

DISSERTATION

A STUDY OF OXIDE CDTE INTERFACES FOR CDTE PHOTOVOLTAICS USING ATOMISTIC
MODELING

Submitted by

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ABSTRACT

A STUDY OF OXIDE/CDTE INTERFACES FOR CDTE PHOTOVOLTAICS USING DENSITY FUNCTIONAL THEORY

Solar photovoltaics (PV) has undergone a dramatic transformation over the past few decades and is now a widespread electricity generation source. Among currently existing PV technologies, the thin film sector led by cadmium telluride is the most promising. Cadmium Telluride (CdTe) PV has experienced unprecedented growth and is now a major commercial player. However, the field has a few challenges to overcome until it reaches its full potential.

The focus of this study is the interface between the CdTe-based absorber and the front window layer. Traditionally, cadmium sulfide has been used as the window layer in such devices. At the Next Generation Photovoltaics (NGPV) center in Colorado State University, superior devices have been demonstrated using magnesium zinc oxide ($\text{Mg}_x\text{Zn}_{1-x}\text{O}$ or MZO) as the window layer. This is attributed to the larger bandgap of MZO causing a pickup in the current and the open circuit voltage. A magnesium to zinc atomic ratio of 23:77 has shown optimal performance characteristics. Alloying CdTe with Se to form cadmium selenium telluride ($\text{CdSe}_x\text{Te}_{1-x}$ or CST) has resulted in further improvements. One way to determine the quality of an interface is to study the electronic band alignment at that interface. Existing band alignment models show only limited features and hence there is a need for a more sophisticated approach to investigate complex characteristics.

This study uses atomistic modeling based on Density Functional Theory (DFT) to investigate certain structural and electronic properties of the oxide and the oxide/absorber

interface. The technique solves for electronic structures of materials based on electron density and predicts the structural properties of materials to a high degree of accuracy. Electronic characteristics are determined using a semi-empirical method known as DFT-1/2. A mathematical formulation called Green's Function (GF) has been incorporated within the model to simulate device structures. The bulk properties of MZO such as lattice constant, band gap, band edges and electron effective mass are established and compared to experiment. Following this, the band alignment at the MZO/CdTe and MZO/CST interfaces is determined, along with band offsets and interface states. The influence of chlorine in the deposition process is also investigated. This work is the first of its kind to study the oxide-CdTe and oxide/CST interfaces using DFT+GF and provides new insights into the electronic characteristics at the interface. Bulk properties of the MZO match experimental reports. Termination chemistry plays a significant role in the band bending and in the presence of defect states at the oxide/absorber interface. Calculations indicate that a Mg/Zn-Te interface is energetically preferred, with experimental reports pointing to the same. Moreover, varying the magnesium composition in the MZO alloy affects the magnitude of the band offsets. The interface band alignment results are close to those seen experimentally. A small amount of chlorine may help alleviate interface defect states by chemical passivation, possibly due to the removal of dangling bonds.

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TABLE OF CONTENTS

ABSTRACT.....	ii
ACKNOWLEDGEMENTS.....	iv
LIST OF TABLES.....	x
LIST OF FIGURES.....	xi
Chapter 1 – Introduction.....	1
1.1 Solar energy as of today.....	1
1.2 Thin Film Solar Cells.....	3
1.2.1. Cadmium Telluride Photovoltaics.....	3
1.2.2. Challenges Facing CdTe Photovoltaics.....	4
1.3 Future of Solar Power.....	5
Chapter 2 – Front contacts in CdTe solar cells.....	7
2.1 Band Alignment Terminology.....	7
2.2 Cadmium Sulfide.....	8
2.3 Oxides.....	9
2.3.1. Transparent conducting Oxide.....	10
2.3.2. Zinc Oxide.....	11
2.3.3. Magnesium Zinc Oxide.....	12

Chapter 3 – Theoretical models to describe band alignment.....	16
3.1 Background.....	16
3.2 Research Questions and Hypotheses.....	17
3.3 First Principles Calculations.....	21
3.4 Atomistic Modeling.....	21
3.4.1. Density Functional Theory.....	21
3.4.2 Band gap corrections.....	25
3.4.3 Hubbard U Correction.....	25
3.4.4 DFT – $\frac{1}{2}$ Correction.....	26
3.4.5 Green’s Function.....	29
Chapter 4 – Bulk calculations.....	31
4.1 CdTe.....	31
4.1.1 Methods.....	31
4.1.2 Results.....	33
4.2 MgZnO.....	36
4.2.1 Methods.....	36
4.2.2. Results.....	37
4.2.3 Gallium doped MZO.....	53

Chapter 5 – Interface simulations.....	55
5.1. ZnO/CdTe.....	55
5.1.1 Methods.....	55
5.1.2 Results.....	59
5.2. MZO/CdTe.....	62
5.2.1 Methods.....	62
5.2.2 Results.....	62
5.3 Effect of Chlorine.....	75
5.4 MZO/CdSeTe Interface Simulations.....	80
5.4.1 Methods.....	80
5.4.2 Results.....	81
Chapter 6 – Conclusions and Future work.....	83
6.1 Research Questions, Hypotheses and Results.....	85
6.2 Future work.....	87
Bibliography.....	88
Appendices.....	96
Appendix A: Optical Measurements for CdS and MZO	96
Appendix B: UPS band measurements of various oxides deposited on FTO	97
Appendix C: 1-D Modeling baseline parameters used for SCAPS simulation of HRT and window material property effects.....	98
Appendix D: DFT Comparison with Expt.....	99

Appendix E: k-point Convergence.....	101
Appendix F: MZO Band Parameters (NOGO).....	102
Appendix G: MZO Bandgaps and Density of States (NOGO).....	103
List of Abbreviations and Symbols.....	108

LIST OF TABLES

1.	CdTe Structural (variable-cell) Relaxation.....	34
2.	CdTe bulk parameters.....	35
3.	Comparison of calculated lattice parameters for w-MZO using GGA and LDA.....	38
4.	w-MZO c/a ratios.....	39
5.	c-MZO lattice constants.....	40
6.	ZnO bulk parameters.....	41
7.	Mg _{0.25} Zn _{0.75} O bulk parameters.....	41
8.	w-MZO band gaps.....	42
9.	c-MZO band gaps.....	45
10.	MZO electron effective masses m_e	46
11.	GMZO Lattice constants and band gaps.....	54
12.	Average electronic charge on atomic layers at the interface (O-Cd termination).....	61
13.	Average electronic charge on atomic layers at the interface (Mg/Zn-Te termination)	61
14.	Average electronic charge on atomic layers at the interface (Mg/Zn-Te termination)	65
15.	Average electronic charge on atomic layers at the interface (O-Cd termination).....	67
16.	Band gaps and band offsets at the MZO/CdTe interface.....	70
17.	Band Gaps and Band Offsets For The MZO-Cl-CdTe Interface.....	79

LIST OF FIGURES

1.	System size vs. cost per watt for different types of solar.....	1
2.	Installed capacity of solar power (MW) in China, US, Germany, and Japan.....	2
3.	Projected solar PV, wind, and storage technology capacities.....	5
4.	Band alignment diagrams and J-V curves for oxide/CdTe interfaces with varying electron affinity.....	7
5.	Band alignment in a TCO/CdS/CdTe solar cell.....	8
6.	Energy band diagram of a generic TCO/buffer/absorber (p-type)/back contact heterojunction solar cell with the front interface, depletion region, quasi-neutral region, and back-contact interface.....	10
7.	Current-voltage characteristics comparison of CdS/CdTe and MZO/CdTe solar cells on the left and the structure of the MZO/CdTe solar cell on the right.....	13
8.	A comparison of the TRPL lifetimes of charge carriers in MZO/CST/Al ₂ O ₃ and Al ₂ O ₃ /CST/Al ₂ O ₃	14
9.	Dark field TEM and EDX showing the elemental composition at the MZO/CdTe interface.....	15
10.	Band alignment for oxide/CdTe based on electron affinity.....	17
11.	Experimental result of band alignment at the MZO/CdTe interface (Mg/Zn-Te termination).....	18
12.	Termination chemistries at the ZnO/CdTe interface.....	18
13.	Illustration of defect states at the MZO/CdTe interface.....	19

14.	Device performance with and without CdCl_2 (left); presence of Cl at the MZO/CdTe interface from NanoSIMS (right).....	20
15.	Comparison of band gaps of elemental and III-V semiconductors as predicted by DFT and DFT-1/2.....	28
16.	Performance of DFT functionals.....	29
17.	Illustration of a CdTe unit cell.....	32
18.	Total energies of SC, BCC and FCC lattices of CdTe.....	33
19.	Lattice constant of CdTe using GGA-PBE functional.....	33
20.	Band structure of CdTe using GGA and GGA-1/2.....	35
21.	Binding energy of CdTe using GGA-PBE functional.....	35
22.	Models showing wurtzite and rocksalt MZO.....	36
23.	Wurtzite MZO lattice constants.....	37
24.	Wurtzite MZO c/a ratio.....	39
25.	Rock salt MZO lattice constants.....	40
26.	Band structure of ZnO using GGA and GGA-1/2.....	41
27.	Band structure of MZO using GGA and GGA-1/2.....	41
28.	Wurtzite MZO band gaps.....	42
29.	Wurtzite MZO valence and conduction band edges.....	43
30.	Wurtzite MZO band parameters.....	43
31.	Wurtzite MZO electron effective masses.....	44
32.	Rock salt MZO band gaps.....	44
33.	Rock salt MZO valence and conduction band edges.....	45
34.	Rock salt MZO electron effective masses.....	46

35.	Wurtzite MZO band structures.....	47
36.	Rock salt MZO band structures.....	48
37.	Wurtzite MZO Density of States.....	49
38.	Rock salt MZO Density of States.....	51
39.	ZnO contribution of orbitals to DOS.....	53
40.	GMZO DOS.....	54
41.	Illustration of the CdTe 111 plane, ZnO 002 plane and the number of atoms in the interface plane vs. initial strain state.....	56
42.	A model of the ZnO/CdTe interface built using QuantumATK.....	57
43.	The ZnO/CdTe device structure built using the two-probe model in QuantumATK.....	58
44.	Density of states at the ZnO/CdTe interface.....	59
45.	The MZO/CdTe interface depicted using QuantumATK.....	62
46.	The MZO/CdTe device structure built using the two-probe model in QuantumATK.....	62
47.	Density of electronic states at the MZO/CdTe interface.....	63
48.	Band alignment at the Mg/Zn-Te terminated MZO/CdTe interface for different Mg percentages.....	64
49.	Band alignment at the O-Cd terminated MZO/CdTe interface for different Mg percentages.....	66
50.	Conduction band offsets for CdTe devices employing MZO of different magnesium concentrations using SCAPS.....	69

51.	PLDOS image, device configuration and Mulliken charge analysis for MZO/CdTe.....	70
52.	PLDOS image, device configuration and Mulliken charge analysis for MZO/Cl/CdTe.....	71
53.	A comparison of atomistic modeling, experimental and SCAPS results for the MZO/CdTe interface.....	73
54.	Grain orientation of CdTe and MZO using Electron Backscatter Diffraction (EBSD).....	74
55.	Effect of CdCl ₂ treatment on CdTe devices and NanoSIMS showing the presence of chlorine at the MZO/CdTe interface.....	76
56.	Illustration of the MZO/CdTe interface with Cl.....	78
57.	Illustration of the MZO/CdTe device configuration for with Cl.....	78
58.	MZO/CdTe band alignment for different Cl concentrations.....	79
59.	Illustration of the MZO/CdTe interface.....	80
60.	Band alignment at the MZO/CST interface.....	81
61.	Band alignment at the MZO/Cl/CST interface.....	82
62.	Dependence of band alignment on termination chemistry (MZO/CdTe).....	85
63.	Dependence of band alignment on termination chemistry (MZO/CdTe).....	86
64.	Dependence of defect states on termination chemistry (MZO/CdTe).....	86
65.	Effect of Cl on band alignment features of the MZO/CdTe interface.....	87

CHAPTER 1. INTRODUCTION

1.1 SOLAR ENERGY AS OF TODAY

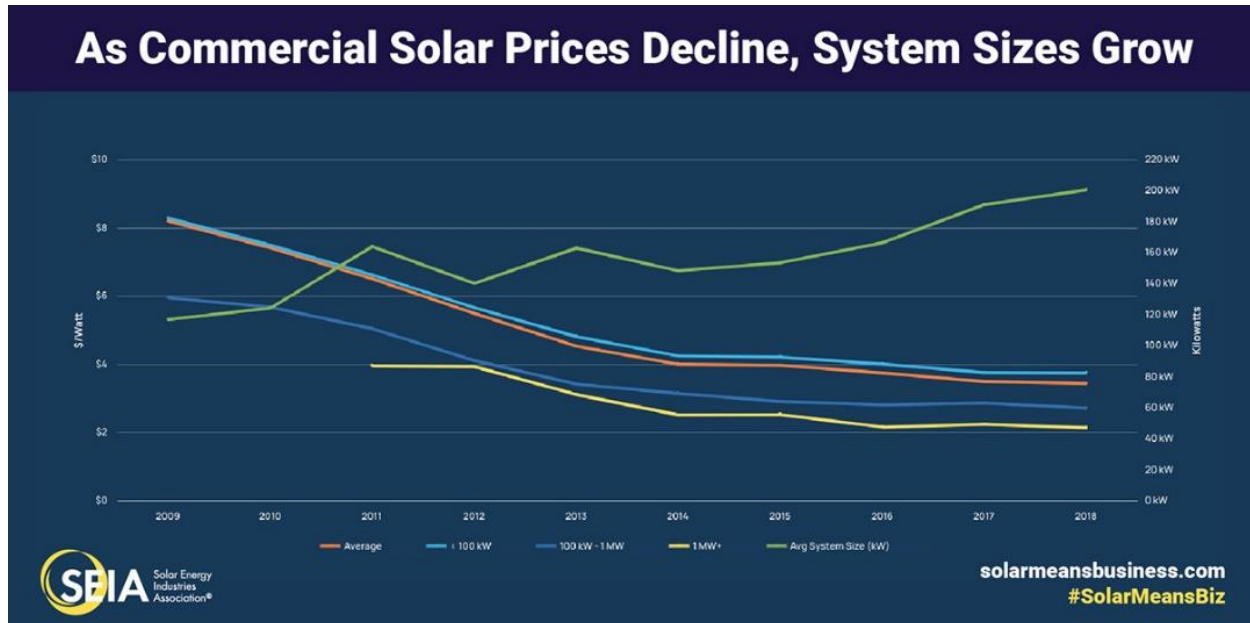


Fig. 1. System size vs. cost per watt for different categories of solar [1].

From merely a research ideology and a vision of the future, solar cells, specifically photovoltaics (PV), have grown to become a significant part of the energy equation today. A 2017 Lazard report shows that thin film utility scale solar PV is cheaper than all forms of conventional energy and cost competitive with wind power [2]. The popularity of solar photovoltaics (PV) can be explained in several ways. It can be powered by an abundant, free, and renewable fuel source, the sun. It possesses a low environmental impact due to minimal carbon emissions that are produced mostly during the manufacturing of parts. The technology has shown good performance and reliability as well as low maintenance costs mainly from the lack of moving parts. Photovoltaics has seen increased penetration due to these reasons but perhaps their least well-known asset is their economic feasibility, especially in large scale power projects. In fact, as of today, PV is already much cheaper than many other conventional energy sources such as coal and

natural gas. Even in the renewables sector, solar PV is rapidly gaining ground on wind in terms of installation capacity in the US, largely due to lower costs. Moreover, the combination of solar energy and storage is also approaching the threshold of the cheaper forms of energy such as coal and natural gas. Additionally, system costs reduce as size increases as shown in the graph in Figure 1. above.

A lot of this credit goes to improving cell efficiencies, which have exceeded 22% and 18.5% for small cells and modules respectively [3,4]. Apart from tweaking the process, the improvement in efficiencies comes also from a better understanding of the mechanism involved in the solar cell physics. Researchers are getting ever closer to the Shockley-Queisser limit that has been established for each type of solar material.

Lower costs are fueled not only by dropping module costs, but also by the lower expenses associated with integrating panels into a new structure such as a house or an office building. This is reflected in the number of solar PV installations in major economies which has been growing rapidly as shown in the chart below.

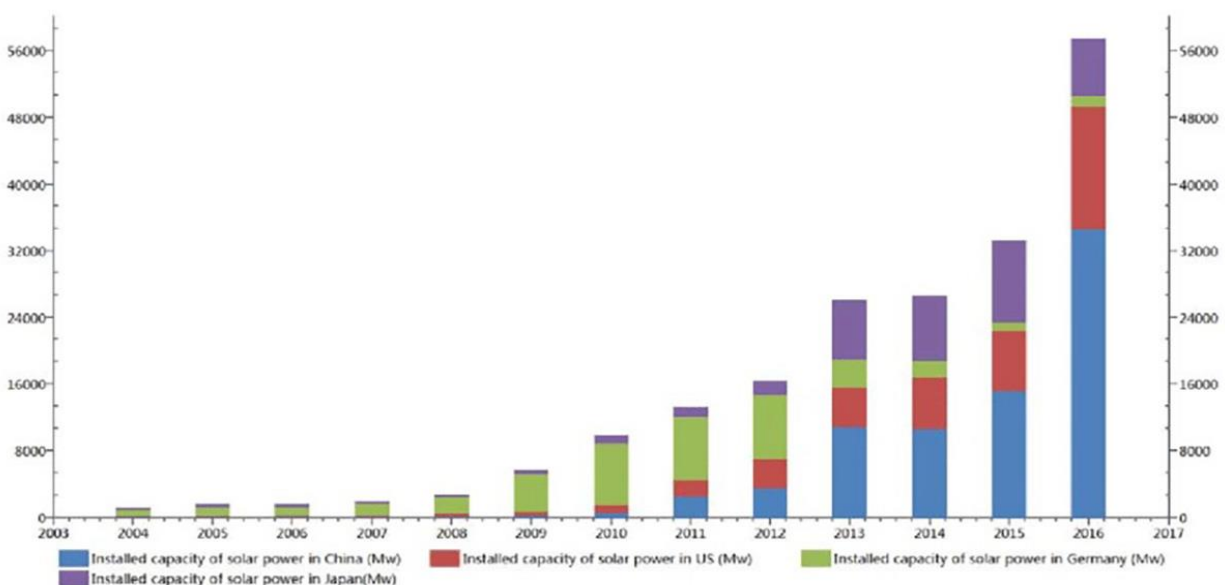


Fig.2 Installed capacity of solar power (MW) in China, US, Germany, and Japan [5]

Although a lot of these modules are imported, typically from Asia, a fair share of them are manufactured in the US and this capacity has also been steadily increasing. Locally in the US, both PV module supply and demand have been rising fast over the last few years fueled by lower costs and higher performance.

1.2 THIN FILM SOLAR CELLS

Silicon is the most common solar cell material in use today. However, silicon solar cell power conversion efficiencies (PCEs) have plateaued for quite some time now. Another disadvantage facing silicon is that it is an indirect band gap material, meaning that it requires several hundred micrometers for enough light to be absorbed to generate carriers and collect current [6]. Thin film solar cells on the other hand, need only a few microns of material for good absorption of the solar spectrum and as a result, they have been gaining ground over silicon at a steady pace over the last few years. Thin films consist of solar cell technologies such as CdTe, CIGS (Copper Indium Gallium Selenide), organics and perovskites and have seen huge boosts in device performances and show potential to reach high power conversion efficiencies.

1.2.1 CADMIUM TELLURIDE PHOTOVOLTAICS

While the other thin film technologies possess questionable stability, chalcogenides do not have such a problem. CdTe in particular, seems to be the most promising class of materials due to several factors; They not only possess high Shockley-Quiesser efficiency limits but also have a lot of potential to reach these values; they have demonstrated the capability for high throughput and ease of large-scale manufacturing [7]; they perform better in harsh environments. In fact, CdTe

solar cells have shown lesser degradation in hot and humid conditions than their silicon counterparts [8].

Most of this local production is led by the CdTe solar cell technology pioneered by First Solar. Within this realm, cadmium telluride (CdTe) solar cells have attracted the attention of the solar research community, as they hold a lot of promise in terms of performance improvement. A part of this evolution comes from its ease of manufacturing; the fabrication of CdTe requires a material purity of 99.999%, which is fairly easy to achieve with current technology; impurities that are found in the cell usually originate from other cell components or the fabrication process itself [9].

Thin films – especially CdTe and its alloys – are expected to play a major role in the development of multi junction systems. At the Next Generation Photovoltaics Center (NGPV) at Colorado State University (CSU), Power Conversion Efficiencies (PCEs) around 20% have been demonstrated and multi junctions are a part of the center's vision for the future. Despite these recent developments, challenges remain.

1.2.2 CHALLENGES FACING CDTE PHOTOVOLTAICS

For all the advances in the field, CdTe photovoltaics is not without its challenges. It is not only bulk characteristics of CdTe that play a critical role; the contacting layers need to be compatible with the absorber in order to extract maximum performance. The back interface also impacts device performance through its ability to draw holes from the absorber. Different materials such as molybdenum oxide have been used as back contact materials [10]. Tellurium has also been tested with CdTe and its effect is being pursued in other closely related works [11]. The third area

of concern is related to the interface between CdTe and the front contact which is the focus of this dissertation. The following are some of the challenges faced by the community [12,13,14,15]:

- The ability to p-dope CdTe, which has historically been challenging, even though the naturally occurring Cd vacancies provide a slight p-type character.
- Presence of defects primarily caused by Cd vacancies and Te at Cd sites.
- A voltage barrier that has plateaued for a few years, partially due to the difficulty in anion doping and low hole density.
- Low lifetimes limited to the order of a few nanoseconds and carrier concentrations of around 10^{14} cm^{-3} on the absorber side.
- Carrier recombination at the grain boundaries due to small grain size, especially in the transport direction
- Low current generation at the front interface mostly due to low absorption of light by the transparent conducting oxide (TCO) layer and/or window layer (traditionally cadmium sulfide) and due to interfacial recombination.
- A poor back contact caused by a mismatch in work function between CdTe and the metal contact.

1.3 FUTURE OF SOLAR POWER

A forecast by Green Tech Media (GTM) has solar installations increasing exponentially over the next few decades and projected to exceed wind by the year 2050. Storage technologies are also forecast to grow steadily. This is shown in the image below.

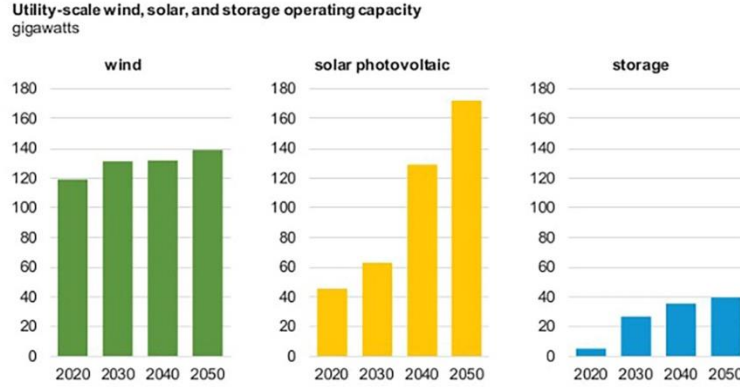


Fig. 3. Projected solar PV, wind and storage technology capacities [16]

Future growth in solar photovoltaics involves not only optimizing existing processes but also exploring new and upcoming technologies. These include but are not restricted to increasing the solar spectrum absorption creating multi junctions, maximizing quantum efficiency by incorporating quantum dots and several other techniques.

However, only refining experimental techniques may not suffice. Computer simulations can now be performed to determine many properties and assist in the development of devices such as transistors and diodes accurately. Such methods are currently being implemented by corporations and academic institutions across the globe and have also been extended to solar cells. Specifically, atomistic modeling techniques can help understand the behavior of many state-of-the-art devices as the latter have undergone miniaturization to a remarkable degree. The ability of such models to describe and predict the properties and behavior of modern-day devices stems from the fact that they involve a microscopic approach that classical methods ignore.

CHAPTER 2. FRONT CONTACTS IN CDTE

2.1. BAND ALIGNMENT TERMINOLOGY

Increasing oxide electron affinity

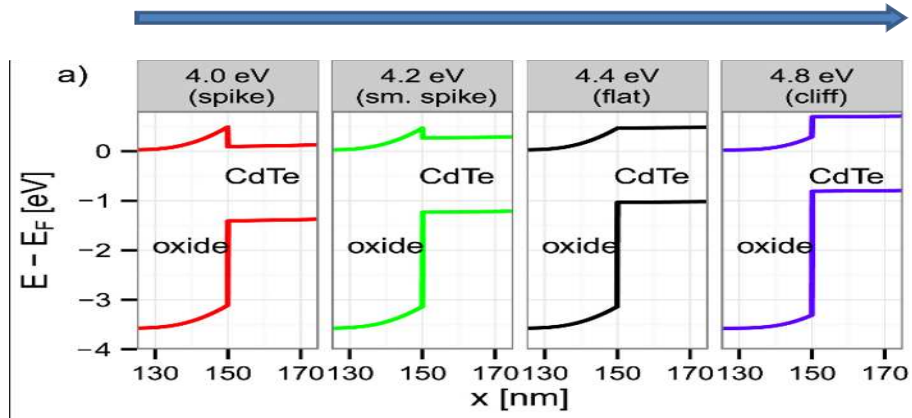


Fig. 4a. Band alignment diagrams for oxide/CdTe interfaces with varying electron affinity [17]

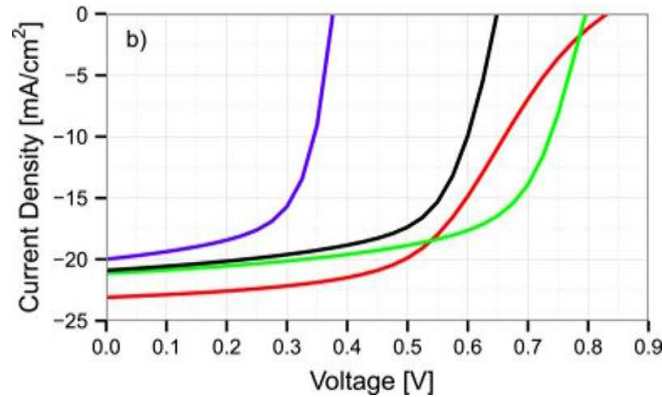


Fig. 4b. J-V curves for devices using oxide/CdTe interfaces with varying electron affinity [17]

Fig. 4a. represents window and absorber band alignments, in this case, for oxide and CdTe layers [17]. A cliff (blue) is formed when the conduction band of the oxide is lower than that of the absorber. This alignment seems to benefit the minority carriers traveling from the CdTe to the oxide because of the drop in the CB. However, it reduces the available open circuit voltage and

can also encourage recombination of such carriers, which is detrimental to the device, as seen in Fig. 4b. A flat band alignment (black) results when the CB levels of both materials are comparable. This reduces band to band recombination and increases the open circuit voltage slightly.

A small spike (green) is formed when the CB of the window layer is slightly higher than that of the absorber. This is considered the most ideal alignment since it results in very low recombination while also retaining open circuit voltage. At the same time, minority carriers moving from the absorber to the oxide require very little energy to climb the small hill which is the spike. This energy (<0.4 eV) is often available at room temperature [18]. On the far end of the spectrum, a large spike (red) is obtained when the CB of the oxide is much higher (≥ 0.4 eV) than that of the absorber. Even though this alignment retains the same open circuit voltage and minimizes carrier recombination, the electrons traveling from the CdTe to the oxide face a significant barrier. This reduces overall current flowing through the device, hampering its efficiency.

2.2. CADMIUM SULFIDE

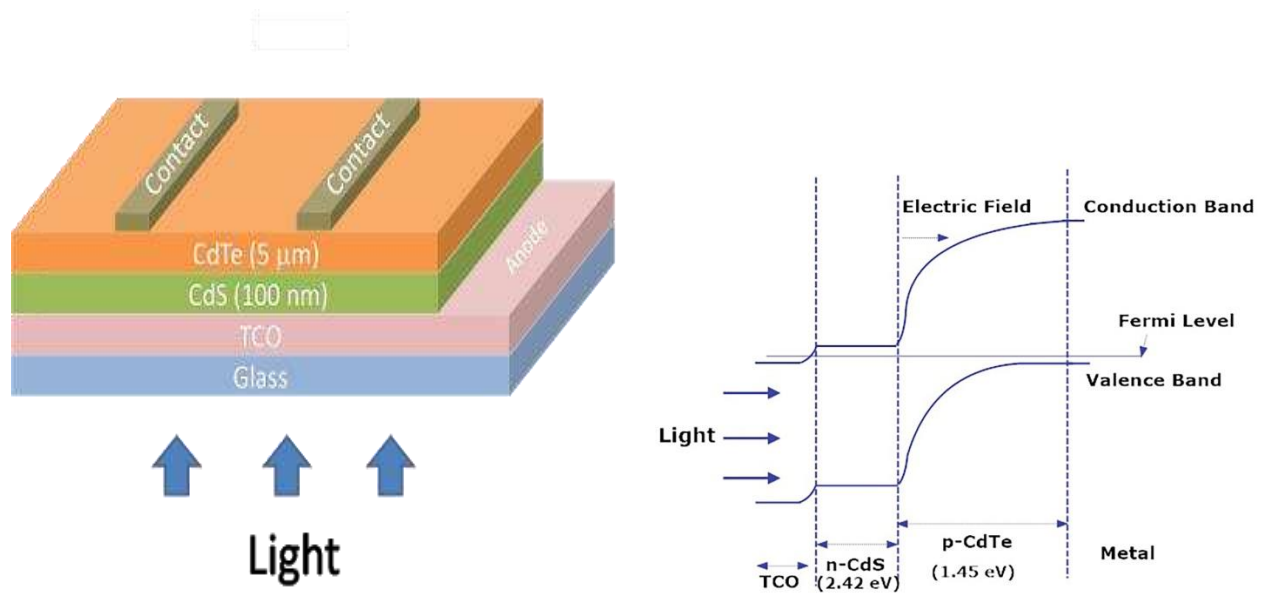


Fig. 5. Band alignment in a TCO/CdS/CdTe solar cell [19]

A wide variety of materials have been tested as front contacts in CdTe photovoltaics. One such semiconductor that garnered some interest was cadmium sulfide (CdS) which has historically been the preferred material of choice as a window layer in CdTe PV research. It possesses a higher direct bandgap (2.42 eV) than CdTe, allowing more of the solar spectrum to pass through it and eventually into the absorber layer. The band alignment at the interface between CdS and CdTe is shown in the figure below.

Despite its advantages, this II-VI material has its drawbacks. The values of open circuit voltage and short circuit current still fell short of their theoretical or maximum potential (Shockley Queisser limit) because the CdS layer does not transmit enough of the light onto the CdTe layer. CdS absorbs a lot of blue photons, leaving a smaller amount of the spectrum to be used by the absorber [20]. The result was a maximum power conversion efficiency of 17% [21]. This makes such cells fall short of their potential, specifically by limiting short circuit current, thus requiring materials with a higher band gap – and lower absorption – to be explored.

2.3. OXIDES

Many decades ago, oxide layers were found to be beneficial for the silicon solar cell, one of the oldest and easily the most prevalent PV technologies. The silicon research community faced challenges with efficiencies plateauing at 17% during the 1970s, despite the theoretical maximum being close to 30%. Thermally grown oxide layers used in the 1980s helped boost the efficiency of these cells to greater than 20%, largely due to a higher V_{OC} resulting from higher passivation [6]. This was after the formation of a beneficial native silicon oxide layer was observed on the surfaces of these cells, prompting their use in photovoltaics – both silicon and thin films.

