Abstract

MOBALLEGH, ALI. Field-Induced Point Defect Redistribution in Metal Oxides: Mesoscopic Length Scale Phenomena. (Under the direction of Prof. Elizabeth C. Dickey).

The spatial redistribution of charged point defects under direct-current (DC) biasing can have significant implications for electroceramic device performance and lifetime. The transport behavior of point defects is regulated by the boundary conditions of the electrodes, which can block electronic charge and/or ion transfer across the interface to varying degrees. When the electrodes are impermeable to mass transport, there will be an accumulation of point defects in the near-electrode region that can lead to significant modifications in the local electronic carrier concentrations. Such defect redistribution is responsible for the long-term increases in leakage current in many capacitor devices via modification of the interface Schottky barrier at the reverse-biased cathode.

While this leakage current enhancement is detrimental in capacitor devices, the phenomenon of lattice defect migration can be utilized to form novel functional behaviors, such as resistive switching in metal-oxides via modulation of the Schottky barrier or formation of nonstoichiometric filaments oriented along the applied field direction.

The present work aims to understand the phenomenon of defect redistribution as a function of the initial defect chemistry state and electrode boundary conditions under the degradation process, using single-crystal rutile TiO$_2$ as a model material. Experiments are performed as a function of degradation voltage and crystallographic orientation since the self-diffusion coefficients of oxygen vacancies and titanium interstitials are known to be highly anisotropic in rutile.
Rutile single crystals are equilibrated at specific oxygen partial pressures and temperatures to define the initial defect chemistry state. Platinum electrodes, which form Schottky contacts and are largely impermeable to oxygen transfer, are deposited on opposite faces of the crystal. The samples are then subjected to up to 200 V/cm electric field at 200°C while the leakage current is continuously monitored. To understand spatial variations in chemistry and possible changes in microstructure, we utilize a combination of cathodoluminescence spectroscopy (CL), transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). After electrical degradation, correlating electrical characterization measurements with electron microscopy analyses provides insight into the redistribution of point defects as a function of electric field and time.

Diode-like rectification behavior was observed in crystals subjected to an applied voltage in the low electric field regime (< 75V/cm). One-dimensional and homogenous defect redistribution along both <010> and <001> results in accumulation of point defects and the formation of highly reduced substoichiometric regions near the cathode, which leads to the Schottky barrier degradation. The CL spectroscopy shows that titanium interstitials dominate the point defect redistribution process in this region. The reversibility of the rectification behavior, examined for both crystallographic directions, shows that the process can be influenced by the anisotropy of rutile. At degradation fields on the order of 56 V/cm at 200°C, although the degradation of Schottky barrier is mostly reversible along <010>, formation of extended structural defects is not recovered during the application of a reverse bias and results in an irreversible rectification behavior along <001> direction.

We also identify electric field regimes (> 175 V/cm) in which the concentrations of point defects become large enough to induce higher-dimensional defects such as dislocations
and the formation of Magnéli phases. We find that the condensation of point defects into Magnéli phases at the electrodes depletes point defect concentration in the bulk, thus increasing the bulk resistivity. The Magnéli phases formed near the cathode are found to be stable, and not reversible, at 200°C for the times and fields studied. The defect condensation processes have significant impacts on the overall I-V behavior of the material and the ability to switch the total resistance.

The electroformation of conductive filaments, another dominant degradation mechanism, is observed on samples with slightly higher initial bulk resistivity (about 80 Ω.cm) at field levels as low as 150 V/cm. The redistribution of ionic carriers leads to heterogeneity in the chemistry of TiO$_2$ in the form of nonstoichiometric filaments oriented along the applied field direction. The CL spectra taken from conductive filaments and non-filaments regions indicate a noticeable increase in the concentration of the titanium interstitials of the filaments. We demonstrate that the filaments can be disconnected from the electrodes with subsequent reverse-polarity biasing, demonstrating switching on a macroscopic crystal.

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Field-Induced Point Defect Redistribution in Metal Oxides:
Mesoscopic Length Scale Phenomena

by
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Dedication

This thesis is dedicated to

my parents, Zohreh Behnia and Asghar Moballegh,

my love, Golsa,

for their endless support and encouragement.

I was always encouraged by my parents, my father a material engineer and my mother an experienced literature teacher, to eagerly explore the unknown and discover its underlying aspects. He always noted me “No matter who I am or who I will be in future; a teacher, a doctor, an engineer or a pilot, I should try to excel in every walk of life”.
Biography

Ali Moballegh was born in Tehran, Iran on May 20th, 1980. After finishing his high school in Danesh, he was admitted in materials engineering (Ceramics) at the Faculty of Material Engineering, Iran University of Science and Technology (IUST) in 1999, the only university in Iran offering ceramics engineering major and accepting only 35 students among all of 1.5 million applicants. His thesis was done under supervision of professor Naghizadeh and professor Sarpoulaki with title of “Effects of CaF$_2$ and BaSO$_4$ Additives on LCC Refractory Castable Properties.” In 2004, he started his master program in material science and engineering at Tarbiat Modarres University (TMU) after getting admitted with a very good rank in the entrance exam. He decided to conduct his thesis, “Synthesizing ZnO Nanoparticles and Investigating the Optical Properties.” with focus on synthesizing and investigating the properties of nanomaterials under the supervision of Professor Shahverdi and Professor Aghababazadeh. During and after the Master’s degree, he worked as a researcher in research and development department in NEPCO (Nasoozin Engineering and Production Company) until he came to the US in August 2009. He started his PhD in Material Science and Engineering department at North Carolina State University in August 2010, and joined Prof. Dickey’s group in May, 2011 and took his PhD in December 2014.
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Chapter 1

Introduction

It is generally understood that the lattice defect disorder (e.g. vacancies, interstitials) significantly affects the electronic properties of semiconducting materials, because there is a coupling between the charged lattice defects and electronic carriers (electrons and holes). The equilibrium point defect concentrations, and thus electronic carrier concentrations, are functions of external environmental conditions: temperature (T), extrinsic dopant concentration and in the case of oxides, the partial pressure of oxygen (PO$_2$). In device applications under direct current (DC) voltage, these charged defects can redistribute, which can lead to detrimental behavior such as leakage current enhancement in capacitor devices [4]. The defect migration can also be utilized to form novel functional behaviors, such as resistive switching in metal-oxides [1-3]. Understanding the phenomenon of point defect redistribution and its implications for a variety electronic properties is thus of great importance to the modern micro-electronics industry.
The drift/diffusion of point defects under applied bias leads to accumulation of the charged point defects at the electrode if it blocks mass transport across interface. If the electrode was initially of Schottky type, these temporal changes in local defect concentrations can lead to increased charge injection via barrier height lowering and depletion layer narrowing [1]. The resulting asymmetrical behavior at the cathode and anode leads to diode-like behavior, also called field-programmable rectification. If the interface behavior can be reversed with the application of an electric field in the opposite polarity, this leads to resistive switching. The nature of resistive switching has been studied in binary transition metal oxides [5] such as TiO$_2$ [6-9], Nb$_2$O$_5$ and Ta$_2$O$_5$ as well as ternary oxides, such as BaTiO$_3$ [4, 10] and SrTiO$_3$ [11, 12] with perovskite structure.

Rutile TiO$_{2-x}$, where x indicates the sub-stoichiometry level, can be utilized as a model system to study point defect transport in response to the electric field [13-16]. The sub-stoichiometry is accommodated by the formation of oxygen vacancies and titanium interstitials [15, 17]. Prior literature reports the migration of oxygen vacancies by an electric field, caused by Schottky barrier annihilation and rectification behavior in rutile single crystals [6, 18]. Field-programmable rectification behavior was observed by Jameson et al [6] on TiO$_2$ single crystals, at fields of 125-375 kV/cm. The retention of the rectifying state depends on the programing voltage, the programming time and the crystallographic orientation. It was found to increase as a function of in-plane crystallographic orientation from the <010> direction toward the <001> direction. After the field-programming process, a dark blue region at the negative terminal formed and was accompanied by a transparent
region at the positive terminal. To describe the degradation process, oxygen vacancies as the mobile point defect have been discussed [15, 19]; however in contrast to the perovskites [4, 12, 20], both oxygen vacancies and cation (Ti) interstitials are highly mobile in TiO₂. Titanium interstitials therefore can be expected to contribute in the interface barrier modulation and even control the degradation process.

The resistance switching for TiO₂ can also occur via formation of conductive filaments. In this mechanism, point defect migration has a non-planar concentration front, the concentration enhancement of accumulated point defects leads to the formation of highly reduced regions that grow along the direction of the electric-field connecting the electrodes by “electroforming” [3]. The electroforming mechanism is studied on TiO₂ and resistance switching is mostly discussed with bipolar resistance switching [21-24]. The conductive filaments can shunt the anode and the cathode and lead to a bipolar switching mechanism between high and low resistance states, as application of subsequent electric fields can “disconnect” the filament from either electrode depending on the field polarity.

The phase transformation from TiO₂ to a Magnéli phase is another possible origin of resistive switching behavior. Extremely high concentrations of point defects, out of the dilute solution approximation, have been shown in several studies to form crystallographic shear planes and/or Magnéli phases to compensate the sub-stoichiometry associated from electrochemical reduction at the cathode [15, 25].

Many important questions remain to understand fundamentally the thermodynamic and transport behaviors of point defects in the metal oxide including:
• What is the role of initial defect chemistry state of TiO$_2$ on resistance degradation? In other words, how do the absolute and relative concentrations of mobile charged point defects, such as oxygen vacancies and titanium interstitials, impact the redistribution process?

• Which factors determining the degradation mechanism, i.e. is it a one-dimensional drift-diffusion problem or does filamentary growth dominate?

• What are the effects of crystallographic orientation on the redistribution process?

• How does the system accommodate large concentrations of point defects, when then electrochemical potential approaches and exceeds the stability of TiO$_2$ near the metal/dielectric interface?

• What is the role of defect concentration, electric field, and crystallographic orientation on the probability of phase transformation to the Magnéli phases (Ti$_n$O$_{2n-1}$)?

• How is the resistance degradation process affected by extended defects and Magnéli phase formation?

In the present work, we aim to answer these questions and provide guidance for future research by developing new and more generalized insight into the defect transport kinetics and resistance degradation mechanisms. Single crystal rutile TiO$_2$, with a well-defined initial defect chemistry state, is utilized to study point defect redistribution and resistance degradation mechanisms under an applied electric field. Over the degradation process, the current-voltage behavior is monitored and local microstructure and microchemistry are analyzed by electron microscopy and electron spectroscopy techniques to gain more insight into point defect transportation.
Both homogenous concentration front redistribution (interface modulation), and filamentary growth mechanisms are observed and studied by controlling experimental variables, temperature and oxygen partial pressure.
Chapter 2

Background

1. Crystal structure of rutile TiO$_2$

Rutile TiO$_2$ is a wide band gap dielectric and is the thermodynamically stable phase at standard temperature and pressure compared to other metastable polymorphs, such as anatase and brookite [26-28]. First studied by Vegard [29], the crystallographic structure of rutile TiO$_2$ corresponds to a tetragonal unit cell where the titanium atoms create a body-centered tetragonal sublattice and oxygen atoms arrange to form a slightly distorted octahedron surrounding each titanium atom (Figure 2-1). Atomic bonding in TiO$_2$ is not purely ionic (ionic-covalent bonding) [30] which results in low solubility in polar solvents, a coordination number of three for the oxygen atoms and high static dielectric constant (89 along $a$ and 187 along $c$ axis) [31]. The bulk properties of the TiO$_2$ polymorphs are summarized in Table 2-1.
Figure 2-1: Rutile crystal structure created with crystal maker software.
Table 2-1: Properties of TiO₂ polymorphs [17, 32, 33].

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<th>Space group</th>
<th>Lattice constants (Å)</th>
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<tr>
<th>Permittivity ($\varepsilon_r$)</th>
<th>Optical (high frequency)</th>
<th>Static (low frequency)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-axis c-axis a-axis c-axis</td>
<td>7.53 8.66 187 89</td>
<td>5.3 5.5 13 43</td>
</tr>
</tbody>
</table>

2 Electrical properties

2.1 Band structure of rutile TiO$_2$

Rutile TiO$_2$, with wide band energy of about 3 eV [34], is one of the most studied dielectrics due to its special optical and electrical properties. An indirect-band transition at 3.03 eV from the electroabsorption measurements by Arntz and Yacoby [35] indicates the direct optical transition edge is somewhere in a range of 3.2-3.5 eV [36]. The electronic behavior of n-type TiO$_2$...
rutile is explained by positively charged point defects, oxygen vacancies, $V_{O}^{+2}$, and Ti interstitials, $Ti_i^{+4}$ and $Ti_i^{+3}$ [37].

In TiO$_{2-x}$, the cathodoluminescence (CL) spectroscopy implemented in a scanning electron microscope (SEM) is able to detect optical transitions associated with the point defect energy levels with high spatial resolution [38-40]. The band structure of (100) and (110)-oriented n-type TiO$_2$ single crystal have been studied by SEM-CL measurements [38]. The CL spectrum, as reported by Fernández et al., shows a broad peak around a wavelength of 410 nm (3 eV), which corresponds to the TiO$_2$ band gap and overlaps with a peak resulting from the oxygen vacancy’s energy level [38]. The energy state of titanium interstitials ($Ti_i^-$) is reported to be about 1.53 eV above the valence band and has an associated emission peak in the infrared region. After Gaussian deconvolution of the spectrum, the energy position of fully ionized oxygen vacancies is around 2.23 - 2.83 eV above the valence band while the associated emission peak lies within the tail of the band-gap emission [38, 40]. The energy levels of titanium interstitials and oxygen vacancies within the band gap of the rutile TiO$_{2-x}$ are shown in Figure 2-2.
Figure 2-2: Schematic of the energy levels of the intrinsic lattice defects of TiO$_2$ [41].

The electronic band structure of rutile is also studied by photoluminescence spectroscopy, which is a powerful technique to investigate the electronic band structure of materials [42-44]. The investigation by Ghosh et al. shows that a direct optical transition occurs at 3.2 eV; however, at lower energies of 3 eV, an indirect transition is observed [42]. At 1.55 eV below the conduction band, a luminescence emission belong to transition to Ti$_i^{3+}$ energy level is detected. At least eight different shallow energy levels (<1 eV) below the conduction band are distinguished, which can be related to oxygen vacancies. Shi et al. recorded an intense photoluminescence emission near-infrared (about 1.5 eV below conduction band) ascribed to titanium interstitials [43].

In the Ti rich case, the combination of titanium interstitials and oxygen vacancies, in the form of $V_o^−$ – Ti$_i^{−−}$ dimer, is also predicted in the electronic band structure of rutile by Zhu et al [45]. Density function theory (DFT) calculations indicate that titanium interstitials have
two energy levels below the conduction band; a deep donor level about 1.25 eV, associated with $Ti_i^{3+}$, and a shallow donor level at 0.28 eV, associated with $Ti_i^{4+}$. Moreover, the dimer has two main energy levels at 0.63 eV and 1.53 eV below the conduction band. The energy level of oxygen vacancies with different charge states is about 0.7 eV below the conduction band based on calculations reported by Lee et al. [46] and is in agreement with study by Park [47]. However, different charge states of titanium interstitials results in formation of four defect states at 0.7-1.3 eV below the conduction band. In another study, Ramamoorthy et al. found that the oxygen vacancy defect state is 0.3 eV below the conduction band within the band gap [48].

2.2 Point defect energetics and carrier concentrations

The formation of intrinsic charged defects in TiO$_2$ can be described by Schottky disorders that lead to oxygen vacancy and titanium vacancy creation (1.3±0.1 eV formation energy), or Frenkel cation disorders comprised of titanium interstitials and titanium vacancies (2.2±0.2 eV formation energy) [49]. Non-stoichiometric and extrinsic point defects define and alter the electrical behavior of semiconductors. The dangling bond remaining after formation of the point defect enables the electronic charge transfer between the host material and the point defect. The direction of electron transfer away or toward the point defects defines formation of donors or acceptors, respectively. The host’s Fermi energy is affected by formation of donors that often have energy levels close to the conduction band while acceptors have energy levels closer to the valence band. By knowing the position of the Fermi level, charge
state and formation energy of the point defect, the defect concentration can be calculated as a function of temperature [50]. Moreover, in the case of oxide semiconductors, the concentration of charged defects can be defined using the law of mass action and also knowing external parameters, such as the oxygen partial pressure and temperature [51-53]. At thermodynamic equilibrium a determinate concentration of point defects are generated and uniformly distributed at any given temperature and oxygen partial pressure. The concentration of the point defects can be calculated by knowing the vibrational entropy, $\Delta S^0_{\text{vib}}$, the enthalpy of formation, $\Delta H^0$, for all charged point defects (intrinsic point defects, dopants and impurities) and charged electron and hole carriers where the charge neutrality condition is satisfied.

In TiO$_2$, the most important point defects are titanium interstitials, $\text{Ti}_i^{***}$ and $\text{Ti}_i^{****}$, oxygen vacancies, $V_{\text{O}}^{**}$, and titanium vacancies, $V_{\text{Ti}}^{****}$ [54]. Compared to oxygen vacancies present within the unit cell, titanium interstitials cause more distortion in the octahedra. Cho et al. presented that the Ti-O bond length distorts in a way that oxygen ions relax toward the interstitials by about 10% while Ti ions pull away from interstitials by 13% [55]. Cation dopants and impurities, which mainly substitute on the titanium site, are classified in two groups based on the valence state of external ions. An impurity or dopant ion can be considered as an acceptor impurity (e.g. trivalent ions on titanium sites, $A^{*}_{\text{Ti}}$) or a donor impurity (e.g. pentavalent ions on titanium sites, $D^{*}_{\text{Ti}}$).
2.2.1 Experimental measurements

The point defect chemistry of oxides is typically measured experimentally either by thermogravimetric analysis (TGA) or electrical conductivity, $\sigma$, as a function of temperature and oxygen partial pressure.

