# Ultra-Thin Oxide Membranes: Synthesis and Carrier Transport

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Ultra-thin Oxide Membranes: Synthesis and Carrier Transport

A dissertation presented

by

Jai Sung Sim

to

The School of Engineering and Applied Sciences

in partial fulfillment of the requirements
for the degree of

Doctor of Philosophy

in the subject of

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Ultra-thin Oxide Membranes: Synthesis and Carrier Transport

ABSTRACT

Self-supported freestanding membranes are films that are devoid of any underlying supporting layers. The key advantage of such structures is that, due to the lack of substrate effects - both mechanical and chemical, the true native properties of the material can be probed. This is crucial since many of the studies done on materials that are used as freestanding membranes are done as films clamped to substrates or in the bulk form.

This thesis focuses on the synthesis and fabrication as well as electrical studies of free standing ultrathin < 40nm oxide membranes. It also is one of the first demonstrations for electrically probing nanoscale freestanding oxide membranes. Fabrication of such membranes is non-trivial as oxide materials are often brittle and difficult to handle. Therefore, it requires an understanding of thin plate mechanics coupled with controllable thin film deposition process. Taking things a step further, to electrically probe these membranes required design of complex device architecture and extensive optimization of nano-fabrication processes. The challenges and optimized fabrication method of such membranes are demonstrated.
Three materials are probed in this study, VO$_2$, TiO$_2$, and CeO$_2$. VO$_2$ for understanding structural considerations for electronic phase change and nature of ionic liquid gating, TiO$_2$ and CeO$_2$ for understanding surface conduction properties and surface chemistry.

The VO$_2$ study shows shift in metal-insulator transition (MIT) temperature arising from stress relaxation and opening of the hysteresis. The ionic liquid gating studies showed reversible modulation of channel resistance and allowed distinguishing bulk process from the surface effects. Comparing the ionic liquid gating experiments to hydrogen doping experiments illustrated that ionic liquid gating can be a surface limited electrostatic effect, if the critical voltage threshold is not exceeded.

TiO$_2$ study shows creation of non-stoichiometric forms under ion milling. Utilizing focused ion beam milling, thin membranes of Ti$_x$O$_y$ of 100-300 nm thickness have been created. TEM studies indicated polycrystallinity and presence of twins in the FIB-milled nanowalls. Compositional analysis in the transmission electron microscope also showed reduced content of oxygen, confirming non-stoichiometry. Temperature dependence of the electrical resistivity of the nanowall showed semiconducting behavior with an activation energy different from that of TiO$_2$ single crystals and was attributed to formation of Ti$_n$O$_{2n-1}$ phases after FIB processing.

The CeO$_2$ study involved high temperature conductivity studies on substrate-free self-supported nano-crystalline ceria membranes up to 800 K. Increasing
conductivity with oxygen partial pressure directly opposing the behavior of thin film devices ‘clamped’ by substrate has been observed. This illustrate that the relaxed nature of free standing membranes, and increased surface to volume ratio enables more sensitive electrical response to oxygen adsorption which could have implications for their use in oxygen storage devices, solid oxide fuel cells, and chemical sensors.

The work in this thesis advances the understanding of materials in freestanding membrane form and advances fabrication techniques that have not been explored before, having implications for sensors, actuators, SOFC, memristors, and physics of quasi-2D materials.
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In the mind’s eye
an untamed sea rages
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Thank you…

All of you for believing in me…
CHAPTER ONE

INTRODUCTION

1.1. Membrane structures and applications

Membranes are ubiquitous, found in almost anything from our cells to most sophisticated nano-technology energy solutions. Despite, being ever present in our lives, most studies probing the materials properties of these membranes have been done in a bulk form or as a film deposited on to a substrate. This was a serious scientific challenge as scientists were using bulk and film studies as proxies to understand properties of materials that are often used in suspended membrane form. For example ionic and electronic conductivity studies of YSZ\(^1\) and GDC\(^2\) are often carried out in the bulk material or as thin films when one of the primary motivation for executing these studies is for understanding carrier transport for applications in solid oxide fuel cells (SOFC).

Using bulk materials and films as a proxy to understand membranes pose two issues. One, films are mechanically and chemically bound by the substrate and two, the surface properties are drowned out by either the substrate or the large bulk contribution. Especially in cases of sputtered films, the residual stress from deposition would be present in the film.\(^3\) With chemical, ionic, and electrical properties dependent on the
strain of the materials, the properties of substrate clamped films would not match the properties of a freestanding membrane. For example, SOFCs are often in membrane architecture which are free of substrate clamping and the surface to volume ratio is much higher than the bulk materials.\textsuperscript{4} The natural approach would be to create membranes and study their properties. However, fabrication challenges in creating freestanding membranes of brittle materials have hampered the efforts to directly probe the membranes.

Enabled by recent fabrication technologies, the number of studies of freestanding membranes on materials such as polymers,\textsuperscript{5} graphene,\textsuperscript{6} and metals\textsuperscript{7} have increased and opened doors into new physics and applications. The studies outlined in this thesis will focus on oxides, as its brittle nature and chemical sensitivity has made it nearly impossible to study in a free standing membrane form.

1.2. Oxide membranes

Oxide membranes are a vital platform for sensors and actuators,\textsuperscript{8} energy conversion devices,\textsuperscript{9} and for investigating new condensed matter science.\textsuperscript{10} Figure 1 shows applications that utilize oxide membranes and benefits of nanoscale membranes in each application.
As seen in figure 1, oxide membranes are of interest in various technologies. Hence a deeper understanding of their properties and discovering new device architectures will have profound impact on our lives. Yet studies of oxide membranes are limited to mechanical studies or informs of hybrid membranes with thick supporting layers. The limitations on studies of membranes is primarily due to the difficulty in fabrication of membranes arising from mechanical considerations, which are laid out in the next section.

Figure 1: Applications of oxide membranes and benefits of nanoscale fabrication

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1.3. Mechanical properties of oxide membranes

Oxides are a brittle class of materials.\textsuperscript{11} Thus, making ultrathin oxide membranes with thickness less than 40nm requires extensive understanding of thin plate mechanics. Earlier understanding of optimizing membrane stability used boundaries stemming from conditions for film buckling and Weibull analysis of failure probability.\textsuperscript{12,13} Such approaches are useful in understanding the underlying fundamental mechanical considerations but were not verified experimentally. Kerman et al have demonstrated fabrication of membranes and have shown that buckling is not a failure mechanism.\textsuperscript{14} It was shown that it was necessary for membranes to buckle to stabilize thin brittle structures. Hence, a modified mechanical design have been introduced.\textsuperscript{15,16} Deeper understanding of the buckling patterns and elastic stability of the membranes were also demonstrated.\textsuperscript{17} In these studies, the key controllable parameter in determining membrane stability is the residual stress. Hence, to fabricate mechanically stable structures, understanding the influence of film growth parameters on film stress is vital.\textsuperscript{18,19} Therefore, film stress in the membrane must be tuned to result in stable elastic buckling configurations and prevent rupture of the membranes. In this study the film growth parameters have been optimized to create mechanically stable membranes but also present a new fabrication design that allows for stable membranes.
1.4. Oxides of choice

As afore mentioned, improved understanding of oxide membranes would lead to advancement in various technologies. This study demonstrates for the first time, rigorous electrical probing of freestanding self-supported nanoscale membranes. The thesis is divided into three main parts examining three materials with each part dedicated to the study of VO\textsubscript{2}, TiO\textsubscript{2}, and CeO\textsubscript{2}. For VO\textsubscript{2} we demonstrate amplified detection of surface effects and show that ionic liquid gating can be a surface limited effect. For TiO\textsubscript{2} we show formation of reduced oxides and Magneli phases due to membrane fabrication by ion milling. For CeO\textsubscript{2} we show changing conduction mechanisms vs. temperature due to stress relaxation of membranes and increased interaction with the oxygen ambient.
CHAPTER TWO

MIT MATERIALS & OXYGEN ION CONDUCTORS

2.1. Theoretical background of MIT

2.1.1. MIT materials

Metal-insulator transition (MIT) in correlated oxide systems has been an active area in condensed matter science since Morin reported an abrupt change in conductivity in binary transition metal oxides.\textsuperscript{20} Despite the efforts of many scientists the mechanisms of MIT have not been firmly explained yet. Figure 2 shows the transition temperature of various materials that undergo phase transitions.\textsuperscript{21}
Figure 2: MIT temperature of various materials. It is to note that magnetic, optical and strain factors may impact the MIT temperature. Reprinted from Ref. 21 with permission from Annual Reviews

As fig. 2 shows, a phase transition can be brought forth by manipulating the temperature of the oxide. It is also to note that phase transitions can also be brought forth by other methods such as, electrical\textsuperscript{22,23}, magnetic\textsuperscript{24}, optical\textsuperscript{25}, and strain\textsuperscript{26} manipulations. The material I will be discussing is vanadium dioxide (VO\textsubscript{2}). What is interesting about VO\textsubscript{2}
is that the phase transition occurs near 68°C with about five orders of magnitude change in resistivity.\textsuperscript{27}

### 2.1.2 MIT theories

The challenge with understanding MIT in correlated electron materials is that, unlike understanding physics of Si or semiconductors,\textsuperscript{28} a simple picture of non-interacting electron systems cannot be used. Hence, theories surrounding the MIT have been pioneered by Sir Nevill Francis Mott\textsuperscript{29}, Sir Rudolf Ernst Peierls\textsuperscript{30}, and Philip Warren Anderson\textsuperscript{31}.

Mott’s theory on MIT is based on electron-electron correlations, where the MIT occurs when the lattice constant becomes larger than a critical value that results in increased electron-electron interaction. In simpler terms, the metallic phase manifests when the carrier density reaches a critical threshold. Mott suggested that the critical density is noted by

\[ n_c^{1/3} a_H \approx 0.2 \]

where the \( a_H \) is the Bohr radius.\textsuperscript{29} This theory was then developed into the Mott-Hubard model, where the insulating phase is manifested by the electron-electron interaction, thus correlation effect of electrons.\textsuperscript{32}
Another theory that was developed to explain MIT excluded electron-electron interactions. The Peierls MIT theory considers the electron-phonon interaction to be the main driver of MIT. In a Peierls MIT, a crystal structure change is observed. The structural change results in the change in the band gap where an opening is created.

Lastly, the Anderson MIT theory illustrates the transition is triggered by disorder and not by electron correlation. For example, a strong disordered system like a heavily doped silicon, an MIT is observed via electron trapping by the defect states. Hence, randomly distributed defects can localize electrons that results in an insulating phase.

The material in question, VO$_2$, observes a transition from an insulating state to a metallic state when heated across the transition temperature of 68°C. In this transition the electronic resistivity drops by five orders of magnitude and a structural change is observed. The crystal structure transitions from an insulating monoclinic phase, M1, to a metallic tetragonal phase, as shown in Figure 3.
Figure 3: 3-D, a and b, and 2-D, c and d, Structural diagrams of VO$_2$ in the insulating phase, a and c, and in the metallic phase, b and d. Reprinted, a and b only, from Ref. 35 with permission from The American Association for the Advancement of Science.

The space group of M1 and R phases are identified as P2$_{1/c}$ and P4$_2/mnm$ respectively.$^{36,37}$ Amidst the structural transition, the vanadium atoms, or vanadium pairs, as shown in figure 2, are tilted from the octahedral planes, but upon heating is tilted towards the planes. Consequently the band structure changes, closing a band gap.$^{38}$ In the insulating phase, the 3d$_{||}$ band is split into a filled bonding 3d$_{||}$ and an empty anti bonding 3d$_{\perp}$.* The anti-bonding 3d$_{\perp}$* band is pushed up with respect to the Fermi energy. Therefore, a gap of about 0.6-0.7ev is created in the insulating state.$^{39,40}$ Going back to our
discussion on MIT theories, presence of both electronic and structural transition have gotten scientists interested on which theory dictates the MIT in VO$_2$.

The existence of an insulating state in VO$_2$ where the 3d energy band is half filled could not have been predicted by the simple band theory. It was the correlation of electrons that was used to explain the MIT in VO$_2$ by Mott in 1968.\textsuperscript{29} Immediately after, Goodenough proposed that a structurally triggered MIT must be the reason for MIT in VO$_2$ as it observes a structural transition.\textsuperscript{36} This kicked off the Mott transition vs. Peierls transition debate that is still an active topic today. More recently, Cavalleri et al observed that transition is delayed with respect to hole injection indicating band insulator characteristics.\textsuperscript{41} On the contrary, Kim et al, demonstrated that MIT and structural transition occur subsequently and not simultaneously, and that a monoclinic metal phase is formed in between the MIT and structural transition, strongly hinting that VO$_2$ is a Mott insulator.\textsuperscript{42} Additionally work by Okazaki et al highlights that MIT in VO$_2$ could be both Mott-Hubbard type and Peierls type.\textsuperscript{40} Biermann et al used theoretical calculations of dynamical mean field theory in conjunction with density functional theory within LDA to show that a combination of Mott and Peierls transition maybe taking place.\textsuperscript{43}
2.1.3. MIT triggers

In understanding theories of MIT, it is important to consider what triggers MIT. Temperature, bandwidth, and band filling are three primary ways to control and trigger MIT.\(^{44}\) As afore mentioned, temperature control is the most widely used to induce MIT and achieved by heating or cooling a sample across the transition temperature. The second method, bandwidth control, is achieved by inducing strain on the sample either through exertion of stress on to the sample or doping of the sample with differently sized impurities. The last method, band-filling, is achieved by altering the energy levels of dopants and acceptors through electronic manipulation.\(^{44}\)

\(\text{VO}_2\), similarly, can go through MIT via different triggers: thermal heating\(^{45}\), electrical field manipulation\(^{46}\), and photo-excitation.\(^{42}\) Application of a strong external field, may create a carrier density enough to reach the critical concentration, thus triggering MIT.\(^{46}\) Understanding these switching mechanisms could enable new electronic and photonic devices that range from sensors, optical switches, and non-volatile memory devices.