2.3.1 TRANSPARENT CONDUCTING OXIDE

Transparent conducting oxide (TCO) – undoped or doped – can be coated directly on glass substrates and contacted with CdTe and many attempts were made at such a configuration. The work done by Tursun et al. has shown that high efficiencies can be achieved from such a setup [22]. However, in most cases, this configuration has an unfavorable band alignment with the CdTe and often results in a very low output voltage. The conduction band offset, although favorable from an electron transport point of view, does not maximize the built in potential available due to high interface carrier recombination. A high bandgap window layer was required for more absorption of light and thus subsequent transmission into the CdTe absorber layer.

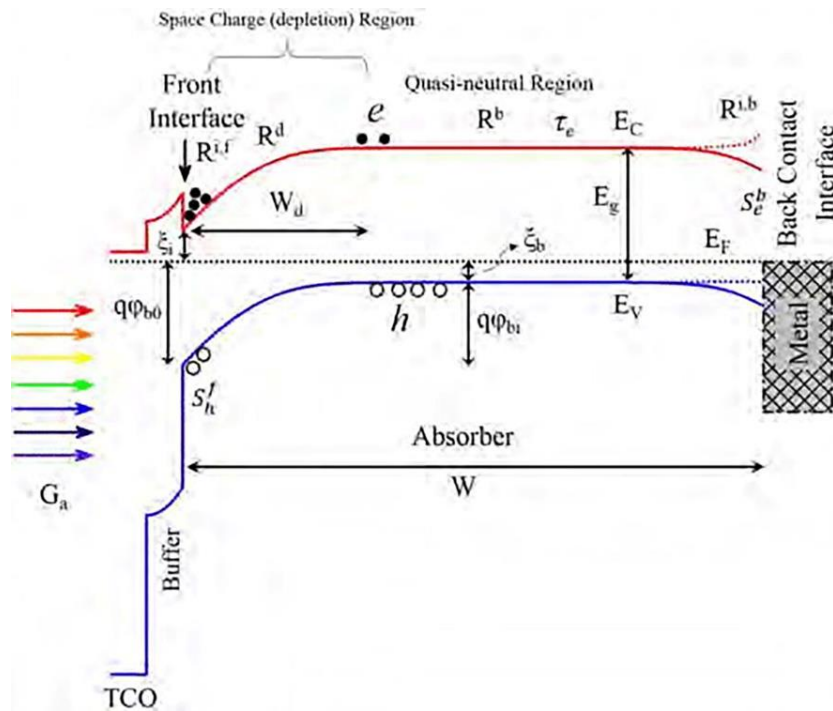


Fig. 6. Energy band diagram of a generic TCO/buffer/absorber (p-type)/back contact heterojunction solar cell with the front interface, depletion region, quasi-neutral region, and back-contact interface [23].

2.3.2 ZINC OXIDE

One class of materials that possess relatively large band gaps are oxides. Moreover, oxides have been a success story in the silicon solar industry which had endured an uphill battle for a long time. Power conversion efficiencies plateaued at around 17% PCE for more than a decade while the Shockley Queisser limit, is around 29%. The next improvements that caused the efficiency to breach the 20% mark were due to increased output voltage from better passivation of electronic activity [6]. On further investigation, it was known that the native silicon dioxide (SiO_2) that formed on the atomic semiconductor was benefitting the device performance by inadvertently passivating the dangling bonds present at the silicon surface. Previous manufacturing attempts had tried to get rid of this oxide layer which proved to be a blessing in disguise.

Naturally, the same idea found its way into the field of thin film photovoltaics and eventually into CdTe research. ZnO was one such a hopeful oxide material. It has a band gap (3.3 eV) much larger than CdS and has been used in other types of solar cell research such as organic PV, both as conventional thin films and as nanorods [24]. It has been known to possess good electron transport properties, although a lot of those depended on how the ZnO was grown. Some experiments even focused on inserting ZnO between the TCO and CdS layers to reduce the voltage barrier and noticed increased power conversion and quantum efficiency [25]. Other literature sources point to the highly resistive ZnO being able to suppress front contact carrier reflection and thus reflective losses [24]. ZnO is also known to possess a better band alignment with CdTe than with CdS. Still, cell parameters were far from the potential limit, again largely due to a restricted band gap and its quantum efficiency at lower wavelengths leaves a lot to be desired. There was a need to push this value even higher.

2.3.3 MAGNESIUM ZINC OXIDE

The ZnO band gap can be increased by adding a certain amount of magnesium to the lattice, yielding the ternary Magnesium alloyed Zinc Oxide ($\text{Mg}_x\text{Zn}_{1-x}\text{O}$, MgZnO or MZO). In addition to lower absorption (higher transmittance), this material has the added advantage of a tunable band gap at low Mg concentrations. Experiments regarding changing magnesium concentration in MZO have been of keen interest for at least twenty years. A series of experiments performed by Minemato et. al. [26] studied the properties of MZO. By varying the ratio of magnesium, they were able to tune the band gap of the alloy ranging from 3.24 eV to 4.20 eV. The upside of this process was that the lattice constants did not change by much. Moreover, for up to about 46% magnesium concentration, the lattice preserved its hexagonal form. Only at higher percentages were a mix of different lattice types seen. They reported that the crystal structure of MZO remained wurtzite up to a magnesium concentration of 46% while the cubic phase began at 62% Mg. Alloys with Mg compositions between the above-mentioned percentage range were a mix of both phases. This work was further validated by Kumar et al. and Reddy et al. in the same decade [27, 28]. Experiments involving MZO as the window layer sandwiched between the FTO and CdTe, thus replacing CdS were performed at the Next Gen Photovoltaics (NGPV) Center in Colorado State University. Work on MZO was initiated by Jason Kephart who fabricated some CdTe devices using the same. Ultraviolet Photoelectron Spectroscopy (UPS) measurements were used to determine band offsets for different oxide/CdTe interfaces, and a comparison was made with SCAPS modeling [29]. It was found that a magnesium ratio of 23% was found to give optimum results in CdTe devices in terms of device performance. This increase was the result of more current generated from higher absorption and a higher open circuit voltage (V_{oc}) largely caused by the greater band gap. This is shown in the illustration below.

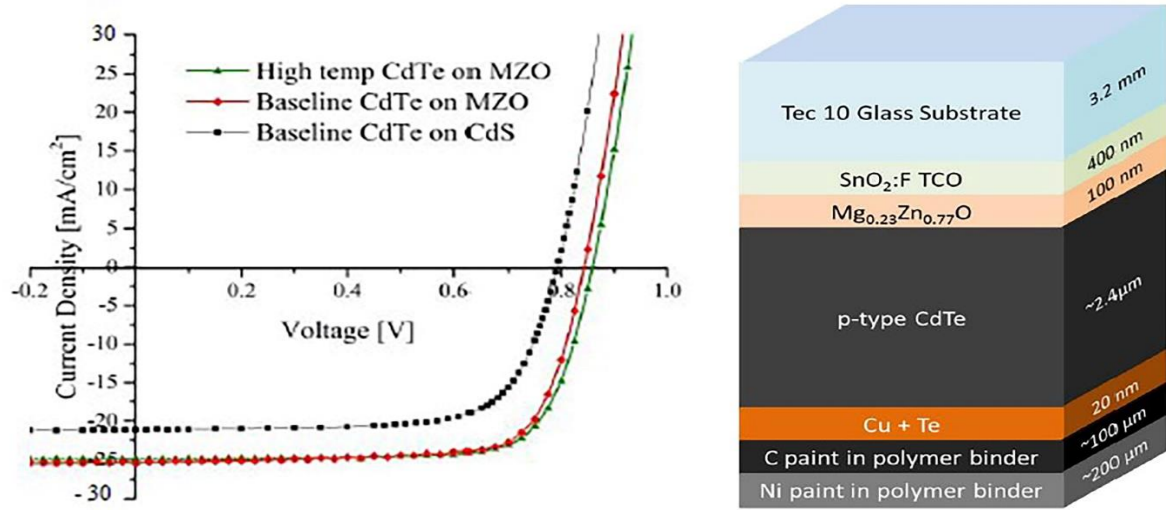


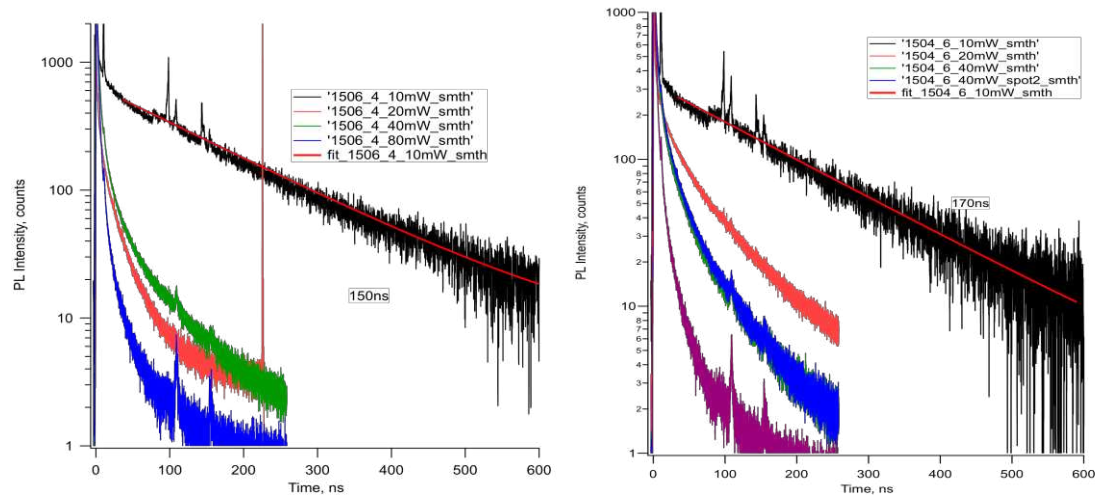
Fig. 7. Current-voltage characteristics comparison of CdS/CdTe and MZO/CdTe solar cells on the left and the structure of the MZO/CdTe solar cell on the right [30]

It is postulated that another reason for the success of MZO is its favorable band alignment with CdTe. MZO, with a lower electron affinity and higher band gap value than ZnO creates a spike in the conduction band. Moreover, the device performance is the best with the small spike, although the available short circuit current is lower. Still, this configuration produces the best J-V curves with reasonable fill factor and no kink or rollover as with higher Mg content (and thereby lower electron affinity). However, the lattice mismatch between CdTe and MZO is greater than 11% which is higher than the CdS/CdTe case [29]. The fact that a higher amount of mismatch produces a better performing device raised more questions than answers and prompted further investigation into the MZO/CdTe interface.

Another alloy that has proven effective is CdSe_xTe_{1-x} or CST which has increased the available short circuit current without losing open circuit voltage [31,32]. Although CST only devices showed lower performance, a combination of CST and CdTe have yielded higher efficiencies. More recently, the incorporation of a graded CST layer has further improved device

parameters. Although the complex methodology of graded CST is not studied in this work, related exercises have involved them. However, simulations containing a fixed ratio of Se in the CST alloy have been performed and the results have been analyzed.

One of the motivations for this experiment derives from the fact that CST possesses extremely high carrier lifetimes comparable to those for CST/ Al_2O_3 interface. This was demonstrated by a technique called Time Resolved Photoluminescence (TRPL) measurement performed at the National Renewable Energy Laboratory (NREL) for devices fabricated at CSU and are illustrated in the figure below.



100 nm MZO/2.5 μm CST/100 nm Al_2O_3	100 nm MZO/3.1 μm CdTe/100 nm Al_2O_3
100 nm Al_2O_3 /3 μm CdTe/100 nm Al_2O_3	100 nm Al_2O_3 /3.4 μm CST/100 nm Al_2O_3

Fig. 8. A comparison of the TRPL lifetimes of charge carriers in MZO/CST/ Al_2O_3 and Al_2O_3 /CST/ Al_2O_3

None of these materials would be as effective as they are without the CdCl_2 treatment, which has been a major boon for CdTe photovoltaics. It is hypothesized that the chlorine alleviates defects present in the cell, mostly at grain boundaries and interfaces. This mechanism is assumed to occur through passivation of dangling bonds, thereby minimizing interface electronic states.

CdCl_2 has been observed to segregate preferentially at the grain boundaries and interfaces through Scanning Electron Microscopy (SEM) and Tunneling Electron Microscopy (TEM) techniques as shown in the diagram below [30].

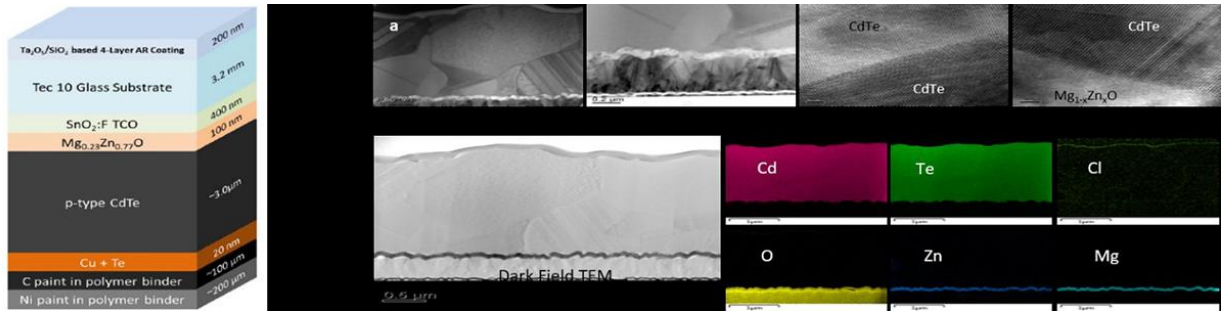


Fig. 9. Dark field TEM and EDX showing the elemental composition at the MZO/CdTe interface

CHAPTER 3. THEORETICAL MODELS FOR BAND ALIGNMENT

3.1 BACKGROUND

The Anderson model is a popular method to describe band alignment at interfaces. However, this model considers the two bulk material properties before the interface has formed. In a practical situation, some atomic rearrangement would be expected to happen at the interface, at least for a few monolayers on each side. This may cause band gaps at the interface to change while also introducing defect states within the band gap. These states could be caused due to interfacial strain states when the second material is deposited on top of the first. Several factors could influence the way the atoms rearrange themselves such as the thickness of each layer, the lattice mismatch between the two materials and the temperature profile of the deposition process. In the case of CdTe deposited on MZO, the latter could undergo some rearrangement since it is only around 100 nm thick, whereas the CdTe absorber thickness is in the order of a few microns. The first few atomic layers of CdTe could conform to the material below it, thereby introducing some strain. In real world conditions, this is probably a combination of the above cases, and capturing these properties will need to involve a more sophisticated approach. The technique will have to consider the strain induced at the interface in both surfaces. Hence, atomistic modeling is used to study the oxide interfaces in CdTe solar cells to understand some of their characteristics.

3.2 RESEARCH QUESTIONS AND HYPOTHESES

The proposed research questions regarding the MZO/CdTe interface are:

1. What is the band alignment at the interface between the ZnO/CdTe and MZO/CdTe from atomistic modeling?
- Hypothesis: band alignment is determined by the electron affinity values

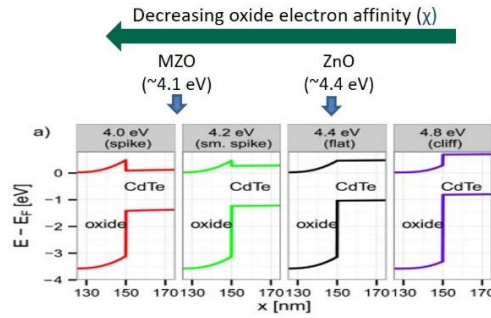


Fig. 10. Band alignment for oxide/CdTe based on electron affinity

Based on electron affinity values (χ), ZnO/CdTe will have a flat conduction band (since $\chi_{\text{CdTe}} = \chi_{\text{ZnO}}$) while MZO/CdTe will have a spike (since $\chi_{\text{CdTe}} > \chi_{\text{MZO}}$). Moreover, it has also been experimentally proved by Duncan et al using a combination of characterization techniques that a flat conduction band forms at the MZO/CdTe interface, shown below [33].

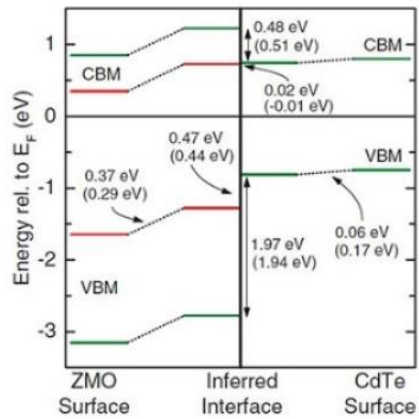


Fig. 11. Experimental result of band alignment at the MZO/CdTe interface (Mg/Zn-Te termination)

2. How does interface termination/chemistry affect band alignment?
- Hypothesis: Termination (O-Cd or Mg/Zn-Te) should exhibit similar band alignment characteristics since the valences of the cation and anion atoms are the same. Following literature references, only anion-cation terminations were considered since terminations with opposite polarities are expected to have lower energy due to lesser like-charge repulsion.

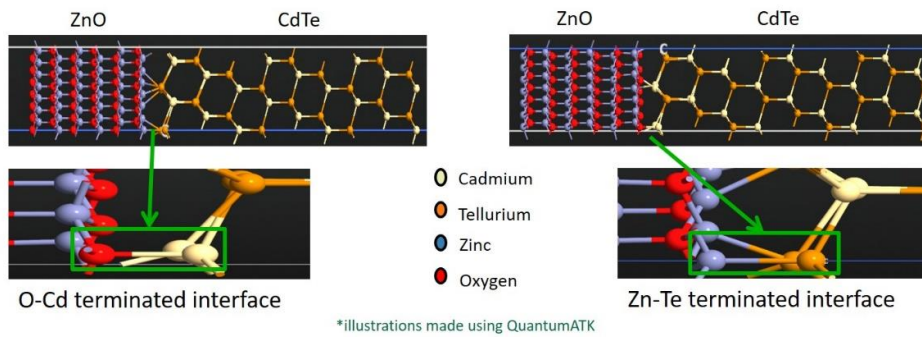


Fig. 12. Termination chemistries at the ZnO/CdTe interface

3. Are defect states present at the MZO/CdTe interface?
- Hypothesis: Defect states are likely to exist irrespective of termination. Defect states are primarily caused due to:
 1. lattice mismatch between the bulk materials
 2. dangling bonds
 3. change in bond lengths
 4. net charge at the interface
 5. difference in electronegativity of the different atoms
 6. presence of electrically charged species.

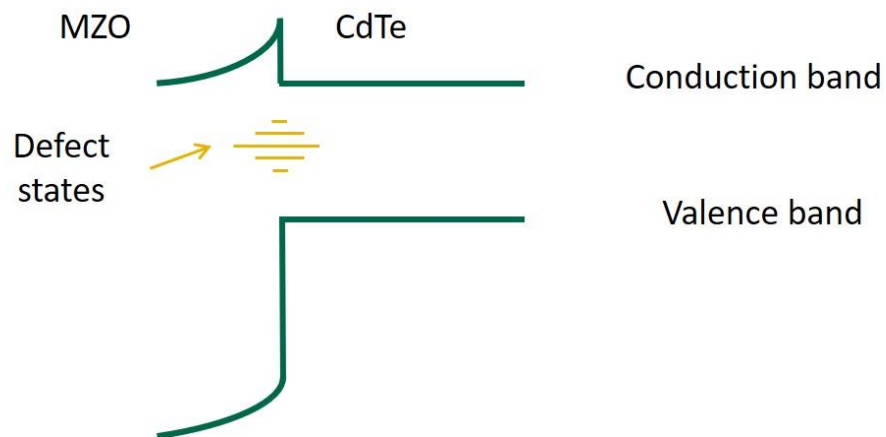


Fig. 13. Illustration of defect states at the MZO/CdTe interface

4. How will chlorine modify the band alignment features at the MZO/CdTe interface?
- Hypothesis: Chlorine is expected to passivate the interface and alter band bending. Cadmium chloride treatment has a remarkable effect on J-V characteristics. Chlorine has been observed at interfaces and GBs as seen in the figure below.

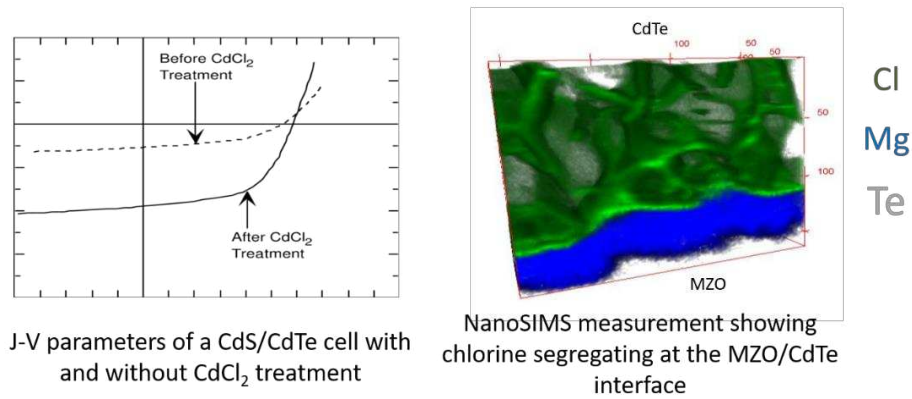


Fig. 14. Device performance with and without CdCl₂ (left); presence of Cl at the MZO/CdTe interface from NanoSIMS (right)

3.3 FIRST PRINCIPLES CALCULATIONS

Ab initio or first principles calculations have been an instrumental tool in capturing many details that simpler models neglect. Since there is no fitted data, these calculations are considered accurate, albeit time consuming. But with the state-of-the-art computational resources available today, these simulations can be performed much faster than many processing or fabrication experiments, thereby providing pointers that dictate such experiments. Not only do such simulations accurately reflect experimental parameters, but they also lessen the chances of a failed or bad experiment, thereby saving valuable time and resources in the process.

3.4 ATOMISTIC MODELING

1-D modeling tools can be very useful to simulate multiple device structures or configurations in a short duration, as opposed to determining performance solely using experimental methods. They often save time and can also act as a guideline for experimental runs. However, they rely on postulates like the Anderson rule for band alignment which can often be very theoretical in nature, not painting an accurate picture of atomic scale phenomena. This is where atomistic modeling using ab initio concepts is very useful. The technique follows a bottom-up approach where no empirical data is fitted to any of the results obtained. They are a result of a series of calculations that use known universal physical constants.

3.4.1 DENSITY FUNCTIONAL THEORY

Density Functional Theory (DFT) is a modeling method that uses electron density to calculate the ground state energy of electrons of a system, from which many other properties may be derived [34]. The method begins with an initial estimate of the electron density from which the

ground state energy is calculated. The density is recalculated from the energy numerically until the difference between the two electron energies or densities lies within a specified threshold value after a certain number of iterations. Such a calculation is said to be converged and one that does not satisfy this condition is un-converged. This process is called a Self-consistent Field (SCF) calculation. It is standard procedure to use only converged results in publications or presentations, or even to extract meaningful results. From the resulting ground state energy configuration, it is possible to calculate other properties such as lattice constants, band gaps, bulk moduli, and density of states (DOS). It has become a widely popular to validate, explain and even predict material properties and behavior using DFT. While the study of bulk materials (point and line defects, grain boundaries etc.) has become ubiquitous, interfaces have not garnered as much attention. This is even more so in the case of thin film photovoltaics, especially CdTe. DFT in its original formulation, even though successful for many situations, is not accurate in some scenarios.

Density Functional Theory is based on the Kohn-Hohenberg theorems which consist of two parts [34, 35]. The first theorem states that “the ground state of any interacting many-particle system with a given fixed inter-particle interaction is a unique functional of the electron density”. In other words, “The ground-state energy from Schrodinger’s equation is a unique functional of the electron density” [36]. The second component states that “A universal functional for the energy $E[n]$ can be defined in terms of the density. The exact ground state is the global minimum value of this functional”. This method too has proved vastly successful in the world of physics, chemistry, and materials sciences. The field has come a long way since it was originally developed by Kohn and Sham. It started out as a series of approximations to the Schrodinger wave equation, which can be solved exactly for a single electron system such as a hydrogen atom or a helium ion. However, when multiple electrons are involved, approximations need to be made to arrive at a

solution. Nowadays, numerical methods are employed by computers to do this. The Kohn-Sham equation forms the basis for DFT, and a description of the steps involved to arrive at the will require extensive mathematical treatment of the subject. A flavor is presented below. This excerpt is taken from the self-consistent equations developed by Kohn and Sham which form the basis for DFT [34].

The non-relativistic Schrodinger equation in the Born-Oppenheimer approximation is described as:

$$\hat{H}\psi = E\psi$$

Where E is the electronic energy,

$\psi = \psi(x_1, x_2, \dots, x_n)$ is the N-electron wave function

And

$$\hat{H} = \sum (-1/2) \nabla_i^2 + \sum v(r_i) + \sum \sum (1/r_{ij})$$

Where $v(r_i)$ is the external potential acting on electron i

$$V(r_i) = -\sum Z_\alpha / (R_\alpha - r_i)$$

The ground state energy of an interacting homogeneous electron gas in a static potential $v(r)$ is:

$$E = \int \frac{1}{2} \frac{v(r)n(r)}{|r - r'|} dr dr' + G[n]$$

Where G is a functional of the electron density and is written as:

$$G[n] = T[n] + E_{xc}[n]$$

Where $T[n]$ = kinetic energy of a system of non-interacting electrons

And $E_{xc}[n]$ is the exchange correlation energy which is given by:

$$E_{xc}[n] = \int n(r) E_{xc}(n(r)) dr$$

The ground state energy subject to the condition

$$\int \delta n(r) dr = 0,$$

The one-particle Schrodinger equation:

$$\left\{ -\left(\frac{1}{2}\right) \nabla^2 + [\varphi(r) + \mu(n(r))] \right\} \psi(r) = \varepsilon \psi(r)$$

Can be solved by setting

$$n(r) = \sum |\psi(r)|^2$$

Once solved self-consistently where $n(r)$ is determined by assuming a starting value of $n(r)$, the energy is given by:

$$E = \sum \varepsilon - \frac{\left(\frac{1}{2}\right) \int \int n(r) n(r') dr dr'}{r - r'} + \int n(r) [\varepsilon(n(r)) - \mu(n(r))] dr$$

If exchange effects are included, then the above equation becomes:

$$E = \sum \varepsilon - \frac{\frac{1}{2} \int \int n(r) n(r') dr dr'}{|r - r'|} + \frac{\left(\frac{1}{2}\right) \int \int n(r, r') n(r', r) dr dr'}{|r - r'|} + \int n(r) \{ \varepsilon(n(r)) - \mu(n(r)) \} dr$$

This can be regarded as a Hartree-Fock method for correlation effects.

For a system of non-interacting electrons in an effective potential $\varphi + \mu$, the solution is determined by the following equation:

$$\left\{ -\left(\frac{1}{2}\right) \nabla^2 + [\varphi(r) + \mu(n(r))] \right\} \psi(r) = \varepsilon \psi(r)$$

With $\mu(n)$ replaced by an effective one-particle potential v_{xc} defined as:

$$v_{xc}(r) = \delta E_{xc}[n] / \delta n(r),$$

The exact total energy is then given by:

$$\sum \varepsilon - \frac{\left(\frac{1}{2}\right) \int \int n(r)n(r')drdr'}{|r-r'|} + E_{XC}[n] - \int v_{xc}(r)n(r)dr$$

3.4.2 BAND GAP CORRECTION

Although traditional DFT methods can be used to predict a lot of material properties such as lattice constants and bulk moduli, there are severe limitations in computing the electrical properties such as band gaps. This has inspired the development of other formulations or extensions recently to bridge these shortcomings. Some of them include corrective methods such as DFT+U (Hubbard U) or semi-empirical additions such as DFT – 1/2 which provide remarkable results which are shown in the illustration below. These methods can be viewed as minor annexures but the basic essence of DFT remains largely unchanged. DFT can predict mechanical properties like lattice constants and bulk moduli accurately but has been known to severely underestimate band gaps. To arrive at a bandgap close to the experimental value, semi-empirical methods are used. One such scheme called the Hubbard U correction can be used to optimize the Coulomb interaction potential (U) [37]. DFT-1/2 uses the half-occupation technique to correct for self-energy and consequently the band gap [38, 39].

3.4.3 THE HUBBARD U CORRECTION

The additive Hubbard U Hamiltonian can be mathematically expressed as [38]:

$$H_{Hub} = t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma} c_{j,\sigma} + h.c.) + U \sum_i n_{i,\uparrow} n_{i,\downarrow}$$

Where c_i , c_j , and n_i are electronic creation, annihilation, and number operators for electrons of spin on site i , respectively.

3.4.4 DFT – ½ CORRECTION

This is a semi-empirical method for improving band gaps by correcting for the Kohn-Sham eigenvalues around the top of the valence band and the bottom of the conduction band. As a result, it is suitable for determining band gaps, but not properties such as total energy. It is obtained by adding an atomic self-energy potential that attempts to correct the self-interaction error by canceling the electron hole self-interaction energy. This potential is the difference between the potential of a neutral atom and that resulting from the removal of a fractional electronic charge from the finite system (e.g. unit cell). In other words, the Kohn-Sham potential is replaced by a modified potential given by [40]:

$$V_{\text{mod-KS}}(r) = V_{\text{KS}}(r) - V_{\text{S}}(r)$$

Where $V_{\text{mod-KS}}(r)$, $V_{\text{KS}}(r)$ and $V_{\text{S}}(r)$ are the modified Kohn-Sham potential, the Kohn-Sham potential and the correction or the self-energy potential respectively. The last “correction” term is calculated through a trimming process defined by:

$$\theta(r) = A \left[1 - \left(\frac{r}{r_{\text{cut}}} \right)^n \right]^3, r \leq r_{\text{cut}}$$

$$\theta(r) = 0, r > r_{\text{cut}}$$

Where r_{cut} is determined variationally,

$$n = 8,$$

$$A = 1.$$

When $r_{\text{cut}} = 0$, this reflects a standard DFT calculation. The suffix “-1/2” is derived from the corrective potential which mimics the Slater half-occupation scheme. The self-energy potential

for each atom is the difference between the Kohn-Sham potential for the neutral atom and that of the half-ionized atom. The shell to be ionized gives rise to the valence band.

DFT-1/2 has its roots in the Janak theorem, which refers to the derivative of the total energy with respect to occupation. This equals the Kohn-Sham eigenvalue. This theorem is applicable when the derivative is linear with the occupation. The half-occupation technique was first used for atoms, later in molecules and clusters, and finally in extended systems such as crystals. Since removing half an electron from an infinite system is not considered perturbation, a special handling is required.

The self-energy is the difference between the ionization energy and the eigenvalue and the Self Interaction Correction (SIC) is half this value. The SIC has been verified numerically.

The half-ion technique is formulated as:

$$\frac{\partial E}{\partial f_{\alpha}} = e_{\alpha}(f_{\alpha})$$

Where f_{α} = occupation of the Kohn-Sham eigenstate.

e_{α} = KS eigenvalue dependent on the occupation

$E(f_{\alpha})$ = total energy of the atom or ion

The proof for this equation is exact for LDA and is also likely to be valid for GGA.

Integrating the above equation from the ion to the atom,

$$E_{\dot{\alpha}}(0) - E_{\dot{\alpha}}(-1) = \int_{-1}^0 \frac{\partial E}{\partial f_{\alpha}} df_{\alpha} = \int_{-1}^0 e_{\alpha}(f_{\alpha}) df_{\alpha} = e_{\dot{\alpha}}(-1/2)$$

The precision of this technique is usually better than 0.1 eV.

A slightly poorer approximation is:

$$\frac{e\dot{\alpha}(0) + e\dot{\alpha}(-1)}{2}$$

There is no explanation for a physical meaning of this technique.

