EFFECT OF INTERFACE STRUCTURE ON FILM POLARIZATION AND SURFACE CHEMISTRY IN ULTRA-THIN TiO$_2$/BaTiO$_3$ HETERO-STRUCTURES

BY

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THESIS

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ABSTRACT

Advances in modern computational techniques have provided us with the ability to develop a fundamental understanding of complex material phenomenon down to an atomic scale and manipulate these properties for desired effects at larger lengths scales. It has become increasingly realistic to optimize and tailor material properties for potential applications in electronics, nanotechnology and energy harvesting.

For example, when disparate oxides are integrated together in a heteroepitaxial system, the atomic-scale structure of the interface can dramatically influence the resulting properties of the material system. In this work, using first-principles total-energy electronic structure methods based on density functional theory, we investigate how the photocatalytic activity of anatase titanium dioxide ultra-thin films can be tuned via heteroepitaxial integration with a polarizable perovskite such as barium titanate.

We explore several titanium dioxide/barium titanate heterostructures with varying interfacial geometry to elucidate how interface composition can control film polarization, in turn tailoring the surface reactivity. The polarization of the BaTiO$_3$ is expected to affect the surface chemistry TiO$_2$ thin film and adsorption energy of water molecules on the surface. However, thin-film perovskites such as BaTiO$_3$ are subject to depolarization fields, and do not display ferroelectricity as in the bulk form. Therefore, the interface between the perovskite and TiO$_2$ needs to be engineered to recover polarization.

To maintain polarization, we perform first principles calculations based on density functional theory (DFT) varying both interface boundary conditions and interfacial composition of the heterostructure. Our first-principles calculations demonstrate that structurally imposed boundary conditions at the interface stabilize preferred orientations and magnitudes of polarization. However, the system is dominated by the interface effects, which eliminate any ferroelectric tendency. The direction and magnitude of this interface-
induced polarization in the film also affects chemisorption of water molecules on surface of titanium dioxide. Tuning the molecular adsorption on surfaces can result in selectively augmented or suppressed reaction pathways, thereby potentially improving photocatalytic efficiency of the semiconductor photocatalyst.
For my parents and Jolly, who have supported me always.
Foremost, I would like to express my gratitude to my advisor Prof. Elif Ertekin for introducing me to the exciting field of computational material science and giving me the opportunity to work on this project. She is a great mix of motivation, enthusiasm and fun, and I am extremely fortunate to have had the chance of learning from her both personally and professionally. Her advice, encouragement and feedback have helped me evolve as a researcher and I remain forever grateful for the opportunity to work with her.

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My final thanks are for my parents and my brother, the three people who mean the most to me. Their sacrifices for my education and career are intangible. To them I owe everything I am today.
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Solar photocatalysis, or the direct conversion of visible light energy to chemical energy, is a promising approach for a number of emerging technologies such as generation of chemical fuels and environmental remediation of organic pollutants. For a semiconductor to be a good photocatalyst, it must absorb a large portion of the incoming solar spectrum, efficiently transfer charge carriers to the surface, and possess a surface chemistry that promotes the targeted chemical reaction (while simultaneously maintaining stability in solution under illumination)[1]. For decades, several semiconducting materials have been considered for solar photocatalysis. While traditional semiconductors have low band-gap energies that enable absorption of a large portion of the solar spectrum, they are not sufficiently stable in solution[2]. By contrast, wide band-gap oxides are often stable, but their large band gaps preclude usage of all but a small portion of the solar spectrum[3]. Therefore, a prevailing approach to optimizing performance is to exploit the advantages of disparate materials by combining them into a single integrated system.

In such structures, the coupling of the functional properties of disparate materials via control of the atomic-scale structure of the interface gives rise to a wide spectrum of interface phenomena that can dramatically influence the resulting properties of the material system[4]. Particularly for oxides, several characteristics such as the ionic character, electronic reconstructions at the interfaces, and correlated electron effects in some cases leads to remarkable properties, such as interfacial superconductivity[5, 6], enhanced magnetoresistivity[7], ultrathin magnetic layers[8], conducting electron gases[9, 10] or a combination of these[11, 12, 13, 14, 15]. Substantial research efforts have focused on mapping out the influence of interface atomic structure on behavior and properties of the materials adjacent to the interface[16, 17, 18, 19, 20, 21, 22, 23]. For example, the generation of a conducting 2d electron gas layer between two insulators at LaAlO$_3$/SrTiO$_3$...
interface and similar systems has been studied extensively[24, 25, 26, 27, 28, 29]. Similarly, the epitaxial SrTiO$_3$/Si system has been studied to determine interface effects on strain induced ferroelectricity in nanoscale oxide structures[30, 31, 32, 33]. Enhanced understanding of oxide interfaces, supplemented with increased ability to grow epitaxial oxide heterostructures down to atomic layer precision [34, 35, 36] has enabled the design of new devices with novel physical properties for a variety of energy applications such as heterogeneous photocatalysts[1, 2, 3], high-T$_c$ superconducting cables[5, 6] and photovoltaics[37, 38, 39].

Figure 1.1: Solar Photocatalysis: Splitting of water on TiO$_2$ surface using solar energy

In this work, we extend this approach to consider the integration of anatase titanium dioxide (TiO$_2$), a promising photocatalyst for solar water splitting, with an underlying polarizable oxide support layer, barium titanate (BaTiO$_3$). We use first-principles electronic structure methods to demonstrate that the surface catalytic properties of the TiO$_2$ can be tuned by successful coupling with polarization of a perovskite across an interface.
Among semiconductors, titanium dioxide in anatase form has been a strong candidate for hydrogen production via photocatalytic water splitting since the discovery of the Fujishima-Honda effect[40]. Although it exhibits photoactivity under UV light irradiation and strong oxidation potential of photo-generated holes, TiO$_2$-based systems continue to exhibit low photocatalytic efficiency[41, 42, 43]. Ferroelectric BaTiO$_3$ provides an opportunity for increased control of catalytic properties by the virtue of its inbuilt polarization[44, 45, 46]. For example, tuning the polarization of the underlayer may induce increased electron injection into or away from the surface of TiO$_2$ layers, thereby allowing for optimization of surface interaction with water molecules. The effect of polarization on reactivity of ferroelectric surfaces has been demonstrated[47, 48, 49]. Studies have also shown increased selectivity of metal catalysts towards preferred reaction pathways when supported by a polarized substrate[50, 51, 52, 53, 54, 55]. Recent efforts in fabricating TiO$_2$ thin films supported on a BaTiO$_3$ substrate have been made, which establish that fields in a ferroelectric substrate influence charge carrier transport in the thin film[56, 57, 58].

Figure 1.2: Using interface properties to alter surface chemistry

However, perovskites such as BaTiO$_3$ are subject to large depolarization fields in thin-film geometries due to uncompensated charges on the two surfaces of the film, and do not display ferroelectricity as in the bulk form [59]. This depolarizing field is inversely proportional to ferroelectric film thickness and can suppress polarization entirely below a critical thickness[60, 61, 62]. Depolarizing fields can be reduced by screening charges at film interfaces [63]. The nature of chemical bonding at the film-electrode/substrate interface governs the effectiveness of the screening and interface induced polarization through the formation of intrinsic dipole moments at the interfaces[64,
Presence of asymmetric interfaces at either side of the film may also impose an electric field on the film resulting in two non-equivalent polarization states or freezing a preferred orientation of polar displacements\cite{67, 31}. Therefore, the interface between the perovskite and TiO$_2$ needs to be engineered to maintain polarization.

We use density functional theory \cite{68, 69} to systematically investigate (i) the effect of chemical interactions at the interface in a TiO$_2$/BaTiO$_3$ thin-film hetero-system on the polarization of the structure as a function of BaTiO$_3$ termination, interface composition, and the presence/absence of metal (Pt) electrodes, and (ii) the effect of this polarized underlayer on the electronic properties and chemistry of TiO$_2$ surface by examining the chemisorption behavior of water molecule. We use the PBE \cite{70, 71} flavor of generalized gradient approximation (GGA) to the exchange-correlation potential as implemented in QUANTUM ESPRESSO \cite{72} package. The core electrons are represented using ultrasoft pseudopotentials and the atomic orbitals are expanded in a plane wave basis set. The system is represented on a Monkhorst-Pack grid. The actual cutoffs and other simulation parameters are mentioned in the individual sections.

Our results demonstrate that breaking the in-plane symmetry on either side of BaTiO$_3$ slab introduces different chemical interactions at the two interfaces and creates unequal interface dipoles that allow the BaTiO$_3$ thin film to maintain polarization. These asymmetrical interactions impose electrostatic boundary conditions on the film, stabilizing large amount of polarization despite the presence of depolarizing fields. The polarization of the system is entirely dominated by the interface effects. We also show that the nature of interface changes the electronic properties of the system, such as interface band alignment and occupied surface states. Finally, we discuss the trends in chemisorption of water molecule on TiO$_2$ surfaces with varying interface structure and magnitude of induced polarization and potential applications to photocatalytic water splitting.

The outline of this thesis is presented below:

In Chapter 2, we review the photocatalytic properties of titanium dioxide, current TiO$_2$ based photocatalytic systems and major causes of low efficiency of these systems. We also present a brief review of ferroelectric perovskites of type ABO$_3$, particularly barium titanate. For both these materials, we also mention bulk properties as predicted by our calculations and compare
them with other published work.

In Chapter 3, we discuss the deleterious effect of depolarizing field in thin film ferroelectrics. We touch on the reason for occurrence of depolarization in ferroelectrics and potential ways to recover polarization. We also introduce the different heterostructures considered in this study and the rationale behind considering the particular representative set.

In Chapter 4, we present a detailed discussion of the interface structure for the various heterostructures considered and the effect of interface geometry on system properties. We compare the nature of chemical bonding at the interface and film polarizations in BaTiO$_3$ layers across different systems. We also present a stability analysis of different structures.

In Chapter 5, we discuss the effect of this interface-induced polarization on electronic properties and surface reactivity of different structures. We present trends in band alignment of the heterostructures as we vary interface composition, and boundary conditions. We also show the effect of varying magnitudes of film polarization on chemisorption of water molecules on TiO$_2$ surface.

In Chapter 6, we provide a brief summary of the work done so far and possible directions for future work that may derive from the progress made here.
CHAPTER 2

BACKGROUND REVIEW

This chapter briefly reviews the photocatalytic properties and prior work on photocatalysis using titanium dioxide. We also present our DFT predicted material properties for bulk TiO$_2$. In the final section, we introduce ferroelectric perovskites and describe the properties that make them good candidates as substrates under TiO$_2$.

2.1 Properties of Titanium Dioxide

2.1.1 Historical Overview

The ability of titanium dioxide to produce hydrogen from water through photocatalysis is a novel method of converting solar energy to useful chemical energy. Fujishima and Honda first discovered the photocatalytic properties of TiO$_2$ in 1972 when they found it to be capable of splitting H$_2$O to H$_2$ and O$_2$ when illuminated by UV light in an electrochemical cell [40]. A schematic of this photoelectrochemical cell is shown in Fig 2.1. In their experiment, they detected a current flow from the platinum electrode to the TiO$_2$ electrode and oxygen evolution at TiO$_2$ anode when irradiated with UV light (≥3.0 eV).