The defect disorder (i.e., titanium interstitials, oxygen vacancies and titanium vacancies) can be described according the following equilibrium point defect equations and equilibrium constants where $n$ and $p$ are concentrations of electrons and holes, respectively [56].

\[ O_2 \rightleftharpoons V_0^{\bullet\bullet} + 2e' + \frac{1}{2}O_2 \quad K_1 = [V_0^{\bullet\bullet}]n^2P^{0.5} \quad (2-1) \]

\[ 2O_2 + Ti_{T_i} \rightleftharpoons Ti_{T_i}^{\bullet\bullet\bullet} + 3e' + O_2 \quad K_2 = [Ti_{T_i}^{\bullet\bullet\bullet}]n^3P \quad (2-2) \]

\[ 2O_2 + Ti_{T_i} \rightleftharpoons Ti_{T_i}^{\bullet\bullet\bullet\bullet} + 4e' + O_2 \quad K_3 = [Ti_{T_i}^{\bullet\bullet\bullet\bullet}]n^4P \quad (2-3) \]

\[ O_2 \rightleftharpoons 2O_2 + V_{T_i}^{\bullet\bullet\bullet\bullet} + 4h^* \quad K_4 = [V_{T_i}^{\bullet\bullet\bullet\bullet}]p^4P^{-1} \quad (2-4) \]

\[ nil \rightleftharpoons e' + h^* \quad K_i = np \quad (2-5) \]

The equilibrium constants for the these equations have been measured experimentally by numerous groups over the past ten years [57-59] and the results have been reviewed by
Nowotny et al. [41], who emphasize the need to equilibrate samples to full equilibrium based on the different diffusion constants of the cation interstitials and oxygen vacancies. The most reliable values for the mass action constants, as reported by Nowotny et al. are listed in Table 2-2. Derivation of point defect diagrams requires solving the above equations by with the equilibrium constants and also considering the charge neutrality condition according to Equation 2-6, where \([A']\) and \([D^\star]\) denote the concentrations of acceptors and donors.

\[
n + 4[V_{Ti}'''] + [A'] = p + 2[V_{O}^\star] + 3[Ti_i^{***}] + 4[Ti_{i}^{****}] + [D^\star]
\]  

(2-6)

According to the oxygen partial pressure exponent, the defect disorder can be studied in different regimes where dominant point defects vary from one regime to another. The concentrations of charged carriers and ionic point defects as a function of equilibrium constants for each regime are presented in Table 2-3.
Table 2-2: The thermodynamic quantities for the intrinsic point defect formation and electronic charge carriers in undoped TiO$_2$.

<table>
<thead>
<tr>
<th>Equilibrium constants</th>
<th>$\Delta H^o$ [kJ mol$^{-1}$]</th>
<th>$\Delta S^o$ [J mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>493.1</td>
<td>106.5</td>
</tr>
<tr>
<td>$K_2$</td>
<td>879.2</td>
<td>190.8</td>
</tr>
<tr>
<td>$K_3$</td>
<td>1025.8</td>
<td>238.3</td>
</tr>
<tr>
<td>$K_4$</td>
<td>354.5</td>
<td>-202.1</td>
</tr>
<tr>
<td>$K_i$</td>
<td>222.1</td>
<td>-44.6$^1$</td>
</tr>
</tbody>
</table>

Table 2-3: Ionic point defects and charge carrier concentrations in undoped TiO$_2$ corresponding to the oxygen activity and the charge neutrality [41, 57, 60, 61].

<table>
<thead>
<tr>
<th>regime</th>
<th>extremely reduced</th>
<th>strongly reduced</th>
<th>reduction-oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>electronic compensation</td>
<td>$n = 3[Ti_i^{***}]$</td>
<td>$n = 2[V_O^{**}]$</td>
<td>$[V_O^{**}] = 2[V_Ti^{''''}]$</td>
</tr>
<tr>
<td>electronic compensation</td>
<td>$p$</td>
<td>$K_i(3K_2)^{-1/4}PO_2^{-1/4}$</td>
<td>$(2K_i)^{1/3}PO_2^{-1/6}$</td>
</tr>
<tr>
<td>[V$_{Ti}^{''''}$]</td>
<td>$3K_4K_2K_i^{-4}PO_2^0$</td>
<td>$(2K_1)^{4/3}K_4K_i^{-4}PO_2^{1/3}$</td>
<td>$(2K_i^2K_4K_i^{-1})^{1/3}PO_2^0$</td>
</tr>
<tr>
<td>[V$_O^{**}$]</td>
<td>$K_3(3K_2)^{-1/2}PO_2^0$</td>
<td>$(K_1/4)^{1/3}PO_2^{1/6}$</td>
<td>$(2K_i^2K_4K_i^{-4})^{1/3}PO_2^0$</td>
</tr>
<tr>
<td>[Ti$_i^{***}$]</td>
<td>$(K_1/27)^{1/4}PO_2^{-1/4}$</td>
<td>$K_2(2K_1)^{-1}PO_2^{-1/2}$</td>
<td>$(2K_i^2K_4K_i^{-1})^{1/2}PO_2^{-1/4}$</td>
</tr>
<tr>
<td>[Ti$_i^{''''}$]</td>
<td>$K_3(3K_2)^{-1}PO_2^0$</td>
<td>$K_3(2K_1)^{-4/3}PO_2^{-1/3}$</td>
<td>$K_3(2K_4K_i^{-4}K_i^{-1})^{2/3}PO_2^0$</td>
</tr>
</tbody>
</table>

$^1$ A typo in the referenced literature [43] has been corrected.
Rutile TiO₂ samples can be annealed under specific oxygen partial pressure (PO₂) and temperature conditions to establish the initial defect chemistry state of the material, taking into account the known equilibration kinetics of TiO₂ [41, 60-62]. At annealing conditions that target n-type conductivity regimes (reducing regime), either titanium interstitials or oxygen vacancies are the dominant defects [41, 61, 62]. At high temperatures (1050-1350°C) in reducing atmospheres (PO₂=10⁻¹⁰-1 atm) Schottky disorder dominates (in ionic compensation region) and the electronic carrier concentration is governed by the titanium interstitials. At low PO₂ (<10⁻¹⁰ atm) the slope of the Ln(conductivity) vs. PO₂ changes to -1/6 and -1/4 which are consistent with charged oxygen vacancies and Ti interstitials, Ti⁺³, respectively [60, 61]. An example defect diagram, shown in figure 2-3, reveals the concentration of specific defects. The ionic compensation regime is distinguished from the electronic compensation regime by a vertical line. As seen, the n-p transition point at 1100°C corresponds to Log(PO₂) of about 0.6 atm.
2.2.2 Theoretical calculations

Theoretically, at a certain T and PO2, the charged point defect formation energies in TiO2 are calculated by combining Density Function Theory (DFT) and thermodynamics. The formation energy of the charged defect is calculated over a range of T and PO2 [47, 63-68]. The oxygen vacancy has a lower formation energy for a large portion of oxygen activity; however, in
extremely reduced region, the titanium interstitial with a lower energy is the dominant defect [47, 63-67].

The defect formation energy can be calculated as a function of Fermi energy, $E_F$, and chemical potential with respect to the valence band energy, $E_V$, by knowing the total energy of a supercell with defect, the total energy of a perfect supercell, the chemical potentials, $\mu_i$, and number of atoms of element $i$, $n_i$, according to Equation 2-7.

$$H_{\text{defect}}(E_F, \mu) = E[\text{defect}] - E[\text{perfect}] + z( E_V + \Delta E_F ) + \sum n_i \mu_i$$

(2-7)

Where $n_i$ can be inserted to, with negative sign, or taken from, with positive sign, supercell to form point defect. In the case rutile TiO$_2$, formation energies of neutral point defects, reported in literatures, are summarized in Table 2-4.

Table 2-4: Comparison of formation energies and transition levels for O vacancy and Ti interstitial, calculated by different methods

<table>
<thead>
<tr>
<th>Method</th>
<th>$V_o$ (eV)</th>
<th>$Ti_i$ (eV)</th>
<th>$V_{Ti}$ (eV)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morgan [69]</td>
<td>0 – poor</td>
<td>0.8</td>
<td>0.26</td>
<td>GGA+U</td>
</tr>
<tr>
<td></td>
<td>0 – rich</td>
<td>4.41</td>
<td>7.5</td>
<td>GGA+U</td>
</tr>
<tr>
<td>Zhu [45]</td>
<td>0 – poor</td>
<td>0.60</td>
<td>-1.29</td>
<td>DFT+U</td>
</tr>
<tr>
<td></td>
<td>0 – rich</td>
<td>5.68</td>
<td>8.90</td>
<td>DFT+U</td>
</tr>
<tr>
<td>Lee [46]</td>
<td>0 – poor</td>
<td>1.9</td>
<td>0.3</td>
<td>Hybrid-DF</td>
</tr>
<tr>
<td>Janotti [64]</td>
<td>0 – poor</td>
<td>1.8</td>
<td></td>
<td>HSE</td>
</tr>
</tbody>
</table>
2.3 Equilibration of point and electronic defects at interfaces

Higher dimensional crystalline defects such as dislocations, grain boundaries and interfaces, can create an electrochemical discontinuity and space-charge zones may be created with concentration profiles of charge carriers. At equilibrium, the electrochemical potential (Eq. 2-8), \( \eta \), for any mobile charge carrier, \( i \), is constant.

\[
\eta_i = \mu_i + z_i e \psi
\]  

(2-8)

The electrochemical potential includes two terms: chemical potential, \( \mu_i = \mu_0 + k_B T \ln(c_i) \), and electrical potential, \( \psi \), where \( z_i, c_i, k_B \) and \( T \) are charge number, carrier concentration, Boltzmann constant and temperature, respectively. The local concentration as a function of position, \( x \), and bulk concentration, \( c_{i\infty} \), is derived from Equation 2-9 (\( \Delta \psi(x) = \psi(x) - \psi_{\infty} \)) [70].

\[
\left( \frac{c_i(x)}{c_{i\infty}} \right)^{1/z_i} = \exp\left( - \frac{e}{k_B T} \Delta \psi(x) \right)
\]  

(2-9)

At one and two dimensional crystalline defects, the standard chemical potential, \( \mu_0 \), may change due to local changes in bonding environments. This discontinuity must be compensated by redistribution of the mobile charge carrier in the space charge zone and local electric potential. In the space-charge region, the electrical potential profile as a function of
local charge density is given by Poission’s equation (Eq. 2-10) where \( \varepsilon \) is the dielectric constant.

\[
\frac{\partial^2}{\partial x^2} \psi(x) = -\frac{Q(x)}{\varepsilon}
\]

\( Q(x) = -\sum_l z_l e c_l(x) \)  

When the local electrical potential, \( \psi(x) \), at interface is higher than the bulk \( \psi(x) > \psi_{bulk} \), the concentrations of all positively charged ionic and electronic defects decrease exponentially from the bulk toward the interface in the space-charge region. For \( \psi(x) < \psi_{bulk} \), the positive defects redistribute toward interface to compensate the electrical potential gradient [45].

Similarly at a metal-semiconductor interface, there may be a discontinuity between the Fermi levels (electron chemical potential) between the two materials. This contact potential, also called built in potential, corresponds to the difference between the work functions of the metal (electrode) and the semiconductor (Section 4.1). At equilibrium, the position of the Fermi energy level within the space charge layer, depletion layer, is determined where the constant electrochemical potential is achieved. Therefore, within the depletion layer (Figure 2-4), the induced electrical potential is a driving force to form the charge profile to keep the electro chemical potential constant. Negative charge builds up at
the metal surface equal to the positive charge in the n-type semiconductor within the depletion region, \( W \) [71].

![Energy-band diagram of interface between metallic electrode and n-type semiconductor.](image)

Figure 2-4: Energy-band diagram of interface between metallic electrode and n-type semiconductor.

2.4 Kinetics of point defects redistribution

2.4.1 Drift and diffusion in electric fields

The 1-D redistribution of point defects under DC voltage and accumulation at the electrode interface were modeled by Waser et al. for perovskites in the 1990 [12, 72]. Under a DC bias,
the temporal ionic redistribution can be solved by the drift-diffusion equation in a time domain [1, 72-75]. The ionic transport behavior across the interface was considered as a variable boundary condition. The defect concentration redistribution is achieved under an applied electric field where there is at least one electrode which blocks or eliminates the ion transport at the interface.

The ionic migration flux is influenced from both drift and diffusion according to Equation 2-11 [76], which can be solved with Poisson’s equation (Eq. 2-12) where \( \psi \) is electrostatic potential, \( n \) is electron charge, \( p \) is hole charge concentration, and \( z \) is the ionic charge \( i \) with concentration \( C_i \). The effects of the electrochemical reaction of TiO\(_2\) and electrode at the interface have been included in modeling the overall electrical behavior of the cell during the degradation process by Jeong [1]. Using proper boundary conditions, the oxygen vacancy distribution can be solved in a time domain by using the drift diffusion equation and Fick’s Second Law.

\[
J = -D \frac{\partial C(x)}{\partial x} + z \mu CE(x) \quad (2-11)
\]

\[
\nabla^2 \psi = \frac{q}{\varepsilon} (n - p + \sum z_i C_i) \quad (2-12)
\]

In TiO\(_2\), the mobile charged point defects that are generated in a reducing atmosphere contribute to the drift-diffusion process under applied electric field. The TiO\(_2\) becomes
oxygen-deficient when annealed at high temperature and low oxygen partial pressure. The deviation from the stoichiometric TiO$_2$ can be calculated by knowing the defect chemistry state of TiO$_{2-x}$ when the equilibrium is achieved (Eq. 2-13).

\[
x = \frac{2([Ti_i^{3+}] + [Ti_i^{4+}] - [V_{Ti}^{4-}]) + [V_{O}^{2+}] + [V_T^{4-}] + [Ti_i^{3+}] + [Ti_i^{4+}] - [V_{Ti}^{4-}])}{1 + [Ti_i^{3+}] + [Ti_i^{4+}] - [V_{Ti}^{4-}]}
\]  

(2-13)

2.4.2 Diffusion mechanisms and structural anisotropy

An overview of the literatures about the diffusivity of the ions in TiO$_2$ indicates that the point defects can be classified in two regimes based on their transport kinetics [61]: (i) fast kinetics (oxygen vacancies and titanium interstitials) and (ii) slow kinetics (titanium vacancies). The chemical diffusion constants were experimentally measured for the transport of fast kinetics and slow kinetics species at 1323K which are $5.4 \times 10^{-9}$ m$^2$/s [61] and $8.9 \times 10^{-14}$ m$^2$/s [77], respectively.

The diffusion coefficients of mobile species are highly anisotropic [63, 78, 79]. In the case of titanium interstitials, the migration barriers have mostly been studied using the ab initio pseudopotential total-energy method [63] and density function theory [80], along perpendicular <110> and <001> crystallographic directions. The titanium interstitials can migrate through an open channel along <001>; however, the migration mechanism along the less open <110> direction is based on kick-out, or interstitialcy, process. Therefore, the diffusion of titanium interstitials along <110> requires construction and destruction of the Ti-
O bonds. Huntington suggested that the open <001> channel is the path with lower migration barrier for titanium interstitials compared to <110> direction [81]. This hypothesis is also supported by transition state theory calculations by He and Sinnott [80]. The open channel in the [001] direction is much easier migration path for titanium interstitials compared to paths along [100] and [110] directions. However, referring to transition-state theory calculations work by Iddir et al., the titanium interstitial has a lower migration energy along <110>, 0.225 eV, than <001>, 0.37 eV, when the interstitialcy process along <110> is considered [63]. In the case of oxygen vacancies, the migration barrier is in general larger and more anisotropic: 0.69 eV along <110> and 1.77 eV along <001>. The energy barrier for migration of oxygen vacancies could not be higher than 1.1 eV along any direction due to the possibility of choosing different paths which are energetically more preferable [63].

Attention is drawn to this fact that between two types of positive charged defects, the titanium interstitials are the higher mobility defects in TiO₂. As shown experimentally by Lee and Yoon [62] two different relaxation times are observed for TiO₂. The two relaxation times are observed when the concentration of oxygen vacancies and titanium interstitials are comparable. When the oxygen activity is pushed to extremely reduced condition ([Ti⁺⁺] ≫ [Vo]), only one relaxation time can be detected. During equilibration with the external oxygen partial pressure at elevated temperature, the experimentally measured diffusivity of oxygen vacancies is about one order of magnitude lower than titanium interstitials. The diffusivities of oxygen vacancy and titanium interstitial at 1000°C and 1100°C are \( D_{Vo} = 1.4 \times 10^{-7} \) and \( D_{Ti} = 1.5 \times 10^{-6} \); \( D_{Vo} = 2.5 \times 10^{-7} \) and \( D_{Ti} = 2.6 \times 10^{-6} \), respectively [62].
The knowledge of transport kinetics for all possible types of defects as a function of temperature is necessary to calculate the electrical and ionic conductivities. Since the mobility term is temperature dependent, at elevated temperature, the ionic conductivity \( \sigma_i \) significantly affects the conductivity. In this case the overall conductivity includes both electronic and ionic components according Equation 2-14. Where \( e \), \( \mu \) and \( N \) are charge, mobility and concentration for electrons (\( n \)) and holes (\( p \)), respectively.

\[
\sigma_T = e\mu_n N_n + e\mu_p N_p + \sigma_i
\]  

(2-14)

2.5 Sub-stoichiometric Ti\(_{n}\)O\(_{2n-1}\) (Magnéli phases)

In rutile TiO\(_2\), the possibility of creating intermediate phases, known as the Magnéli phases [82, 83], Ti\(_{n}\)O\(_{2n-1}\), should also be considered as an important factor to study when the oxygen activity is lower than limit of phase stability of TiO\(_2\) over the defect redistribution process.

The electronic structure of Magnéli phases change the oxygen-titanium ion distance, influenced from ordering the point defects in shear planes. It is reported that most Magnéli phases have an insulator-metallic transition of about 150 K temperature [84, 85].

The resistance switching via formation of conductive filaments in polycrystalline TiO\(_2\) is reported by Choi et al. [9]. An atomic force microscope (AFM) with a conductive probe is utilized to map local conductivity of TiO\(_2\) after electroforming and also after switching back to a high-resistance state by reversing the polarity.
There is a potential interest to address what the nature of the conductive filaments are, where they initiate and how they form to shunt the electrodes. Kwon et al discussed the possibility of phase transformation of amorphous TiO$_2$ to a Magnéli phase, Ti$_4$O$_7$, as an origin of filament formation and consequential resistive switching [15]. Transition to the on-state with low resistance occurs via formation of the metallic Magnéli phase that connects the electrodes. It is reported that reversing the polarity of bias voltage results in migration of point defects away from the interface of electrode that leads to conductive filament contraction via formation of amorphous phase assisted by Joule heating effect.