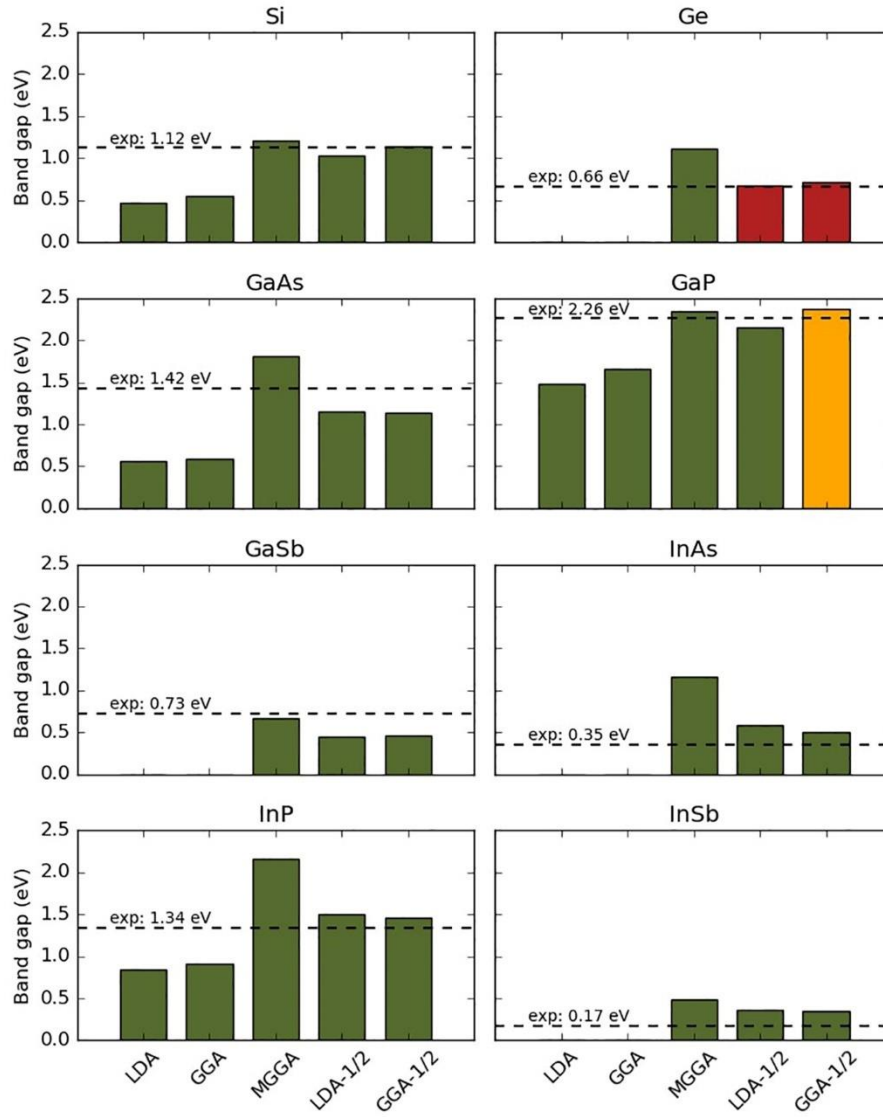


Fig. 15. Comparison of band gaps of elemental and III-V semiconductors as predicted by DFT (LDA, GGA, MGGA) and DFT-1/2 (LDA-1/2, GGA-1/2) [41]

Performance of DFT functionals

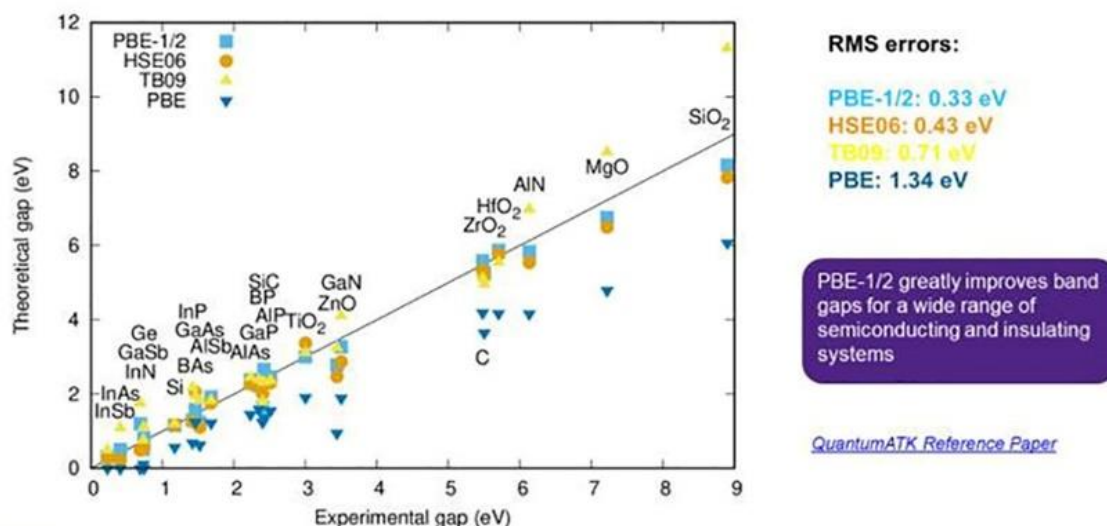


Figure 16. Performance of DFT functionals

An illustration of band gaps for some III-V semiconductors using different DFT schemes is shown in figure 10. Figure 11 displays the band gap results that have been extended to also include some II-VI semiconductors using the same methods. More about those schemes is discussed in the following sections.

3.4.5 GREEN'S FUNCTION (GF)

Traditional DFT packages use the slab model to examine interfaces, but such calculations are long and hard to perform. The most common way to study interfaces has been the slab model which involves building an interface between the two materials and introducing a vacuum on both sides along the transport direction or perpendicular to the interface plane. The atoms in all three coordinate axes are repeated infinitely. However, such a model has limitations. The slab must be made long enough for the bulk material properties to converge along the transport direction. This means that the system needs to consist of a larger number of atoms, making the process

computationally expensive. An alternate method that incorporates a mathematical parametrization called Green's Function (GF) can be used to obtain faster and more accurate results and is a great asset for interfaces [42]. More recently, these methods have been used to study more complex systems such as interfaces. This method involves matching chemical potentials of the respective materials and providing a mathematical formulation to model the system in such a way that the number of atoms along the transport direction are finite. The model now consists of two semi-infinite electrodes (infinite only on either the positive or negative axis in the transport direction) and a finite central region which does not repeat along the transport direction. Along the planes perpendicular to the transport direction (or parallel to the interface plane) however, the system is repeated infinitely in both the positive and negative axes. This method instantly yields better results in terms of convergence of the simulation, the accuracy of results obtained as well as the computational expense involved.

CHAPTER 4. BULK CALCULATIONS

4.1. CDTE

4.1.1 METHODS

Structural and electronic properties of the bulk CdTe absorber were established. DFT (Quantum Espresso) was used to predict the crystal structure, lattice constant, binding or cohesive energy and band gap of the material. The energies of different types of cubic structures (Simple Cubic or SC, Body Centered Cubic or BCC, and Face Centered Cubic or FCC) were computed across a range of lattice constant values. Some of the initial calculations with CdTe were carried out using the Quantum Espresso DFT software package [43] since it was an open source code and had a lot of online documentation available at the time. Crystal structure, lattice constants and bulk moduli of the individual materials were verified and were found to be within reasonable limits of literature and experimental data.

However, there were some challenges. The electronic properties such as band gap were being heavily underestimated using plain GGA or LDA exchange correlation functional calculations [44, 45]. Although Quantum Espresso was a well-documented and widely used plane wave code at the time, there were limitations pre- and post-processing techniques. A more advanced learning curve was required, which was outside the realm of expertise in the lab. Hence a switch to a more sophisticated software package was necessary. Most of the results presented use QuantumATK (versions O-2019.03, P-2019.12 and Q-2020.06) [46] a product of Synopsys, primarily because of code's ability to handle interface modeling better. This is made possible due to the presence of the Linear Combination of Atomic Orbitals (LCAO) description and the

implementation of DFT in combination with Green's Function (GF) [47, 48]. Moreover, the package possesses an extremely user-friendly Graphic User Interface (GUI).

As with the case of Quantum Espresso, the modeling process started with bulk material validations. Both the Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) exchange correlation functionals were used for interface calculations [49, 50]. However, due to the chronic underestimation of band gaps by standard DFT, a band gap correction method must be used [51, 52]. A Hubbard U band gap correction was investigated to obtain a value closer to the theoretical and experimental range, but the convergence of those computational simulations proved challenging and time consuming. Hence, an alternative approach known as DFT-1/2 was employed. Simulations for the bulk materials and the device employed GGA and LDA in combination with DFT-1/2. When combined with the GGA or LDA functional, this method is referred to as GGA-1/2 or LDA-1/2 respectively. All Self Consistent Field (SCF) calculations for bulk, interface geometry optimization and device configuration were converged to a threshold of 0.0001 eV.

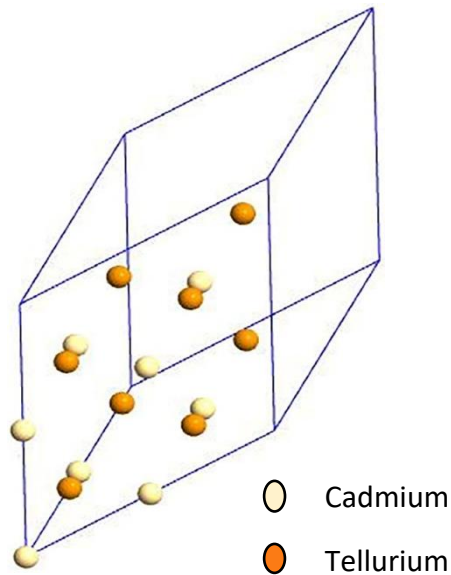


Fig. 17. Illustration of a CdTe unit cell

Using the former, both Ultrasoft and Norm-conserving pseudopotentials were employed. In the latter, CdTe was modeled using 4x4x4 k points (corresponding to a density of 3.09x3.09x3.09 Å). An illustration of the CdTe unit cell is shown in fig. 16 above. The SG15 Pseudopotential was used for all calculations [53].

4.1.2 RESULTS

It was determined that the FCC produced the lowest energy value indicating highest stability as shown in Figure 17 below. This can also be verified from experimental reports.

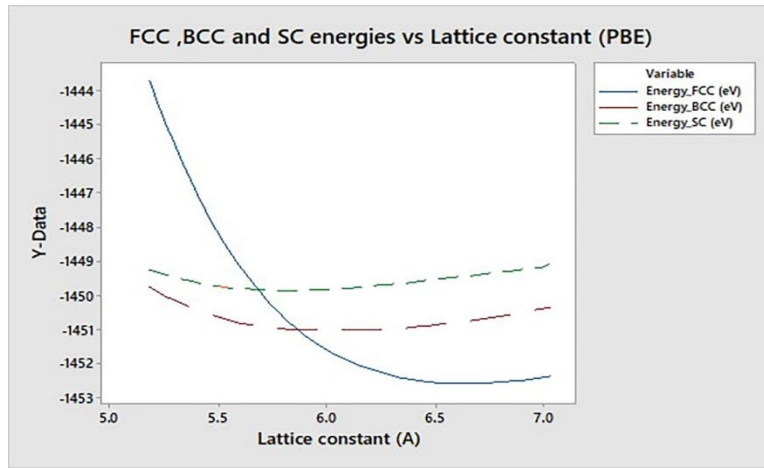


Fig. 18. Total energies of SC, BCC and FCC lattices of CdTe

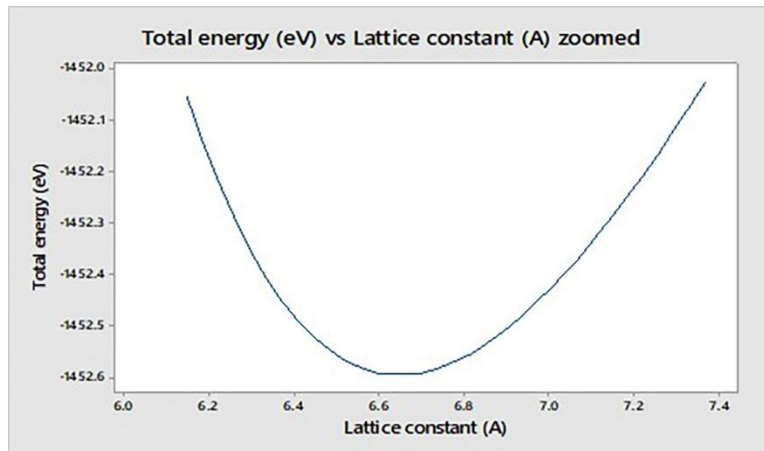


Fig. 19. Lattice constant of CdTe using GGA-PBE functional

The Cd and Te atoms – which are normally displaced from each other by a length equal to one-fourth of the body diagonal – were placed at different relative positions from one another, thus constituting a zincblende structure. To verify this, another set of calculations were performed. The Cd and Te atoms were placed at different separations ranging from 0.2 to 0.35 times the length of the body diagonal. However, every time this was done, the system brought itself back to a state where both atoms were apart by a length of 0.25 times the body diagonal or very close to this value. This is illustrated in Table 1 below.

Table 1. CdTe Structural (variable-cell) Relaxation

Initial Cd positions	Initial Te positions	Final Cd positions	Final Te positions	Difference
All entities are in multiples of the body diagonal				
0	0.2	-0.025	0.225	0.25
0	0.21	-0.02	0.23	0.25
0	0.22	-0.015	0.235	0.25
0	0.23	-0.01	0.24	0.25
0	0.24	-0.005	0.245	0.25
0	0.25	0	0.25	0.25
0	0.26	0.005	0.255	0.25
0	0.27	0.01	0.26	0.25
0	0.28	0.015	0.265	0.25
0	0.29	0.02	0.27	0.25
0	0.3	0.025	0.275	0.25
0	0.31	0.03	0.28	0.25
0	0.32	0.035	0.285	0.25
0	0.33	0.04	0.29	0.25
0	0.34	0.045	0.295	0.25

After determining the crystal structure, the lattice constant was computed, as shown in figure 18. Like the above methodology of identifying the lattice type, this step also uses the lowest energy principle. A range of lattice constants were input into the system and the total energies at each value were calculated. The lattice parameter corresponding to the minimum energy is the lattice constant. This was found to be 6.66 Å using the GGA XC and 6.55 Å with the LDA XC. These values deviate by only 1-2% from experimental reports as shown in Table 2 below.

Table 2. CdTe bulk parameters

Parameter	Method					Error %
	LDA	LDA-1/2	GGA	GGA-1/2	Experiment	
Lattice constant (Å)	6.55	-	6.66	-	6.48	2.7
Band gap (eV)	0.84	1.63	0.77	1.47	1.49	1.3

The band gap values of CdTe were also calculated using both GGA and LDA functionals. As a band gap correction method, GGA-1/2 and LDA-1/2 were compared with traditional GGA and LDA methods respectively. It can be seen from both Table 1 and the band diagrams in figure 19 that the DFT-1/2 correction increases the band gaps pushing them closer to experimental values.

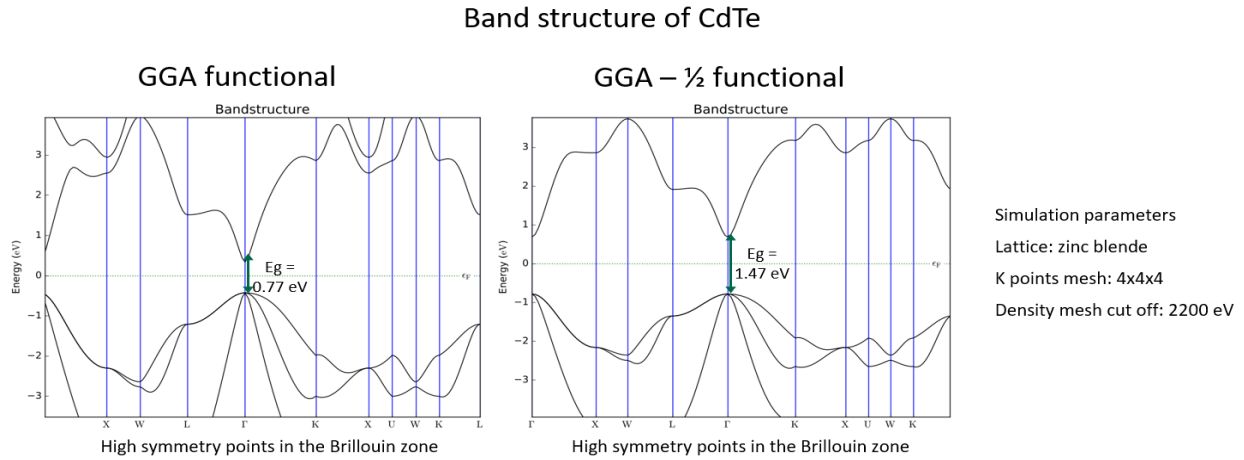


Fig. 20. Band structure of CdTe using GGA (left) and GGA-1/2 (right)

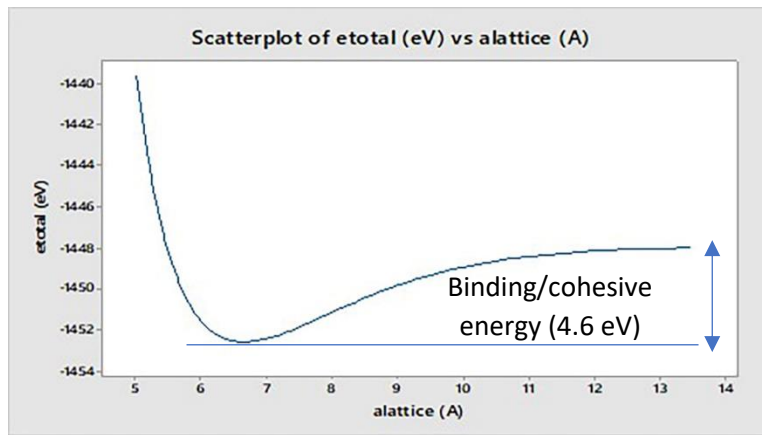


Figure 21. Binding energy of CdTe using GGA-PBE functional

The binding energy was calculated as the difference between the lowest energy and the asymptote (where the energy value plateaus on increasing the lattice constant). The result is plotted in figure 20. This matches well with other DFT reports [54].

4.2 MAGNESIUM ZINC OXIDE

4.2.1 METHODS

Bulk properties of both ZnO and MZO were also established. ZnO was constructed in the hexagonal lattice while MgO was configured in the zinc blende structure as depicted in figures. 16a and 16b [26]. Moreover, since a magnesium-zinc ratio of 0.23 or 23% produced optimal device results, it was decided that a 25% magnesium ratio would be incorporated in the cationic lattice points of the structure for convenience in being able to construct smaller models. It is also known that the alloy MZO maintains a hexagonal crystal structure up to a 46% magnesium ratio at the cationic sites. Since the magnesium concentration falls below the upper limit, the MZO alloy is also modeled as hexagonal. Initially, many different magnesium positions in the alloy were experimented with to find the configuration with the lowest energy. It was determined that the configuration which had any two magnesium atoms furthest apart from each other was the most stable (least energetic). However, as an afterthought, it was deemed more appropriate that the magnesium atoms be randomly placed in the lattice. This was because such a situation was more likely to occur in practice during the evaporation of MZO.

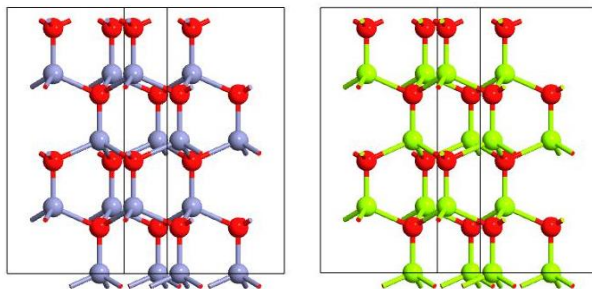


Fig. 22a. Models showing wurtzite ZnO and MgO

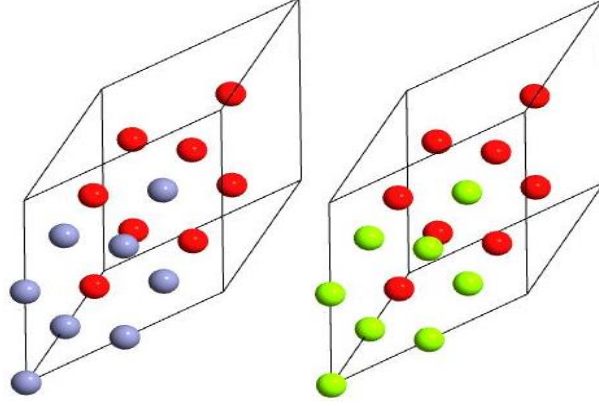


Fig. 22b. Models showing rock salt ZnO and MgO

A Monkhorst-Pack grid of $5 \times 5 \times 3$ k points was employed for w-MZO due to the inherent asymmetry of the former hexagonal lattices while a mesh of $4 \times 4 \times 4$ k points was used for MgO bulk simulations with highly symmetric cubic lattices [55].

4.2.2. RESULTS

Bulk lattice constants were within 3% of experimental values in all three cases (CdTe, ZnO and MZO). Bulk modulus values of CdTe were also comparable to those reported [26-28]. Band gap values, when calculated using the GGA or LDA exchange correlation functional deviated considerably from those found in theory and experiment. However, these values agreed with values previously reported using traditional DFT methods incorporating the GGA or LDA functional. This correction produces values very close to experimental results as shown below in Table 3. Certain simulation parameters such as the k point grid and density mesh cut off were optimized for convergence, typically with respect to energy [56].

Table 3. Comparison of calculated lattice parameters for w-MZO using GGA and LDA

Compound or Alloy	Lattice constant (a, GGA) [Å]	Lattice constant (a, LDA) [Å]	Lattice constant [23] (a, expt.) [Å]	Lattice constant (c, GGA) [Å]	Lattice constant (c, LDA) [Å]	Lattice constant [23] (c, expt.) [Å]
ZnO	3.30	3.22	3.245	5.28	5.16	5.21
Mg _{0.0625} Zn _{0.9375} O	3.30	3.22	3.24	5.28	5.16	5.20
Mg _{0.125} Zn _{0.875} O	3.30	3.22	3.25	5.27	5.16	5.18
Mg _{0.1875} Zn _{0.8125} O	3.30	3.22	3.26	5.27	5.15	5.16
Mg _{0.25} Zn _{0.75} O	3.30	3.22	3.255	5.27	5.15	5.15
Mg _{0.375} Zn _{0.625} O	3.30	3.23	3.27	5.24	5.13	5.14
Mg _{0.50} Zn _{0.50} O	3.31	3.23	-	5.23	5.12	-
Mg _{0.625} Zn _{0.375} O	3.31	3.24	-	5.21	5.09	-
Mg _{0.75} Zn _{0.25} O	3.32	3.26	-	5.18	5.05	-
Mg _{0.875} Zn _{0.125} O	3.33	3.28	-	5.16	4.98	-
MgO	3.34	3.46	-	5.10	4.17	-

Table 3 lists the lattice constants for w-MZO. Very little change is seen in the MZO lattice constant as the ratio of Mg increases. Only for MgO, there is a considerable change in the ‘a’ parameter and a drastic change in the ‘c’ parameter. It is known that replacing Zn with Mg in the ZnO lattice introduces minimal strain. This is because the atomic radii (Mg = 0.71 Å, Zn = 0.74 Å) and ionic radii (Mg²⁺ = 0.57 Å, Zn²⁺ = 0.60 Å) of both the elements are very similar to each other. Hence, the Mg atoms sits well in the Zn lattice [18,28]. This characteristic represents pseudo-morphic growth – a single crystal structure composed of different materials but with fully coherent atomic bonds [57,58]. The deviation from experimental values for higher concentrations of Mg can be explained by the fact that MgO does not exhibit the wurtzite structure naturally. For ZnO and MZO with low and mid-range values of Zn, the lattice parameters resemble those seen in experiment.

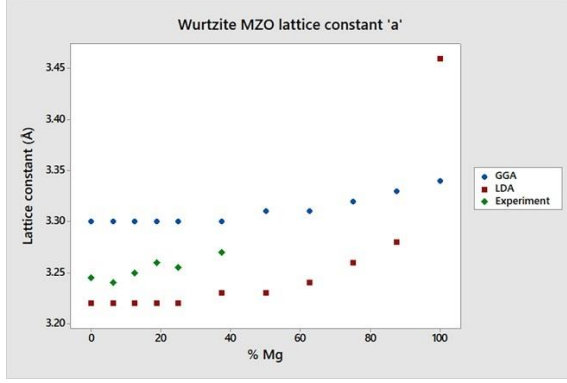


Fig. 23a. w-MZO 'a' lattice constant

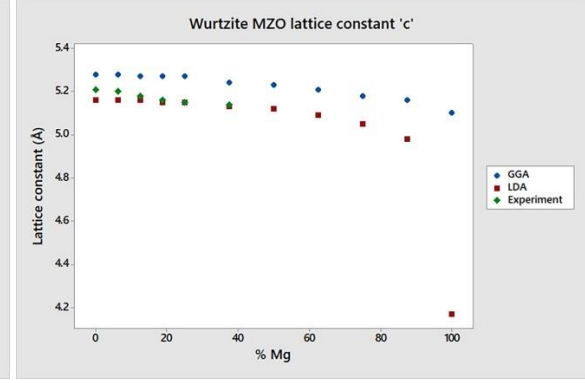


Fig. 23b. w-MZO 'c' lattice constant

Table 4. w-MZO c/a ratios

Compound/Alloy	c/a (GGA)	c/a (LDA)	c/a (expt.)
ZnO	1.60	1.60	1.605 [59], 1.614 [60]
Mg _{0.0625} Zn _{0.9375} O	1.60	1.60	1.606 [59]
Mg _{0.125} Zn _{0.875} O	1.60	1.60	1.597 [59]
Mg _{0.1875} Zn _{0.8125} O	1.60	1.60	1.59 [59]
Mg _{0.25} Zn _{0.75} O	1.60	1.60	1.591 [59], 1.599 [60]
Mg _{0.375} Zn _{0.625} O	1.59	1.59	1.575 [59]
Mg _{0.50} Zn _{0.50} O	1.58	1.59	1.585 [60]
Mg _{0.625} Zn _{0.375} O	1.57	1.57	-
Mg _{0.75} Zn _{0.25} O	1.56	1.55	1.569 [60]
Mg _{0.875} Zn _{0.125} O	1.55	1.52	-
MgO	1.53	1.21	1.538 [60]

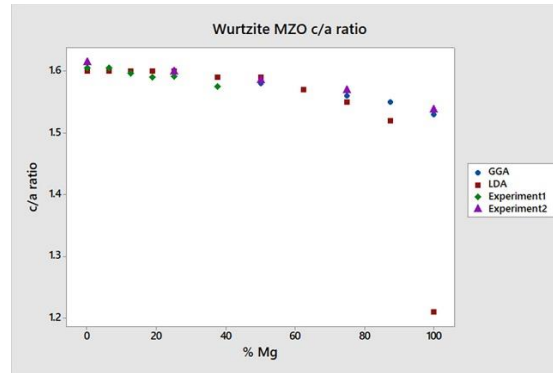


Fig. 24. w-MZO c/a ratio

c-MZO lattice constants show a decreasing trend with increasing Mg concentration as seen in Fig. 19. This can be explained by the smaller sizes of both the magnesium atom and ion

compared to their zinc counterparts. This is also observed experimentally as shown in Table 5 below, which represents cubic MZO lattice constants.

Table 5. c-MZO lattice constants

Compound/Alloy	Lattice constant (a, GGA) [Å]	Lattice constant (a, LDA) [Å]	Lattice constant (a, literature) [Å]
ZnO	4.332	4.218	4.298 [60], 4.28[61]
Mg _{0.125} Zn _{0.875} O	4.319	4.214	-
Mg _{0.25} Zn _{0.75} O	4.312	4.209	4.292 [60]
Mg _{0.375} Zn _{0.625} O	4.307	4.206	-
Mg _{0.50} Zn _{0.50} O	4.296	4.199	4.286 [60]
Mg _{0.625} Zn _{0.375} O	4.287	4.192	-
Mg _{0.75} Zn _{0.25} O	4.283	4.187	4.279 [60]
Mg _{0.875} Zn _{0.125} O	4.279	4.182	-
MgO	4.270	4.177	4.272[60], 4.21[61], 4.24 [62]

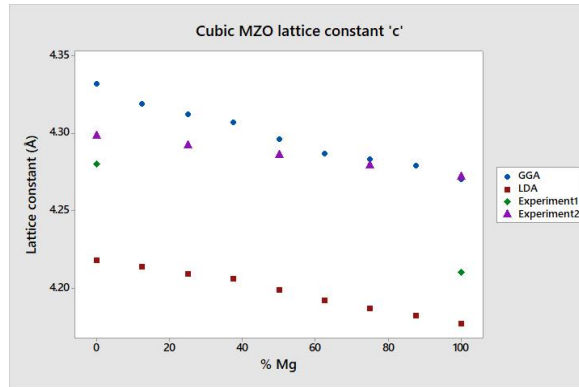


Fig. 25. Rock salt MZO lattice constants

A summary of both structural and electronic properties for ZnO and Mg_{0.25}Zn_{0.75}O are shown in Table 2 and Table 3 respectively. The ‘a’ lattice parameter predicted by GGA is closer to experimental values while the ‘c’ lattice constant calculated under LDA matches reported values better. However, for band gap calculations, GGA-1/2 is the better choice.