This concludes this section on basic background information on \(\text{VO}_2\). In subsequent parts of the discussion, we will explore how stress, substrate, and electrostatic gating via ionic liquids impact the MIT and what the underlying mechanism of ionic liquid gating is.
2.2. Mixed Ionic and Electronic Conductors

When one speaks of conductivity, the most common picture we conjure up is charge carried out by electrons. However Michael Faraday in 1833 discovered that Ag$_2$S observes an increase in electrical conductivity with rising temperature, contradicting typical trend of metallic conductors.$^{47}$ This discovery and studies of oxides led to the development of ionic conduction theory: current generated by movement of ions. With the understanding of electrical conductivity being carried out by ions in addition to electrons the total conductivity is expressed as

$$\sigma_{total} = \sigma_{ionic} + \sigma_{electronic}$$

This equation implies three types of electrical conductors. One pure electronic conductors, two pure ionic conductors, and three mixed conductors. This study looks at mixed conductors, primarily TiO$_2$ and CeO$_2$ for their ubiquitous use in various applications.

2.2.1. TiO$_2$

Perhaps of all wide band gap materials, TiO$_2$ is one of the most important materials technologically as it has diverse applications such as water splitting$^{48}$, photocatalysis$^{49}$, dye sensitized solar cells$^{50}$, sensors$^{51}$, memristors$^{52}$, and anodes for batteries$^{53}$. TiO$_2$ has at minimum of six polymorphs but the most commonly occurring
polymorphs are amorphous, anatase, and rutile, shown by fig. 4.\textsuperscript{54,55,56} Rutile is known to be the most stable phase macroscopically\textsuperscript{57} and at the nanometer scale, anatase is the most stable, thermodynamically speaking.\textsuperscript{58,59} Both rutile and anatase structures are tetragonal, where each titanium atom is octahedral coordinated by six oxygen atoms and each oxygen atom is surrounded by three titanium atoms as shown in fig 4.

![Structural diagram of rutile and anatase](image)

Figure 4: Structural diagram of rutile, a, and anatase, b, TiO$_2$ Reprinted from Ref 60 with permission of IOP Publishing, © IOP Publishing. All rights reserved.

The octahedron containing TiO$_6$ is slightly elongated in that the two Ti-O bonds are slightly longer.\textsuperscript{61} The distinguishing factor between the two structures is the way the octahedra are connected. In rutile phase they share two edges with other octahedral with
space group of $p4_{2/mnm}$ space group with lattice constants $a=0.4584\text{nm}$ and $c=0.2953\text{nm}$. In anatase form, they share four edges with space group $I4_{1/amd}$ with lattice constants $a=0.3733\text{nm}$ and $c=0.937\text{nm}$. The band gaps for rutile and anatase have been found to be $3.1\text{ eV}$ and $3.23\text{ eV}$ respectively.\textsuperscript{61,62,63} TiO$_2$ is known to be a mixed conductor that can have electrons or ions acting as the main carriers depending on stoichiometry. As such, the main conduction mechanisms in TiO$_2$ are facilitated by defects. The subsequent parts in this chapter will illustrate defect types and defect chemistry in TiO$_2$.

### 2.2.2. Types of point defects in TiO$_2$

At a finite temperature, there is a concentration of point defects that are always present due to entropy.\textsuperscript{64} For ionic solids, like TiO$_2$, charge neutrality is facilitated by simultaneous creation of oppositely charged defects. Hence, the concentration of a defect pair can be represented by

$$[C_+][C_-] = \exp\left(\frac{\Delta S^\circ}{k}\right) \exp\left(-\frac{\Delta H^\circ}{kT}\right)$$

Where $\Delta S$ is the entropy and $\Delta H$ is the enthalpy per defect. The reader will recognize that this equation can be written in terms of free energy.

$$[C_+][C_-] = \exp\left(-\frac{\Delta G^\circ}{kT}\right)$$

The point defects thus far discussed are intrinsic point defects that occur naturally in a material. There are other types of point defects that are extrinsic, doped or injected
impurities. The defects are often represented using the Kroger-Vink convention. In this study the intrinsic and extrinsic defects are noted as follows.

**Intrinsic**

- $V_0^{**}$: Oxygen vacancies
- $T_{i_l}^{****}$: Titanium interstitials
- $V_{Ti}^{****}$: Titanium vacancies
- $O_{i_l}^{**}$: Oxygen interstitials

**Extrinsic**

- $A_{Ti}^{'}$: Trivalent atom in Ti site
- $B_{Ti}^{*}$: Pentavalent atom in Ti site

### 2.2.3. Defect Chemistry in TiO$_2$

The defect chemistry of TiO$_2$ is complex when compared to other wide band gap oxides such as SrTiO$_3$ and CeO$_2$. The complexity is mainly due to the existence of two mobile defects $V_0^{**}$ and $T_{i_l}^{****}$, that can have comparable concentrations. This poses challenges in defect identification as typical experimental procedure for understanding defect chemistry is performing conductivity measurements over a range of partial pressure of oxygen. One can imagine, if there was only one mobile defect, the
conductivity change with respect to oxygen partial pressure could directly be linked to the concentration of the mobile defect being created. However, with a mix of two mobile defects it is difficult to gauge, which defect contributes how much to the conductivity. Furthermore, the m-value, value which the relationship between conductivity vs. pO\textsubscript{2}, defined as $\sigma = pO^{m}_2$, for $V^m_0$ and $Ti_l^m$ are very similar at reducing pO\textsubscript{2}, m= -1/6 and -1/5 respectively. Hence, this led to a debate about the defect chemistry of TiO2 in the past.\textsuperscript{67,68,69,70}

The intrinsic defect reactions of bulk TiO\textsubscript{2} are cation Frenkel and Schottky reactions. Anion Frenkel defects are not considered since they are unlikely to form as indicated by theoretical studies.\textsuperscript{71} The electron and hole defects created by excitation across the band gap is also included in the discussion.

The cation Frenkel defect reaction with the mass action law is,

$$Ti_i^X + V_i^X \rightleftharpoons V_{Ti}^{''''} + Ti_l^{****}$$

$$K_F = [V_{Ti}^{''''}][Ti_l^{****}] = \exp\left(\frac{-\Delta G_F^o}{RT}\right)$$

Similarly the Schottky defect reaction with the corresponding mass action law is

$$Ti_i^X + 2O_2^{X} \rightleftharpoons V_{Ti}^{''''} + 2V_{O}^{**} + TiO_2$$

$$K_S = [V_{Ti}^{''''}][V_{O}^{**}]^2 = \exp\left(\frac{-\Delta G_S^o}{RT}\right)$$

The carrier equilibrium of for electron and hole pair is

$$Null \rightleftharpoons e^+ + h^+$$
\[ K_i = [e'][h^+] = np \]

These defects are known to be dependent on \( pO_2 \). Thus the following sections will illustrate defect chemistry in three conditions, extremely reducing, strongly reducing, and near neutral/oxidizing conditions.

**Extreme reduction regime**

Extremely reducing atmosphere where \( pO_2 \) is below \( 10^{-12} \) bar with \( T > 1000^\circ C \), presents a higher concentration of titanium interstitials vs. oxygen vacancies.\(^{66}\) The titanium interstitial formation equation is given by

\[
Ti^X_{Ti} + 2O^X_\emptyset \rightarrow Ti^{****}_i + 4e' + O_2
\]

\[
K_{ER}^{Ti} = [Ti^{****}_i][e']^4pO_2
\]

The charge neutrality condition is satisfied when

\[
[e'] = 4[Ti^{****}_i]
\]

Combining the equations we obtain

\[
[e'] = (4K_{ER}^{Ti})^{1/5}pO_2^{1/5}
\]

What this shows is that the majority defects \( Ti^{****}_i \) are electrically compensated by electrons with \( m = -1/5 \). It is to note that high concentration of electrons and \( Ti^{****}_i \) there are charge trapping of electrons by \( Ti^{****}_i \) giving rise to \( Ti^{***}_i \) species as well. In the case \( Ti^{***}_i \) exist, then \( m = -1/4 \).
**Strongly reducing regime**

In this regime where \(10^{-12} < \text{pO}_2 < 10^{-5}\) bar, \(T \sim 1000^\circ\)C, oxygen vacancy concentration is slightly higher than titanium interstitials. The defect equation with charge neutrality condition is

\[
O^+_0 \rightleftharpoons V^{**}_0 + 2e' + \frac{1}{2}O_2
\]

\[
K^0_{SR} = [V^{**}_0][e']^2 pO_2^{1/2}
\]

\[
[e'] = 2[V^{**}_0]
\]

Giving rise to

\[
[e'] = (2K^0_{SR})^{1/3} pO_2^{1/6}
\]

We can see that in this regime the m value results in -1/6 where electrons are compensating \(V^{**}_0\).

**Neutral regime and oxidizing regime**

In this regime the defects \(Ti^{****}_i\) and \(V^{**}_0\) are compensated by \(V^{****}_i\).

\[
Ti^{X}_Tl + O_2 \rightleftharpoons V^{****}_Tl' + 4h^* + TiO_2
\]

\[
K_{OX} = [V^{****}_Tl'][h^*]^4 pO_2^{-1}
\]

With the charge neutrality condition now being

\[
4[V^{****}_Tl'] = 2[V^{**}_0]
\]

combining with above equations and equations from strongly reducing case we obtain
\[ K_{ox} = \left[ \frac{K^0_{SR}}{[e']^{1/2} pO_2} \right] [h^*]^4 pO_2^{-1} \]

Solving for electron concentration we obtain

\[ [e'] = \left[ \frac{K^2 L K^0_{SR}}{K_{ox}} \right]^{1/6} pO_2^{-1/4} \]

As we can see, by measuring conductivity vs. \( pO_2 \) we are able to discern the reducing regime and the corresponding defect chemistry by looking at the \( m \) value. A more in-depth science pertaining to our specifics of the study are discussed in subsequent chapters.

2.2.4. Ce\( \text{O}_2 \)

Cerium dioxide, Ce\( \text{O}_2 \) has been extensively studied for the past half a century.\(^{72} \)

Due to its ubiquitous use, Ce\( \text{O}_2 \) has been established as a model system for understanding mixed ionic-electronic conduction and for understanding fluorite structures. Similar to applications of Ti\( \text{O}_2 \) above, Ce\( \text{O}_2 \) is prominently found in SOFCs\(^{73} \), catalysis\(^{74} \), sensors\(^{75} \), and memristors.\(^{76} \)

Ce\( \text{O}_2 \) has a fluorite structure which is shown in figure 5.
Each Ce atom is surrounded by eight equivalent nearest O atoms. Alternatively all of the tetrahedral sites of an FCC oxygen matrix have been filled with Ce atoms. Consequently CeO$_2$ has a space group Fm$ar{3}$m, with a melting point of 2475°C, lattice parameter of 0.541135nm.$^{77}$
2.2.5. Defect chemistry of CeO$_2$

Charge conduction is facilitated by defects in CeO$_2$. The following equations show three types of defect creation scenarios in CeO$_2$.

\[
2O_0^\times + Ce_{Ce}^\times \rightleftharpoons 2V_0^{\bullet\bullet} + V_{Ce}^{''''} + CeO_2
\]

\[
O_0^\times \rightleftharpoons V_0^{\bullet\bullet} + O_i^{'''}
\]

\[
Ce_{Ce}^\times \rightleftharpoons Ce_{Ce}^{'''''} + V_{Ce}^{''''''}
\]

The first equation shows creation of a Schottky defect while the 2$^{\text{nd}}$ and 3$^{\text{rd}}$ shows creation of anion Frenkel and cation Frenkel defects. The formation energy for these defects in a perfect crystal are 3.33 eV, 2.81 eV, and 8.86 eV for Schottky, anion, and cation Frenkel defects respectively.\textsuperscript{78} Just from comparing the energies one can see that creating a Frenkel defect is less likely. Consequently, it is rarely observed in nature.

Based on oxygen self-diffusion studies, it has been accepted that the charge compensating defect in CeO$_2$ are oxygen vacancies and not interstitial Ce species.\textsuperscript{79} The ionic conduction in ceria are hence carried out via oxygen vacancy conduction.

Above illustrates the defect chemistry and defect creation for ionic conduction, however, being an MIEC it is important to consider electronic conductivity in CeO$_2$ which occurs via polaron hopping between the 3+ and 4+ states. The reduction of Ce$^{4+}$ atoms to Ce$^{3+}$ from one Ceria atom to another facilitates polaron hopping. Figure 6
shows an illustration of polaron hopping coupled with the movement of oxygen vacancies.

![Figure 6: Illustration of Polaron Hopping in CeO$_2$](image)

Orange spheres depict Ce, blue spheres depict O, purple spheres show Ce$^{3+}$, and white sphere shows an oxygen vacancy.

The hopping mechanism can be written in an equation form

$$O_0^X + 2Ce_{ce}^X \rightleftharpoons V_{o}^{*} + 2Ce_{ce}' + \frac{1}{2}O_2$$

$$Ce^{3+} \rightleftharpoons Ce^{4+} + e'$$

As one can see the hopping of an electron from Ce atom to another coupled with the motion of positively charged oxygen vacancies facilitates electronic conduction. As seen in equation above low pO$_2$ would create more Ce$^{3+}$ leading to an increased electron
conduction. Figure 7 shows increasing conductivity of CeO\textsubscript{2} with decreasing pO\textsubscript{2} across a wide range of temperatures.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Conductivity of CeO\textsubscript{2} vs. pO\textsubscript{2}}
\end{figure}

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To have a better understanding of conductivity of CeO\textsubscript{2} and its relationship to pO\textsubscript{2}, the figure, consider the following

The partial conductivities of electronic conduction and ionic conduction can be expanded as so,

\begin{align*}
\sigma_{ionic} &= 2q[V_0^{**}]\mu_{V_0^{**}} \\
\sigma_{electronic} &= nq\mu_e = nq \left(\frac{\mu_0}{T}\right) \exp\left(-\frac{E_H}{kT}\right)
\end{align*}
Where $\mu_0$ is the temperature independent mobility constant, $E_H$ is the hopping energy.

Considering the equilibrium constant and the charge neutrality condition at low oxygen pressure,

$$O_2^x \rightleftharpoons V_0^{**} + 2e' + \frac{1}{2}O_2$$

$$K_{\text{redux}} = [V_0^{**}] [e']^2 pO_2^{1/2} = K_{\text{redux}}^0 \exp \left( -\frac{\Delta H}{kT} \right)$$

$$[e'] = 2[V_0^{**}]$$

We arrive to

$$[e'] = (2K_{\text{redux}})^{1/3} pO_2^{-1/6}$$

From the above equation, similar to TiO$_2$ in strongly reducing regime, the electron concentration is related to the oxygen pressure by $m=-1/6$

Taking into account the electronic conductivity and relating it to the above equation,

$$E_A = \frac{\Delta H_R}{3} + E_H$$

The electrical conductivity of pure CeO$_2$ was studied by Ruloph who found an $m$ number of -1/5.6.\textsuperscript{81} As noted in our equations above, such a negative slope obtained by Ruloph’s experiments indicate electron mediated conduction via polaron hopping.\textsuperscript{82}
CHAPTER THREE

EXPERIMENTAL METHODS

Before diving into the specifics of each of the studies, and experimental designs, this chapter sheds light on some common experimental techniques used.

