respective atomic charge distribution for the various grain boundaries mentioned above. The green line in figure 8.3 highlights the mapping of the defect states in the energy band alignment diagram based on the 10⁻⁵/eV local density of states cutoff value [92]. The defect state character (donor

or acceptor) for $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (110)/(100) grain boundaries was determined using the mulliken population analysis method described by *Shah et. al.* [92].

Table 8.1: Salient electronic features in the energy band alignment of various CdTe (110)/(100) and $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (110)/(100) grain boundaries.

(110)/(100) grain-boundary type	E_{110}^g (eV)	E_{100}^g (eV)	E_{peak} (eV)	E_{cusp} (eV)	E_{dip} (eV)
Bare CdTe	1.44	1.51	0.18	0.66	-0.33
Bare $\text{CdSe}_{0.25}\text{Te}_{0.75}$	1.15	1.07	-0.15	0.15	-
Cl_{Te} CdTe	1.51	1.49	-0.64	-	-0.52
Cl_{Te} $\text{CdSe}_{0.25}\text{Te}_{0.75}$	1.08	1.12	0.01	0.18	-

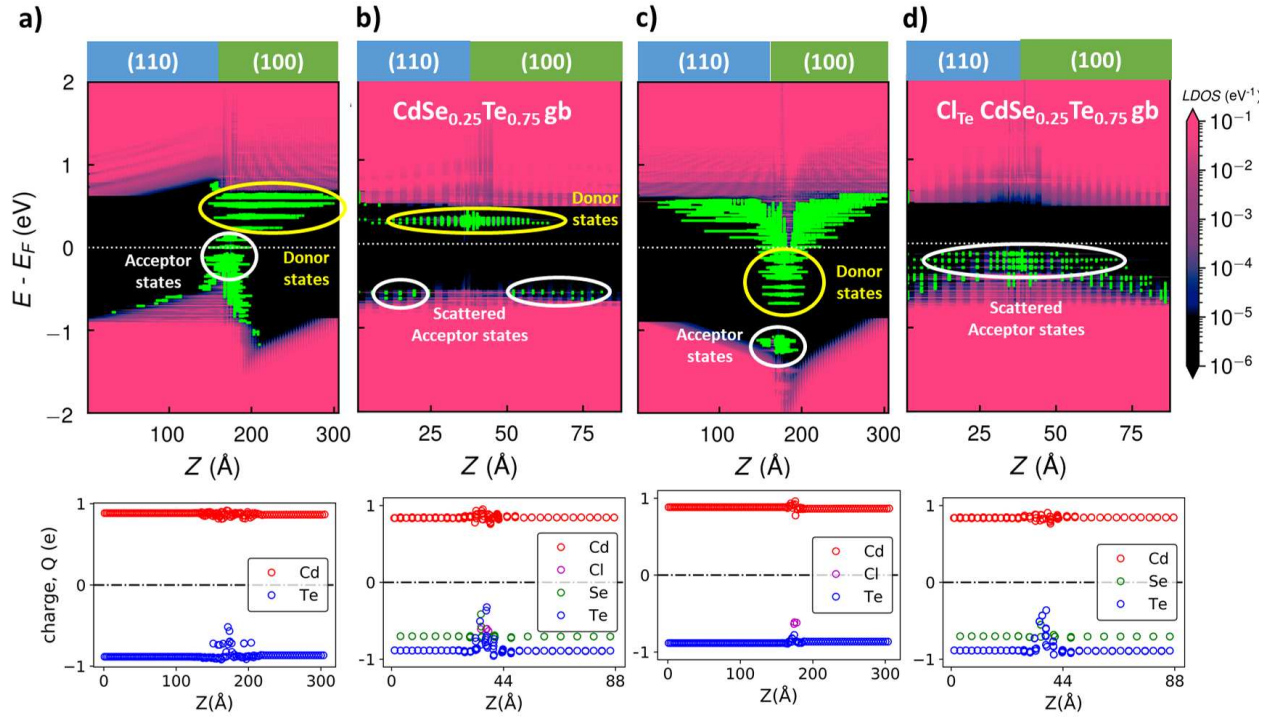


Figure 8.3: grain-boundary defect state comparison for (a) bare CdTe (110)/(100) grain-boundary (gb), (b) bare $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (110)/(100) grain-boundary, (c) Cl_{Te} CdTe (110)/(100) grain-boundary (gb), and (d) Cl_{Te} $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (110)/(100) grain-boundary

Comparing figure 8.2 (a) and (b), it was noted that while the bare CdTe grain-boundary showed a sharp cusp (0.66 eV) followed by a sharp dip (-0.33 eV) in the VBM, bare CdSe_{0.25}Te_{0.75} grain-boundary indicated milder cusp (0.15 eV) and no dip feature in VBM. The CBM showed opposite features in the bare CdSe_{0.25}Te_{0.75} and CdTe grain boundaries. While the bare CdTe grain-boundary indicated a positive E^{peak} value (0.18 eV) suggesting an electron reflector effect in the CBM, an opposite effect was observed in the bare CdSe_{0.25}Te_{0.75} grain-boundary. The CBM in the bare CdSe_{0.25}Te_{0.75} grain-boundary showed a negative E^{peak} value (-0.15 eV) indicating slight inversion to n-type in the bare CdSe_{0.25}Te_{0.75} grain-boundary. Further mapping of the defect states indicated that density of grain-boundary defect states in bare CdSe_{0.25}Te_{0.75} grain-boundary is lower than that observed in bare CdTe grain-boundary (see figure 8.3 (a) and (b)). While bare CdTe grain-boundary had high density of acceptor and donor states, bare CdSe_{0.25}Te_{0.75} grain-boundary inherently showed passivated acceptor states with scattered acceptor states near the VBM. However, few donor states were found near the CBM that bent the CBM down toward the fermi level causing slight p-n inversion in the bare CdSe_{0.25}Te_{0.75} grain-boundary. The presence of such low density of grain-boundary defect states in CdSe_{0.25}Te_{0.75} grain-boundary could be one of the reason for higher bulk lifetime observed for CdSeTe DHs than CdTe DHs.

For the Cl_{Te} at the grain boundaries, it was found that CdTe grain boundaries showed higher density of donor states and lower density of acceptor states leading to p-n inversion at the Cl_{Te} CdTe grain-boundary (see figure 8.2 (c) and figure 8.3 (c)). However, Cl_{Te} at CdSe_{0.25}Te_{0.75} grain-boundary indicated that chlorine substitution completely passivates the donor states and introduces more scattered acceptor states near the VBM (see figure 8.3 (d)). The presence of acceptor states near VBM leads to cusp feature in the VBM and would cause the localization of hole charge carriers (see figure 8.2 (d)). The localization of hole charge carriers at the CdSeTe grain boundaries would still lead to an effective charge carrier extraction. Such a passivation mechanism could be thought of as p-p* inversion at CdSeTe grain boundaries which is different from p-n type inversion observed in the CdTe grain boundaries. Nonetheless, the passivation of donor states followed by p-p* type inversion at CdSeTe grain boundaries would indicate better passivation in the CdSeTe

grain-boundary than CdTe grain-boundary leading to higher CL intensity and carrier lifetimes observed in the CdSeTe absorber layer.

8.3.2 $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{Al}_2\text{O}_3$ interface

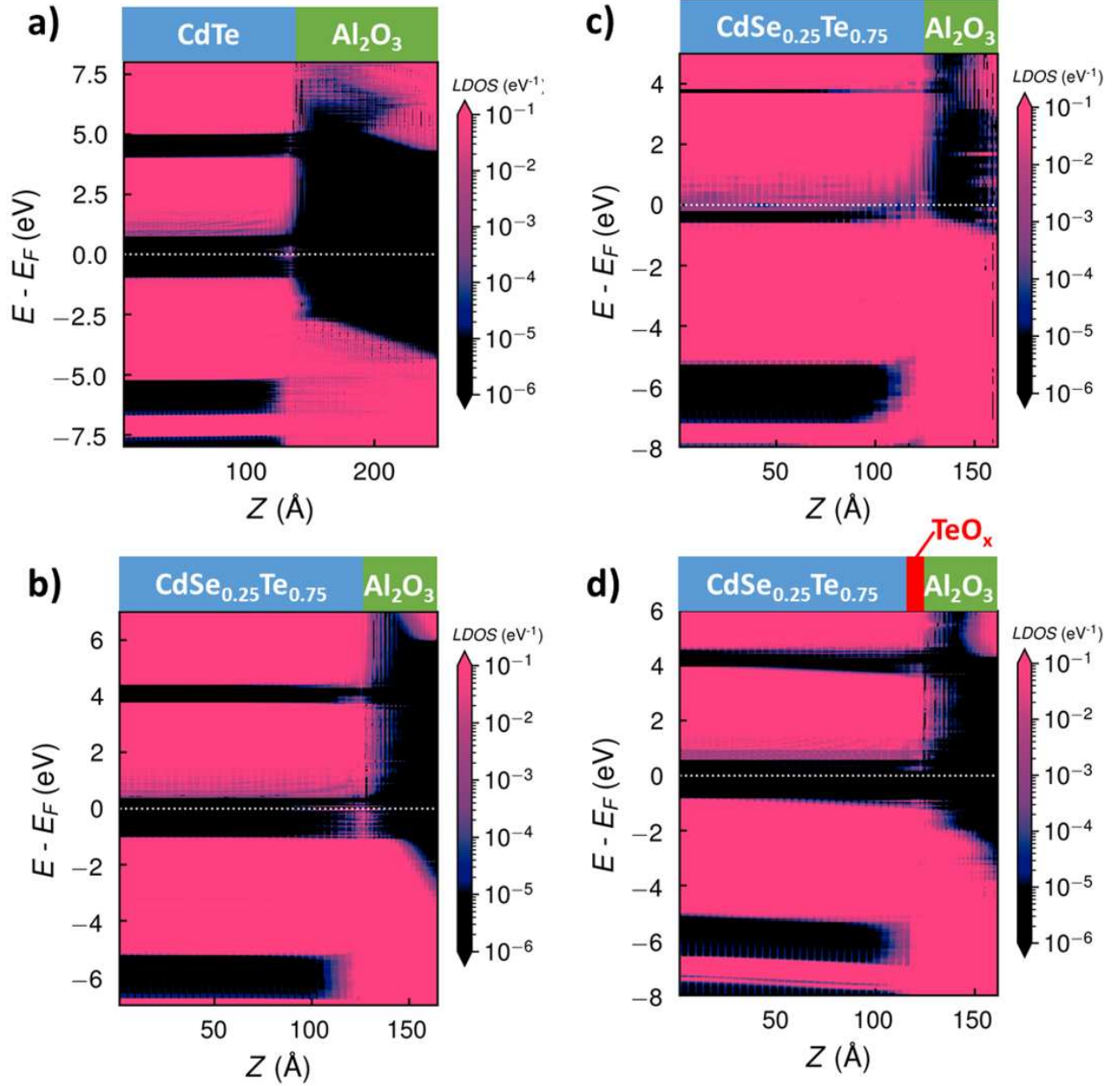


Figure 8.4: Energy band alignment comparison of (a) P-I CdTe/ Al_2O_3 , (b) S-I $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{Al}_2\text{O}_3$, (c) P-I $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{Al}_2\text{O}_3$, and (d) $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{TeO}_x/\text{Al}_2\text{O}_3$. CdTe and $\text{CdSe}_{0.25}\text{Te}_{0.75}$ had (111) orientation. Al_2O_3 had (0001) orientation in all simulations.

The DFT modeling of CdTe(110)/(100) and CdSe_{0.25}Te_{0.75}(110)/(100) grain boundaries indicated lower density of defect states and different defect passivation mechanism in CdSe_{0.25}Te_{0.75}(110)/(100) grain-boundary. To further understand the interface passivation mechanism enabling high carrier lifetime in DHs, CdTe/Al₂O₃ and CdSe_{0.25}Te_{0.75}/Al₂O₃ interfaces were simulated using the DFT atomistic models. Figure 8.4 (a) and (c) respectively represents P-I CdTe/Al₂O₃ and CdSe_{0.25}Te_{0.75}/Al₂O₃ interfaces. While P-I CdTe/Al₂O₃ interface converged to give a meaningful energy band alignment diagram, P-I CdSe_{0.25}Te_{0.75}/Al₂O₃ interface did not converge well. Since the fermi level in figure 8.4 (c) was found to be inside the CBM, it was deemed that the P-I CdSe_{0.25}Te_{0.75}/Al₂O₃ interface did not converge well and therefore was not considered for further analysis. *Shah et. al.* in past have described a different method of making a two probe atomistic model using Surface-Interface (S-I) approach known as S-I model [91]. Therefore to understand the electronic properties of the absorber/oxide interface, S-I atomistic model of the CdSe_{0.25}Te_{0.75}/Al₂O₃ was simulated and energy band alignment was calculated using the DFT-1/2 method. Table 8.2 summarizes the electronic properties of various interfaces formed with Al₂O₃.

