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# Electric-field-induced point defect redistribution in single-crystal $TiO_{2-x}$ and effects on electrical transport

Ali Moballegh* and Elizabeth C. Dickey

*Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27606, USA*

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**Abstract**—The spatial redistribution of non-stoichiometric point defects in rutile $TiO_2$ is studied as a function of voltage and time. Single crystals are equilibrated initially to a well-defined stoichiometry with n-type conductivity and a carrier concentration on the order of $10^{18}$ $cm^{-3}$. The crystals are subsequently electroded with Pt contacts that exhibit Schottky behavior. When subjected to an applied voltage of 15 V, a time-dependent increase and saturation in the leakage current is observed, which is associated with an accumulation of point defects and an attendant decrease in stoichiometry at the cathode electrode. This local change in stoichiometry degrades the Schottky barrier, leading to asymmetric electrodes and thus macroscopic rectifying behavior. Cathodoluminescence spectroscopy shows that Ti interstitials dominate the point defect redistribution process. Under larger applied voltages, of around 30 V, qualitatively different behavior is observed in which the resistivity increases as a function of time. This behavior is associated with condensation of point defects into a region of extended defects and Magnéli phases near the cathode, sufficient to increase the bulk stoichiometry and resistivity. These experiments demonstrate that a one-dimensional drift-diffusion process, as opposed to filamentary growth, dominates in these experimental conditions and that the Pt–$TiO_2$–Pt system remains closed, with no significant oxygen transport across the Pt–$TiO_2$ interfaces. We believe this is the first observation of a second higher-voltage regime in which the bulk stoichiometry and thus resistivity is increased as large concentrations of defects condense into metallic Magnéli phases in the near-electrode regions.

*Keywords:* Oxides; Electromigration; Point defects; Electrical properties; Analytical electron microscopy

## 1. Introduction

The performance of electroceramic devices is largely determined by the thermodynamic and transport behaviors of coupled point and electronic defects in the material. Under direct current (DC) voltage these charged defects can redistribute spatially as a function of time. This phenomenon has been studied in numerous dielectric materials, such as $TiO_2$ [1–3], $BaTiO_3$ [4,5] and $SrTiO_3$ [6,7]. Although lattice defect migration can lead to detrimental behavior such as leakage current enhancement in capacitor devices [4], it can also be utilized to form novel functional behaviors, such as resistive switching in metal oxides [8–10].

Typically, electrodes for dielectric materials are chosen such that they lead to interface Schottky barriers that limit charge carrier injection into the dielectric. Seminal work in the 1990s by Waser et al. showed that point defect migration under applied bias in $BaTiO_3$ and $SrTiO_3$ leads to an accumulation of charged point defects at the dielectric-electrode interface, modifying the interface characteristics [6,11]. The local accumulation of point defects near the interface can modify the Schottky barrier and width of the depletion layers [12] which increases the electron injection. The conduction mechanism itself can be modified in these highly defective regions [13]. Further, the asymmetrical behavior at the anode and cathode can lead to diode-like rectification behavior [1,2,4]. This functionality can be utilized for electronic devices, such as cross-bar array-type memory devices [14,15].

Several studies have quantitatively modeled the temporal ionic point defect redistribution under voltage biasing by solving the drift-diffusion equation in a time domain and considering ionic transport behavior across the interface as a boundary condition within the dilute solution approximation [8,11,16–18]. If, however, the electrodes block or limit mass transport across the interface, then very high concentrations of point defects may accumulate, well beyond a dilute concentration, and may even push the ion activity outside of the material's stability range. Several experimental studies have, in fact, shown condensation of point defects into higher-dimensional defects or ordered structures near electrodes as a consequence of DC biasing [3,19–22].

The present work focuses on point defect migration in $TiO_2$, a material that has attracted intense interest in diverse applications such as capacitors, where its high dielectric constant is influenced from the unique arrangement of the $TiO_6$-octahedra, and memristor/resistive switching memory, with the ability of unipolar [23] or

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* Corresponding author. Fax: +1 919 515 7724; e-mail: amoball@ncsu.edu

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bipolar [8,15,24] switching. Regardless of the form of $TiO_2$ (amorphous, polycrystalline, single crystal), the governing model for resistive memory behavior has been the electroformation of conductive (substoichiometric) filaments that shunt the anode and cathode, leading to a low-resistance state. As the local stoichiometry near the electrodes is modulated with subsequent applied fields, the rectification behavior of the Schottky contacts can be manipulated [15]. Jameson et al. [1] demonstrated Schottky barrier modulation at the electrodes via local reduction/oxidation of $TiO_2$, with electrical measurements on $TiO_2$ single crystals with surface-patterned Pt electrodes. The field-programmable rectification behavior was observed after voltage biasing at fields of 125–375 kV $cm^{-1}$ at room temperature. The behavior was also demonstrated to be reversible by reversing the polarity of the programing voltage. Szot et al. [10] provided a critical review of resistive switching in $TiO_2$ and emphasized the need for more fundamental research aimed at understanding the mechanisms of defect transport and phase stability in these materials, since prior work on $TiO_2$ spanned materials with various degrees of crystallinity, purity, etc. They emphasized the significance of the small stoichiometry range for rutile $TiO_{2-x}$ and the formation of crystallographic shear planes and Magnéli phases to accommodate the substoichiometry resulting from electrochemical reduction at the cathode. The authors presented further work on heavily reduced single-crystal $TiO_2$, annealed under different conditions with concomitant differences in initial stoichiometry. It was demonstrated with surface Pt electrodes that conductive, substoichiometry filaments were formed as well as crystallographic shear defects and Magnéli phases at the cathode interfaces.