Table 6. ZnO bulk parameters

Parameter	LDA	LDA - ½	GGA	GGA – ½	Expt.	Error %
Lattice constant (Å)	a = 5.29 c = 3.27	-	a = 5.28 c = 3.30	-	a = 5.2 c = 3.25	1.5 1.5
Band gap (eV)		2.87	0.41	2.98	3.24	8

Table 7. $\text{Mg}_{0.25}\text{Zn}_{0.75}\text{O}$ bulk parameters

Parameter	LDA	LDA - ½	GGA	GGA – ½	Expt.	Error %
Lattice constant (Å)	a = 5.29 c = 3.27	-	a = 5.28 c = 3.30	-	a = 5.18 c = 3.25	1.5 1.5
Band gap (eV)		2.88	0.65	3.56	3.70	4

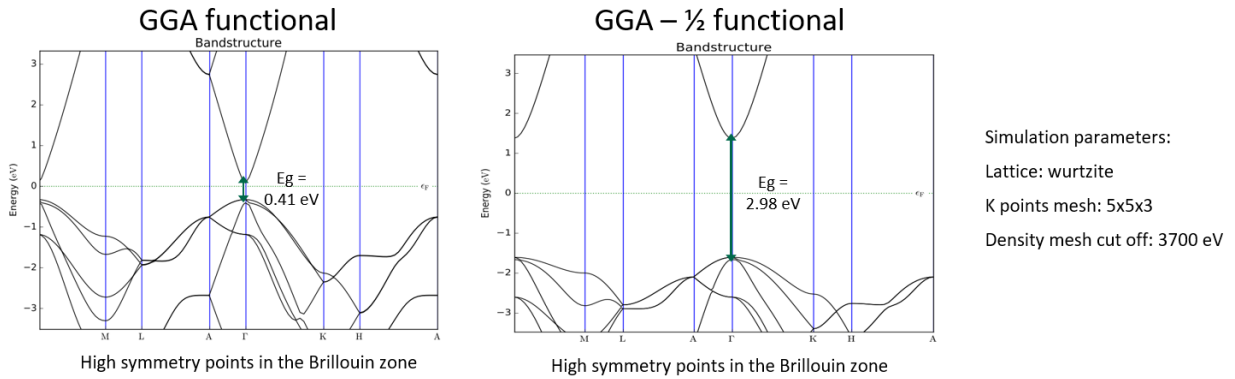


Fig. 26. Band structure of ZnO using GGA (left) and GGA-1/2 (right)

Band structure of MZO

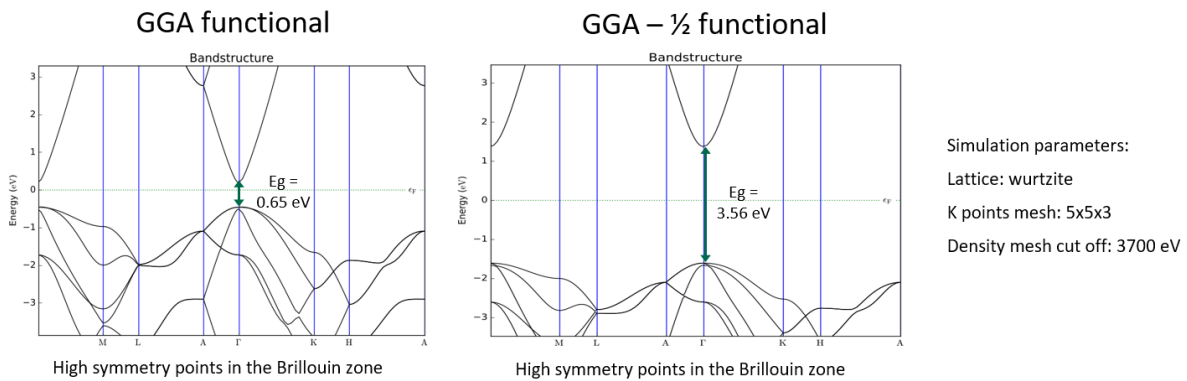


Fig. 27. Band structure of MZO using GGA (left) and GGA-1/2 (right)

The band structures of ZnO and $\text{Mg}_{0.25}\text{Zn}_{0.75}\text{O}$ are displayed in figures 25 and 26 above. Yet again, the difference that the DFT-1/2 correction makes is evident.

The band gaps of different MZO compositions using GGA-1/2 and LDA-1/2 XCs, along with experimental reports are depicted in listed in Table 8 and plotted in figure 27 below.

Compound or Alloy	Band gap (GO, GGA-1/2) [eV]	Band gap (GO, LDA-1/2) [eV]	Band gap (expt.) [eV]
ZnO	2.99	3.27	3.24 [21], 3.37 [62]
$\text{Mg}_{0.0625}\text{Zn}_{0.9375}\text{O}$	3.11	3.39	3.38 [21]
$\text{Mg}_{0.125}\text{Zn}_{0.875}\text{O}$	3.21	3.49	-
$\text{Mg}_{0.1875}\text{Zn}_{0.8125}\text{O}$	3.31	3.64	3.60 [21]
$\text{Mg}_{0.25}\text{Zn}_{0.75}\text{O}$	3.36	3.75	3.76 [21], 3.87 [62]
$\text{Mg}_{0.375}\text{Zn}_{0.625}\text{O}$	3.65	4.13	-
$\text{Mg}_{0.50}\text{Zn}_{0.50}\text{O}$	4.21	4.48	4.1 [62]
$\text{Mg}_{0.625}\text{Zn}_{0.375}\text{O}$	4.56	4.83	4.97[21]
$\text{Mg}_{0.75}\text{Zn}_{0.25}\text{O}$	4.79	5.06	-
$\text{Mg}_{0.875}\text{Zn}_{0.125}\text{O}$	5.34	5.61	-
MgO	5.92	6.22	-

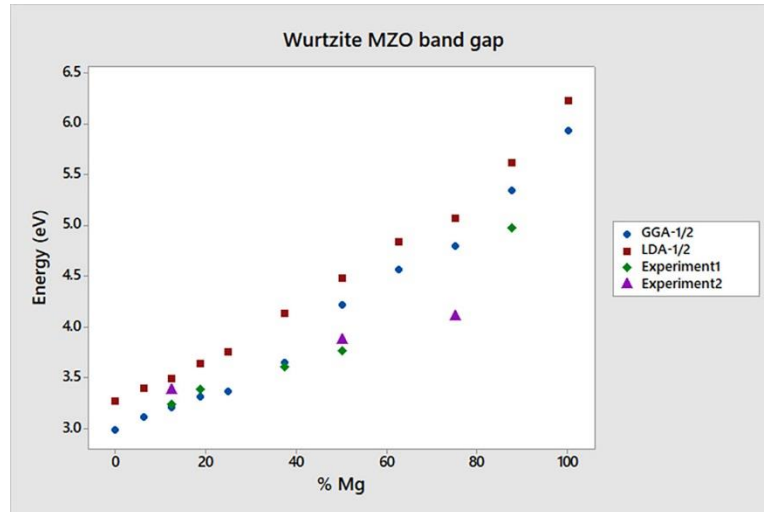


Fig. 28. Wurtzite MZO band gaps

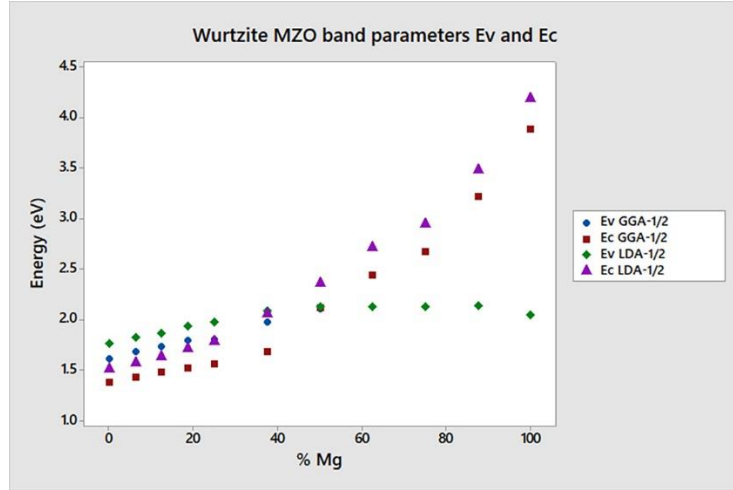


Fig. 29. Wurtzite MZO valence and conduction band edges

Another way of looking at the band parameters was to split the band gap into conduction and valence band edges which, were also determined for the whole range of MZO compositions. These results are shown in figures 28. The valence and conduction band edges at low Mg concentrations are similar; however, at higher concentrations, the conduction band edges increase in magnitude in comparison to the valence band edges. This is depicted in figures 29a and 29b. Electron effective masses were another set of parameters that were computed. These values are shown in figure 30.

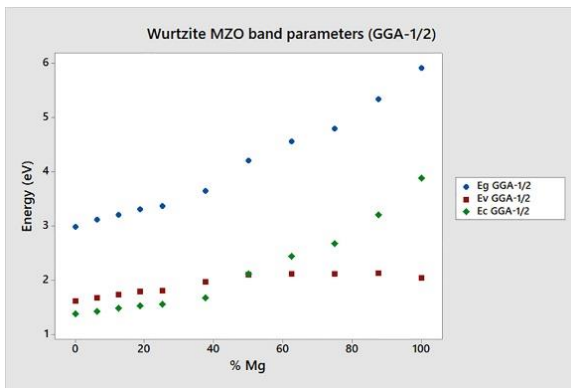


Fig. 30a. w-MZO band parameters (GO, GGA-1/2)

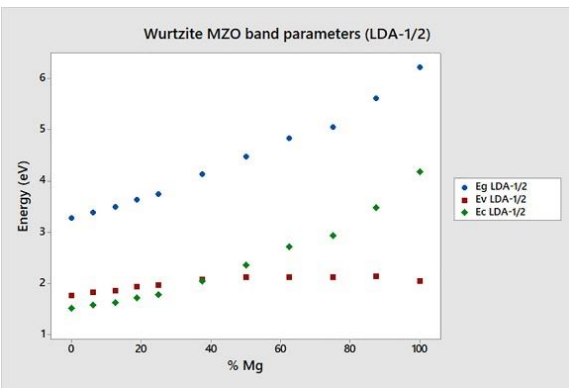


Fig. 30b. w-MZO band parameters (GO, LDA-1/2)

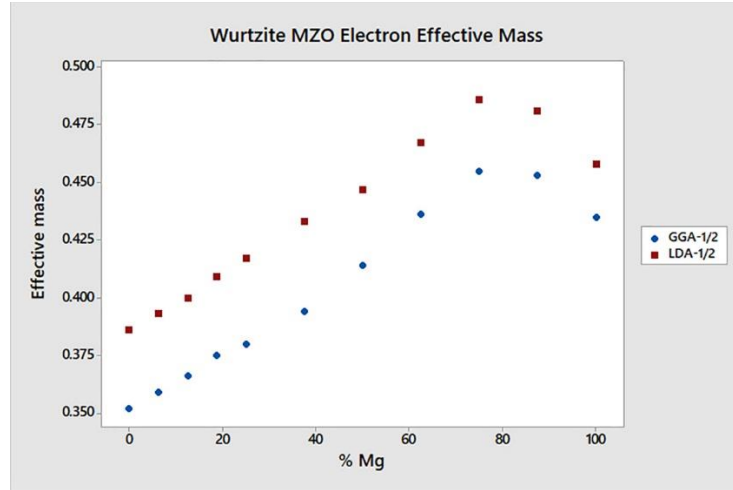


Fig. 31. Wurtzite MZO electron effective masses

Band gaps for the rock salt MZO compositions are displayed in figure 31 and table 9 below.

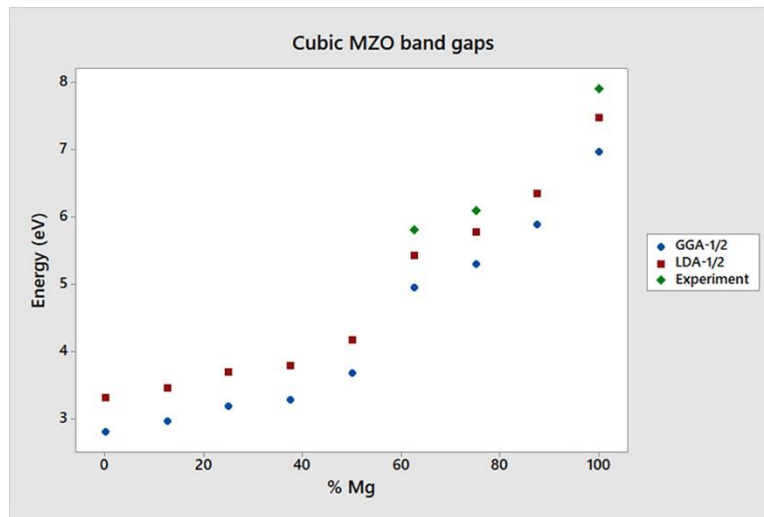


Fig. 32. Rock salt MZO band gaps

The band gap increases with increasing Mg concentration. This happens slowly at low Mg levels but picks up significantly for Mg > 50%, giving the curve a parabolic/quadratic nature. The simulations are slightly below experimental values with LDA being the better predictor.

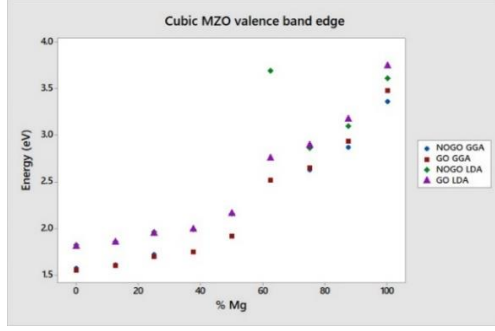


Fig. 33a. Rock salt MZO valence band edges

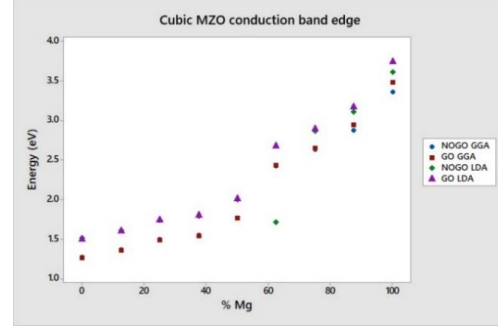


Fig. 33b. Rock salt MZO conduction band edges

Table 9. c-MZO band gaps

Compound or Alloy	Band gap (GO, GGA-1/2) [eV]	Band gap (GO, LDA-1/2) [eV]	Band gap (expt.) [eV]
ZnO	2.81	3.31	-
Mg _{0.125} Zn _{0.875} O	2.96	3.45	-
Mg _{0.1875} Zn _{0.8125} O	3.19	3.69	-
Mg _{0.375} Zn _{0.625} O	3.29	3.79	-
Mg _{0.50} Zn _{0.50} O	3.68	4.17	-
Mg _{0.625} Zn _{0.375} O	4.95	5.42	5.80 [58]
Mg _{0.75} Zn _{0.25} O	5.3	5.78	6.09 [58]
Mg _{0.875} Zn _{0.125} O	5.88	6.34	-
MgO	6.96	7.48	7.9 [58]

Like the w-MZO case, valence and conduction band edges were determined for c-MZO. These are plotted in figures 32a and 32b. Electron effective masses are also calculated as seen in Table 10 and figure 33. Results like those seen with w-MZO are observed. The curve is linear to begin with and increases at higher Mg values. However, close to 100% Mg, the m_e values show a slight dip.

Table 10. MZO electron effective masses m_e

Compound or Alloy	w-MZO, GGA	w-MZO, LDA	c-MZO, GGA	c-MZO, LDA
ZnO	0.352	0.386	0.295	0.336
Mg _{0.0625} Zn _{0.9375} O	0.359	0.393	-	-
Mg _{0.125} Zn _{0.875} O	0.366	0.400	0.306	0.345
Mg _{0.1875} Zn _{0.8125} O	0.375	0.409	-	-
Mg _{0.25} Zn _{0.75} O	0.380	0.417	0.32	0.359
Mg _{0.375} Zn _{0.625} O	0.394	0.433	0.329	0.368
Mg _{0.50} Zn _{0.50} O	0.414	0.447	0.351	0.392
Mg _{0.625} Zn _{0.375} O	0.436	0.467	0.4	0.448
Mg _{0.75} Zn _{0.25} O	0.455	0.486	0.416	0.465
Mg _{0.875} Zn _{0.125} O	0.453	0.481	0.443	0.493
MgO	0.435	0.458	0.441	0.479

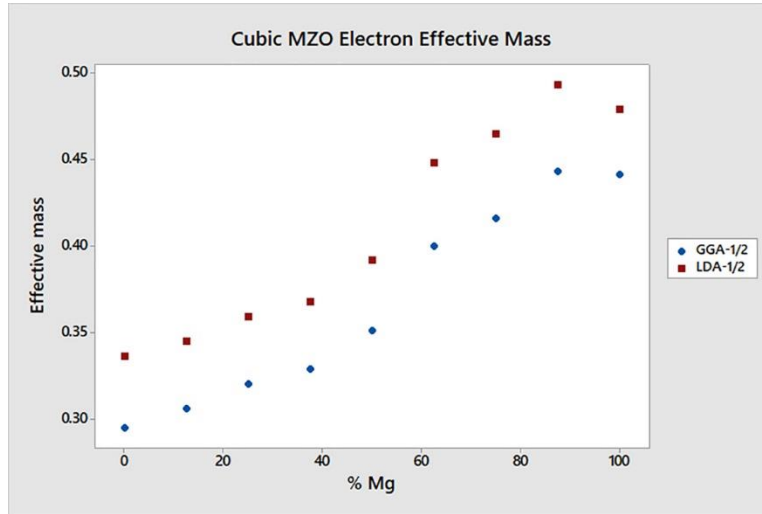


Fig. 34. Rock salt MZO electron effective masses

Band structures for w-MZO and c-MZO with and without GO have been plotted as shown in the figures 34a-j below. The electron masses have been derived from the curvature of the conduction band. For w-MZO, a trend of decreasing curviness is seen in the CB which indicates higher electron effective masses as the Mg composition is increased [63]. This can be verified from the m_e plots as well.

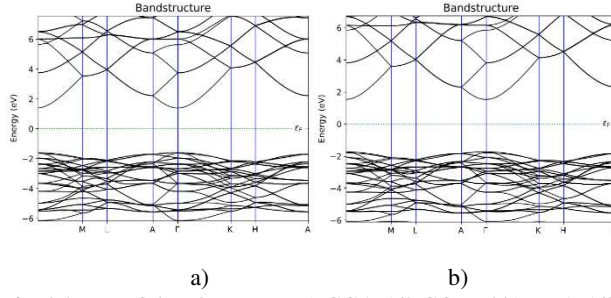


Fig. 35. w-ZnO band structure a) GGA-1/2 GO and b) LDA-1/2 GO

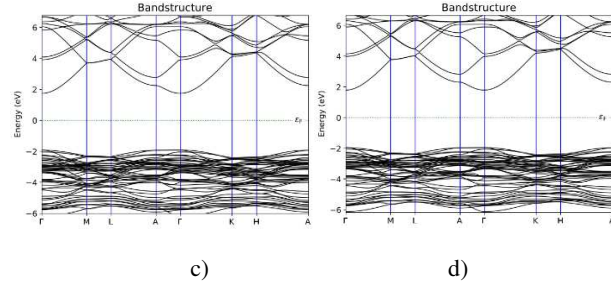


Fig. 35. w-Mg_{0.25}Zn_{0.75}O band structure a) GGA-1/2 GO and b) LDA-1/2 GO

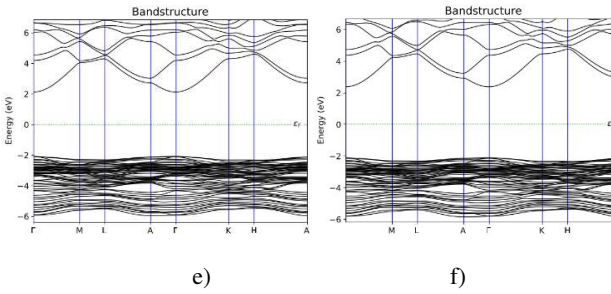


Fig. 35. w-Mg_{0.50}Zn_{0.50}O band structure a) GGA-1/2 GO and b) LDA-1/2 GO

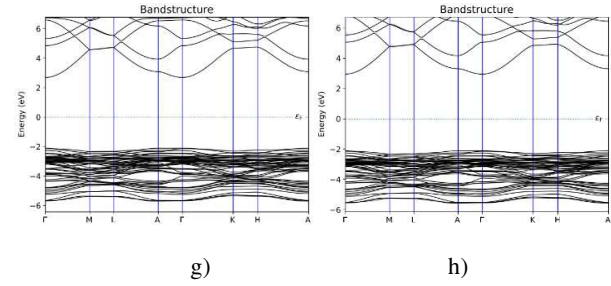


Fig. 35. w-Mg_{0.75}Zn_{0.25}O band structure a) GGA-1/2 GO and b) LDA-1/2 GO

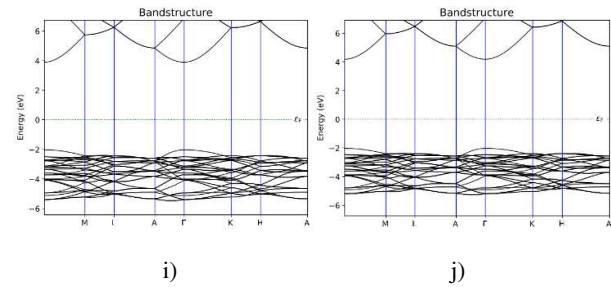


Fig. 35. w-MgO band structure a) GGA-1/2 GO and b) LDA-1/2 GO

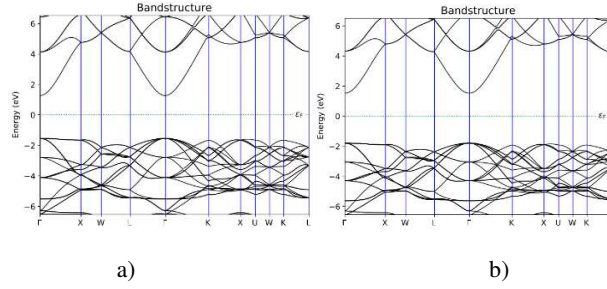


Fig. 36 c-ZnO band structure a) GGA-1/2 GO and b) LDA-1/2 GO

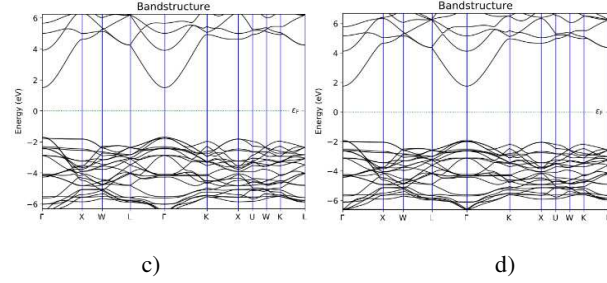


Fig. 36. c- $\text{Mg}_{0.25}\text{Zn}_{0.75}\text{O}$ band structure c) GGA-1/2 GO and d) LDA-1/2 GO

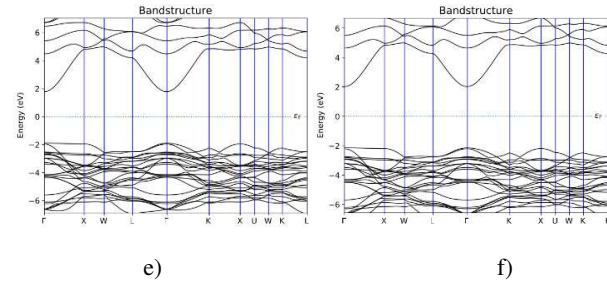


Fig. 36. c- $\text{Mg}_{0.50}\text{Zn}_{0.50}\text{O}$ band structure e) GGA-1/2 GO and f) LDA-1/2 GO

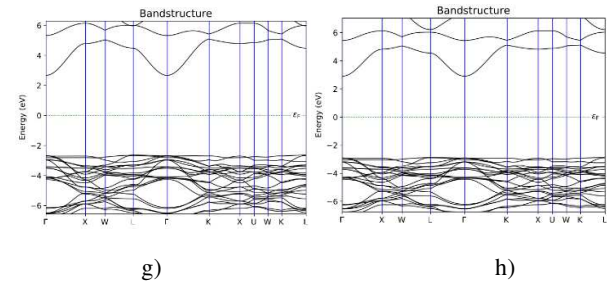


Fig. 36. c- $\text{Mg}_{0.75}\text{Zn}_{0.25}\text{O}$ band structure g) GGA-1/2 GO and h) LDA-1/2 GO

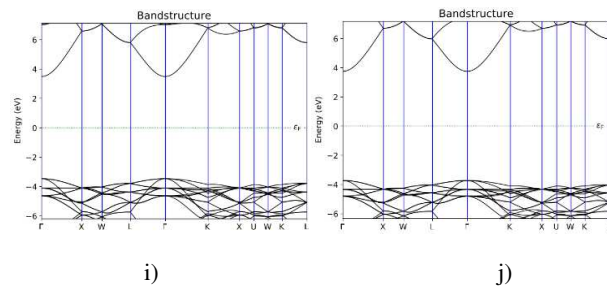
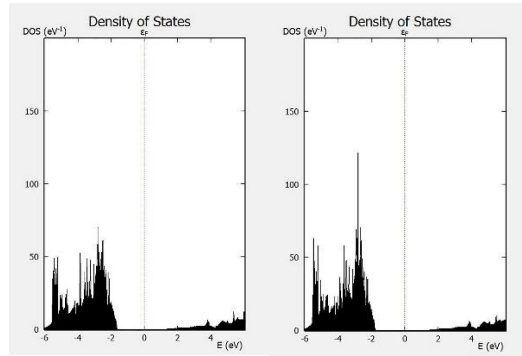


Fig. 36. c- MgO band structure i) GGA-1/2 GO and j) LDA-1/2 GO

Displayed above in figs. 35 a-j are band structures for c-MZO. The band gaps widen with increasing magnesium content as expected. Like the w-MZO scenario, the CB shows increasing non-parabolicity with higher Mg composition. This corresponds to increasing effective masses of electrons which can be inferred from figure 27.

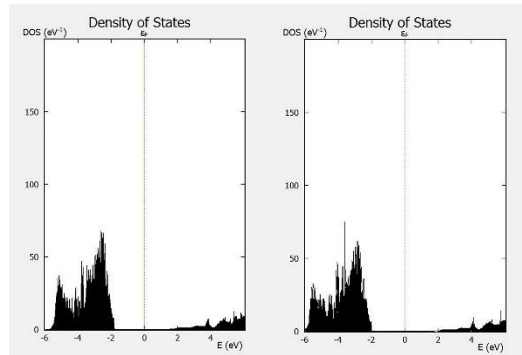
Density of States (DOS) plots are shown below in figures 36a-j for w-MZO alloys ranging from ZnO through MgO at increments of 25% atomic composition. The band gap widens gradually with the VB showing a more marked increase. The VB also exhibits a higher density of states than the CB.



a)

b)

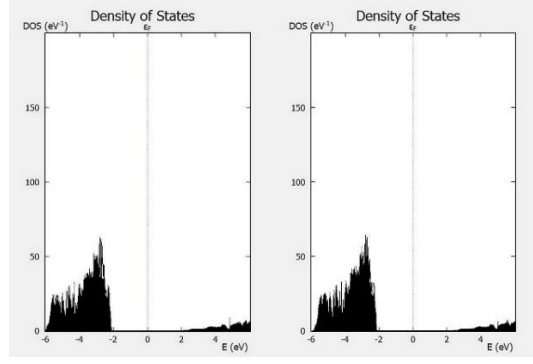
Fig. 37. w-ZnO DOS a) GGA-1/2 GO and b) LDA-1/2 GO



c)

d)

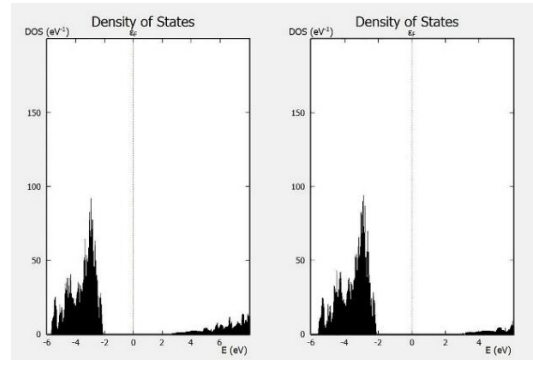
Fig. 37. w-Mg_{0.25}Zn_{0.75}O DOS c) GGA-1/2 GO and d) LDA-1/2 GO



e)

f)

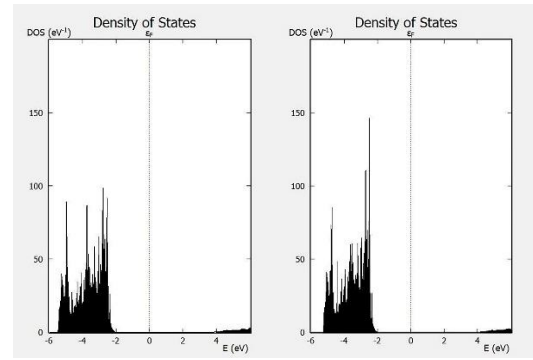
Fig. 37. w-Mg_{0.50}Zn_{0.50}O DOS e) GGA-1/2 GO and f) LDA-1/2 GO



g)

h)

Fig. 37. w-Mg_{0.75}Zn_{0.25}O DOS g) GGA-1/2 GO and h) LDA-1/2 GO



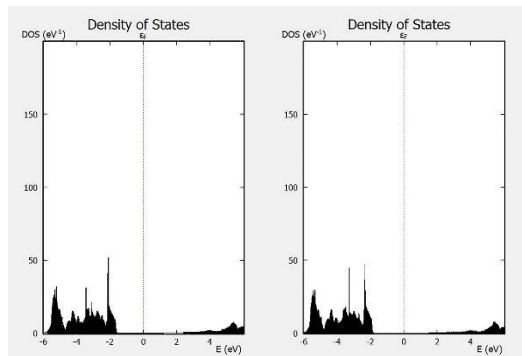
i)

j)

Fig. 37. w-MgO DOS i) GGA-1/2 GO and j) LDA-1/2 GO

Density of States (DOS) plots for c-ZnO are illustrated below in figs. 37a-j. Again, as with w-MZO, the band gap increases gradually with increasing Mg concentration. However, unlike w-

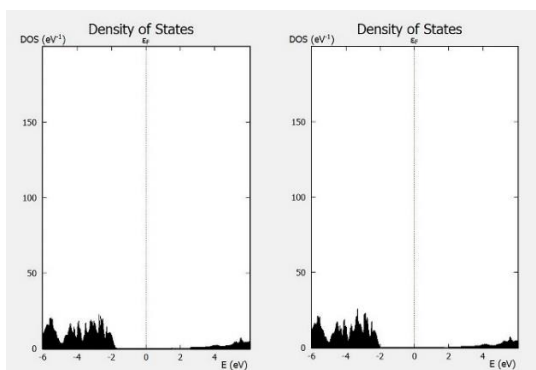
MZO, at higher concentrations of Mg ($> 75\%$), the band gap contributions from both the VB and CB become equal.



a)

b)

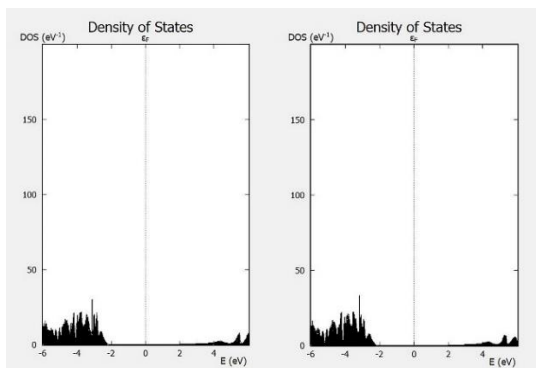
Fig. 38. c-ZnO DOS a) GGA-1/2 GO and b) LDA-1/2 GO



c)

d)

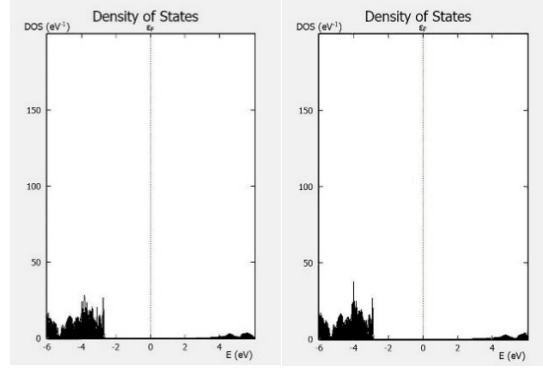
Fig. 38. c-Mg_{0.25}Zn_{0.75}O DOS c) GGA-1/2 GO and d) LDA-1/2 GO



e)

f)

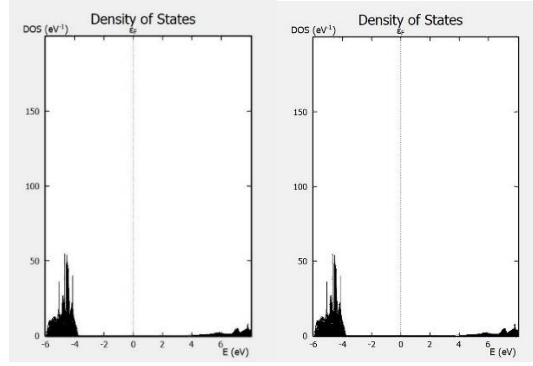
Fig. 38. c-Mg_{0.50}Zn_{0.50}O DOS g) LDA-1/2 NOGO and h) LDA-1/2 GO



g)

h)

Fig. 38. c-Mg_{0.75}Zn_{0.25}O DOS g) GGA-1/2 GO and h) LDA-1/2 GO



i)

j)

Fig. 38. c-MgO DOS i) GGA-1/2 GO and j) LDA-1/2 GO

Using Newton's law, the force on an electron in the CB can be written as [64]:

$$F = m_e^* a = dp/dt$$

For a free electron, energy and momentum are related by the parabolic law:

$$E = p^2/2m$$

For electrons in the CB at energies close to the minimum E_c in direct gap semiconductors such as ZnO and MgO,

$$E - E_c = p^2/2m_e^*$$

The 2p orbital of the oxygen makes the highest contribution to the Density of States, as seen from figures 38 a and 38b below. This is because they form the valence electrons, which tend to be the

most reactive. The contribution from the corresponding 3d orbitals in zinc and the 2s orbitals in magnesium is lower than that of oxygen 2p.