Table 8.2: Salient electronic features in the energy band alignment of CdTe/Al₂O₃, CdSe_{0.25}Te_{0.75}/ Al₂O₃, and CdSe_{0.25}Te_{0.75}/TeO_x/Al₂O₃ interface.

Interface type	E _{absorber} ^g (eV)	E _{Al₂O₃} ^g (eV)
CdTe/Al ₂ O ₃	1.10	8.80
CdSe _{0.25} Te _{0.75} /Al ₂ O ₃	1.36	8.76
CdSe _{0.25} Te _{0.75} /TeO _x /Al ₂ O ₃	1.34	7.63

The literature report suggests bulk band-gap values of CdTe, CdSe_{0.25}Te_{0.75} and Al₂O₃ as 1.50 eV, 1.44 eV, and 7.76 eV respectively [88, 93]. Although the interfacial electronic properties converged with the DFT calculation, the band-gap for bulk-like (far away from interface) CdTe, CdSe_{0.25}Te_{0.75} and Al₂O₃ did not (see table 8.2). This suggests that the atomistic model are not long enough to achieve the bulk-like properties far away from the interface. However, as increasing the

model size further presents computational challenges, the analysis of interfacial properties were done with the current setup.

The CdTe/Al₂O₃ interface showed high density of defect states (see figure 8.4 (a)). The presence of defect states at the CdTe/Al₂O₃ interface and at the CdTe grain boundaries suggests higher recombination in the bulk and at the interface. Similarly, high density of defect states was also observed at CdSe_{0.25}Te_{0.75}/Al₂O₃ interface (see figure 8.4 (b)). It was noted that presence of back layer Al₂O₃ does not bend the valence and conduction bands upwards in the CdTe absorber. An upward bending of the bands would reflect the minority electron charge carriers from reaching the back contact and therefore the presence of defect states would be benign. This effect of passivation by band bending is referred to as field passivation effect [90]. Such an observation of absence of field passivation effect and presence of high density of defect states at interfaces contradicted the earlier theory of Al₂O₃ by itself is passivating the interface.

In past, *Perkins et. al.* had made similar observation through XPS and TRPL measurements and suggested the formation of native TeO_x between the CdTe/Al₂O₃ interface [90]. In another work, *Ablekim et. al.* also showed formation of native TeO_x between the oxide/CdSeTe layers [94]. In order to incorporate the above findings in the atomistic model, a monolayer of TeO_x was included in the two probe atomistic as has been described in the section 8.2.1. Figure 8.4 (d) shows the energy band alignment results for the CdSe_{0.25}Te_{0.75}/TeO_x/Al₂O₃ interface. The inclusion of TeO_x between the CdSe_{0.25}Te_{0.75}/Al₂O₃ clearly passivates the defect states at the interface (see figure 8.4 (c) and (d)). This indicates that the passivation occurring at the oxide/CdSeTe interface is indeed a chemical passivation. Furthermore, *Ablekim et. al.* has shown that native TeO_x readily forms with the CdSeTe absorber than CdTe absorber [94]. This would imply that lower density of defect states in the CdSeTe grain-boundary and the chemical passivation due to formation of native TeO_x at the CdSeTe/Al₂O₃ interface leads to higher lifetime in the CdSeTe DHs than the CdTe DHs.

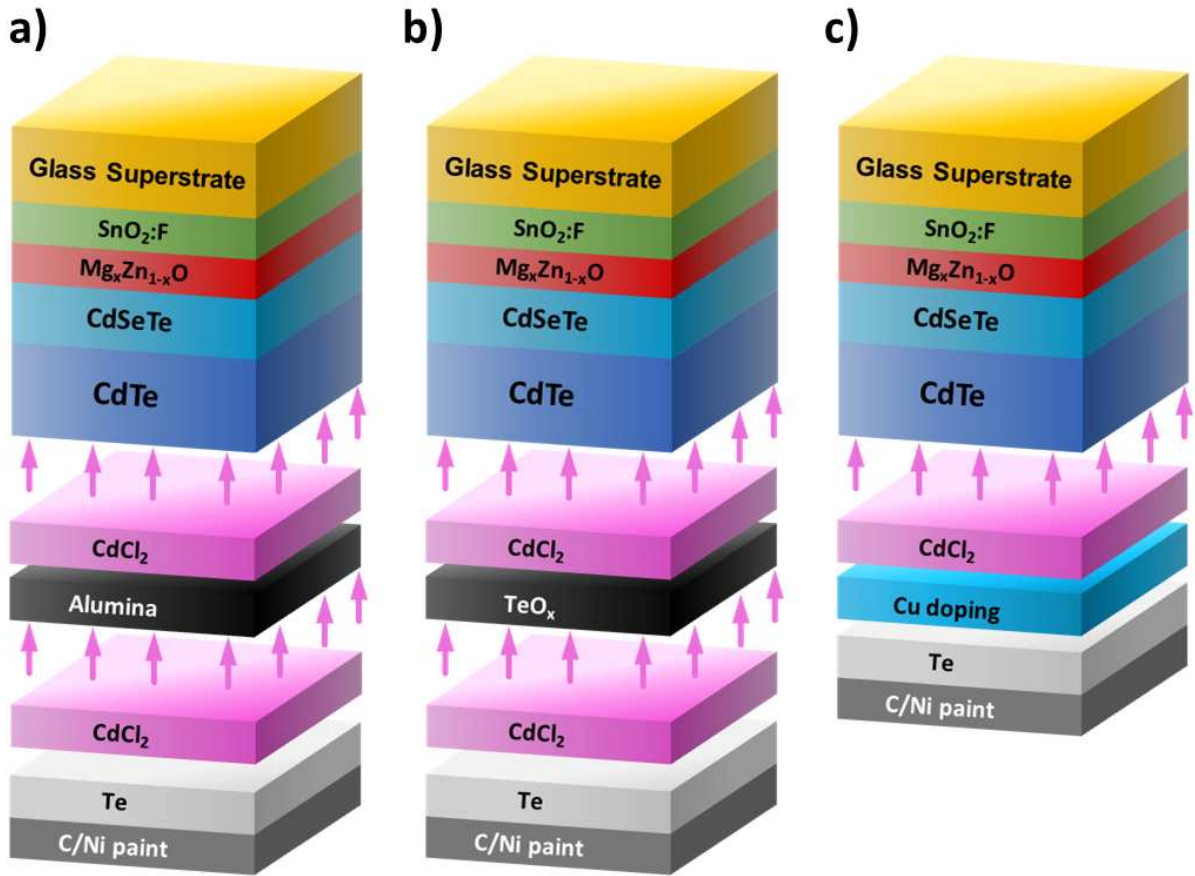


Figure 8.5: Schematic structure of PV-devices with (a) Al_2O_3 , (b) TeO_x , and (c) copper doping as back contact conditions.

8.3.3 PV-device fabrication

To incorporate the learning from DFT models and further understand how the above oxide passivation at the back contact affects the device performance, two substrates were fabricated with 4-5 nm Al_2O_3 and TeO_x as the back contact layer without any copper doping. These devices were also compared with the standard copper doped CdSeTe/CdTe PV-devices to understand how the back contact conditions could influence the performances in the CdSeTe/CdTe PV-devices. Figure 8.5 shows the schematic of different back contact conditions used in fabrication of various CdSeTe/CdTe PV-devices.

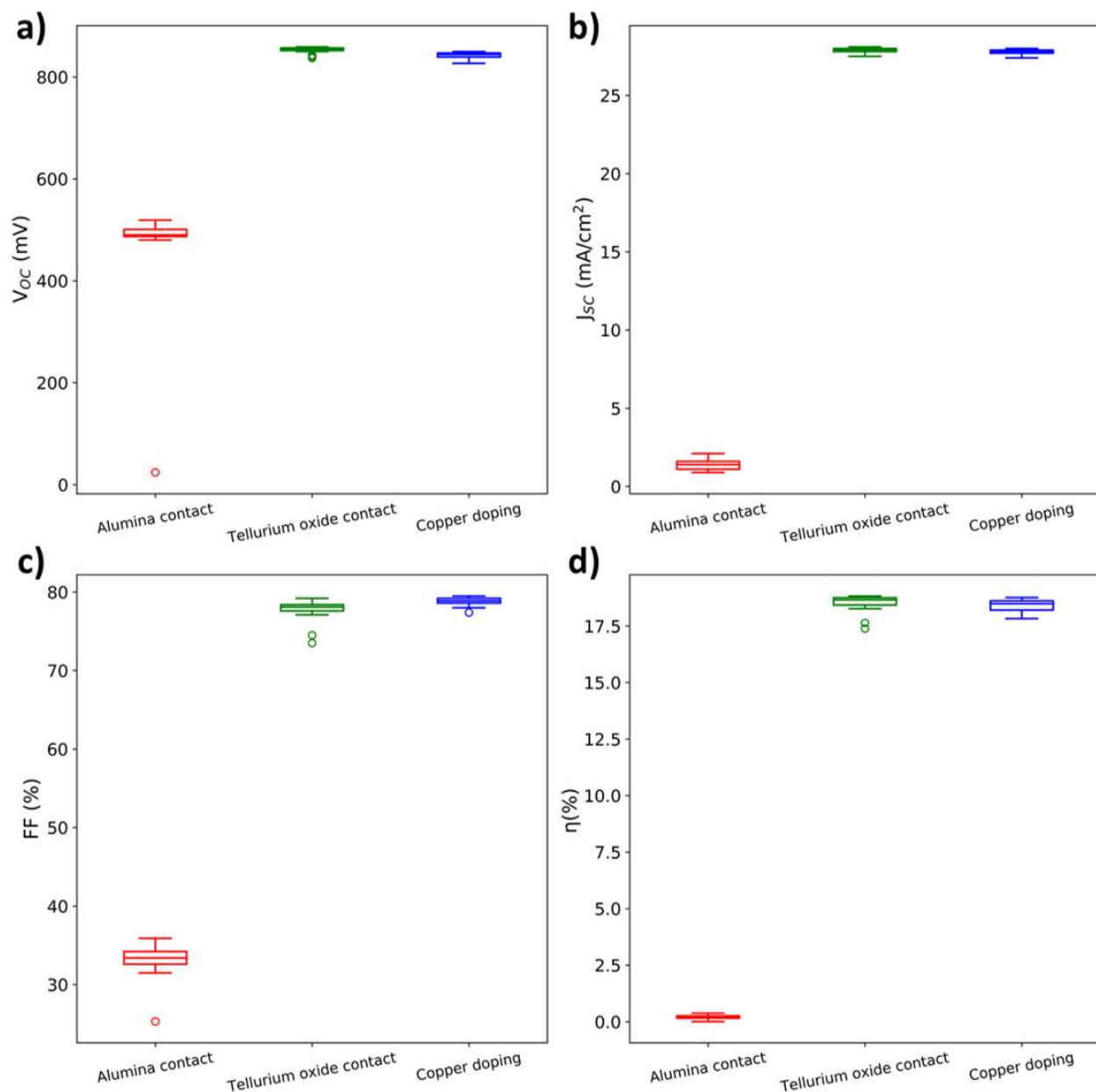


Figure 8.6: Box plots showing (a) Open-circuit voltage (V_{OC}), (b) Short-circuit current density (J_{SC}), (c) Fill Factor (FF), and (d) Efficiency (η). Each box plot contains the data from 25 devices.

Figure 8.6 shows the box plots of open-circuit voltage (V_{OC}), Short-circuit current density (J_{SC}), Fill Factor (FF), and Efficiency (η) for various back contact configurations. It was noted that PV-devices with Al_2O_3 back contact had very low short circuit current density values, while the devices with TeO_x had comparable J_{SC} to the standard copper doped solar cells. Similar effects were also seen for V_{OC} , FF, and efficiency values. Figure 8.7 shows the diode curve for different back contact

conditions. The diode curve for the alumina back contact clearly shows high series resistance and poor shunt resistance thereby decreasing the J_{SC} , V_{OC} , FF, and efficiency values. This phenomena of such low diode curve parameters could be explained with the energy band alignment diagram of CdTe/ Al_2O_3 (see figure 8.4 (a)). The high band-gap of Al_2O_3 layer doesn't allow better hole charge carrier extraction thereby giving high series resistance and lower parameter values in the diode curve.

However, undoped devices with TeO_x as a back contact would passivate the back of the CdTe layer helping in better extraction of the hole charge carriers. Comparing the performances of the devices with TeO_x back contact to the copper doped devices, it could be stated that TeO_x back contact is the potential candidate for replacing the copper doping process in the CdSeTe/CdTe bilayer PV-devices. Usage of TeO_x as a back contact would not only help to increase the stability of the CdTe solar cells but will also pave the path for further improvement in the device performance of CdTe solar cells.