3.1. Basics of sputtering

Vapor phase film deposition has been extensively used due to three main factors, the substrate temperature could be controlled, the wide variety of deposition materials, and opportunities for in-situ sample analysis.\textsuperscript{83,84} The properties of the film are critically affected by the temperature of the substrate during deposition. To this fact, the benefit of being able to control the substrate temperature in a vapor phase film deposition was critical in the advancement of film synthesis.

There are different types of vapor phase deposition techniques, however they are typically classified as physical vapor deposition PVD, which includes e-beam evaporation, laser ablation, MBE, PLD, and sputtering. Sputtering is a film growth process where a deposition material is bombarded by Ar+ plasma to create the vapor. The main advantages of sputtering are, any material could be sputtered, a uniform film could be created in terms of thickness and composition, and the composition of the film
could be controlled by controlling the reactive gases and co-sputtering different materials.

The sputtering with a DC power source is the simplest technique that just requires two electrodes: a cathode where the target is placed and the plasma is bombarded and at the anode where the substrate is held for deposition. By applying a voltage across these two electrodes, the sputtering discharge is maintained and the positive Ar ions are accelerated to the cathode.

In the case of insulating materials such as oxides, the DC technique would not work as one would observe build up of charge on the surface of the oxide target. To sustain a plasma discharge on an insulating target a RF power source is used with a frequency of 13.56 MHz. At such high frequencies, ions can not follow the switching and electrons can neutralize the positive charge buildup on the surface of the oxide target. The Ar plasma generated by the power source bombard the target ejecting “vapor” of atoms.

To increase the efficiency and the rate of Ar bombardment, magnets are placed below the target. Due to the effects of electric and magnetic fields, electrons are held near the target showing cycloidal motion, thus increasing the plasma density right near the target leading to increased sputtering rate.
3.2. Photolithography

Photolithography is one of the most widely used techniques in micro-fabrication for patterning films and electrodes down to the sub-micron regime. This is achieved by using optical imaging techniques and photosensitive materials. The general procedure of photolithography involves the following steps: Preparing the sample, photoresist coating, alignment, UV light exposure, development of exposed areas, desired processing such as etching or deposition of additional materials, and resist removal.

Photoresist is a class of polymers whose solubility is manipulated by exposure to UV. Two types of photo resist exist, positive and negative photoresist. A positive resist is the type where the UV exposed area is made insoluble and a negative resist is the type where UV exposed area is made soluble. Typically positive photoresists give rise to smaller feature lengths that may aid in creating smaller devices. The UV sourced used in this study is a mercury vapor lamp with a wavelength ranging from 310nm to 440nm. The step by step recipe for photolithography used in this study is as follows.
1) Prepare the sample by acetone and isopropyl alcohol cleaning

2) Apply s1813 photoresist on the sample via spin coating at 3000rpm for 40 s

3) Pre exposure bake for 2 minutes at 115C

4) Place the sample into the aligner

5) Align the sample features to the desired features on the mask

6) Apply UV for about 2 seconds to 4 seconds depending on the power of the lamp

7) Develop the photo resist with CD26 for 50s and rinsing with deionized water for 90s

8) Apply desired fabrication techniques, either KOH etch, RIE, or deposition of metal

9) Remove the remaining photoresist using Remover PG, acetone, and IPA
3.3. **Scanning electron micrography**

An SEM is a microscope that uses electrons instead of photons to image small features. A typical schematic of an SEM is shown in Figure 8.

In an SEM, an electron beam is emitted from an electron gun with energies ranging from 0.1keV to 40keV. This beam is focused by a couple of condenser lenses to make a small beam with few nanometers in diameter. This beam is passed through what’s...
called a scanning coil that scans an area much like how older CRT TV screens worked. When the beam interacts with the sample, the electrons lose energy and are either absorbed or scattered. The scattered electrons are collected by electron detectors. The collection of amount of scattered electrons over very small areas put together generates an image, much like optical imaging where scattered photons are detected by our eyes or cameras.

Backscattered electrons BSE are high energy electrons that are scattered out of the sample by elastic scattering with the sample atoms. The heavier elements backscatter electrons more strongly than lighter elements and therefore appear brighter in the image created. It is a useful technique to generate contrast between areas with different chemical compositions.

3.4. Focused Ion Beam

FIB is a technique that uses local ablation or deposition of materials to create features at the nano-scale. Similar to an SEM charged particles are focused into a very small beam that then interact with the sample. Instead of using electrons as charged particles FIB typically uses gallium ions.

To generate the ions, gallium metal is placed with a tungsten needle and is heated until the gallium melts and coats the tungsten. The force of surface tension and
electric field forces the melted gallium into a Taylor cone. The tip of the cone is extremely small ranging few nanometers in diameter. This creates a huge electric field that causes ionization of the gallium atoms. The ions are accelerated to an energy of 1-50 keV and is focused by a series of electrostatic lenses. The focused beam is then passed through a scanner that manipulates the beam to scan over a defined area.

The ion beam bombarding a sample can be used as a source to sputter a small area. Figure 9 shows a diagram of a substrate being sputtered. This enabled patterning of an area by effectively “etching” away the unwanted material.

The ion beam can also be used to deposit materials in gas assisted metal deposition. At lower powers, instead of sputtering away the material, the ion beam is able to dissociate precursor gases. The dissociated species that are immediately next to the sample adsorb to the surface completing the deposition. Figure 9 shows FIB milling and gas assisted metal deposition.

![Diagram of FIB milling and gas assisted metal deposition](image)

Figure 9: Diagram of FIB milling, a, and gas assisted metal deposition, b.

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3.5. Transmission Electron microscopy

TEM is an imaging technique that uses electrons to imagine very small feature sizes even down to sub nm range. Unlike SEM, a TEM uses transmitted electrons instead of surface scattered electrons to image. An overview of TEM can be found in work by William and Carter.\(^5\)

A TEM consists of an electron gun that is typically a tungsten filament or lanthanum hexaboride. Once the electrons are emitted they are accelerated through a voltage of 100kV to 300kV. The emitted beam is then focused and manipulated by electromagnetic lenses that focus the beam to a very small area. Usually there are three stages of lensing: the condenser lens, objective lens, and projector lens. The condenser focuses emitted electrons to a primary beam. The objective lens focus the beam through the sample to converge the electrons to a tiny spot. Then the projector lens takes the beam and expands it to an imaging device. Figure 10 shows a schematic of a TEM setup.
Figure 10: Diagram outlining the internal components of a basic TEM system

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Bright field TEM

Bright field imaging is an imaging mode where the contrast is formed directly by occlusion and absorption of electrons in the sample. Regions with heavier elements will appear dark while regions with no materials or lighter elements will appear bright. The image can be described as a simple 2d projection of the material down the optic axis.

Electron Diffraction,

TEMs can also be used to obtain electron diffraction patterns. This can be achieved by adjusting the magnetic lenses such that the back focal plane of the lens is placed on the imaging plane.
3.6. X-Ray Diffraction

Taking advantage of Braggs law, \( m\lambda = 2d \sin \theta \), also shown in figure 11, one setup for XRD is defining the rotating axis of the sample and detector as \( \theta \) and \( 2\theta \). The detector can be rotated about the sample to scan at different angles. In single crystals, the crystal planes that are parallel to the surface and that satisfy Braggs law are detected and the scattered beams are intense in few points in space. For polycrystalline samples, since the grains are randomly oriented, all grains should satisfy the Bragg law distributing the scattered beam into a cone. However, highly textured or epitaxial films, some diffraction peaks will be missing due to the orientation of the grains. This poses challenges in the \( \theta - 2\theta \) scans.

![Figure 11: Schematic of x-ray diffraction; a, illustration of the conditions required for Bragg diffraction to occur and, b, relationship of the incident \( \mathbf{k}_0 \), diffracted \( \mathbf{k}_h \), and scattering \( \mathbf{k} \) with respect to the crystal. Planes of atoms are indicated by dotted lines](image-url)
Glancing incidence

A glancing incident scan is used to remove substrate peaks and any peaks arising from texturing. In a glancing incidence scan, the detector is sweeping across the 2θ while the source, incident beam, is only a few degrees off of the surface of the sample.
3.7. Electrical measurement techniques

Linear 2/4 point measurement

An easy way to take resistivity measurements when the geometry of the sample is well known is to take a 2 point or 4 point linear measurement. A current is fed from a source contact A to drain contact B and probing contacts C and D measure the voltage. A 2 point measure is when the source contact A and the drain contact B become probing contacts as well simultaneously measuring current and voltage.

Van der Pauw

The above mentioned technique is limited in that the geometry of the sample has to be well known and in a linear shape. A more sophisticated technique has been developed to determine the resistivity of a sample. In the Van der Pauw technique a square sample is needed with corners of the square sample being connected to a metal contact. By applying current through two adjacent contacts and measuring voltage across the opposing contacts in all possible combinations, and combining the results with the following equations we are able to obtain the sheet resistance $R_S$.

$$R_{\text{vertical}} = \frac{R_{12,34} + R_{34,12} + R_{21,43} + R_{43,21}}{4}$$

$$R_{\text{horizontal}} = \frac{R_{23,41} + R_{41,23} + R_{32,14} + R_{14,32}}{4}$$

$$e^{-\pi R_{\text{vertical}}/R_S} + e^{-\pi R_{\text{horizontal}}/R_S} = 1$$
CHAPTER FOUR

FREESTANDING SUB-50nm VANADIUM DIOXIDE MEMBRANE TRANSISTORS: FABRICATION AND IONIC LIQUID GATING STUDIES

4.1. Introduction

This section illustrates a robust lithographic patterning method to fabricate self-supported sub-50nm VO$_2$ membranes that undergo a phase transition. Utilizing such self-supported membranes, shift in metal-insulator transition temperature arising from stress relaxation and consistent opening of the hysteresis have been observed. Electric double layer transistors are then fabricated with the membranes and compared to thin film devices. The ionic liquid allowed reversible modulation of channel resistance and allowed distinguishing bulk process from the surface effects. From the shift in the metal-insulator transition temperature, the carrier density doped through electrolyte gating is estimated to be $1 \times 10^{20}$ cm$^{-3}$. Hydrogen annealing studies showed little difference in resistivity between the film and the membrane indicating rapid diffusion of hydrogen in the vanadium oxide rutile lattice consistent with previous observations. The ability to fabricate electrically wired suspended VO$_2$ ultra-thin membranes create new opportunities to study mesoscopic size effects on phase transitions and may also be of interest in sensor devices.
4.2. Previous studies on VO$_2$ membranes

Self-supported ultra-thin oxide nanostructures are gaining increased attention due to their potential use in energy and environmental technologies, micro-electromechanical systems, and sensors.$^{90,91}$ For example, structures where functionality is determined by surface to volume ratio (such as but not limited to chemical sensors) could benefit greatly from ultra-thin suspended device architectures. Furthermore, creating such quasi 2-dimensional free standing membrane with correlated oxides may also lead to new insights into mesoscopic electronic phenomena.

Vanadium oxide (VO$_2$) is of contemporary interest as a model material to investigate correlated electron phenomena, metal-insulator phase transition mechanisms, and as well as for potential applications in switching devices. While studies have been conducted on thin films, hybrid layers of VO$_2$ supported on other materials,$^{92,93}$ and various nanosized and microscale crystals, fundamental phase transition properties and electrical measurements of self-supported VO$_2$ thin film membranes removed from substrate confinement have not been reported yet to the best of our knowledge, in part due to the experimental challenges in the fabrication of such a structure.

Previous attempts of fabricating self-supported VO$_2$ thin film membranes primarily exist in a VO$_2$/supporting layer architecture where a thin VO$_2$ film is
deposited on a thicker underlayer. For example, VO$_2$ supported on Si$_3$N$_4$ membranes, attempted by Viswanath et al., proved to be difficult due to lattice distortion and sharp stress changes accompanying MIT in VO$_2$ that results in micro-cracks and morphology changes.\textsuperscript{93} Figure 12 shows micro-cracks present on a VO$_2$ film on Si$_3$N$_4$.

![Image](image-url)

Figure 12: Optical image of VO$_2$ film on Si$_3$N$_4$ showing micro-cracks resulting from phase transitions. Reprinted from Ref. 93 with permission from Cambridge University Press.

A recent example of stable VO$_2$/ supporting layer architecture was demonstrated by Pellegrino et al. in which a 70nm VO$_2$ film deposited on 200nm thick TiO$_2$ membrane show mechanical stability across the MIT.\textsuperscript{92}
This study demonstrates, for the first time, fabrication of self-supported edge clamped sub-50 nm vanadium dioxide membrane through an arduous optimization of fabrication processes, and report its electrical properties in Van der Pauw measurements as well as three-terminal field effect device geometry using ionic liquid gate dielectric. There is interest in electrostatic doping of correlated materials due to the possibility to induce electronic phase transitions by carrier doping. However, gating of VO$_2$ using traditional gate oxide architectures proved to be challenging due to the short screening length. Hence, ultra-thin VO$_2$ channels are desirable while being experimentally challenging. Consequently, electrolyte gating using ionic liquids, which enables large carrier accumulation compared to solid gate dielectrics and gate-controlled phase transitions, is of interest. It is however important to note that due to complexity of potential electrochemical reactions or interface instability at large voltages and the slow gating dynamics, one has to exercise caution in interpretation of the device response. Here, we investigate electrolyte gating with ionic liquid on the electrical properties of VO$_2$ films and membranes and compare the results with annealing VO$_2$ films and membranes in hydrogen to provide insight into the doping mechanism.

We find consistent difference in the VO$_2$ electrical properties in thin film versus free standing membrane and attribute it to the relaxation of strain. We find that the membrane is more sensitive to ionic liquid gating than a thin film on a substrate and explain these observations by distinguishing the bulk process from the surface effects.
Comparing the ionic liquid observations to the hydrogen exposure experiments also suggest that hydrogen doping and electrolyte gating are likely based on different mechanisms. The results show that mechanically stable free-standing membrane of VO$_2$ can be fabricated, could enhance surface effects, and be of potential interest in devices. Further, the techniques presented here are broadly relevant to fabricate self-supported nanostructures for electrical interrogation.