2.1.2 Photocatalysis with TiO$_2$

Semiconductors such as TiO$_2$ can absorb light to generate charge carriers. When a photon of energy greater than the material’s band gap is absorbed, an electron is excited from the valence band to the conduction band, leaving behind a positive charge in the valence band, or a hole. These photo-generated charged carriers take part in the photocatalytic splitting of water, which is
Figure 2.1: A Photoelectrochemical cell

a 3-step process: (i) the semiconductor photocatalyst absorbs a photon with energy larger than its band gap, leading to creation of an electron-hole pair, (ii) the charge carriers do not recombine, but migrate to the surface, and (iii) a redox reaction takes place, with photo generated holes oxidizing water to oxygen and H\textsuperscript{+} ions and the photo-generated electrons reducing the H\textsuperscript{+} ions to hydrogen on the surface [1].

The overall photochemical reaction to produce hydrogen from water using light is:

\[ 2H_2O + h\nu \rightarrow 2H_2 + O_2 \]  \hspace{1cm} (2.1)

This reaction can be divided into two half reactions as:

\[ 4H^+ + 4e^- \rightarrow 2H_2 \]  \hspace{1cm} (2.2)

\[ 2H_2O + 4h^+ \rightarrow 4H^+O_2 \]  \hspace{1cm} (2.3)

Reaction (2.2) is the reduction half reaction, which consumes electrons to produce hydrogen. Reaction (2.3) utilizes holes to produce oxygen [41].

The equilibrium cell potential for water electrolysis at room temperature
and pressure is 1.23eV, therefore the band gap of the semiconductor used for photocatalysis should at least be 1.23 eV. Also, a semiconductor with a band gap around 1.35eV would provide optimum utilization of solar energy. Moreover, for a semiconductor to be a photocatalyst, it is desirable that the conduction band energy is higher than the redox level of H⁺/H₂ (hydrogen evolution potential) to allow photo-generated electrons to flow to the counter electrode without an applied potential (-0.4V versus SHE in acid solution). Similarly, the valence band edge should be lower than the redox level of H₂O/O₂ (oxygen evolution potential).

Anatase and rutile phases of TiO₂ which are stable at room temperature satisfy two of the above requirements [41]. They have a band gap greater than 1.23 eV (3 eV for rutile and 3.2 eV for anatase), and they have both reduction and oxidation over-potential. Of the two, anatase gives better results than rutile possibly due to the higher reduction potential of photo-generated electrons (the conduction band minimum of anatase is 0.1V more negative than that of rutile).

2.1.3 Inefficiencies of TiO₂ as a photocatalyst and possible remedies

Despite much research effort since the discovery of Fujishima-Honda effect, hydrogen production with TiO₂ has not yet found commercial application. There are two approaches to produce hydrogen with TiO₂. The first is to use photoelectrochemical (PEC) cell as shown in Figure 2.1. The other approach is to use powdered catalysts such as Pt-deposited TiO₂ particles which form tiny PEC cells. In both the approaches, photo-generated electrons migrate to Pt electrode where they reduce hydrogen while holes on TiO₂ oxidize water to oxygen. PEC cells were found more efficient than simultaneous production of H₂ and O₂ in the powdered systems because the photo-generated charge carriers in PEC cells are well separated, lowering their recombination rate, as well as the rate of back-reaction of H₂ and O₂ to form water. One approach to solve this problem is to add organic compounds to an aqueous suspension of the powdered catalyst, such that water is reduced at Pt sites to produce H₂ while the organic compounds are oxidized by photogenerated holes at TiO₂ sites. This increases the quantum yield of H₂ production to more than
50% in the presence of ethanol.

Despite high reaction efficiency, large band gaps of TiO$_2$ phases (rutile and anatase) imply that they can only utilize the UV portion (3%) of the solar spectrum making TiO$_2$ photocatalysis unattractive for commercial purposes. A number of approaches have been used to improve the photocatalytic efficiency of TiO$_2$. Strategies include reducing the effective band gap of the material by extrinsic doping to extend the absorption edge into the visible range and addition of adsorbed molecular species to absorb visible light and donate an electron or a hole to the TiO$_2$. Extrinsic doping can add electronic levels in the band gap of TiO$_2$ to increase the photocatalytic activity of TiO$_2$ in 400 - 600 nm range. For example, N-doped TiO$_2$ has been shown to have electronic states approximately 0.75 eV above the valence [42]. However, dopants also become recombination centers that decrease the efficiency of the photochemical process. An alternative approach to increase the adsorption range is dye sensitization of TiO$_2$, although most photosensitizer dyes have low stabilities in solution. However, conversion efficiencies of 10-11% have been achieved using porous TiO$_2$ electrodes and ruthenium complexes as sensitizers [43]. Other approaches to improve photocatalytic activity of TiO$_2$ include use of nano-particles to increase surface areas and allow for fast diffusion of charge carriers to surfaces.

Even if a semiconductor captures most of the incident photons, efficient photocatalysis also requires efficient separation of photo-generated carriers, which may otherwise recombine before any redox reaction can take place. Therefore, to enhance the overall quantum efficiency of the process, effective charge separation is essential. A popular approach to enhance charge carrier separation is to form a heterojunction of TiO$_2$ with an appropriate substrate. A hetero-system with correct band alignment at the interface will aid in separation of charge carriers at the interface towards the different semiconductors, increasing charged carrier lifetimes. Recently, ferroelectric materials have also been utilized as substrates in TiO$_2$ based heterojunction [57, 58]. Such systems utilize the inbuilt polarization of the ferroelectric for modified TiO$_2$ surface properties and increased electron injection to the surface. We discuss properties of ferroelectric materials that allow for this effect and this approach in the next section.
2.1.4 DFT predicted properties of anatase TiO$_2$

All calculations are performed using density functional theory\[68, 69\] with the PBE\[70, 71\] approximation to the exchange-correlation potential as implemented in the QUANTUM ESPRESSO\[72\] package. Core electrons are represented using ultrasoft pseudopotentials, and the orbitals are expanded in a plane wave basis set with a cutoff of 250 Ry. All bulk properties of TiO$_2$ are converged for a Monkhorst-Pack 8x8x8 k-grid. The DFT-predicted lattice constants and band gaps for bulk TiO$_2$ are shown in Table 2.1, and compared against other published results. The DFT predicted band structure is shown in Figure 2.2. The predicted band gap is 2.17 eV versus experimental gap of 3.2 eV, due to well known DFT error of underestimating band gaps. For workfunction calculations a 5-layer thick TiO$_2$ slab is used, which is sufficiently large such that the two free surfaces are non-interacting, to best represent an isolated free surface. Periodic images of the slabs are separated by $\approx 13 \text{ Å}$ vacuum and a dipole correction\[73\] is applied to the middle of vacuum region to correct for spurious electrostatic effects arising from periodic boundary conditions. All atoms in the supercell are relaxed until forces on each of the atoms are < 2.5 meV/Å. We calculate the workfunction of (001) surface as 5.33 eV.

Table 2.1: Computed lattice constants, band gap and work function for TiO$_2$ vs other DFT and experimental values

<table>
<thead>
<tr>
<th>Property</th>
<th>DFT-PBE Value</th>
<th>Experimental[74]</th>
<th>Other DFT (GGA)[75]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Constant</td>
<td>$a = 3.79\text{Å}$</td>
<td>$a = 3.78\text{Å}$</td>
<td>$a = 3.78\text{Å}$</td>
</tr>
<tr>
<td>Lattice Constant</td>
<td>$c = 9.55\text{Å}$</td>
<td>$c = 9.51\text{Å}$</td>
<td>$c = 9.51\text{Å}$</td>
</tr>
<tr>
<td>Bandgap</td>
<td>2.17$eV$</td>
<td>3.2$eV$</td>
<td>2.1$eV$</td>
</tr>
</tbody>
</table>

2.2 Barium Titanate and its properties

2.2.1 Ferroelectricity

Ferroelectric materials have a spontaneous inbuilt polarization. This polarization exists in the absence of an electric field and can be switched by the
Figure 2.2: Computed band structure and band gap of TiO$_2$
application of a field. Perovskites of type ABO$_3$ such as barium titanate have a tetravalent cation at the center of a octahedron of oxygen ions, as shown in Figure 2.3. At high temperatures, the structure is cubic and centrosymmetric. Below a critical temperature, called the Curie temperature ($T_c$), the oxygen octahedron distorts and the cations shift to off-center positions resulting in a tetragonal structure. This results in a non-centrosymmetric system with positive and negative ions having different centers of symmetry [44, 45]. Each atomic plane of atoms has a relative displacement of cations with respect to anions, resulting in a polarized crystal. This polarization is not uniform throughout a crystal; for example it may be variable in the neighborhood of defects and foreign ions and typically goes to zero at the surface. Variation in polarization gives rise to a discontinuity in electrostatic potential through the crystal and is the origin of depolarizing field. This phenomenon is discussed in the next chapter.

![Displacement of atoms for cubic to tetragonal transition](image)

Figure 2.3: A typical perovskite of type ABO$_3$

2.2.2 Use as substrate

Recent experimental work has established the possibility of enhancing photocatalytic activity of TiO$_2$ by using ferroelectric BaTiO$_3$ as substrate [56, 57, 58]. The underlying polarization of BaTiO$_3$ can drive the photo-generated electrons and holes in opposite directions, increasing carrier lifetimes and reducing recombination rate. This can allow for spatially distinct oxidation
and reduction sites on TiO$_2$ surface supported by BaTiO$_3$ film of alternating polarizations. Experiments have been performed to reduce Ag from silver salts (AgNO$_3$) and oxidize PbO$_2$ from lead salts (Pb(CH$_3$COO)$_2$) on TiO$_2$ surface with BaTiO$_3$ substrate. The pattern of Ag products and PbO$_2$ products has been found to be consistent with polarization of underlying BaTiO$_3$ and complementary to each other [57, 58]. This suggests that the inbuilt polarization of BaTiO$_3$ can significantly influence the photocatalytic activity of TiO$_2$. In this work, we examine the possibility of tailoring the surface reactivity of TiO$_2$ over layers towards water molecules by tuning the polarization of the underlying BaTiO$_3$ substrate via interface engineering.

