

Damage-free and atomically precise surface preparation of SrTiO₃



Yong Su Kim^{*}, Dong Jin Yun, Seong Heon Kim, Yong Koo Kyoung, Sung Heo

Analytical Science Laboratory of Samsung Advanced Institute of Technology, Suwon, Gyeonggi-do 443-803, South Korea

ARTICLE INFO

Article history:

Received 15 June 2016

Received in revised form

23 August 2016

Accepted 25 August 2016

Available online 27 August 2016

Keywords:

Oxide surface and interface

SrTiO₃

XPS

GCIB

ABSTRACT

Atomically flat and clean (i.e., defect- and contaminant-free) oxide surfaces are essential to fabricating new interfaces with emerging properties and analyzing the surface electronic structure. We investigated how to apply Ar-sputtering techniques to surface preparation. Defect-related peaks were not observed in the spectra collected from the SrTiO₃(001) surface prepared via time and energy controlled Ar-ion and Ar-gas cluster ion beam sputtering. In addition, surface with a step-and-terrace structure had sub-Angstrom root-mean-square roughness indicating structurally and morphologically fine surface. This work demonstrates that sputtering techniques can be used as pre-cleaning and in-situ preparation processes for fabrication of atomically precise oxide surface and interfaces.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The preparation of clean and damage-free oxide surfaces is essential to the application and analysis of functional oxide materials. In fact, the fabrication of sharp heterointerfaces is one of key requirements to achieving high-performance oxide devices [1–8]. Moreover, analysis of the surface electronic structure is vital to understanding device characteristics [9–11] and industrially relevant catalytic reactions in renewable energy and environmental technology [12,13].

Smooth oxide surfaces are typically produced via a chemical etching process followed by thermal annealing [14–20]. Chemical etching selectively removes the topmost sub-layer, and subsequent high-temperature annealing in an oxygen environment produces an atomically flat surface. This prepared oxide surface should be annealed in a vacuum environment in order to remove contaminants prior to oxide device fabrication or analysis of the surface electronic structure; these contaminants are generated during fabrication and from air-exposure [12,13,21]. However, the annealing process typically leads to layer intermixing and the formation of defects such as oxygen vacancies in the oxide materials [22].

Over the years, analytical surface science techniques have been developed and applied in various fields, such as in the study of batteries [23,24], fuel cells [12,13], and oxide devices [6–11]. Photoelectron spectroscopy is used extensively for the analysis of

electronic structures. A cleaning process constitutes the first step in the spectroscopic characterization of surface chemical properties, and therefore, oxide materials are commonly treated by a thermal annealing or an ion-beam bombardment to remove the surface contaminants. However, cleaning process-induced changes in the surface structure (i.e., defect generation) and deformation of the electronic structure have yet to be solved.

In this paper, we present how to prepare and clean the surface, particularly for a prototype model for perovskite oxide: SrTiO₃(001). We show detailed spectroscopic and morphological studies and a method of controlling the surface properties. The results show that the well-established sputtering method constitutes a simple means of preparing a pristine oxide surfaces and interfaces for device fabrication and spectroscopic exploration of the surface electronic structure.

The sputtering of oxide materials using inert gas ions is a conventional method to investigate the surface and bulk chemical compositions. Ar-ion sputtering, which uses high-energy Ar⁺ ions, is the most frequently used technique for removing surface contaminants and obtaining information on the depth distribution of chemical composition in a sample. The recently developed Ar gas cluster ion beam (GCIB) technique uses ionized gas clusters that consist of several hundreds or thousands of weakly bound Ar atoms. The gas cluster ions are highly energetic; acceleration voltage is in the range of 5 kV–20 kV. Since the energy of each atom is the total energy divided by its cluster size, a larger cluster has a lower momentum than a smaller one. Therefore, a low-energy cluster beam can gently remove the surface elements during depth profiling. These sputtering methods, however, all suffer from one drawback, i.e., the surface is degraded and defects are

^{*} Corresponding author.