4.3. Experimental details

4.3.1. Fabrication method

Nano-scale self-supported free standing membranes of VO$_2$ have been prepared by the method outlined below. Fig. 13 shows a detailed flow diagram of the processing steps.
Figure 13: Process diagram of the ultra-thin membrane fabrication process

(a) S1813 is spun and patterned, (b) The Si$_3$N$_4$ is etched using RIE (c) The Si substrate is etched using KOH, leaving behind a small Si$_3$N$_4$ membrane (d) Functional Oxide, VO$_2$, is deposited (e) S1813 is spun on and patterned leaving a diamond patterned resist over the Si$_3$N$_4$ membrane, (f) The oxide in the unwanted area is etched away using RIE, (g) S1813 is spun on and patterned for metal contacts at the corners of the oxide, (h) Desired metal (Ti/Au) is deposited and lifted off to create metal contacts, (i) The Si$_3$N$_4$ under the oxide is etched away by RIE from the back side of the wafer.
Double side polished 500um thick Si wafer with 200nm of low stress low pressure chemical vapor deposition (LPCVD) Si$_3$N$_4$ on both sides was obtained from University Wafers. Shipley S1813 photoresist is spun on one side of the wafer and squares with desired sizes are patterned using a Karl-Suss MJB4 mask aligner and CD-26 as a developer. The Si$_3$N$_4$ on the patterned areas is etched using a South Bay reactive ion etcher (RIE) to expose the Si substrate. By taking advantage of anisotropic etch of Si in KOH, a membrane of Si$_3$N$_4$ on the un-patterned side of the wafer is created. A thin layer of VO$_2$ is deposited on top of the Si$_3$N$_4$ membranes by radio frequency (RF) sputtering from a V$_2$O$_5$ target. VO$_2$ films were grown under different oxygen pressure conditions as a means to tune their electrical properties and experimental conditions are listed in Table 1.

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Table 1: Deposition Parameters of Conditions A, B, and C
Once the VO$_2$ film is grown, Shipley S1813 is patterned and used as a mask for etching VO$_2$ film in unwanted areas, leaving a desired diamond pattern on top of the Si$_3$N$_4$ window in such a way that the corners of the diamond pattern are at the midpoint the Si$_3$N$_4$ membrane edge. Fig. 14 (a) shows the desired diamond pattern VO$_2$ on the Si$_3$N$_4$ membrane.
Figure 14: Figure 14: Optical Images of Si$_3$N$_4$ Membrane and VO$_2$ Film and Membrane Devices. (a) VO$_2$ film patterned into a diamond, (b) Si$_3$N$_4$ membrane buckling (c) 80um diagonal VO$_2$ film on Si$_3$N$_4$, (d) 80um diagonal free standing VO$_2$ membrane, (e) 20µm diagonal free standing VO$_2$ membrane.
The images are in false color. (a) Note how only the corners of the oxide touch the edge of the Si$_3$N$_4$ Membrane. This is a crucial step for the oxide to be robust during RIE. (b) The purple area is Si$_3$N$_4$ on Si and the blue area is Si$_3$N$_4$ membrane. Note that there is large distortion from Si$_3$N$_4$ buckling due to low stress Si$_3$N$_4$ being clamped to the Si at the edge of the membrane. The buckling occurs during RIE as the thickness of Si$_3$N$_4$ membrane is reduced. Any oxide present near the edge of the Si$_3$N$_4$ membrane results in cracking during RIE due to this buckling. Hence, our geometry was chosen from numerous experiments to minimize contact with the edge of the Si$_3$N$_4$ membrane. The black spaces in (c) and (d) are free space. Note that the distorted shape of the VO$_2$ membrane in (d) is from relaxation of tensile stress. (e) the device in this figure has minimal distortion.

The selection of a diamond geometry with only the corners touching the substrate is chosen to make Van der Pauw measurements possible. Furthermore, the chosen shape allows the relaxation of stress of the Si$_3$N$_4$ during the back side RIE etch. As the low stress LPCVD Si$_3$N$_4$ is made thinner, it begins to deform and buckle causing mechanical stress on whatever film is layed on top. Fig. 14(b) shows the buckling pattern of the Si$_3$N$_4$ as it is made thinner. From attempting different geometries, it was found that if the VO$_2$ film had a significant contact with the edge of the Si$_3$N$_4$ window, the VO$_2$ film will crack during the backside RIE of the Si$_3$N$_4$ and hence is an important design parameter in fabricating robust membranes. Metal contacts are made at the
corners of the diamond pattern by RF sputtering of 6nm Ti and DC sputtering of 200nm
of Au for four probe Van der Pauw measurement. Finally, the Si$_3$N$_4$ under the VO$_2$ is
etched away from the backside by using RIE leaving a self-supported free standing
nano-scale VO$_2$ membrane as shown in Fig. 14 (d) and (e).

4.3.2. Measurement techniques

Van der Pauw measurements as a function of temperature were repeated for both
VO$_2$ film on Si$_3$N$_4$ and the suspended VO$_2$ membrane for a comparison of the resistivity
($\rho$) vs. temperature (T) curves. Afterwards, the VO$_2$ film on Si$_3$N$_4$ (film device), Fig.
14(c), and VO$_2$ free standing membrane (membrane device), Fig. 14(d), were subjected
to systematic ionic liquid gating as well as hydrogen exposure treatments.

Ionic liquids are molten salts with high ionic conductivity but negligible
electronic conductivity and have been used to modify carrier densities in various
semiconducting materials.$^{97,98}$ When applying a gate voltage above its melting
temperature, ions can move within the liquid to the ionic liquid/VO$_2$ interface, forming
an electric double layer and inducing carrier density change in VO$_2$. After cooling
below its melting temperature, the mobility of ions in the ionic liquid becomes lower
and the ions become frozen at the interface and carrier modulation is preserved even
without a gate bias as long as the ambient temperature does not approach the melting
temperature. The ionic liquid used in the electrolyte gating experiments is 1,2,3,4,5-pentamethylimidazolium bis(pentafluoroethylsulfonyl)imide (M₅I-Beti) from Covalent Associates Incorporated, USA with a melting temperature of ~ 98°C. First, the electrolyte was dropped onto the sample surface at room temperature. Then the temperature was raised to 115 ºC, where the ionic liquid melted and covered the entire surface of VO₂ film/membrane. Gate bias was applied from a probe inserted into ionic liquid while one of the four electrodes was grounded as shown in Fig. 15.

Figure 15: Schematic of Electrolyte Gating of VO₂ forming an electric double layer transistor. The VO₂ membrane is completely submerged in the ionic liquid.
The system was kept under a fixed gate bias for 15 minutes at 115 °C and then cooled down to room temperature with gate bias applied. Afterwards, the gate bias was removed and Van der Pauw measurements were performed with temperature ranging from 20°C to 90°C. Another set of both film and membrane devices, (grown at the same time as previous samples,) were fabricated and exposed to 5% H$_2$ in Ar balance in an environmental probe station for an hour at 100°C and 150°C. Then Van der Pauw measurement was performed to obtain $\rho$ vs. $T$ curves and the effect of H$_2$ on VO$_2$ film and membrane is compared to that of ionic liquid gating.
4.4. Results and Discussion

4.4.1. Electrical probing of VO$_2$ membranes

Fig. 16 (a), (b), and (c) show the temperature dependent resistivity of films and membranes grown under conditions A, B, and C respectively. Fig 16 (d), (e), and (f) show the dlog($\rho$)/dT of films and membranes of samples A, B, and C respectively.

Figure 16: (a), (b), (c) Temperature vs. Resistivity $\rho$ plots, (d), (e), (f) Temperature vs. Derivative of the Log($\rho$). Note that for (a) and (b), the transition temperature is depressed due to the relaxation of tensile stress. The tensile stress originates from lack of O2 during deposition. In (c) the O2 partial pressure is optimized during deposition to yield a nearly stress-free VO2 and the transition temperature is comparable to that of bulk single crystals. One trend that is consistent in all of the samples was that the width of the hysteresis increased. Gaussian fitting did not yield a good fit for (d)
The transition temperatures were determined by Gaussian peak of the dlog(ρ)/dT curves. One major difference in the electrical properties between a VO₂ film and a free standing membrane grown with no oxygen is that the transition temperature is depressed. In Fig. 16(a) the transition temperature is shifted for the membrane by -6°C and -8°C during heating and cooling respectively. In Fig. 16 (b) the transition temperature difference for heating and cooling curves between a film and a membrane (T_{membrane} - T_{film}) are -3°C and -4.9°C respectively. A decrease in the VO₂ transition temperature is indicative of manifestation of compressive stress or relaxation of tensile stress.⁹⁹,¹⁰⁰ The deformation of the membrane’s shape from a square, Fig 14(c), to an asteroid, Fig 14(d), is indicative of relaxation of tensile stress in the membrane, which is in agreement with the shift in the transition temperature going from a film to a membrane in our devices.

4.4.2. Effect of strain on MIT temperature

The dependence of MIT temperature on strain has been attributed to strain on the c axis. Figure 17 shows the MIT temperature with varying C axis lattice parameter.
Figure 17: MIT temperature $T_{MI}$ vs. lattice parameter $c$ for the VO$_2$ films deposited on TiO$_2$ (001) and TiO$_2$ (110) substrates. Reprinted from ref. 100 with permission from AIP Publishing

As one can see from Figure 17, there is a strong correlation between the lattice parameter along the C axis and MIT. Compression along the C axis illustrates decrease in the MIT temperature while expansion along the C axis illustrates increase in MIT temperature. This clearly illustrates that there is a driving force that makes the metallic
state more easily accessible. One thing to note about the C axis is that the $V^{4+}$ to $V^{4+}$ distance is measured along it. Hence, the $V^{4+}$ to $V^{4+}$ distance would decrease with decreasing lattice parameter along the C axis. This reduction in the $V^{4+}$ to $V^{4+}$ distance would cause larger overlap of the d orbitals. Figure 18 shows an orbital diagram of V atoms with corresponding band energies.
Figure 18: a, A schematic of the rutile (three units along the c axis, \( C_R \), are shown) and the monoclinic (shaded) crystal structures in VO\(_2\). b, An octahedron at the center of a rutile unit cell of VO\(_2\) showing orthorhombic distortion and the different apical and equatorial V–O bond lengths. The vanadium t\(_{2g}\) d orbitals are also shown. c,d, Schematic of the VO\(_2\) band structure in the metallic (c) and insulating (d) states.

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In Figure 18 it is to note that the oxygen octahedra at the body-center and the corners of the rutile unit cell are related by a 90° rotation about C_R. In the MIT, the vanadium ions move away from the octahedral-site center as shown by the black arrows. This creates the structural change that is accompanied in the MIT.

Another aspect to note is the orbitals of V atoms in figure 18 b. One can imagine, as the lattice is compressed along the c axis, these orbitals will see a larger overlap, pushing the d_|| bands together to create a metallic state and shifting the d_ʌ bands. Hence, compressive strain along the c axis lowers the MIT temperature.

It has been previously noted that oxygen composition can be tuned to induce/modify stresses in thin film oxides (see for example a detailed study on this problem by Bhatia and Sheldon).^102 Hence, in condition C, the deposition parameters were optimized (through background oxygen partial pressure tuning achieved by oxygen flow control) to yield a nearly stress-free VO_2 film on Si_3N_4. The correlation between oxygen partial pressure during the deposition and the oxygen content in the film has been studied previously by X-ray photoelectron spectroscopy^103 and was used to optimize the growth condition. This is evident in fig. 16(c) where the transition temperature during heating is close to that of bulk single crystal VO_2 (~ 68 °C) for both films and membranes. In addition, the transition temperature does not shift much between the film and membrane. Also from fig. 16(c) the activation energy is found to be 0.191eV and 0.196eV for the insulating state and 0.098eV and 0.103eV for the
metallic state of the film and the membrane respectively, showing that the conduction mechanism does not change between the film and membrane. The reduced activation energy of the insulating state may be attributed to inhomogeneous oxygen stoichiometry, which introduces defect states in the VO$_2$ band gap.\textsuperscript{103} Similarly, the negative d$\rho$/dT of the metallic phase is also likely due to mixed valence states of vanadium in the film, that is often present in growth on non-oriented substrates. There is observable hysteresis widening after making membranes from the stress-free films. Fig. 16 (f) shows the hysteresis width changing from 7°C to 11°C for the film grown with condition C. Fig. 16 (d), (e), and (f) all show an increase in the width of the hysteresis regardless of the deposition conditions. In fig. 16 (d) the hysteresis opens up from 14°C to 16°C and in fig. 16 (e) the hysteresis opens up from 5.5°C to 7.4°C. The opening of the hysteresis can be explained by amplified surface effect in a self-supported membrane. Chang et al. observed that the phase transition in the bulk of the film is much sharper with narrower hysteresis than right at the surface of the film.\textsuperscript{104} The broader hysteresis observed on the surface of the film was attributed to inhomogeneity in the oxidation state of the V atoms, (for example, electronic in-homogeneity on VO$_2$ surfaces has been noted by scanning tunneling microscopy),\textsuperscript{105} and also inhomogeneity in the stress relaxation of the grains at the surface. The opening of the hysteresis in our self-supported membranes is suggestive of this hypothesis and illustrates surface contribution that is reflected in amplified changes in electrical properties.
4.4.3. Ionic Liquid Gating

Fig. 19 shows the log(\(\rho\)) vs. T for film and membrane devices at various bias voltages in electrolyte gating experiments.

Figure 19: Temperature vs. Resistivity \(\rho\) Plot of VO\(_2\) Devices with Various Ionic Liquid Gate Voltages. At gate bias of 2V the resistivity of the insulating state at 25 \(^\circ\)C of the film and the membrane are 0.97\(\Omega\)-cm and 0.761\(\Omega\)-cm respectively. At a gate bias of 2.5V the resistivity of the film and the membrane are further reduced to 0.12\(\Omega\)-cm and 0.067\(\Omega\)-cm respectively. Note that the membrane is consistently more sensitive to the ionic liquid gating from the increased surface coverage.
In a previous study,\textsuperscript{106} we have determined safe voltage ranges to probe ionic liquid gating without chemical reactions that often lead to irreversible resistance changes. Here, we are within this range and only representative results are discussed. At gate bias of 2V the resistivity of the insulating state at 25 $^\circ$C of the film and the membrane are 0.97$\Omega$-cm and 0.761$\Omega$-cm respectively, showing a slight decrease from the original insulating state resistance. At a gate bias of 2.5V the resistivity of the film and the membrane are further reduced to 0.12$\Omega$-cm and 0.067$\Omega$-cm respectively. There is a clear trend that the resistivity of the membranes is much lower than that of the film, which is clearly evident in fig. 19. This could be explained by carrier doping near the ionic liquid-VO$_2$ interfaces. Thus, having two exposed surfaces in the membrane naturally increases its response. This is demonstrated extremely well when the film and the membrane are gated at 2.5V in that the resistivity of the insulating state of the membrane is only $\sim$56% of the insulating state of the film. Fig. 20 illustrates the doping from the ionic liquid is not a permanent chemical change but a reversible process.
Figure 20: Temperature vs. Resistivity $\rho$ Plot of VO$_2$ Film Cycled at applying gate voltage $V_g=0$ and after $V_g=2.5$ for 15min. The ionic liquid doping is a reversible process. Here the VO$_2$ film returns to its original value after two cycles. This reversibility is due to the ions detaching themselves with $V_g=0$ and being heated close to its melting temperature.

