

Surface segregation of bulk oxygen on oxidation of epitaxially grown Nb-doped SrTiO₃ on SrTiO₃(001)

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We studied the epitaxy of 10 mol% Nb:SrTiO₃ on a SrTiO₃(100) substrate under an interrupted pulsed-laser-deposition condition. By monitoring the recovery behaviors of reflection high-energy electron diffraction intensity and an optical reflectance difference signal from the growth surface, we observed that, at temperatures above 630 °C, the oxidation of an as-deposited Nb:SrTiO₃ monolayer was achieved by the diffusion of oxygen vacancies in the monolayer into the substrate. © 2002 American Institute of Physics. [DOI: 10.1063/1.1473694]

Perovskite oxides are expected to play important roles in future generations of microelectronics, optoelectronics, and spintronics. Considerable efforts have been made to understand and improve the epitaxial growth of perovskite oxides.^{1–7} Under pulsed-laser-deposition (PLD) conditions, as-grown perovskite-oxide films are, typically, oxygen deficient and the deficiency is usually removed by postgrowth annealing treatments. It is important to understand the origin of oxygen deficiency in terms of oxidation kinetics during as well as after the growth. As reported recently by Zhu and co-workers, kinetic parameters that characterize the *oxidation reaction of an as-grown monolayer with ambient oxygen* vary from oxide to oxide by orders of magnitude even under identical growth conditions.^{8,9} In this letter, we report an observation of *oxidation of an as-grown perovskite oxide monolayer via diffusion of oxygen vacancies in the monolayer into the substrate*.

We grow Nb-doped SrTiO₃ on a SrTiO₃(100) substrate in a PLD chamber with a base pressure of 1×10^{-7} Torr. The substrate is a 1-mm-thick plate with a width of 5 mm and a length of 10 mm. The chamber is equipped with a reflection high-energy electron diffraction (RHEED) apparatus and an oblique-incidence optical reflectance difference measurement system.^{10,11} The incidence plane of the RHEED electron beam coincides with the [010] axis of the SrTiO₃(001) substrate, and the incidence angle of the beam is adjusted to the out-of-phase condition during the growth experiment. The substrate is attached to a heater plate and its temperature is monitored directly with an optical pyrometer. The laser-ablation target is a ceramic disk made of stoichiometric SrTiO₃ doped with 10 mol% Nb. The deposition is done either in a molecular oxygen ambient or in an *oxygen-free* ambient under base pressure. Molecular oxygen is introduced to the chamber through a nozzle that is directed at the substrate surface at a distance 10 cm away. The oxygen partial pressure is monitored with an ion gauge. The actual oxygen pressure at the substrate surface is higher than the ion gauge reading. To investigate the recrystallization and oxida-

tion kinetics, we interrupt the deposition at the completion of one monolayer (ML) and monitor the properties of the monolayer with RHEED and the optical reflectance difference signal.

The oblique-incidence optical reflectance difference (OI-RD) system is the same as reported in Refs. 10 and 11. In our present experiment, the incidence angle is $\theta_{\text{inc}} \approx 79^\circ$. Let r_{p0} and r_{s0} be the reflection coefficients for *p*- and *s*-polarized light at wavelength $\lambda = 632.8$ nm from the substrate before deposition. And let r_p and r_s be the reflection coefficients during and after the deposition of Nb:SrTiO₃. Let $\Delta_p \equiv (r_p - r_{p0})/r_{p0}$ and $\Delta_s \equiv (r_s - r_{s0})/r_{s0}$. Our OI-RD system enables us to measure the reflectance difference $|r_p/r_{p0}|^2 - |r_s/r_{s0}|^2$. Since we detect the signal change in response to deposition of one monolayer with a unit-cell height of $d_0 = 0.39$ nm, we have approximately $|r_p/r_{p0}|^2 - |r_s/r_{s0}|^2 \cong 2 \text{Re}\{\Delta_p - \Delta_s\}$. As shown by Zhu and co-workers, $\text{Re}\{\Delta_p - \Delta_s\}$ monitors the optical absorption in the deposited monolayer.^{9,12–15}