2.2.3 DFT predicted properties of tetragonal BaTiO$_3$

The plane wave basis set cutoff is set at 250 Ry and the results are converged for a Monkhorst-Pack 6x6x6 k-grid. The DFT-predicted lattice constants and band gaps for tetragonal (ferroelectric) phase of bulk BaTiO$_3$ are shown in Table 2.2, and compared against other published results. The bulk cation-oxygen displacements are also mentioned. The DFT predicted band structure is shown in Figure 2.4. The predicted band gap is 1.88 eV versus experimental gap of 3.3 eV, due to underestimation of band gaps by DFT. For workfunction calculations a 7.5-layer thick BaTiO$_3$ slab is used, which is sufficiently large such that the two free surfaces are non-interacting, to best represent an isolated free surface. Periodic images of the slabs are separated by $\approx$ 13 Å vacuum and a dipole correction[73] is applied to the middle of vacuum region to correct for spurious electrostatic effects arising from periodic boundary conditions. All atoms in the supercell are relaxed until forces on each of the atoms are < 2.5 meV/Å.
Table 2.2: Computed lattice constants $a$ and $c$, cation-oxygen displacements in fractional coordinates ($z/a$, band gap and work function for BaTiO$_3$ vs other DFT and experimental values

<table>
<thead>
<tr>
<th>Property</th>
<th>DFT-PBE Value</th>
<th>Experimental[76]</th>
<th>Other DFT(GGA)[77]</th>
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<tr>
<td>Lattice Constant</td>
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<td>$a = 3.99\text{Å}$</td>
<td>$a = 3.98\text{Å}$</td>
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<tr>
<td>Lattice Constant</td>
<td>$c = 4.10\text{Å}$</td>
<td>$c = 4.03\text{Å}$</td>
<td>$c = 4.03\text{Å}$</td>
</tr>
<tr>
<td>Ba-O displacement</td>
<td>0.25</td>
<td>0.0105</td>
<td>0.0186</td>
</tr>
<tr>
<td>Ti-O displacement</td>
<td>0.044</td>
<td>0.0468</td>
<td>0.045</td>
</tr>
<tr>
<td>Bandgap</td>
<td>1.88eV</td>
<td>3eV</td>
<td>1.92eV</td>
</tr>
</tbody>
</table>

Figure 2.4: Computed band structure and band gap of BaTiO$_3$
CHAPTER 3

DEPOLARIZING FIELDS IN THIN FILM FERROELECTRICS

In the previous chapter, we reviewed the properties of titanium dioxide and barium titanate, and suggested the possibility of utilizing the inbuilt polarization in BaTiO$_3$ as a way to modify properties of TiO$_2$. However, when a heterosystem consisting of 4 atomic layers (1 unit cell) of TiO$_2$ in (001) orientation in contact with 3-unit cell thick BaTiO$_3$ also in (001) is modeled, the ion displacements of bulk BaTiO$_3$ that lead to polarization vanish. This is shown in Figure 3.1, which shows no polarization in BaTiO$_3$ despite the interfacial charge rearrangements, as would be expected from integration of dissimilar materials.

This occurs due to depolarization, a well known phenomenon in thin-film geometries of ferroelectric perovskites like BaTiO$_3$ [59, 63]. This chapter is devoted to understanding depolarization and ways to mitigate the effect. We begin by describing the origin of these fields and discuss the unwanted effects of this phenomenon and ways to overcome the effect. The heterostructures considered in this study to determine the effect of interface structure on heterosystem properties are introduced towards the end.

3.1 The origin of depolarizing fields

Depolarization occurs due to the field applied by uncompensated charges on the surface of the film induced by the spontaneous polarization of the film. If we cut out a finite sized film of a material with a spontaneous polarization $P$ from bulk, we introduce a discontinuity in electrostatic potential on the surface. This discontinuity leads to appearance of surface charges, which if not compensated induce an internal electric field $E$ in a direction opposite to that of the material polarization. This field, whose intensity scales with the magnitude of $P$, counteracts the $P$ and is called the depolarizing field.
Figure 3.1: A simple heterostructure of TiO$_2$/BaTiO$_3$: On integrating these two materials from their bulk geometry, the system loses its polarization. The slabs on the left show bulk TiO$_2$ and bulk BaTiO$_3$. The slab on the right show final relaxed geometry and charge rearrangement due to interface formation.
Figure 3.2: Compensating Surface Charges: Origin of depolarizing field

An alternate argument can be provided on the basis of total charge in a system. The total charge density $\rho_t$ in a system is a sum of free charge density $\rho_f$ due to free carriers such as electrons, and bound charge density $\rho_b$ due to distortion of electron cloud around the nucleus. The field due to free charge density is the dielectric displacement $D$ and the field due to bound charge density is the polarization $P$. Together, the total charge density is cause of the internal electric field $E$ of the material. These three fields are linked as [17]:

$$D = E + 4\pi P \quad (3.1)$$

In the absence of an external electric field, the free charges will be randomly distributed throughout the materials, resulting in zero net field, \textit{i.e.} $D = 0$ in the absence of an external field. In this case, a non zero polarization $P$ would imply an opposing non zero internal electric field, $E = -4\pi P$. This is the depolarizing field in the system.
3.2 Instability due to depolarizing fields

Since a non-compensated polarization implies a non-zero internal electric field, or depolarizing field, thin film ferroelectric materials lose their polarization, or depolarize and become paraelectric to avoid these fields. The destabilizing nature of these fields can be verified by a simple computation.

![Figure 3.3: Free, bound and total charge in a material](image)

Figure 3.3: Free, bound and total charge in a material

**Plots of Electrostatic Potential in absence of External Electric Field**

![Plots of Electrostatic Potential in absence of External Electric Field](image)

Figure 3.4: Macroscopic averaged electrostatic potential for a test heterosystem made of TiO$_2$/BaTiO$_3$/TiO$_2$ with a) the system free to relax b) middle layer in BaTiO$_3$ film frozen in the bulk polarized geometry

Figure 3.4 shows the plots of electrostatic potential for two test systems of the same composition - 3.5 layer thick BaTiO$_3$ film terminated by BaO on both sides and sandwiched between 4 atomic layer of TiO$_2$. One of the systems free to relax in $x, y, z$ directions (Figure 3.4 (a) ) and the other
system is constrained to have a polarization by freezing the central BaTiO$_3$ layers in their bulk ferroelectric geometry. This system is chosen because it has similar material on both sides of the film, therefore avoiding any effects due to dissimilar interfaces. We find that the BaTiO$_3$ film in the system on the left loses all of its polarization (which can be verified by zero relative displacements of cations with respect to anions in the atomic planes). The plot of electrostatic potential of BaTiO$_3$ film also has a zero slope, indicating no internal electric field in the system. On the other hand, the BaTiO$_3$ film in the system which is constrained to remain polarized has a non zero slope, indicating the presence of internal electric fields, or depolarizing fields in the system. The system on the left is found to be more stable than the system on the right, indicating that if unconstrained, a system would prefer to be in a state with no-internal electric field. This is consistent with the electrostatic stability criteria for thin films by Noguera[17], which states that the plot of electrostatic potential should have a zero slope across the system for stability.

3.3 Asymmetric Interfaces: Possible solution

A symmetric heterosystem in the absence of an external electric field prefers a non-polarized state. One possible way to overcome this problem is by creating asymmetric interfaces on either side of the polarizable film [64, 65, 67, 66]. Integration of two different materials across an interface creates a discontinuity in potential at the interface due to different average bulk internal potentials of the materials on either side of the interface. The drop in potential at the interface in a plot of electrostatic potential in the $z$-direction is indicative of this, and creates a dipole at the interface. These interface dipoles are marked in Figure 3.5. Ideally, the potential drop at the interface should be proportional to the difference in average bulk potentials. However, charge redistribution due to interface formation creates an additional interfacial dipole leading to an additional drop in potential at the interface than that expected in the absence of any charge transfer. The formation of interface dipoles has been observed for many systems which require dissimilar materials to form an interface such as LaAlO$_3$/SrTiO$_3$ or Si/SrTiO$_3$ heterojunctions and Ge/-GaAs and AlAs/GaAs superlattices [78, 79], and the effects of this dipole on film properties have been extensively studied [10, 27, 30, 31].
Figure 3.5: Macroscopic averaged electrostatic potential for a test heterosystem made of TiO$_2$/BaTiO$_3$/TiO$_2$ with symmetric interfaces on both ends of BaTiO$_3$ film.
This suggests that modifying the interface composition would modify charge distribution at the interface, affecting the interface dipole as well. The system shown in Figure 3.5 has symmetric interfaces on either side of the film, and therefore symmetric and opposing interface dipoles, which cancel out. If one of the interfaces is modified, we would expect dissimilar dipoles at the two interfaces, and the difference in these dipoles may be seen as an external electric field by the BaTiO$_3$ film. This could potentially allow the system to retain a polarization.

There are many ways to create asymmetric interfaces. We can modify the stoichiometry of the interface, or apply dissimilar materials on either side of the film. This idea is tested by first modifying the interface ion concentration. The phase space of possible interface configurations is huge, and it is impossible to know what the interfacial structure should look like a priori. Such oxide heterostructures in general exhibit large interfacial reconstruction and complicated geometries and have been the focus of many computational and theoretical studies [16, 17, 24, 25, 27, 33]. For computational feasibility, we choose to vary oxygen concentration as oxygen vacancies are known to exist both in TiO$_2$ and BaTiO$_3$ [80, 81, 82] and serving as electron donors and local disturbances of polarization [83, 84, 85, 86]. The interfacial BaO layers are fully depleted of oxygen atoms (one oxygen vacancy per barium atom) to create a depleted Ba layer at the interface. The plot of electrostatic potential for this system is shown in Figure 3.6. Various other interfacial compositions are also possible, such as non stoichiometric cation vacancies or a combination of both anion and cation vacancies, but are not considered here. Fully oxygen-depleted Ba layers are chosen for computational reasons since lower vacancy concentrations will require increasing the simulation cell size, but lower degrees of depletion are more probable than the extreme case considered here. However, we use this as a test system to gain an insight on the feasibility of using asymmetry to suppress depolarization.

We observe unequal interface dipoles on both sides of the film as a result of modifying interface structure. The relative displacements of cations with respect to anions indicate that the BaTiO$_3$ film now maintains a polarization. Also, despite a non-zero polarization, there is no slope in electrostatic potential plot for BaTiO$_3$. This supports our theory that the difference in unequal interface dipoles is seen as an external field by the film which allows it to maintain a polarization.
Figure 3.6: Macroscopic averaged electrostatic potential for a test heterosystem made of TiO₂/BaTiO₃/TiO₂ with the left interfacial Ba layer depleted of oxygen atoms.