When heated close to the melting temperature of the ionic liquid with no gate bias applied, the accumulated ions at the ionic liquid/VO$_2$ interface will approach the equilibrium state by detaching from the VO$_2$ surface, reversing the resistivity of the insulating state back to its original value.$^{100}$ In addition, the resistance could also be
reversed to its original value by removing the ionic liquid with acetone. Also note that there is no modification of the metallic state resistance because the intrinsic carrier density in the metallic phase is larger compared with induced carrier density.

### 4.4.4. Ionic liquid gating vs. hydrogen studies

Recent experiments have suggested that electrolyte gating using water contaminated DEME-TFSI includes electrochemical process, in which the hydrogen in the ionic liquid diffuse into the VO\textsubscript{2} film or accumulate at the interface.\textsuperscript{107} Hydrogen annealing studies were conducted on the film and membrane devices to compare the results to the ionic liquid gating results to better understand the doping mechanism.

Fig. 21 shows the Log(\(\rho\)) vs. T for film and membrane devices exposed to hydrogen for one hour at various temperatures in an environment controlled probe station with a hot stage.
The films were exposed to H\textsubscript{2} for 1hr at the temperatures indicated in the legend. The change in the resistivity of the insulating phase is ~22% for the film and 21% for the membrane for hydrogen exposure at 100 °C. For 150 °C exposure, the resistivity change is about 64% for the film and 70%. The membrane does not seem to be more sensitive to the H\textsubscript{2}, unlike the behavior observed in ionic liquid studies.

The change in the resistivity of the insulating phase is about 22% for the film and 21% for the membrane for hydrogen exposure at 100°C. The membrane does not seem to be more sensitive to the H\textsubscript{2} than the film at this temperature. For 150°C
exposure, the resistivity change is about 64% for the film and 70% for the membrane, again not a large difference between the film and the membrane unlike observed in ionic liquid gating. The lack of a large difference in change of resistivity of the insulating state in H\textsubscript{2} between the film and the membrane is likely due to the rapid diffusion of H\textsubscript{2} throughout thickness of VO\textsubscript{2}. This is noted in previous work by Wei et al.,\textsuperscript{108} in which a single crystal VO\textsubscript{2} nanowire is readily doped by baking it in H\textsubscript{2} at 150°C for 20 minutes. The doping increases the conductivity of the nanowire and is attributed to fast diffusion of H\textsubscript{2} along the C axis of the rutile phase.\textsuperscript{108} It is possible that accumulation of hydrogen at the ionic liquid-VO\textsubscript{2} interface is not the primary gating mechanism in our case given the uniform improved response of the membrane compared to the film over the insulating state range. If hydrogen dominates the electrolyte gating experiments, one may not expect large difference in the resistance modulation between membranes and films, again due to the rapid diffusion of hydrogen in VO\textsubscript{2}. Furthermore, the observation that the resistivity of the gated film reverses back to its original value at 0V bias close to the melting temperature in our experiments, (which is different from carrier depletion due to reversing gate bias polarity), further suggests that the doping mechanism could be different. The large difference in the channel resistance between the film and the membrane and the reversibility of the doping without a negative bias suggest that the doping mechanism of M\textsubscript{5}I-Beti ionic liquid is likely due to near-surface electrostatic carrier doping.
The transition temperature of the film during heating decreases slightly from 68.0 °C to 67.0 °C at 2V gate bias and 64.3 °C at 2.5V. On the other hand, the transition temperature of the membrane changes from 67.3 °C to 66.0 °C at 2 V gate bias and is further reduced to 62.1 °C at 2.5 V gate bias. Utilizing experimentally determined relationships between transition temperature of doped vanadium dioxide and carrier density one can estimate the accumulated carrier density from the change in the metal-insulator transition temperature. In general, chemically reducing $V^{4+}$ into $V^{3+}$ and therefore doping VO$_2$ with electrons could destabilize insulating M1 phase with respect to metallic rutile phase and decrease the transition temperature. In compounds such as V$_{1-X}$M$_X$O$_2$ (M = Mo, W), the metal-insulator transition temperature changes with the chemical doping as $dT_{MI}/dx \sim -2300$~$2570$K/ atomic %. Based on this relation, we can extrapolate the electron doping density for the membranes. If 0.2 % electron doping per vanadium atom is roughly assumed, which corresponds to $\sim 1 \times 10^{20}$ cm$^{-3}$ bulk carrier density change, it could lead to decrease in transition temperature of $\sim 5$ K. Using this value, the accumulated sheet carrier density for a 40 nm thickness membrane is $4 \times 10^{14}$ cm$^{-2}$. From this value we can estimate the effective capacitance of the ionic liquid could be estimated as $\sim 12$-15 µF/cm$^2$ in the free-standing membrane device geometry, comparable to results previously reported. We have observed larger modulation in the transition temperature for a membrane than film under the same gate voltage and attributed this to the increased surface contribution.
4.5. Conclusion

In summary, we have demonstrated a robust fabrication process for self-supported edge clamped sub-50nm VO$_2$ membranes that are stable under rigorous electrical characterization. The fabrication process can be adapted to a range of nano-scale materials systems that require electrical characterization. Utilizing such suspended membranes, we have directly observed shift in metal-insulator transition temperature likely arising from stress relaxation and opening of the hysteresis. Ionic liquid gating of the membrane transistors allowed reversible modulation of channel resistance. The doping of VO$_2$ with hydrogen at 100°C and 150°C showed little difference in sensitivity between the film and the membrane, indicating that hydrogen diffusion is rather a rapid process in VO$_2$, consistent with previous reports. From a comparison of ionic liquid gating and hydrogen annealing studies, it is suggested that the reversible resistance modulation in the insulating state with ionic liquid MI$_5$-Beti is likely due to near-surface electrostatic carrier doping.
CHAPTER FIVE

FABRICATION AND PHYSICAL PROPERTIES OF THIN Ti$_x$O$_y$ MEMBRANES FROM SINGLE CRYSTAL TiO$_2$

5.1. Introduction

Utilizing focused ion beam (FIB) milling, we have fabricated thin membranes (also referred to as nanowalls) of Ti$_x$O$_y$ of 100-300 nm thickness starting from rutile titania bulk single crystals. Low probe currents (~80 pA) in conjunction with XeF$_2$-assisted milling enables minimal contamination during the fabrication process. Transmission electron microscopy studies indicated polycrystallinity and presence of nano-twins in the FIB-milled nanowalls. Formation of such nanoscale twinned structures may be related to high degree of nonstoichiometry, i.e. reduction as a result of milling in TiO$_2$ that is consistent with observations in other oxides in the literature. Compositional analysis in the transmission electron microscope also showed reduced content of oxygen, confirming non-stoichiometry after milling. We have studied the temperature dependence of the electrical conductivity behavior in such ultra-thin walls in the temperature range of 300 K < T < 520 K. Temperature dependence of the electrical resistivity of the nanowall showed semiconducting behavior with an activation
energy different from that corresponding to TiO$_2$ single crystal and was attributed to formation of Ti$_n$O$_{2n-1}$ phases with n<4 after FIB processing. The results suggest a pathway to fabricate quasi-two dimensional oxide structures for probing mesoscopic conduction phenomena.

5.2. TiO$_2$ and nonstoichiometric variants

There is great interest in studies on thin films of non-stoichiometric oxides from scientific and technological perspectives. Contemporary problems include understanding defect conduction at mesoscopic lengthscales and the role of free surface proximity on charge transport as well as a range of two-terminal electronic devices for resistive switching and in a broader context for non-linear transport properties. Of particular interest is the titanium oxide material system, including near-stoichiometric TiO$_2$, and the various non-stoichiometric phases of the general form Ti$_n$O$_{2n-1}$.

Increasing the density of oxygen vacancies, x, in the TiO$_2$ host results in generation of several Ti$_n$O$_{2n-1}$ phases, in which the point defects are eliminated by crystallographic shear planes and their subsequent ordering. In other words, the electrons which are created by reducing TiO$_2$ are trapped in such shear planes.

Ref. 114 has reviewed and summarized the structural transformations that rutile TiO$_{2-x}$ may undergo as a result of varying oxygen stoichiometry. It has been previously reported that only a
slight change as much as 0.001 in x may lead to creation of a new phase structure, $\text{Ti}_n\text{O}_{2n-1}$.\textsuperscript{115,116} Several of these nonstoichiometric Ti$_x$O$_y$ phases have different phase transition characteristics depending on the symmetry change upon heating or cooling at corresponding temperatures.\textsuperscript{117,118,119} For instance, Ti$_3$O$_5$ shows a first-order structural transition from insulating monoclinic phase at low temperature (below 460 K in heating) to a metallic orthorhombic phase at higher temperatures.\textsuperscript{120} Other Magneli type phase (Ti$_n$O$_{2n-1}$, n>3) also typically show a characteristic phase transition at much lower temperature (<RT) and thus have metallic behavior at close to room temperature. Such metallic behavior is associated with delocalizing the unpaired electron and their distribution over d levels of the each Ti atom.\textsuperscript{114} Since such transition is a characteristic of the structure and composition of Ti$_x$O$_y$, observation of the phase transition and/or the semiconducting/metallic/insulating behavior can be used as a way to investigate the phase along with other compositional and structural characterizations.

Obtaining nanoscale single crystals in membrane form to study electrical transport is quite challenging. For example, TiO$_2$ is non-reactive to several conventional etchants, such as HCl or BOE. Reported low etch rates for TiO$_2$ single crystals makes it extremely challenging to achieve ultra-thin layers.\textsuperscript{121} Therefore, dry etching techniques such as Reactive Ion Etching (RIE) and/or Focused Ion Beam milling (FIB) are required to etch titania. The goals of this study include advancing experimental approaches to fabricate high purity ultra-thin Ti$_x$O$_y$ membranes (or referred to as nanowalls) starting
from single crystals and to study their physical properties. Fabrication of such nano-sized membranes in the titania system has not been reported previously to the best of our knowledge. Our approach involves Focused Ion Beam (FIB) milling, utilizing Ga-ion bombardment for etching TiO$_2$. Numerous experiments were carried out to optimize the fabrication process. High temperature electrical conduction studies were carried out in an environmental probe station chamber.

5.3. Experimental step

Single crystals of (100) TiO$_2$ (from MTI Crystal) were used as starting material. The samples were placed in Focused Ion Beam microscope (FIB) with Ga ion beam normal to the surface of the sample. Milling was operated at 30 kV accelerating voltage and beam currents in the range of 80-1500 pA. XeF$_2$ and H$_2$O gases were used in situ to assist the milling operation. The substrate was then taken out of the FIB and annealed in ozone for 1 hour at 300°C. SiO$_2$ precursor was then deposited at the bottom of the trenches as an insulating layer using Ga-induced gas-break down deposition in FIB. Subsequently, Pt precursor was used to form contacts to the sides of the wall, similar to SiO$_2$ deposition. Pt was also deposited to form wires connecting the trenches to larger electrodes, as detailed in the following section, for electrical measurements. Scanning electron microscope (SEM, Ultra) was used to determine the morphology, while the
chemical composition of the membrane was determined by the Energy Dispersive X-ray spectroscopy (EDX) in conjunction with SEM. In order to make contacts for electrical measurements, square electrodes were deposited on the bare surface of TiO$_2$ substrates by DC-sputtering, using a metal shadow mask. This step was carried out prior to fabrication of the nanowall in the FIB. Square electrodes of different sizes with 100 µm separations were formed on the sample surface. Pt films were grown at 250 W for 15 minutes in 4 mTorr to form stable dense electrodes. Plane view TEM specimens were prepared by Focused Ion Beam milling. Utilizing Omniprobe, the milled nanowall was removed and lifted off the substrate surface. The nanowall was then glued to a special TEM grid by depositing Pt. Figure 22 (a) demonstrates the schematic configuration of the device (referred to as a nanowall) for electrical measurements.
Figure 22: a) Single crystal TiO$_2$ nanowall fabricated using Focused Ion Beam (FIB) milling. Side walls are coated with Pt for electrodes. Front and rear sides were milled to ensure isolation for electrical pathways. B) Schematic illustration of measurement setup, including environmental chamber, temperature controller and Keithley 2000 digital multimeter.
Deposited Pt on the side walls are marked by arrows. The temperature dependence of electrical conduction was investigated in a probe station capable of high temperature measurements, schematically illustrated in Figure 22 (b) in the temperature range of 300-520 K in air. The resistance value was derived from the slope of the linear I-V curve at each temperature during cooling down, using a Keithley 2000 digital multimeter. The sample was held at each temperature for few minutes to stabilize before the measurement was carried out.