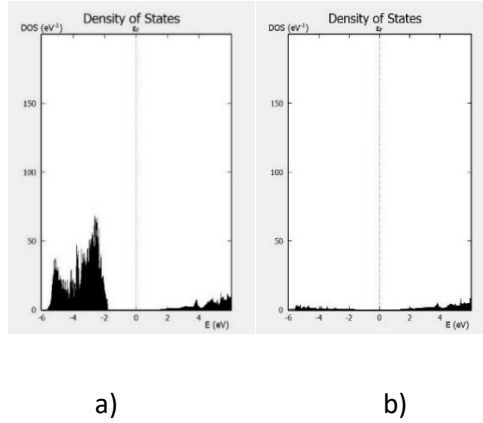


Fig. 39. w-ZnO GGA-1/2 a) total DOS and b) s-orbital contribution to the DOS

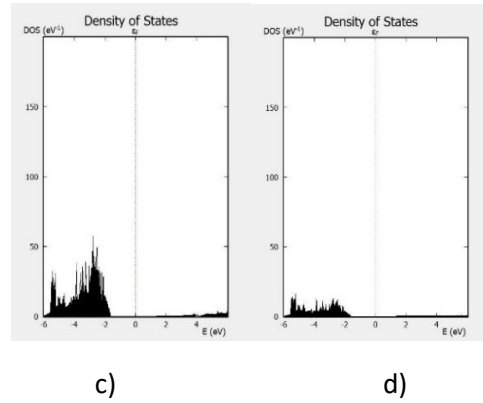


Fig. 39. w-ZnO GGA-1/2 c) p-orbital and d) d-orbital contribution to the DOS

4.2.3. GALLIUM DOPED MGZNO (GMZO)

Following experiments performed by Dr. Jason Kephart at the NGPV, bulk properties of GMZO for two compositions were simulated [21]. One had a low Ga content with relatively high Mg and low Zn ratios ($\text{Ga}_{0.01}\text{Mg}_{0.22}\text{Zn}_{0.77}\text{O}$) while the other had a higher Ga ratio, low Mg and high Zn compositions ($\text{Ga}_{0.03}\text{Mg}_{0.02}\text{Zn}_{0.95}\text{O}$). Lattice constants and band gaps are displayed in the table below. The DOS plots are illustrated in fig. 39. The carrier concentration in GMZO is so high that

the band gap appears degenerate i.e. the Fermi level sits slightly above the CB. This is indicative of degenerate n-type doping.

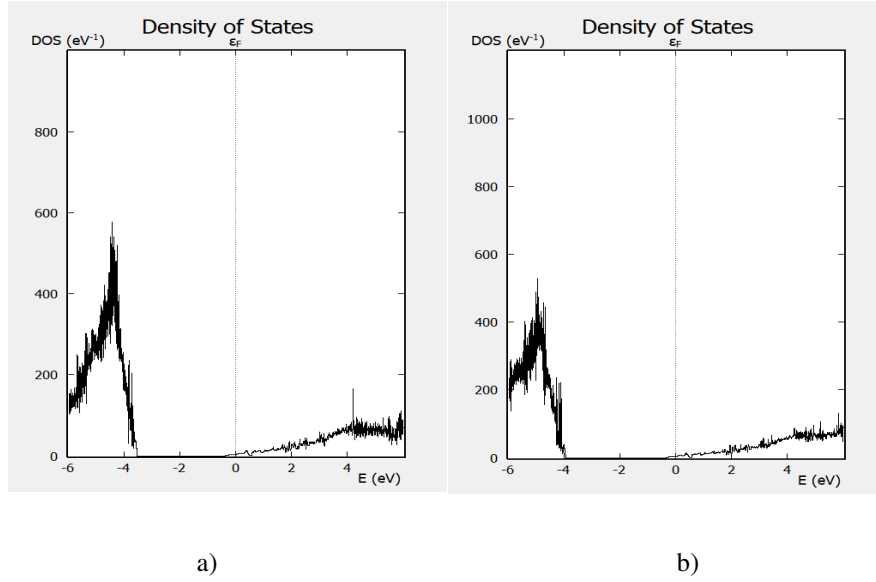


Fig. 40. GMZO DOS a) GGA-1/2 and b) LDA-1/2

Table 11. GMZO Lattice constants and band gaps

Compound/Alloy	Lattice constant (a, GGA) [Å]		Lattice constant (c, GGA) [Å]		Lattice constant (a, LDA) [Å]		Lattice constant (c, LDA) [Å]	
$\text{Ga}_{0.01}\text{Mg}_{0.22}\text{Zn}_{0.77}\text{O}$	3.302		5.27		3.222		5.158	
$\text{Ga}_{0.03}\text{Mg}_{0.02}\text{Zn}_{0.95}\text{O}$	3.305		5.282		3.222		5.175	

Compound/Alloy	Band gap (No GO, GGA-1/2) [eV]			Band gap (GO, GGA-1/2) [eV]		
	VBM	CBM		VBM	CBM	
$\text{Ga}_{0.01}\text{Mg}_{0.22}\text{Zn}_{0.77}\text{O}$	3.13	-3.43	-0.30	3.16	-3.53	-0.37
$\text{Ga}_{0.03}\text{Mg}_{0.02}\text{Zn}_{0.95}\text{O}$	2.60	-3.52	-0.92	2.72	-3.68	-0.96

Compound/Alloy	Band gap (No GO, LDA-1/2) [eV]			Band gap (GO, LDA-1/2) [eV]		
	VBM	CBM		VBM	CBM	
$\text{Ga}_{0.01}\text{Mg}_{0.22}\text{Zn}_{0.77}\text{O}$	3.39	-3.66	-0.27	3.59	-3.94	-0.35
$\text{Ga}_{0.03}\text{Mg}_{0.02}\text{Zn}_{0.95}\text{O}$	2.85	-3.70	-0.85	3.10	-4.05	-0.95

CHAPTER 5. INTERFACE AND DEVICE SIMULATIONS

5.1. ZNO/CDTE INTERFACE SIMULATIONS

5.1.1. METHODS

Once the bulk material properties were determined, the same simulation parameters were then used in interface calculations. The two materials are brought together using the interface builder in QuantumATK [65]. The macro allows several possibilities of forming an interface between the two bulk materials. One aspect is the surface chemistry or termination. In this exercise, for both the ZnO and the MZO, only the anion-cation or opposite polarity terminations were considered primarily in order to reduce the complications involved [66]. In other words, terminations involving the same polarities were disregarded. An illustration of an interface built using the QuantumATK interface builder is shown below.

A second aspect to consider is the grain orientation of both bulk materials. Most simulations were performed with the CdTe(111) and ZnO/MZO(0002) configuration as they were the most preferred grain orientations as determined experimentally [30].

Yet another attribute is the initial strain state and the type of strain (tensile or compressive) either material experiences with respect to the other. The interface builder feature does this by comparing the number of atoms in the interface plane and the strain is determined by rotating one surface with respect to another in small incremental angles. The lattice vectors are extracted, and the strain tensors are computed to arrive at several possible combinations of the initial strain state and the number of atoms along the interface plane.

This can be done in three ways:

- straining the first surface
- straining the second surface,
- applying equal strain to both surfaces

In this case, the first surface is the oxide (ZnO or MZO) and so the first alternative involves applying a tensile strain since the lattice parameter of the oxide is lesser than that of CdTe. The second option is straining the CdTe compressively as it would have to lower its lattice parameter to conform to the oxide layer below it. The last possibility is to strain both surfaces equally.

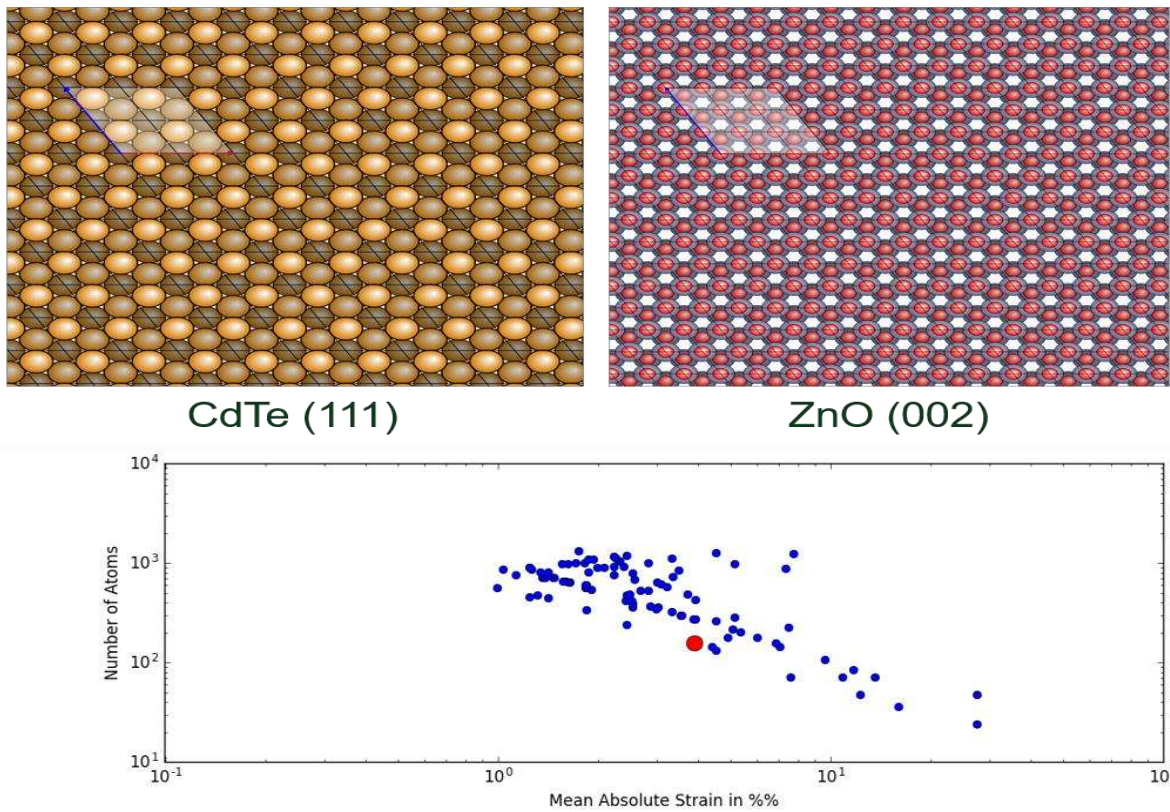


Fig. 41. Illustration of the CdTe 111 plane (top left), the ZnO 002 plane (top right) and a plot of the number of atoms in the interface plane vs. initial strain state (bottom).

A plot of the number of atoms in the interface plane against the initial strain state is then generated as shown above in fig. 40, and a suitable configuration is then chosen for the interface. This is chosen based on the desired strain value and the number of atoms that can be handled in such a way that the system size is not too large to make the calculations computationally expensive. Since this value of strain usually varies inversely with the number of atoms, this is done in such a way that there is a balance between these two parameters. The interface can then be extended in either direction by a certain number of atomic/molecular layers or unit cells with the same amount of strain maintained. The atoms undergoing structural relaxation can also be chosen. They are usually the atoms closest to the interface but can go all the way till the end. Vacuum is then added to either side. The length of this vacuum region is usually about 15% of the length of the interface super cell so that when repeated along the transport direction, the end of one cell does not have an influence on the other end as shown in the depiction below (fig. 41).

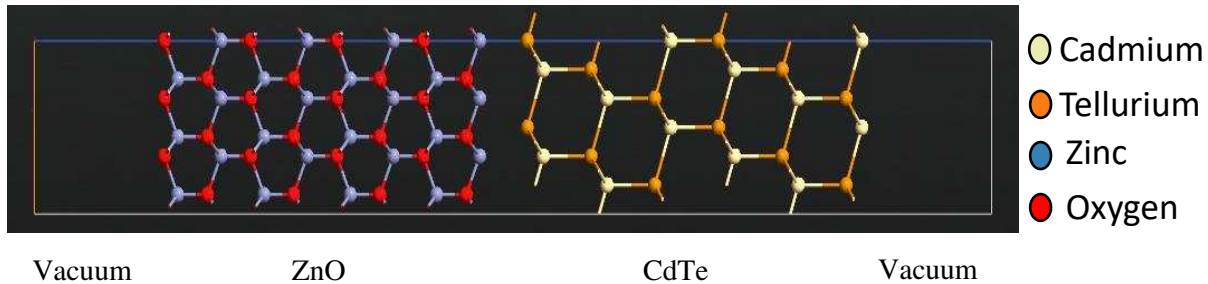


Fig. 42. A model of the ZnO/CdTe interface built using QuantumATK

Structural relaxation is then performed, and the resulting configuration is used to generate a device in the two-probe model which consists of the central region that has been relaxed and two semi-infinite bulk electrode regions. This is done using DFT + GF applying open boundary conditions to the bulk electrodes. A SCF loop is then calculated to determine electron densities and energies for the device following which other properties such as band gaps and density of

states can be obtained. The structure of the device as constructed in the two-probe configuration is shown below in fig. 42.

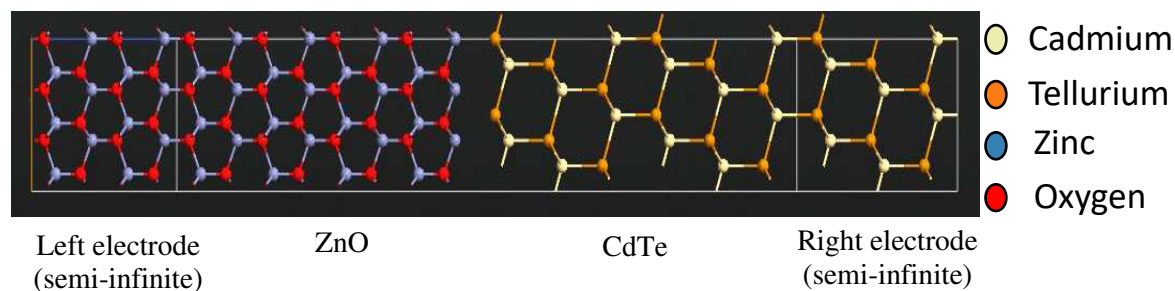


Fig. 43. The ZnO/CdTe device structure built using the two-probe model in QuantumATK

By and large, the same k point grid and density mesh cut off values used in bulk calculations were carried forward into the interface and device simulations. The only exception is the number of k points used in the transport direction in either case. For the structural relaxation, the default number of k points in the transport direction is 1, whereas in the device configuration, the number of k points is very high in the bulk electrodes (typically 100 – 200) for easier convergence of the properties (mainly band gap) in the central region with those of the bulk.

An alternate method involves bringing the geometry optimized bulk configurations together. However, the interfaces thus formed were larger than those in the initial procedure and would prove to be computationally more expensive. As a result, this method was avoided. The first method also took care of geometry optimization so the need for an alternative was deemed unnecessary.

5.1.2. RESULTS

Since the primary interest of this work is band alignments at the interface, most of the results, if not all, are Projected Local Device Density of States (PLDDOS) plots. These show the electronic states at the interface and a short distance on either side. However, the size of the model and resource constraints made it difficult for such convergence to be attained within the scale of the plots. The system size of greater than 800 atoms meant that a large amount of memory was necessary for the calculations and exceeding this number of atoms proved challenging from both a hardware and convergence standpoint.

The SCF calculations converged for most simulations and the structural relaxation calculations were well behaved. The density of electronic states plot has been shown in figs 43a and 43b.

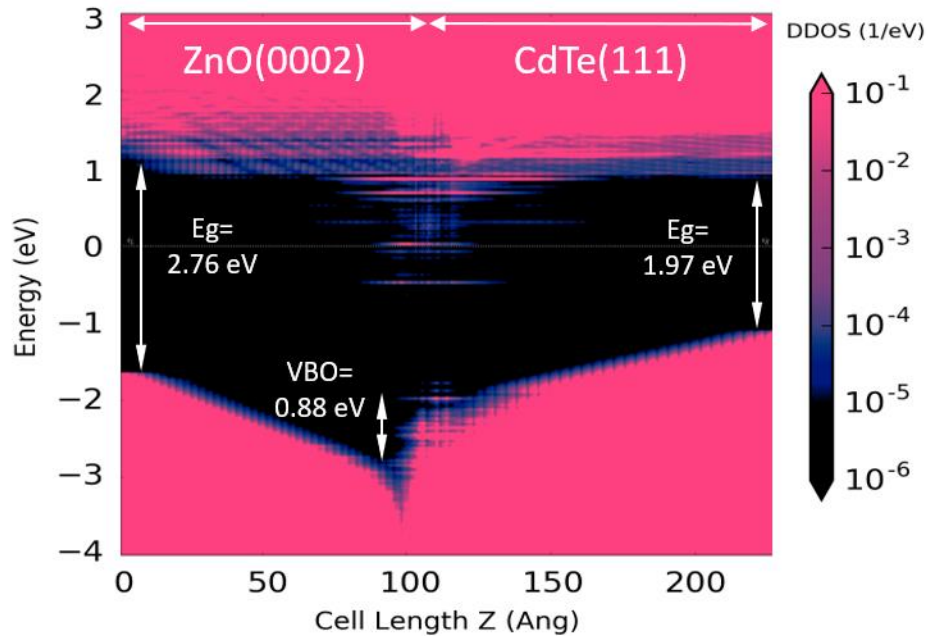


Fig. 44a. Density of states at the ZnO/CdTe interface for Zn-Te termination

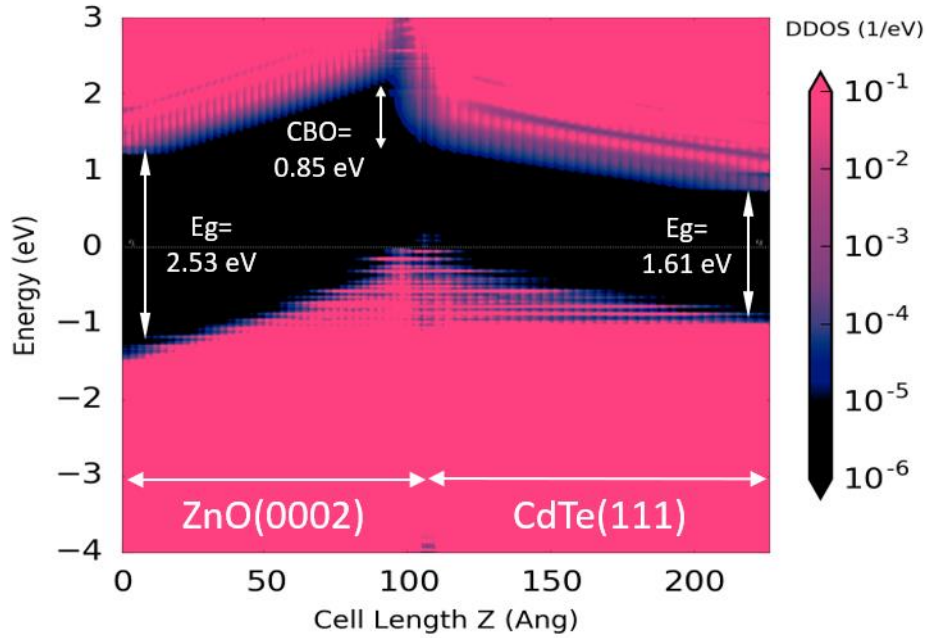


Fig. 44b. Density of states at the ZnO/CdTe interface for O-Cd termination

Probably the most striking feature of the results is the differences between the termination chemistries – O-Cd and Zn-Te. In the case of the O-Cd terminated interface, it is seen that the bands bend up. It can also be seen that this bending induces too much of a spike (1 eV) or barrier for the electrons, which are the majority carriers in the ZnO, to cross. The electrons that are generated in the CdTe near the interface would find it hard to flow through the ZnO layer and be collected in the TCO side. However, this interface is largely free of electronic states within the bandgap except for a few close to and below the fermi level.

On the other hand, for the Zn-Te terminated interface, the bands bend downward. The dip in the valence band forms a barrier for holes generated on the CdTe side close to the interface from moving towards the ZnO side. Holes, being the majority charge carriers in CdTe would move towards the back of the device from a lower to a higher energy since this is a favorable hole

transport mechanism. However, interface states are more prominent in this case, extending from the conduction band to below the fermi level.

The results are also consistent with reports in literature that suggest an upward band bending when there is a net positive charge accumulation. A Mulliken charge population analysis reveals that the O-Cd bonds at the interface are less polar than the Zn-O bonds, causing a lower electron density over the O atoms. On the CdTe side, the Cd-O bonds are more polar than the Cd-Te ones, creating a higher positive charge accumulation around the Cd atoms near the interface. The differences in polarity can be attributed to the electronegativities of the elements involved. The effect of this behavior creates a barrier for electrons moving from the absorber to the window layer. The net charges for each atomic layer close to the interface are provided in Tables 12 and 13.

Table 12. Average electronic charge on atomic layers at the interface (O-Cd termination)

Atom	Mg/Zn (bulk)	O (bulk)	Mg/Zn (interface)	O (interface)	Cd (interface)	Te (interface)	Cd (bulk)	Te (bulk)
Charge	+1.37	-1.39	+1.36	-1.33	+0.89	-0.45	+0.54	-0.54
Average (cation+anion)	-0.01		+0.02		+0.22		0.00	
Interface charge	-0.22							

Table 13. Average electronic charge on atomic layers at the interface (Zn-Te termination)

Atom	O (bulk)	Zn (bulk)	O (interface)	Zn (interface)	Te (interface)	Cd (interface)	Te (bulk)	Cd (bulk)
Charge	-1.46	+1.51	-1.34	+1.10	-0.57	+0.44	-0.53	+0.53
(cation+anion)/2	+0.03		-0.12		-0.07		0.00	
Interface charge	+0.27							

5.2. MZO/CDTE INTERFACE SIMULATIONS

5.2.1. METHODS

The interface (fig. 44) is constructed the same way as that of the ZnO/CdTe scenario except that magnesium now occupy 25% of the cationic lattice sites. Initial strain states at the interface remained the same. The Mg/Te termination was considered equivalent to the Zn/Te situation.

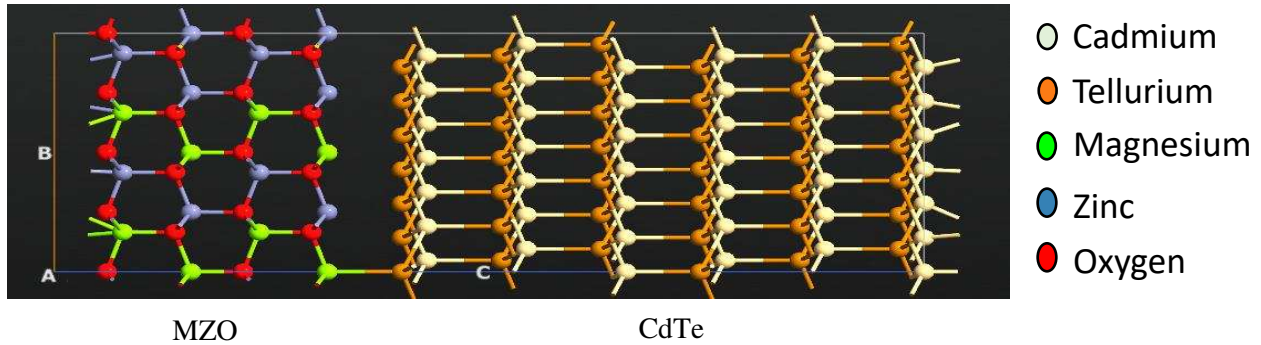


Fig. 45. The MZO/CdTe interface depicted using QuantumATK

As in the case of ZnO/CdTe, a device was configured in the two-probe model with bulk electrodes of MZO and CdTe on each side. This is shown in the figure 45 below.

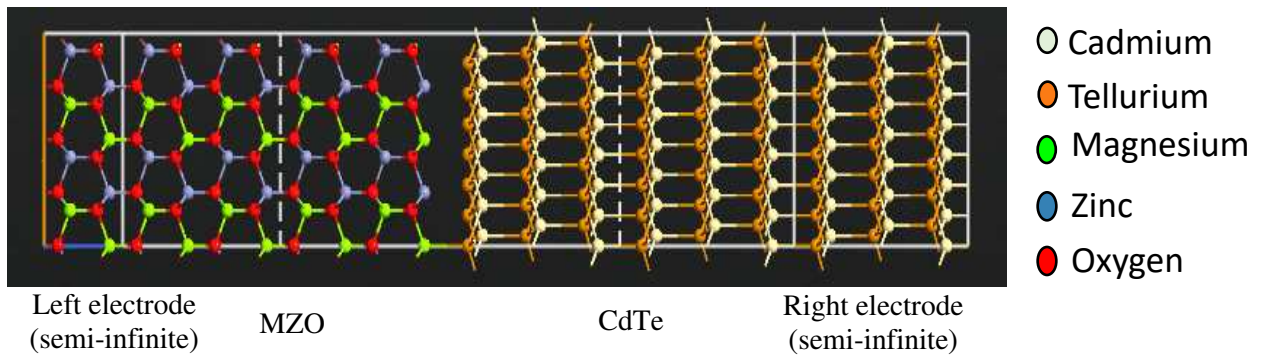


Fig. 46. The MZO/CdTe device structure built using the two-probe model in QuantumATK

5.2.2 RESULTS

Experimental reports suggest that the formation of a Mg/Zn-Te interface may be more likely [66]. Moreover, the calculations proved harder to converge due to the presence of a fifth

different element in the system and the system size. Regarding band alignment at the interface, a more pronounced band bending is noticed in the case of MZO as shown in the figure 46 below.

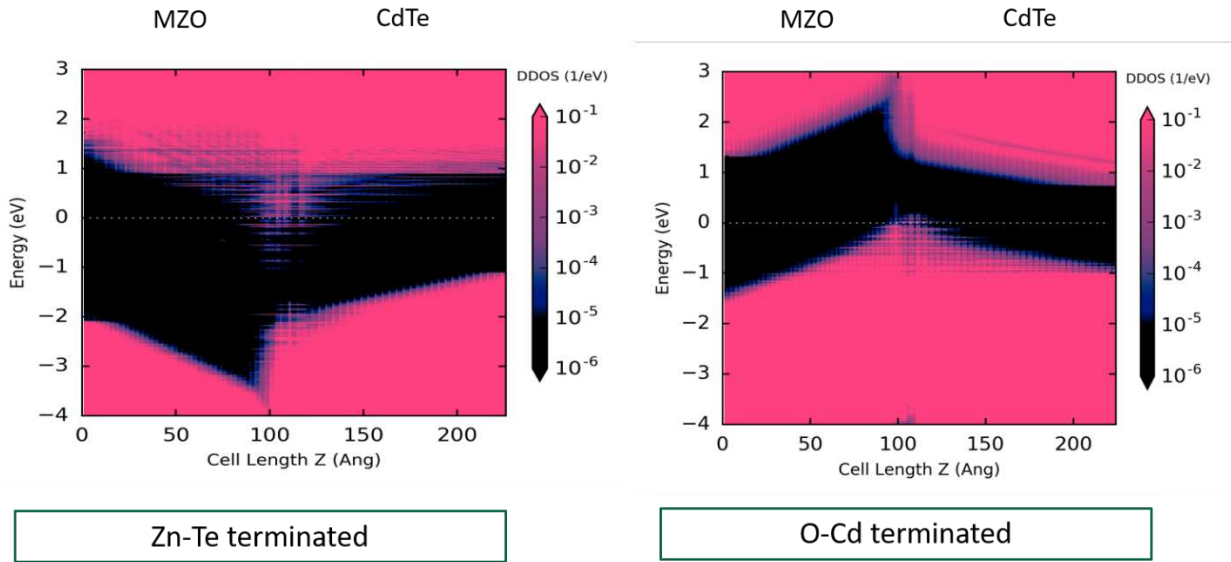


Fig. 47. Density of electronic states at the MZO/CdTe interface for Mg/Zn-Te termination (left) and O-Cd termination (right)

For consistency, the results of the analyses were shown with MZO on the left and CdTe on the right. The interfaces were brought together using the interface builder by straining the CdTe surface since it was deposited on MZO. It was assumed that MZO would undergo relaxation during the geometry optimization step. The case for CdTe being strained is that it is the layer deposited second. The case for MZO being strained is that it has a thickness of only 100 nm as compared to the CdTe with a standard thickness of more than 2 microns. The Zn/Mg-Te termination was easily achieved by direct use of the interface builder. However, in order to generate the O-Cd termination, the process had to start out with having the CdTe on the left and then flipping the entire structure by 180 degrees about the axis perpendicular to the interface or transport direction (z axis). This was performed using a simple feature in the software.

The amount of band bending observed is different than in the case of ZnO/CdTe. This behavior could be used to explain the movement or lack thereof of charge carriers through the device. In the case of the Mg/Zn-Te termination, it is the valence band that primarily bends down at the interface. It is believed that this behavior prevents the holes – which are the majority charge carriers in the p-CdTe absorber side – generated close to the interface from diffusing into the MZO window layer. On the other hand, the Cd-O termination causes band bending in the upward direction. Moreover, a spike is caused in the conduction band, which can form a barrier to the electrons (majority carriers in the n-MZO side) generated close to the interface in the CdTe side. The barrier that electrons are capable of crossing reasonably comfortably is around 0.4 eV from thermionic emission at room temperature [67]. However, this value of the barrier (or conduction band offset in this case) was measured at closer to 1 eV and as a result, most electrons would not possess the energy capable to cross this barrier and contribute to a significant amount of electron current. As in the case of ZnO/CdTe, only anion-cation terminations were investigated, and same polarity terminations were ignored.