$\begin{align*}
I_1 < I_2 & \implies D = I_2 - I_1 \\
E &= 0 \\
\Rightarrow P &= D/4\pi
\end{align*}$
Finally, to verify if this recovered polarization varies with the interface structure, the oxygen ion concentration in several different layers of the heterosystem is modified, at and away from the interface. We find that the polarization recovered is contingent on both oxygen vacancy position and concentration. A comparison of the magnitude of polarization and stability of heterosystems with oxygen vacancies is shown in Figure 3.7.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Symmetric</th>
<th>Vacancy in Plane 3</th>
<th>Vacancy in Plane 2</th>
<th>Vacancy in Plane 4</th>
<th>Vacancy in Plane 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovered Polarization (as % of Bulk)</td>
<td>0%</td>
<td>83%</td>
<td>58%</td>
<td>41%</td>
<td>30%</td>
</tr>
</tbody>
</table>

* Spontaneous Bulk Polarization of BaTiO3 is 0.15C/m²

Figure 3.7: Possible vacancy positions, recovered polarization and relative stabilities

A comparison of system stabilities indicates that it is energetically most favorable to create oxygen vacancies at the interface. Systems depleted of oxygen atoms at the interfacial layers recover maximum polarization as opposed to layers away from the interface. Therefore, we choose to very oxygen ion concentration at the interface for the remaining sections of our study. Since it is established that breaking in-plane symmetry to create unequal dipoles is a potential way to recover polarization, we now proceed to study various systems with asymmetric interface. In the final section, the heterostructures considered to estimate the effect of interface structure on heterosystem properties are described in detail.
3.4 Representative Heterostructures

A representative simulation cell as shown in Figure 3.8 is composed of 4 atomic layers (1 unit cell) of TiO$_2$ in (001) orientation in contact with 3-unit cell thick BaTiO$_3$ also in (001) orientation with BaO-terminated interfacial layer. For the rest of this study, we will refer to the TiO$_2$ surface (exposed to vacuum or Pt) as the top surface, the BaTiO$_3$ surface (exposed to vacuum or Pt) as the bottom surface and the TiO$_2$/BaTiO$_3$ interface as the interface. The top surface in Figure 3.8 is in contact with vacuum, the bottom surface in contact with Pt electrodes and the interface is composed of a Ba layer depleted of oxygen atoms. For each structure considered here, the system is initialized from two distinct bulk BaTiO$_3$ ferroelectric configuration with initial polarization oriented towards and away from the TiO$_2$/BaTiO$_3$ interface in order to determine the preferred polarization orientation and avoid potential metastable configurations. The in-plane lattice constant of systems without Pt electrodes is fixed at the computed BaTiO$_3$ lattice constant (3.96 Å) and at the computed Pt lattice constant (3.98 Å) for systems with Pt electrodes. This results in a moderate epitaxial strain of ∼ 5% in anatase TiO$_2$. Pt electrodes if present are 4 atomic layers thick. For systems in contact with Pt electrodes, the energetically favored registry of Pt atoms at the interface is found adjacent to surface Ba and O ions in a BaO terminated layer and adjacent to surface O ions in TiO$_2$ terminated layer. The heterostructures are considered with these configurations at the interface. The plane wave basis set cutoff is set at 250 Ry and the system is converged with a k-point mesh of 6x6x6. Periodic copies of the supercell are separated by ≈ 13 Å vacuum and a dipole correction [73] is applied to the middle of vacuum region to correct for any spurious electrostatic effect arising from periodic boundary conditions. All atoms in the supercell are relaxed until forces on each of the atoms are < 2.5 meV/Å.

To study the effect of the presence of an electron reservoir on polarization, the heterostructures surfaces are either exposed to vacuum or capped with Pt electrodes. Three variations are considered: (i) TiO$_2$/BaTiO$_3$ system with vacuum on both surfaces, (ii) TiO$_2$/BaTiO$_3$/Pt system with top surface in contact with vacuum and the bottom surface in contact with Pt electrodes or (iii) Pt/TiO$_2$/BaTiO$_3$/Pt system with Pt electrodes on both surfaces. The BaTiO$_3$ surface can have different work function based on it’s termination
Figure 3.8: Example of a simulation supercell showing computed relaxed atomic structure. Here the TiO$_2$ surface is in contact with vacuum and Pt electrodes are provided at BaTiO$_3$ surface. The TiO$_2$/BaTiO$_3$ interface is depleted of oxygen atoms; computations are performed both with a stoichiometric layer and a depleted layer.

(BaO or TiO$_2$). The effect of this difference in work function on film polarization is studied by terminating the bottom surface (adjacent to vacuum or Pt electrodes) with either a BaO layer or a TiO$_2$ layer.

Since the structure of the interface can potentially play a dominant role in deciding film properties, for all of these systems, the atomic geometries at the TiO$_2$/BaTiO$_3$ interface are modified by varying ion composition. As noted earlier, the phase space of possible interface configurations is huge, but for computational feasibility, we choose to vary oxygen concentration between a stoichiometric BaO layer (one oxygen per barium atom) at the TiO$_2$/BaTiO$_3$ interface and a fully depleted Ba layer (one oxygen vacancy per barium atom) at the TiO$_2$/BaTiO$_3$ interface. Although lower degrees of depletion are more probable than the extreme case considered here, we hope to still get some valuable insights into how off-stoichiometric interfacial composition can affect heterostructure polarizations and properties from the compositions considered here. It is expected that the trends in film polarizations and properties we observe for these systems are likely to persist at lower defect concentrations as well. Also, fully oxygen depleted system have been observed for some heterostructures, such as interface in a Si/SrTiO$_3$ heterosystem [30, 31, 32]. This gives us a total of twelve set of systems (3x2x2=12) considered, which are discussed in detail in the next chapter.
CHAPTER 4

DETAILED ANALYSIS OF INTERFACE STRUCTURE OF DIFFERENT HETEROSTRUCTURES

In the previous chapter, we outlined the different types of heterosystems we chose for the purpose of this study. In this chapter, the trends in some universal properties of these heterostructures such as interfacial charge rearrangement and film polarization are explored in detail. In the first section, the properties of a simple heterojunction of TiO$_2$/BaTiO$_3$ with vacuum on both ends are presented. In the subsequent sections, we add Pt electrodes to one or both ends of this heterojunction and discuss it’s effect on system properties.

4.1 Systems with vacuum on both ends

4.1.1 Stoichiometric Interfaces

We begin by studying stoichiometric interfaces at TiO$_2$/BaTiO$_3$ systems in the absence of electrodes on both ends, for the two possible terminations of BaTiO$_3$ film. The relaxed atomic configurations for these structures are depicted in Figure 4.2(a,b). The key phenomena observed in these structures are the rearrangement of charge at the interface and cation-oxygen displacements, or polarization, in the BaTiO$_3$ film.

Film Polarization

Figure 4.1 shows the layer-by-layer cation/anion displacements in the BaTiO$_3$ layers in the relaxed configuration.

In our convention, positive values of displacements indicate that oxygen is closer to the TiO$_2$/BaTiO$_3$ interface than cation (i.e. the polarization due to these displacements points away from TiO$_2$ towards BaTiO$_3$ at the interface).
Figure 4.1: Polarization profiles showing cation-oxygen displacement $\Delta z$ in each layer of BaTiO$_3$ film for TiO$_2$/BaTiO$_3$ systems in contact with vacuum on both ends. Terminations of BaTiO$_3$ surface adjacent to vacuum and interface compositions are as marked in the figure. S denotes that the system has a stoichiometric BaO layer and V denotes a depleted Ba layer at the TiO$_2$/BaTiO$_3$ interface.

A key observation here is the rearrangement of charge at the interface and the recovery of a negligibly small polarization in the BaTiO$_3$ film as a result of the formation of the interface. This is in comparison to an isolated slab of BaTiO$_3$, which exhibits no polarization in any layer. We estimate the local polarization in BaTiO$_3$ film using a Born effective charges based model [87]. The polarization in each layer is computed using cation/anion displacements as:

$$P = \frac{e}{V} \sum Z_n \delta z_n$$  \hspace{1cm} (4.1)

where $Z_n$ is the Born effective charge for the $n^{th}$ atom, $\delta z_n$ is the displacement of the $n^{th}$ atom away from its position in the centrosymmetric structure, $V$ is the volume of the unit cell and the summation is over all the atoms in a unit cell. The Born effective charges are 2.77 for Ba, 7.25 for Ti, -5.71 for O atoms in the BaO plane and -2.15 for O atoms in the TiO$_2$ plane [88]. This local polarization can then be averaged over BaTiO$_3$ film to obtain an average film polarization, which is then converted to an average dipole using the relation

$$P = \frac{p}{S a}$$

where $p$ is the dipole moment and $Sa$ is the volume of the unit cell. Using these parameters, the bulk dipole from polarization is calculated.
as 0.060 eÅ/surface area. Since these Born effective charges are calculated for bulk ferroelectrics, this method will not provide a quantitatively accurate description due to absence of interface effects and local distortions in the bulk. We can however draw some qualitative insights into the effects of interface structures on film polarization using this simple model. The values of average dipole moments, \( p_{BTO_{avg}} \) for these systems are shown in Table 4.1.

We find a small recovery of polarization corresponding to an average dipole of \(-0.001\) eÅ/surface area for the BaO terminated system and 0.003 eÅ/surface area for TiO \(_2\) terminated system.

Table 4.1: Average dipole due to polarization \( p_{BTO_{avg}} \) in BaTiO \(_3\) (in eÅ/surface area), Interface dipoles (\( \Delta p_{int} \), \( \Delta p_{bot} \) and \( \Delta p_{film} \)) in eÅ/surface area and relative system energies \( E_{rel} \) (in eV) with respect to a reference for relaxed interface geometries. \( \Delta p_{int} \) is the contribution from TiO \(_2\)/BaTiO \(_3\) interface, \( \Delta p_{bot} \) is the contribution from terminal oxide layers computed using the displacements in the bottom-most BaTiO \(_3\) layer (these layers are not included in the calculation for \( p_{BTO_{avg}} \)), and \( \Delta p_{film} = \Delta p_{int} + \Delta p_{bot} \) is the dipole across BaTiO \(_3\) film. Positive values for dipoles indicate dipole pointing from interface into BaTiO \(_3\) film or away from BaTiO \(_3\) film at bottom surface. S denotes that the system has a stoichiometric BaO layer and V denotes a depleted Ba layer at the TiO \(_2\)/BaTiO \(_3\) interface.

<table>
<thead>
<tr>
<th>Top</th>
<th>Bottom</th>
<th>Heterosystem</th>
<th>( p_{BTO_{avg}} )</th>
<th>( \Delta p_{int} )</th>
<th>( \Delta p_{bot} )</th>
<th>( \Delta p_{film} )</th>
<th>( E_{rel} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vac</td>
<td>Vac</td>
<td>S, BaO Terminated</td>
<td>-0.001</td>
<td>0.013</td>
<td>-0.013</td>
<td>0.001</td>
<td>Ref</td>
</tr>
<tr>
<td>Vac</td>
<td>Vac</td>
<td>S, TiO (_2) Terminated</td>
<td>0.003</td>
<td>0.013</td>
<td>-0.020</td>
<td>-0.007</td>
<td>0.07</td>
</tr>
<tr>
<td>Vac</td>
<td>Vac</td>
<td>V, BaO Terminated</td>
<td>0.059</td>
<td>0.024</td>
<td>-0.016</td>
<td>0.008</td>
<td>7.44</td>
</tr>
<tr>
<td>Vac</td>
<td>Vac</td>
<td>V, TiO (_2) Terminated</td>
<td>0.056</td>
<td>0.021</td>
<td>-0.017</td>
<td>0.004</td>
<td>7.51</td>
</tr>
</tbody>
</table>

Charge Rearrangement

To understand the origin of this polarization, we consider the influence of electron charge redistribution resulting from the formation of the TiO \(_2\)/BaTiO \(_3\) interface. The electron rearrangement due to the formation of the interface can be seen clearly in the electron density plots overlaid over atomic geometries in Figure 4.2(a,b). The electron density rearrangement, \( \delta \rho_{system} \) due to interface formation is determined from first-principles computations as:

\[
\delta \rho_{system} = \rho_{system} - (\rho_{TiO_2} + \rho_{BaTiO_3})
\]  

(4.2)
Figure 4.2: Relaxed atomic structures showing electron rearrangement in the xz plane (summed over y) due to interface formation for TiO$_2$/BaTiO$_3$ systems in contact with vacuum on both ends. Terminations of BaTiO$_3$ surface adjacent to vacuum and interface compositions are as marked in the figure.
where $\rho_{\text{system}}$ is the DFT-computed electronic charge density of the actual heterostructure, and $\rho_{\text{TiO}_2}, \rho_{\text{BaTiO}_3}$ are the DFT-computed electronic charge densities of isolated TiO$_2$ and BaTiO$_3$ slabs frozen in the atomic geometry identical to the heterosystem. The electron density shown in Figure 4.2 is $\delta\rho_{\text{system}}$ integrated in the direction of $y -$ axis (perpendicular to the page). From this figure, we see that as a result of interface formation between the TiO$_2$ and the BaTiO$_3$, electrons are transferred from Ba and Ti ions to the O ions. We attribute this observation to the larger chemical electronegativity of the O atoms, which pull charge away from the more electropositive Ba and Ti ions.