5.4. Results and Discussion

5.4.1 FIB milling and incorporation of Ga

Figure 23 (a) shows the SEM image of the trenches immediately after etching by XeF$_2$-assisted milling, while Figure 23 (b) shows the electroded nanowall after Pt deposition. Two trenches of 2 µm in depth and various separations were milled to form nano-walls of various thicknesses. As seen from the image (Figure 23 (a)), the side walls show no visible indication of structure damage. The front and back side of the wall were subsequently isolated by XeF$_2$-assisted milling to exclude fringe effects, as shown in Figure 23 (c). Pt was also deposited to form wires connecting the trenches to larger electrodes for electrical measurements. Figure 23 (d) shows the final semi-free standing isolated nanowall after Pt wiring.
Figure 23: SEM micrographs of TiO$_2$ nanowalls after a) milling deep trenches (2 µm), b) Pt deposition onto the side walls, c) isolation of front and rear electrical pathways, d) Pt wires deposited to connect to larger electrodes for electrical measurements

Initial milling of the trenches was done using higher probe currents of 1.5 nA to create deep trenches with a larger spacing between them, followed by fine milling with 80 pA to thin the nano-wall down to 200-4000 nm. This is due to the damage created by the larger probe currents on the structure and composition of TiO$_2$ crystal. Figure 24 (a) shows the SEM micrograph of a milled trench with 1.5 nA of probe current. As observed from the image, it is clear that the structure of TiO$_2$ in the vicinity of the side
walls were damaged, leading to formation of a likely disordered layer, as previously reported.\textsuperscript{122,123}

Figure 24: a) SEM micrograph and b) EDX spectrum of deep trench FIB milled with 1.5 nA probe current. Ga peak indicates a significant Ga implantation.
This is associated with the high energy bombardment of Ga ions which disrupts the TiO$_2$ lattice. The composition of the crystal in the amorphous region is also expected to vary due to the defects generated by the highly energetic Ga ions. Also, Ga incorporation rate is greater at higher beam currents. This was confirmed by the EDX spectrum of the nanowall fabricated with 1.5 nA probe current, plotted in Figure 24 (b). As observed in the plot, the Ga peak intensity is high and corresponds to roughly 8 at%. The EDX spectra of the TiO$_2$ nanowalls collected upon FIB milling is shown in Figure 4. Figure 25 (a) shows the EDX spectrum corresponding to the as-received TiO$_2$ substrates for reference, whereas Figure 25 (b) indicates the composition of the nanowall milled at 1.5 nA of probe current.
Figure 25: EDX spectra of single crystal TiO$_2$ a) as-received substrates, and milled trenches with b) 1.5 nA probe current, c) 80 pA probe current with XeF$_2$-assisted milling, d) 80 pA probe current with H$_2$O-assisted milling.
The trenches etched to define the nanowalls were approximately 500 nm deep. As can be seen from these two plots, oxygen intensity is reduced after FIB, while a small Ga peak is observed at around 2 kV. This shows the Ga ion implantation during milling process in FIB and is consistent with previous reports on FIB-milled oxide surfaces. The depth of Ga implantation is estimated as ~15 nm.\textsuperscript{123} Ga implantation can result in changes in electrical properties of nanowalls. Also, it is believed that Ga-ion milling amorphizes a thin layer of oxide crystal where it is exposed to high energy ion beam. The percentage of Ga incorporation is calculated as approximately 7 at% while Ti/O ratio is ~1.7. This is significantly higher than the stoichiometric value of 0.5. Figure 25 (c) corresponds to the nanowall fabricated at a low probe current of 80 pA using XeF\textsubscript{2}-assisted milling. As can be seen from the plot, the Ga intensity has been greatly reduced to ~1 at%. Even at such low probe currents, oxygen vacancies are likely to be generated. However, the Ti/O ratio shows a closer value to 0.5 (~0.7). The chemical analysis in this work is primarily for comparative purposes between the samples to improve processing, since it was very difficult to confine the electron beam to the vicinity of sidewalls for a more accurate EDX measurement. Figure 25 (d) shows the EDX spectrum of the nanowall fabricated by probe current of 80 pA using H\textsubscript{2}O-assisted milling. As seen, Ga ion peak is almost invisible with an approximate 0.7 at% atomic percent and Ti/O ratio shows an increase to around 0.7. Table 2 summarizes of EDX
results for the as-received, etched by high-beam current, low-beam current and XeF$_2$-assisted milling on TiO$_2$ substrates.

<table>
<thead>
<tr>
<th>Probe current/element</th>
<th>Ti (at%)</th>
<th>O (at%)</th>
<th>Ga (at%)</th>
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<tr>
<td>as-received</td>
<td>34</td>
<td>66</td>
<td>0</td>
</tr>
<tr>
<td>1.5 nA</td>
<td>59</td>
<td>34</td>
<td>7</td>
</tr>
<tr>
<td>80 pA (XeF$_2$)</td>
<td>43</td>
<td>56</td>
<td>1</td>
</tr>
<tr>
<td>80 pA (H$_2$O)</td>
<td>42</td>
<td>57</td>
<td>&lt;1</td>
</tr>
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</table>

Table 2: Chemical composition of sidewalls, FIB milled in TiO$_2$ single crystal substrate using different probe currents for relative comparison.

Therefore, it is concluded that the lower probe currents and gas-assisted milling are required to obtain TiO$_2$ nanowalls with a near-stoichiometric composition. In order to make samples suitable for electrical conduction studies, the trenches were etched down to 2 µm depth, in which case, XeF$_2$ and H$_2$O-assisted milling showed no significant difference in Ga diffusion or Ti/O ration, being close to 1 at% and 0.7 at%, respectively. However, XeF$_2$-assisted milling showed sharper etching profile and higher etch rates. Therefore, it was used to fabricate the nanowalls for further electrical conduction studies.
5.4.2. Formation of twins and Magneli phases

Figure 26 represents a bright field TEM image of a FIB milled nanowall from a commercial single crystal TiO$_2$ substrate.

![Figure 26: a) Bright field image of TEM sample prepared from a nanowall, showing a high density of nano-twins with white arrows and b) Formation of nano-twins and presence of polycrystalline grains.](image)

As can be seen from the image, the wall is of polycrystalline nature with a high density of nano-twin formation within a relatively small area. The polycrystallinity is most likely originated from the damage caused by ion beam milling, generation of oxygen vacancies and nucleation of reduced phases. Such phases have been observed
previously in the literature as a result of reducing stoichiometric TiO$_2$ and thought to be of Magneli phase structure with formula Ti$_n$O$_{2n-1}$.$^{124-130}$

Also, a high density of nano-twins marked by the arrows in the figure evidences a distribution of nonstoichiometric TiO$_x$ phases in the wall. It has been reported that such nano-twin structures in oxides are linked to non-stoichiometry.$^{131}$ HREM lattice images of the wall are shown in Figure 27, more clearly indicating the polycrystalline phases present with various d-spacing in small-sized grains. Also, twinned regions are clearly visible as well. In order to confirm the formation of Magneli phase in the wall, lattice image is used to identify the d-spacing corresponding to each grain.
Figure 27: High-resolution TEM images of a) polycrystalline grains in the nanowall, used to extract the d-spacing and b) Twins formed and distributed across the wall. Inset shows the FFT of lattice image indicating mirror reflection, corresponding to twinning.
Additionally, the FFT image in the inset of each figure shows a mirror reflection symmetry which indicates twinning as well. A summary of d-spacings and corresponding phases they may correspond to is shown in Table 3.

<table>
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<tr>
<th>d-spacing (Å)</th>
<th>Possible structure/phase</th>
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<tr>
<td>4.6</td>
<td>Ti$<em>7$O$</em>{13}$ (Magneli)</td>
</tr>
<tr>
<td>3.7</td>
<td>Ti$<em>8$O$</em>{15}$ (Magneli), TiO</td>
</tr>
<tr>
<td>2.12</td>
<td>Ti$_2$O$_3$, Ti$_3$O$_5$</td>
</tr>
<tr>
<td>2.08</td>
<td>TiO$_2$ (rutile)</td>
</tr>
<tr>
<td>2.0</td>
<td>Ti$_3$O, Ti$_3$O$_5$</td>
</tr>
<tr>
<td>1.9</td>
<td>TiO, Ti$_3$O$_5$</td>
</tr>
<tr>
<td>1.77</td>
<td>TiO$_2$ (rutile)</td>
</tr>
</tbody>
</table>

Table 3: Summary of d-spacing from TEM lattice images and corresponding structures.

Several Ti$_n$O$_{2n-1}$ phases with varying n can be present in coexistence with rutile TiO$_2$. It is however interesting that such phases are observed in a small scale and are distributed widely across the sample. It is important to note that specifying the structure of these grains with just the d-spacing from TEM lattice images is not feasible. Nevertheless,
certain d-spacing values listed in Table 3, are clearly distinct from those corresponding
to just TiO$_2$ and this suggests the presence of secondary phases formed after the milling.
The EDX profile of the nanowall taken in the TEM is plotted in Figure 28.

![EDX profile of the nanowall taken from the TEM specimen](image)

Figure 28: EDX profile of the nanowall taken from the TEM specimen, indicating oxygen deficiency in the nanowall, as compared to single crystal TiO$_2$ substrate. Inset shows the FIB-prepared nanowall for TEM.

As can be seen from the profile, the oxygen content of the wall is much reduced as compared to stoichiometric TiO$_2$. This is further supported by the work of Brusil and
Hyde, where they studied the maximum amount of tolerable oxygen nonstoichiometry, $x$ in TiO$_{2-x}$, describable as point defects in rutile structure. Such $x$ value was found to be less than 0.001 and therefore, upon reaching this critical value, a new structure was created. In formation of Magneli phase structures, increased number of point defects is stabilized via formation of shear planes. Additional references discuss this transformation further.$^{132-135}$

Normalized resistance for two different membranes of nominal 100 nm thickness is plotted as a function of temperature in Figure 29.
Figure 29: Temperature dependence of the normalized resistance for two different samples of similar 100 nm thickness in the range of 300-520 K. Inset shows the normalized resistance of TiO$_2$ bulk single crystal vs. inverse of temperature.
Consistent trend was seen in the 300nm thick membrane as well. As seen from the figure, the resistance decreases weakly with activation energy of 0.06-0.08eV. The inset of Figure 29 shows the behavior of starting TiO2 single crystal normalized surface resistance for reference. Pt contacts were directly deposited onto the TiO2 substrate surface and the resistance was measured as a function of temperature. As seen, the resistance decreases with temperature smoothly with activation energy of ~0.72 eV, with similar range reported in literature.136 This is different from the resistance behavior as well as the activation energy of conduction of the nanowall and is an indication of phase change as a result of FIB processing which dominates the electrical characteristic.

We hypothesize that in case of nanowalls, local heterogeneity in the composition may lead to a distribution of related Ti\textsubscript{n}O\textsubscript{2n-1} phase structures. According to Figure 29, the present phase(s) in the nanowall show insulating properties at RT with no transition up to 250 °C. Although there may be more than one non-stoichiometric phase formed during FIB milling, the electrical resistivity of the order of 10\textsuperscript{4} -10\textsuperscript{5} Ω-cm at 200 °C suggests that the dominant phase was most likely comprised of Ti\textsubscript{n}O\textsubscript{2n-1} phase(s) with n<4 which shows insulating behavior at room temperature and above.114-119 This is also consistent with the non-stoichiometry in the samples measured by energy dispersive spectroscopy discussed above.
5.5. Conclusion

Thin non-stoichiometric structures of titanium oxide with varying thickness were fabricated utilizing focused ion beam (FIB) milling. It was found that Ga incorporation occurs at high probe currents (> 1.5 nA) and Ga content was found to be substantially high in the exposed etched areas. Through the use of low probe currents (80 pA) in conjunction with XeF$_2$-assisted milling fabrication processes for thin membranes were developed. TEM studies indicated polycrystallinity and presence of nanotwins in FIB-milled regions. Formation of such nanoscale twinned structures may be related to high degree of non-stoichiometry, i.e. reduction as a result of milling in TiO$_2$ consistent with previous reports on other oxides in the literature. Temperature dependence of the electrical resistance showed semiconducting behavior in the temperature range of 300 K< T< 520 K with activation energy different from that of single crystal TiO$_2$ substrate and is likely related to formation of Magneli phases after FIB processing.
CHAPTER SIX

ULTRA-THIN FREESTANDING CERIA MEMBRANES: LAYER TRANSFER TECHNIQUES AND HIGH TEMPERATURE CONDUCTIVITY STUDIES

6.1. Introduction

As our previous study on TiO$_2$ showed, using FIB to create freestanding membranes was not feasible. A new architecture had to be designed. This chapter shows interrogation of conduction mechanisms in quasi two-dimensional (2D) brittle or highly resistive materials that are in suspended form, which presents a formidable experimental challenge. High temperature conductivity studies on substrate-free self-supported nano-crystalline ceria membranes up to 800 K utilizing a layer transfer method that enables four-terminal carrier transport studies under extreme environments have been carried out. Utilizing such structures increasing conductivity with oxygen partial pressure directly opposing the behavior of thin film devices ‘clamped’ by substrate has been observed. This illustrate that the relaxed nature of free standing membranes, and increased surface to volume ratio enables more sensitive electrical response to oxygen adsorption on the surface which could have implications for their use in oxygen storage devices, solid oxide fuel cells, and chemical sensors.
6.2. Background science on CeO$_2$

6.2.1. Previous work on CeO$_2$ nano-structures

The electronic and ionic properties of ceria have been under investigation dating well back to the 1950’s.\textsuperscript{137} However, understanding the role of interfaces on ionic-electronic conduction and exploration of new opportunities in manipulating charge transport through dimensionality reduction has recently put ceria in the spotlight. Consequently, nanostructured ceria is an active area of study due to potential charge inversion from ionic to electronic carriers at the interface.\textsuperscript{138} Thus far, studies on nanostructured ceria have been performed on nanocrystalline ceria,\textsuperscript{138} thin films,\textsuperscript{139} nanowires,\textsuperscript{140} and nanoparticles.\textsuperscript{141} Previous studies on freestanding ceria membranes have focused on synthesis of nanosheets,\textsuperscript{142} and chemo-mechanical properties of freestanding membranes.\textsuperscript{143, 144}

Understanding conduction phenomena and surface chemistry are relevant to designing solid oxide fuel cells and sensors as these devices can have metal oxides in a freestanding architecture.\textsuperscript{145} Transport, charge carrier, and surface studies are often done on rigid thin films clamped by the substrate.\textsuperscript{146} Due to residual stresses that arise from film growth,\textsuperscript{147} such interaction with the substrate can influence surface phenomena and ionic and electronic conduction properties. For example, strain may alter the surface chemistry of ceria, which may be important in understanding creation of oxygen
radicals.\textsuperscript{148} The effect of the strain on defect mobility in ceria has been previously investigated through modeling by De Souza et al, who illustrate that strain may alter the migration thermodynamics and enhance the ionic conductivity.\textsuperscript{149} Schweiger et al have investigated altered ionic conduction by strain engineering.\textsuperscript{150} In ceria nanoparticles the lattice parameters were observed to increase, attributed the nanoparticles ability to accommodate large strain, distortions, and, thus, large concentration of $V_0^-\text{in CeO}_2$.\textsuperscript{151} A recent study on iron oxide nanoparticles has also pointed out the importance of strain in influencing ionic conduction.\textsuperscript{152} Similar to modifying ionic conduction in bulk ceria, strain may play a role in surface defect mobility and creation. In particular, surface adsorption and desorption, via creation or filling of surface vacancies\textsuperscript{153} could be altered by strain.