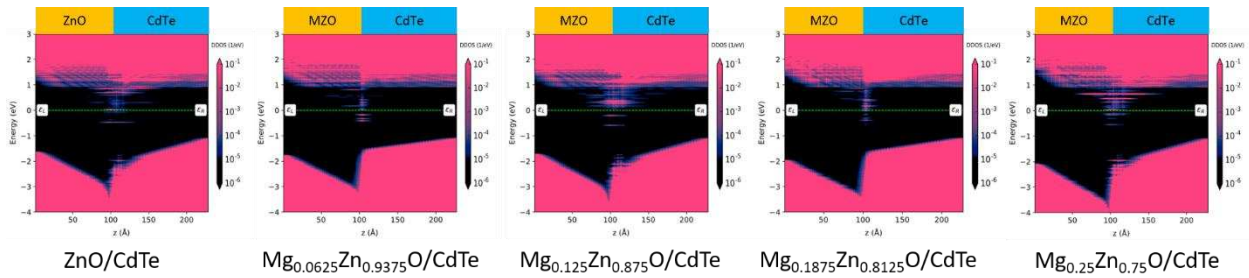


Fig. 48. Band alignment at the Mg/Zn-Te terminated MZO/CdTe interface for varying Mg

Table 14. Average electronic charge on atomic layers at the interface (Mg/Zn-Te termination)

Atom	O (bulk)	Mg/Zn (bulk)	O (interface)	Mg/Zn (interface)	Te (interface)	Cd (interface)	Te (bulk)	Cd (bulk)
Charge	-1.44	+1.43	-1.35	+1.15	-0.57	+0.51	-0.54	+0.54
(cation+anion)/2	-0.01		-0.10		-0.03		0.00	
Interface charge	+0.29							

Displayed above in fig. 47 are PLDOS plots of the Mg/Zn-Te terminated MZO-CdTe interface for various Mg ratios in MZO. The Mg/Zn-Te termination creates a dip in the valence band in both materials and is seen for all Mg ratios. The value of this dip which is the Valence Band Offset or VBO increases with higher Mg content, as does the band gap on the MZO side. Common knowledge suggests that bands bend down when there is an excess positive charge (holes or a deficiency of electrons) at any region. Since the interface atoms are of different polarities, one would expect the charge net charge to be dependent on how electronegative/electropositive the respective elements are. Indeed, a quantitative charge distribution calculation performed using a Mulliken population analysis suggests the same. Table 15 gives this distribution for four atomic layers from the interface on either side; beyond four layers, the differences in charge distribution were found to be negligible. The charges on each atomic layer have been averaged out for the sake of convenience. For example, the Mg and Zn atoms accumulate varying magnitudes of positive charge due to their different electro-positivity; also, atoms bonded at the interface will carry a slightly different charge than neighboring atoms of the same species.

At the Mg/Zn-Te interface, a hole generated in CdTe experiences repulsion at the Mg/Zn layer due to the positive charge on it (+1.16). A closer examination reveals that the Mg/Zn layer closest to the interface has a smaller positive charge compared to the immediate next such layer (+1.43), yielding a difference of -0.27. However, the oxygen layers do not see as much difference (-1.35 vs -1.44) which amounts to -0.09. This variation is not compensated for (at least in the

immediate neighboring layers), causing a net electron build-up at the interface. Similar behavior is observed on the CdTe side, although this magnitude is not as high, possibly due to the lower polarity of the bonds. Both Cd (0.54 to 0.51) and Te (-0.54 to -0.57) lose a 0.03 electronic charge. It is believed that this charge imbalance is redistributed over the entire device.

Considering charge balance by grouping alternating layers (anion and cation) within the same material (MZO or CdTe) results in increased electron density (lower positive/higher negative charge) than the neighboring atoms. This may contradict the fact that the bands bend down. However, taking only the contacting interface atoms (Mg/Zn and Te) into consideration reveals different results. The Mg/Zn and Te together average a positive charge of +0.22, thus causing the downward bending of the bands which agrees with literature reports.

The overall reduction in net charge at the interface (increase in electron density) causes the bands to bend down. Since this intensity is higher on the MZO side, the bands bend down to a higher degree. The O atoms near the interface have lower electronic charge (-1.35) than those 100 Å away (-1.44). Correspondingly, the Mg and Zn atoms average a +1.13 charge near the interface and the Te atoms at the interface exhibit a marginally higher negative charge (-0.566) than those in the bulk (-0.543). Similarly, the Cd atoms contain a charge of +0.544 at the bulk and (+0.514) at the center. Moreover, the gradient in the VB on the CdTe side would aid holes to drift towards the back contact.

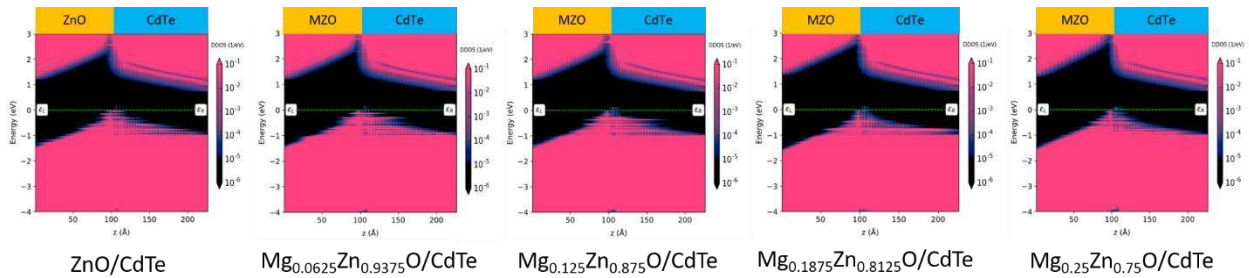


Fig. 49. Band alignment at the O-Cd terminated MZO/CdTe interface for different Mg percentages

Table. 15. Average electronic charge on atomic layers at the interface (O-Cd termination)

Atom	Mg/Zn (bulk)	O (bulk)	Mg/Zn (interface)	O (interface)	Cd (interface)	Te (interface)	Cd (bulk)	Te (bulk)
Charge	+1.37	-1.39	+1.36	-1.33	+0.89	-0.45	+0.54	-0.54
Average (cation+anion)	-0.01		+0.02		+0.22		0.00	
Interface charge				-0.22				

Shown above in fig. 48 are PLDOS plots of the O-Cd terminated MZO-CdTe interface for different concentrations of Mg in the MZO alloy. Bulk band gaps for MZO and CdTe approach theoretically calculated values but are yet to fully converge with respect to device length. Those for CdTe are closer to the results shown in Table 1. Band offsets generally increase with higher Mg content for both terminations and are summarized in Table. 5. This increase, however, does not appear to be linear. There seems to be an abrupt increase when the Mg concentration is increased from 12.5 to 18.75%. The CBO increases with more Mg. As observed with Mg/Zn-Te, this increase is non-linear. There is a sharp jump when just 6.25% Mg is added to the lattice. A rather large increase is also seen going from 12.5 to 18.75% Mg. A spike in the conduction band is produced in all simulation results. This is consistent with reports in literature that suggest an upward band bending when there is a net positive charge accumulation.

A Mulliken charge population analysis reveals that the O-Cd bonds at the interface are less polar than the Mg/Zn-O bonds, causing a lower electron density over the O atoms. On the CdTe side, the Cd-O bonds are more polar than the Cd-Te counterparts, creating a higher positive charge accumulation around the Cd atoms near the interface. The differences in polarity can be attributed to the electronegativities of the elements involved. The effect of this behavior creates a barrier for electrons moving from the absorber to the window layer. The net charges for each atomic layer close to the interface are provided in Table 16.

A net positive charge is seen to accumulate on the CdTe side of the interface. This effect is most prominent in Cd (+0.89 vs +0.54) where a difference of +0.35 is observed. In Te, this equates to +0.09 and in oxygen, +0.06. It is minimal in Mg/Zn (-0.01). However, the charge on O and Cd average a negative charge of -0.29, bending the bands upward at the interface. In this case, the band bending is uniform as opposed to that in Mg/Zn-Te where the bending was more prominent in MZO.

At the Mg/Zn-Te interface, a hole generated in CdTe experiences repulsion at the Mg/Zn layer due to the positive charge on it (+1.16). This seems to contradict the fact that the bands bend down. However, a closer examination reveals that the Mg/Zn layer closest to the interface has a smaller positive charge compared to the immediate next such layer (+1.43), yielding a difference of -0.27. The oxygen layers do not see as much difference (-1.35 vs -1.44) which amounts to -0.09. This variation is not compensated for (at least in the immediate layers), causing a net electron build-up at the interface. Similar behavior is observed on the CdTe side, although this magnitude is not as high, possibly due to the lower polar nature of the bonds. Both Cd (0.54 to 0.51) and Te (-0.54 to -0.57) lose a 0.03 electronic charge. It is assumed/believed that this charge imbalance is redistributed over the entire device. The overall reduction in net charge at the interface (increase in electron density) causes the bands to bend down. Since this intensity is higher on the MZO side, the bands bend down to a higher degree.

Even though looking at the anion and cation of the same material (MZO or CdTe) results in lowered or increased electronic charge, taking only the interface atoms into consideration reveals different results. The Mg/Zn and Te together average a positive charge of +0.22, causing the bands to bend down which agrees with literature reports. On the contrary, the charge on O and Cd average a negative charge of -0.29, bending the bands upward at the interface.

For the O-Cd termination, the opposite effect is seen. A net positive charge seems to have accumulated at the interface. This effect is most prominent in Cd (+0.89 vs +0.54) where a difference of +0.35 is observed. In Te, this equates to +0.09 and in oxygen, +0.06. It is minimal in Mg/Zn (-0.01). In this case, the bands bend up almost uniformly. On the other hand, the Mg/Zn-Te termination creates a dip in the valence band in both materials. The O atoms near the interface have lower electronic charge (-1.35) than those 100 Å away (-1.443). Correspondingly, the Mg and Zn atoms average a +1.13 charge near the interface and the Te atoms at the interface exhibit a marginally higher negative charge (-0.566) than those in the bulk (-0.543). Similarly, the Cd atoms contain (+0.544) at the bulk and (+0.514) at the center. Moreover, the gradient in the VB on the CdTe side would aid holes to drift towards the back contact.

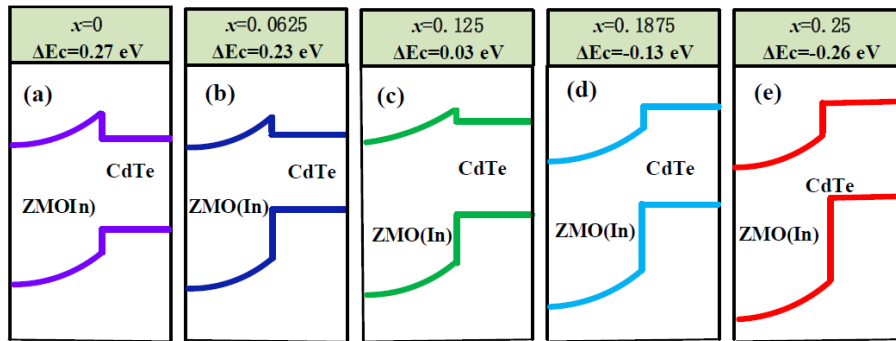


Fig. 50. Conduction band offsets for CdTe devices employing MZO of different magnesium concentrations [68].

DFT results are different from those predicted by SCAPS (fig. 49). However, the DFT models portrayed intrinsic semiconductor materials while the SCAPS study incorporated a certain amount of p and n type doping to the absorber and window layers respectively. Although the CdTe doping was minimal ($\sim 10^{14} \text{ cm}^{-3}$), the MZO doping levels ranged from 10^{15} to 10^{17} cm^{-3} , which are higher than those observed practically by a magnitude of one to three orders. Despite these differences, SCAPS models do not bring out the finer nuances in the band alignment. Minor interface states and variations in the conduction and valence bands are not observed. These features

could provide more detail about charge transport behavior and eventually device performance. One way of looking at the band bending behavior is by analyzing the charge rearrangement at the interface. Table 16. gives this distribution for four atomic layers from the interface on either side; beyond four layers, the differences in charge distribution were found to be negligible. The charges on each atomic layer have been averaged out for the sake of simplicity/convenience, especially since the Mg and Zn atoms accumulate varying magnitudes of positive charge due to their different electro-positivity.

Table 16. Band gaps and band offsets at the MZO/CdTe interface

Composition	MZO Eg (O-Cd)	MZO Eg (Mg/Zn-Te)	CBO (O-Cd)	VBO (Mg/Zn-Te)	CdTe Eg (O-Cd)	CdTe Eg (Mg/Zn-Te)
ZnO	2.56	2.81	0.85	0.89	1.72	2.02
Mg _{0.0625} Zn _{0.9375} O	2.57	2.94	0.88	1.31	1.73	2.00
Mg _{0.125} Zn _{0.875} O	2.62	2.98	0.92	1.35	1.73	2.00
Mg _{0.1875} Zn _{0.8125} O	2.76	3.3	1.14	1.51	1.74	2.00
Mg _{0.25} Zn _{0.75} O	2.80	3.48	1.21	1.56	1.74	2.00

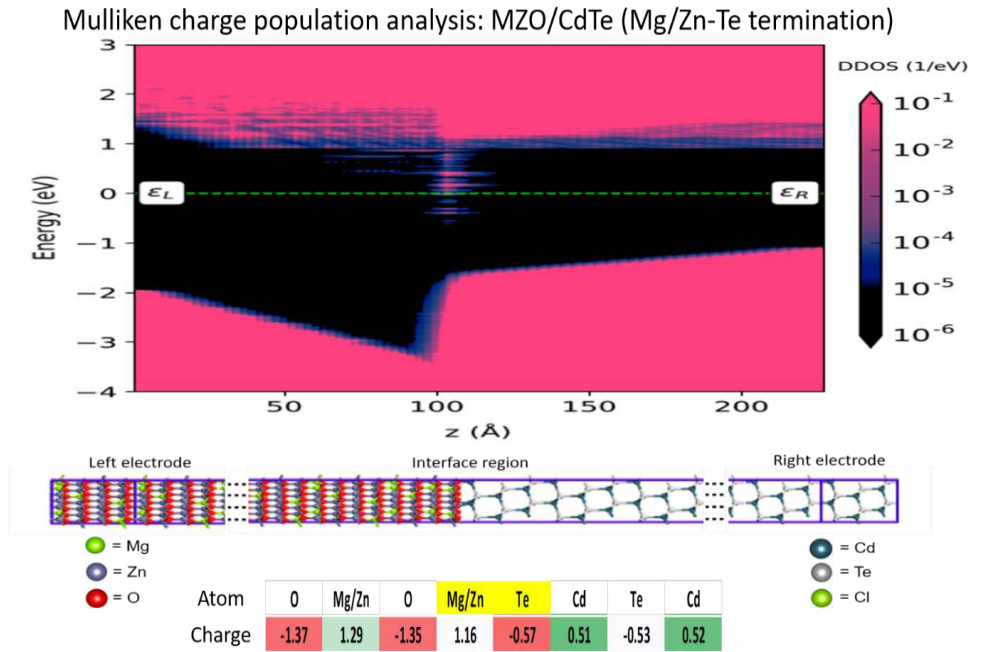


Fig. 51a. PLDOS image (above), device configuration (middle) and Mulliken charge analysis (bottom) of Mg/Zn-Te terminated MZO/CdTe

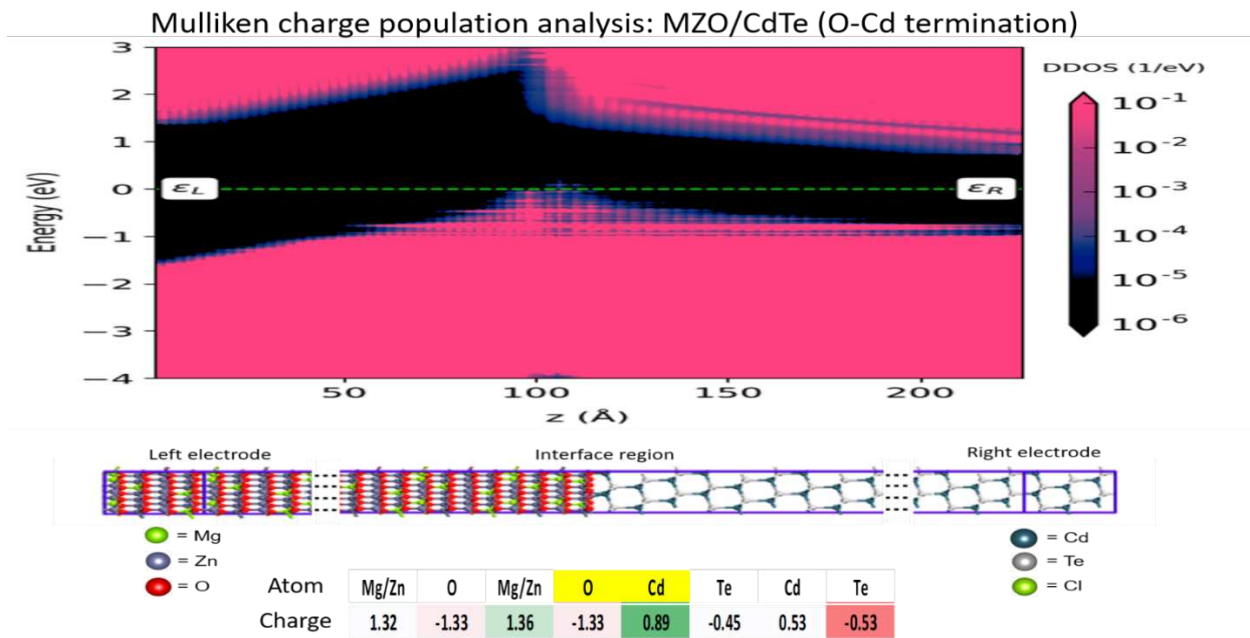


Fig. 51b. PLDOS image (above), device configuration (middle) and Mulliken charge analysis (bottom) of O-Cd terminated MZO/CdTe

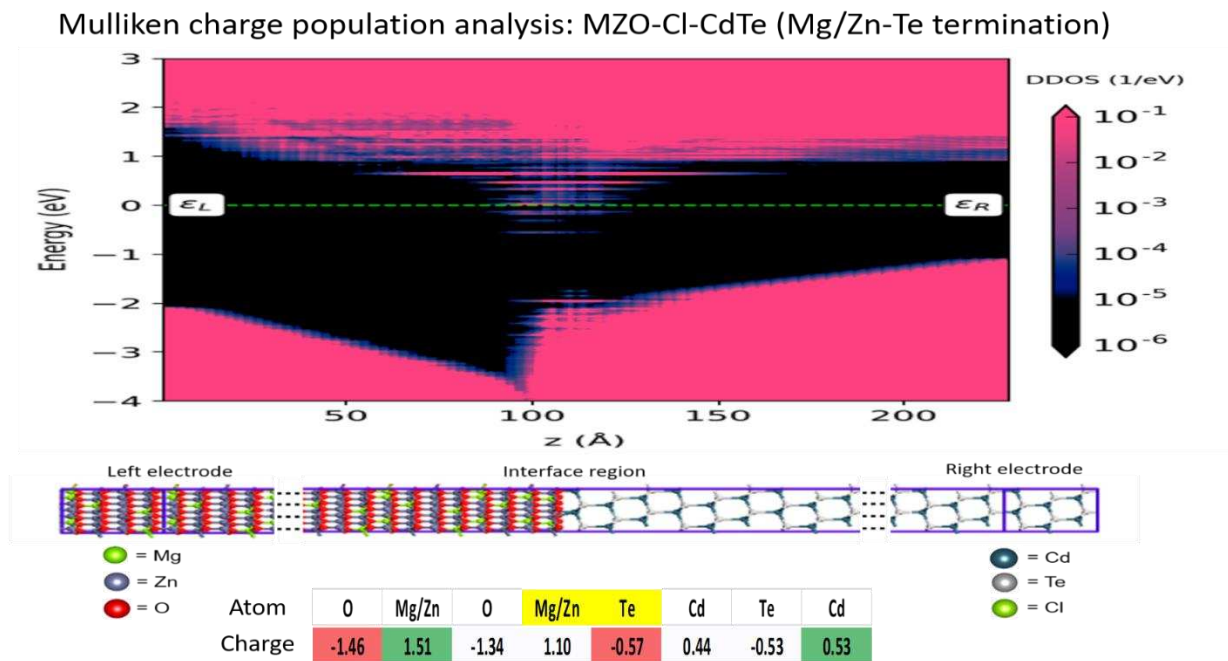


Fig. 52a. PLDOS image (above), device configuration (middle) and Mulliken charge analysis (bottom) of Mg/Zn-Te terminated MZO/Cl/CdTe

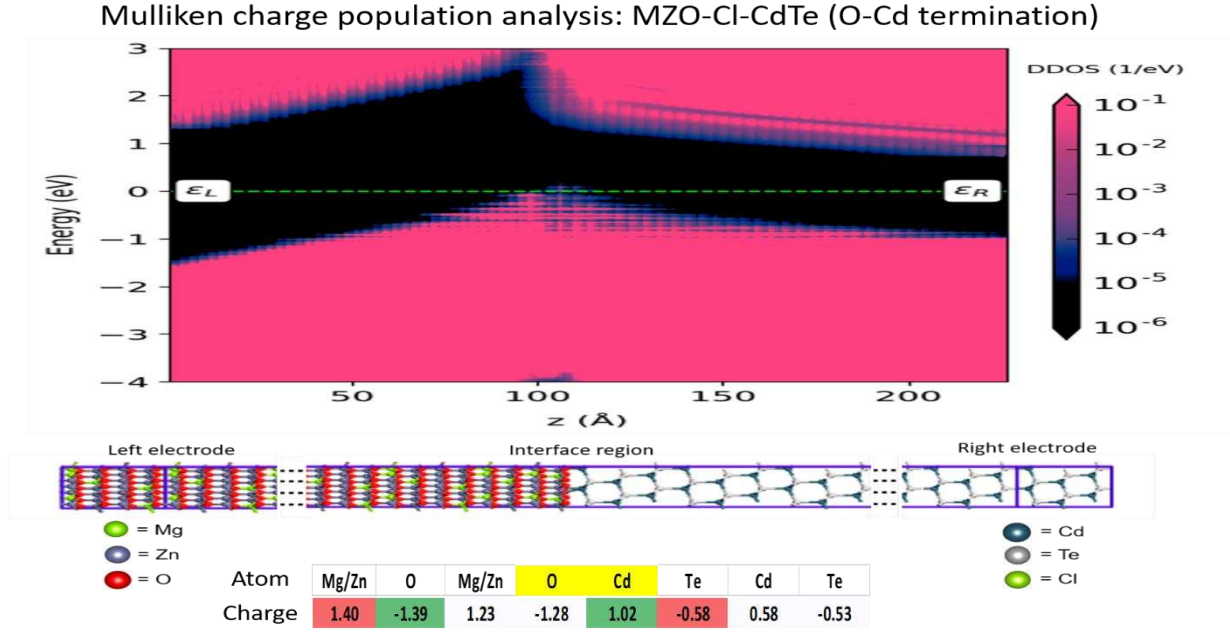


Fig. 52b. PLDOS image (above), device configuration (middle) and Mulliken charge analysis (bottom) of O-Cd terminated MZO/Cl/CdTe

The main takeaway from these calculations is that interface termination has a major role to play in the way the bands align themselves, which is not considered in existing models. The conduction band on the MZO side bends up in the case of an O-Cd termination creating a barrier for electrons moving from the absorber to the window. On the other hand, the valence band bends downward in the case of a Mg/Zn-Te termination thus providing a hole barrier that prevents them from moving into the MZO, thereby retaining them within the CdTe.

It has also been experimentally proven that the MZO-CdTe interface does indeed terminate as Mg/Zn-Te. Research done by Clemens et al detected the above elements at the interface using a combination of different techniques [33]. These included Ultraviolet Photoelectron Spectroscopy (UPS), X-ray excited Auger Electron Spectroscopy and Inverse Photoemission Spectroscopy. Using the above measurements, a peak energy value equivalent to those reported for ZnTe was observed, thus confirming the existence of a Zn-Te bond at the interface. A secondary peak speculated to be equivalent to Mg-Te was also seen but there were no literature data to compare

with. A distinction was made between the optical and electronic band gap and it was theorized that the latter was primarily responsible for charge transport. An optical gap is defined as the gap between the band edges whereas an electronic gap excludes defect states. These defect states could form due to the influence of the interface. The CdTe is expected to have low defect concentrations and the electronic gap is close to the optical gap. For MZO, the defect concentration is higher since it must allow for conductivity. However, since it is also transparent, the optical states are separated by a large gap. This is indeed the case for the band alignment results determined experimentally shown in figure below. These band alignment results match those calculated from DFT.

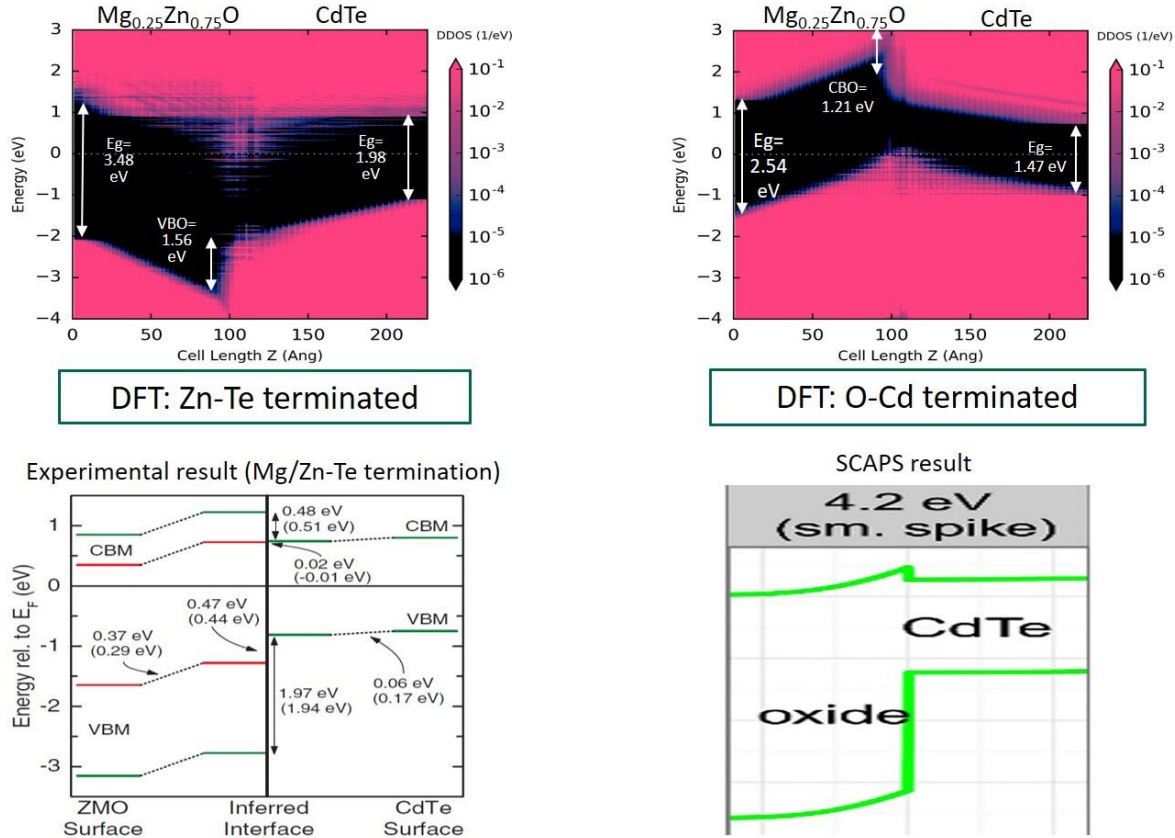


Fig. 53. A comparison of atomistic modeling, experimental and SCAPS results for the MZO/CdTe interface

It is our hypothesis that for this grain orientation of CdTe 111 and MZO 0002, the Zn-Te terminating interfaces are predominant as they would aid flow of current. These are the highest

peak intensities as observed by X-Ray diffraction (XRD) and Electron Backscatter (EBSD) measurements for the CdTe and MZO respectively. The (101) is the second most common grain orientation observed in MZO deposited on glass. In the case of CdTe deposited on MZO, the 111 is the clear winner, with the second most predominant grain much lower in XRD peak intensity. These are shown in the images below.

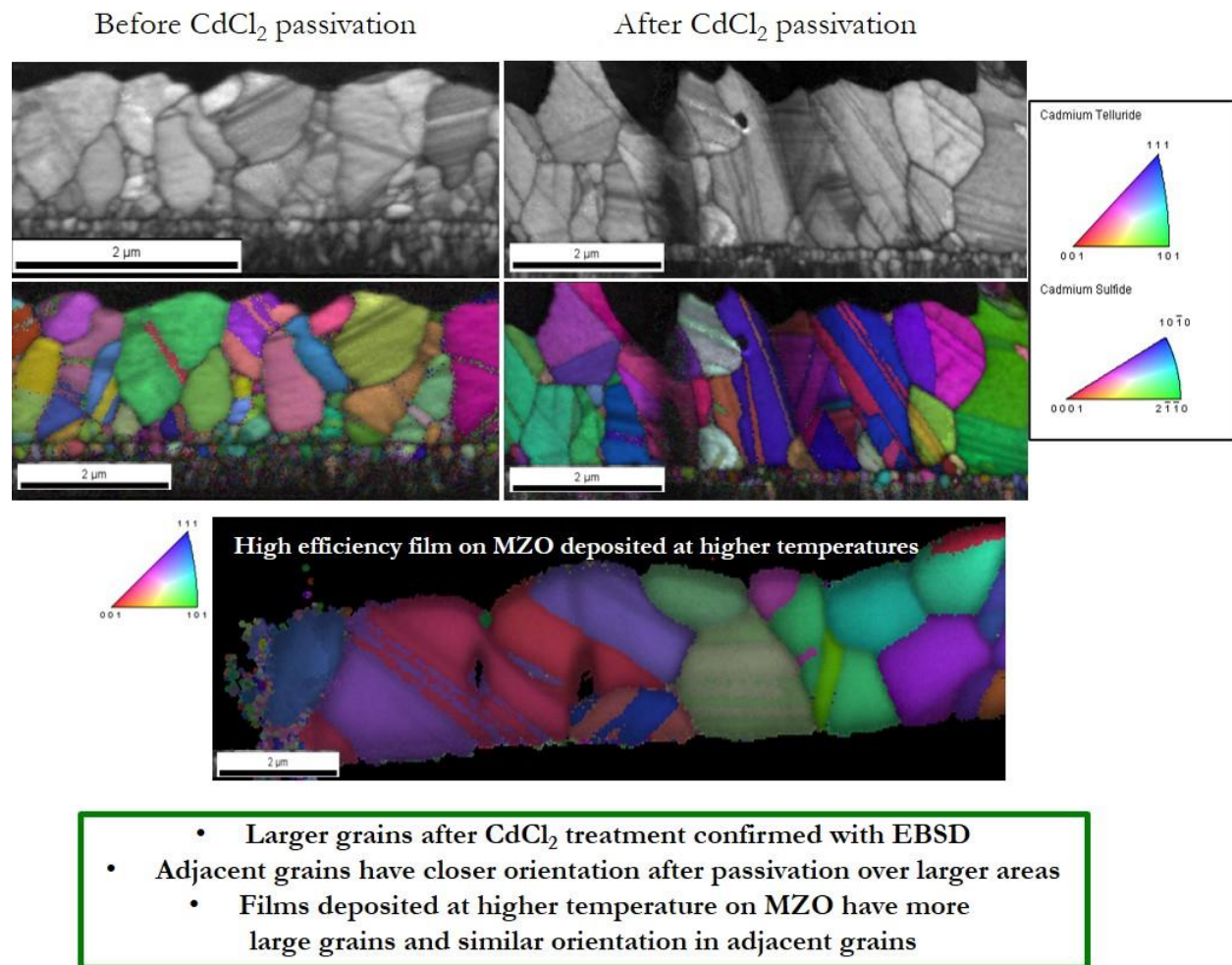


Fig. 54. Grain orientation of CdTe and MZO using Electron Backscatter Diffraction (EBSD)

It is hypothesized that for this grain orientation of CdTe (111) and MZO (0002), the Zn-Te terminating interfaces are more predominant as they would aid the flow of hole current, establishing solid device performance as we know from experimental data. The mild gradient also

favors hole drift across the absorber. Electron current may be limited, but a fair number would make it past the moderate barrier using thermionic emission, for $E < 0.4$ eV. For O-Cd terminated interfaces, the electron barrier is too high to overcome. A hole barrier exists too, although it is not as steep as the electron barrier. In any case, holes generated near the interface would find it difficult to move towards the back due to the gradient opposing them. One possible explanation for the high performance of these devices assuming they are largely intrinsic stems from the observation that CdTe grain size is about twelve hundred times that of MZO. It is postulated that the preferred interface configuration of Mg/Zn atoms contacting Te carry the bulk of the current. Another explanation is that the (002) crystal direction of MZO forms only a fraction of the interface orientations, with the (101) representing the next most common plane. The MZO (101)/CdTe (111) interface may exhibit properties different from those seen with MZO (002)/CdTe (111) with the O-Cd termination less hostile to electron transport. Preliminary investigations on the (101)/CdTe (111) interface indicate that it is computationally more expensive than corresponding MZO (002)/CdTe (111) simulations.