The electrochemical potential influences the concentration of titanium interstitials and oxygen vacancies are enhanced at the interface of the TiO$_2$ and electrode. While the level of oxygen non-stoichiometry, X, in TiO$_{2-x}$ increases above morphological stability level of TiO$_2$, X=0.001, the phase transformation to intermediate phases creates the Magnéli phases [85, 86]. Based on the level of oxygen sub-stoichiometry, permanent structure Ti$_n$O$_{2n-1}$ is formed, with range of n=2 to 37 in the Magnéli formula [84, 85], to compensate high concentrations of point defects, via condensation into the shear planes (SP) [86-91]. The ordering of point defects into the shear planes decreases the energy of system that is increased by accumulation of point defects, while the relaxation of ionic point defects results in the elimination of the cation-cation repulsion [92, 93]. The formation of shear planes is followed by trapping the electrons that induce a positive charge in the SP. In fact, this positive charge is playing an important role in ordering the shear planes via the electrostatic repulsion [93].
The electronic structure of TiO$_2$ was investigated by Paxton, who showed that the conduction band formed by Ti 3d-states is empty of electrons; however, the filled valence band is influenced by O 2p-states which results in the formation of an indirect band gap of 3eV [94, 95]. The phase transformation from TiO$_2$ to Ti$_n$O$_{2n-1}$ should alter the band structure, where the wide band gap will become much narrower to achieve metallic conduction at room temperature via ordering of the shear planes.

Described by the Verway model [96], when Ti$_4$O$_7$ is cooled down below the insulator-metal transition temperature, the titanium interstitials form a bipolaron ordering of electrons close to the shear planes. Heating Ti$_4$O$_7$ above the critical temperature delocalizes and distributes the electrons.

X-ray characterization verifies that a range of Magnéli phases, Ti$_n$O$_{2n-1}$, with n= 6-9, is formed within a rutile single crystal after annealing at 1200°C and under a reducing atmosphere of 10$^{-20}$ mbar oxygen partial pressure for approximately 10 hours. However, reducing single crystals under 10$^{-6}$-10$^{-12}$ mbar PO$_2$ is not sufficient to form Magnéli phases [7].

3 Metal-Oxide contacts

The leakage current in dielectric or semiconductor materials is controlled by numerous different conduction mechanisms [97]. The electrical conduction at the electrode interface is generally categorized as Ohmic or Schottky (rectifying) based on the work function, electron affinity and the charge carrier density values. Schottky conduction is observed when the
metal (electrode) work function is higher than the electron affinity of the insulator (Eq. 2-14) [71, 98], resulting in formation of a potential barrier that eliminates and controls the electron injection from the electrode to the semiconductor/insulator (Fig 2-5.a). The electrical behavior at this type of interface is also known as rectifying behavior. In contrast, when the metal work function is less than the electron affinity of the dielectric, an Ohmic contact is formed that does not have resistance in front of the electrical conduction (Fig 2-5.b).

Figure 2-5: The lining up of the Fermi energy levels at the metal-insulator (n-type) interface, (a) formation of Schottky contact ($\Phi_M > \Phi_{SC}$), (b) formation of ohmic contact ($\Phi_M < \Phi_{SC}$).

At the interface of the metal/dielectric, the Schottky barrier height is defined by the electron affinity of the dielectric and metallic work function difference (Eq. 2-15) [71, 98].
\[ \Phi_B = S(\Phi_M - \Phi_S) + (\Phi_S - \chi_S) \]  

(2-15)

Here \( \Phi_B, S, \Phi_S, \Phi_M \) and \( \chi_S \) are the Schottky barrier, Schottky barrier pinning factor, the metallic work function, charge neutrality level of dielectric and the electron affinity of dielectric, respectively. Knowing the optical dielectric constant, the Schottky barrier pinning factor is calculated via the empirical formula from Clark (Eq. 2-16) [98].

\[ S = \frac{1}{1 + 0.1(\varepsilon_\infty - 1)^2} \]  

(2-16)

The Schottky barrier shows weak dependence on the Fermi-level pinning when \( S \) converges toward one. However, in the case of strong Fermi level pinning, regardless of electrode work function, the formed Schottky barrier is invariable since the Fermi level is pinned deep in the band gap. Interface Schottky barriers between metals and TiO\(_2\) have not been as rigorously studied as in the perovskites, but it is confirmed by Kim that the work function of electrodes (Pt, Au, and Ag), deposited on TiO\(_2\), influences on the Schottky barrier height formed at the metal/TiO\(_2\) interface [99]. The variation of the defect concentration at the interface of the TiO\(_2\)/electrode has be shown to alter the Schottky barriers in several studies [23, 100].

### 3.1.1 Thermionic emission conduction

Electron injection over the Schottky barrier, formed at the dielectric/metal interface, can occur through thermionic excitation [101]. The electron thermionic emission from the
electrode side into the conduction band of the dielectric is called reverse-bias Schottky conduction. Forward-bias Schottky conduction occurs when the electron injection arises from the dielectric/semiconductor side into the metal. Both reverse and forward Schottky conduction are shown in Figure 2-6.

Figure 2-6: The electron conduction over the Schottky barrier formed at the metal-insulator interface via thermionic emission mechanism, (a) reverse bias conduction, (b) forward bias conduction.

The leakage current density due to the reverse-bias Schottky conduction is shown in Equation 2-17, taking into account the effects of image charge lowering (Eq. 2-18). The forward-bias Schottky controlled current density is shown in Equation 2-19 where $\Phi_B$, $A^*$, $n$, $\varepsilon_s$, $\varphi_{bi}$, $E_m$ and $N_D$ are the barrier height, effective Richardson constant, ideality factor,
dielectric permittivity, built-in potential, maximum electric field at the interface, and carrier concentration at the interface, respectively.

\[
J_R = A^{**}T^2 \exp\left[-\frac{q(\phi_B - \sqrt{qE_m/4\pi\varepsilon_s})}{kT}\right]
\]  

(2-17)

\[
E_m = \sqrt{\frac{2qN_D}{\varepsilon_s} \left(V_R - \phi_B - \frac{kT}{q}\right)}
\]  

(2-18)

\[
J_F = A^{**}T^2 \exp\left(-\frac{q\phi_B}{kT}\right) \left[\exp\left(\frac{qV_F}{nkT}\right) - 1\right]
\]  

(2-19)

3.1.2 Fowler Nordheim tunneling conduction

The temperature independent Fowler-Nordheim tunneling conduction results in a linear \((J/E^2\) vs. \(1/E\)) curve with a negative slope. The conduction mechanism at the interface can be changed from thermionic emission to the field emission (Fowler-Nordheim tunneling) at higher electric fields.

Fowler-Nordheim Tunneling is observed when the electron can tunnel through the Schottky barrier at the dielectric/metal interface [102]. The significant band bending is induced by high bias voltage, applied to the electrode and/or high concentration of charged point defects or doping at the interface, which can lead to the narrowing of the depletion
region that is inversely related to the square root of the donor density in n-type semiconductors. The electron tunneling phenomenon by Fowler-Nordheim conduction is shown in Figure 2-7.

Figure 2-7: The electron conduction though the Schottky barrier formed at the metal-insulator interface via the Fowler-Nordheim tunneling mechanism.

The relation between the current density, electric field and barrier height is obtained from the Fowler-Nordheim tunneling current density equation where $K_1$ and $K_2$ are constants associated with the electron effective mass (Eq. 2-19).

$$J_{FN} = K_1 \frac{E}{\Phi_B} \exp \left( -K_2 \frac{\Phi_B^2}{E} \right)$$  \hspace{1cm} (2-20)
4 Implications of defect redistribution on properties

The time-dependent redistribution of point defects under an applied electric field is often accompanied by leakage current enhancement after a period of time. In addition to the studies by Waser [12], Yang et al [4] showed the degradation in polycrystalline BaTiO$_3$ was affected by the resistance drop in the grain boundaries and grains; however, the decrease in interface resistance played the most significant role [4]. Moreover, the accumulation of the defects at the electrode interface changed the microstructure and microchemistry, as shown by electron microscopy [103, 104] and electron spectroscopy [20]. How the local chemistry near the electrode can change the interface resistance requires an understanding of charge transport process at semiconductor-metal interfaces. The most significant mechanisms will be discussed below.

The lowering of the Schottky barrier potential and narrowing of the barrier width are influenced from the accumulation of oxygen vacancies at the interface during the degradation. The degradation process is affected by the grain boundaries which behave as a barrier against the migration of charged and mobile point defects. Furthermore, the contact resistance associated with the Schottky barrier controls the leakage current [4].

Some of the seminal work studying resistance degradation in oxides as a result of point defect migration was by Waser’s group in the early 1990s. The conductivity changed associated with temperature and voltage stress in doped or un-doped BaTiO$_3$ and SrTiO$_3$ single crystals were studied as a function of electric field, temperature and time [12].
The electrocoloration study on 0.15-mol% Fe-doped SrTiO$_3$ revealed that a doped single crystal with an initial reddish color, transformed to show two distinct regions during degradation. The migration of oxygen vacancies toward the cathode resulted in local variation of the stoichiometry and valence state of the Fe ions. The oxidation of the Fe-doped region formed a dark-red color near the anode (Fe$^{4+}$ ion valence state) while the reduction of Fe ions resulted in a colorless region at the cathode (Fe$^{2+}$ ion valence state). Over the degradation, the reduced and oxidized regions moved toward each other until they were eliminated somewhere between two electrodes. The motion of the color front changed, and as a consequence the leakage current, slowed down after the two regions met within the bulk.

Waser et al. showed on 0.15 mol% Fe-doped SrTiO$_3$ single crystal reversing the polarity of the bias voltage is followed with color change at another electrode (anode during forward biasing) which was colorless at the beginning of reverse biasing step [12].

The point defect redistribution induced by DC voltage was quantitatively modeled for the acceptor-doped and undoped materials. Over the degradation process, the equilibrated system with uniformly distributed point defects started to demix by migration of the charged point defects, i.e. oxygen vacancies in the perovskite-type titanates. The local resistance was influenced by the variation of the local point defect concentration, in which the time evolution of field distribution occurred during the degradation process. Defect transport was modeled considering the continuity, Poisson and mass action equations [72]. The concentration of the generated oxygen vacancies was considered constant in a low-temperature regime ($T < 700K$) because oxygen transport through the solid/gas interface
was slow and approximately negligible, especially when the electrodes blocked ion transfer at the interface [12].

The type of acceptor-dopant strongly altered the mobility of the oxygen vacancy. Higher degradation rates were obtained by adding the acceptors that showed different valence states over the annealing process [12, 72]. In the case of Al-doped titanates, Al ions were substituted with Ti ions, and were not affected by the annealing conditions due to a stable 3 valence state. Donor-doped titanates such as SrTiO$_3$ resisted degradation compared to acceptor-doped titanates due to the low level of oxygen concentration.

X-ray absorption near-edge structure (XANES) had been utilized to probe the oxygen vacancy distribution in Pt/SeTi$_{0.95}$Fe$_{0.05}$O$_3$/Nb:STO [105]. The variation in the valence state of the transition-metal dopant was monitored by XANES via an intensity increase in the pre-edge peak of the Fe K-edge. A homogeneous increase in the concentration of oxygen vacancies was observed at the interface over the electroforming process.

In contrast to rutile TiO$_2$, the field-programmable rectification behavior is observed on the (110) and (100) surfaces but not on the (001) surface [6]. In particular, the rectification behavior is studied along the platinum electrodes deposited on the surface of the rutile TiO$_2$ single crystal. The drift/diffusion of the charged ionic carriers induced by an electric field results in accumulation of point defects at the interface. Ionic carriers amass when the electrode blocks the ion transfer at the interface during degradation. The annihilation of the barrier at the interface on one side causes the reverse bias Schottky resistance eradicates the leakage current when the voltage with the opposite sign of the programing voltage applies to
the device. The device behaves as a rectifier so long as the voltage sign agrees with the programing voltage. An electric field of about 37.5 KV/cm acts as a programming field, and is applied to the electrodes with a 2 µm gap between the electrodes at room temperature. The retention time enhances by increasing the programing voltage and time. As a result, on the (100) surface, the retention time is longest along the <001> crystallographic orientation, and decreases as the programing voltage direction is rotated away from the <001> direction. The reversibility of the rectification mechanism is studied by applying a bias voltage with opposite polarity. By forcing the positive charged ions away from the reduced side, and moving them to the other electrode, the rectification direction is reversed. The degradation process can be accelerated by elevating the temperature through Joule heating.

This was modeled by Jeong et al., in their endeavor to understand the resistance degradation process in Pt/TiO₂/Pt [1]. That enhancement in the defect concentration led to formation of sub-stoichiometric TiO₂, Magnéli phase [83, 106].

The investigation into the nature of the resistance switching and field-programmable rectification behavior in TiO₂ single crystals is limited to three works [6, 7, 18]. In each study, oxygen accumulation under applied electric field is presented as an origin of the Schottky barrier modification and resistance switching (RS) mechanism. Further, the defect redistribution and RS behavior is highly anisotropic and observed only in specific crystallographic orientations.
5 Conductive Filament Formation and resistive switching

Whereas prior discussions have focused on one-dimensional drift-diffusion process, it has been served frequently especially in the resistive memory literatures, that conductive filaments can form during the degradation process. Although the nucleation of these filaments are not well understood, many have argued that microstructural defects, such dislocations, can provide defect diffusion paths and thus nucleate the perturbations to the concentration front.

The resistive switching phenomenon is governed by formation and migration of charged point defects within the dielectric layer. The total process is usually classified in three steps; point defect formation, redox reactions related to the defect distribution variation, and annihilation reaction at one electrode (usually the cathode) to form reduced region also called conductive filament.

As shown in Figure 2-8, the accumulation of the charged defects at one electrode results in the formation of a conductive region that will grow toward the other electrode. Under applied electric fields, the migration of mobile charged defects toward the electrode is followed with redox reaction at the interface. The formed reduced region has higher conductivity compared to the bulk. This region will grow toward the other electrode until it reaches the anode. The conducting filament connecting the electrodes is known as electroforming. When the two electrodes are connected by this conducting channel, a transition from a high resistance state to a low resistance state takes place. When the polarity of bias voltage is reversed, deformation of the channel results from repelling the charged
point defects from the interface, thus annihilating the conductive filament (switching back to the high resistance state). The electroforming process is influenced by the bias polarity [22, 107], dielectric properties [107], cell dimensions [108] and oxygen partial pressure [109, 110]. The random formation and rupture of the conductive filaments is controlled by doping the dielectric [111, 112]. The local redox-reaction near the dopants improves the reversibility of the resistance switching process.

Figure 2-8: shows a basic scheme of resistance switching via formatting of conductive filaments. The SET operation occurs on one polarity (switching from high-resistance to low-resistance states), the RESET operation requires the opposite polarity (switching from low-resistance to high-resistance states).
Electroforming is influenced by the symmetry and asymmetry of the electrodes. In addition, the reactivity, geometry and position of the electrodes alter the switching properties. Non-reactive metals, e.g. Pt, Au, and Ni, with usually high work functions, are utilized to form Schottky contacts at the metal/electrode interface [9, 113]. These metals are widely used in RRAM devices to block ion transport at the interface. Consequently, the filaments nucleate as a result of accumulation of the defects at the interface. When the conductive filaments connect both electrodes, the $R_{\text{off}}/R_{\text{on}}$ ratio drops dramatically due to the annihilation of resistance at the interfaces. In case of TiO$_2$, the high resistance ratio, with excellent switching endurance, is observed when the Pt is used to form the top electrode, compared to Ni, Al and stainless steel [114].

A large number of dielectrics (generally transition metal oxides, such as perovskites) have been investigated for resistive switching applications. Moreover, TiO$_2$ is a potential candidate due to its remarkable properties including a high dielectric constant, ease of non-stoichiometric and sub-stoichiometric material formation, temperature stability, and ability to have both unipolar and bipolar switching [1].

In sub-stoichiometric TiO$_2$, the electron charge density distribution is high enough to form a metallic channel to shunt the lateral electrodes. While the oxygen vacancies are reported as the origin of the conductive filament formation within TiO$_2$ [14, 115, 116]; titanium interstitials can dominate the redistribution process for both thermodynamic and kinetic reasons [117]. They are energetically favorable at low oxygen activities as encountered in the near-cathode region and have higher diffusivity [41, 63, 80].
randomness in filaments formed during the electroforming process can be eliminated by tightly controlling the concentration and redistribution of the point defects within TiO$_2$ [13, 14].
Chapter 3

Experimental procedure

1 Establishing initial defect chemistry

In this study, high-purity single-crystal rutile TiO$_2$ samples, made by Verneuil growth process, were purchased from Shinkosha, Co. with a reported intrinsic dislocation density of $10^5$ to $10^6$ /cm$^2$. Aluminum is reported as the most significant impurity at $\sim$ 50 ppm by weight. After cutting crystals to the desired dimensions ($\sim$ 3 x 3 x 0.5 mm), they were well polished with 1 µm diamond lapping films and annealed under specific oxygen partial pressure (PO$_2$) and temperature conditions to establish the initial defect chemistry state of the material.

PO$_2$ was controlled in a high-temperature tube furnace (Thermolyne 59300) using appropriate mixtures of pure Argon and forming gas (Ar/H$_2$) controlled by mass-flow controllers. The PO$_2$ was monitored by a commercial zirconia-based oxygen gas sensor, purchased from Ceramic Oxide Fabricators.
To achieve the equilibrium condition, the annealing time, $\tau$, is inversely related to diffusion constant, $D$, by $\sqrt{\langle x^2 \rangle} = \sqrt{6D\tau}$, where $x$ is the root-mean-square displacement.

The temperature dependent diffusivity follows the Arrhenius equation $D = D_0 \exp(-\frac{E_a}{k_B T})$.

Considering oxygen vacancies as the dominant diffusing species, with lower diffusivity comparing to the titanium interstitials [63], along with the effect of oxygen activity ($PO_2$) on the activation energy of the diffusion constant [61], 22 hours annealing at 1300°C and 36 hours annealing at 1100°C were needed to reach the equilibrium condition. Figure 3-1 shows the set-up designed for annealing samples at the required conditions.

Figure 3-1: Image of set-up of facilities designed and used to anneal the samples at high temperature under low oxygen partial pressure.
The equilibrated crystals were pulled to a region of the tube held at 150°C in flowing gas. Under these conditions, the heat transfer was limited by the thermal conductivity, geometry of the sample holder (since it was larger than the TiO₂ crystal and therefore took longer to achieve steady state) and gas flow rate (100 sccm). Based on the cooling profile (Figure 3-2), measured from 1100°C to 250°C, the approximate quench rate was about 40°C/s (1100°C-900°C), 7.5°C/s (900°C-700°C), 2°C/s (700°C-400°C) and 0.5°C/s (700°C-250°C).

Figure 3-2: shows the cooling profile of the single crystals after annealing at 1100°C.
2 Degradation of TiO$_2$ single crystals

2.1 Contact deposition

Contacts were applied to the annealed and equilibrated samples by magnetron DC sputtering (Figure 3-3). Tightly controlled parameters were electric power, chamber vacuum level (back pressure), gas flow rate, and target-substrate distance. These parameters determine the deposition rate, allowing for reproducible high quality films with good electrical contact.