6.2.2. Mechanical studies of CeO$_2$ membranes

Therefore, to overcome substrate effects, one natural approach is to pursue substrate-free samples, such as self-supported, freestanding, thin membranes. Freestanding membranes have been observed to relax their stress, often mechanically distorting the film creating non-uniform stress profiles.\textsuperscript{154} Releasing the film from the substrate could have profound changes in defect and charge carrier mobility. Rupp has illustrated processing dependent lattice strain and its effects on conduction
mechanisms.\textsuperscript{139} We hypothesize that similar effects may be observed for surface species, where strain would affect gas adsorption, hence, changing the conduction mechanism near the surface.

Prior examples of self-supported ceria films can be found in literature. Nair et al., demonstrated lateral expansion in CeO\textsubscript{2} films once they have been released from the substrate, irrespective of mechanical stress of the film.\textsuperscript{143} The expansion was measured by optical spectroscopy to obtain height of the membrane deflection. Nair et al, note that strain in their samples originate from two sources, one from variation of the lattice constant with thickness, or two from within/in between grains.\textsuperscript{143} The variation of the lattice constant with thickness is believed to be caused by microscopic strain at the film-substrate interface originating from substrate clamping. They attribute the expansion to removal of substrate clamping that triggers a structural change from CeO\textsubscript{20/11} with ordered $V_\text{O}^-$ to CeO\textsubscript{2-x} with disordered $V_\text{O}^-$. Similarly, Kossoy et al. report on elastic anomalies, spontaneous changes in the lattice parameter/local lattice distortions, in thin self-supported CeO\textsubscript{2} films.\textsuperscript{144} The change in lattice parameters and strain is deduced from X-ray diffraction (XRD) and extended X-Ray absorption fine structure (EXAFS) measurements. It was demonstrated that even for pure ceria, if it contains a large amount of oxygen vacancies, local lattice distortions are possible where Ce-O bond lengths decreases and Ce-$V_\text{O}^-$ length increases. Kossoy et al, interpret this as expansion
of the empty cation tetrahedra and compression in the region of the oxygen containing tetrahedra, thus leading to local lattice distortions.

Lattice distortions prevalent in free standing CeO$_2$ membranes, impact the defect creation and conduction mechanism via altered ionic bond strengths from strain.$^{155}$ Paier et al showed varying surface adsorption energies for (111) and (110) surface of ceria. Furthermore, Paier et al illustrate, from first principle calculations, electron density distribution over surface oxygen vacancy$^{155}$ The calculation notes an ideal case where perfect symmetry is obtained. However, in strained ceria or extended defects would provide different electron density distribution, hence energies for surface adsorption of oxygen would be impacted.

6.2.3. Case for suspended membranes

In some of the works discussed above, the self-supported structures were realized by local substrate release, where the edges of the film was still bound to the substrate. In the case of edge clamped membranes as demonstrated by Kerman et al, the energy contained in the biaxial film stress is converted to an out-of-plane displacement. The stresses created by buckling is approximately equal to the biaxial residual film stress.$^{154}$ To realize relaxation, membranes were created by a layer transfer method.$^{156}$
Figure 30 shows a diagram of a substrate clamped nano-crystalline film, a free standing nano-crystalline membrane, and resulting possible changes in surface adsorption energies.

Figure 30: Diagram of (a) a substrate clamped nano-crystalline film, (b) a free standing nano-crystalline membrane in buckled form with varying local strain, (c) Surface adsorption (green) and desorption (purple) in unstrained and (d) strained oxide with fluorite structure, (e) qualitative surface adsorption and desorption energy plot versus lattice distortion $a^*$, dotted lines indicate possible deviation of adsorption/desorption energy from that of relaxed crystal due to strain (f) schematic of a fully fabricated free standing membrane device with buckling.
To investigate the surface-dominated properties, a method to conduct electrical measurements on suspended nanometric membranes should be developed first. Such a measurement strategy is substantial to concurrently understand the transport information and mechanical status.

A substrate clamped oxide, as shown in Fig. 30a and 30c, under compressive stress would result in a lattice parameter that is altered from that of a relaxed crystal. However, as seen in Fig. 30b, 30d, 30e and 30f, the buckled membrane would exhibit varying lattice parameters, providing sites with significantly different chemical bonds with different bond angles and lengths.\textsuperscript{155} Hence, these lattice distortions and surface defect sites could likely impact the surface adsorption and desorption of oxygen, which would make the oxidation state more sensitive to ambient oxidizing potentials. Such effects would manifest in change in overall conductivity, and increased response to changing external environment.

6.3. Membrane Fabrication and Layer Transfer Methods

The processing challenges in fabricating oxide membranes that can accommodate lattice distortions during chemical treatments or heating have to date limited electrical conduction studies on free standing membranes. In this section, we outline processing methods pursued in this study in detail. Careful process optimization
has been demonstrated in our previous work for self-supported VO$_2$ membranes that undergo structural phase transitions.$^{157}$ However, this fabrication process does not work for insulating samples like CeO$_2$ due to large leakage through the Si$_3$N$_4$ to the Si substrate. The transfer method had to be completely modified such that a membrane was on an extremely insulating substrate like fused silica. This proved to be difficult since, the advantage of creating membranes on Si$_3$N$_4$ was that a back etch technique could be used to create self-supported oxide membranes. Such back etching techniques cannot be used for fused silica or alumina substrates. To circumvent this problem, we developed a membrane transfer technique where an oxide membrane is deposited on a Si$_3$N$_4$ membrane, and transferred on to a desired substrate by etching away the Si$_3$N$_4$ while the oxide film is in contact with the substrate surface. Fig. 31 illustrates the detailed flow diagram of the processing steps.
Figure 31: Flow diagram for CeO$_2$ membrane fabrication and four-terminal electrical wiring. Purple, light gray, light blue, dark gray, and peach, denotes Silicon Nitride (SN), Silicon (Si), Oxide, Platinum (Pt), and Fused Silica (SiO$_2$). (a) desired oxide (in this case CeO$_2$) is deposited on the un-etched side of the wafer with a shadow mask, (b) The Si$_3$N$_4$ wafer is placed with the desired oxide side facing the fused silica substrate. (c) The Si$_3$N$_4$ is etched away using RIE, (d) FIB metal contacts are made to ensure good contact with the desired oxide.
As shown in Fig. 31a, a thin layer of CeO$_2$ is deposited by radio frequency (RF) sputtering from a CeO$_2$ target on top of the patterned Si$_3$N$_4$ windows prepared by the KOH etching technique. CeO$_2$ films were grown at 4mtorr, 10% O$_2$, 90% Ar, at 400 °C. The film thicknesses were in the range of 35nm as determined from X-ray reflectivity. The ceria film is subsequently transferred over a trench, shown in fig. 32a, with pre-deposited metal contacts on the fused silica substrate by etching away the nitride membrane using reactive ion etching. However, this is non-trivial due to the fragile nature of oxide membranes. The oxide membranes often buckle as the thick Si$_3$N$_4$ is etched away due to differences in stress between the Si$_3$N$_4$ and the deposited oxide. Furthermore, the gradient of stress within the oxide film arising during film growth$^{154}$ can result in buckling. Figure 32b shows a buckled CeO$_2$ membrane as the Si$_3$N$_4$ is etched completely.
Figure 32: Optical images of (a) deep trench etched into a fused silica substrate, (b) buckling of CeO$_2$ membrane after back etch of Si$_3$N$_4$, (c) successfully transferred CeO$_2$ membrane onto a flat piece of fused silica, (d) shattered CeO$_2$ membrane.

The buckling can sometimes result in cracking of the oxide membrane that often makes transfers difficult, but at the same time, buckling enables good contact with the underlying substrate as the Si$_3$N$_4$ is etched. This contact from buckling results in Van der Waals bonding between the substrate and the transferred membrane.$^{156}$ Figure 32c shows a successfully transferred CeO$_2$ membrane onto a flat fused silica substrate.
Figure 32d illustrates a transferred membrane with a part of it shattered to illustrate the extreme care required.

Performing RIE for a prolonged time removes any residual Si$_3$N$_4$ leaving a transferred CeO$_2$ membrane held on to the fused silica substrate. As demonstrated by Bieberle-Hütter et al. RIE does not impact the microstructure and conductivity.$^{158}$ The placement of this transferred membrane over a trench gives a portion of the membrane that is free standing over the fused silica trench. An inherent hurdle in this process is the creation of a membrane device directly over a pre-patterned trench. In our design, the freestanding portion of the membrane is realized by transferring an oxide membrane over a deep trench. Van der waals force positions the membrane in its place right after the transfer. Since transferring over a trench results in minimized contact with the substrate, only at the corners of the oxide membrane, the membrane often would blow away or crumple due to the lack of adhesion with the substrate right after the transfer. The transfer technique, therefore, has to align the membrane within 5 micron precision.

Figure 33a shows a transferred oxide membrane over a trench with misalignment.
Figure 33: (a) optical image of a mis-aligned CeO$_2$ membrane and (b) SEM image of a broken CeO$_2$ membrane during FIB on a practice sample. (c) optical image of a fully fabricated free standing membrane device with buckling.

Once the membrane is transferred focused ion beam (FIB) metal deposition is used to ensure good contact between underlying metal contact and the membrane. Due to the fragile nature of the membranes, no wet processing is possible. Hence, we utilized FIB assisted metal deposition to make contact between the transferred membrane and the metal contact on the substrate. Figure 33b shows a ruptured membrane after non-optimal FIB. An additional challenge during the FIB metal deposition process is drift of the ion beam. Since the sample is on an insulating substrate (CeO$_2$/SiO$_2$ at this stage), charging effects during metal deposition can occur, causing the ion beam to drift. To remedy this problem, we segment the total required deposition time into 30s intervals. In total, the metal deposition using FIB took about 20 hours per sample. The details of membrane fabrication presented here can be applied to
a variety of materials systems, particularly ones that are mechanically fragile and highly resistive.

Fig. 33c shows a schematic of a free standing membrane device and its inset shows an optical image of the transferred CeO$_2$ membrane with metal contacts and with a freestanding portion over the fused silica trench. The depth of the trench (20+ $\mu$m) is much larger than the deflection of the membrane from buckling ($<3$ $\mu$m), consistent with previous findings,$^{154}$ ensuring that the film is self-supported.

The CeO$_2$ membrane device was subjected to systematically varying gas environments, (Ar, atmosphere, O$_2$, O$_3$) at similar gas flow rate of 1 liter/min into a sealed high temperature chamber with electrical contacts. The order of the experiments is as introduced in the Discussion section. In this custom environmental probe station the device was electrically probed by the Van der Pauw method with voltage ranging from few tenths of a volt to few volts with current ranging from 1-100 nA, at various temperatures ranging from 653 K to 803 K. TEM studies (200 kV JEOL 2100) have been performed by obtaining bright field high resolution images and diffraction patterns to observe any changes in the crystal structure of CeO$_2$ in this temperature range by in-situ experiments. Gas switching experiments have also been performed as a two point measurement, where the probes are on opposite corners of a membrane device.
6.4. Results and Discussion

6.4.1. Conductivity vs. temperature in Ar, 20\% O_2, 100\% O_2, and O_3

Figure 34a shows the log resistivity vs. inverse temperature plots of membrane and film devices in 100\% oxygen compared to literature values published for n-type and p-type conduction, similar grain sizes, and same atmospheric conditions: Panhans et al (orange shows n-type and green shows p-type both in 1atm O_2),\textsuperscript{159} Suzuki et al (red shows 20 nm grains)\textsuperscript{160} and Gobel et al. (black shows 50-100 nm grains and blue shows 16 nm grains).\textsuperscript{161} In Fig. 34a the dots and lines represent measured data and extrapolated values from literature respectively. The resistivity and activation energy values of the membrane and film devices are comparable to previous literature values as seen in Fig. 34a.
Figure 34: Log(resistivity) vs. 1/T of (a) 100% oxygen environment and comparison with literature values from Panhans et al (orange shows n-type and green shows p-type both in 1atm O\textsubscript{2})\textsuperscript{23}, Suzuki et al (red shows 20 nm grains)\textsuperscript{24} and Gobel et al. (black shows 50-100 nm grains and blue shows 16 nm grains)\textsuperscript{25}. The dots represent data measured and lines show extrapolated values. Our results are shown in cyan and magenta, which represent measured values for film and membrane device respectively. (b) the membrane device in Ar, 20% oxygen atmosphere, 100% oxygen, and ozone (c) the film device in Ar, 20% oxygen, and 100% oxygen atmosphere. (d) CeO\textsubscript{2} membrane exposed to ozone at a high temperature and left on for subsequent cycles.
Interestingly, there is an anomaly in the membrane sample where an increase in the resistivity at about 753 K is observed. This increase in the resistivity is present in various partial pressures of oxygen. Figure 34b shows the log resistivity vs. inverse temperature plots of the membrane device subjected to Ar, 20% oxygen, 100% oxygen, and ozone environments respectively. As seen in Fig. 34b, the jump in resistivity as the sample is heated up is present in 20% oxygen and 100% oxygen atmosphere, but is absent for Ar and O₃ atmospheres. This may be due to changing oxygen interaction with the surface of the CeO₂ membrane which affects the dominant carrier type depending on the chemical environment. Hole conduction has been noted in ceria under high oxygen partial pressure and at temperatures well below 973K.¹⁶² In our sample, the high oxygen partial pressures of 20% and 100% at 1 atm may promote surface adsorption of oxygen to create hole carriers. The subsequent jump would be indicative of surface desorption of oxygen where concentration of p-type carriers are decreased. The low oxygen partial pressure during Ar annealing at high temperatures would infer significantly reduced oxygen interaction, thus limiting the transition. Furthermore, extreme oxygen activity in O₃ would greatly promote oxygen interaction with the surface of the membrane to create hole carriers through surface adsorption of oxygen.

Previously published literature values measure thin film nanocrystalline pure CeO₂ in the high temperature range (973-1373 K).¹⁶³,¹⁶⁴ There are literature reports in the 573-873 K range, however, these are on doped ceria.¹³⁸,¹⁶¹ Mamontov et al,
observed that oxygen vacancy and interstitial concentration was greatly reduced at higher temperatures (1090 K) due to recombination in ceria powders.\textsuperscript{165} Abazari et al, have noted decrease in concentration of oxygen radicals on the surface of yttria doped ceria film at temperatures above 873K due to desorption.\textsuperscript{166} Such adsorption/desorption would be facilitated and its effect magnified in our free standing membrane structure leading to jumps observed in figure 34b.