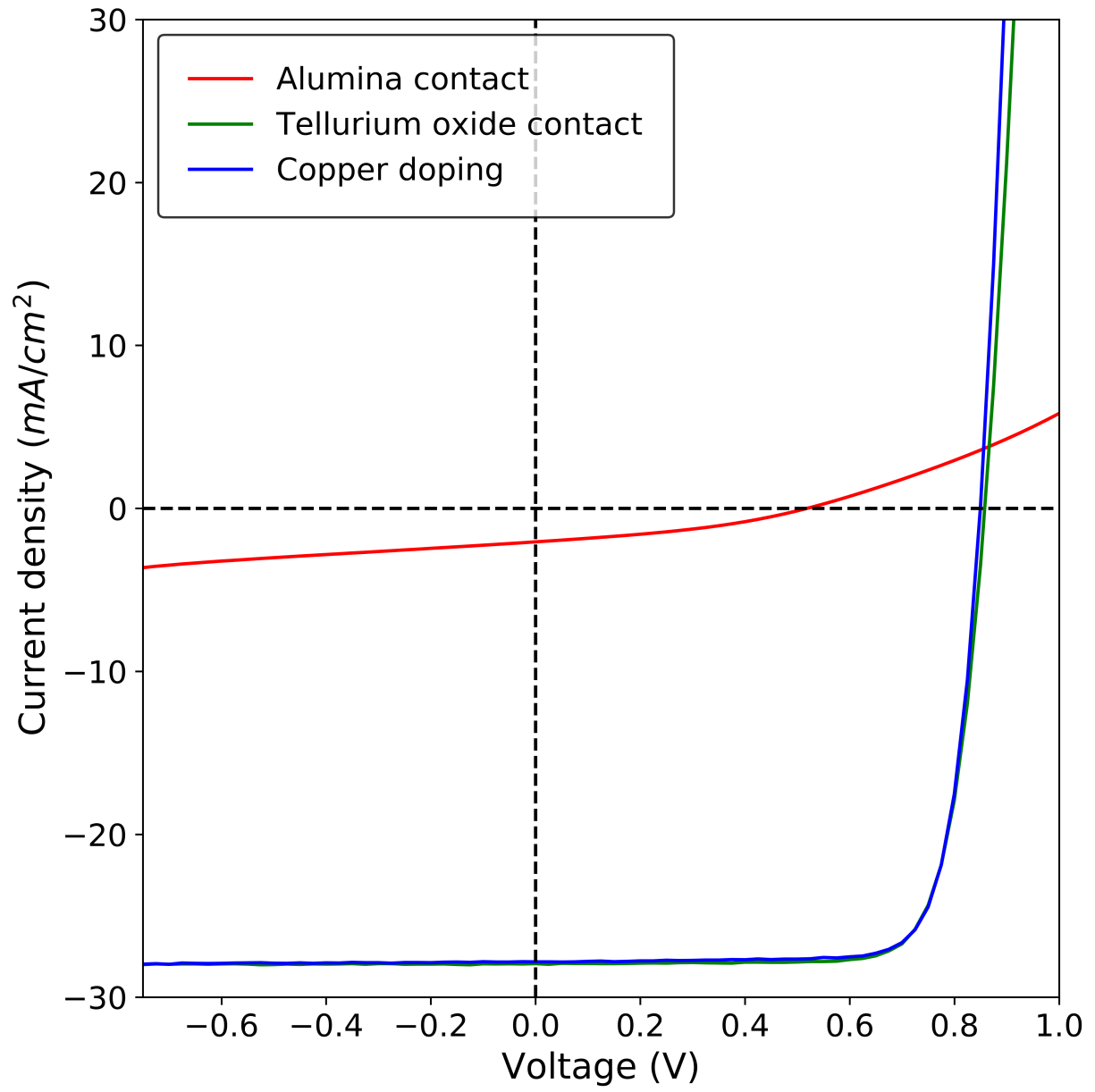


Figure 8.7: Current density-Voltage diode curve for various back contact conditions.

Chapter 9

Solar cells with CdSeTe absorber¹

9.1 Introduction

The theoretical Shockley-Queisser efficiency limit for CdTe PV-device is 32% [95]. Most of the recent device efficiency improvements have been achieved by lowering the band-gap of the absorber layer and increasing the short-circuit current. The lowering of the band-gap of the absorber has been accomplished by Se alloying of the CdTe absorber. CdSeTe/CdTe bilayer absorber based research scale devices have achieved efficiencies of 22.1% in 2016 [17]. Further improvement in the device performance is expected to come from increasing the fill factor and open-circuit voltage of CdTe solar cells [96].

Researchers in past have shown higher carrier lifetimes, lower recombination velocities, and better passivation in the bulk absorber and interface with Se-alloyed CdTe absorbers [16,21,31,63, 89,92]. For a Se-graded CdSeTe/CdTe bilayer structure, *Fiducia et. al.* used cathodoluminescence to show brighter intensity in the CdSeTe region in comparison to CdTe layer [21]. Such high lifetimes and better passivation with CdSeTe layer suggests that fabricating solar cells with CdSeTe absorber should give higher open-circuit voltage and fill factor in addition to higher short circuit current density.

¹This chapter has been modified from a peer-reviewed journal article: A. Shah, R. Pandey, , A.P. Nicholson, Z. Lustig, A. Abbas, A. Danielson, J. M. Walls, A. H. Munshi, W. S. Sampath (2021). Understanding the Role of CdTe in Polycrystalline CdSexTe1-x/CdTe Graded Bilayer Photovoltaic Device, Solar RRL, 2100523.

A. Shah: Conceptualization, Methodology, cell fabrication, Software, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization.

R. Pandey: UPS characterization, Data analysis, Writing - review editing.

A. P. Nicholson: Software, Data curation, Writing - review editing.

Z. Lustig, A. Danielson: Cell fabrication, Writing- Review and editing.

A. Abbas: TEM-EDS characterization.

J.M. Walls, A. H. Munshi, W. S. Sampath: Conceptualization, Resources, Project administration, Funding acquisition

However, from one of the earlier work, the PV-devices made with the CdSeTe-only absorber (fabricated with same parameters used for high efficiency CdSeTe/CdTe bilayer devices) demonstrated efficiencies of 9-12% [91]. It has been hypothesized in chapter 6 that lower efficiencies in CdSeTe-only absorber based cell results from the absence of cusp feature observed at CdTe back surface. This chapter delve into understanding the electronic features of various CdSeTe interfaces and explore different processing conditions to fabricate high efficiency CdSeTe-only devices.

9.2 Experimental and Computational details

9.2.1 Computational details

CdSe_{0.25}Te_{0.75}(111)/Te(0001) interfaces were simulated using the two probe atomistic models described in earlier chapters. The energy band alignment were calculated for different doping levels of CdSe_{0.25}Te_{0.75} to understand the effect of doping on the energy band alignment at CdSe_{0.25}Te_{0.75}/Te interface. Similarly, to understand the electronic properties of CdSeTe/CdTe bilayer absorber, Se-graded CdSe_{0.25}Te_{0.75}/CdTe interface was simulated using the S-I model (see figure 9.1) described by *Shah et. al.* [91]. CdSe_{0.25}Te_{0.75}/CdTe interface models were simulated in three major principal orientation of (100), (110), and (111). The S-I two probe atomistic model was based on the EDS line profile obtained from TEM-EDS analysis of the CdSeTe/CdTe film.

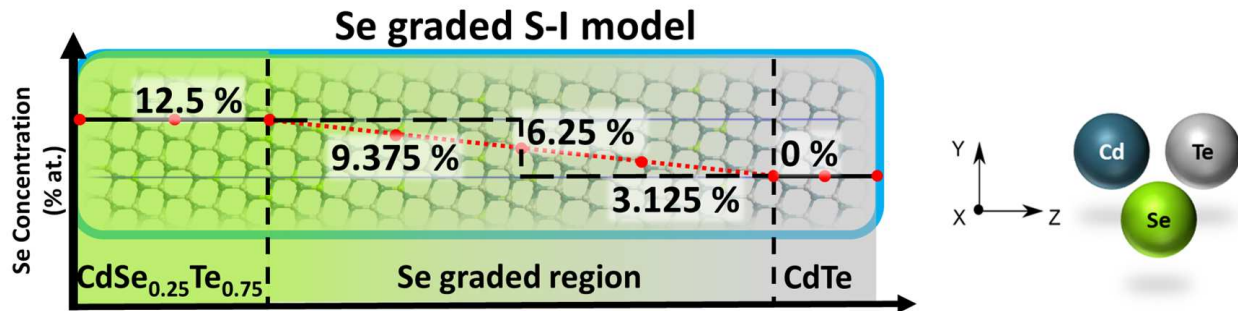


Figure 9.1: Schematic showing the Se-graded CdSe_{0.25}Te_{0.75}/CdTe two probe S-I model. The black dash line represents % Se atomic concentration before grading Se in the CdSe_{0.25}Te_{0.75}/CdTe layer. The graded Se at. % was determined as a decrease of a Se atom for every 32 chalcogenide-based elements over two CdSe_{0.25}Te_{0.75} unit cells. Figure is not drawn to scale

9.2.2 Experimental details

CdTe solar cells with thin film materials such As doped $\text{CdSe}_{0.4}\text{Te}_{0.6}$, $\text{CdSe}_{0.2}\text{Te}_{0.8}$, $\text{CdSe}_{0.4}\text{Te}_{0.6}$, TeO_x were fabricated in various configurations in a bid to incorporate the learning gained from DFT modeling and improve the device performance. The fabrication of PV-devices were done with closed space sublimation method using the methods described before [91]. Ultraviolet photoelectron spectroscopy was done for CdSeTe and CdTe films to construct the energy band alignment diagram for CdSeTe/CdTe interface. TEM-EDS and SEM-EDS line/ surface profiling on structures were done on the absorber films to understand the atomic distribution of various elements post CdCl_2 -annealing process step and has been described in details in the earlier works by *Shah et. al.* [91].

9.3 Results and Discussion

9.3.1 $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{Te}$ interface

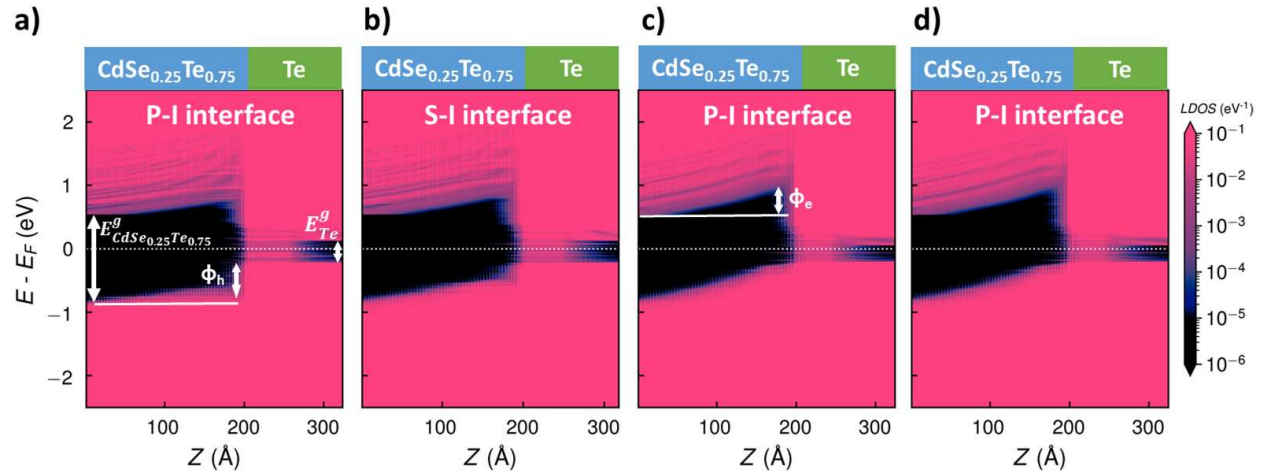


Figure 9.2: Energy band alignment diagrams showing (a) undoped Pristine-Interface (P-I) $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{Te}$, (b) undoped Surface-Interface (S-I) $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{Te}$, (c) $10^{16}/\text{cm}^3$ $\text{CdSe}_{0.25}\text{Te}_{0.75}$ doped P-I $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{Te}$, and (d) $10^{18}/\text{cm}^3$ $\text{CdSe}_{0.25}\text{Te}_{0.75}$ doped P-I $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{Te}$. Te in all the above cases were doped to $10^{19}/\text{cm}^3$.

CdSe_{0.25}Te_{0.75}/Te atomistic models were simulated using the P-I and S-I methods discussed in chapter 8. It was important to simulate the P-I and S-I CdSe_{0.25}Te_{0.75}/Te models since CdSe_{0.25}Te_{0.75}/Al₂O₃ showed significantly different band alignment with the above two modeling methods. Figure 9.2 (a) and (b) compares the difference in the energy band alignment of CdSe_{0.25}Te_{0.75}/Te P-I and S-I models. Table 9.1 summarizes the bulk like band-gap values for CdSe_{0.25}Te_{0.75} ($E_{\text{CdSe}_{0.25}\text{Te}_{0.75}}^g$) and Te (E_{Te}^g) as per the labels shown in figure 9.2. Two other parameters Φ_h and Φ_e were defined as the hole enabler and electron barrier respectively.