Interface Dipole

![Graph showing potential distribution](image)

Figure 4.3: Macroscopic averaged potential in z direction for TiO$_2$/BaTiO$_3$ systems in contact with vacuum on both ends. Terminations of BaTiO$_3$ surface adjacent to vacuum and interface compositions are as marked in the figure. The offset between vacuum potential to the left and right of the slab is also marked. S denotes that the system has a stoichiometric BaO layer and V denotes a depleted Ba layer at the TiO$_2$/BaTiO$_3$ interface.

The redistribution of charge due to interface formation can be considered to be equivalent to the formation of an interface dipole which induces an additional potential drop across the interface. The formation of interface dipoles has been discussed previously in Chapter 3. When two dissimilar
materials are joined at an interface to form a heterostructure, there is an offset in the vacuum levels at the left and right side of the slab due to a difference in work functions of the two materials and a discontinuity in potential at the interface due to a difference between the average potential in the bulk of the two materials. We can see this as the drop in potential due to a difference in average potential on the left hand side (TiO$_2$ film) and the right hand side (BaTiO$_3$ film) of the interface in the plot of electrostatic potential in the $z$-direction for the structures shown in Figure 4.2. Ideally, the vacuum level offset, $\Delta_{\text{vacuum}}$ should be difference in work functions of the two materials (2.4 eV for system with BaO terminated bottom surface and 0.1 eV for system with TiO$_2$ terminated bottom surface) and the drop in potential at the interface would be the difference in average bulk potentials. However, charge redistribution due to interface formation creates an interfacial dipole leading to an additional drop in potential at the interface than that expected in the absence of any charge transfer. By virtue of the nature of charge redistribution here (small net transfer of charge from BaTiO$_3$ to TiO$_2$), the interface dipole should point into BaTiO$_3$ at the interface. The interface dipoles, in addition to surface dipoles formed due to surface charges are also responsible for deviation of vacuum level offset from difference in work functions of surface terminations.

We can quantitatively estimate the interface dipole moment per surface due to charge redistribution at the interface from electron density rearrangement, $\delta\rho_{\text{system}}$:

$$\Delta p = \int \delta\rho_{\text{system}} z dz \quad (4.3)$$

where the integration is from TiO$_2$ side of the interface where $\delta\rho_{\text{system}} \to 0$ to BaTiO$_3$ side of the interface where $\delta\rho_{\text{system}} \to 0$ again. A representative plot of macroscopic averaged charge density difference, $\delta\rho_{\text{system}}(z)$ in $z$ direction for TiO$_2$/BaTiO$_3$ system with BaO terminated bottom surface is shown in Figure 4.4, showing clear transfer of charge across the interface from BaTiO$_3$ to TiO$_2$. The computed values for the interface dipoles for all system considered here are tabulated in Table 4.1. A positive value of $\Delta p$ implies that the dipole is oriented into BaTiO$_3$ at the interface. For the two TiO$_2$/BaTiO$_3$ surfaces under consideration here, we find that the dipole moment, $\Delta p_{\text{int}}$ is 0.013 $e\AA$/surface area, indicating a net small transfer of electron charge from the BaTiO$_3$ to the TiO$_2$. This interface dipole is the same for both
the TiO$_2$ and BaO terminated systems (Figure 4.1a,b). We again note that while this method will not provide a quantitatively accurate description since the value of $\rho_{\text{system}}$ is estimated from isolated slabs frozen in heterostructure geometry, ignoring effects due to distortions from bulk geometry, we can use this approach for a semiquantitative study of interface related phenomena.

The small polarization induced in the BaTiO$_3$ slab can now be understood as a response to the formation of the interface dipole. The positive ions in BaTiO$_3$ film are repelled away from the interface due charge transfer across the interface. We notice that despite the presence of an interface dipole, these two structures display negligible cation-oxygen displacements in the oxide layers adjacent to the interface and displacements in the terminal oxide layers of the BaTiO$_3$ film in directions that offset the dipole at TiO$_2$/BaTiO$_3$ interface. The film polarization profiles depicting cation-oxygen displacement in each atomic layer of BaTiO$_3$ film in Table 4.1 show that the terminal oxide layers polarize in opposite direction (cations towards the interface, anions away). The calculated dipoles due to polarization in terminal layers using (1) are $-0.013$ eÅ/surface area for the BaO terminated system and $-0.020$ eÅ/surface area for TiO$_2$ terminated system.

The absence of a screening mechanism for these internal electric fields
causes an equal and opposing dipole moment to develop at the bottom surface that completely suppresses the interface dipole and prevents the development of any internal electric field. As discussed in Chapter 3, an uncompensated polarization in the film would lead to an internal electric field (depolarizing field) in the film, leading to a slope in the electrostatic potential. The absence of internal fields in these films can be witnessed from a zero slope in potential in BaTiO$_3$ film in the electrostatic potential plots of Figure 4.3.

### 4.1.2 Oxygen-depleted Interfaces

To explore the effect of interface composition on the charge rearrangement and resulting polarization profile of the BaTiO$_3$ slab, we introduce oxygen vacancies to the interfacial BaO layer. We have already mentioned the computational considerations of choosing this particular interface composition in the previous chapter.

#### Film Polarization

Introduction of oxygen vacancies dramatically changes the polarization and charge distributions in these systems. The cation-oxygen displacements for oxygen-depleted systems in atomic planes close to the interface are now greatly enhanced compared to the stoichiometric case, as seen in film polarization profiles (Figure 4.1). The average layer-by-layer displacements in these oxygen-depleted systems are 0.13Å, with $p_{BTO_{avg}}$ of 0.059 eÅ/surface area and 0.056 eÅ/surface area for BaO terminated system and TiO$_2$ terminated systems respectively.

#### Charge Rearrangement

A substantial transfer of charge away from interfacial Ba layer can also be observed from charge densities in Figure 4.2. As a result, the calculated $\Delta p_{int}$ is also larger in magnitude (0.024 eÅ/surface area and 0.021 eÅ/surface area for BaO and TiO$_2$ terminated surface respectively versus 0.013 eÅ/surface area for stoichiometric case) at the interface for these systems (Table 4.1).

The introduction of oxygen vacancies at the interface leads to the presence of excess electrons in the Ba layer due to the absence of Ba-O bonds in that
layer. These excess electrons cause the interfacial Ba layer to act as a source of negative charge carriers. This strongly affects the charge distribution at the interface causing the more electronegative oxygen ions at the interfacial TiO$_2$ layers to pull this charge away from the Ba atoms at the interface. As a result the Ba layer at the interface has a slight positive charge, and repels the cations in the subsequent layers of BaTiO$_3$ film causing them to displace away from the interface. As a result, the observed cation-oxygen displacements in these systems are larger than those in the stoichiometric case.

**Interface Dipole**

As is the case with stoichiometric systems, the direction of displacements in terminal oxide layers at the bottom surface is opposite to those enforced by the TiO$_2$/BaTiO$_3$ interface, to suppress formation of an internal electric field. The calculated dipoles here are $-0.016 \ e\text{Å}/\text{surface area}$ for the BaO terminated system and $-0.017 \ e\text{Å}/\text{surface area}$ for TiO$_2$ terminated system. However, the electrostatic potential in BaTiO$_3$ film for these systems has a non-zero slope, suggesting some net electric field is present in the BaTiO$_3$ film. The oxygen depleted interface has a larger interface dipole due to stronger charge rearrangement which is not completely offset by opposing dipole from the displacements at bottom surface.

Therefore, systems with oxygen depleted interfaces have a noticeable slope in electrostatic potential plot due to insufficiency of opposing dipoles applied by the bottom surface in suppressing interface induced polarization and absence of a screening mechanism (Figure 4.3). Electrostatic stability criteria for thin film states that a non-zero slope in potential will lead to 'polar catastrophe' in the thermodynamic limit [17]. Therefore we expect these structures to have lower stability than those with stoichiometric compositions.

**4.1.3 Energetics**

Given the observed slope in the electrostatic potential and the large value of the interface dipole, it is interesting to consider the relative energies of
the stoichiometric systems in Figure 4.2(a,b) in comparison to the fully-depleted systems in Figure 4.2(c,d). This helps elucidate the energetic cost of introducing a large dipole and resulting polarizations. Taking the BaO-terminated, stoichiometric case (Figure 4.2a) as a reference, we calculate the relative energies of the four systems considered as:

\[
E_{\text{rel}} = E_{\text{sys}} - (E_{\text{ref}} + n_O \mu_O + n_Ti \mu_{Ti})
\]

where \(E_{\text{sys}}\) is the DFT-computed total energy of the system under consideration, \(E_{\text{ref}}\) is the DFT-computed total energy of the reference system, and \(n_i\) is the number of atoms of species \(i (i = O, Ti)\) to be added to \((n_i > 0)\) or removed from \((n_i > 0)\) the reference system to create the system under consideration. We analyze stabilities for oxygen poor growth conditions by setting the chemical potential for O atom \(\mu_O\) equal to half the energy of an oxygen molecule \((\mu_O = E_{O_2}/2, E_{O_2}\) is the corrected energy of an oxygen molecule [89]) . The chemical potential \(\mu_{Ti}\) can then be obtained by requiring the chemical potentials to satisfy \(\mu_{Ti} + 2\mu_O = \mu_{TiO_2}\) and \(\mu_{Ti} < 0\) at equilibrium. This is equivalent to restricting our analysis to phase space where \(TiO_2\) is stable but the precipitation of bulk Ti is not. The calculated relative energies for all the systems studied are shown in Table 4.1 as \(E_{\text{rel}}\).

The heterostructures with stoichiometric interface compositions have comparable stability for different terminations for BaTiO\(_3\) film, with the TiO\(_2\) terminated bottom surface being 0.07eV higher in energy. As expected, depleting the interface of oxygen atoms is not energetically favorable, requiring high energy to create these systems and support the large polarization enforced by the interface (7.44 eV for BaO terminated bottom surface and 7.51 eV for TiO\(_2\) terminated bottom surface)

Since compensating fields can be screened by the introduction of free charges at at the surface [63], we now consider the possibility of introducing metallic electrodes at one or both of the surfaces of the TiO\(_2\)/BaTiO\(_3\) heterojunction to study the effect of screening charges as well as asymmetric interfaces on the polarization through the heterojunction. The nature of chemical bonding between the heterojunction and electrode governs the effectiveness of the screening, and hence the capability of the structure to support the interface-induced polarization, through the formation of intrinsic dipole moments at the surfaces [64, 65, 66]. Presence of asymmetric interfaces at
either side of the film may also impose an electric field on the film resulting in two non-equivalent polarization states or freezing a preferred orientation of polar displacements [67, 31]. Therefore, we add platinum electrodes to one or both surfaces of all four heterosystems discussed above since presence of Pt electrodes adjacent to BaTiO$_3$ film is expected to provide compensating charges to screen depolarizing fields. We discuss these systems in the next sections.

