

Investigation of Intrinsic Defects in Sputtered Titanium Oxide Surfaces

Peter Chang, 2018 CNF iREU Intern

Physics, University of Dallas

REU Program: 2018 Cornell NanoScale Facility International Research Experience for Undergraduates (CNF iREU) Program at the National Institute of Material Science (NIMS), Tsukuba, Ibaraki, Japan

CNF iREU Principal Investigators: Dr. Takeo Ohsawa, Dr. Naoki Ohashi, NIMS

CNF iREU Mentor: Dr. Takeo Ohsawa, NIMS

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Contact: pchang@udallas.edu, ohashi.naoki@nims.go.jp, ohsawa.takeo@nims.go.jp

Website: http://www.cnf.cornell.edu/cnf_2018reu.html

Abstract:

The discovery of a quasi-two-dimensional electron liquid (q2DEL) formed at metal-oxide surfaces has motivated research with applications towards next generation oxide electronics. The preparation of well-defined surfaces is important for generating these interesting electronic states. However, unintentional defects and their roles in determining surface properties remain an area of debate. Near surface oxygen vacancies have long been held responsible for reduced surface defects in titanium oxides (TiO_2). However, many previous experimental results have highlighted the persistence of reduced states in sputtered TiO_2 even after surface vacancies were removed, thereby indicating that the intrinsic nature of these surfaces is still controversial. Consequently, further investigation of intrinsic defects in TiO_2 surfaces is still needed. In this study, we present rutile TiO_2 as a model oxide. Surface defects in niobium-doped TiO_2 single crystals with different crystal orientations are monitored using x-ray and ultraviolet photoelectron spectroscopy (XPS/UPS) as a function of Ar^+ exposure and annealing temperature. In agreement with previous studies, XPS spectra show an increase with sputtering time in reduced Ti^{3+} and Ti^{2+} surface states in addition to the standard Ti^{4+} state. These reduced peaks are removed and surface stoichiometry is restored under annealing at only 300°C and 400°C for $\text{Nb}:\text{TiO}_2$ $\langle 110 \rangle$ and $\langle 001 \rangle$, respectively, suggesting a bulk-assisted re-oxidation. These results indicate that interstitial titanium and not oxygen anions are the primary movers for re-oxidizing reduced TiO_2 at relatively low temperatures.

Introduction:

Due to its high dielectric constant, titanium oxide (TiO_2) has been proposed as a potential replacement for silicon dioxide as a gate insulator material [1]. This idea has received increased attention with the discovery of a quasi-two-dimensional electron liquid (q2DEL) that exists at metal-oxide surfaces, resulting in a number of useful properties applicable towards the development of oxide electronics [2].

These surface states are responsible for defects that result from doping electrons into TiO_2 . These excess electrons are observed through reduced states of Ti which normally has a charge of plus four in pristine TiO_2 . Photoelectron spectroscopy is best suited to detect reduced surface states, since the binding energy of electrons ejected through the photoelectric effect carries information about the element, electron orbital and chemical environment. Reduced states in TiO_2 show up via a chemical shifting of the Ti $2p$ peak and through the rise of the Ti $3d$ peak inside the band gap.

In order to generate these electronic states, it is necessary to form well-defined surfaces obtained through ion

radiation and subsequent annealing. However, this process induces intrinsic defects into TiO_2 that must be taken into account if using XPS to study the q2DEL states.

Near surface oxygen vacancies have long been held responsible for intrinsic defects in TiO_2 . However, past experimental results have shown the persistence of reduced surface states even after oxygen vacancies were removed through oxygen exposure. In this study, we further clarify the properties of intrinsic defects in TiO_2 by monitoring their amount as a function of Ar^+ radiation, annealing temperature and crystal orientation.

Experimental Procedure:

Rutile niobium-doped TiO_2 ($\text{Nb}:\text{TiO}_2$) samples with $\langle 001 \rangle$, $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ crystal planes were sputtered with Ar^+ for thirty seconds, one minute, two minutes and three minutes. The Ti $2p$, O $1s$ and valence band photoelectron peaks were observed using Al $K\alpha$ X-ray. Defect ratios in the Ti $2p$ peaks and the area under the Ti $3d$ peaks were used to quantify the amount