Table 9.1: Salient electronic features in the energy band alignment of CdSe_{0.25}Te_{0.75}/Te interface.

Interface type	$E_{\text{CdSe}_{0.25}\text{Te}_{0.75}}^g$ (eV)	E_{Te}^g (eV)	Φ_h	Φ_e
P-I undoped	1.32	0.21	0.34	0.13
S-I undoped	1.27	0.22	0.52	0.18
P-I 10 ¹⁶ /cm ³	1.24	0.17	0.72	0.28
P-I 10 ¹⁸ /cm ³	1.26	0.18	0.84	0.36

Similar band alignment features were observed for both the undoped P-I and S-I models (see figure 9.2 (a) and (b)). The bulk like band-gap value for the respective CdSe_{0.25}Te_{0.75} and Te were found to be 0.2 eV and 0.13 eV lower than the expected bulk band-gap values (see table 9.1). Nonetheless, the P-I and S-I models still gave valuable information about the CdSe_{0.25}Te_{0.75}/Te interfacial electronic properties. High density of defect states were observed at the CdSe_{0.25}Te_{0.75}/Te interface. Similar observation has been made by *Nicholson et. al.* for the CdTe/Te interface [6]. Since the electronic features were found to be similar in the P-I undoped and S-I undoped CdSe_{0.25}Te_{0.75}/Te interfaces, doping of the CdSe_{0.25}Te_{0.75} layer was done in the P-I model to make one to one comparison with the CdTe/Te interface. For the CdTe/Te case, *Nicholson et. al.* found a hole charge transport aiding cusp feature at the CdTe/Te interface [6]. However, no such feature was present at the CdSe_{0.25}Te_{0.75}/Te interface. This also correlates to the CdSe_{0.25}Te_{0.75} surface simulations (see chapter 5), where no cusp feature was observed at the back of CdSe_{0.25}Te_{0.75} sur-

face. However, the doping of $\text{CdSe}_{0.25}\text{Te}_{0.75}$ layer increased the electron barrier (Φ_e , see table 9.1) at the interface (see figure 9.2 (c) and (d)). The hole enabler energy also increase with the increased doping of the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ layer (Φ_h , see table 9.1).

The above results indicated the presence of high density defect states at the $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{Te}$ interface and lower value of Φ_e . Due to this, there would high recombination at the back surface of the undoped $\text{CdSe}_{0.25}\text{Te}_{0.75}$ layer. However, as the doping is increased the electron barrier becomes stronger and would reflect the electron from reaching the back of the recombination prone $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{Te}$ interface. Based on the above the results and Se passivating the grain boundaries (as discussed before in earlier chapters), CdSeTe-only based PV-devices were fabricated with copper and arsenic doped layers and were compared to CdSeTe/CdTe bilayer absorber based devices.

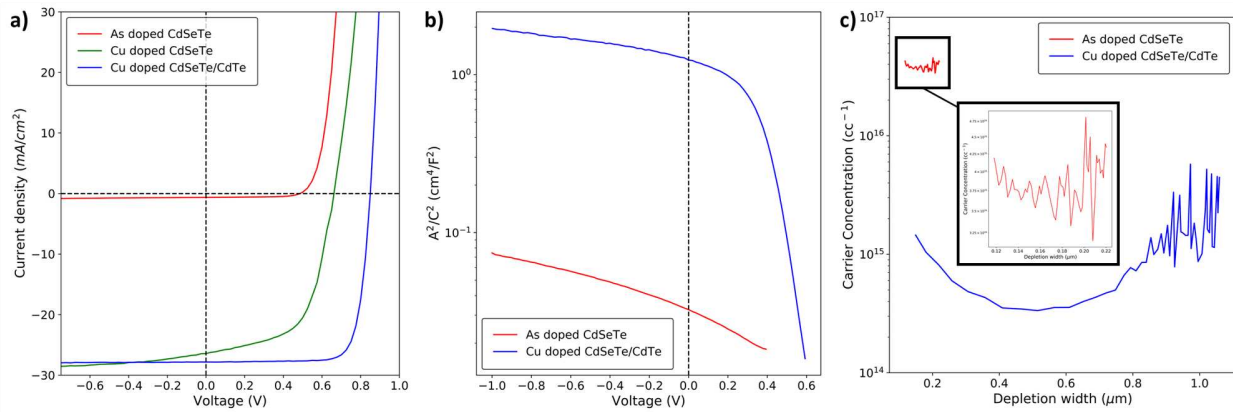


Figure 9.3: (a) Current-density vs Voltage diode curves for copper (Cu) doped CdSeTe, arsenic (As) doped CdSeTe, and copper (Cu) doped CdSeTe/CdTe PV-devices, (b) Mott-Schottky plots for As doped CdSeTe, and Cu doped CdSeTe/CdTe PV-device, and (c) carrier concentration vs depletion width plots for As doped CdSeTe, and Cu doped CdSeTe/CdTe PV-device

Figure 9.3 shows the device characteristics for the copper (Cu) doped CdSeTe, arsenic (As) doped CdSeTe, and copper (Cu) doped CdSeTe/CdTe PV-devices. Table 9.2 summarizes the diode parameters for various PV-device configurations. The copper doping recipe was the same for the CdSeTe-only and CdSeTe/CdTe based PV-devices. The arsenic doping was done by depositing the As doped CdSeTe layer behind the undoped layer. This stack was then treated with CdCl_2 and Te was deposited to make the back contact. It was noted that the As doped CdSeTe cell

Table 9.2: Device parameters for copper (Cu) doped CdSeTe, arsenic (As) doped CdSeTe, and copper (Cu) doped CdSeTe/CdTe PV-devices.

Device type	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF (%)	η (%)	N_A (cc ⁻¹)
As doped CdSeTe	487	0.6	62.0	0.19	4.3×10^{16}
Cu doped CdSeTe	662	26.4	58.7	10.27	-
Cu doped CdSeTe/CdTe	850	27.8	79.3	18.76	7.8×10^{14}

gave the poor J_{SC} , V_{OC} , and FF values in comparison to copper doped CdSeTe-only and CdSeTe/CdTe bilayer PV-devices (see figure 9.3(a) and table 9.2). However, the Mott-Schottky plot (see figure 9.3 (b)) showed that As doped CdSeTe device had a linear line in comparison to the Cu doped CdSeTe/CdTe device, indicating uniform doping with arsenic than copper [97]. The carrier-concentration vs depletion width measurements further showed higher carrier concentration in the As doped CdSeTe device in comparison to Cu doped CdSeTe/CdTe device (see table 9.2). Based on the CdSeTe/Te and previous CdSeTe interface DFT models, highly p-type doped CdSeTe/Te in principle should have given better device efficiencies. However, as this was not realized in the actual PV-devices, it was decided to understand the role of CdTe in the bilayer CdSeTe/CdTe PV-devices using various DFT models and experiments.

9.3.2 CdSe_{0.25}Te_{0.75}/CdTe interface

Microstructural analysis

CdTe films and CdSeTe/CdTe films were fabricated using the methods described by *Shah et. al.* for the TEM-EDS analysis [91]. Figure 9.4 shows the TEM images and the elemental profiles of atoms in the CdCl₂ treated CdTe and CdSe_xTe_{1-x}/CdTe absorber films. The EDS line scan indicated no diffusion of Mg, Zn, or O from the Mg_{0.23}Zn_{0.77}O into any of the absorber layer. Elemental line scan for CdSe_xTe_{1-x}/CdTe bilayer absorber revealed 8 At. % of Se in the CdSeTe layer with a diffused Se profile extended towards the CdTe layer. Similar effects have been observed with the CdSe_xTe_{1-x}/CdTe bilayers by *Fiducia et. al.* and *Guo et. al.* where the Se diffusion lowers the

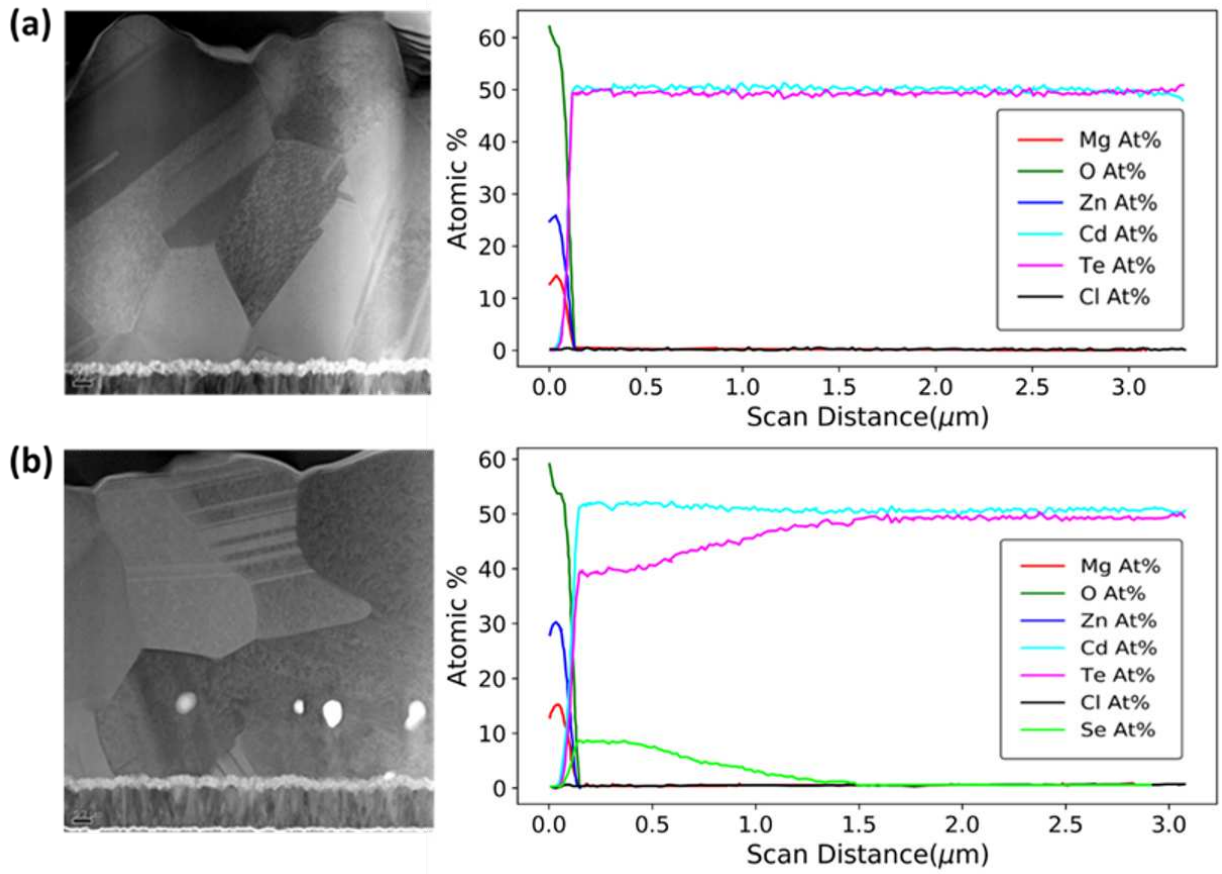


Figure 9.4: TEM image of the cross section showing the microstructure and EDS line scans for (a) CdTe-only and (b) CdSeTe/CdTe based absorber films. The TEM microstructure also suggests presence of voids (white spots) in the CdSeTe absorber film.

bandgap of the $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ bilayer absorber [21, 31]. The comparison of TEM images show the grain size near the front junction in the CdSeTe layer to be relatively smaller than the CdTe only device. The CdSeTe film was deposited at lower substrate temperature of 420C while the CdTe film was deposited at the higher substrate temperature of 500C [91]. This is consistent with previous studies by *Munshi et al.* who have shown that the grain size in the CdTe-based absorber films depend on the substrate temperature [98]. Further, the images show voids in the CdSeTe layer near the front interface of the bilayer $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ absorber. *Baines et al.* and coworkers have made similar observations, where they attributed the formation of voids in the $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ structure due to the intermixing of Se and Te atoms [99]. The presence of such voids and relatively

small CdSeTe grains is expected to limit the open-circuit voltage and has been reported previously for several different thin-film solar cells [98,99].