4.2 Systems with Platinum electrodes on one end

We first consider the incorporation of a platinum electrode only at the BaTiO$_3$ side of the heterojunction, resulting in a TiO$_2$/BaTiO$_3$/Pt stack. This model system may be representative of, for example, an oxide heterojunction used for catalysis, in which one side of the junction is supported by a metal electrode, and the other side is not completely exposed to vacuum or a metal electrode, but perhaps to a weak electrolytic solution or redox couple.

4.2.1 Stoichiometric Interfaces

Film Polarization

The film polarization profiles in Figure 4.5 demonstrate that the BaO terminated system shows small, positive values of cation-oxygen displacements in all atomic planes as compared to it’s counterpart with no electrodes. The polarization profile still stays negligible in TiO$_2$ terminated system in all except the terminal planes. The average layer-by-layer displacements in BaO terminated system is $0.07\, \text{Å}$, while it is $\sim 0$ for TiO$_2$ termination. The average dipoles, $p_{BTO_{avg}}$ are $0.018\, e\text{Å}/\text{surface area}$ and $0.002\, e\text{Å}/\text{surface area}$ respectively. The magnitude of the interface dipole, $\Delta p_{int}$ also remains the same in TiO$_2$ terminated system as before the electrode appeared while it changes to $0.008\, e\text{Å}/\text{surface area}$ for the BaO terminated system. This suggests that Pt electrodes are better suited to support the polarization from the induced cation-oxygen displacements in a BaO terminated system as compared to a TiO2-terminated system.
Figure 4.5: Polarization profiles showing cation-oxygen displacement $\Delta z$ in each layer of BaTiO$_3$ film for TiO$_2$/BaTiO$_3$ systems in contact with vacuum at TiO$_2$ surface and the BaTiO$_3$ surface adjacent to Pt electrodes. Terminations of BaTiO$_3$ surface adjacent to vacuum and interface compositions are as marked in the figure. S denotes that the system has a stoichiometric BaO layer and V denotes a depleted Ba layer at the TiO$_2$/BaTiO$_3$ interface.
Charge Rearrangement and Interface Dipole

The electron density plots for TiO$_2$/BaTiO$_3$ systems with Pt electrodes at bottom surface are shown in Figure 4.6. Similar to the systems with no dipole, the electron density rearrangement, $\delta \rho_{\text{system}}$, is calculated as:

$$\delta \rho_{\text{system}} = \rho_{\text{system}} - (\rho_{\text{TiO}_2} + \rho_{\text{BaTiO}_3} + \rho_{\text{Pt}}) \quad (4.5)$$

where $\rho_{\text{system}}$ is the DFT computed electronic charge density of the actual heterostructure, and $\rho_{\text{TiO}_2}$, $\rho_{\text{BaTiO}_3}$, and $\rho_{\text{Pt}}$ are the DFT computed electronic charge densities of separated TiO$_2$, BaTiO$_3$, and Pt slabs, calculated by freezing them in the atomic geometry identical to the heterosystem. These plots in Figure 4.6 (a,b) for stoichiometric interfaces at TiO$_2$/BaTiO$_3$ highlight that there is a significant difference in the nature of chemical interaction between TiO$_2$ surface and platinum and BaO surface and platinum at the bottom surface. While the platinum electrodes pull charge from BaTiO$_3$ film in both cases, Figures 4.6(a,b) show that the bonding between TiO$_2$/Pt has a covalent nature with charge sharing between Ti at bottom surface and four Pt atoms, while it is weakly ionic in nature between BaO/Pt with large distance between the BaO plane and Pt plane. We therefore expect the BaO terminated surface to exhibit larger dipole ($\Delta p_{\text{bot}} = -0.018 \, e\text{Å}/\text{surface area}$ for BaO terminated system and $-0.012 \, e\text{Å}/\text{surface area}$ for TiO$_2$ terminated system). Since the dipole at the BaO terminated surface is large and opposite in direction to that at the TiO$_2$/BaO interface, the net dipole across BaTiO$_3$ film, which is a summation of these two dipoles, points from the bottom surface to the interface in BaO terminated bottom surface ($\Delta p_{\text{film}} = -0.010 \, e\text{Å}/\text{surface area}$). As discussed in Chapter 3, this is seen as an external field by the film, and this system can support a film polarization that points from interface to bottom surface such that the net slope in electrostatic potential is zero, eliminating any internal electric field. On the other hand, for the TiO$_2$-terminated system, the dipole is still opposite, but smaller in magnitude leading to a negligible net dipole across BaTiO$_3$ film ($\Delta p_{\text{film}} = 0.001 \, e\text{Å}/\text{surface area}$). Consequently, this system shows suppressed cation-oxygen displacements and small (almost zero) polarization to prevent the development of any internal electric field. Our observations are in concurrence with previous work which demonstrates that AO-terminated
Figure 4.6: Relaxed atomic structures showing electron rearrangement in the xz plane (summed over y) due to interface formation for TiO$_2$/BaTiO$_3$ systems in contact with vacuum at TiO$_2$ surface and the BaTiO$_3$ surface adjacent to Pt electrodes. Terminations of BaTiO$_3$ surface adjacent to vacuum and interface compositions are as marked in the figure.
perovskite ferroelectrics can show a strong interfacial enhancement of the ferroelectric properties when weakly bonded to a simple metal [64].

We note that while we recover some polarization in BaO terminated BaTiO$_3$ film (non-zero $\Delta z$), there is no slope in the electrostatic potential plot from the system in Figure 4.7. This suggests that screening is provided by Pt electrodes in the form of charge rearrangement at the bottom surface such that the net dipole across the film points in a direction opposite to the polarization enforced by the interface.

![Figure 4.7: Macroscopic averaged potential in z direction for TiO$_2$/BaTiO$_3$ systems in contact with vacuum at TiO$_2$ surface and the BaTiO$_3$ surface adjacent to Pt electrodes. Terminations of BaTiO$_3$ surface adjacent to vacuum and interface compositions are as marked in the figure. The offset between vacuum potential to the left and right of the slab is also marked. S denotes that the system has a stoichiometric BaO layer and V denotes a depleted Ba layer at the TiO$_2$/BaTiO$_3$ interface.](image)

**4.2.2 Oxygen depleted Interfaces**

Given the influence of the dipole between the heterojunction and Pt electrode on polarization profiles, we explore how the presence of the electrode affects film polarization for the oxygen-depleted heterojunctions. The polarization profiles and associated charge redistributions are shown in Figure 4.6. We observe positive polarizations, substantially larger in magnitude
than the previous cases considered, for both terminations of BaTiO$_3$. For
the BaO-termination, the average layer-by-layer cation oxygen displacement
is 0.36Å, and for the TiO$_2$-termination it is 0.27Å. The average dipoles,
$p_{BTO_{avg}}$ are 0.111 eÅ/surface area and 0.088 eÅ/surface area respectively,
larger than the bulk value of 0.060 eÅ/surface area. These large polariza-
tions arise in concert with large dipoles at the BaTiO$_3$/TiO$_2$ interface, and
at the Pt/BaTiO$_3$ surface. For the BaO-termination, $\Delta p_{int}$ is computed
as 0.186 eÅ/surface area and $\Delta p_{bot}$ as $-0.247$ eÅ/surface area leading to
$\Delta p_{film}$ of $-0.06$ eÅ/surface area, which supports the large positive polarization
in the film. Similarly, for the TiO$_2$-termination, $\Delta p_{int}$ is computed as
0.151 eÅ/surface area and $\Delta p_{bot}$ as $-0.176$ eÅ/surface area leading to $\Delta p_{film}$
of $-0.025$ eÅ/surface area, which, while smaller than that in BaO terminated
system, can still support a positive polarization. For both terminations, we
attribute the large polarizations to the fact that the Pt electrode provides free
charges that effectively screen large compensating internal fields and thus sta-
bilize large polarizations. As in the previous case where the interfacial BaO
layer was completely depleted of oxygen atoms, the removal of the oxygen
atoms results in an excess of negative charge at the interface. As a conse-
quence, the electronegative O species in the adjacent layers relax towards,
and the more electropositive species (Ba, Ti) relax away from, this interface.
When the Pt electrode is present, the observed relaxations are much larger,
because the internal electric fields can now screened by the metal electrodes.
This is also evident in the electrostatic potential plots, which show no slope
across the slab components despite the large polarizations.

4.2.3 Energetics

Comparing the relative energies of these systems in Table 4.2, we find that the
TiO$_2$ termination of BaTiO$_3$ film with Pt electrode is more stable compared
to the BaO termination by 0.11eV at stoichiometric interface compositions,
indicating that Pt binds favorably with Ti atoms of the TiO$_2$ layer. However,
the TiO$_2$ termination of the same structure with oxygen depleted interface
is higher in energy than BaO termination of BaTiO$_3$ film (relative energy of
TiO$_2$ terminated film is 6.69eV and BaO terminated film is 6.31eV). This
is in agreement with our earlier conclusion that weakly bonded BaO/Pt at
Table 4.2: Average dipole due to polarization $p_{BTO_{avg}}$ in BaTiO$_3$ (in eA/surface area), Interface dipoles ($\Delta p_{int}$, $\Delta p_{bot}$ and $\Delta p_{film}$) in eA/surface area and relative system energies $E_{rel}$ (in eV) with respect to a reference for relaxed interface geometries. $\Delta p_{int}$ is the contribution from TiO$_2$/BaTiO$_3$ interface, $\Delta p_{bot}$ is the contribution from BaO/Pt or TiO$_2$/Pt bottom surface and $\Delta p_{film} = \Delta p_{int} + \Delta p_{bot}$ is the dipole across BaTiO$_3$ film. Positive values for dipoles indicate dipole pointing from interface into BaTiO$_3$ film or away from BaTiO$_3$ film into Pt at bottom surface. S denotes that the system has a stoichiometric BaO layer and V denotes a depleted Ba layer at the TiO$_2$/BaTiO$_3$ interface.

<table>
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<tr>
<th>Top</th>
<th>Bottom</th>
<th>Heterosystem</th>
<th>$p_{BTO_{avg}}$</th>
<th>$\Delta p_{int}$</th>
<th>$\Delta p_{bot}$</th>
<th>$\Delta p_{film}$</th>
<th>$E_{rel}$ (eV)</th>
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<td>0.186</td>
<td>-0.247</td>
<td>-0.060</td>
<td>6.31</td>
</tr>
<tr>
<td>Vac</td>
<td>Pt</td>
<td>V, TiO$_2$ Terminated</td>
<td>0.088</td>
<td>0.151</td>
<td>-0.176</td>
<td>-0.025</td>
<td>6.69</td>
</tr>
</tbody>
</table>

bottom surface is conducive to aid the polarization in BaTiO$_3$ film induced by TiO$_2$/BaO interface. We also note that the relative energies of the depleted interface (although still prohibitively high) are now lower by around 1eV relative to the no electrode case, illustrating that addition of electrodes to configurations that induce large film polarizations makes them marginally less unstable by providing compensating charges to support the large polarization enforced by the interface.