Figure 3-3: Direct current (DC) magnetron sputtering system
Contamination during the deposition process was avoided by maintaining a clean substrate and target material. The crystals were cleaned in acetone and isopropanol to remove contaminates from the surfaces. In this work, electrodes were deposited on a pair of opposite lateral surfaces of the crystal. A marker applied a thin layer of ink on the other four sides, which aided in removal of undesired sputtered material after contact deposition.

The reduced TiO$_2$-x single crystals had titanium contacts deposited, as ohmic contacts, to measure the bulk resistivity. To deposit titanium, a power density of 6.11 W/cm$^2$, back pressure below $10^{-5}$ Torr, gas pressure of 10 mTorr (pure Ar), and substrate to target distance of 3.4 cm were used resulting in a deposition rate of 15 nm/min for titanium.

To form Schottky contacts platinum electrodes with a significantly higher work function, compared with the electron affinity of TiO$_2$ were deposited on both sides. The deposition parameters were set to 6.11 W/cm$^2$, 30 mTorr (pure Ar) and 3.4 cm for power, gas pressure and substrate to target distance, respectively, that resulted in a deposition rate of 75 nm/min for Platinum. The deposited contact was annealed at 200°C for 3 hours to form a better connection at the TiO$_2$-x/Pt interface.

2.2 Electrical Characterization

2.2.1 Current-Voltage (I-V) Measurements

Electrical characterization was performed using a high-precision Keithley 617 Electrometer. The station can source voltage and measure current with a high degree of precision. To control the Keithley Electrometer a LabView program was written with two primary
functions. First, the program can sweep through a voltage range and measure the current response. Second, the program can source a static voltage and measure how the current changes over time, which was needed for degradation studies.

During current-voltage measurement, the voltage was stepped in increments of 0.05V and current measurements were made after 10 s to achieve steady state and avoid the effects of polarization currents. To perform I-V characteristic measurements, two probe positioners were used, as shown in Figure 3-4.
2.2.2 Current-Time (I-T-t) Measurements

TiO$_{2-x}$ samples were subjected to an applied DC voltage to study the degradation process. Influenced by the electric field (100-400 V/cm) at 200°C temperature, positively charged ionic carriers, such as titanium interstitials and oxygen vacancies, are expected to migrate with the electric field toward the cathode. The oxygen transport through the solid/gas interface is slow and approximately negligible in a low-temperature regime ($T < 700K$), especially when the electrodes block ion transfer at the interface [12].

A HP-6634B power supply was used to apply the DC voltage. A program was written in LabView to record and monitor the leakage current as a function of time. The degradation process was performed in a box furnace to provide uniform temperature during the experiment. A stage with conductive and adjustable probes was designed to be used at high temperature in the furnace (Figure 3-5).
3 Microstructure and microchemistry characterization

3.1 Scanning/Transmission Electron Microscopy and spectroscopy

The local microstructure and micro chemistry were studied through electron microscopy and electron spectroscopy experiments to acquire insight about the defect transport and contact behavior as a function of the degradation process.
3.1.1 Sample Preparation

In this study, TEM samples are created by mechanical polishing and lift-out technique using a FEI Quanta 3D focused ion beam (FIB). Figure 3-6 shows a slice of TiO$_2$ which was lifted out from the region close to the cathode while making TEM sample by FIB.

![Figure 3-6: Shows TEM sample preparation of TiO$_2$ by FIB.](image)

After finding the region of interest, a 15x2x2 μm Pt bar was deposited to protect that region from ion beam damage while the sample is tilted to 52°. As it is shown in Figure 3-5, the regions beside to the Pt bar were milled by 30 kV, 7 nA Ga ion, down to 8 μm from the surface. At 0° tilt, the 3 nA was used for the U-shape cut to disconnect the region of interest.
from the rest of the sample. The sample was lifted out by using the Omni probe and it was attached to a cupper grid (TEM sample holder). At 52° tilt, the final polishing was performed with 0.3 to 0.1 nA ion beam currents, on both sides by tilting the sample ±1°, until the sample looked bright at 5KV electron beam. The sample was tilted toward the sides ±4° to remove the ion beam damage at 5 kV and 48 pA Ga ion.

3.1.2 TEM/STEM Analysis

High-resolution phase-contrast and Z-contrast scanning transmission electron microscopy (STEM) imaging of the TiO$_2$-x/cathode interface were performed to study the accumulation and clustering of oxygen vacancies and titanium interstitials at the interface.

Microstructural defects were studied using a JEOL transmission electron microscope (JEOL 2010F) equipped with a field emission gun operated at 200 kV. Atomic resolution STEM images were taken by the aberration corrected FEI Titan 80-300 microscope.

3.2 Electron spectroscopy

3.2.1 Electron energy loss spectroscopy (EELS)

Electron energy loss spectroscopy (EELS) was utilized to investigate the nonstoichiometry of TiO$_2$-x in a reduced region formed after the degradation process. EELS and scanning transmission electron microscopy (STEM) were performed in a monochromated FEI G2 Titan operated at 200 kV. The EEL spectra were acquired in STEM mode with a collection angle of 39.1 mrad. The energy resolution of the monochromated-EELS was measured to be
below 0.2 eV, as determined with the full width at half maximum of the zero-loss peak (Figure 3-7). An energy dispersion of 0.1 eV/channel was used to record both Ti-L\textsubscript{2,3} and O-K edges simultaneously. The Ti:O ratio was quantified by integrating the respective edges, after appropriate background subtraction for both Ti-L\textsubscript{2,3} and O-K edges and using Hartree-Slater inelastic scattering cross sections [118].

Figure 3-7: Zero-loss spectrum showing the energy resolution can be achieved as well as 0.12 eV taken by monochromated-EELS/STEM microscope. Acquisition parameters: energy dispersion of 0.01 eV/channel, camera length of 38mm, collection semi angle of 42mrad and exposure time of 0.001s.
3.2.2 Cathodoluminescence (CL) spectroscopy

Cathodoluminescence (CL) spectroscopy was accomplished using a Gatan MonoCL4 with a highly sensitive photo multiplier tube (PMT) (160-930 nm) detector on a Zeiss Evo 50 SEM with a tungsten emitter. The microscope was performed at 20kV and the CL results were acquired at room temperature with 2.5 second dwell time and 2nm step size.
Chapter 4

Electric-Field-Induced Point Defect Redistribution in Single-Crystal TiO$_{2-x}$ and Effects on Electrical Transport

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1 Abstract

The spatial redistribution of non-stoichiometric point defects in rutile TiO$_2$ is studied as a function of voltage and time. Single crystals are equilibrated initially to a well-defined stoichiometry with n-type conductivity and a carrier concentration on the order of 10$^{18}$/cm$^3$. The crystals are subsequently electroded with Pt contacts that exhibit Schottky behavior.
When subjected to an applied voltage of 15 V, a time-dependent increase and saturation in the leakage current is observed, which is associated with an accumulation of point defects and an attendant decrease in stoichiometry at the cathode electrode. This local change in stoichiometry degrades the Schottky barrier, leading to asymmetric electrodes and thus macroscopic rectifying behavior. Cathodoluminescence spectroscopy shows that Ti interstitials dominate the point defect redistribution process. Under larger applied voltages, around 30 V, qualitatively different behavior is observed in which the resistivity increases as a function of time. This behavior is associated with condensation of point defects into a region of extended defects and Magnéli phases near the cathode, sufficient to increase the bulk stoichiometry and resistivity. These experiments demonstrate that a one-dimensional drift-diffusion process, as opposed to filamentary growth, dominates in these experimental conditions and that the Pt-TiO2-Pt system remains closed, with no significant oxygen transport across the Pt-TiO2 interfaces. We believe this is the first observation of a second higher-voltage regime in which the bulk stoichiometry and thus resistivity is increased as large concentrations of defects condense into metallic Magnéli phases in the near-electrode regions.

2 Introduction

The performance of electroceramic devices is largely determined by the thermodynamic and transport behaviors of coupled point and electronic defects in the material. Under direct current (DC) voltage these charged defects can redistribute spatially as a function of time.
This phenomenon has been studied in numerous dielectric materials such as TiO$_2$ [6-8], BaTiO$_3$ [4, 10], and SrTiO$_3$ [11, 12]. Although lattice defect migration can lead such detrimental behavior as leakage current enhancement in capacitor devices [4], it can also be utilized to form novel functional behaviors, such as resistive switching in metal-oxides [1-3].

Typically, electrodes for dielectric materials are chosen such that they lead to interface Schottky barriers that limit charge carrier injection into the dielectric. Seminal work in the 1990s by Waser et al. showed that point defect migration under applied bias in BaTiO$_3$ and SrTiO$_3$ leads to an accumulation of charged point defects at the dielectric-electrode interface, modifying the interface characteristics [12, 72]. The local accumulation of point defects near the interface can modify the Schottky barrier and width of the depletion layers [71] which increases the electron injection. The conduction mechanism itself can be modified in these highly defective regions [119]. Further, the asymmetrical behavior at the anode and cathode can lead to diode-like rectification behavior [4, 6, 8]. This functionality can be utilized for electronic devices such as the cross-bar array type memory devices [23, 120].

Several studies have quantitatively modeled the temporal ionic point defect redistribution under voltage biasing by solving the drift-diffusion equation in a time domain and considering ionic transport behavior across the interface as a boundary condition within the dilute solution approximation [1, 72-75]. If, however, the electrodes block or limit mass transport across the interface, then very high concentrations of point defects may accumulate, well beyond a dilute concentration, and may even push the ion activity outside of the
material’s stability range. Several experimental studies have, in fact, shown condensation of point defects into higher dimensional defects or ordered structures near electrodes as a consequence of DC biasing [7, 91, 103, 121, 122].

The present work focuses on point defect migration in TiO\textsubscript{2}, a material that has attracted intense interest in diverse applications such as capacitors, where its high dielectric constant is influenced from the unique arrangement of the TiO\textsubscript{6}-octahedra, and as memristor/resistive switching memory, with the ability of unipolar [24] or bipolar [1, 23, 123] switching. Regardless of the form of TiO\textsubscript{2} (amorphous, polycrystalline, single crystal), the governing model for resistive memory behavior has been the electroformation of conductive (substoichiometric) filaments that shunt the anode and cathode, leading to a low-resistance state. As the local stoichiometry near the electrodes is modulated with subsequent applied fields, the rectification behavior of the Schottky contacts can be manipulated [23]. Jameson et al. demonstrated Schottky barrier modulation at the electrodes, via local reduction/oxidation of TiO\textsubscript{2}, with electrical measurements on TiO\textsubscript{2} single crystals with surface-patterned Pt electrodes. The field-programmable rectification behavior was observed after voltage biasing at fields of 125-375 kV/cm at room temperature. The behavior was also demonstrated to be reversible by reversing the polarity of the programing voltage [6]. Szot et al. provided a critical review of resistive switching in TiO\textsubscript{2} and emphasized the need for more fundamental research aimed at understanding the mechanisms of defect transport and phase stability in these materials, since prior work on TiO\textsubscript{2} spanned materials with various degrees of crystallinity, purity, etc. They emphasized the significance of the small stoichiometry
range for rutile TiO$_{2-x}$ and the formation of crystallographic shear planes and Magnéli phases to accommodate the substoichiometry resulting from electrochemical reduction at the cathode. The authors presented further work on heavily reduced single-crystal TiO$_2$, annealed under different conditions with concomitant differences in initial stoichiometry. It was demonstrated with surface Pt electrodes, that conductive, substoichiometric filaments were formed as well as crystallographic shear defects and Magnéli phases at the cathode interfaces.

While a substantial body of literature already exists on point defect dynamics in TiO$_2$, there has been significant disconnect between this body of literature and the abundant information known about point defect energetics and mobilities in rutile TiO$_2$ [41, 57, 60, 61]. This work aims to help bridge that gap by providing new and more generalized insight into the mechanisms of point defect electromigration in TiO$_2$. Ultimately, we aim to provide experimental data and guidance for future studies, which could predict quantitatively the time-dependent evolution of point defect redistribution under an applied electric field. We specifically focus on point defect transport behavior in single-crystal rutile TiO$_2$ with well-defined initial-state defect chemistries and electrode geometries that interrogate the bulk (as opposed to surface) defect transport kinetics.

In addition, while prior literature almost exclusively considers the role of oxygen vacancies in the transport process, we also consider the role of titanium interstitials, which are known to dominate the point-defect equilibria at low oxygen activities [41, 57, 60, 61]. Further, in contrast to the many perovskites in which cation interstitials are relatively
immobile [4, 12, 20, 124, 125], both oxygen vacancies and titanium interstitials have significant mobility in rutile TiO$_{2-x}$ [126, 127]. Referring to transition-state theory calculations, the titanium interstitial has a lower migration energy, 0.225 eV along <110> and 0.37 eV along <001> [63], as compared to the oxygen vacancy, 0.69 eV along <110> and 1.77 eV along <001>. As shown experimentally by Lee and Yoon [62] two different relaxation times are observed for TiO$_2$ during equilibrium with the external oxygen partial pressure due to the diffusivity of oxygen vacancies being one order of magnitude lower than titanium interstitials.

In the present work, the local interface microstructure and microchemistry are studied as a function of the degradation process via electron microscopy, diffraction and spectroscopy to gain insight into point defect transport and its role in the contact and electrical transport evolution. We make no a priori assumptions about mechanisms of defect redistribution (i.e. homogenous or filamentary growth) and show that in these well-defined and largely homogeneous materials, a 1-D homogeneous modulation of the interface chemistry dominates under the conditions studied and is sufficient to describe the degradation process. In this mode of degradation we observe two regimes: one in which the electrical transport is dominated by local changes near the electrodes and another in higher-voltage regimes where large concentrations of point defects condense near the electrodes. In these higher-voltage ranges, the bulk stoichiometry is altered to the extent that it begins to dominate the electrical transport.
3 Experimental procedure

High-purity (100)-oriented rutile TiO₂ single crystals, made by the Verneuil growth process, were purchased from Shinkosha Company (Japan). The most significant impurity was reported to be Al at ~ 50 ppm by weight. The crystals, well-polished with 1 µm diamond paper, were annealed under specific oxygen partial pressure (PO₂) and temperature conditions to establish the initial defect chemistry state of the material, taking into account the known equilibration kinetics in TiO₂ [41, 57, 60, 61].

Specifically, a series of single-crystal rutile samples were annealed and equilibrated at an oxygen partial pressure (PO₂) of 10⁻⁴ atm at 1100°C for 36 hr. In this temperature range and reducing atmosphere (1050-1350°C and PO₂=10⁻²-10⁻⁴ atm), TiO₂ is an n-type semiconductor with the ln(conductivity) vs. PO₂ having a -1/4 slope, consistent with fully charged oxygen vacancies as the dominant point defects which are compensated by titanium vacancies [57, 60, 61]. The PO₂ was controlled in a high-temperature tube furnace using an Argon and Argon/H₂ forming gas and monitored by a commercial zirconia-based oxygen gas sensor. After equilibration, the samples were quenched to T < 300°C in the flowing reducing atmosphere to establish the initial defect chemistry state. The approximate quench rate was measured to be ~40°C/s (1100°C-900°C), 7.5°C/s (900°C-700°C), 2°C/s (700°C-400°C) and 0.5°C/s (700°C-250°C). While the oxygen vacancies and titanium interstitials are mobile in TiO₂, the titanium vacancies are relatively immobile [60, 61] and are not expected to participate in the subsequent lower-temperature, field-induced redistribution.
Pairs of electrodes were deposited on opposite lateral (010) surfaces (~3 mm x 0.5 mm) by magnetron DC sputtering to study transport along the [010] direction. A power density of 6.11 W/cm², a gas pressure of 30 mTorr (pure Ar), and a substrate to target distance of 3.4 cm, were used in the deposition process, which resulted in a deposition rate of 75 nm/min for Platinum. The deposited contacts, which covered the two lateral surfaces, were annealed at 200 °C for 3 hours to establish reproducible contacts at the TiO₂ₓ/Pt interface [128]. Since the work function of Pt (5.1-5.3 eV [99, 129]) is larger than the electron affinity for rutile TiO₂ (~4.0 - 4.8 eV) [99, 130, 131], a Schottky barrier is expected to form at the interface.

The defect migration studies were performed at 200 °C by applying a DC voltage using a HP-6634B power supply with 15-70 V, corresponding to average electric fields ranging from 100-500 V/cm. Throughout various points in the degradation process, the I-V behavior was measured at room temperature over a voltage range of ±8 V by a high-precision Keithley 617 electrometer. The voltage was stepped in increments of 0.05V and current measurements were made after 10 s to achieve steady state and avoid the effects of polarization currents.

Local microstructure and microchemistry in the near-electrode regions were studied by electron microscopy and spectroscopy. Cathodoluminescence (CL) spectroscopy was accomplished using a Gatan MonoCL4 with a highly sensitive photo multiplier tube (PMT) (160-930 nm) detector on a Zeiss Evo 50 SEM with a tungsten emitter. Site-selective TEM samples were prepared by focused ion beam (FIB) from the TiO₂ₓ/Pt interfaces before and
after the degradation studies. Microstructural defects, formed after the degradation process, were studied using a JEOL transmission electron microscope equipped with a field emission gun (JEOL 2010F) operated at 200 kV. Electron energy loss spectroscopy (EELS) and scanning transmission electron microscopy (STEM) were performed in a monochromated FEI G2 Titan operated at 200 kV. The EEL spectra were acquired in STEM mode with a collection angle of 39.1 mrad. The energy resolution of the EELS was measured to be about 0.2 eV, as determined with the full width at half maximum of the zero-loss peak. A energy dispersion of 0.1 eV/channel was used to record both Ti-L$_{2,3}$ and O-K edges simultaneously. The Ti:O ratio was quantified by integrating the respective edges, after appropriate background subtraction for both Ti-L$_{2,3}$ and O-K edges and using Hartree-Slater inelastic scattering cross sections.

4 Results

4.1 Initial defect chemistry state and electrode boundary conditions

Figure 4-1 shows a defect equilibrium diagram of TiO$_2$, calculated from published equilibrium constants \cite{41, 57}, considering the Al impurity level ([Al]$' = 1.47 \times 10^{-6}$ per site) and the charge neutrality condition (Appendix). The diagram includes the concentration of charged point defects and electronic carriers over a wide range of oxygen activities ($10^{-20} - 10^2$ PO$_2$). In the reduced region, three regimes are identified as a function of oxygen partial pressure: (i) the reduced regime, which is dominated by oxygen vacancies and titanium vacancies compensation ($[V_\text{O}] = 2[V_\text{Ti}]$), but where the electron
carrier concentration is governed by Ti interstitials, (ii) the strongly reduced regime in which doubly ionized oxygen vacancies dominate with an associated electron carrier concentration exponent equal to \(-1/6\) \((2[V_{O}^{2-}] = n)\), and (iii) the extremely reduced regime in which trivalent titanium interstitials are the dominant point defects with the \(PO_{2}\)- dependent electronic carrier concentration exponent equal to \(-1/4\) \((3[Ti^{3+}] = n)\).