While a substantial body of literature already exists on point defect dynamics in $TiO_2$, there has been significant disconnect between this body of literature and the abundant information known about point defect energetics and mobilities in rutile $TiO_2$ [25–28]. This work aims to help bridge that gap by providing new and more generalized insight into the mechanisms of point defect electromigration in $TiO_2$. Ultimately, we aim to provide experimental data and guidance for future studies, which could predict quantitatively the time-dependent evolution of point defect redistribution under an applied electric field. We specifically focus on point defect transport behavior in single-crystal rutile $TiO_2$ with well-defined initial-state defect chemistries and electrode geometries that interrogate the bulk (as opposed to surface) defect transport kinetics.

In addition, while prior literature almost exclusively considers the role of oxygen vacancies in the transport process, we also consider the role of titanium interstitials, which are known to dominate the point-defect equilibria at low oxygen activities [25–28]. Further, in contrast to the many perovskites in which cation interstitials are relatively immobile [4,6,29–31], both oxygen vacancies and titanium interstitials have significant mobility in rutile $TiO_{2-x}$ [32,33]. Referring to transition-state theory calculations, the titanium interstitial has lower migration energies, 0.225 eV along <1 1 0> and 0.37 eV along <0 0 1> [34], compared to the oxygen vacancy, 0.69 eV along <1 1 0> and 1.77 eV along <0 0 1>. As shown experimentally by Lee and Yoo [35], two different relaxation times are observed for $TiO_2$ during equilibrium with the external oxygen partial pressure due to the diffusivity of oxygen vacancies being one order of magnitude lower than titanium interstitials.

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

## 2. Experimental procedure

High-purity (1 0 0)-oriented rutile $TiO_2$ single crystals, made by the Verneuil growth process, were purchased from Shinkosha Company (Japan). The most significant impurity was reported to be Al at ~50 ppm by weight. The crystals, well polished with 1 μm diamond paper, were annealed under specific oxygen partial pressure ($pO_2$) and temperature conditions to establish the initial defect chemistry state of the material, taking into account the known equilibration kinetics in $TiO_2$ [25–28].

Specifically, a series of single-crystal rutile samples were annealed and equilibrated at a $pO_2$ of $10^{-4}$ atm at 1100 °C for 36 h. In this temperature range and reducing atmosphere (1050–1350 °C and $pO_2 = 10^{-2}$–$10^{-4}$ atm), $TiO_2$ is an n-type semiconductor with the ln(conductivity) vs. $pO_2$ having a −1/4 slope, consistent with fully charged oxygen vacancies as the dominant point defects, which are compensated by titanium vacancies [25–27]. The $pO_2$ was controlled in a high-temperature tube furnace using an argon and argon/$H_2$ forming gas and monitored by a commercial zirconia-based oxygen gas sensor. After equilibration, the samples were quenched to $T < 300$ °C in the flowing reducing atmosphere to establish the initial defect chemistry state. The approximate quench rate was measured to be ~40 °C $s^{-1}$ (1100–900 °C), 7.5 °C $s^{-1}$ (900–700 °C), 2 °C $s^{-1}$ (700–400 °C) and 0.5 °C $s^{-1}$ (700–250 °C). While the oxygen vacancies and titanium interstitials are mobile in $TiO_2$, the titanium vacancies are relatively immobile [26,27] and are not expected to participate in the subsequent lower-temperature, field-induced redistribution.

Pairs of electrodes were deposited on opposite lateral (0 1 0) surfaces (~3 mm × 0.5 mm) by magnetron DC sputtering to study transport along the [0 1 0] direction. A power density of 6.11 W $cm^{-2}$, a gas pressure of 30 mTorr (pure Ar) and a substrate to target distance of 3.4 cm were used in the deposition process, which resulted in a deposition rate of 75 nm $min^{-1}$ for platinum. The deposited contacts, which covered the two lateral surfaces, were annealed at 200 °C for 3 h to establish reproducible contacts at the $TiO_{2-x}$/Pt interface [36]. Since the work function of Pt (5.1–5.3 eV [37,38]) is larger than the electron affinity for rutile $TiO_2$ (~4.0–4.8 eV) [38–40], a Schottky barrier is expected to form at the interface.