Experimental energy band alignment

To measure the band offsets between the CdTe and $\text{CdSe}_x\text{Te}_{1-x}$, UPS measurement was performed in the valence band region at low binding energy as shown in figure 9.5(a). The inset in figure 9.5(a) shows the onset of the signals and has been extrapolated to extract the valence band maxima to be 0.8 ± 0.1 eV for both CdTe and $\text{CdSe}_x\text{Te}_{1-x}$. Similar measurement was performed at voltage bias of 10 V to measure the secondary electron edge as shown in figure 9.5(b). It shows the cutoff energy for CdTe and CdSeTe to be 7.06 eV and 6.81 eV respectively. This was used to measure the work function which was calculated to be 4.15 eV and 4.4 eV respectively. The work function for the Au calibration sample was measured to be 5.16 eV. There are two key points to be discussed here. First, the work function of CdSeTe is larger than that of CdTe, meaning that it would be harder to make a hole contact with CdSeTe surface in comparison to a CdTe surface. Another, the measured work function of Au calibration sample of 5.16 eV is close to the relative valence band maxima of CdTe (4.95 eV) and CdSeTe (5.2 eV) measured with UPS. This suggests that Au and other high work function metals like Ni will form a good ohmic metal back contact with the CdTe based solar cells.

Using these values from UPS and the optical energy band-gap of 1.48 eV (820nm) for CdTe, and 1.40 eV (870nm) for CdSeTe from PL measurements, an energy band diagram relative to the vacuum level is predicted as shown in figure 9.6. Fig. 9.6 (a) shows the relative position of the energy bands for the isolated case of CdSeTe and CdTe films. In equilibrium, the Fermi level should coincide in both sides of a junction. To comply to this, the initial difference in Fermi position of 0.25 eV in isolated cases was distributed such that the Fermi in CdSeTe was pushed towards EC by 0.13 eV and in the CdTe region pushed towards the valence band by 0.12 eV respectively which puts the equilibrium Fermi level at 4.28 eV. Based on this, a simple energy band-diagram at the CdSeTe/CdTe interface is presented in fig 9.6 (b) where there is a conduction band offset of 0.2 eV and a valence band offset of around 0.1 eV. Such a band offset would mean

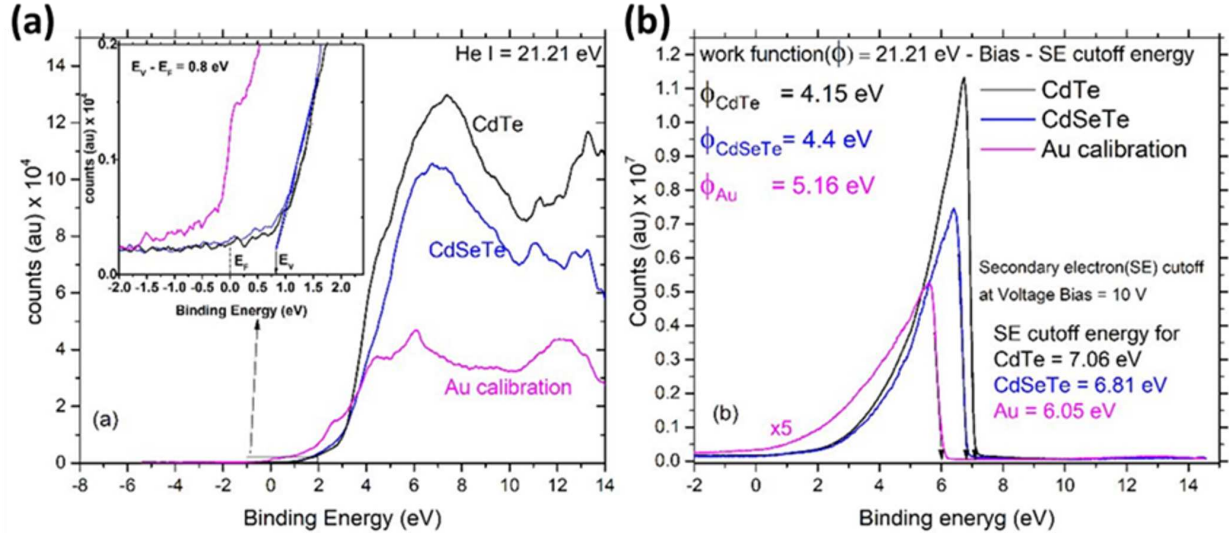


Figure 9.5: (a) UPS measurement to find the VBM, and (b) UPS measurement to measure the secondary electron cut off region.

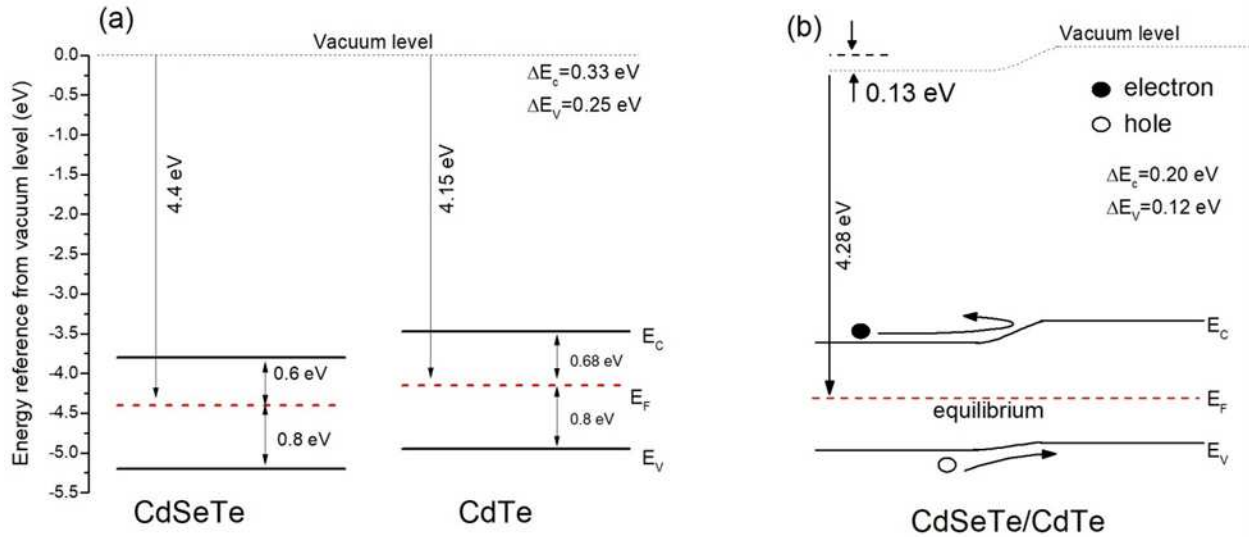


Figure 9.6: Schematic showing (a) energy band position of CdSeTe and CdTe based on the UPS measurement, and (b) projected band alignment at CdSeTe/CdTe interface.

that the electrons would be reflected towards the CdSeTe region while the holes would be moving towards the CdTe region. In the real device configuration, the Se was graded leading to a graded band-gap. Also, the relative position of the energy bands is measured from the fermi level, this means that the vacuum level either gets pushed up in the CdSe_xTe_{1-x} region or gets pulled down in the CdTe region. In either case the band bending was such that it created a barrier for the electrons

to move from $\text{CdSe}_x\text{Te}_{1-x}$ to CdTe region in conduction band and assisted the hole collection in the valence band.

Energy band alignment from Density Functional Theory

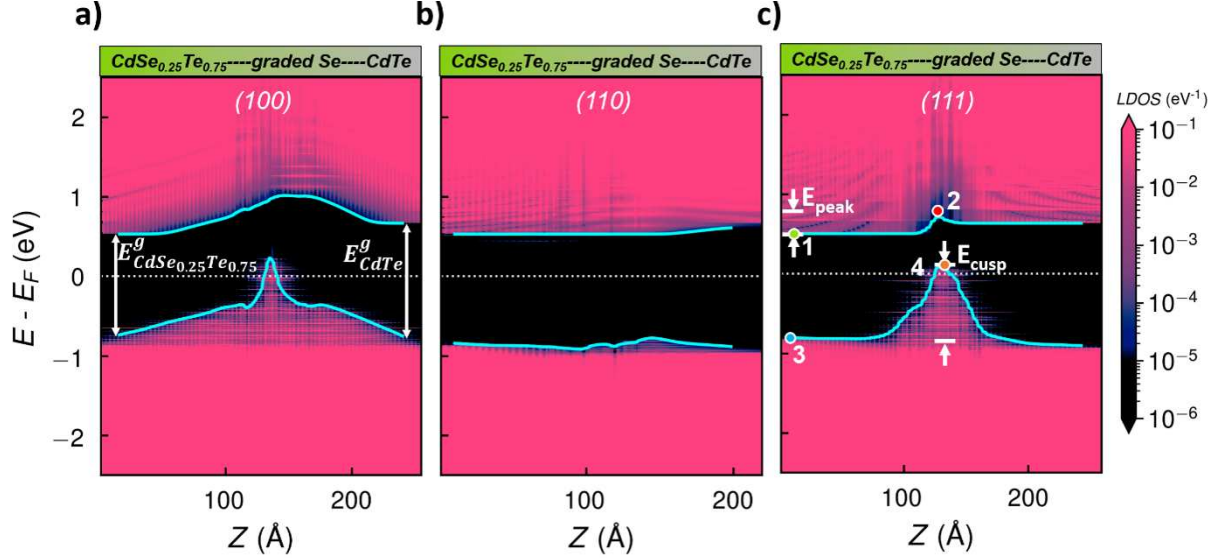


Figure 9.7: Energy band alignment diagram of Se-graded $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{CdTe}$ S-I model in (a) (100), (b) (110), and (c) (111) grain orientation. The blue curves are the trace of the macroscopic average curve fits of the valence band maximum and conduction band minimum, respectively.

Pertinent electronic features of the Se-graded S-I model were studied to understand the energy band alignment of the Se-graded $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{CdTe}$ interface using the methods described by *Shah et. al.* [91]. The band-gap energy, $E_{\text{CdSe}_{0.25}\text{Te}_{0.75}}^g$ and E_{CdTe}^g was determined from the energy differences of the VBM and CBM at positions located close to the bulk-like $\text{CdSe}_{0.25}\text{Te}_{0.75}$ and CdTe regions, respectively. It was noted that bulk-like band-gap energy of CdTe matched with different experimental band-gap values (see table 9.3). However, bulk like $\text{CdSe}_{0.25}\text{Te}_{0.75}$ band-gap energy deviated by 3.5-8.4 % from the experimentally reported band-gap values [36, 55]. Such deviations in the bandgap energy values are noted due to limitation of the system size. Extending the bulk-like $\text{CdSe}_{0.25}\text{Te}_{0.75}$ region further could have helped to resolve this issue but would make the simulation computationally expensive. Nonetheless, it can still be inferred from these results

that DFT-1/2 correction scheme works well with the band-gap correction of cadmium selenium telluride ternary alloy.

Table 9.3: Salient geometrical and electronic features of the Se-graded $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{CdTe}$ S-I models along different grain orientations. All the energy potential values are reported in eV. $L_{z,\text{CdTe}}$, $L_{z,\text{CdSeTe}}$ denotes the respective bulk electrode length of CdTe and $\text{CdSe}_{0.25}\text{Te}_{0.75}$. $L_{z,\text{central}}$ and N_{atoms} denotes the central region length and number of atoms within the central region. All the lengths are reported in Å.

Orientation	$E_{\text{CdSe}_{0.25}\text{Te}_{0.75}}^g$	E_{CdTe}^g	E_{peak}	E_{cusp}	$L_{z,\text{CdTe}}$	$L_{z,\text{CdSeTe}}$	$L_{z,\text{central}}$	N_{atoms}
(100)	1.27	1.42	0.49	0.97	5.79	5.62	259.35	637
(110)	1.37	1.49	0.07	0.05	3.51	8.08	219.53	759
(111)	1.31	1.54	0.21	0.94	10.04	9.67	281.30	598

In accordance with the labels provided in fig. 9.7, the conduction band peak potential E_{peak} is defined as the energy difference between the peak of the curve fit CBM (labeled point 2) and the curve fit CBM value of the bulk-like $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (labeled point 1). In reference to the macroscopically averaged curve fit of the VBM, the cusp energy potential E_{cusp} is defined as the energy difference between the peak of the curve fit VBM (labeled point 4) and the curve fit VBM value of the bulk-like $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (labeled point 3). Table 9.3 summarizes all the electronic features described above for the Se-graded $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{CdTe}$ S-I model.