Figure 4-1: Defect diagram for single crystal TiO\(_2\) at 1100 °C, where the concentration of the impurity, Al, is \(1.47 \times 10^{-6}\) /site.
The defect equilibria expected for annealing conditions of $10^{-4}$ PO$_2$ and 1100 °C are denoted by the vertical dashed line and correspond to: $[\text{V}_0] = 4.58 \times 10^{-3} \text{ (per site)}$, $[\text{V}''''_{\text{Ti}}] = 2.29 \times 10^{-3} \text{ (per site)}$, $[\text{Ti}^{4+}] = 6.36 \times 10^{-7} \text{ (per site)}$, $[\text{Ti}^{-}] = 1.37 \times 10^{-5} \text{ (per site)}$, $n = 3.73 \times 10^{-5} \text{ (per site)}$ or $1.79 \times 10^{18} \text{ cm}^{-3}$ and $p = 4.46 \times 10^{-7} \text{ (per site)}$. Based on the electron carrier concentration, the bulk electrical resistivity, $\rho_B$, is calculated to be 52 $\Omega \cdot \text{cm}$, considering an electron mobility ($\mu_e$) of $6.7 \times 10^{-2} \text{ cm}^2 / \text{V} \cdot \text{s}$ [41].

To corroborate the expected defect chemistry state, the bulk resistivities of equilibrated crystals were measured using Ti electrodes, which form ohmic contacts to TiO$_2$. Figure 4-2a (dashed red line) presents the resulting I–V characteristics measured at room temperature. The bulk resistivity is measured to be 60.6 $\Omega \cdot \text{cm}$, which is within 16.5% of the expected value based on Fig. 4-1.

For the remainder of the studies, approximately 300 nm thick, symmetrical Pt contacts were used, as shown in the bright-field TEM image in Figure 4-2b. The I-V curve of Pt/TiO$_{2-x}$/Pt (solid curve in Fig. 4-2a) shows an initial exponential behavior, indicative of reverse-biased Schottky barriers at the TiO$_{2-x}$/Pt interfaces.

The I-V behavior of the Pt/TiO$_{2-x}$/Pt cell was modeled by an equivalent circuit consisting of two Schottky barriers in series with the bulk (ohmic) resistance, assuming thermionic emission over the interface barriers [71]. One of the Schottky interfaces is forward biased (Eq. 4-1), while the other is reverse biased (Eq. 4-2) and modeled by the Schottky equation taking into account the effects of image charge lowering (Eq. 4-3).
\[ J_F = A^{**}T^2 \exp \left(- \frac{q\phi_{Bn}}{kT} \right) [\exp \left( \frac{qV_F}{nkT} \right) - 1] \]  

\[ J_R = A^{**}T^2 \exp \left[- \frac{q(\phi_{Bn} - \sqrt{\frac{qE_m}{4\pi\varepsilon_s}})}{kT} \right] \]  

\[ E_m = \frac{2qN_D}{\varepsilon_s} \left( V_R - \varphi_{bi} - \frac{kT}{q} \right) \]  

\( \phi_{Bn}, A^{**}, n, \varepsilon_s, \varphi_{bi}, E_m, \) and \( N_D \) are the barrier height, effective Richardson constant, ideality factor, dielectric permittivity, built-in potential, maximum electric field at the interface, and carrier concentration at the interface, respectively. The model was fitted to the experimental I-V data by setting the parameters to independently measured or literature values (i.e. measured bulk resistivity = 60.6 \( \Omega \cdot \text{cm} \), \( A^{**} = 1.2 \times 10^6 \, (A m^{-2} K^{-2}) \) [132], \( \varepsilon_s = 7.5 \) [33], and \( n = 1 \)). The fitted values for the barrier height, built-in potential and carrier concentration at the reversed-biased electrode were 0.78 eV, 0.5 eV, and \( 1.13 \times 10^{19} \, \text{cm}^{-3} \), respectively. The dashed blue line in Figure 4-2a is the fitted curve with an R^2 value of 0.9984 and is almost indistinguishable from the experimental curve (solid black line).

In the lower voltage range, the reverse-biased electrode limits the conduction through the TiO₂, and the fitted value of the Schottky barrier height is reasonable within the reported ranges for the electron affinity of TiO₂ and work function of Pt. The total resistivity
converges to the bulk resistivity around 20 V/cm as evidenced by the converging slope of the I-V curve (solid curve in Fig. 4-2a) to the bulk linear resistivity (dashed red line in Fig. 4-2a). It should be noted that since both the bulk and reversed-biased electrodes significantly affect the I-V response, it was necessary to fit the experimental data to an equivalent circuit model with these two elements to extract the interface characteristics. The contributions of the forward bias electrode are insignificant for these samples.
Figure 4-2: (a) Conductivity of TiO$_2$ single crystal, annealed at 1100°C for 36 h and $10^{-4}$ PO$_2$, with ohmic contacts (Ti/TiO$_{2-x}$/Ti) is compared to the Pt deposited electrodes (Pt/TiO$_{2-x}$/Pt) with Schottky barriers formed at the interfaces. (b) TEM image of single crystal TiO$_2$ after Pt contact deposition.
4.2 Low electric-field degradation regime

The Pt/TiO$_{2-x}$/Pt sample was then subjected to DC field degradation studies at 200°C. Figure 4-3a shows the leakage current gradually increasing during the degradation process at 15V bias voltage (75V/cm) until it reaches a saturation of 1.3 A/cm$^2$ after several hours. An optical image of the negative terminal (Fig. 4-3b) shows that the TiO$_{2-x}$ near the cathode interface becomes a dark blue color over a length scale of approximately 120 µm, indicative of an increased concentration of Ti$^{3+}$ in that region [133]. In contrast, Figure 4-3c shows an optical image of the TiO$_{2-x}$/anode interface, where the TiO$_{2-x}$ remains colorless and transparent. The current-voltage response of the degraded sample in Figure 4-3d displays a diode-like rectification behavior, with nearly ohmic behavior in the positive bias direction when the cathode serves as the reverse-biased Schottky barrier. The bulk resistivity remains constant at 60.6 Ω.cm. [134]
Figure 4-3: (a) Conductivity of TiO$_{2-x}$ as a function of time for 5 V, 10 V and 15 V biasing. (b) An optical image of Pt-TiO$_{2-x}$ cathode region after 15 V degradation. (c) An optical image Pt-TiO$_{2-x}$ anode region after 15 V degradation. (d) Current-voltage (I-V) measurement before and after 15 V forward degradation.
Although the sample in the degraded state had an inhomogeneous distribution of point defects, we still attempted to model the I-V data in Figure 4-3d to the three-element equivalent circuit model. The model was fitted to the positive part of the I-V curve with the barrier height for the un-degraded sample, 0.78 eV, used as the forward-biased electrode (anode during degradation). The parameters for the reverse-bias electrode (cathode during degradation) were refined, resulting in a fitted barrier height of 0.75 eV, a carrier concentration of $9.41 \times 10^{19} \text{ cm}^{-3}$, a built-in potential of 0.1 eV, and a $R^2$ fit value of 0.9999. The most significant difference in the contact characteristics from the un-degraded samples is found in the built-in potential term, which may be associated with the accumulation of positively charged point defects (titanium interstitials and oxygen vacancies) in that region, compensated by electrons that raise the local Fermi level. It should be mentioned that this interpretation is considered only speculative at this point, as the interface barrier only affects a small portion of the total I-V behavior and the fit to the linear part of the curve dominates the $R^2$.

In principal, we should be able to use the fitted values from the positive part of the I-V curve and reverse the polarity on the equivalent circuit model to predict the I-V response on the negative part of the I-V curve. This approach does not, however, adequately reproduce the current response, achieving an $R^2$ value of only 0.6887. While the nearly ohmic contact, now in the forward biased polarity, accounts for some of the increased current density in this polarity, it does not account for all.
To investigate changes in the local microchemistry, site-selective TEM samples were made via FIB lift-out from the TiO$_{2-x}$/cathode interface region after the 1$^{\text{st}}$ step forward-degradation process. The Ti valence state and oxygen stoichiometry as a function of position from the cathode were measured using monochromated EELS mapping. Figure 4-4a shows a set of EEL spectra acquired from the interface to 200 nm from the interface. The onset of the O K edge (532 eV) was used to calibrate the energy position of the spectra. Figure 4-4b presents the quantified stoichiometry of TiO$_{2-x}$ as a function of position from the interface toward the bulk. The stoichiometry reaches as low as TiO$_{1.67}$, which is far outside the stability region of rutile and should correspond to a Magnéli phase of Ti$_3$O$_5$ [135, 136]. The phase transformation to the Magnéli phase has not been detected in these regions by TEM or electron diffraction, which may indicate a nucleation barrier to the phase formation. However, the extended defects formation, i.e. dislocations, is observed at the interface.
Figure 4-4: (a) EEL spectra of single-crystal TiO$_2$ after 15 V degradation from a region adjacent to the cathode. (b) shows the oxygen content and chemical shift of the Ti L$_{2,3}$ edge after degradation as a function of distance from the interface.
Also apparent in the EEL spectra of figure 4-4a is a significant change in the energy onset and fine structure of the Ti-L$_{2,3}$ edges near the interface, as compared to 200 nm from the interface. As shown in figure 4-4b, a 0.7 eV chemical shift of Ti-L$_{2,3}$ edge toward lower energy is observed near the interface. This is consistent with a lowering of the Ti oxidation state, concomitant with the change in local stoichiometry [137, 138].

While EELS is useful for measuring local stoichiometry, it does not provide information regarding the type of point defects that are responsible for the substoichiometry, and EELS is not sensitive to subtle changes in stoichiometry that can lead to quite large changes in carrier concentrations. Cathodoluminescence (CL) spectroscopy is a complementary technique to investigate energy levels related to the point defects and has been used to study defect states in n-type TiO$_2$ single crystals [38]. The rutile TiO$_2$ CL spectrum, exhibits a broad peak around 410 nm wavelength, ~3 eV, which corresponds to the TiO$_2$ band gap [139]. The energy level of titanium interstitials (Ti$^{i-}$) is reported to be about 1.53 eV above the valence band and has an associated emission peak in the infrared region. The energy position of fully ionized oxygen vacancies is around 2.23 - 2.83 eV above the valence band where the associated emission peak lies within the tail of the band-gap emission [38, 40].

Figure 4-5 presents the cathodoluminescence (CL) spectra taken from various regions in the TiO$_{2-x}$ crystal after the first-step forward-degradation process: adjacent to the cathode (solid black line), from the center of the sample (red dotted line) and adjacent to the anode (blue dashed line). The inset shows a CL spectrum from an as-received rutile single crystal,
in which the peak intensity at 1.6 eV corresponds to Ti interstitials and is small relative to the intensity in the annealed sample (dashed red line in main figure). The spectra from the anode and sample center after degradation are almost identical, while a significant increase in the peak intensity at ~1.6 eV is observed in the cathode region. Note the spatial resolution of the CL spectra is ~ 1 µm based on the interaction volume of the electron beam with the sample, much larger that the region probed by the EELS measurements. The CL spectra thus probe the broader darkened regions evident in Figure 4-3b. These data suggest that $Ti_i^{2-}$ dominates the defect chemistry in the near-cathode region, even though oxygen vacancies were the dominant defect in the as-equilibrated state. This finding is consistent with the facts that Ti interstitials are more mobile than oxygen vacancies in the rutile lattice [62] and that Ti interstitials become the preferred substoichiometric defects at low oxygen activities (Fig. 4-1).
Figure 4-5: (a) Cathodoluminescence spectra of a degraded single-crystal TiO$_2$ sample. Black curve is taken near the TiO$_{2-x}$/cathode interface. Red and blue curves are from the bulk and TiO$_{2-x}$/anode interface regions, respectively. (b) CL spectrum of as-received rutile TiO$_2$ single crystal.
To assess the reversibility of the defect migration in the low electric field regime, another crystal was prepared identically and studied in a forward and subsequent reverse degradation cycle. At 200°C, the leakage currents are monitored at 15V bias voltage as a function of time for both forward and reverse biasing, are shown in figure 4-6a. After approximately 250 min, during the reverse polarity the current density (dashed line in blue) saturates to 0.6 A/cm², which is about the same value to that is observed in the forward-bias direction (in black). The forward biased I-V characteristics (Fig. 4-6b) are very similar in comparison to the data presented in Fig. 4-3. When subjected to reverse biasing (dashed line in blue), the electrode behavior is nearly inverted with the original cathode (as defined during forward degradation) approaching, but not fully converging to, its original I-V behavior (in black), suggesting that the stoichiometry changes in the near-cathode region are nearly reversible.
Figure 4-6: (a) Conductivity of TiO$_{2-x}$ over forward biasing and reverse biasing at 15 V. (b) I-V characteristics before degradation, after 15 V forward biasing and after 15 V reverse biasing.
4.3 Moderate electric-field regime

At higher levels of applied bias, qualitatively different behavior is observed and will therefore be discussed separately. A different set of thermally equilibrated samples were biased at higher voltage levels, 35-60 V (175-300 V/cm electric field). After similar increases in leakage current at low fields, the samples then exhibit a *decrease* in the leakage current as a function of time at higher fields (Fig. 4-7a). Figure 4-7b compares the I-V curves of the as-annealed sample after the 2\textsuperscript{nd} step (60 V) forward degradation. At high electric fields, where the total resistance is dominated by contributions from the bulk resistivity, we find the field-degraded sample to be much more resistive, which is unexpected. Fitting the I-V curve on the positive voltage side yields a barrier height of 0.74 eV with negligible built-in potential, bulk resistivity of 203.01 Ω.cm, and an $R^2$ value of 0.9997.
Figure 4-7: (a) Conductivity of TiO$_{2-x}$ as a function of time up to 60 V biasing. (b) I-V characteristics before degradation with after 60 V forward biasing.
To understand the origins of this qualitatively different behavior, we analyzed the microstructure and microchemistry of the TiO$_{2-x}$/cathode region. The TEM image in figure 4-8a shows that microstructural defects are formed near the interface, as a result of clustered point defects. Figure 4-8b shows an electron diffraction pattern from the area, which exhibits superlattice reflections associated with 3d$_{011}$ periodicity. This stacking sequence is seen in the STEM image, figure 4-8c, and is associated with point defect ordering into ordered crystallographic shear planes, or Magnéli phases [15, 56, 136]. A model of the Ti$_3$O$_5$ Magnéli phase associated with the 3d$_{011}$ sequence is inset in Fig. 4-8d. Magnéli phase formation in severely degraded TiO$_2$ has been reported by Kwon et al. and investigated by using the HRTEM and electron diffraction [15]. The Magnéli phases are formed in extremely reduced TiO$_{2-x}$ to accommodate the large concentrations of point defects. Important to this study is the fact that the Magnéli phases exhibit a metal-insulator transition and most are metallic at room temperature, including Ti$_3$O$_5$ [15, 135].
Figure 4-8: (a) TEM image revealing microstructural defects induced from clustering of positively charged point defects near the cathode. (b) Diffraction patterns showing long range ordering of point defects near the cathode with a periodicity of $3d_{011}$. (c) STEM images showing corresponding crystallographic shear planes corresponding to Magnéli phases (d) at the electrode.
We can rationalize the decrease in the leakage current (Fig. 4-7a) in terms of the point defect condensation into Magnéli phases near the cathode, which leaves the bulk crystal with lower defect concentrations and thus higher bulk resistivity. The voltage drop across the metallic Magnéli phase is negligible and in effect serves to extend the contact. As the bulk resistivity increases, – an almost three-fold increase is measured experimentally– the bulk starts to dominate the I-V behavior.

Figure 4-9 shows a schematic illustration of defect redistribution over the degradation process. Using a simple mass-balance calculation, the following analysis helps validate our hypothesis that the bulk defect concentrations are lowered by the defect condensation process near the cathode. First, the electron concentration and substoichiometry in the bulk necessary to explain the \(203.01 \, \Omega \cdot \text{cm}\) bulk resistivity are \(n = 1.1 \times 10^{18} \, (\text{cm}^{-3})\) and \(\text{TiO}_{1.9998}\), respectively. Then, we consider the oxygen vacancy concentration needed to form \(\text{Ti}_3\text{O}_5\) to be \(5.8 \times 10^{21} \, \text{cm}^{-3}\), while the initial concentration of the oxygen vacancies before the degradation process was \(7.8 \times 10^{17} \, \text{cm}^{-3}\). Assuming no significant oxygen transfer at the electrodes or solid/gas interface, a simple mass balance would predict a thickness of the highly conductive Magnéli phase to be about 200nm at the cathode interface, which is in excellent agreement with the thickness of the extended defect phase in Fig. 4-8a. Not only does this explain the origins of the observed increase in leakage current in the moderate field degradation regime, but it also points to the fact that the dense Pt electrodes are impermeable to oxygen transfer across the interface.
Figure 4-9: A schematic of defect redistribution over the high-field degradation process. The red dotted line corresponds to initial defect concentration and the blue solid line to the spatial distribution after 60 V biasing. The accumulation of defects near the cathode region depletes the bulk concentration of defects.

The final experiment tested the reversibility of the defect migration in this moderate-field regimen by applying an equivalent bias (350 V/cm) to the sample but in the reverse polarity. Figure 4-10a shows the leakage current as a function of time, monitored over the reverse-bias degradation at 200°C. As observed in the forward-bias degradation, the leakage current significantly decreases at 70 V. Figure 4-10b compares the corresponding I–V curves of the sample before degradation, after the 2nd step forward bias and after reverse bias, where we
see that the bulk resistivity continues to increase. After reverse degradation, TEM analysis of both electrodes (not shown) revealed extended defects at both electrodes. Thus under the conditions studied, the extended defects at the original cathode are metastable and do not convert back to rutile TiO$_{2-x}$, while extended defects form at the opposite electrode, analogous to their formation in the forward-bias experiment. The result of this defect condensation process is that the bulk defect concentration continues to drop, driving up the bulk resistivity.
Figure 4-10: (a) Conductivity of TiO$_2$-x as a function of time up to 70 V after reversing the polarity with respect to that shown in Fig. 7. (b) I-V characteristics before degradation, after 60 V forward biasing and after 70 V reverse biasing.
5 Conclusions

At low electric-field degradation, there is clear evidence for the accumulation of substoichiometric point defects at the cathode electrode in single-crystal TiO$_2$. The defect redistribution is largely homogeneous (a 1-D drift-diffusion mechanism) with no evidence for sub-stoichiometric filament formation. While oxygen vacancies are widely implicated as the important point defect in the kinetics of this process, this work points to the significance of titanium interstitials, even when they are a minority defect in the virgin sample. Titanium interstitials dominate the redistribution process for both thermodynamic and kinetic reasons: they are energetically favorable at low oxygen activities as encountered in the near-cathode region and have higher diffusivity [62, 63]. Even at relatively low applied voltages (15 kV), the stoichiometry within 100 nm of the cathode region is well below the stability of TiO$_2$, as measured by EELS. This is indicative of Magnéli phase formation, however there appears to be a nucleation barrier to their formation, which was not overcome in low-field studies. The accumulation of defects near the cathode results in significantly altered Schottky barrier characteristics via the built-in potential and macroscopic rectification behavior.