\textbf{6.4.2. Strain considerations in CeO$_2$ conductivity}

Sheldon et al. present a striking result in a recent study that space charge at interfaces often are accompanied with stresses that significantly alter defect concentrations and transport properties.\textsuperscript{167} Rodriguez et al. notes that the surface of nanocrystalline Zr doped CeO$_2$ was more reactive to H$_2$ and SO$_2$ than a corresponding single crystal surface.\textsuperscript{168} Near a grain boundary or a free surface of a self-supported membrane such stresses would relax having an effect on the surface chemistry and transport, altering the rate of oxygen adsorption/desorption.

Another feature to note in Fig. 34b is the difference in activation energies above and below the transition temperature. Below and above the transition temperature the activation energy is about 1.08 eV and 0.7 eV respectively. The activation energy for conductivity in ceria varies greatly depending on the charge carrier, film thickness,
grain size, and strain. For example, the activation energy varies from 0.9eV to 1.55 eV for CeO$_2$ thin films with grain sizes from 38nm to 230nm respectively.$^{169}$ The change in the activation energy in our study as the sample is heated could be indicative of changing conduction mechanism. In perspective, Suzuki et al. reports activation energies in the range of 1 eV to 1.4 eV for nanocrystalline ceria films that are believed to be in the electronic conduction regime.$^{160}$ Panhans et al, notes the activation energy to be 1.13-1.16 eV in the hole conduction regime.$^{159}$ The enhanced conductivity seen above is well explained in literature where grain boundaries in nanocrystalline ceria lowers defect formation and migration energies for oxygen vacancies.$^{138, 163, 164}$ Furthermore, the proximity to an unclamped free surface with nano-crystalline structure would lead to reduction in migration energies. Recent findings by Marrocchelli et al,$^{170}$ De Souza et al,$^{149}$ Rupp et al,$^{171}$ and Hinterberg et al,$^{172}$ all have noted strain-altered defect migration energies arising from chemical expansion of different ionic states of ceria. Samples used in this study have an average grain size of ~20nm and thickness of ~30nm. The comparable grain size and thickness would present a complex strain profile that would enhance surface adsorption and desorption processes.

To compare the effect of the substrate clamping on film versus self-supported membranes Log(resistivity) vs. inverse temperature of CeO$_2$ films grown directly on SiO$_2$ substrates were obtained. The experiments performed in Ar, 20% O$_2$ and 100% O$_2$ are shown in figure 34c. As seen in Fig. 34c the plots for film devices in these
atmospheres closely resemble that of literature results shown in Fig. 34a, with the resistivity values and activation energy values reflecting that of Suzuki et al. and Gobel et al.\textsuperscript{160,161}

The comparison between membrane and film devices at the lower temperature regime illustrates a difference in electrical response of the devices to changing oxygen partial pressures. As seen in Fig. 34c, the resistivity of the film device increases with increasing oxidizing environment, and decreases with lower oxidizing environment, complementing results from literature.\textsuperscript{166, 167} However, in Fig. 34b, for lower temperature range, the behavior is the opposite. The resistivity seems to increase with lower oxidizing environment and decrease with increasing oxidizing environment. This phenomenon suggests that conduction in membrane devices in lower temperatures is influenced by increasing p-type charge carriers via surface oxygen adsorption. This can be noted by looking at resistivity vs. inverse temperature for a device in 100\% Ar atmosphere and ozone atmospheres wherein the membrane device is clearly less resistive in ozone than in Ar.

To examine the oxygen interaction in membrane devices at high temperatures, ozone is introduced at 773 K after the resistance jump is observed in oxygen environment. Figure 5d shows the log resistivity vs. inverse temperature plots for the membrane device in various heating and cooling cycles. In Fig. 34d the first heating cycle in O\textsubscript{2} shows the same resistivity jump as observed before. After the jump is
observed, the membrane is exposed to ozone atmosphere. Interestingly, despite the strong oxygen activity of ozone the resistivity of the membrane device did not drop suggesting limited oxygen adsorption at elevated temperatures. At high temperatures, the decrease of oxygen radical concentration on the surface due to desorption may further explain the limited oxygen interaction.\textsuperscript{166} With the ozone gas left on, the sample is cooled to 673 K. On the first cooling cycle, reduction in resistivity in the lower temperature regime, dropping from 4547 \, \Omega\cdot\text{cm} to 3639 \, \Omega\cdot\text{cm}, is observed. Subsequent heating, shown in heating cycle 2, showed further drop in resistivity in the lower temperature regime. The drop in resistivity is possible from additional hole carrier generation from oxygen adsorption at lower temperatures.\textsuperscript{159}

Figure 34d also demonstrates that this effect is reversible and reproducible, the plots shown in Fig. 34d was taken after our initial ozone experiments, which is shown as - O3 Meas. By the time the first and second cycles were performed for figure 34d, the sample has been left out in atmosphere for over a week, and was subjected to argon tests prior to the final ozone cycle experiment.

6.4.3. TEM studies of CeO\textsubscript{2} structure at various temperatures

To investigate whether there is any structural transformation present as the membrane was heated, in-situ TEM on a CeO\textsubscript{2} membrane (membrane prepared by the
procedure outlined in our previous work followed by transfer to a TEM grid) during heating was performed. Figure 35 shows the electron diffraction (ED) patterns and bright field (BF) images from the membranes obtained with the help of my colleague J. Shi.

Figure 35: Electron diffraction patterns at (a) 20 °C, (b) 300 °C, and (c) 500 °C and bright field, (d) low resolution and (e) high resolution, images of CeO$_2$ membrane. (a-c) Note no change in diffraction pattern indicating absence of structural phase transformation. (d) and (e) distribution of grain sizes ranging of the order of 15nm.
Diffraction patterns collected from the same region of ceria membrane at three different temperatures (300 K, 573 K and 773 K) are essentially identical, suggesting the fluorite structure of ceria remains unchanged across the temperature range of interest, ruling out the contribution of structural phase transition on conduction mechanism switching. BF and high-resolution TEM images at room temperature show that the grain size of CeO$_2$ ranges from 5 to 20 nm without any textured crystal orientation.

### 6.4.4. Gas switching experiments

Ar/O$_2$ switching experiments were then carried out to examine membrane device’s sensitivity to oxygen, by examining changes in resistance. Figure 36 shows the normalized resistance vs. time for various Ar/O$_2$ switching cycles for the CeO$_2$ membrane device and film devices.
Figure 36: Ar/oxygen gas switching experiment results for (a) membrane device at 703 K shown by normalized resistance vs. time. (b) membrane device at 803K shown by normalized resistance vs. time. (c) film device at 703K shown by normalized resistance vs. time. (d) film device at 803K shown by normalized resistance vs. time.
The oxygen incorporation rate, seen from the rate of resistivity change in % when O\textsubscript{2} is turned on is similar for two representative temperatures shown. In Fig. 36b, 36c, and 36d a hump when O\textsubscript{2} is switched on and a dip when Ar is switched on are observed. We attribute these features to the fact that the specific heat capacity of oxygen is higher than that of Ar. This would imply that when O\textsubscript{2} replaces Ar at the same flow rate, the heating stage will need to adjust to accommodate for the increased heat loss to the O\textsubscript{2} to maintain the same temperature. This hump is the transient from fluctuating temperature for our device when the gases are switched. As seen in Fig. 36a, the resistance vs. time in O\textsubscript{2} shows a large peak and subsequent drop down of resistance to a much lower value, which is a different signature compared to the rise followed by steady state saturated resistance in Fig. 36b, 36c, and 36d. We attribute this peak as a point where the oxygen adsorption begins to create more p-type carriers. The initial peak signifies carrier annihilation, thus minimizing the carrier concentration in the membrane. The subsequent drop in resistance to a lower value is attributed to additional adsorption of oxygen where p-type carriers are generated, increasing the overall carrier concentration. In the high temperature regime, similar to the bound film devices, shown by figure 36b, 36c, and 36d, no sharp peak and corresponding drop are observed in the resistance curve taken in flowing oxygen atmosphere. This suggests limited oxygen adsorption at higher temperatures which is consistent with literature.\textsuperscript{159}
Another observation from the switching experiments can be seen by comparing fig. 36b and 36d. In the high temperature regime, the percent resistance change in membrane and film devices are 66% and 24% respectively. The membrane device shows larger resistance changes and is more sensitive to changing environments. The increased sensitivity is attributed to amplified surface to volume ratio (i.e. two free surfaces in the membrane) and the un-constrained nature of the membrane.

### 6.4.5. Interaction with oxygen

To further investigate the membrane interaction with the environment, the normalized I-V curves of the membrane sample at 703 K and 803 K in 100% O₂ atmosphere are shown in Figure 37a. The I-V curves taken at 703 K, shows hysteretic behavior while the I-V curve at 803 K, shows linear behavior. Hysteretic behavior in the I-V curve is most indicative of defects trapping carriers.¹⁷³ In our study, the hysteresis could be arising from charge compensation from interaction with the oxygen ambient. For example, the oxygen would adsorb on the CeO₂ membrane and trap electrons in the process, acting as a charge trapping defect.¹⁵³ To validate this hypothesis, the I-V curves were taken in 100% Ar atmosphere. Figure 8b shows the normalized I-V curves for the membrane sample in 100% Ar and 100% O₂ atmosphere at 703 K. As one can see in Fig. 8b the I-V curve in Ar shows little to no hysteretic behavior.
Figure 37: Normalized I-V curves for (a) membrane device in O$_2$ at 723 K and 803 K (b) membrane device in O$_2$ and Ar at 703 K (c) membrane device in O$_2$ at 703 K and film device in Ar and O$_2$ at 703 K (d) membrane device in O$_2$ at 803 K and film device in Ar and O$_2$ at 803 K. The curves are normalized the maximum current for each sample for visual comparison of hysteretic behavior of I-V curves in different environment for the different samples.
I-V curves of the membrane in O$_2$ and of the film in Ar and O$_2$ at 703 K and 803 K are shown in fig. 37c and 37d respectively. Note that in 37c and 37d negligible hysteretic behavior is observed for the film devices and the absence of hysteretic behavior in 100% Ar atmosphere supports charge interaction with surface oxygen species.

6.5. Conclusion

A layer transfer technique has been developed to investigate high temperature conduction in freestanding ceria membranes. The method is well suited to investigate transport in highly resistive materials that are mechanically fragile. We have directly observed resistivity modulation in suspended ceria membranes that is not present in substrate-clamped thin film devices. The membrane devices, free from substrate confinement, are able to show greater response to the chemical environment. Such quasi-2D layers could launch new research directions in exploring confinement effects on ionic and electronic transport, and the use of ultra-thin ionic conductors for intermediate temperature transistors and sensors.
CHAPTER SEVEN

SUMMARY & FUTURE WORK

7.1. Summary

Synthesis and fabrication as well as electrical studies of free standing ultrathin <40nm oxide membranes have been demonstrated. As shown in this study, fabrication of such membranes proved to be a challenge.

Some of the key conclusions of this study are

1) Nanoscale freestanding membranes amplify surface properties of materials

The VO$_2$ study showed shift in consistent opening of the hysteresis that resulted from variability in the oxidation state of the vanadium atom near the surface. The creation of membrane structure increased the contribution of surface properties over the bulk. The CeO$_2$ study showed increasing conductivity with oxygen partial pressure directly opposing the behavior of thin films ‘clamped’ by substrate and bulk crystals. This illustrates increased surface to volume ratio enables more sensitive electrical response to oxygen adsorption on the surface. TiO$_2$ study showed creating of non-stoichiometric forms of TiO$_2$ as the membrane was milled down to smaller thicknesses. Showing activation energy different from that of TiO$_2$ single crystals
The above studies have shown that identifying and amplifying surface limited effects are feasible through freestanding nanoscale membranes.

2) Remove substrate effects

The VO$_2$ study showed shift in metal-insulator transition temperature arising from stress relaxation. Additionally, the study on ceria showed increased sensitivity to changing atmospheres due to the stress free nature of the membrane. As shown before reduction of CeO$_2$ causes natural expansion of the lattice, which would have been limited if the film was clamped down on to a substrate.

3) Effectively study surface limited effects

The unique geometry of membranes allowed the identification of surface limited processes. The ionic liquid studies showed reversible modulation of channel resistance and allowed distinguishing bulk process from the surface effects.

The work in this thesis advances the understanding of materials in the freestanding membrane form and advances fabrication techniques that have not been explored before. The membrane fabrication method and device architecture developed here allows almost any material to be made into a membrane. The studies pioneered by this method could have profound implications for sensors, actuators, SOFC, memristors, and physics of quasi 2D materials.
7.2. Future Work

The exciting implications of this work is that the fabrication technique could be expanded to other systems. Here I outline some crucial experiments that could be done in the future.

**Single Crystal Nanoscale Membranes**

In this study we examined polycrystalline materials. However, there are profound questions that are left unanswered regarding behavior of ultra-thin single crystal materials. Just like super-lattice structures have shown, single crystal membranes with the air-oxide interfaces separated by a few nanometers may lead to enhanced ionic conductivity.\(^7\) Low temperature studies of 2-d oxide membranes could open doors to a slew of new physics as much as graphene has\(^6\).

**Dependence of ionic conductivity on stress**

This study has shown that there is a relationship between ionic conductivity vs. stress. Oxide membranes are well poised as research platforms to provide extensive study on the influence of different degrees of stress on conduction of different ionic types.
Oxide Electrodes

Metallic electrodes are excellent conductors even at high temperatures. However, these electrodes are morphologically unstable over time. This study has shown that unlike previous studies, oxide materials exhibited significant conduction at lower temperatures. This could lead to design of electrodes that are stable, catalytically active, and store charge for later use.

Application of oxides as gas separators

Gas separation technologies have existed for some time and oxide membrane based devices have been of great interest due to the benefits of thickness reduction for higher output. For example mixed conducting oxides, such as LSCF, and BSCF are used for conversion of CH$_4$.$^{175}$ Simultaneous generation and separation of H$_2$ and N$_2$ can be achieved using several mixed conducting membrane layers in series.$^{176}$ As one can imagine to maximize the output, the thickness of the membrane needs to be smaller while the area of the membrane needs to be larger. Additionally, such a structure needs to be stable under pressure gradients. Oxide membranes may facilitate such feats and should be investigated going forward.
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