Fig. 9.7 shows the energy band alignment of Se-graded $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{CdTe}$ S-I model in the three different low index grain orientation. Irrespective of the orientation, the band alignment exhibits a peak in the CBM and a cusp in the VBM at the interface. However, this effect is more pronounced in the polar (100), and (111) grain orientation with the respective E_{peak} value of 0.49 eV and 0.21 eV than non-polar (110) grain orientation. Nonetheless, all the three orientations have the existence of the peak and cusp in the CBM and VBM respectively. The presence of peak in CBM indicates an electron reflector effect created at the $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{CdTe}$ interface. For a p-type absorber, such an effect in the CBM would confine the minority electron charge carriers, where they would move toward the front contact of the device. The confinement and subsequent transport

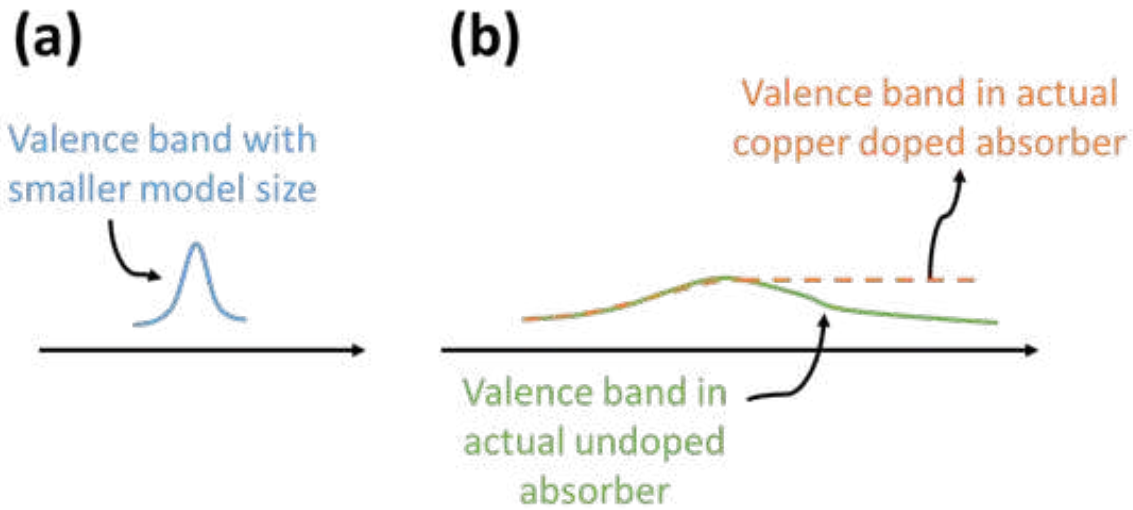


Figure 9.8: Schematic showing the valence band maximum for (a) the current S-I model (27 nm) utilized for DFT calculation in this study, and (b) expected valence band maximum for actual undoped and copper doped absorber (3.2-3.4 μm).

of the minority charge carriers to the front would lead to an increase in the current collection as observed experimentally. The energy band alignment diagrams also show minimal defect states at the $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{CdTe}$ interface indicating a lower interface recombination. Further, the cusp in the VBM at the $\text{CdSe}_{0.25}\text{Te}_{0.75}/\text{CdTe}$ interface indicates a p-type doping at the interface. It can be thought that the sharp cusp feature observed in the VBM would initially aid the hole charge transport up the cusp hill but later would impede the same toward the back electrode (see figure 9.8 (a)). However, it is to be noted that the current atomistic model spans only up to 27 nm with Se grading happening over 5-7 nm (see Figure 9.1 and Figure 9.7) which is much smaller than the actual absorber thickness (3.2-3.4 μm) where actual Se grading profile spans over 1.5 μm (from EDS plot in figure 9.4). The calculation in figure 9.7, shows that the sharp cusp in the valence band maximum occurs in the 5-7 nm of Se-graded region. If the similar cusp feature was to occur in the 1.5 μm , it wouldn't be this sharp and the effect will be much less pronounced in the valence band. It is also to be noted that the current models used in this study are undoped whereas the actual absorbers have copper doping. The doping of the absorber would further improve the p-type characteristics and enhance the hole charge transport towards the back electrode. We have

also added a schematic in figure 9.8 (b) explaining that photo-generated holes would climb up the extended cusp hill in the valence band initially. The copper doping would further assist an efficient extraction of the hole charge carriers which is reflected in the high device efficiencies. Meanwhile, the presence of peak feature in the conduction band keeps the minority electrons away from the back reducing the recombination yielding highly efficient CdSeTe/CdTe solar cells (see table 9.2).

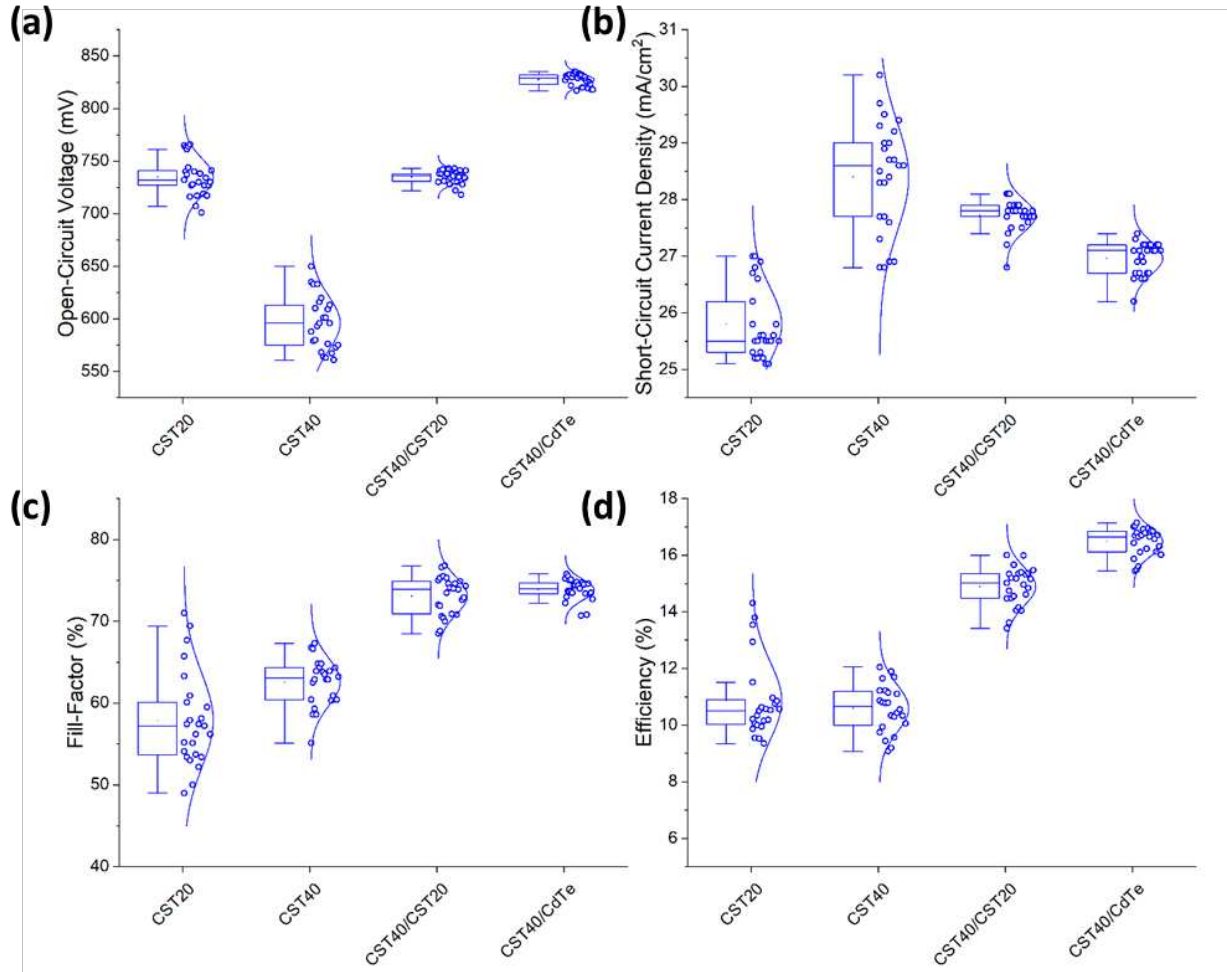


Figure 9.9: Box plot comparing the (a) Open-Circuit Voltage (V_{OC}) (b) Short-Circuit current density (J_{SC}) (c) Fill Factor (%) (d) Efficiency (%) between CdSeTe20 (CST20), CdSeTe40 (CST40), CdSeTe40/CdSeTe20, and CdSeTe40/CdTe bilayer PV-devices. Each box plot contains device data for 25 solar cells.

The above experimental characterization and theoretical analyses confirmed that putting a higher bandgap CdTe film behind the lower bandgap CdSeTe absorber created an electron reflector type effect which further aided in improving the efficiencies of the CdTe based solar cells.

Swanson et. al. and others in their work have suggested that the bandgap of Se-alloyed CdTe absorber could be altered based on the Se composition [21, 36]. In this regard, devices with two different source charge viz CdSeTe-20 (molar fraction of CdSe is 20%) and CdSeTe-40 (molar fraction of CdSe is 40%) were used to make higher and lower bandgap CdSeTe absorber. Based on the analyses presented above, it was further predicted that a bilayer of CdSeTe 40/CdTe absorber (with smaller bandgap CdSeTe absorber grown from CdSeTe 40 absorber material in front) based PV-devices would have better electron reflector type effect and therefore would lead to higher efficiencies. Therefore, 4 more substrates viz. CdSeTe-20 only, CdSeTe-40 only, CdSeTe 40/ CdSeTe 20 bilayer, and CdSeTe 40/ CdTe bilayer based PV-devices were fabricated.

The boxplot in Figure 9.9 shows the Open-circuit Voltage, Short-circuit current density, Fill Factor (%), and Efficiency comparison between the CdSeTe-20 only, CdSeTe-40 only, CdSeTe 40/ CdSeTe 20 bilayer, and CdSeTe 40/ CdTe bilayer absorber based PV-devices. The V_{OC} and J_{SC} values followed the expected trend with respect to the absorber's bandgap. As the absorber's bandgap decreased with increasing Se composition (CdTe > CdSeTe 20 > CdSeTe 40), the V_{oc} values dropped from CdSeTe 20-only to CdSeTe 40-only device and then again improved for CdSeTe 40/ CdSeTe 20 and CdSeTe 40/CdTe bilayer devices. Similarly, as the lower bandgap material allows for higher current extraction, the J_{SC} values increased from CdSeTe 20-only to CdSeTe 40-only devices and then again decreased for CdSeTe 40/ CdSeTe 20 and CdSeTe 40/CdTe bilayer devices. The FF and the respective efficiency increased from CdSeTe-only PV-devices to CdSeTe40/ CdSeTe20 followed by highest efficiency values recorded in CdSeTe40/CdTe bilayer absorber based devices.

9.3.3 Device fabrication

Based on the analyses discussed in above sections, it was hypothesized that although higher selenium content in CdSeTe passivates the defect states in the absorber, presence of higher bandgap material (such as CdTe) is required at the back to achieve higher better device performance. Also, it was noted that arsenic doping increases the carrier concentration while copper doping allows

for better charge carrier extraction leading to higher device performance (see figure 9.3, copper doped CdSeTe and arsenic doped CdSeTe). Combining the above findings, it was thought that selenium diffusion is required all the way through the CdTe to passivate the CdTe absorber. Also, it was thought that arsenic and copper doping together would improve the carrier concentration and provide better selectivity of charge carriers.

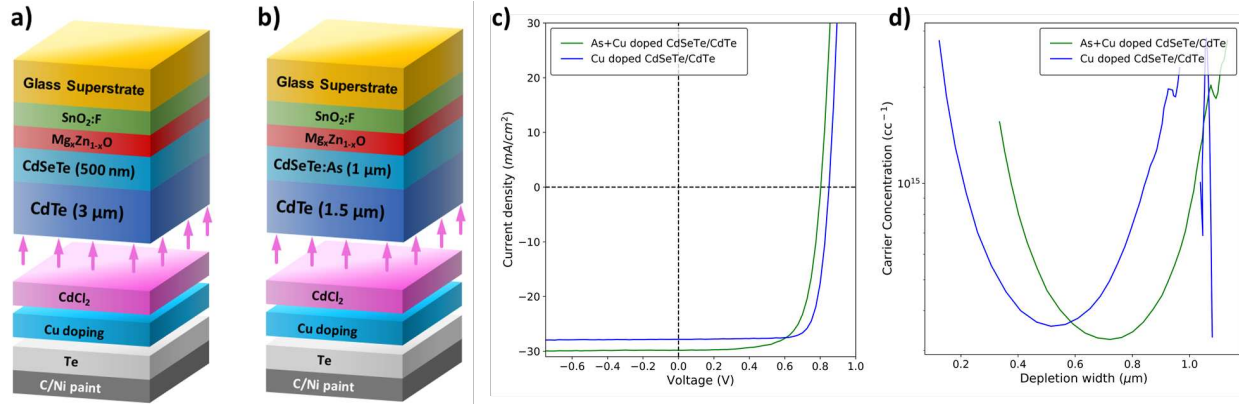


Figure 9.10: Schematic showing device structure of (a) copper doped CdSeTe/CdTe baseline PV-device, and (b) arsenic and copper doped CdSeTe/CdTe PV-device. (c) J-V diode curve, and (d) carrier concentration-depletion width curve comparison comparison of the arsenic+copper and copper doped CdSeTe/CdTe PV-device.