At higher applied voltages (~50 V) we observe qualitatively different temporal behavior of the leakage current. In this regime, the high-field current is found to decrease with time. As a result of the severe degradation, microstructural defects are induced by the condensation of large concentrations of point defects to the extent that the bulk stoichiometry is significantly altered, making it more stoichiometric and thus more resistive. Interpretation
of the I-V behavior via simple mass-balance calculations explains the observed behavior and shows dense Pt electrodes block ion transfer, leading to a closed system.

Finally, reverse degradation shows that the Magnéli phase formation near the cathode is not reversible at 200°C for the times and fields studied, indicative of a nucleation barrier associated with the phase transition.

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Chapter 5

Investigation of Defect Transport Along <001> in Single Crystal Rutile TiO$_{2-x}$

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1 Introduction

To study point defect redistribution in metal oxides, rutile single crystal TiO$_2$ has been used as a model system [13-16]. The initial defect chemistry state can be defined by annealing the crystals under reducing atmosphere at elevated temperature. Charged point defects with lower migration barriers, i.e. titanium interstitials and oxygen vacancies, can migrate in response to an electric field [61]; however, titanium vacancies with significantly high diffusivity are relatively immobile under DC bias [15, 17].
An overview of the literature on the diffusivity of the lattice defects in TiO$_2$ indicates that the mobilities of titanium interstitials and oxygen vacancies are highly anisotropic [63, 78, 79]. In the case of titanium interstitials, the crystallographic direction with the lowest migration barrier is still a matter of debate.

The titanium interstitials are located at the octahedral sites in a rutile TiO$_2$ unit cell. The migration of titanium interstitials through an open channel along <001> is suggested by Huntington [81] as a path with highest diffusivity as compared to other crystallographic orientations; this is also supported by Sinnott who calculated the formation energies of titanium interstitials via density functional theory [80]. More recent studies, however, by Iddir et al. [63], showed by DFT transition-state theory calculations that interstitial diffusion along the less open <110> direction occurs by an interstitialcy mechanism resulting in a lower migration energy of 0.225 eV in comparison to 0.37 eV along <001>. The calculations, however, were conducted on Ti$^{4+}$ ions only and the values would be expected to be higher for Ti$^{3+}$ (but less than 0.7 eV) along <001> [63]. In the case of oxygen vacancies, with overall slower transport kinetics [62], the migration barriers are 0.69 eV along <110> and 1.77 eV along <001> for the fully charged (2+) species [63].

The computational studies, indicating a significant difference in the diffusion kinetics between titanium interstitials and oxygen vacancies, have been realized experimentally by Lee and Yoon [62] who observed two different relaxation times during the equilibration of single crystal TiO$_2$. The two distinct relaxation times are observed when the concentration of oxygen vacancies and titanium interstitials are comparable. When the oxygen activity was
pushed to extremely reduced conditions ($[\text{Ti}^{\cdot\cdot}] \gg [\text{V}_0]$), only one relaxation time could be detected. During equilibration with the external oxygen partial pressure at elevated temperature, the experimentally measured diffusivity of oxygen vacancies is about one order of magnitude lower than titanium interstitials. The diffusivities of oxygen vacancy and titanium interstitial at 1000°C and 1100°C are $D_{\text{Vo}} = 1.4 \times 10^{-7} \text{cm}^2/\text{s}$ and $D_{\text{Ti}_i} = 1.5 \times 10^{-6} \text{cm}^2/\text{s}$; $D_{\text{Vo}} = 2.5 \times 10^{-7} \text{cm}^2/\text{s}$ and $D_{\text{Ti}_i} = 2.6 \times 10^{-6} \text{cm}^2/\text{s}$, respectively [62].

Field-induced interface modulation and rectification behavior in single crystal TiO$_2$ was observed by Jameson et al. after applying electric field of 125-375 kV/cm across Pt surface electrodes at room temperature. The reversibility of the field-programmable rectification behavior is examined by reversing polarity of bias voltage. The results indicate that the rectification behavior is reversible where the positive charge defects redistribute toward the cathode (anode during forward biasing) [6]. However, {001} surface-oriented crystals did not show rectification behavior along any in-plane orientation.

In this chapter, we explore anisotropy effect by combining electrical characterization measurements with electron microscopy analyses on defect migration along the <001> crystallographic orientation as a function of electric field and time. In addition, we introduce real-time optical imaging analysis to study real-time the redistribution process.

The Ti valence state and oxygen stoichiometry near the cathode are determined using monochromated electron energy loss spectroscopy (EELS). Using diffraction contrast and high-resolution phase-contrast TEM imaging, the microstructure of reduced regions are investigated. The reversibility of the diode-like rectification behavior of Pt/TiO$_2$/Pt sample is
examined by reversing the polarity of the bias voltage. Moreover, monitoring the drift and diffusion of positively charged defects real-time under DC bias clearly shows that two regions with different diffusivities migrate toward the cathode.

2 Experimental

A single-crystal rutile sample was prepared by annealing at $8.7 \times 10^{-5}$ PO$_2$ at 1100 °C for 36 hr. The samples were quenched to $T < 200$ °C after the equilibrium is achieved. The concentration of the charged point defects and charge carriers are expected to be: $[V_{O}] = 4.58 \times 10^{-3}$ (per site), $[V_{Ti}'''] = 2.29 \times 10^{-3}$ (per site), $[Ti_i^-] = 6.59 \times 10^{-7}$ (per site), $[Ti_{i''}^-] = 1.37 \times 10^{-5}$ (per site), $n = 3.86 \times 10^{-5}$ (per site) or $1.84 \times 10^{18}$ cm$^{-3}$ and $p = 4.31 \times 10^{-7}$ (per site). The bulk electrical resistivity, $\rho_B$, is calculated to be 50.63 $\Omega \cdot cm$ based on the electron carrier concentration.

As an ohmic contact, Ti electrodes are deposited on the reduced TiO$_2$. The bulk resistivity is measured to be 36 $\Omega \cdot cm$, which is within the same order of magnitude of the predicted value. Figure 5-1 presents the resulting I-V characteristics of Ti/TiO$_2$/Ti (dashed red line) and the exponential I-V curve of Pt/TiO$_2$/Pt (solid black line), indicative of Schottky barriers formed on both sides.
Figure 5-1: Conductivity of TiO$_2$ single crystal, annealed at 1100°C for 36 h and 8.7x10$^{-5}$ p(O$_2$), with ohmic contacts (Ti/TiO$_{2-x}$/Ti) is compared to the Pt deposited electrodes (Pt/TiO$_{2-x}$/Pt) with Schottky barriers, formed at the interfaces.

Along the <001> crystallographic direction, a DC field is applied to the Pt/TiO$_2$/Pt to study the possible anisotropy in defect transport and degradation process as compared to the <010> direction (Chapter 4). The leakage current gradually increases at 15V bias voltage (56 V/cm) until it reaches a saturation of 1.8 A/cm$^2$ (Fig. 5-2a). An increased concentration of point defects at the negative terminal results in formation of a dark blue region, evidenced in the optical image (Fig. 5-2b). An optical image from the anode side shows that the TiO$_{2-x}$
remains colorless (Fig. 5-2c). After the forward-bias degradation at low voltage, the measured current-voltage characteristic displays a diode-like rectification behavior, shown in Figure 5-2d.
Figure 5-2: (a) Conductivity of TiO$_{2-x}$ over the 1$^{st}$ step forward-bias degradation. (b) An optical image of TiO$_{2-x}$ after formation of reduced region at the cathode. (c) An optical image of TiO$_{2-x}$/anode interface. (d) Current-voltage (I-V) measurement before and after 1$^{st}$ step forward degradation.
The time that it takes the system to reach an equilibrium conductivity at 15 applied volts is about three times faster along <001> in comparison to the <010> direction (Figure 4-3a). This observed behavior is kinetically consistent with the literatures [80, 81] that suggest the c-axis as an easy path for titanium interstitials to migrate with lower migration barrier.

To assess the reversibility of the defect migration in the low electric field regime, after the 1st step forward biasing, the same crystal is subjected to an applied voltage with reversed polarity, again at 200°C. The leakage current monitored at -15V bias voltage as a function of time, is shown in figure 5-3a. After approximately 200 min the total current density saturates to 1.8 A/cm², which is an identical value to that is observed in the forward-bias direction. Figure 5-3b presents an optical image of the interface of TiO₂ₓ/anode (the cathode in the forward bias), which shows that the transparency recovers during the reverse-biasing process. Figure 5-3c shows the other side of crystal, at the TiO₂ₓ/electrode (cathode during reverse biasing) interface, which now exhibits a bluish region ~ 150 µm in extent. From these data, it appears that the defect migration process is reversible in these voltage and temperature regimes, however, the resulting room-temperature current-voltage characteristics (Figure 5-3d) shows that the process is not completely reversible.
Figure 5-3: (a) Conductivity of TiO$_{2-x}$ over the 1$^{\text{st}}$ step reverse-bias degradation. (b) An optical image of TiO$_{2-x}$ shows the formed reduced region is annihilated, caused by the reverse-bias voltage. (c) An optical image of TiO$_{2-x}$/cathode interface after formation of reduced region. (d) Comparing I-V characteristics before degradation, after 1$^{\text{st}}$ step forward degradation and 1$^{\text{st}}$ step reverse-bias voltage.
The local microchemistry of both the TiO$_2$-$x$/cathode and TiO$_2$-$x$/anode interface regions is investigated by the monochromated EELS mapping on the crystal after forward and reverse degradation. Figure 5-4a shows the chemical shift of Ti L$_{2,3}$ edge and the change in local stoichiometry from the TiO$_2$-$x$/Pt interface (cathode during the reverse biasing) to 200 nm from the interface. To compare the local microchemistry of both sides, similar characterization is done from the TiO$_2$-$x$/Pt interface (anode during the reverse biasing) presented in figure 5-4b. The quantified stoichiometry of TiO$_2$-$x$ at both interfaces and relative chemical shift of Ti L$_{2,3}$ edge are almost identical for both interface regions of a forward and reverse biased sample, however, the TiO$_2$-$x$/cathode region (during the reverse biasing) is more substoichiometric. From the I-V behavior, it appears that the defect migration process in this low electric-field regime is not completely reversible, even though the optical images indicate show that the bluish region disappears with the reverse biasing.
Figure 5-4: (a) EELS quantification analysis indicates the oxygen content and chemical shift of the Ti L₂,₃ edge as a function of distance from the cathode interface (during the reverse biasing), (b) the anode interface (during the reverse biasing).
The TEM image in figure 5-5a shows the microstructure of the TiO$_{2-x}$/cathode region (during the reverse biasing). As a result of clustered charged point defects, the microstructural defects are formed near the interface at low electric field regime. Figure 5-5b shows an electron diffraction pattern from the area. The superlattice reflections associated with Magnéli phases, as seen in the <010> oriented specimens (Figure 4-8b), are not observed at the cathode interface at low electric field. The microstructure of the TiO$_{2-x}$/anode (during the reverse biasing) in figure 5-5c indicates microstructural defects at the interface formed during the forward biasing are stable and prevent full oxidation of that interface during the reverse biasing process.
Figure 5-5: (a) TEM image reveal microstructural defects after reversing DC field polarity near the cathode, (b) Diffraction pattern of the TiO$_{2-x}$/cathode region after degradation and (c) the microstructural defects near the anode (during the reverse biasing).
The findings from the I-V measurements, EELS spectroscopy and transmission electron microscopy are consistent with the fact that close to the interface, in the nanoscale range, the concentration of the reduced region does not change back to the initial state after reversing the polarity of the bias voltage and that the extended defects stabilize the local non-stoichiometry.

As shown in Figure 5-6, the real-time one-dimensional drift-diffusion is monitored where the positive charge defects redistribute toward cathode under applied electric field (56 V/cm) at 200°C. The crystal, used to study the rectification behavior and reversibility at low voltage along <001> direction, is utilized for this experiment.

First of all, the crystal is subjected to 15 V bias voltage (56 V/cm) at 200°C to redistribute and accumulate the point defects at top electrode resulting in the formation of a dark blue region (Figure 5-6a). After accumulating the defects at one side, the polarity of the bias voltage is reversed to redistribute the defects toward the other electrode. At $t = 0$, in response to the electric field the point defects, the positively charged oxygen vacancies and titanium interstitials migrate toward the cathode (bottom electrode). During the degradation process the highly reduced region expands and a concentration front forms that is shown in Figures 5-4c, 5-4d and 5-4e with red line. The region with higher concentration of defects migrate until the point defects are accumulated at the cathode terminal, shown in Figure 5-6f ($t = 103.3 \text{ min, at } 200^\circ C$).
Figure 5-6: Series of different states during the electromigration of charged point defects along <001> direction at $T = 473$ K and $E = 56$ V/cm of a TiO$_{2-x}$ single crystal. (a) $t = 0$ min, (b) $t = 5.7$ min, (c) $t = 15.1$ min, (d) $t = 33.9$ min, (e) $t = 62.0$ min and (f) $t = 103.3$ min.
Figure 5-7 shows the leakage current gradually increasing during the degradation process at 15V bias voltage (56V/cm) until it reaches a saturation of 1.7 A/cm² after 100 minutes. This conduction enhancement is caused by modification of the barrier at the reverse bias electrode (bottom electrode) and ionic conduction; however, a layer of extended defects about 200nm remained from previous degradations on both sides.

Figure 5-7: Conductivity of TiO$_{2-x}$ as a function of time measured during 15 V biasing (E = 56 V/cm) at T = 473 K. (a) t = 0 min, (b) t = 5.7 min, (c) t = 15.1 min, (d) t = 33.9 min, (e) t = 62.0 min and (f) t = 103.3 min.
The point defects migration is also monitored at higher temperature (300°C). Surprisingly, two distinguished regions with different diffusivity are observed that migrate from the top electrode (anode) toward the bottom electrode (cathode), observable in Figure 5-8b and 5-8c via red-line (concentration front of region with higher diffusivity) and blue-line (concentration front of region with slower diffusivity).

Figure 5-9 shows the leakage current monitored as a function of time. The current increases while 15 V DC bias is applied to the electrodes which results from electron injection enhancement over the barrier at the cathode and also the ionic conduction that impacts the total electrical conductivity at this temperature. After about 77 seconds (Figure 5-8d), the point defects start to accumulate at the negative terminal (bottom electrode). As a consequence, the ionic migration slows down by repulsion force between the accumulated defects and migrating defects. After about 70 seconds, the leakage current decreases until it reaches a saturation of about 1.7 A/cm² after 246 seconds. The $\text{Ti}^{4+}$ with lower migration barrier, comparing to the $\text{Ti}^{3+}$ and $\text{VO}^{2+}$, may be the origin of the region that reaches the bottom electrode quickly after about 1.17 min (Figure 5-8d).
Figure 5-8: Series of different states during the electromigration of charged point defects along <001> direction at $T = 573$ K and $E = 56$ V/cm of a TiO$_{2-x}$ single crystal. (a) $t = 0$ min, (b) $t = 0.52$ min, (c) $t = 0.82$ min, (d) $t = 1.17$ min, (e) $t = 1.97$ min and (f) $t = 4.1$ min.
The average drift velocity is measured for both migration regions during the applied voltage at 300°C. The first region with 44 μm/s velocity has higher mobility comparing to 18 μm/s velocity for the second region. If the electric field, $E$, is considered constant then the mobility, $\mu$, of charged point defect can be calculated according the equation 5-1.
\[ \nu_i = \mu_i E \]  

Kinetically, the mobility for the fast and slow regions is $7.8 \times 10^{-5} \frac{cm^2}{Vs}$ and $3.2 \times 10^{-5} \frac{cm^2}{Vs}$, respectively. However, $Ti_{i}^{4+}$ dominates the redistribution process with significantly higher diffusivity and higher charge in comparison to $Ti_{i}^{3+}$ and $V_{O}^{2+}$. Therefore, the origin of the fast drifting region can be $Ti_{i}^{4+}$ while either $Ti_{i}^{3+}$ or $V_{O}^{2+}$ is forming the other region with slower drift.

3 Conclusions

The one-dimensional defect redistribution is studied in single-crystal TiO$_2$ along <001> crystallographic orientation. At low applied voltages (15 kV), the point defects homogenously migrate (a 1-D drift-diffusion mechanism) and accumulate at the cathode electrode (where Pt electrodes block ion transfer) with no evidence for conductive filament formation. The diode-like rectification behavior, observed after the forward-bias degradation, indicates that Schottky barrier at the reverse bias electrode is annihilated. A region with high concentration of titanium interstitials and oxygen vacancies is formed at the cathode in blue color. The transparency recovers during the reverse-biasing process, while a new reduced region is formed at the other electrode (anode during forward-biasing process). However, the current-voltage measurement, electron microscopy and electron spectroscopy characterizations show that the point defects condense into extended defects, which do not
recover during the application of a reverse bias. Thus the modulation of the Schottky barrier is not reversible at the fields and temperatures studied. Comparison of the forward-bias degradation process along <010> and <001> indicates that the leakage current saturates about 3 times faster along <001> which can be kinetically related to migration of titanium interstitials along the open channel (c-axis) with a lower migration barrier. The EELS quantification analysis from both TiO₂/cathode and TiO₂/anode interfaces shows the quantified stoichiometry of TiO₂₋ₓ at the electrodes are almost identical, indicating the extended defects formed near the electrode that were stable even after reversing the polarity of bias voltage. The substoichiometry of TiO₂₋ₓ quantified by EELS at the cathode interface along <001> is slightly more stoichiometric in comparison with the cathode interface along <010>, that is thermodynamically in agreement with lower electric field, 56 V/cm, along <001> comparing to 75 V/cm along <010>. The Magnéli phase formation at TiO₂/Pt interfaces at 200°C and electric field of 56 V/cm along <001> was not observed.

