Role of step edges in oxygen vacancy transport into SrTiO$_3$(001)

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Using a combination of oblique-incidence optical reflectivity difference and specular reflection high energy electron diffraction techniques, we studied vacuum annealing of pulsed-laser deposited Nb-doped SrTiO$_3$ monolayers on SrTiO$_3$(100) near 730 °C. In oxygen-free ambient, the as-grown monolayers are oxygen deficient. The excess oxygen vacancies in the monolayers are reduced by vacancy diffusion into the bulk. We found that the reduction rate is characterized by an activation energy $E=1.0$ eV. More interestingly, the pre-exponential factor decreases significantly as the annealing time interval increases between two successive monolayer depositions. We propose that the indiffusion of excess surface oxygen vacancies takes place at step edges, and the Oswald ripening governs the density of the latter during vacuum annealing. © 2005 American Institute of Physics. [DOI: 10.1063/1.2005398]

Heterostructures of perovskite oxides have emerged as promising materials for material research and device applications. The structure compatibility has enabled successful fabrication of epitaxial heterostructures of these oxides. Since perovskite oxides take on a wide range of properties (e.g., insulators, superconductors, ferromagnets, ferroelectrics, optically nonlinear crystals), integration and interplay of these properties through properly grown heterostructures promise exciting materials and new device application. As demonstrated by Hwang et al. and others, heterostructures of perovskite oxides with high degree of crystallinity and interfaces as sharp as one molecular layer can be fabricated with pulsed laser deposition (PLD) and reactive molecular beam epitaxy. In addition to crystallinity, properties of oxide films are subject to oxygen content. Films grown under pulsed-laser-deposition conditions are typically oxygen deficient, even when the deposition is carried out in oxygen ambient. Excess oxygen vacancies in as-grown oxide films are usually removed by post-growth annealing in oxygen-rich ambient. Understanding the mechanisms and kinetic details of oxidation reactions is essential for preparation stoichiometry oxide films.

In oxygen-free ambient, driven by chemical potential disparity, excessive oxygen vacancies in as-grown oxide films diffuse into the bulk so that the films still become oxidized even at typical growth temperatures. Though the indiffusion of excess surface oxygen vacancies can take place on terraces or preferentially at chemically active sites such as step edges, our investigation shows that the latter is the case. In this letter we report the findings of such an investigation.

The experiment was carried out in a pulsed laser deposition chamber with a base pressure of $1 \times 10^{-5}$ Pa (7.5 $\times 10^{-9}$ Torr). The chamber is equipped with a standard reflection high-energy electron diffraction (RHEED) apparatus and an oblique-incidence optical reflectance difference measurement system. The SrTiO$_3$(001) substrate of $10 \times 5 \times 0.5$ mm$^3$ is attached to a stainless heater block. The substrate temperature is monitored with an optical pyrometer. A sintered ceramics of stoichiometric Nb: SrTiO$_3$ (10 mol %) is used as the target. A 308-nm XeCl excimer laser at a repetition rate of 2 Hz is used for ablation. We deposit one monolayer of Nb: SrTiO$_3$ at a time in oxygen-free ambient using 38 laser pulses. At the completion of one monolayer, we interrupt the deposition and continue to monitor the properties of the as-deposited monolayer. In particular, we examine how the reduction rate of excess oxygen vacancies varies with temperature and the annealing time interval between two successive monolayer depositions by monitoring the oblique-incidence optical reflectivity difference (OI-RD) from the growth surface.

The experimental setup and procedures have been described previously. Briefly let $r_{p0}$ and $r_{s0}$ be the respective reflectivity from the bare substrate for $p$- and $s$-polarized light at the wavelength of a He–Ne probe laser $\lambda =632.8$ nm. Let $r_p$ and $r_s$ be the respective reflectivity during and after the deposition. Fractional changes in reflectivity are defined as $\Delta_p=(r_p-r_{p0})/r_{p0}$ and $\Delta_s=(r_s-r_{s0})/r_{s0}$. We measure the difference defined as $\Delta_p-\Delta_s$. Let $\varepsilon_{p0}=\varepsilon_{s0}+\varepsilon_{d0}$ be the optical dielectric constant of a Nb: SrTiO$_3$ monolayer. The measurable Re$\{\Delta_p-\Delta_s\}$ is proportional to $\varepsilon_{p0}^2$. For an as-deposited Nb: SrTiO$_3$ monolayer, $\varepsilon_{p0}$ comes from (1) an intrinsic absorption of a stoichiometric Nb: SrTiO$_3$, and (2) an extra absorption associated with the oxygen vacancies in the monolayer. By monitoring Re$\{\Delta_p-\Delta_s\}$, we follow the buildup and removal of excess oxygen vacancies.