Table 9.4: Device parameters for Cu doped CdSeTe/CdTe and As+Cu doped CdSeTe/CdTe PV-devices.

Device type	V _{OC} (mV)	J _{SC} (mA/cm ²)	FF (%)	η (%)	N _A (cc ⁻¹)
As+Cu doped CdSeTe	804	29.8	71.2	17.07	3.1 x 10 ¹⁴
Cu doped CdSeTe/CdTe	850	27.8	79.3	18.76	7.8 x 10 ¹⁴

Figure 9.11 (a) and (b) further shows the SEM-EDS cross section profile of various elements done for thick Cu doped CdSeTe/CdTe and thin As+Cu doped CdSeTe/CdTe PV-device respectively. It was observed that Se was mainly concentrated in the front CdSeTe layer for the thick device, the thin device had a more diffused Se profile towards the back of the CdTe layer (see Se

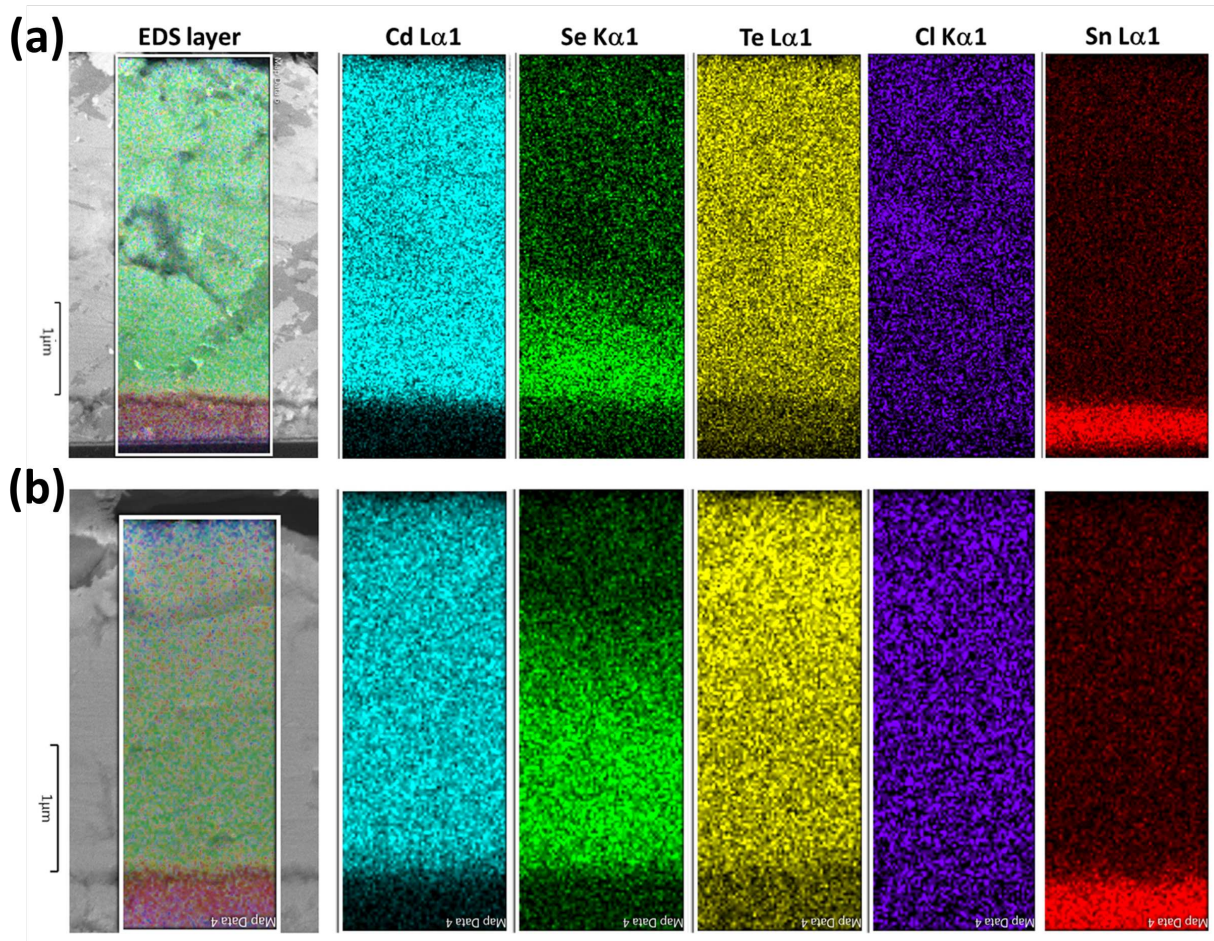


Figure 9.11: EDS profile showing the cross section of (a) copper doped CdSeTe/CdTe baseline PV-device, and (b) arsenic and copper doped CdSeTe/CdTe PV-device.

profile in figure 9.11 (a) and (b)). Such diffusion profile of Se at the back of CdTe layer would passivate the CdTe grain boundaries further improving the carrier lifetime while still leaving a thin CdTe layer at the back of the device for creating a better contact.

For the device parameters, while the open-circuit voltage of the thin device was lower than the thick device, thin device showed higher short-circuit current density (see table 9.4 and figure 9.10 (c)). This could be again explained from the SEM-EDS profiles as the thin device had more diffused Se content in the absorber leading to lower bandgap of the absorber. The carrier concentration vs depletion width curve showed that the depletion width of the copper only doped device is shifted toward the front of the device in comparison to the arsenic and copper doped device (see figure 9.10 (d)). This could be one of the potential reason for lower open circuit voltage measured

in the As+Cu doped thin CdSeTe/CdTe device. Nonetheless, the above results pave path for the future experiments where process parameters would need to be optimized to make high efficiency CdSeTe-only absorber devices.

Chapter 10

Summary and Future Work

An extensive literature review involving the understanding of DFT concepts and experimental progress made in the field of CdTe photovoltaics has been done. This has led to several thought provoking research questions mentioned in section 4.2. The answers to these questions will generate the fundamental understanding of the device efficiency improvements caused by CdCl₂ treatment and selenium alloying of CdTe absorber layer.

10.1 Summary

- **Q 1: How do structural and electronic features in bulk CdSe_xTe_{1-x} alloys modeled using LCAO basis set compares with those modeled using plane wave basis sets?**

Hypothesis: The bulk properties of CdTe binary alloy modeled using LCAO basis sets have matched well with the existing experimental and theoretical results. Therefore, the structural and electronic properties of bulk CdSe_xTe_{1-x} ternary alloy modeled using LCAO basis sets should also be in good agreement with the properties modeled using Plane wave basis sets.

Methodology: For the bulk CdSe_xTe_{1-x} alloy (with varying Se composition (x)), properties such as lattice parameters, band-gap values, and band-structure diagrams were calculated using LCAO based DFT-1/2 methods. The data generated in this study were then compared to the existing experimental and Plane wave basis set results. Such an approach ensured that the LCAO modeling parameters could be used to model the bulk properties of ternary CdSe_xTe_{1-x} alloys.

Key finding: The structural and electronic properties of the bulk CdSe_xTe_{1-x} structures modeled using LCAO basis sets in conjugation with DFT-1/2 correction scheme is in good agreement with the existing literature. The lattice parameter for both the Zinc-blende and the wurtzite phase follows the Vegard's law. The band-gap value yields a classical U-curve na-

ture with respect to the Se composition of the alloy. The band-structure diagrams further reveals shifts in the CBM with the changing Se composition in the $\text{CdSe}_x\text{Te}_{1-x}$ alloy as the main reason for change in the band-gap values.

• **Q 2: Are structural and electronic features of $\text{CdSe}_x\text{Te}_{1-x}$ surfaces like those of the CdTe surface?**

Hypothesis: The structural and electronic properties of CdTe surfaces have been shown to depend on the surface polarity and the termination layer. The surface relaxation of Cd-terminated CdTe(100) surface have shown the formation of surface Cd-dimers [4]. Similarly, a non-polar CdTe(110) shows an atomic chain tilt at the surface [59]. Also, the polar CdTe(111) plane orientation indicates that a (2×2) reconstruction of the CdTe(111) surface will be energetically favorable [4]. Previous DFT simulations done for unreconstructed polar CdTe(100) and (111) surfaces by Nicholson et. al. shows the presence of cusp feature in the surface VBM [4]. Since, $\text{CdSe}_x\text{Te}_{1-x}$ like CdTe is also a II-VI compound alloy, its surface structural properties in various orientations is expected to match to those of CdTe surfaces. With regards to the electronic properties, the polar $\text{CdSe}_x\text{Te}_{1-x}$ (111) and $\text{CdSe}_x\text{Te}_{1-x}$ (100) unreconstructed and reconstructed surfaces is expected to have a presence of hole charge transport aiding cusp-feature in the VBM as observed in CdTe polar surfaces. The non-polar $\text{CdSe}_x\text{Te}_{1-x}$ (110) surface is expected to give a flat energy band alignment diagram.

Methodology: The EDS characterization of the cadmium-selenium-telluride absorber grown with closed space sublimation have shown ~ 11 at.% of Se ($x \sim 0.22$) in the film. In order to match the experimental Se composition, bulk $\text{CdSe}_{0.25}\text{Te}_{0.75}$ was cleaved in simulation along three major low index surface viz. (100), (110), and (111) plane orientations. The study included an in-depth analysis of the geometrical and electronic properties observed in the unreconstructed and reconstructed Cd-terminated polar (100), (111), and non-polar (110) surfaces. The surfaces were relaxed and energy band alignment diagrams were calculated using the modeling parameters derived for bulk $\text{CdSe}_x\text{Te}_{1-x}$. The structural properties of the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface in all three low index plane orientation were compared to the existing

experimental and theoretical literature for CdTe surface. Further, the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface-energy band alignment was calculated via DFT-1/2 method. The $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface-energy band-alignment results were then compared with those of the CdTe surfaces. Such a procedure helped to get insights into how Se alloying of CdTe changes its geometrical and electronic surface properties.

Key finding: The DFT + SGF approach was applied to three principle low indexed $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface facets. The non-polar (110) surface facet due to a charge neutral surface generated a flat CBM and VBM. The polar (100) and (111) surfaces were studied with the Cd-termination layer. In general, the (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (100) and (111) unreconstructed surfaces showed the downward bending in the VBM. The resulting downward bend in the VBM was due to the positively charged surface as observed in the Mulliken population analysis. However, the $c(2 \times 2)$ and (2×2) reconstructed $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (100) and (111) surfaces result in the cleaner energy band diagrams with minimal surface states. The comparison between unreconstructed and reconstructed surfaces depicts the importance of different surface defects in their respective plane orientations.

Further comparison of the CdTe surface electronic features with those of $\text{CdSe}_{0.25}\text{Te}_{0.75}$ revealed the possible reason for lower performance of $\text{CdSe}_x\text{Te}_{1-x}$ -only devices observed experimentally. Earlier studies have shown the prominence of the additional cusp feature observed in the CdTe surface and CdTe/Te interface for hole carrier transport in CdTe PV-device. The absence of the cusp feature from $\text{CdSe}_{0.25}\text{Te}_{0.25}$ surface may lead to a lower device performance. These results also suggest the importance of including the CdTe layer at the back of $\text{CdSe}_x\text{Te}_{1-x}$ absorber for effective charge transport.

Overall, the atomistic modeling perspective of $\text{CdSe}_x\text{Te}_{1-x}$ surfaces provides insight into spatial distribution of the electronic features. A good understanding of the $\text{CdSe}_x\text{Te}_{1-x}$ surfaces would lead to a better comprehension of the different $\text{CdSe}_x\text{Te}_{1-x}$ interfaces and will help in further improving the device performance of II-VI absorber based solar cells.

• **Q 3: How does Se grading in CdTe absorber lead to an improved device performance?**

Hypothesis: Se is graded into the CdTe film from $\text{CdSe}_x\text{Te}_{1-x}$ due to the CdCl_2 treatment of the absorber layer [14]. Literature reports by *Fiducia et al.* and *GuO et al.* suggests that Se and Cl passivates the defect levels in the polycrystalline CdTe [31,60]. DFT analysis by *Li et al.* has revealed that chlorine occupies the Te sites at grain boundaries and causes an inversion from p-type absorber grain interior to n-type grain boundaries [22]. Such an inversion leads to electrostatic field between the grain and grain-boundary and helps in better extraction of the charge carriers. *Mhirech et al.* made similar observation, where a p-type absorber was inverted to n-type at the absorber/oxide interface [61]. It is thought of that the presence of high density of donor states at an interface will cause such an inversion [61, 62]. However, the mechanism elucidating the cause of inversion at the CdTe grain boundaries have not been identified yet. In this study, it is hypothesized that the Se alloying and Cl passivation of CdTe will lead to high density of donor states at the CdTe grain-boundary. The presence of high donor density should be the major cause of p-n type inversion at grain boundaries (as found in other published literature [61, 62]). Moreover, Se-alloyed, Cl-passivated CdTe grain-boundary should depict higher density of donor states (leading to higher p-n inversion) in comparison to Cl-passivated CdTe grain-boundary. The higher p-n inversion caused by alloying Se and Cl at the CdTe grain boundaries could be the main reason for high efficiencies observed in the Se-graded CdTe PV-devices.