The kinetics of defect transport in response to the electric field is studied by observation of drift/diffusion of charged point defects migration in real time. At 300°C and 15V, two concentration fronts with different mobility can be distinguished. Since the titanium interstitials dominate the redistribution process for both thermodynamic and kinetic reasons, the region with higher diffusivity should be related to the Ti⁺ redistribution [62, 63].
Chapter 6

Origin of Electroformed Conductive Filaments in Reduced Rutile TiO$_2$ via Cathodoluminescence Spectroscopy

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1 Abstract

The present work reports the role of intrinsic point defects on the degradation and electroforming process relevant to resistive switching in rutile TiO$_2$. To study this phenomenon, high-purity single crystals of TiO$_2$ are annealed at low oxygen partial pressures to establish the initial defect chemistry state and thus self-doping of the material. The point defect redistribution process under applied field is studied by monitoring the leakage current
as a function of time, investigating the current-voltage behavior and analyzing optical microscopy images. In addition, cathodoluminescence (CL) spectroscopy and electron energy loss spectroscopy are utilized to understand the origins of the formed conductive filaments.

2 Introduction

Recently, there has been an intense interest to develop a new generation of non-volatile memory (NVM) [140] to extend Moore’s law for the next few decades. As a potential candidate, electrically switchable resistance memories have attracted special attention due to their high performance, high density and scalability [3, 7, 15].

In transition metal oxides, resistive switching can result from a redistribution of charged point defects in response to an applied electric field. Local inhomogeneities in stoichiometry are accompanied by changes in cation valence and local resistivity. If these redistribution processes are reversible, switching behavior can be realized [3]. A wide variety of transition metal oxides has been studied to understand the dominant mechanisms associated with the resistive switching process [6, 8, 21-23, 141-145]. In general, two different mechanisms have been established: field-programmable rectification switching [6, 117, 141, 142, 146] and filamentary switching [8, 21-24, 143, 144].

Field-programmable rectification switching behavior results from the asymmetry in the defect distributions near the anode and the cathode formed under an applied bias. In this case, the leakage current is believed to be controlled by the modulation of the interface
Schottky barrier at the reverse-biased cathode that is homogeneous and proportional to the electrode area. The formation of a strongly reduced region underneath the cathode leads to a change in the effective Schottky barrier height and width of the depletion layer at the metal/semiconducting oxide interface, which governs the electron injection into the dielectric [6, 117, 145]. The anisotropy effects of TiO$_2$ single crystals on diode-like rectification behavior has been studied in single-crystalline TiO$_2$[6].

As the concentration of accumulated positive charged defects at the cathode increases, a morphological instability in the concentration front can appear which leads to filamentary growth of highly reduced regions. This process is usually termed as an “electroforming” process in the context of resistive switching [3]. The formation of the conductive filaments is responsible for the switch between a high-resistance to a low-resistance state as the filaments connect the two electrodes, serving as shunts. Several experimental reports discuss the mechanism of electroforming on bipolar switching in TiO$_{2-x}$ [21-24] and other transition metal oxides [2, 147].

A summary of what is known about TiO$_2$ shows that most literatures have been concerned with the formation of filaments, although the switching mechanism can be influenced by the anisotropy of rutile [6], extended structural defects as fast transport paths [24, 91, 148], the defect condensation, and phase transformation to highly conductive phases [15, 56]. The intrinsic ionic defects, oxygen vacancies and titanium interstitials, are expected to be the origins of the observed filaments. Under applied voltage, the large concentration of point defects can be induced and ordered into shear defect phases, termed “Magnéli” phases.
Recently, filaments of Magnéli phases have been detected by the transmission electron microscope (TEM) in severely degraded TiO$_2$ samples [15].

In contrast to the perovskites [4, 12, 20], both oxygen vacancies and cation (Ti) interstitials are highly mobile in TiO$_2$. Our prior work (Chapter 4 and 5) shows that titania interstitials, although largely ignored in the previous literature, are dominant in the redistribution process [117]. In this study, we demonstrated experimental conditions under which filaments did not form during the degradation process; rather the redistribution was largely governed by a one-dimensional drift diffusion process resulting in modulation of the Schottky barrier at the interface. The objective of the current study is to explore conditions under which filament formation dominates the degradation or “electroforming” process and to distinguish which type of point defect is responsible for the filament formation and if the filaments are switchable.

3 Experimental procedure

High-purity (100)-oriented single-crystal rutile TiO$_2$ samples made by a Verneuil growth process were purchased from Shinkosha Ltd., Japan. The most significant impurity was Al at ~ 50 ppm by weight. Knowing the chemical diffusion kinetics of TiO$_2$ [61, 62], a series of well-polished crystals were annealed and equilibrated at an oxygen partial pressure of $10^{-4}$ at 1300 °C for 22 hours and then with the rate of 10 °C/min cooled to room temperature to explore the effects of the dominant point defect type on the redistribution process in subsequent biasing studies. The PO$_2$ was controlled in a high-temperature tube furnace using
an Argon and Argon/H₂ forming gas and monitored by a commercial zirconia-based oxygen gas sensor. Based on this annealing condition, oxygen vacancies and titanium interstitials were expected to be the mobile charged point defects.

Platinum contacts were deposited by magnetron direct current (DC) sputtering on a pair of opposite lateral (010) surfaces to study transport along the [010] direction. A power density of 6.11 W/cm², a gas pressure of 30 mTorr (pure Ar), and a substrate to target distance of 3.4 cm, were used in the deposition process, which resulted in the deposition rate of 75 nm/min. This allowed 350 nm of platinum to layer onto the substrate evenly. The deposited contacts were annealed at 200 °C for 3 hours to obtain reliable and reproducible contacts.

The annealed Pt/TiO₂-x/Pt single crystal was established in the DC-bias redistribution studies. Degradation was induced by applying a bias electric field (200-400 V/cm) at 200 °C, performed by a HP-6634B power supply. The bias was expected to induce positively charged defects, i.e. oxygen vacancies and titanium interstitials, to migrate toward the cathode. The current-voltage behavior of the TiO₂-x was measured before and after degradation by a high precision Keithley 617 electrometer.

The formation of the conductive filaments has been studied by taking optical images before and after the degradation. A Gatan MonoCL4 with a highly sensitive PMT (160-930 nm) detector on Zeiss Evo 50 SEM with tungsten source was utilized for cathodoluminescence studies to distinguish the type of defects present in the filament regions.
4 Results

Figure 6-1 presents an I–V curve measured at room temperature after the annealing process. After Pt deposition on the sides of the crystal with about 300 nm thickness, as expected, the contacts displayed non-linear I-V characteristics, consistent with a Schottky barrier at the interface. Since the work function of Pt, about 5.3 eV, is significantly larger than the electron affinity for TiO₂ (~ 4 eV) [130, 149], a Schottky barrier is anticipated [150]. The height and width of this potential barrier at the cathode contact (the reverse-biased electrode) generally controls the electron injection into the oxide and consequently limits the electronic transport over a large applied voltage range.
The samples were then subjected to a DC bias voltage at 200°C temperature. Figure 6-2a shows the change in the leakage current as a function of time, over the duration of the degradation process. The leakage current increases gradually until a sudden jump in the current occurs at 30 V (150 V/cm electric field), which is followed by a series of similar current spikes. An optical microscope image taken after the electroforming process is presented in figure 6-2b and shows well-oriented conducting filaments along the electric field.
direction. The I-V curve, measured after the degradation, is compared with the curve before degradation in figure 6-2c. It is clear that the device is more conductive, as a result of the filament formation.
Figure 6-2: (a) Conductivity of TiO$_{2-x}$ over the degradation. (b) An optical image of TiO$_{2-x}$ after formation of conductive filaments. (c) Comparing I-V characteristics before and after degradation.
Cathodoluminescence (CL) spectroscopy was performed in a scanning electron microscope (SEM) to further investigate the nature of the degradation process and filament formation. The CL spectra in Figure 6-3 shows a broad peak around 410 nm in wavelength, which corresponds to the band gap of TiO₂ (~3.1 eV). In addition, a peak at 780 nm is evident in the infrared portion of the spectrum and has been associated with titanium interstitials [38]. A less intense peak at 610 nm is believed to result from radiative transitions from states associated with oxygen vacancies [38]. After Gaussian deconvolution of the spectrum, it is found that the energy state of oxygen vacancies should be in the range of 0.2 - 1 eV below the conduction band.

In figure 6-3, the CL spectra taken from filament (the blue curve) and non-filament areas (the red curve) from the TiO₂₋ₓ/anode interface, clearly shows a difference in intensity of the peaks about 1.6 eV or 780 nm wavelength which is associated with titanium interstitials in TiO₂₋ₓ.
Figure 6-3: Cathodoluminescence spectra of a reduced single-crystal TiO₂ sample. Red curve is taken from the bulk and blue curve is from a filament region.

The CL-SEM system is equipped with RGB filters: the blue filter has a wavelength range of 185-510 nm, green filter with the range of 495-575 nm, and red filter with the wavelength range of 595-850 nm. Figure 6-4a is an image taken by a secondary electron SEM from the anode region as a reference. Figure 6-4b shows a CL image made by the emission of the main peak which excludes the emission belonging to the titanium interstitials energy levels.
by inserting the blue filter. The green filter is inserted to exclude the emissions which belong to the band gap and titanium interstitials energy level within the band gap. It is expected that the CL image with the green filter is related to the oxygen vacancies energy level (Fig. 6-4c). In order to distinguish the titanium interstitial rich region, a CL image is taken by inserting the red filter that allows the emission of the wavelength belongs to the titanium interstitials and oxygen vacancies pass through the detector (Fig. 6-4d). By comparing the CL images taken with red, green and blue filters, it is concluded that the bright regions in figure 6-4d which belong to the conductive filaments, are dark in figure 6-4b and 6-4c.
Figure 6-4: (a) A SEM image of a field-degraded TiO$_{2-x}$ crystal. (b) A CL image is taken by using UV-blue filter, (c) UV-green filter and (d) is taken by red filter at 750x with an electron-beam energy of 20keV.
Electron energy loss spectroscopy (EELS) was utilized to compare the Ti valence state and oxygen stoichiometry from filament (highly reduced region) and non-filament areas. Site-selective TEM samples were prepared by focused ion beam (FIB) lift-out from both regions. Comparing the EEL spectra acquired from the TEM samples did not show significant variation in the stoichiometry. This is attributed to the difficulty of accurately finding the position of conductive filaments since they were not observable in secondary electron microscope (SEM) during FIB sample preparation. This technique is capable of making a TEM sample from a region very close to the surface (about 5 µm in depth) and the filaments, formed in the bulk, might not be close enough to the surface.

The samples were subsequently subjected to a reverse-bias voltage to understand the reversibility of the degradation process. As shown in Fig. 6-5a, the current decreases as a function of time and applied reverse-bias voltage. Figure 6-5b is an optical image of the single crystal after reverse biasing at 20 V (100 V/cm electric field) at 200 °C temperature, and shows evidence of the filaments’ migration away from the original cathode electrode (now positively biased). Figure 6-5c shows the corresponding I–V curve measured at room temperature after the reverse biasing and compares it to the prior I-V curves before degradation and after forward biasing. These curves show that the resistivity of the TiO$_2$-$x$ after reverse biasing is similar to the original state of the crystal, although some filaments may remain connected across the electrode.
Figure 6-5: (a) Conductivity of TiO$_{2-x}$ over the reverse biasing. (b) An optical image of TiO$_{2-x}$ after annihilation of conductive filaments at the anode. (c) Comparing I-V characteristics before degradation, after forward biasing, and after reverse biasing.
(c) Current density (Amp/cm²) vs. Electric field (V/cm)
The resistance degradation is studied in two forms, the annihilation of the Schottky barrier at
the interface (discussed in chapter 4) and formation of conductive filaments (presented in this
chapter). Compering these two sets of data, the only difference is related to the cooling
process from elevated temperature during annealing the crystals after the equilibrium is
achieved. To study interface modulation mechanism, the TiO$_2$ single crystals are reduced at
$10^{-4}$ PO$_2$ and quenched from the 1100$^\circ$C to T$<300^\circ$C in the flowing reducing atmosphere to
establish the initial defect chemistry state. However, the conductive filament formation is
observed where the crystals are slowly cooled down ($10^0$C/min) from 1300$^\circ$C to the room
temperature. Except the cooling procedure, other parameters, such as electric field direction
degradation (along-<010>) and temperature during the degradation process, were identical.

The first hypothesis to describe the resistance degradation change was uniformity of
generated point defects concentrations cross the quenched-samples comparing to point
defects concentrations variation for slowly cooled-samples. The inhomogeneity of defect
concentrations (with lower defect concentration at the interface) behaves like a barrier
against accumulation of the defects at the interface that results in formation of highly reduced
regions in the bulk (with lower defect concentration in the bulk) which connects the
electrodes when it grows along the electric field direction. We tested this hypothesis by
annealing the crystals and cooling down with the same profile. Surprisingly, we have not
seen the electroforming in these sets of crystals even after changing the annealing
temperature and oxygen partial pressure from the conditions that we observed that behavior
initially.
Another hypothesis that was studied to understand the electroforming mechanism, was the impact of the defect chemistry state of TiO$_2$ single crystals on the conductive filaments formation. As it is shown and discussed in Figure 2-2, the concentration of intrinsic point defects varies by changing the temperature and oxygen partial pressure during annealing. Decreasing the temperature results in p-n transition shift to the lower PO$_2$ and defect concentration shift to the lower concentration.

A series of single-crystal rutile samples were annealed and equilibrated at an oxygen partial pressure (PO$_2$) of 4.7x10$^{-3}$ atm at 1100°C for 36 hr. After equilibration, the samples were quenched to T < 300°C in the flowing reducing atmosphere. After annealing, the defects concentrations are expected to be: $[V_0] = 4.58 \times 10^{-3}$ (per site), $[V''''_{Ti}] = 2.29 \times 10^{-3}$ (per site), $[Ti_i^+] = 4.30 \times 10^{-7}$ (per site), $[Ti_i^-] = 1.37 \times 10^{-5}$ (per site), $n = 2.52 \times 10^{-5}$ (per site) or $1.21 \times 10^{18}$ cm$^{-3}$ and $p = 6.60 \times 10^{-7}$ (per site). Based on the electron carrier concentration, the bulk electrical resistivity, $\rho_B$, is calculated to be 77 $\Omega$. cm, considering an electron mobility ($\mu_e$) of $6.7 \times 10^{-2}$ cm$^2$/V.s [41].

The samples were then subjected to a DC bias voltage at 200°C temperature. Figure 6-6a shows the change in the leakage current as a function of time, over the duration of the degradation process.

The leakage current increases significantly at 30 V (175 V/cm electric field). The I-V curve, measured after the degradation, is compared with the curve before degradation in figure 6-6b.
Figure 6-6: (a) Conductivity of TiO$_{2-x}$ over the degradation. (b) Comparing I-V characteristics before and after degradation.
The I-V curve, measured after the degradation, is compared with the curve before degradation in figure 6-2c. It is clear that the device is more conductive, as a result of the filament formation.

Optical microscope images taken after the electroforming process are presented in figure 6-7 and show well-oriented conducting filaments along the electric field direction. Figure 6-7a shows the cathode side where the titanium interstitials and oxygen vacancies are clearly distributed at the interface. The conductive filaments are formed and growth toward the other electrode (anode) along the electric field direction. Figure 6-7b and Figure 6-7c are taken from the anode side. The filaments are parallel and barely connected to the anode electrode. The filament formation results in switching to the low resistance state that is observed in Figure 6-6b.
Figure 6-7: (a) An optical image of TiO$_{2-x}$ after formation of conductive filaments, taken from the cathode side, (b and c) Optical images from the anode side.
Figure 6-8a shows dissociation of the conductive filaments after electroforming process when negative polarity is applied to the anode (during the electroforming process). High current density is passing through the filaments where they are weakly connected to the electrode (Figures 6-7b and 6-7c). As a result, the Joule heating impacts on drifting the ionic carriers away and the filaments get disconnected from the electrode (Figures 6-8a). The bulk resistivity enhances when the current is passing through the bulk instead of conductive filaments (Figure 6-9. During the reverse biasing, the positively charged ionic carriers migrate toward the cathode (anode during the electroforming) and the filaments shrink shown in Figures 6-8(b-g). Consequently, the leakage current suddenly increases at the same electroforming voltage (35 V) where a filament shunts the electrodes (Figure 6-8h).
Figure 6-8: Monitoring annihilation and formation of conductive filaments by applying DC bias along $<100>$ direction to an electroformed TiO$_{2-x}$ single crystal at $T = 473$ K. (a) $t = 2.5$ min, (b) $t = 15.8$ min, (c) $t = 18.3$ min, (d) $t = 30.8$ min, (e) $t = 30.3$ min and (f) $t = 44.1$ min, (g) $t = 46.6$ min and (h) $t = 57.1$ min.
Figure 6-9: Conductivity of TiO$_{2-x}$ as a function of time measured during annihilation and formation of conductive filaments at $T = 473$ K. (a) $t = 2.5$ min, (b) $t = 15.8$ min, (c) $t = 18.3$ min, (d) $t = 30.8$ min, (e) $t = 30.3$ min and (f) $t = 44.1$ min, (g) $t = 46.6$ min and (h) $t = 57.1$ min.

5 Discussion

Applied electric fields at 200°C induce degradation and the formation of conductive filaments in reduced TiO$_{2-x}$ single crystals. Microscopic CL analysis on degraded TiO$_{2-x}$ samples shows that the conductive electroformed filaments are associated with a high concentration of titanium interstitials. Even though the overall concentration of oxygen vacancies is believed to be larger than the concentration of titanium interstitials based on the
annealing conditions, the mobility of the interstitials is expected to be higher. First, the
coulombic interactions are higher for the $Ti_i^{3+}$ or $Ti_i^{4+}$ interstitials as compared to $Vo^{2+}$. Secondly, the migration energy for titanium interstitial diffusion (0.225 eV along [110]) is reported to be smaller than that of oxygen vacancies (0.69 eV along [110]) [63].

Over the degradation process, the non-stoichiometric and conductive filaments serve
to shunt the electrodes, thus increasing the overall leakage current. The sudden increase in
the leakage current following some oscillations in the current might be due to the tunneling
of the current to the electrostatic barrier between the cathode and the tip of the conductive
filament. It is expected that the electric field at the tip of the filament right before connecting
to the anode is much higher than the surrounded area which causes an abrupt raise in
diffusivity of the titanium interstitials influenced by the Joule heating effect [147, 151-153].
The Joule heating impact on assisting positively charged ionic carriers, drifting toward the
anode to shunt the electrodes and away from the anode to annihilate the filament, has been
studied by Infrared thermal micrograph on Cr-doped SrTiO$_3$ [151]. It is reported that the
temperature of the filament at the anode electrode rises up to several hundred degrees.