Although the band properties away from the interface play a part in device performance, only band behavior right at the interface (a few monolayers) was considered here. The band bending towards the bulk materials are a result of the valence and conduction bands of the materials on either side of the window and absorber materials. In this case, they would be Fluorinated Tin Oxide (FTO) and Te respectively. However, since the focus of this study is primarily interfaces, any detailed consideration of the band behavior away from the interface has been omitted.

5.3. EFFECT OF CHLORINE

The CdCl_2 treatment remarkably improved device efficiency due to several postulated reasons [69]. These include but are not limited to:

- Lessening of point defect concentrations
- Passivation of recombination centers at the grain boundaries
- Stacking fault correction
- Formation of n-type regions that facilitate electron-hole separation
- Reduction of mid-gap states while maintaining charge separation

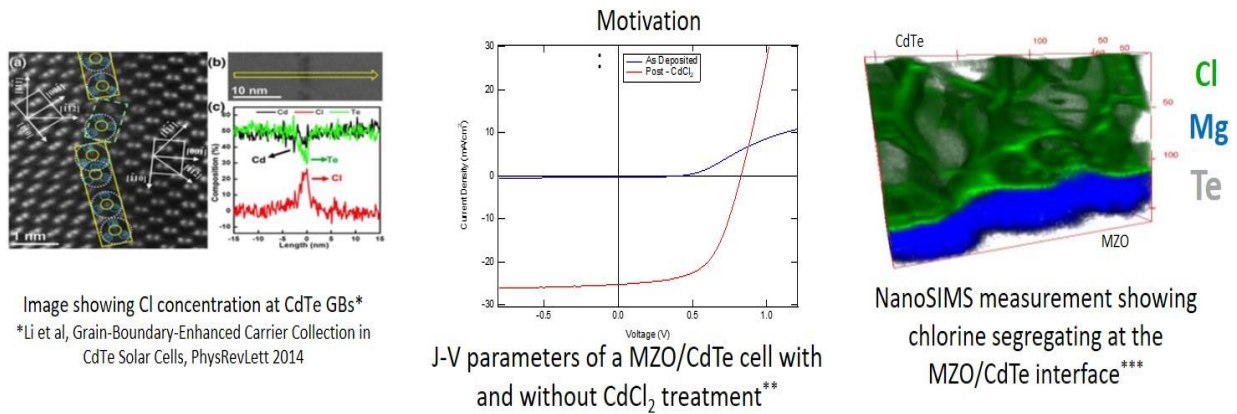


Fig. 55. Effect of CdCl_2 treatment on CdTe devices (left) and NanoSIMS showing the presence of chlorine at the MZO/CdTe interface (right)

The effect of the CdCl_2 treatment can be simulated in two ways. One of them is by replacing tellurium with elemental chlorine at the interface. This is expected to passivate dangling bonds at the interface by alleviating the electronic states close to the valence band in the case of Mg/Zn-Te termination and by cleaning the states close to the conduction band in the Cd-O termination scenario. The idea was to perform simulations with chlorine replacing tellurium at the MZO/CdTe interface for the most commonly occurring chlorine concentrations as measured by NanoSIMS (Secondary Ion Mass Spectroscopy) techniques. This was done to determine the passivating effect of the CdCl_2 treatment. Such a measurement is shown in the figure in the page above.

Another method is to simulate the effect of molecular CdCl_2 . Since this was difficult to model, the first method was chosen – atomic Cl was introduced into the Te site as seen in CdTe grain boundary results [70]. Other reports also show Cl replacing Te to be energetically favorable [71]. A monolayer of chlorine was added at the interface, occupying 25% of the tellurium sites, following research published by Chen Li who performed measurements at CdTe grain boundaries. Li et al. observed 20-30% of the Te sites substituted by chlorine. However, it was decided to simulate different chlorine concentrations to see its effect on the band alignment. These results can also be compared with other studies on the effects of Cl in CdTe solar cells.

Other literature reports indicate the existence of a monolayer of cadmium chloride at the MZO/CdTe interface but modeling three compounds within the same device (two interfaces) was out of the scope of this project. However, it was also seen that atomic chlorine segregated preferentially at the grain boundaries in CdTe where the chlorine concentration was estimated to be between 20 and 30%, almost all of them occupying a tellurium site. As a result, it was decided that the simulations would involve chlorine replacing 25% of the tellurium atoms at the interface. For a Mg/Zn-Te terminated interface, chlorine seems to alleviate a few states just above the valence band but those below extend further out into the bulk. Specifically, it is seen that chlorine removes states present at 0.8 eV above and 2.1 eV below the Fermi level possibly creating more at 0.3 and 0.9 eV below the Fermi level.

For an O-Cd terminated interface, the effect is less obvious. However, a few states just above the valence band seem to get cleaned up but those below extend further out into the bulk. Specifically, it is seen that chlorine removes states present between 0.2 and 0.3 eV below the Fermi level while possibly creating more between 0.4 and 0.5 eV below the Fermi level.

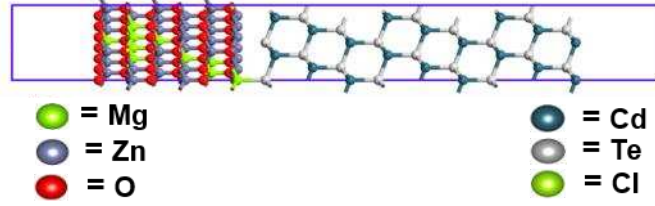


Fig. 56a. Illustration of the MZO/CdTe interface for with Cl (Mg/Zn-Te terminated)

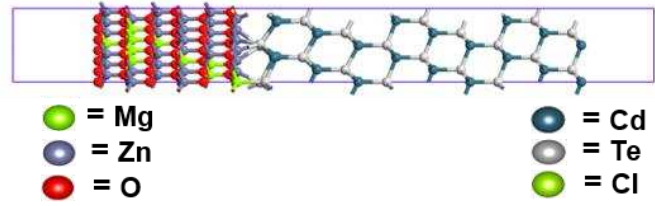


Fig. 56b. Illustration of the MZO/CdTe interface for with Cl (Mg/Zn-Te terminated)

TABLE 17. BAND GAPS AND BAND OFFSETS FOR THE MZO-CL-CdTe INTERFACE

Band alignment comparison	Values (eV)		
	<i>MZO bulk E_g</i>	<i>Band offset</i>	<i>CdTe bulk E_g</i>
O-Cd terminated, No Cl	2.81	1.23	1.70
O-Cd terminated, 25% Cl _{Te}	2.81	1.21	1.67
O-Cd terminated, 50% Cl _{Te}	2.82	1.81	1.73
O-Cd terminated, 75% Cl _{Te}	2.90	1.96	1.74
O-Cd terminated, 100% Cl _{Te}	3.05	1.88	1.73
Mg/Zn-Te terminated, No Cl	3.48	-1.53	1.98
Mg/Zn-Te terminated, 25% Cl _{Te}	3.45	-1.62	2.00

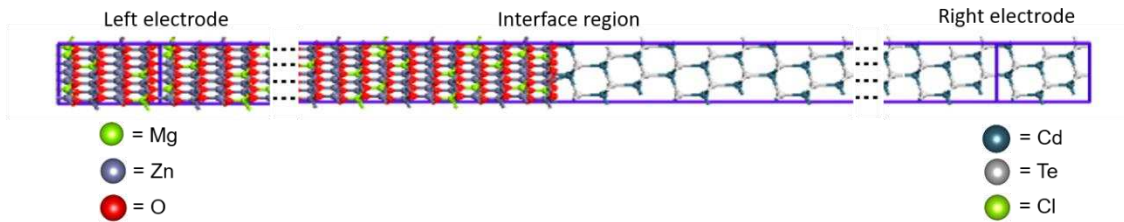


Fig. 57. Illustration of the MZO/CdTe device configuration for with Cl (Mg/Zn-Te terminated)

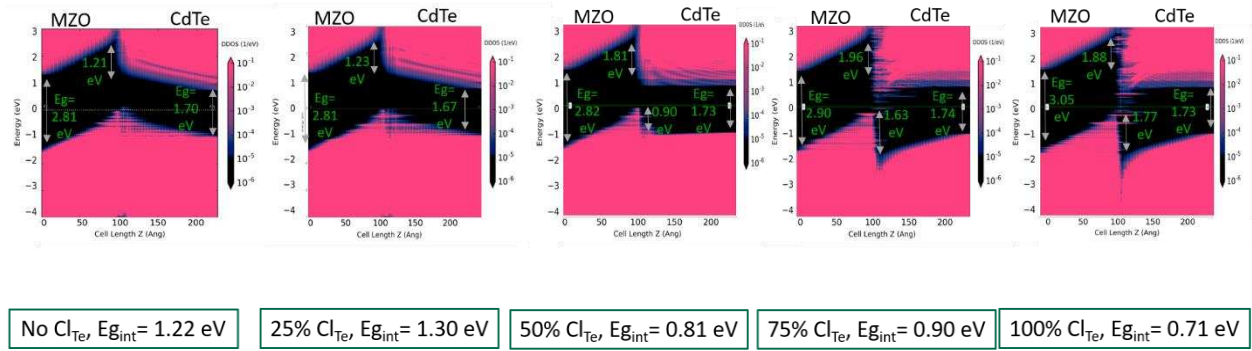


Fig. 58a. MZO/CdTe band alignment for different Cl concentrations (O-Cd terminated)

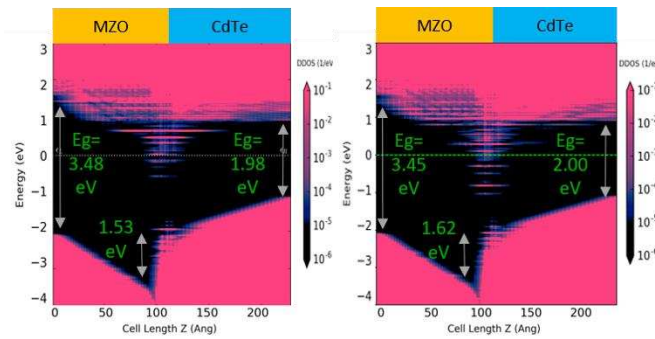


Fig. 58b. PLDOS plots for Mg/Zn-Te terminated MZO-CdTe a) without Cl b) with 25% Cl_{Te} .

Displayed above are PLDOS plots of different chlorine concentrations at the MZO-CdTe interface. Comparing the different images, Cl concentrations of 0% and 25% lead to clean band gaps. The latter has a higher E_g value at the interface as the states around the Fermi level have been erased. This suggests that Cl up to a concentration of 25% passivates the interface chemically by removing states close to the valence and conduction bands. As the number of Cl atoms at the interface increases, thereby increasing the ratio, the effect is more detrimental as several interface states begin to form.

The above figures indicate that the band alignment may not favor electron transport through the MZO to the front of the device. This is due to a very high CBO (>1 eV). Electrons assisted by thermionic emission may possess enough energy to cross a lower barrier (<0.4 eV) at room

temperature. Movement of holes will also be restricted due to the VB on the CdTe side bending down away from the interface.

In the case of Mg/Zn-Te terminations, only 0% and 25% Cl have been simulated. Convergence has not yet been reached for calculations involving higher amounts of Cl. Efforts are currently being undertaken to achieve this. This trend has been observed in the O-Cd termination case and is expected to follow a similar trend with the Mg/Zn-Te terminated models. A narrowing of the band gap can also be observed. Moreover, a dip in the valence band on the CdTe side is noticed as the amount of Cl goes up. Cl at a concentration of 25% provides the best band alignment. This may indicate that Cl concentrations at the MZO-CdTe interface resemble those at the grain boundaries as determined by the experimental findings of Li et al.

5.4. MZO/CDSETE INTERFACE SIMULATIONS

5.4.1. METHODS

The MZO/CST interface construction involved both layers consisting of alloys as opposed to just one in the previous section (MZO/CdTe). Only one alloy composition of CST was tested ($\text{CdSe}_{0.375}\text{Te}_{0.625}$) since it provided the most optimal results from a device standpoint [32]. The interface consisting of the same number of atoms (156 – 84 on the MZO side and 72 on the CST side) was geometry optimized to the same tolerance as in the previous cases. Shown below is an image of the MZO-CST interface (Mg/Zn-Se-Te terminated and O-Cd terminated).

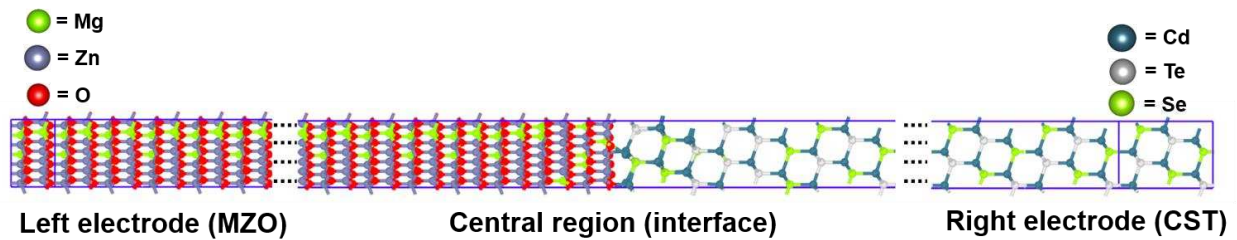


Fig. 59a. Illustration of the MZO/CdTe interface for O-Cd termination

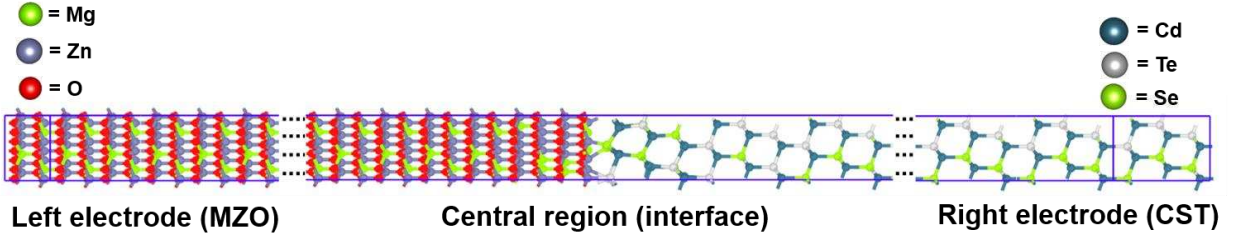


Fig. 59b. Illustration of the MZO/CdTe interface for Mg/Zn-Se/Te termination

5.4.2 RESULTS

Very few differences were observed between the PLDOS results for MZO/CdTe and MZO/CST. The electron barrier in the CB is still present in the case of the O-Cd termination, although not as high. The VB magnitude is also lower. As with MZO/CdTe, the interface is clean for the O-Cd termination while some states are observed for Mg/Zn-Se/Te.

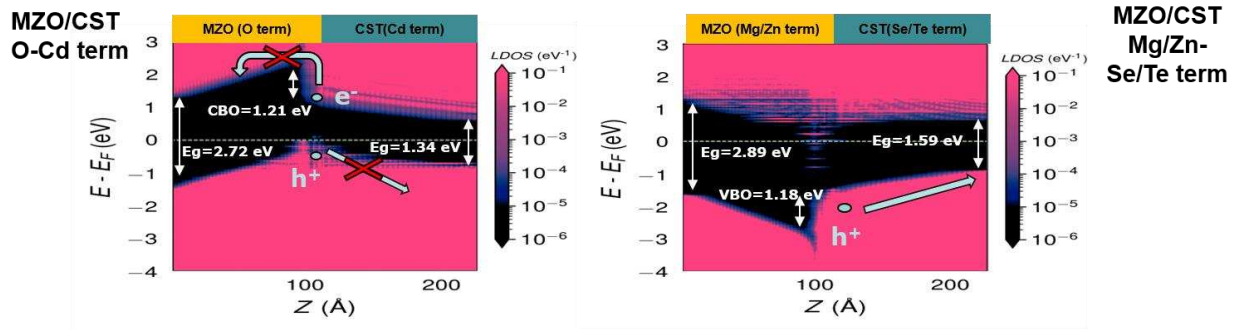


Fig. 60. Band alignment at the MZO/CST interface

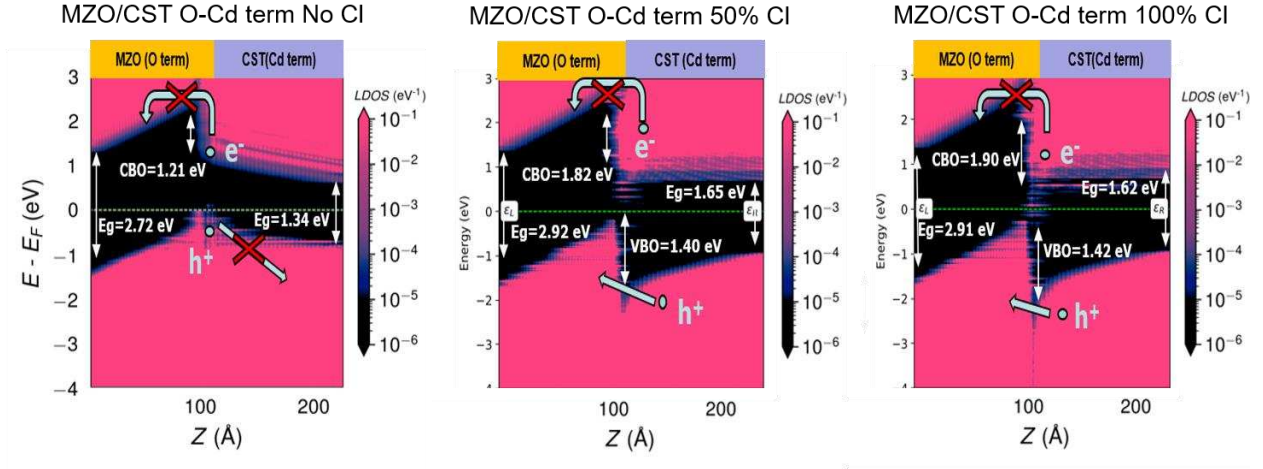


Fig. 61a. Band alignment at the MZO/CI/CST interface (O-Cd termination)

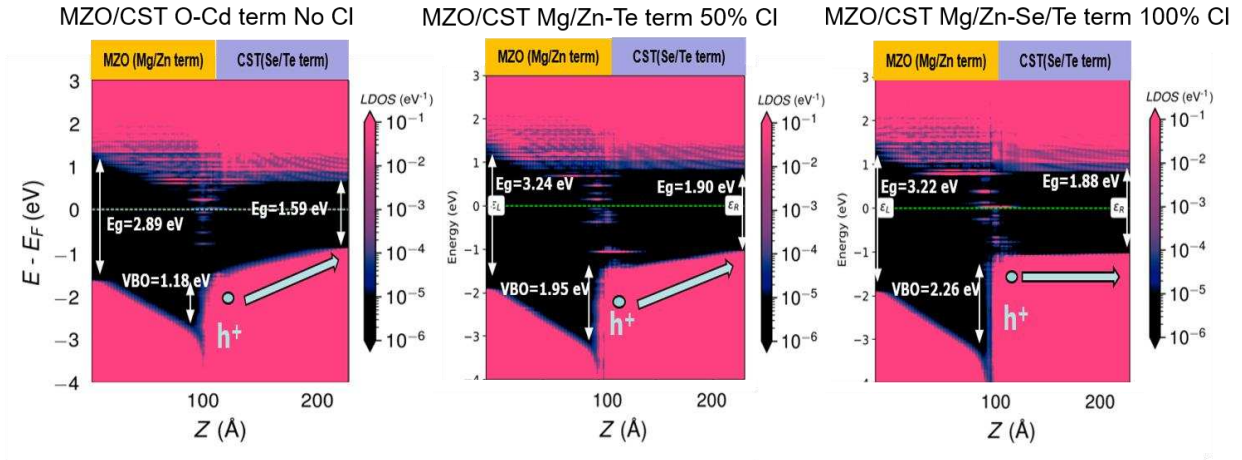


Fig. 61b. Band alignment at the MZO/CI/CST interface (Mg/Zn-Se/Te termination)

CHAPTER 6. CONCLUSIONS AND FUTURE WORK

Atomistic simulations were performed for a range of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ compositions in wurtzite and rock salt phases using LDA and GGA XC functionals with and without GO. The LCAO representation of the Kohn Sham equations in the DFT methodology were used in combination with semi empirical band gap correction methods. Calculated structural parameters include lattice constants – a for both hexagonal and cubic structures as well as c and c/a ratios for the latter. The electronic parameters of band gap, valence, and conduction band edges as well as electron effective masses were also computed. The models were in good agreement with reported experimental values for both structural and electronic properties. LDA-1/2 in combination with structural relaxation (GO) showed the best results.

DFT+GF was used to calculate bulk properties and interface band alignment of $\text{MZO}(0002)/\text{CdTe}(111)$ and $\text{MZO}(0002)/\text{CST}(111)$ for O-Cd and Mg/Zn-Te(Se) terminations. Atomistic simulations reveal material characteristics not observed in other models. The most prominent feature seen from the PLDOS images is that the band alignment at the MZO/CdTe interface is largely dependent on the termination of atoms in both layers. In the intrinsic case, the Mg/Zn-Te termination may be more favorable, or at least less detrimental for charge transport by providing a barrier for the holes generated in the CdTe. The O-Cd termination, on the other hand, appears to create a barrier for electrons moving from the absorber to the MZO, thus impeding electron current. This has practical implications for fabricating devices that consistently produce higher currents by being able to control the deposition of MZO such that it terminates with the cation. This way, it is more probable that the CdTe/CST layer, when deposited on the MZO,

terminates as Te or Se, forming this desirable interface, as has been shown both experimentally as well as in theoretical calculations [66].

Simulations involving elemental chlorine replacing the anion atoms of CdTe/CST at the interface suggest that small amounts of chlorine may reduce interface states through chemical passivation. The band alignment values are quantified. The models can be used to substantiate present experimental data and even possibly guide parameters pertaining to MZO deposition in thin film CdTe based processes. These simulations could also serve as a good platform for moving to more sophisticated interface modeling techniques combining DFT and TCAD (Technology Computer Aided Design) simulation tools. Such modelling efforts are expected to throw more light on specific properties such as interface band alignment and possible mechanisms for carrier transport in those devices.

The results depicted in this study represent a case where both materials are intrinsic. Low doping had little effect on band alignment. A device where one or both materials are doped to higher levels than seen practically is expected to reveal different characteristics. In the case of n doped MZO, the Fermi level would be pushed up closer to the conduction band, which may flatten out. This might cause the bandgap to converge faster with respect to length, thus reaching closer to the experimental value within a shorter distance from the interface/into the bulk. For Mg/Zn-Te terminated MZO/CdTe, such doping might cause the electron barrier to be alleviated while still retaining the hole barrier, both of which are beneficial. Simulations using higher amounts of doping could be performed for a more precise understanding. There is already a focus to increase doping in the fabrication process at CSU. If such calculations result in better band alignments, these efforts could be bolstered further. For simplicity, models studying the effect of chlorine at the interface involved elemental chlorine replacing the anion in the absorber. However, layers of

molecular CdCl_2 have been reported in literature [72]. Complex oxides of CdTe have also been observed to form at CdTe interfaces with alumina and MZO. Simulating these configurations would involve more sophisticated approaches.

6.1 RESEARCH QUESTIONS, HYPOTHESES AND RESULTS

Below is the list of research questions and hypothesis formed at the beginning of this work, along with the results.

1. What is the band alignment at the interface between the ZnO/CdTe and MZO/CdTe from atomistic modeling?

- Hypothesis: band alignment is determined by the electron affinity values
- Result: Band alignment is influenced more by termination chemistry than by electron affinity.

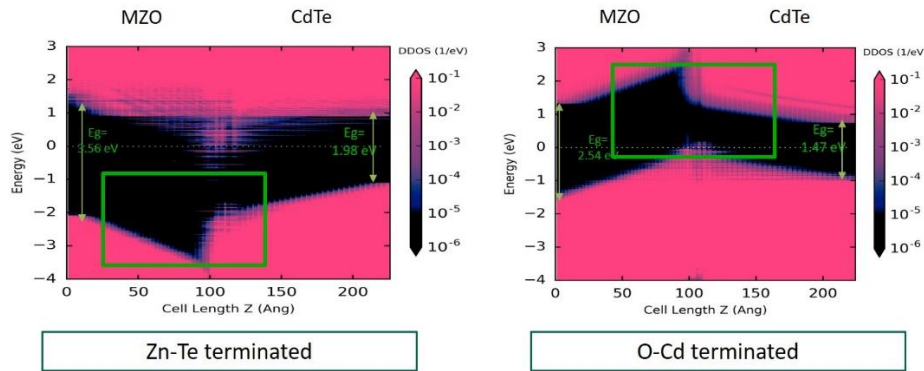


Fig. 62. Dependence of band alignment on termination chemistry (MZO/CdTe)

2. How does interface termination/chemistry affect band alignment?

- Hypothesis: Termination (O-Cd or Mg/Zn-Te) should exhibit similar band alignment characteristics since the valences of the cation and anion atoms are the same.

- Result: Termination chemistry dictates band alignment characteristics.

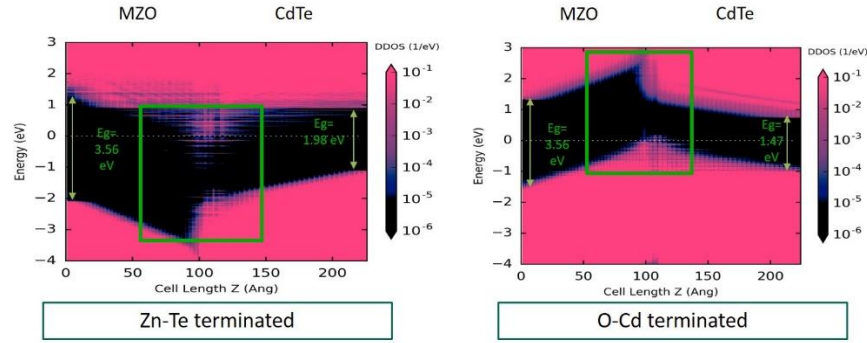


Fig. 63. Dependence of band alignment on termination chemistry (MZO/CdTe)

3. Are defect states present at the MZO/CdTe interface?

- Hypothesis: Defect states are likely to exist irrespective of termination
- Result: Termination plays a big role in the existence of defect states

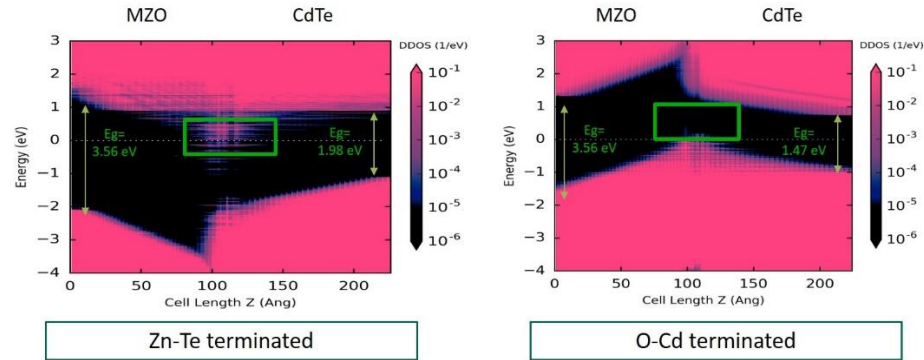


Fig. 64. Dependence of defect states on termination chemistry (MZO/CdTe)

4. How will chlorine modify the band alignment features at the MZO/CdTe interface?

- Hypothesis: Cl is expected to passivate the interface and alter band bending.
- Result: Cl passivates the interface chemically by removing dangling bonds. High amounts of chlorine result in electrical passivation through band bending.

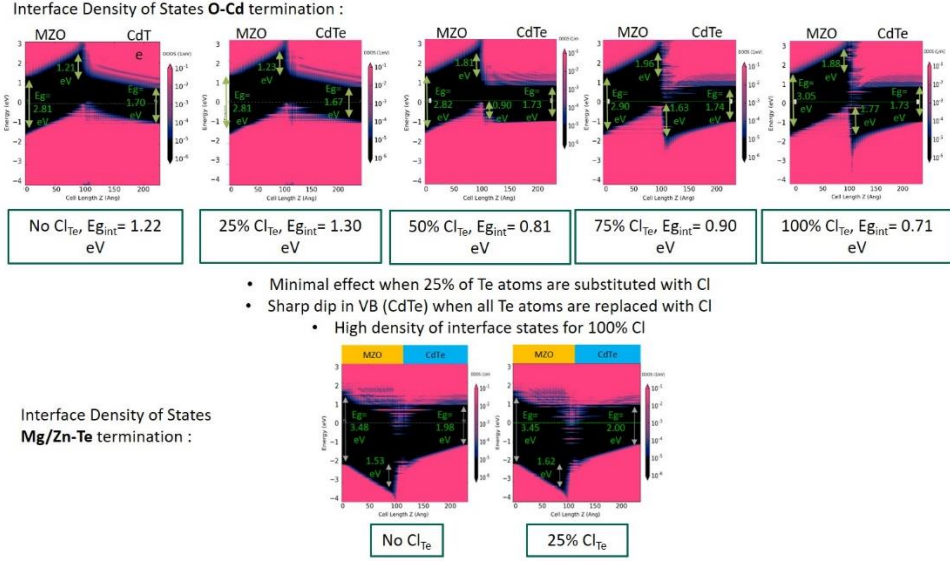


Fig. 65 Effect of Cl on band alignment features of the MZO/CdTe interface

6.2 FUTURE WORK

Future work beyond the PhD research would involve characterize and quantify interface defects and use the results as input in device modeling software such as SCAPS and Sentaurus TCAD. Another region of interest is the modeling of thin film deposition processes using Molecular Dynamics (MD). The above steps will be focused on optimizing single junction solar cells, following which multi-junctions would be studied. This will lead to the realization of the full potential of CdTe based photovoltaics.