Methodology: PV-devices based on three different conditions: untreated CdTe, CdCl_2 -treated CdTe, and CdCl_2 -treated $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ devices were fabricated to compare the respective performances in the unpassivated, Cl-passivated CdTe and Se-alloyed, Cl-passivated CdTe absorbers. Nano-SIMS characterization was performed on CdCl_2 -treated $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ films to understand the Se and Cl atomic distribution at the CdTe grain boundaries. Further, EBSD analysis of the CdTe surface formed the basis of selecting a particular atomistic grain-boundary model. Four CdTe grain-boundary models: bare (no Cl or Se), Cl alloyed, Se-alloyed and Se and Cl alloyed were studied to understand the effect of Se and Cl atoms

on the electronic properties of the CdTe grain-boundary. The elemental concentration profile for Se, Cl atoms were based on the existing literature [21, 22, 31] and the nano-SIMS characterization performed in this study. First principle simulations based on DFT-1/2 methods were utilized to calculate the electronic properties such as energy band alignment results, existence of defect states in the bare, Cl alloyed, Se-alloyed and Se and Cl alloyed CdTe grain boundaries. The defect states were further characterized using the Mulliken population analysis. The characterization and quantification of the grain-boundary defect states calculated using first-principle techniques explained the defect passivation mechanisms in the CdCl₂-treated CdSe_xTe_{1-x}/CdTe PV-devices. Such an approach further aided in comprehending the PV-device performance fabricated with varied absorber conditions.

Key finding: The device performance parameters of the untreated CdTe, CdCl₂-treated CdTe, and CdCl₂-treated CdSe_xTe_{1-x}/CdTe PV-devices were compared. Nano-SIMS characterization of highly efficient CdSe_xTe_{1-x}/CdTe devices reveals the atomic distribution of the selenium and chlorine atoms. While chlorine was found to be concentrated in the CdTe grain boundaries, selenium atoms were found to diffuse into CdTe grains via the grain-boundary regions. The surface EBSD analysis of the CdTe film showed various grain orientations forming distinct grain-boundary regions from which a random CdTe(110)/(100) grain-boundary was chosen for the atomistic modeling. Various CdTe(110)/(100) grain-boundary models including the bare, Cl_{Te} alloyed, and Se_{Te} + Cl_{Te} alloyed CdTe grain-boundary were simulated. The energy band alignment and the defect state properties evaluated using DFT calculations aids in deducing the mechanism for highly efficient CdSe_xTe_{1-x}/CdTe absorber based PV-devices. The presence of selenium and chlorine atoms passivates the acceptor level defect states and induces high density of donor states. The passivation of acceptor defect states reduces the recombination while the high density donor states leads to n-type inversion at the grain-boundary. The inversion from p-type grain interior to n-type grain-boundary enhances the minority charge carrier collection, leading to a higher open-circuit voltage and short-circuit current density observed in highly efficient CdSe_xTe_{1-x}/CdTe PV-devices.

- **Q 4: Why does a polycrystalline $\text{CdSe}_x\text{Te}_{1-x}$ absorber-based double heterostructure have a higher minority charge carrier lifetime than polycrystalline CdTe based heterostructure?**

Hypothesis: Characterization techniques such as Time-Resolved Photoluminescence (TRPL) has been used to report that CdCl_2 -treated polycrystalline $\text{CdSe}_x\text{Te}_{1-x}$ absorber/Alumina based double heterostructure has higher carrier lifetime in comparison to the CdTe absorber/Alumina based double heterostructure [21,63]. A higher minority charge carrier lifetime would imply less carrier recombination in the bulk $\text{CdSe}_x\text{Te}_{1-x}$ and $\text{CdSe}_x\text{Te}_{1-x}$ /Alumina interface than its CdTe counterpart. It could be theorized that Se alloying of CdTe would lead to defect passivation in the $\text{CdSe}_x\text{Te}_{1-x}$ grain boundaries, making $\text{CdSe}_x\text{Te}_{1-x}$ a better bulk material than CdTe. Furthermore, the insights gained from the double heterostructure results could also be thought of as less defect state assisted charge carrier recombination should occur at the $\text{CdSe}_x\text{Te}_{1-x}$ /Alumina interface in comparison to CdTe/Alumina interface.

Methodology: CdCl_2 -treated $\text{CdSe}_x\text{Te}_{1-x}$ /Alumina and CdTe/Alumina double heterostructures (het.) have been fabricated, and TRPL measurements were done to determine the minority charge carrier lifetime by colleagues at Colorado State University and the National Renewable Energy Lab [41, 63]. Atomistic models of the $\text{CdSe}_x\text{Te}_{1-x}$ grain-boundary with Cl distribution (from nano-SIMS), $\text{CdSe}_x\text{Te}_{1-x}$ /Alumina and CdTe/Alumina interfaces were simulated to evaluate the electronic properties of various interfaces. The defect characterization was done using the methods described in Chapter 7. It was found that alumina by itself does not passivate the CdSeTe interface. The literature was investigated to understand the $\text{CdSe}_x\text{Te}_{1-x}$ /Alumina interface. It was found that native TeO_x is formed at the absorber/oxide interface [90]. Therefore, native TeO_x was incorporated in the atomistic simulation to study its effect on the electronic properties of the $\text{CdSe}_x\text{Te}_{1-x}$ /Alumina interface. The learning from the atomistic modeling was further incorporated in the fabrication of CdTe PV-devices to make high efficiencies undoped CdSeTe/CdTe solar cells.

Key finding: The DFT-based simulations indicated that grain boundaries were passivated better in the bulk CdSeTe than in the bulk CdTe absorber. For the double heterostructures, it was found that both CdSe_{0.25}Te_{0.75}/Al₂O₃ and CdTe/Al₂O₃ interface had high density of defect states at the interface. Moreover, the presence of Al₂O₃ does not appear to bend the bands in either the CdTe or CdSe_{0.25}Te_{0.75} absorbers. This suggested the absence of any field passivation effect in the DHs. However, literature has suggested the formation of native TeO_x in between the absorber/oxide interface. Inclusion of the monolayer of native TeO_x in between CdSe_{0.25}Te_{0.75}/Al₂O₃ showed pasivation of defect states at the interface which further indicated chemical passivation at the absorber/oxide interface. The combination of defect-passivated CdSeTe grain boundaries and interfaces explained higher lifetimes in the CdSeTe DHs. Further, based on the literature and the above results, PV-devices were fabricated with TeO_x and Al₂O₃ back contact layers. It was found that devices with Al₂O₃ back contact layer had higher series resistance and lower device performance than the devices that had TeO_x back contact. While the devices with Al₂O₃ back contact layer were 0.5% efficient, TeO_x devices showed efficiencies of 18.9% and were comparable to standard copper doped PV-devices. The high efficiencies with TeO_x back passivation layer is a potential candidate to replace the copper doping in the CdTe PV-device and could further increase the stability of CdTe solar cells.

- **Q 5: How does the CdSe_xTe_{1-x}/Te-interface energy band alignment compare to that of the CdTe/Te interface?**

Hypothesis: It has been observed experimentally that CdSe_xTe_{1-x}-only absorber based PV-devices shows lower performance than CdTe-only solar cells [55]. Nicholson et. al have previously reported the presence of hole charge carrier transport aiding cusp feature in CdTe surfaces and CdTe/Te interface [4]. Based on the CdSe_{0.25}Te_{0.75} surface energy band alignment obtained to answer Q2 and work done by *Nicholson et al.*, it could hypothesized that the absence of cusp of feature in the VBM of CdSe_{0.25}Te_{0.75} surface will translate to CdSe_{0.25}Te_{0.75}/Te interface. A higher density of defect states is also expected at the

CdSe_{0.25}Te_{0.75}/Te interface leading to high charge carrier recombination and therefore overall lower PV-device performance in CdSe_xTe_{1-x}-only absorber based PV-devices.

Methodology: DFT simulations were performed on CdSe_{0.25}Te_{0.75}/Te interface using the modeling parameters identified for Cd, Se and Te atoms in earlier studies. The electronic properties of CdSe_{0.25}Te_{0.75}/Te interface were calculated for various doping level of the CdSe_{0.25}Te_{0.75} layer. The energy-band-alignment results calculated for CdSe_{0.25}Te_{0.75}/Te interface were compared with those available for CdTe/Te interface. Based on the insights gained from DFT simulations of CdSe_{0.25}Te_{0.75}/Te interface, PV-devices were fabricated with different doping conditions. However, it was found that CdSeTe-only absorber based devices with various doping conditions still gave lower solar cell efficiencies. Various experiments such as TEM-EDS, SEM-EDS, UPS, atomistic modeling and device characterization methods were employed to understand the cause of high efficiencies in CdSeTe/CdTe bilayer absorber based PV-devices. Such an approach helped to comprehend the electronic properties of CdSeTe/CdTe PV-devices, and solar cells mimicking the CdSeTe-only absorbers were fabricated with comparable device performance to CdSeTe/CdTe bilayer PV-device.

Key finding: Electronic properties of the CdSe_{0.25}Te_{0.75}/Te interface calculated using DFT showed a high density of defect states at the interface. It was found that higher p-doping of the CdSe_{0.25}Te_{0.75} layer would create an electron reflector effect and could mitigate the charge carrier recombination at the CdSe_{0.25}Te_{0.75}/Te interface. Based on this, arsenic doped CdSeTe-only devices were fabricated and compared to copper-doped CdSeTe/CdTe bilayer devices. It was found that arsenic-doped CdSeTe-only device had high carrier concentration of 10¹⁶/cm³ in comparison to 10¹⁴/cm³ for copper doped CdSeTe/CdTe devices. However, the CdSeTe-only devices despite of the high carrier concentration showed poor device efficiency while the copper doped CdSeTe/CdTe bilayer gave devices above 18.5%. Further analysis of CdSeTe/CdTe interface was done to understand the role of CdTe in the high efficiency bilayer absorber based devices. Atomistic models based on TEM-EDS profile were simulated to calculate the electronic properties at the CdSeTe/CdTe interface in the three

major orientations. Energy-band-alignment results showed an electron reflector effect at the CdSeTe/CdTe interface and was also verified experimentally using UPS technique. Devices were then fabricated with lower band-gap absorbers followed by different high band-gap absorbers in the stack. It was found that open-circuit voltage values tracked the bandgap of the back absorber layer, while short circuit current density tracked the band-gap of the front absorber material. It was hypothesized that since selenium alloying of CdTe passivates the defect states, bare CdTe would still be needed to make better back contact. In view of this, thin CdSeTe/CdTe devices were fabricated with a new process recipe that showed that selenium diffuses towards the back of CdTe while still leaving thin CdTe layer for contacting. The thin CdSeTe/CdTe gave an efficiency of 17%, which is one of the highest observed till date. Further optimization of the process is needed to improve the efficiencies of CdTe PV-devices beyond 20%.

10.2 Future Work

Selenium alloying of CdTe absorber has improved the efficiency of CdTe PV-devices. The findings of this work establishes the passivation effect of selenium and explains the improved device performance observed in the selenium alloyed CdTe PV-devices. This work also demonstrates that high efficiency can be achieved in the undoped CdTe PV-devices by passivating the back surface with tellurium oxide. Based on the learnings gained from this research work, following things could be tried in the future:

- More work needs to be done to further understand the effect of tellurium oxide as the back passivation layer. Stability testing of the devices with for the undoped CdTe devices with tellurium oxide back layer is also recommended.
- Based on the results from this work and other literature, it is recommended to fine tune the fabrication process parameters for thin CdSeTe/CdTe PV-devices forming CdSeTe-only absorber based devices to improve the efficiency of CdTe solar cells beyond 20%.

- Usage of higher band-gap material behind the low band-gap absorber has shown to create an electron reflector effect and improves the open-circuit voltage of the devices. Therefore, CdTe PV devices with new materials (such as $\text{Cd}_x\text{Zn}_{1-x}\text{Te}$) having band-gaps higher than CdTe absorber should be fabricated to realize an improvement in the open-circuit voltage.
- On the atomistic modeling side, machine learning could also be used to simulate large models. The larger models simulated using an amalgamation of the machine learning and DFT methods would lead to better convergence of the bulk like properties while still calculating useful interface properties.
- Machine learning in conjunction with DFT atomistic modeling should also be used to calculate the electronic properties of new interfaces such as CdTe/ZnTe, CdTe/ NiO_x , and other possible passivating layers. This would generate an advance understanding of the interface electronic properties based on which devices could be fabricated to improve the efficiencies of the CdTe solar cells beyond 20%.

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