Reversing the bias leads to partial recovery of the original resistivity and the
conductive filaments are observed to migrate away from the positively charged electrode,
indicating that the degradation is at least partially reversible. The electroformed conductive
filaments are investigated by infrared thermal microscopy. It can be clearly seen, while a DC-
voltage is applied, the filaments with less resistivity, have higher temperature compared to
the rest of the sample. This is consistent with our description of the conductive filaments
made from highly non-stoichiometric TiO$_{2-x}$. The higher leakage current passes through the filaments and increases the temperature of the filament regions.

6 Conclusion

TiO$_2$ resistive switching behavior, through an electroforming process, results from a redistribution of charged point defects in response to an applied electric field. In TiO$_2$, both oxygen vacancies and cation (Ti) interstitials are significantly mobile. Here, the CL spectroscopy and CL imaging are utilized to investigate the nature of the electroformed conductive filaments and to determine the spatial distribution of point defects in TiO$_2$. The CL images resolve the conductive filaments from its surrounding regions and suggest that the drift of titanium interstitials appears to be the dominate factor in the point defect redistribution process and is responsible for the formation of the conductive filaments, despite the fact that the majority of defects in the original samples was oxygen vacancies. This behavior can be understood as a consequence of smaller migration energy associated with the titanium interstitial diffusion in comparison to that of oxygen vacancies.
Chapter 7

Conclusion and Future Directions

1 Conclusions:

Point defect distribution in rutile TiO$_2$ single crystal under direct-current (DC) biasing is studied from well-defined initial state equilibrium concentrations of both lattice and electronic defects. It is shown when the electrodes block ion transfer across the interface, this defect redistribution has significant implications for the electron injection characteristics of the electrodes.

In response to the electric field, the redistribution of the defects under DC bias leads to positively charged defects accumulating at the cathode. Furthermore, the Schottky barrier and width of the depletion layer are changed in such a way that the electron injection increases at the reverse-biased electrode. The defect redistribution of the crystals with resistivities on the order of 60 $\Omega$.cm is homogeneous (1-D transport) with no evidence of conductive filament formation (2-D) in either the <010> or <001> directions. The initial defect chemistry, well-defined after annealing at 1100°C and $10^{-4}$ PO$_2$ shows that oxygen
vacancies are the dominant point defects; however, titanium interstitials dominate the redistribution process near the cathode, as indicated by CL spectroscopy. Thermodynamically, titanium interstitials are energetically favorable at low oxygen activities as encountered in the near-cathode region and from kinetic perspective, and these interstitials have higher diffusivity comparing to the oxygen vacancies. As measured quantitatively by EEL spectroscopy, the substoichiometry is well below the stability of TiO$_2$ at the TiO$_2$-x/cathode interface, although no Magnéli phases are found in the low-electric-field (75 V/cm) regime, indicating a nucleation barrier to the phase transformation. The local stoichiometry analysis by EELS indicates that reduction in Ti ions valence state results in a chemical shift of the Ti L$_{2,3}$ edge to lower energies. The asymmetry in the defect distributions near the anode and cathode leads to diode-like rectification behavior, which has been attributed to the modulation of the interface Schottky barrier at the reverse-biased cathode.

Along the <010> crystallographic direction, the reversibility of the diode-like behavior, observed at low electric field regime, is examined by reversing the DC bias polarity. When the crystal is subjected to reverse biasing, the electrode behavior is nearly inverted, with the original cathode (as defined during forward degradation) approaching its original I-V behavior with no evidence of formation of Magnéli phase, suggesting that the stoichiometry changes in the near-cathode region are nearly reversible.

The anisotropy in defect transport and degradation process is studied by applying the DC bias along <001> crystallographic direction. Diode-like rectification behavior is observed after the forward-bias degradation at low voltage, similar to the <010> orientation, however
the leakage current saturates about three times faster along <001> than along <010> direction. In addition, reverse-bias degradation studies indicate that the degradation process is not reversible along the <001> orientation for similar applied fields, in contrast to the <010> orientation. Since the optical images of the TiO$_2$-x/(cathode and anode) interfaces after each degradation show that the processes appear reversible (based on color changes), the irreversibility must be local to the electrode and below the optical resolution limits. It is concluded from TEM analysis that formation of the microstructural defects at the cathode interface during the forward bias is not recovered when the polarity of the bias voltage is reversed.

Real-time optical studies of the electric field degradation provide additional insight into the redistribution process. At 300°C, two concentration fronts with different diffusivities are observed as point defects migrate toward the cathode. The front with higher diffusivity may be influenced from titanium interstitials ($Ti^4_1$) where the origin of the other region can be either titanium interstitials ($Ti^3_1$) or oxygen vacancies ($O^2_1$), although future CL studies will be necessary to confirm the hypothesis.

At higher electric field regimes, > 150 V/cm, the accumulated point defects at the cathode interface with low oxygen chemical potentials induces coalescence of point defects into shear defect phases, termed “Magnéli phases”. The condensation of large concentration of point defects to the extent that the bulk stoichiometry is significantly altered, making the bulk more stoichiometric and thus more resistive. The electron microscopy measurements of local microstructure and microchemistry provide nonstoichiometry data, defect clustering
and interfacial phase transformation at the interface. When these samples are subsequently subjected to reverse biasing, the results show that the Magnéli phase formation near the cathode is not reversible at 200°C for the times and fields studied.

Studying the defect transport and resistance degradation phenomenon on the rutile single crystals with resistivity about 80 Ω.cm showed that the redistribution of the point defect leads to filamentary growth of highly reduced regions. The continuous filaments bridge the electrodes, and this “electroforming” leads to the high-resistance state converting to the low-resistance state via electrode shunting. The role of the ionic defect redistribution during the resistance switching process between low- and high-resistance states is monitored. The CL spectroscopy of different regions after electroforming indicates that nature of the conductive formed filaments is distribution of titanium interstitials in TiO$_2$. The CL images, taken by utilizing different energy filters, resolve the conductive filaments from its surrounding regions. The red filter with the wavelength range of 595-850 nm shows the conductive filaments where a CL image is formed by the emission of the peak belonging to the titanium interstitials energy levels and excludes the emission of the main peak.

The reversibility of the substoichiometric filaments is examined by reversing the DC bias polarity. As a result, the filaments migrate away from the cathode (anode during the electroforming) and the resistivity switches back to high resistance state. Attempts to identify defect coalescence or Magnéli phase formation in these samples has been unsuccessful, suggesting that reversibility and switching behavior does not involve a phase transformation process, as has been suggested by literature.
2 Future directions:

- Further real-time optical and CL studies can provide additional quantitative insight into the redistribution kinetics over multiple length scales (nm- mm). Studies as a function of temperature and field, will allow us to extract diffusion coefficients and activation energies. Moreover, this data will be useful for guiding and verifying phase-field simulations of the process, which are being pursued by our collaborators.

- The impact of higher dimensional defects, i.e dislocations, on the nucleation of the filaments can be studied by purposefully varying the dislocation density where the initial defect chemistry state is well-defined.

- The formation of microstructural defects at the interface on the nanometer and sub-nanometer length scale and reversibility of the process can be studied *in situ* in the TEM. Samples will need to be carefully extracted from the near-electrode region by focused ion beam (FIB) technique and integrated onto the in situ platform.

- The transition between 1-D and 2-D defect redistributions can be further studied as a function of the electric field and the initial defect chemistry to understand the origins of the transition.
The redistribution of the charged point defects can be modeled by using drift and diffusion equations, taking into account the accumulation of the defects at the electrodes that are blocking the defect transport, the mass balance, and condensation of the point defects into the metallic Magnéli phases at the interface.

The thermal transport during degradation process as a function of defect chemistry state, temperature, electric field and time can be studied by utilizing infra-red imaging microscopy for interface modulation and filamentary growth mechanisms.

The one dimensional electromigration of titanium interstitials (3+ and 4+ charge states) and oxygen vacancies and their diffusivities along different crystallographic directions can be studied in-situ via cathodoluminescence spectroscopy.
References


[38] I. Fernández, A. Cremades, and J. Piqueras, "Cathodoluminescence study of defects in deformed (110) and (100) surfaces of TiO$_2$ single crystals," *Semiconductor Science and Technology*, vol. 20, p. 239, 2005.


Appendices
Appendix A

Defect diagram for rutile TiO$_2$

Defect diagram for TiO$_2$ is calculated and modeled by Matlab as a function of PO$_2$/atm and temperature. A Matlab code for both undoped (part a) and doped (part b) conditions is presented in this chapter. Each part is divided into three regions based on the level of reduction (oxygen partial pressure). From higher to lower PO$_2$, the first region is ionic compensation region that both oxygen vacancies and titanium vacancies dominate. The second region, strongly reduced region, the oxygen vacancy is dominating and in the third region, extremely reduced, titanium interstitials are dominant point defects. An example of defect diagram of TiO$_2$ solved at 1100°C is presented in Figure 2-3.

1. clear;clc;close;

   % Parameter Definition

2. H1=493.1e3;S1=106.5;% Reduction_Vo (Equation 2-1)
3. H2=879.2e3;S2=190.8;% Reduction_Ti3 (Equation 2-2)
4. H3=1025.8e3;S3=238.3;% Reduction_Ti4 (Equation 2-3)
5. \[ H_s = 452.3 \times 10^3; S_s = -167.5; \]

6. \[ H_i = 222.1 \times 10^3; S_i = -44.6;\] % e-h (Equation 2-5)

7. \[ H_4 = 354.5 \times 10^3; S_4 = -202.1;\] % Oxidation (Equation 2-4)

8. \[ T = 1373;\] ; % Annealing temperature (Kelvin)

9. \[ K = 0.008314462175 \times 10^3; \]

10. \[ K_1 = \exp(-1 \times (H_1 - T \times S_1) / (K \times T)); \]

11. \[ K_2 = \exp(-1 \times (H_2 - T \times S_2) / (K \times T)); \]

12. \[ K_3 = \exp(-1 \times (H_3 - T \times S_3) / (K \times T)); \]

13. \[ K_i = \exp(-1 \times (H_i - T \times S_i) / (K \times T)); \]

14. \[ K_4 = \exp(-1 \times (H_4 - T \times S_4) / (K \times T)); \]

15. \[ K_s = K_1^2 \times K_4 / K_i^4; \]

16. \[ A_L = 1.47 \times 10^{-6};\] % Aluminum concentration as an impurity

17. \[ a = \text{logspace}(-13.5604, 2);\] %[PO2]

18. \[ VO = \text{ones}(\text{length}(a), 1) \times (2 \times K_s)^{(1/3)}; \]

19. \[ VT_i = \text{ones}(\text{length}(a), 1) \times 0.5 \times (2 \times K_s)^{(1/3)}; \]

20. \[ T_i_3 = (K_2 \times (2 \times K_s / (K_1.^3)).^(1/2)) \times a.^(^-1/4); \]

21. \[ T_i_4 = \text{ones}(\text{length}(a), 1) \times (K_3 / (K_1.^2)) \times (2 \times K_s)^{(2/3)}; \]

22. \[ n = (K_1)^{0.5 \times (2 \times K_s)^{(-1/6)}} \times a.^(^-1/4); \]

23. \[ p = K_i \times n.^-1; \]
24. \[ VO_s=(2*K_s)^{(1/3)}; \]
25. \[ \text{loglog}(a,VO,'or');hold on; \]
26. \[ \text{loglog}(a,VTi,'b');hold on; \]
27. \[ \text{loglog}(a,Ti3,'g');hold on; \]
28. \[ \text{loglog}(a,Ti4,'y');hold on; \]
29. \[ \text{loglog}(a,n,'ms');hold on; \]
30. \[ \text{loglog}(a,p,'kh');hold on; \]
31. \[ hleg1 = \text{legend}('Vo','VTi','Ti3','Ti4','n','p'); \]
32. \[ \text{xlabel('PO}_2\text{ Concentration');ylabel([']);} \]

% Part(a)-2%
33. \[ a=\text{logspace}(-17.4322,-13.5604); \%[PO_2] \]
34. \[ VO=(K1/4)^{(1/3)}*a.\p(-1/6); \]
35. \[ VTi=K_s*(K1/4)^{(-2/3)}*a.\p(1/3); \]
36. \[ Ti3=(K2/(2*K1))*a.\p(-1/2); \]
37. \[ Ti4=(K3*(2*K1)^{(-4/3)})*a.\p(-1/3); \]
38. \[ n=2*(K1/4)^{(1/3)}*a.\p(-1/6); \]
39. \[ p=K_i*n.\p-1; \]
40. \[ \text{loglog}(a,VO,'or');hold on; \]
41. \[ \text{loglog}(a,VTi,'b');hold on; \]
42. \[ \text{loglog}(a,Ti3,'g');hold on; \]
43. \[ \text{loglog}(a,Ti4,'y');hold on; \]
44. loglog(a,n,'ms'); hold on;
45. loglog(a,p,'kh'); hold on;
46. hleg1 = legend('Vo','VTi','Ti3','Ti4','n','p');
47. xlabel('PO_2 Concentration'); ylabel('[]');

%%%%%%Part(a)-3%%%%%%%
48. a=logspace(-25,-17.4322); [%PO_2]
49. VO=ones(length(a),1).*(K1/(3*K2)^0.5);
50. VTi=ones(length(a),1).*(3*K4*K2/(Ki)^4);
51. Ti3=(K2/27)^(1/4)*a.^(-1/4);
52. Ti4=ones(length(a),1).*(K3/(3*K2));
53. n=(3*K2)^(1/4)*a.^(-1/4);
54. p=Ki*n.^(-1);
55. loglog(a,VO,'or'); hold on;
56. loglog(a,VTi,'.b'); hold on;
57. loglog(a,Ti3,'.g'); hold on;
58. loglog(a,Ti4,'.y'); hold on;
59. loglog(a,n,'ms'); hold on;
60. loglog(a,p,'kh'); hold on;
61. hleg1 = legend('Vo','VTi','Ti3','Ti4','n','p');
62. xlabel('PO_2 Concentration'); ylabel('[]');

%%%%%% Transitions(a)%%%%%%
63. Trans_undoped_1 = (((K1/4)^(1/3))/((2*Ks)^(1/3)))^6;
64. Trans_undoped_2 = (((K1/4)^(1/3))/((K1/(3*K2)^(0.5)))^6;

% Part(b)-1

65. figure;
66. a = logspace(-1.5,-13.5604); % [PO2]
67. VO = ones(length(a),1)*(VOs-AL/2);
68. VTi = ones(length(a),1)*Ks*(VOs-AL/2)^2;
69. Ti3 = (K2*(2*Ks/(K1.^3)).^(1/2))*a.^(-1/4);
70. Ti4 = ones(length(a),1).*(K3/(K1^2))*(2*Ks)^(2/3);
71. n = (K1)^0.5*(2*Ks)^(-1/6)*a.^(-1/4);
72. p = Ki*n.^-1;
73. loglog(a,VO,'or'); hold on;
74. loglog(a,VTi,'.b'); hold on;
75. loglog(a,Ti3,'.g'); hold on;
76. loglog(a,Ti4,'.y'); hold on;
77. loglog(a,n,'ms'); hold on;
78. loglog(a,p,'kh'); hold on;
79. hleg1 = legend('Vo','VTi','Ti3','Ti4','n','p');
80. xlabel('PO_2 Concentration'); ylabel('[]');

% Part(b)-2

81. a = logspace(-13.5604,-17.4322); % [PO2]
82. \( VO = \left(\frac{K_1}{4}\right)^{1/3}a.\wedge(-1/6) \);
83. \( V_Ti = K_s\left(\frac{K_1}{4}\right)^{(-2/3)}a.\wedge(1/3) \);
84. \( Ti_3 = \left(\frac{K_2}{2*K_1}\right)a.\wedge(-1/2) \);
85. \( Ti_4 = \left(\frac{K_3\left(2*K_1\right)^{(-4/3)}}{4}\right)a.\wedge(-1/3) \);
86. \( n = 2\left(\frac{K_1}{4}\right)^{1/3}a.\wedge(-1/6) \);
87. \( p = K_i n.\wedge(-1) \);
88. \( \text{loglog}(a,VO,'or');\text{hold on}; \)
89. \( \text{loglog}(a,VTi,'.b');\text{hold on}; \)
90. \( \text{loglog}(a,Ti3,'.g');\text{hold on}; \)
91. \( \text{loglog}(a,Ti4,'.y');\text{hold on}; \)
92. \( \text{loglog}(a,n,'ms');\text{hold on}; \)
93. \( \text{loglog}(a,p,'kh');\text{hold on}; \)
94. \( hleg1 = \text{legend('Vo','VTi','Ti3','Ti4','n','p');} \)
95. \( \text{xlabel('PO_2 Concentration');ylabel('[]');} \)
96. \( \text{xlabel('PO_2 Concentration');ylabel('[]');} \)

%%Part(b)-3%%

97. \( a = \text{logspace(-17.4322,-20);} \% \text{[PO}_2\text{]} \)
98. \( VO = \text{ones(length(a),1).}\wedge(\text{K}_1/(3*\text{K}_2)^{0.5}); \)
99. \( V_Ti = \text{ones(length(a),1).}\wedge(3*\text{K}_4\text{K}_2/(\text{K}_i)^{4}); \)
100. \( Ti_3 = (\text{K}_2/27)^{1/4}a.\wedge(-1/4) \);
101. \( Ti_4 = \text{ones(length(a),1).}\wedge(K_3/(3*K_2)); \)
102. \( n = (3K_2)^{(1/4)}a.\(^{-1/4}; \)
103. \( p = K_i n.\(^{-1}; \)
104. \( \text{loglog}(a, VO,'or');\text{hold on}; \)
105. \( \text{loglog}(a, VTi,'b');\text{hold on}; \)
106. \( \text{loglog}(a, Ti3,'g');\text{hold on}; \)
107. \( \text{loglog}(a, Ti4,'y');\text{hold on}; \)
108. \( \text{loglog}(a,n,'ms');\text{hold on}; \)
109. \( \text{loglog}(a,p,'kh');\text{hold on}; \)
110. \( h\text{leg1} = \text{legend}('Vo','VTi','Ti3','Ti4','n','p'); \)
111. \( \text{xlabel('PO}_2\text{ Concentration');ylabel('[]');} \)

%%%%%%%Transitions(b)%%%%%%%n
112. \( \text{Trans\_doped\_1} = (((K1/4)^{(1/3)}/(AL/2))\^6; \)
113. \( \text{Trans\_doped\_2} = (((K1/4)^{(1/3)}/(K1/(3*K2)^0.5))\^6; \)