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APPENDIX

APPENDIX A: OPTICAL MEASUREMENTS FOR CDS AND MZO

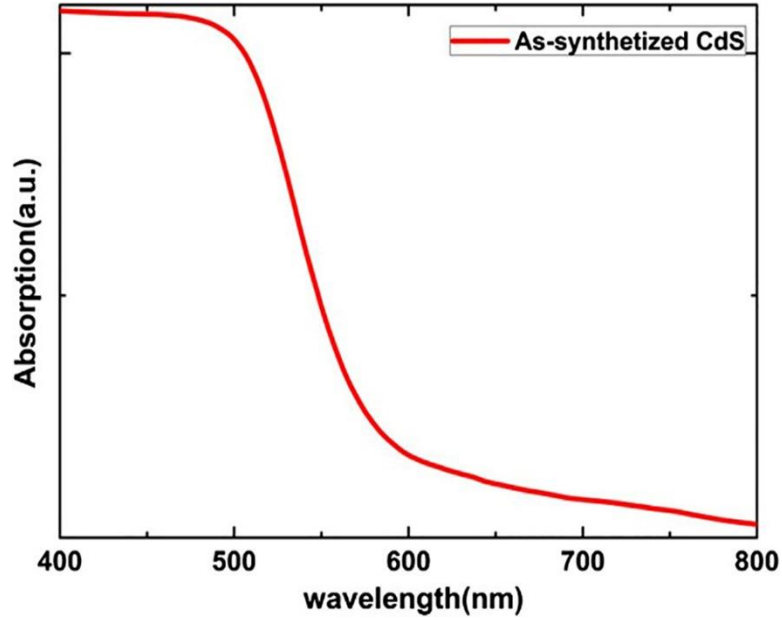


Fig. A1. CdS Absorption vs Wavelength: CdS absorbs most of the light below 500 nm

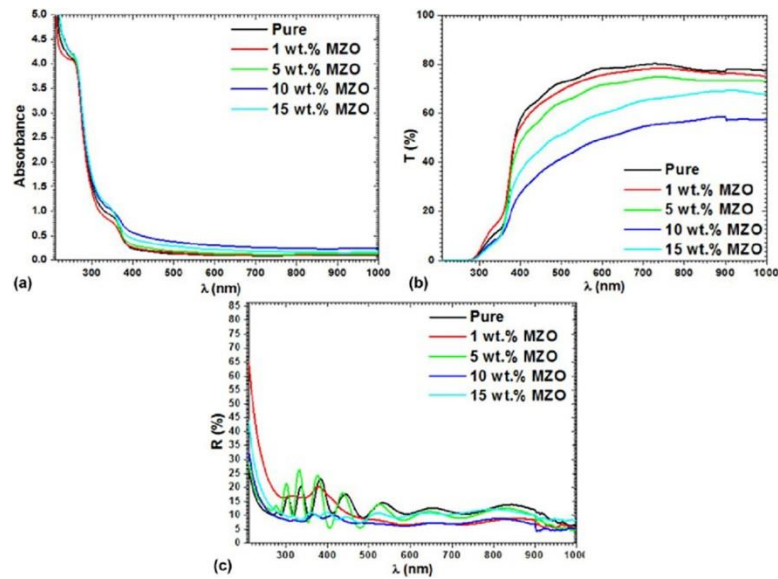


Fig. A2. Absorbance, Transmission and Reflectance of ZnO/MZO [73]

ZnO/MZO transmits most of the light above 300 nm

ZnO/MZO utilize the spectrum in the near UV range better than CdS

APPENDIX B: UPS BAND MEASUREMENTS OF VARIOUS OXIDES DEPOSITED ON FTO [29]

Table B1. UPS band measurements of various oxides deposited on FTO [29]

OXIDE	Φ [eV]	E_F-E_V [eV]	χ [eV]	D [nm]	P [Ω -cm]	ALLOY COMPOSITION [at%]
SnO ₂ :Zn (LOW)	4.1	3.9	4.4	150	5	0.8
SnO ₂ :Ga	4.3	3.9	4.6	150	10	0.9
SnO ₂ :In	4.4	3.8	4.6	150	80	0.5
SnO ₂ :Zn (HIGH)	4.7	3.7	4.8	150	100	3.3
SnO ₂ :F,N	4.9	3.9	5.2	95	100	0.2
SnO ₂	5	3.9	5.3	150	NA	0
SnO ₂ :F (TCO)	5	3.9	5.3	400	0.0005	0.3
ZnO	4.3	3.3	4.4	50	10000000	0
Mg _x Zn _{1-x} O	4	3.8	4.1	50	10000000	23

**APPENDIX C: 1-D MODELING BASELINE PARAMETERS USED FOR SCAPS
SIMULATION OF HRT AND WINDOW MATERIAL PROPERTY EFFECTS [29]**

**Table C1. 1-D Modeling Baseline Parameters used for SCAPS Simulation of HRT and Window
Material Property Effects [29]**

PARAMETER	OXIDE	CDS	CDTE
X [NM]	150	NONEOR50	2500
EG [eV]	3.6	2.4	1.5
X [eV]	VARIES	4.5	4.4
E/E0	9	10	9.4
NC [CM ⁻³]	2.2x10 ¹⁸	2.2x10 ¹⁹	8.0x10 ¹⁷
NV [CM ⁻³]	1.8x10 ¹⁹	1.8x10 ¹⁹	1.8x10 ¹⁹
M _E [CM ⁻² /V S]	1	100	320
M _H [CM ⁻² /V S]	25	25	40
T _N , T _P [NS]	0.1	0.1	2
N OR P [CM ⁻³]	N=1x10 ¹⁸	N=1x10 ¹⁵	P=2x10 ¹⁴
PARAMETER	OXIDE/CdTe	CdS/CdTe	CdTe/BACK
SN OR SP [CM/S]	1x10 ⁷	1x10 ⁵	1x10 ⁷

APPENDIX D: DFT – 1/2 COMPARISON WITH EXPT.

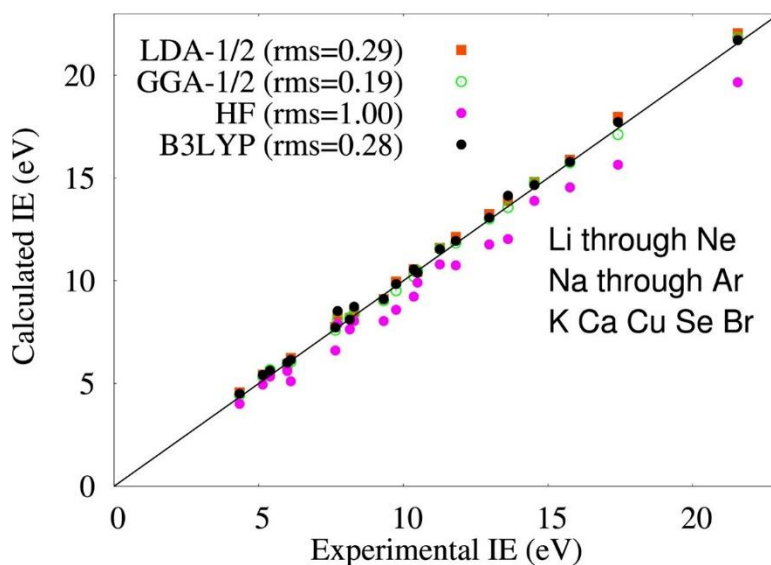


Fig. D1. DFT – 1/2 comparison with expt. 1 [38]

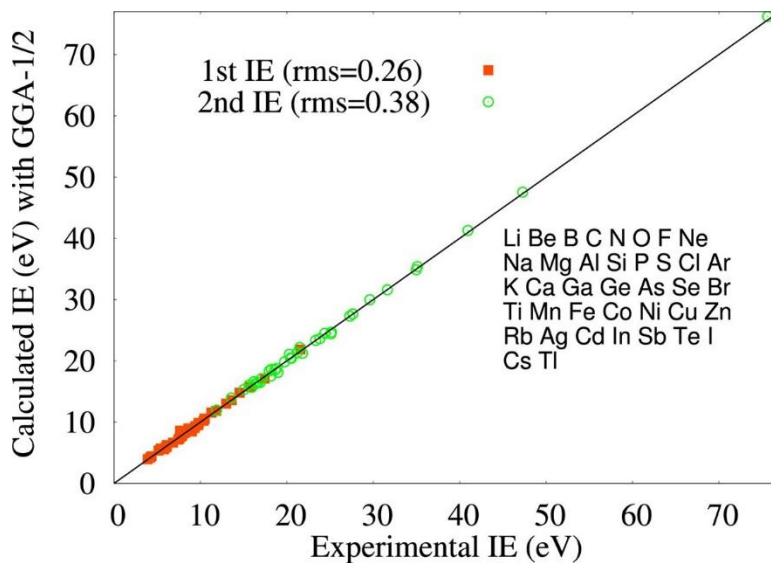


Fig. D2. DFT – 1/2 comparison with expt. 2 [38]

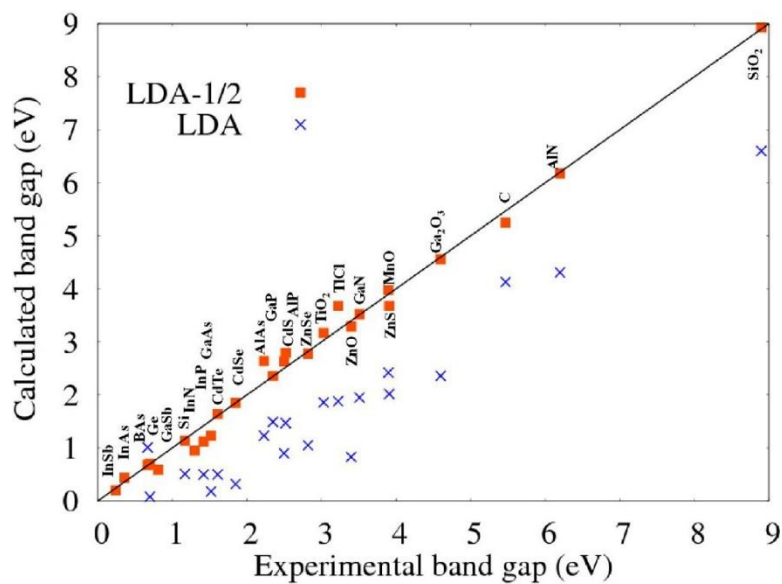


Fig. D3. DFT – 1/2 comparison with expt. 3 [38]

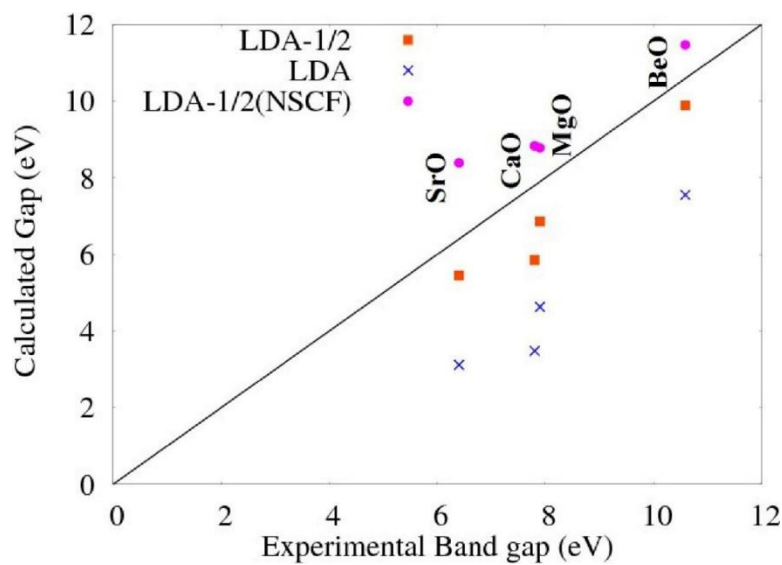


Fig. D4. DFT – 1/2 comparison with expt. 4 [38]

APPENDIX E: K-POINT CONVERGENCE

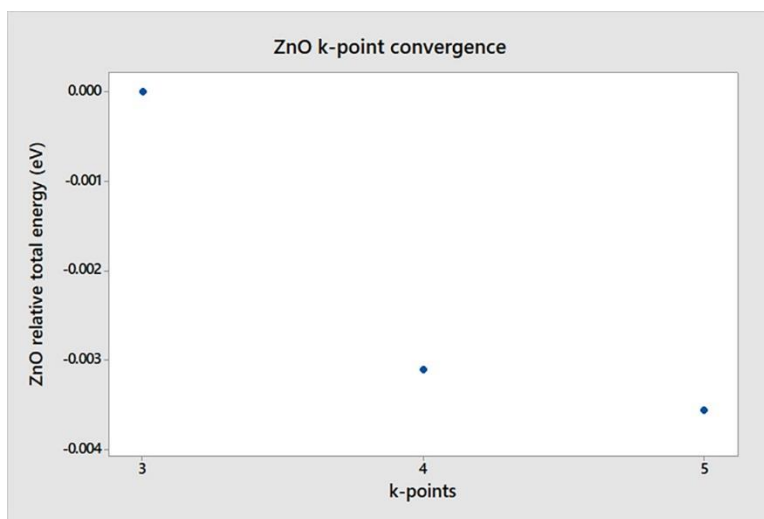


Fig. E1. k-point convergence for ZnO

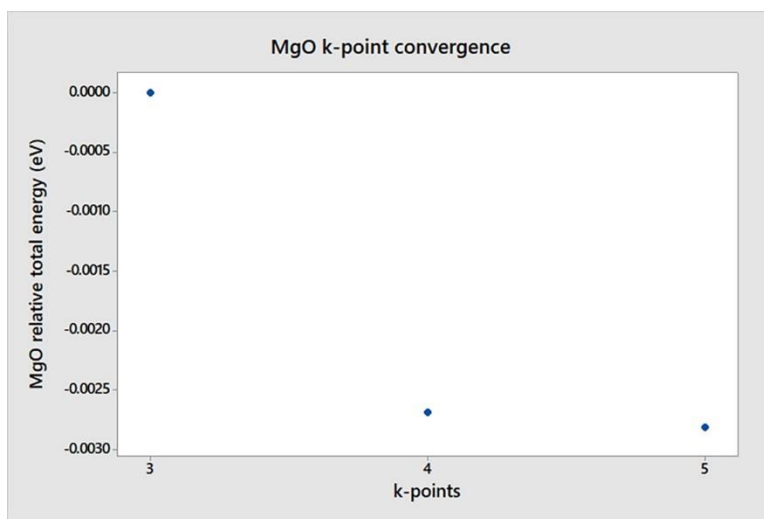


Fig. E2. k-point convergence for MgO

APPENDIX F: MZO BAND PARAMETERS (NOGO)

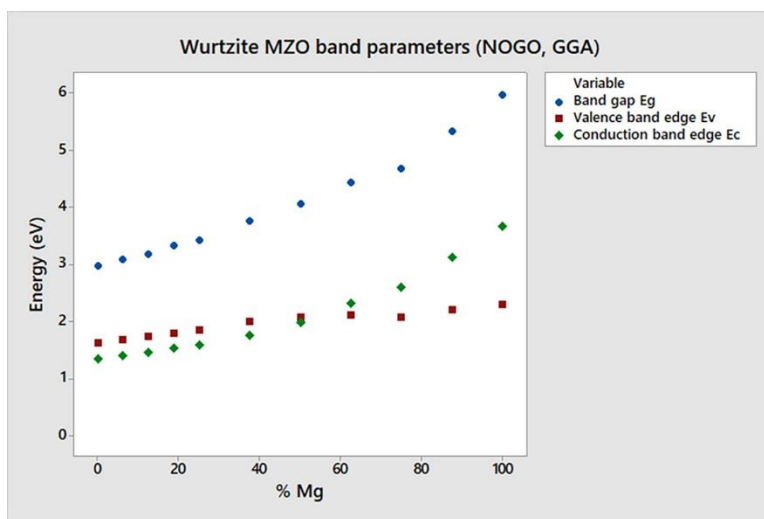


Fig. F1. MZO band parameters NOGO GGA

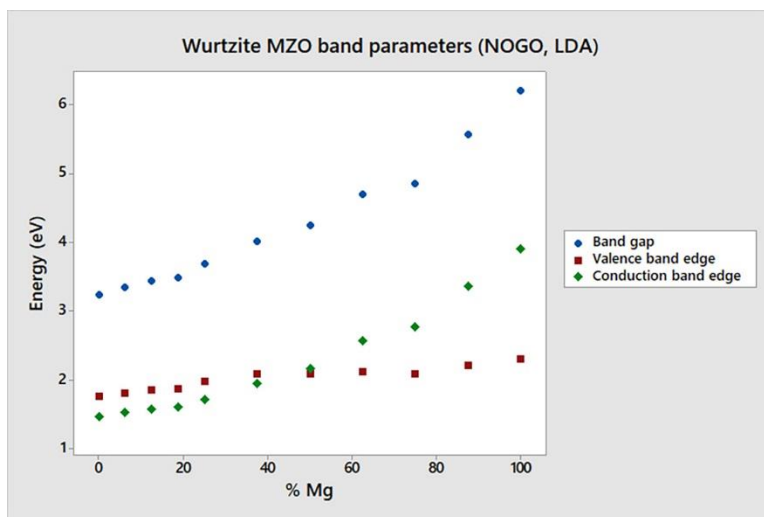
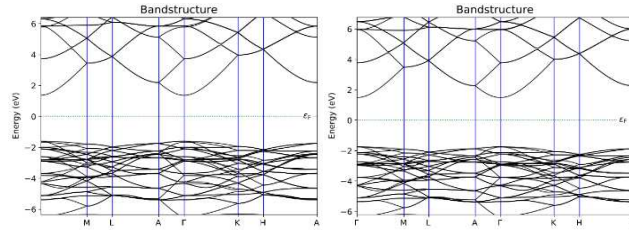


Fig. F2. MZO band parameters NOGO LDA

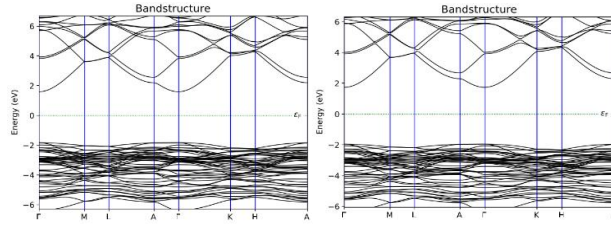
APPENDIX G: MZO BANDGAPS AND DENSITY OF STATES (NOGO)



a)

b)

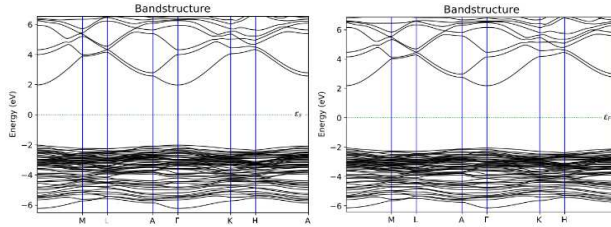
Fig. G1. w-ZnO band structure a) GGA-1/2 NOGO, b) LDA-1/2 NOGO



a)

b)

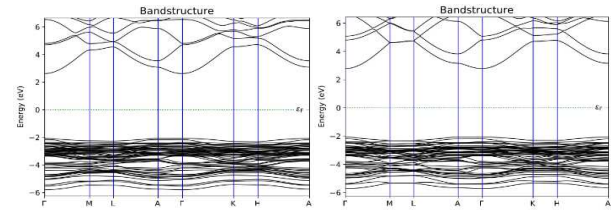
Fig. G2. w-Mg_{0.25}Zn_{0.75}O bandstructure a) GGA-1/2 NOGO, b) LDA-1/2 NOGO



a)

b)

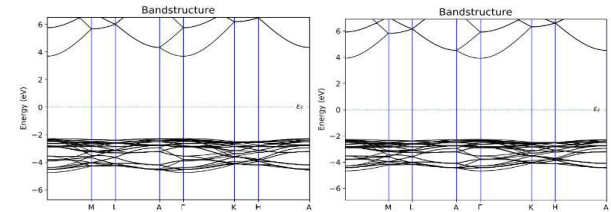
Fig. G3. w-Mg_{0.50}Zn_{0.50}O bandstructure a) GGA-1/2 NOGO, b) LDA-1/2 NOGO



a)

b)

Fig. G4. w-Mg_{0.75}Zn_{0.25}O bandstructure a) GGA-1/2 NOGO, b) LDA-1/2 NOGO



a)

b)

Fig. G5. w-MgO bandstructure a) GGA-1/2 NOGO, b) LDA-1/2 NOGO

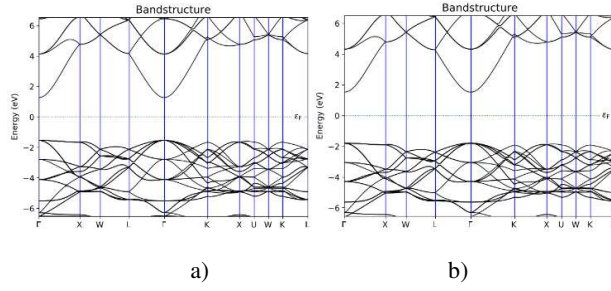


Fig. G6. c- ZnO band structure a) GGA-1/2 NOGO, b) LDA-1/2 NOGO

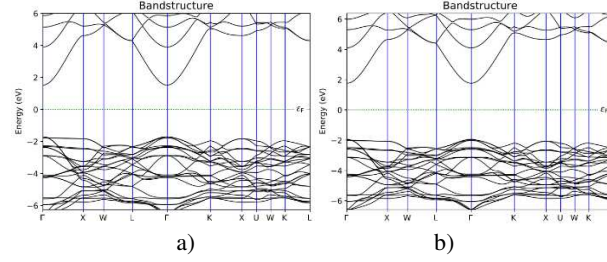


Fig. G7. c- $\text{Mg}_{0.25}\text{Zn}_{0.75}\text{O}$ band structure a) GGA-1/2 NOGO, b) LDA-1/2 NOGO

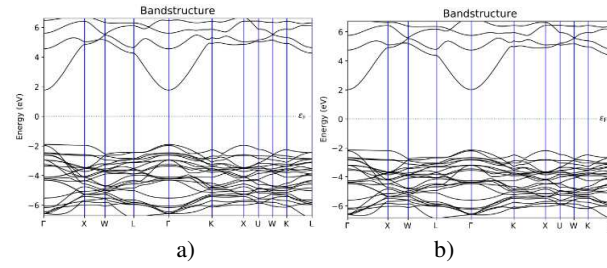


Fig. G8. c- $\text{Mg}_{0.50}\text{Zn}_{0.50}\text{O}$ band structure a) GGA-1/2 NOGO, b) LDA-1/2 NOGO

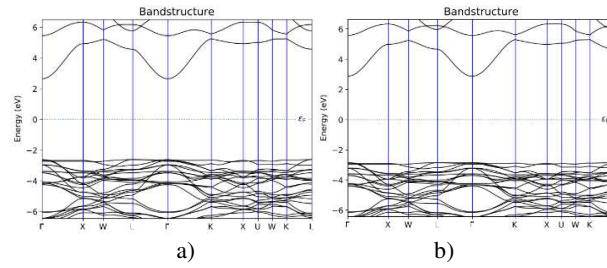


Fig. G9. c- $\text{Mg}_{0.75}\text{Zn}_{0.25}\text{O}$ band structure a) GGA-1/2 NOGO, b) LDA-1/2 NOGO

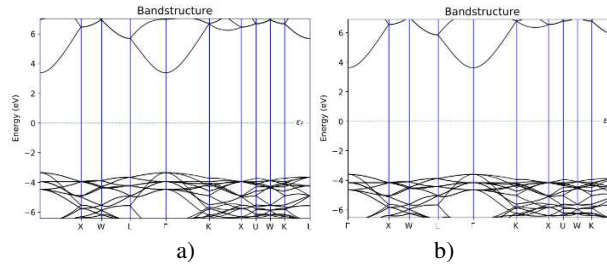


Fig. G10. c- MgO band structure a) GGA-1/2 NOGO, b) LDA-1/2 NOGO

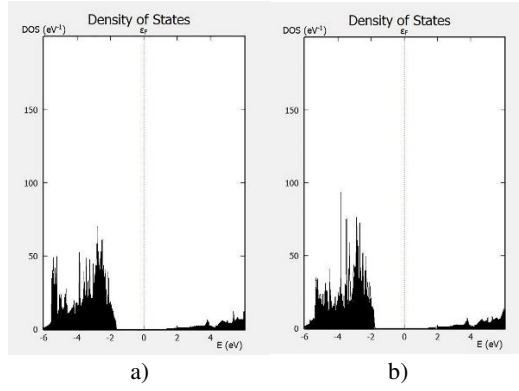


Fig. G11. w-MgO DOS a) GGA-1/2 NOGO, b) LDA-1/2 NOGO

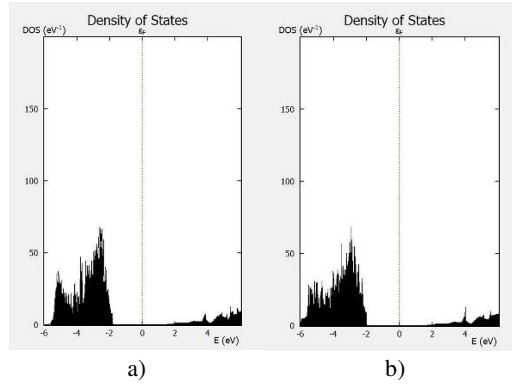


Fig. G12. w-Mg_{0.25}Zn_{0.75}O DOS a) GGA-1/2 NOGO and b) LDA-1/2 NOGO

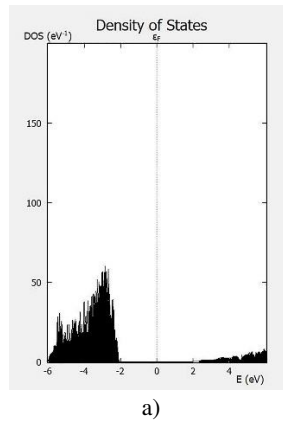


Fig. G13. w-Mg_{0.25}Zn_{0.75}O DOS a) GGA-1/2 NOGO

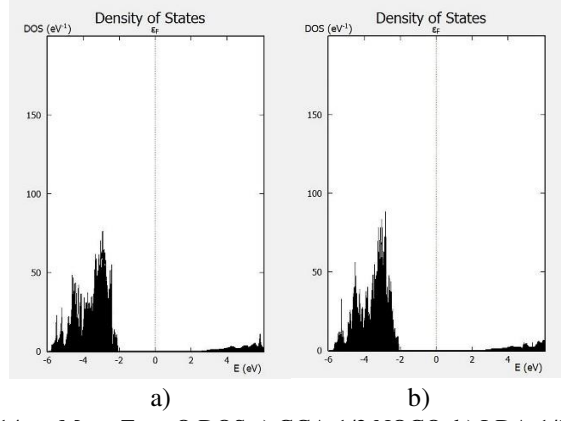


Fig. G14. w-Mg_{0.75}Zn_{0.25}O DOS a) GGA-1/2 NOGO, b) LDA-1/2 NOGO

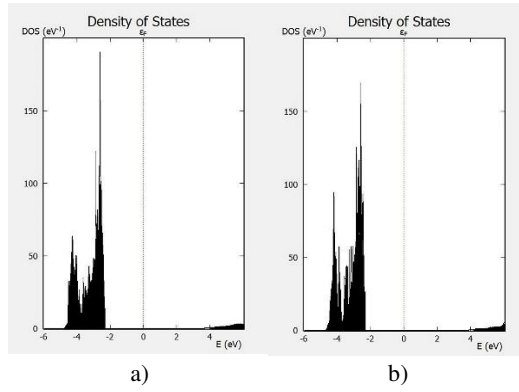


Fig. G15. w-MgO DOS a) GGA-1/2 NOGO, b) LDA-1/2 NOGO

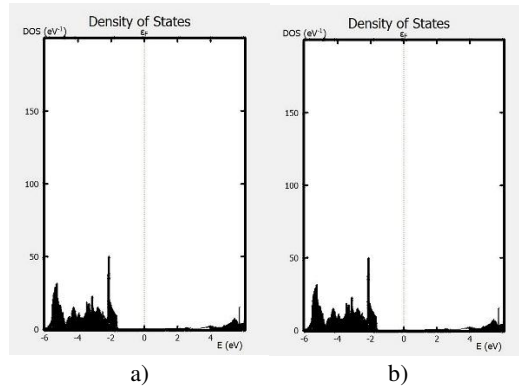


Fig. G16. c-ZnO DOS a) GGA-1/2 NOGO, b) LDA-1/2 NOGO

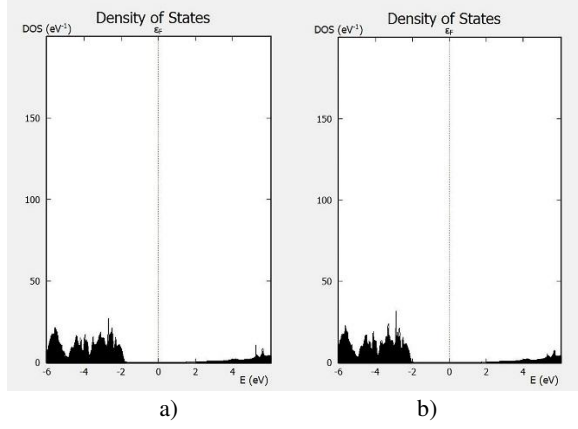


Fig. G17. c-Mg_{0.25}Zn_{0.75}O DOS a) GGA-1/2 NOGO, b) LDA-1/2 NOGO

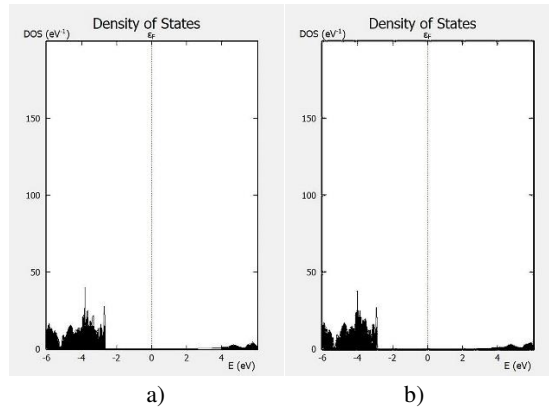


Fig. G18. c-Mg_{0.75}Zn_{0.25}O DOS a) GGA-1/2 NOGO, b) LDA-1/2 NOGO

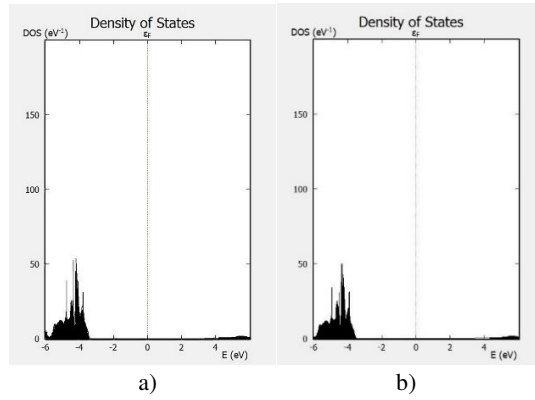


Fig. G19. c-MgO DOS a) GGA-1/2 NOGO, b) LDA-1/2 NOGO

LIST OF ABBREVIATIONS AND SYMBOLS

PV.....	Photovoltaics
Cd.....	Cadmium
Te.....	Tellurium
CdTe.....	Cadmium Telluride
NGPV.....	Next Generation Photovoltaics
TCO.....	Transparent Conducting Oxide
CdS.....	Cadmium Sulfide
Zn.....	Zinc
Mg.....	Magnesium
O.....	Oxygen
ZnO.....	Zinc Oxide
MgO.....	Magnesium Oxide
MZO.....	Magnesium Zinc Oxide
CST.....	Cadmium Selenium Telluride
Cl.....	Chlorine
CdCl ₂	Cadmium Chloride
DFT.....	Density Functional Theory

XC.....	Exchange Correlation
LDA.....	Local Density Approximation
GGA.....	Generalized Gradient Approximation
GF.....	Green's Function
PBE.....	Perdew-Burke-Ernzerhof
a.....	Lattice parameter 'a'
c.....	Lattice parameter 'c'
w-MZO.....	Wurtzite MZO
c-MZO.....	Rock salt MZO
E_g	Band Gap
E_v	Valence Band Edge
E_c	Conduction Band Edge
eV.....	Electron Volt(s)
VB.....	Valence Band
CB.....	Conduction Band
VBO.....	Valence Band Offset
CBO.....	Conduction Band Offset
$\hat{H}$	Hamiltonian
ψ	N-electron wave function

∇	Laplacian
V	Potential Energy
Σ	Sigma/summation
r	Radius/interatomic distance
Z	Atomic Number
$n(r)$	Electron density
E_{xc}	Exchange Correlation Energy
$T[n]$	Kinetic Energy
ϵ	Permittivity of Free Space
c_i	Electron Creation Operator
c_j	Electron Annihilation Operator
n_i	Number Operator