E-mail address: yongsu12.kim@samsung.com (Y.S. Kim).

generated during sputtering, thereby resulting in changes in the chemical states.

2. Results and discussion

Fig. 1 shows the typical core-level spectra of the SrTiO₃ surface and irradiation effects resulting from the Ar-ion and Ar-GCIB sputtering processes. The core-level were measured using a PHI Quantera-II with Al-K α as the excitation source (1486.6 eV) and 45° of take-off angle. The XPS probing depth depends on a take-off angle and inelastic mean free path (λ) of an electron in a solid. (λ varies with materials) The probing depth can be estimated to be around 5–10 nm. Core-level spectra of the initial state of SrTiO₃ surface (black solid line) present a single oxidation state of Ti⁴⁺ (Ti 2p) [25], carbon residues (C 1s), and the corresponding surface contaminant (O 1s). In this case, we sputtered the SrTiO₃ using Ar GCIB and Ar-ions with various acceleration voltages for 5 and 10 min, respectively. Although both methods effectively remove most of the surface contaminants, they also reduce the Ti state to lower oxidation states. After sputtering, the C 1s peaks almost disappeared and the O 1s spectra displayed two typical components of SrTiO₃, i.e., the main peak centered at ~529.3 eV and the shoulder peak at ~531.35 eV correspond to bulk oxygen and surface oxygen in the termination layer, respectively [22].

Fig. 2 shows the irradiation-induced defect states and the change in chemical states. In Fig. 2(a), the Ti 2p peak of the initial state of SrTiO₃, as denoted by the gray-shaded area, represents the Ti⁴⁺ valence state. The Ar GCIB sputtering at an acceleration voltage of 10 kV resulted in a reduced Ti state, i.e., Ti³⁺ valence state (as denoted by the magenta shaded peak). When the voltage is increased from 10 kV to 20 kV, the density of defects (i.e., oxygen vacancies) generated by the cluster ion beam increases; as a result, the Ti⁴⁺ state is reduced to its significantly lower oxidation states (blue-shaded peak) [26]. The oxygen vacancies are easily generated in SrTiO₃ during ion-beam sputtering, i.e., theoretically, they have the lowest formation energy. The formation of oxygen vacancies nearest-neighbor and next-nearest-neighbor sites of Ti ion causes the reduced and intermediate oxidation states of titanium oxide

[26].

The sputtering-induced generation of defect states depends strongly on the sputtering time and the momentum of the incident beam. When an ion beam is irradiated on the surface, the kinetic energy of individual atoms in a beam ion is equal to the total energy of the beam divided by the number of its constituent atoms. Therefore, for the same acceleration voltage, the incident momentum of the Ar⁺ ion beam is one to three orders of magnitude higher than that of the Ar GCIB, which uses a cluster ion beam that is comprised of tens of thousands of Ar atoms. Accordingly, in Fig. 2(a), we could observe that Ar⁺ ion sputtering at an acceleration voltage of 500 V results in lower Ti oxidation states than those resulting from Ar GCIB one. By increasing acceleration voltage, it generates notable Ti³⁺, Ti²⁺, Ti¹⁺, and Ti⁰ states [26], which correspond to magenta-, blue-, green-, and light-blue-shaded peaks, respectively.

In addition, ion beam bombardment leads to changes in the surface structure, as revealed by the Sr 3d core-level spectra of sputtered surface, shown in Fig. 2(b). These spectra consist of two components, which are represented by the dash-dotted and solid orange lines after the curve fittings. The Sr 3d_{2/5} and 3d_{3/3} peaks that occur at ~132.7 eV and 134.4 eV, respectively, as denoted by the gray-shaded area, are attributed to the Sr bulk. The peaks occurring at ~133.2 eV and 135 eV, as denoted by the solid orange lines, are attributed to the Sr–O bonds at the surface termination. Note that when the surface is sputtered, the surface to bulk intensity ratio increases. It is well-known that the prepared surface of SrTiO₃ (001) is terminated with TiO₂-layer [14,21,22]. However, the results indicate that the surface undergoes a morphological change owing to the incident ionized beam, and the SrO layer therefore emerges as the surface layer after the sputtering process. As shown in the above results, typical sputtering processes can not prepare the clean and damage free oxide surface.

