Investigation of Intrinsic Defects in Sputtered Titanium Oxide Surfaces

Peter Chang
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
Primary Source of CNF iREU Funding: National Science Foundation under Grant No. OISE-1559368
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 (TiO₂). However, many previous experimental results have highlighted the persistence of reduced states in sputtered TiO₂ 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 TiO₂ surfaces is still needed. In this study, we present rutile TiO₂ as a model oxide. Surface defects in niobium-doped TiO₂ 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 Ti³⁺ and Ti²⁺ surface states in addition to the standard Ti⁴⁺ state. These reduced peaks are removed and surface stoichiometry is restored under annealing at only 300°C and 400°C for Nb:TiO₂ <110> and <001>, 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 TiO₂ at relatively low temperatures.

Introduction:
Due to its high dielectric constant, titanium oxide (TiO₂) 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 TiO₂. These excess electrons are observed through reduced states of Ti which normally has a charge of plus four in pristine TiO₂. 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 TiO₂ 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 TiO₂ 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 TiO₂. 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 TiO₂ by monitoring their amount as a function of Ar⁺ exposure. Reduced states in TiO₂ are then annealed at 300°C and 400°C, respectively, to determine whether oxygen anions or interstitial titanium are the primary movers for re-oxidizing reduced TiO₂.

Experimental Procedure:
Rutile niobium-doped TiO₂ (Nb:TiO₂) samples with 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 Kα X-ray. Defect ratios in the Ti 2p peaks and the area under the Ti 3d peaks were used to quantify the amount

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Experimental Procedure:
Rutile niobium-doped TiO₂ (Nb:TiO₂) samples with <001>, <100>, <110> and <111> 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 Kα X-ray. Defect ratios in the Ti 2p peaks and the area under the Ti 3d peaks were used to quantify the amount
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:TiO$_2$ <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 Ti$^{3+}$ and Ti$^{2+}$. Defects increased with sputtering time and titanium to oxygen ratio decreased indicating that defect generation was accompanied by the formation of oxygen vacancies.

**Future Work:**

Future experiments can study why the formation of doubly reduced Ti$^{2+}$ 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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**References:**