4.2.4 Depolarization

We plot the macroscopic average of electrostatic potential in $z$ – direction for three isolated BaTiO$_3$ slabs, calculated by freezing them in the atomic geometry identical to the heterosystem they are derived from in Figure 4.8. The systems compared here are BaO terminated at the bottom surface with (i) stoichiometric interface and vacuum on both ends, (ii) depleted interface and vacuum on both ends and (iii) stoichiometric interface and Pt on bottom surface. We see that the system with stoichiometric interface and vacuum on both ends has no slope in the electrostatic potential plot in the absence of the interface, suggesting that the displacements of the bottom surface completely suppress depolarizing fields. The system with depleted interface
Figure 4.8: Macroscopic averaged potential in z direction for isolated BaTiO$_3$ film frozen in heterosystem geometry. Boundary conditions on both surfaces/terminations of BaTiO$_3$ surface/interface compositions of the original heterosystem are as marked in the figure. S denotes that the system has a stoichiometric BaO layer and V denotes a depleted Ba layer at the TiO$_2$/BaTiO$_3$ interface.
and vacuum on both ends has a slope in the electrostatic potential similar to the system with the TiO$_2$ film, in agreement with our earlier assertion that while the polarizations are enforced by stronger dipoles, displacements of the bottom surface cannot suppress depolarizing fields, leading to a slope in potential. Interestingly, when we remove the interface and Pt electrode from the heterosystem with stoichiometric interface and Pt on bottom surface, the BaTiO$_3$ film now has a slope in the potential plot, which was absent in the original heterosystem. This corroborates that this depolarizing field was screened by the addition of Pt electrode in the original system.

4.3 Systems with Platinum electrodes on both ends

To complete the study of the influence of boundary conditions on the interface dipoles and polarizations in ferroelectric oxide heterojunctions, we now consider systems with Pt electrodes on both ends. The relaxed atomic configurations, polarization profile and charge redistributions for these structures are depicted in Figures 4.9-4.11. The magnitude of average dipoles induced by polarization, interface dipoles and relative system energies are in Table 4.3. For the sake of comparison, all other systems are also included in Table 4.3.

4.3.1 Stoichiometric Interfaces

Film Polarization

We note in the film polarization profiles in Figure 4.9 that for the stoichiometric case, the average layer-by-layer cation-oxygen displacement for TiO$_2$ terminated system is now $-0.10\text{Å} \ (p_{BTO_{avg}} = -0.033 \text{ eÅ/surface area})$ as opposed to almost zero polarization in the one electrode case, while it is $0.14\text{Å}$ for BaO terminated system ($p_{BTO_{avg}} = 0.045 \text{ eÅ/surface area}$), similar to the one electrode case.
Figure 4.9: Polarization profiles showing cation-oxygen displacement $\Delta z$ in each layer of BaTiO$_3$ film for TiO$_2$/BaTiO$_3$ systems in contact with Pt electrodes on both ends. Terminations of BaTiO$_3$ surface adjacent to vacuum and interface compositions are as marked in the figure. S denotes that the system has a stoichiometric BaO layer and V denotes a depleted Ba layer at the TiO$_2$/BaTiO$_3$ interface.

Charge Rearrangement and Interface Dipole

For this set of systems, we observe an additional chemical interaction between TiO$_2$/Pt on the top surface, which is covalent in nature as before and contributes an additional dipole. For the TiO$_2$-termination, $\Delta p_{int}$ is computed as 0.008 eÅ/surface area and $\Delta p_{bot}$ as $-0.007$ eÅ/surface area leading to negligibly small $\Delta p_{film}$ of 0.001 eÅ/surface area. The dipole created due to charge rearrangement by TiO$_2$/Pt bonding at top surface $\Delta p_{top}$ is 0.005 eÅ/surface area. For this system, since $\Delta p_{film}$ is almost zero, only the dipole at the top surface can support a polarization in BaTiO$_3$ film.

Since the dipole points from Pt electrode into the heterojunction, the supported polarization points from bottom surface into the heterojunction. For the BaO-termination, $\Delta p_{int}$ is computed as 0.007 eÅ/surface area and $\Delta p_{bot}$ as $-0.012$ eÅ/surface area leading to $\Delta p_{film}$ of $-0.005$ eÅ/surface area. For this system, $\Delta p_{top}$ is 0.003 eÅ/surface area and it seems that the positive polarization in the film is supported by $\Delta p_{film}$, with $\Delta p_{top}$ having negligible to no effect on polarization in the film due to the presence of a non-zero $\Delta p_{film}$. For both these systems, the potential in BaTiO$_3$ film has a zero slope, de-
Figure 4.10: Relaxed atomic structures showing electron rearrangement in the xz plane (summed over y) due to interface formation for TiO$_2$/BaTiO$_3$ systems in contact with Pt electrodes on both ends. Terminations of BaTiO$_3$ surface adjacent to vacuum and interface compositions are as marked in the figure.
noting this arrangement of polarizations and dipoles is required to eliminate internal electric field. This set of systems demonstrates how interface dipoles fully determine the stable polarization in the system.

4.3.2 Oxygen depleted Interfaces

When we deplete these systems of oxygen atoms at the interface, the average layer-by-layer cation oxygen displacement for TiO\textsubscript{2} termination changes to 0.21Å ($p_{\text{BTOavg}} = 0.069$ eÅ/surface area), and for the BaO-termination it is 0.33Å ($p_{\text{BTOavg}} = 0.110$ eÅ/surface area). The computed dipoles now are $\Delta p_{\text{int}} = 0.016$ eÅ/surface area, $\Delta p_{\text{bot}} = -0.023$ eÅ/surface area ($\Delta p_{\text{film}} = -0.007$ eÅ/surface area for TiO\textsubscript{2} terminated system and $\Delta p_{\text{int}} = 0.017$ eÅ/surface area, $\Delta p_{\text{bot}} = -0.026$ eÅ/surface area ($\Delta p_{\text{film}} = -0.009$ eÅ/surface area) and $\Delta p_{\text{top}} = 0.021$ eÅ/surface area for BaO terminated system. In this case, both terminations have non-zero $\Delta p_{\text{film}}$ which supports the positive polarization. The fact that displacements in TiO\textsubscript{2} terminated film are of a reduced magnitude but not completely reversed as in its stoichiometric counterpart implies that the effect induced by oxygen depleted interface is stronger than that induced by top surface/Pt bonding. Also, as before, the electrostatic potential plots have zero slope indicating mitigation of internal electric fields due to screening by Pt electrodes.

4.3.3 Energetics

To complete our analysis we compare the relative energies of these systems and find that for the stoichiometric case, these systems again favor TiO\textsubscript{2} termination of BaTiO\textsubscript{3} film which is lower in energy than BaO termination by 0.51eV. Similar to the one electrode case, the oxygen depleted interfaces favor BaO termination of BaTiO\textsubscript{3} film, which is 6.85eV higher in energy from the reference, as compared to the TiO\textsubscript{2} termination which is 8eV higher in energy from reference, since BaO/Pt at bottom surface is superior in supporting polarization in BaTiO\textsubscript{3} film. Comparing relative stabilities of oxygen depleted interfaces for one electrode and two electrode case, we observe that the relative energies of the depleted interface are higher for systems with two
Figure 4.11: Macroscopic averaged potential in z direction for TiO$_2$/BaTiO$_3$ systems in contact with Pt electrodes on both ends. Terminations of BaTiO$_3$ surface adjacent to vacuum and interface compositions are as marked in the figure. The offset between vacuum potential to the left and right of the slab is also marked. S denotes that the system has a stoichiometric BaO layer and V denotes a depleted Ba layer at the TiO$_2$/BaTiO$_3$ interface.
Table 4.3: Average dipole due to polarization $p_{BTO_{avg}}$ in BaTiO$_3$ (in eÅ/surface area). Interface dipoles ($\Delta p_{top}$, $\Delta p_{int}$, $\Delta p_{bot}$ and $\Delta p_{film}$) in eÅ/surface area and relative system energies $E_{rel}$ (in eV) with respect to a reference for relaxed interface geometries. $\Delta p_{top}$ is the contribution from Pt/TiO$_2$ top surface, $\Delta p_{int}$ is the contribution from TiO$_2$/BaTiO$_3$ interface, $\Delta p_{bot}$ is the contribution from BaO/Pt or TiO$_2$/Pt bottom surface and $\Delta p_{film} = \Delta p_{int} + \Delta p_{bot}$ is the dipole across BaTiO$_3$ film. Positive values for dipoles indicate dipole pointing from interface into BaTiO$_3$ film, away from BaTiO$_3$ film into Pt at bottom surface or from Pt into TiO$_2$ film at top surface. S denotes that the system has a stoichiometric BaO layer and V denotes a depleted Ba layer at the TiO$_2$/BaTiO$_3$ interface. *$\Delta p_{bot}$ for systems with no bottom electrodes are computed using the displacements in the bottom-most BaTiO$_3$ layer. These layers are not included in the calculation for $p_{BTO_{avg}}$

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electrodes. This suggests that presence of Pt electrodes only at the bottom surface helps in stabilizing structures with oxygen depleted interfaces compared to those with no electrodes, while presence of Pt electrodes at both the surfaces has an opposite effect, possibly because the dipole created by charge redistribution from addition of Pt electrode to TiO$_2$ surface, $\Delta p_{\text{top}}$ opposes the displacements enforced by the TiO$_2$/BaTiO$_3$ interface.
5.1 Application of interface engineering to water splitting reaction

Water molecule splitting on the surface of a catalyst consists of two successive processes: dissociative chemisorption as H and OH ions as decreed earlier, followed by desorption [90]. Extremely favorable H\(_2\)O chemisorption on TiO\(_2\) surface will bind the molecule too strongly to the surface, impeding desorption. If it is not favorable enough, then there will be a lack of reactants on the surface, slowing further reaction.

Hence, the plot of reaction rate versus dissociative chemisorption energy is a volcano shaped curve, shown schematically in Figure 5.2 [90]. This picture of the dependance of reaction rate on binding energy is oversimplified, and based only on thermodynamic criteria, ignoring reaction kinetics. However, similar plots generated for rates of surface oxidation/reduction reactions of various molecules (O\(_2\), H\(_2\) etc) on different surfaces experimentally tend to follow a similar volcano trend [91].

In this chapter, we discuss the effect of engineering interfacial charge distribution and substrate polarization in TiO\(_2\)/BaTiO\(_3\) system via varied boundary conditions on surface reactivity of TiO\(_2\) film. Tailoring the surface reactivity of TiO\(_2\) film can tune the chemisorption energy of water on TiO\(_2\) film surface, thereby affecting water molecule dissociation on the surface.

5.2 Band Alignment

Band alignment at a typical semiconductor-semiconductor heterointerface is determined by assuming a common vacuum level for the two materials
Figure 5.1: Steps in dissociation of water molecule on a surface
Figure 5.2: (a) A schematic volcano plot describing reaction rate versus chemisorption energy [90]
and taking a difference of their electron affinities in bulk (electron affinity rule\cite{92}). However, the electronic charge redistribution caused by chemical interactions at the interface can cause additional offsets in electronic potential between the two materials. Figure 5.3 shows the DFT-computed density of states projected across different oxide layers for structures which are in contact with vacuum on both ends. The valence band edges and the Fermi energy level are also marked. Interfacial bonding and magnitude of film polarization directly affect the alignment of the valence and conduction bands across the interface and the Fermi energy level in these systems. Work function difference between the two terminations of BaTiO$_3$ films cause the bands to bend differently at the BaTiO$_3$ surface. TiO$_2$ terminated BaTiO$_3$ films with higher surface work function bend upward at the surface while BaO terminated film with lower work function bend downward.