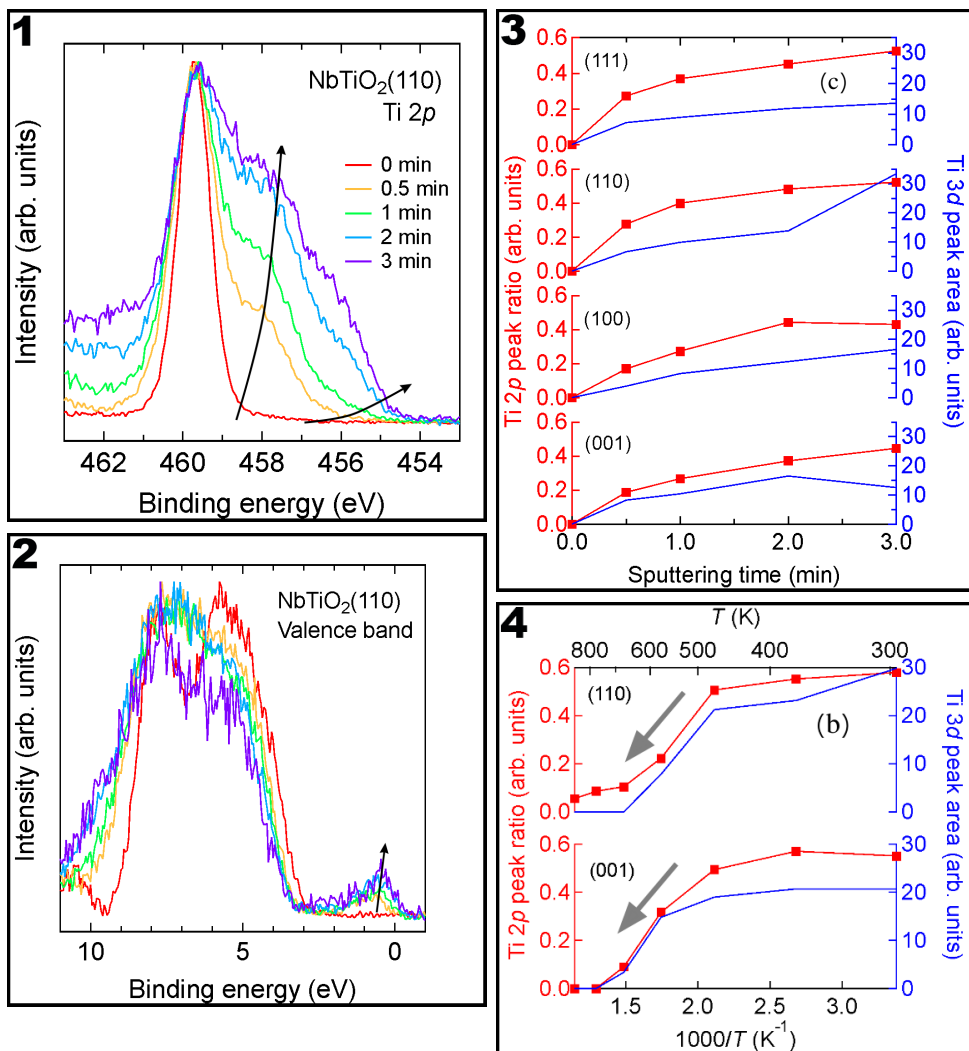


Figure 1, top left: XPS Ti 2p scans of Nb:TiO₂ <110> surface under increasing Ar⁺ sputtering time. Figure 2, bottom left: XPS valence band scans of Nb:TiO₂ <110> surface under increasing Ar⁺ sputtering time. Figure 3, top right: Defect ratios in Ti 2p spectra and Ti 3d peak area plotted as a function of sputtering time. Figure 4, bottom right: Defect ratios in Ti 2p spectra and Ti 3d peak area plotted as a function of annealing temperature after sputtering time for three minutes.

of surface defects, and surface stoichiometry was determined by calculating the titanium to oxygen ratio.

Temperature dependence of the reduced surface states was investigated using Nb:TiO₂ <110> and <001> by first sputtering the sample for three minutes. XPS scans of the Ti 2p and 3d peaks were then conducted at 100°C intervals ranging from 25°C to 600°C.

Results and Discussion:

Figures 1-3 show how XPS spectra change with Ar⁺ sputtering time. Reduced states were evident through the Ti 3d peak inside the bandgap and in the Ti 2p scan through two shifted photoelectron peaks corresponding to Ti³⁺ and Ti²⁺. Defects increased with sputtering time and titanium to oxygen ratio decreased indicating that defect generation was accompanied by the formation of oxygen vacancies.

Figure 4 shows the temperature dependence of surface defects for the <110> and <001> crystal planes. Reduced states disappeared and surface stoichiometry was recovered under annealing at relatively low temperatures with 300°C for <110> and 400°C for <001>. These results suggested that interstitial titanium, which is mobile at lower temperatures, and not oxygen anions, is the primary mover at lower temperatures, migrating from the surface into the bulk.

The temperature experiments suggested that in addition to oxygen vacancies, interstitial titanium also contributes largely to reduced surface states in TiO₂. This is indicated by the significant decrease of defects observed under XPS as titanium cations migrated into the bulk.

Future Work:

Future experiments can study why the formation of doubly reduced Ti²⁺ states under Ar⁺ sputtering were more prone to occur in the <110> and <111> crystal planes. Additional studies can also investigate why surface

defects disappeared at different temperatures for <001> and <110>.

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