In order to apply Ar-sputtering techniques to a surface preparation of oxide materials, we established the sputtering processes via time and energy controlled Ar-ion and Ar-gas cluster ion beam sputtering. For oxide surface preparation, it should provide clean, damage-free and atomically flat oxide surfaces after treatment. The AFM images (Fig. 3) of the SrTiO₃ surface after the controlled sputtering process, verifies that both sputtering techniques can be applied as cleaning process for spectroscopy measurements, and can be used in the in-situ preparation of oxide materials for atomically precise surfaces and interface fabrications. Bare SrTiO₃ substrate (<0.1° mis-cut angle) was treated with buffered HF solution, and then, was annealed at high temperature for sufficient time, i.e., T = 1000 °C for 48 h. The surface was sputtered using Ar-ion and Ar GCIB at various acceleration voltages for 10 and 30 s, respectively. In Fig. 3(a), the so-called “as-is” state of SrTiO₃ shows step-and-terrace surface structure. Each terrace has an uneven surface that is composed of sub-nano-sized structures, as indicated by the line profile (black line in Fig. 3(i)) along the yellow dashed line on the AFM image. A plot of the root mean square (RMS) roughness as a function of the acceleration voltage (Fig. 3(j)) reveals that the terrace of the “as-is” sample has an RMS value (in the area of 0.3 × 1 μm²) of ~0.187 nm. Low-kinetic-energy (i.e., low-acceleration-voltage) sputtering removes the surface contaminant. However, as Fig. 3(b) and (e) show, this sputtering is ineffective in fabricating precise surface, as evidenced by the comparable RMS values of the sputtered surfaces compared to that of the “as-is” surface (Fig. 3(j)). When the acceleration voltage is increased to 1 kV (Ar-ion) and 10 kV (GCIB), the RMS roughness is reduced to about 0.073 (in the area of 0.5 × 1 μm²) and 0.089 nm (in the area of 0.7 × 1 μm²), respectively. These RMS values are comparable to those recently reported by Woo et al. [20] The AFM images in Fig. 3(c) and (f) and the line profile (blue line in Fig. 3(i))

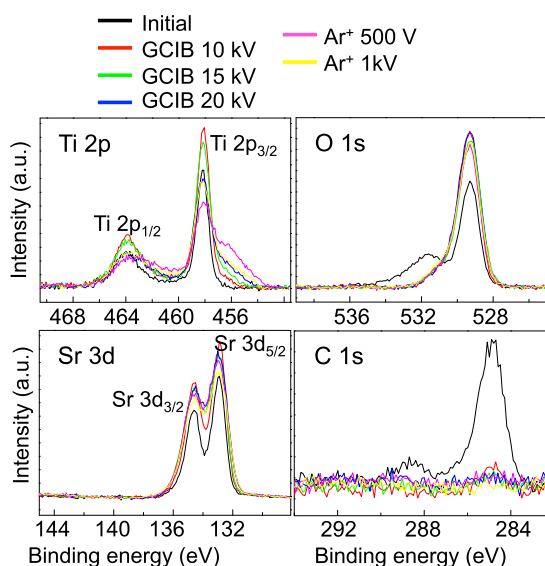


Fig. 1. Ti 2p, O 1s, Sr 3d, and C 1s core-level spectra of SrTiO₃ (001) after typical Ar-ion and GCIB sputtering processes. The C 1s and O 1s spectra show that the conventional sputtering processes effectively remove most of the surface contaminants. However, ion-beam irradiation leads to a reduction from the Ti⁴⁺ (Ti 2p) to lower oxidation states.

Download English Version:

<https://daneshyari.com/en/article/1785358>

Download Persian Version:

<https://daneshyari.com/article/1785358>

[Daneshyari.com](https://daneshyari.com)