The interplay between interface dipoles and surface terminations also affects the Fermi energy of the system. Strong interface dipoles in films with oxygen depleted interfaces push the Fermi level to the conduction band edge. This can be seen as a direct consequence of the partially filled states at the interface in both materials due to charge redistribution from Ba layer to oxygen atoms. It is also evident from Figure 5.3 that bands at TiO$_2$ surface bend downward in the presence of non-polarized stoichiometric films, but strong interface dipoles due to depleted interfaces cause sharp upward bending of bands in the system. The redistribution of charge at the interface causes some charge migration to the surface as well, which leads to presence of surface states that bend the bands upwards. Systems with Pt electrodes on one or both ends also follow similar trends but are not shown here. This is because of band alignment problem at the BaTiO$_3$/Pt interface due to inaccurate predictions of DFT bandgap where the Fermi level of the metal is erroneously aligned with the conduction band of BaTiO$_3$, causing unphysical population of conduction band and metallization in the BaTiO$_3$ layers adjacent Pt. Such an anomaly has also been reported in previous partial density of state analyses of metal/ferroelectric interfaces \cite{93}.
Figure 5.3: Density of states in each oxide layer for TiO$_2$/BaTiO$_3$ system with a) BaO terminated surface b) TiO$_2$ terminated surface c) BaO terminated surface with a Ba layer at interface b) TiO$_2$ terminated surface with a Ba layer at interface, in contact with vacuum on both ends. Both the surfaces are labeled and the interface is denoted by shaded red region. The solid blue line indicates the Fermi Energy and the dashed blue line shows the valence band edge.
Figure 5.4: Dissociative adsorption of water: Charge rearrangement due to the presence of a water molecule on surface
5.3 Chemisorption

Finally, we look at chemisorption of water molecules on the surfaces of systems which have an exposed TiO$_2$ surface. The adsorption of H$_2$O on the surface of TiO$_2$ is dissociative. There is a migration of charge from the O-H bond of water molecule to form a bond between the O atom of water molecule with the surface Ti atom. Similarly, there is a migration of charge from a surface Ti-O bond to form a bond between the bridging O-atom of TiO$_2$ surface and H atom. This is depicted in Figure 5.4.

The chemisorption energy $\Delta E_{H_2O}$ is calculated as:

$$\Delta E_{H_2O} = E_{\text{system}} - (E_{\text{slab}} + E_{H_2O})$$ (5.1)

where $E_{\text{system}}$ is the DFT-computed total energy of the system with water molecule adsorbed on the surface, $E_{\text{slab}}$ is the DFT computed energy of the same system without a water molecule and $E_{H_2O}$ is the DFT computed total energy of a free water molecule. For reference, we also calculate chemisorption energies of water molecule on a 5 layer TiO$_2$ slab. The slab thickness of TiO$_2$ has been converged such that the two surfaces are far away and non interacting, as in a bulk-like system. First principles calculations to study chemisorption of water molecules are performed by placing one water molecule (per unit surface) at a distance of 5 Å from TiO$_2$ surface and allowing the system to relax. In all the systems studied, water molecules interact with TiO$_2$ surface displaying charge sharing between O atom of H$_2$O and Ti atom of TiO$_2$ surface, and one of the H atoms of H$_2$O and bridging O atoms of TiO$_2$ surface. This charge rearrangement for a bulk like TiO$_2$ slab and a representative heterosystem is shown in Figure 5.4. The computed chemisorption energies for a full ML coverage of water molecules and distances between atoms of H$_2$O and TiO$_2$ for all of the systems are recorded in Table 5.1.

We see that water molecule chemisorption is favorable when systems have an interface dipole compared to bulk TiO$_2$ geometry. Within these systems also, film polarizations and boundary conditions affect chemisorption energy. Systems with vacuum boundary conditions on both ends and stoichiometric interface show similar chemisorption energies irrespective of BaTiO$_3$ film termination due to similar interface dipoles and suppression of film polarizations.

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Table 5.1: Computed chemisorption energies for a water molecule $\Delta E_{H_2O}$ (in eV) and interatomic distances between surface ions and water molecule (in Å). $O_{H_2O}$ is the oxygen atom in H$_2$O that bonds with surface Ti atoms and $O_{TiO_2}$ is the bridging oxygen atom on surface that binds with H atom for water molecule. S denotes that the system has a stoichiometric BaO layer and V denotes a depleted Ba layer at the TiO$_2$/BaTiO$_3$ interface.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta E_{H_2O}$ (eV)</th>
<th>Ti - O$_{H_2O}$ (Å)</th>
<th>$O_{TiO_2}$ - H (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ Slab</td>
<td>0.51</td>
<td>2.41</td>
<td>1.76</td>
</tr>
<tr>
<td>Type 1, S, BaO Terminated</td>
<td>0.77</td>
<td>2.26</td>
<td>1.57</td>
</tr>
<tr>
<td>Type 1, S, TiO$_2$ Terminated</td>
<td>0.77</td>
<td>2.26</td>
<td>1.57</td>
</tr>
<tr>
<td>Type 1, V, BaO Terminated</td>
<td>0.78</td>
<td>2.33</td>
<td>1.60</td>
</tr>
<tr>
<td>Type 1, V, TiO$_2$ Terminated</td>
<td>0.60</td>
<td>2.36</td>
<td>1.86</td>
</tr>
<tr>
<td>Type 2, S, BaO Terminated</td>
<td>0.81</td>
<td>2.26</td>
<td>1.57</td>
</tr>
<tr>
<td>Type 2, S, TiO$_2$ Terminated</td>
<td>0.80</td>
<td>2.26</td>
<td>1.57</td>
</tr>
<tr>
<td>Type 2, V, BaO Terminated</td>
<td>1.00</td>
<td>2.25</td>
<td>1.56</td>
</tr>
<tr>
<td>Type 2, V, TiO$_2$ Terminated</td>
<td>0.89</td>
<td>2.26</td>
<td>1.57</td>
</tr>
</tbody>
</table>

by depolarizing fields. However, systems with vacuum boundary conditions on both ends and oxygen depleted interface have very different chemisorption energies despite the presence of similar interface dipoles due to the polar nature of these films. We have seen in Chapter 4 that these films have a slope in electrostatic potential due to a depolarizing field from uncompensated polarization. This downward slope in potential increases the offset in vacuum levels on two sides of the system. From Figure 5.5, we notice that the dipole moment of the water molecule reduces the net potential drop across the BaO terminated system. However, in the TiO$_2$ terminated system, it overcompensates and reverses the magnitude of potential offset across the slab. This suggests that addition of water molecule helps with polarity compensation in the BaO terminated system, while it overcompensates in the TiO$_2$ system, making adsorption less favorable.

Chemisorption energies in systems supported with Pt electrodes vary monotonically with film polarization, with chemisorption of water molecule being most favorable on the heterosystem with BaO terminated BaTiO$_3$ film and an oxygen depleted interface. These trends can be explained by considering the effect of interfacial charge rearrangement on electronic structure of TiO$_2$ film. Strong interfacial redistribution of charge towards TiO$_2$ film creates sur-
Figure 5.5: Macroscopic averaged potential in z direction for TiO$_2$/BaTiO$_3$ systems with a water molecule adsorbed. The system has a depleted Ba layer at the TiO$_2$/BaTiO$_3$ interface and is in contact with vacuum on both ends. The potential plots of corresponding systems with a water molecule are also shown for reference.
face states and bends the bands in TiO$_2$ film upwards and created partially filled states close to the Fermi level in the conduction band. The increased availability of these states close to the Fermi level allows for stronger Ti - O covalent bonding and O-H bonding. For a better comparison, we plot the difference in charge density due to adsorption of water molecule for a 5-layer TiO$_2$ slab as well as a BaO terminated heterosystem with Pt electrodes at bottom surface and depleted interface in Figure 5.6. We can clearly see the increased transfer of charge to the bond between surface Ti-O atom of water molecule for the heterosystem.

![Figure 5.6: Charge rearrangement due to H$_2$O adsorption for a) 5 layer TiO$_2$ slab b) BaO terminated TiO$_2$/BaTiO$_3$ system with a Ba layer at interface and in contact with Pt electrodes at BTO termination and vacuum at TiO$_2$ surface. The red and blue regions denote gain and loss of electrons respectively. The xz plane for charge density is chosen to show bonds between surface ions and water molecule.](image)

Therefore the overall rate of water dissociation on TiO$_2$ surface can be optimized by tuning chemisorption energy to the desired range. These interface
induced changes in chemisorption energies can have a large effect on water molecule dissociation reaction kinetics.
Density Functional Theory calculations were performed with plane wave (Quantum Espresso) basis sets to demonstrate the possibility of tuning polarization of BaTiO$_3$ thin film via interface engineering of TiO$_2$/BaTiO$_3$ hetero-junction and utilizing this interface induced polarization to influence electronic properties and chemistry of TiO$_2$ surface for photocatalytic applications.

A total of twelve different hetero-systems with varying interface geometry on either side of BaTiO$_3$ film were considered in this work. The interface was varied by modifying BaTiO$_3$ termination, interface composition, and the presence/absence of metal (Pt) electrodes. We analyzed the effect of different interface configurations on interfacial charge rearrangement, induced interface dipoles and subsequent suppression of depolarizing fields and recovery of polarization in BaTiO$_3$ film.

Our results demonstrate that interfacial charge rearrangement is influenced by the interface geometry, which in turn affects the induced dipole at the interface. Therefore, asymmetrical interface geometries on either side of BTiO$_3$ film can help suppress depolarizing fields and recover polarization by creating unequal interface dipoles. We have shown that altering these end conditions creates chemical and electrostatic boundary conditions across the slab, stabilizing varied amounts of film polarization. This polarization is entirely induced by interface effects, and is non-switchable, as demonstrated by the absence of a stable opposite polarized state for the system.

Our analysis of the electronic properties of the system shows that a combination of film polarization and varied boundary conditions also alters the electronic structure of the system, such as interface and surface band alignment and occupied surface states. Furthermore, we show that these changes at the interface propagate to the film surface and modify the reactivity of TiO$_2$ surfaces, providing a tunable range of chemisorption energies of water.
molecules on the surface. Therefore our results provide a way of optimizing the reactivity of TiO$_2$-based catalysts by tailoring the interface structure for optimal chemisorption energy to enhance surface water splitting.

We have only modeled two interface compositions in this work, but it would be interesting to explore the effect of other interface compositions on surface reactivity, such as cation vacancies, mixed cation-anion vacancies, foreign dopants etc. This work only studied the effect of polarization on ground state properties such as surface reactivity but the effect on excited state properties and carrier transport should also be explored. Finally, it would be interesting to observe some of the phenomenon we observe in our calculations in experimentally fabricated similar thin film heterojunctions.
REFERENCES