At substrate temperatures above 630 °C, even in an oxygen-free ambient, the specular RHEED intensity recovers to the prepdeposition level essentially right after a monolayer-equivalent of Nb: SrTiO$_3$ is deposited. This shows that the deposited layer is recrystallized and “smooth” over the coherent length of the RHEED system. However the postgrowth monolayer contains excess oxygen vacancies as revealed in the optical reflectivity difference signal. In Fig. 1, we display the measured Re$\{\Delta_p-\Delta_s\}$ during and after the deposition at 730 °C and under a base pressure of $1 \times 10^{-5}$ Pa. The three curves correspond to different time in-

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We propose that transport of excess surface oxygen vacancies into a bulk SrTiO3 crystal takes place at or near step edges; either the surface diffusion towards step edges or the indiffusion at step edges determines the reduction rate of the oxygen vacancies. This mechanism operates independently from the oxidation reaction with ambient oxygen (through a precursor-state as reported by Zhu et al. and Tanaka et al.8). It explains why the preexponential factor in the excess oxygen vacancy reduction rate depends on the annealing time. As we show below, the steady-state density of step edge atoms is governed by the balance between the post-growth Oswald ripening and the accumulation of small-radius isomers. It usually takes the growth surface a long time (compared to the time needed for depositing a monolayer) to become flat with terraces determined only by the miscut angle.17,18 Driven by the Gibbs–Thompson effect, small islands decompose while large islands grow through Oswald ripening so that the mean radius of the island distribution increases with time as $r(t) \propto (1 + t/\tau_e)^{1/3}$.19 $\tau_e$ is a decreasing function of temperature.

Even in a layer-by-layer growth, a post-growth surface contains a distribution of two-dimensional (2D) islands (or clusters) and shallow three-dimensional (3D) islands. It usually takes the growth surface a long time (compared to the time needed for depositing a monolayer) to become flat with terraces determined only by the miscut angle.17,18 Driven by the Gibbs–Thompson effect, small islands decompose while large islands grow through Oswald ripening so that the mean radius $r(t)$ of the island distribution increases with time as $r(t) \propto (1 + t/\tau_e)^{1/3}$.19 $\tau_e$ is a decreasing function of temperature. If Oswald ripening is governed by surface diffusion of unit cells, $\tau_e \propto \exp(E_{\text{diff}}/k_B T)$ with $E_{\text{diff}}$ being the energy barrier for unit cell diffusion on terraces. On average one ex-
pects the density of step edge atoms to be approximately $\theta_s \sim 1/r(t) - (1+t/\tau)^{-1/3}$. Starting from a smooth substrate surface, the deposition of one monolayer-equivalent Nb:SrTiO$_3$ increases the density of small-radius islands slightly. If the time interval $\tau$ between two successive monolayer depositions is long so that Oswald ripening is completed, the density of step edge atoms will remain small. If the time interval $\tau$ is insufficient, the islands with small radii will accumulate. The accumulation stops when Oswald ripening, whose rate increases with the density of small-radius islands, balances the net accumulation from one monolayer deposition in and out of a bulk crystal have also been observed indirectly on NiAl by McCarty and co-workers$^{22}$ and on Co/Cu(100) by Schmid and co-workers.$^{23}$

In conclusion, we find that step edges act as pathways for excess oxygen vacancies in Nb: SrTiO$_3$ monolayers to diffuse into the bulk of the substrate during vacuum annealing. Depending upon whether surface diffusion or indiffusion at the step edges dominates, the reduction rate of excess oxygen vacancies is expected to vary quadratically or linearly with the density of step edge atoms, $\theta_s$.

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