Figure 1 shows the specular RHEED intensity measured

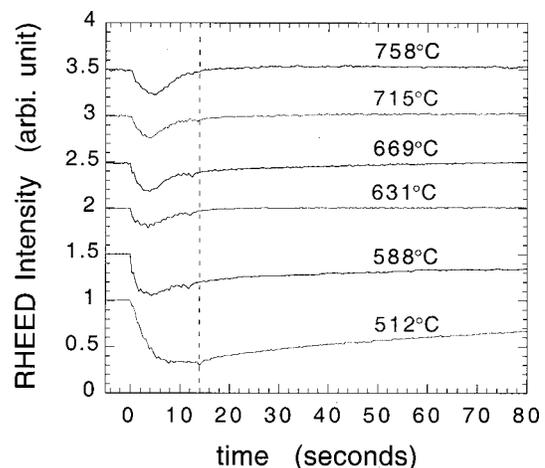


FIG. 1. Specular RHEED intensity from the surface of a SrTiO₃(100) substrate during one cycle of interrupted deposition of Nb:SrTiO₃ in an *oxygen-free* ambient. The measurement is performed in the temperature range from 512 to 758 °C. The dotted line marks the completion of deposition of 1 ML.

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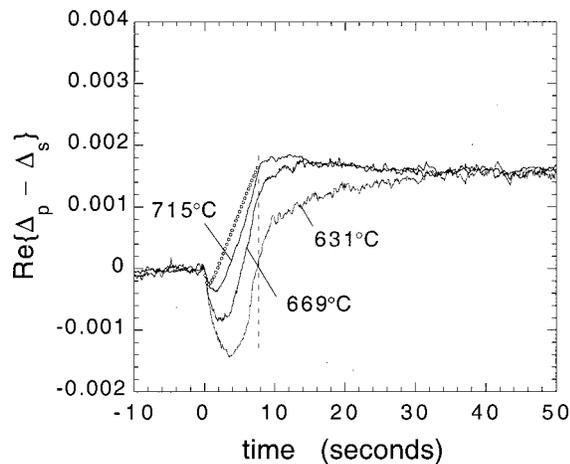


FIG. 2. Optical reflectance difference signal $\text{Re}\{\Delta_p - \Delta_s\}$ from the surface of a $\text{SrTiO}_3(100)$ substrate during one cycle of interrupted deposition of Nb:SrTiO_3 in an *molecular oxygen ambient* of 1.6×10^{-6} Torr. Measurement is performed in the temperature range from 630 to 715 °C. The dotted line marks the completion of deposition of 1 ML. Open circles are calculated $\text{Re}\{\Delta_p - \Delta_s\}$ using the complex refractive index for stoichiometric 10 mol % Nb:SrTiO_3 .

before and after the deposition of 1 ML of Nb:SrTiO_3 in an *oxygen-free* ambient under a base pressure of 1×10^{-7} Torr. Above 630 °C, the RHEED intensity restores to the predeposition level at the completion of deposition. Usually, this indicates that the growth of Nb:SrTiO_3 proceeds in a nearly perfect layer-by-layer mode. Below 630 °C, however, the RHEED intensity no longer recovers fully immediately after the deposition and the residual change in RHEED intensity continues to recover. It means that below 630 °C and in the absence of ambient oxygen the epitaxy of Nb:SrTiO_3 proceeds in a three-dimensional mode. If we flow molecular oxygen of 1.6×10^{-6} Torr through the deposition chamber, the layer-by-layer growth extends to lower temperatures, indicating that the recrystallization kinetics depends partly on the oxidation state of the as-deposited layer.

The optical reflectance difference signal responds to both recrystallization and oxidation processes. In Fig. 2, we show $\text{Re}\{\Delta_p - \Delta_s\}$ over one interrupted deposition cycle in a molecular oxygen ambient at 1.6×10^{-6} Torr. Above 670 °C, the optical signal dips initially and then rises above the predeposition level by $\text{Re}\{\Delta_p - \Delta_s\} \sim 0.0016$. The signal levels off almost immediately afterward, indicating that the recrystallization and oxidation of the monolayer film are complete. The net change in reflectance difference is expected of heteroepitaxy when the deposited material is different from the host. We have separately measured the complex refractive index $n_{\text{Nb:STO}} = 2.61 + i0.074$ for stoichiometric Nb:SrTiO_3 at the He-Ne laser wavelength.¹⁶ Knowing also the refractive index $n_{\text{STO}} = 2.379$ for the substrate (e.g., stoichiometric SrTiO_3), we computed $\text{Re}\{\Delta_p - \Delta_s\}$ assuming that the as-deposited monolayer of Nb:SrTiO_3 forms a smooth, compact film. The calculated value (open circles in Fig. 2) reproduces the experiment very well, and thus confirms the conclusion of a complete layer-by-layer epitaxy including oxygen stoichiometry. Below 630 °C, $\text{Re}\{\Delta_p - \Delta_s\}$ dips down further during the deposition and rises back only to a lower level at the completion of monolayer deposition. The signal continues to recover to the equilibrium value of 0.0016. This is

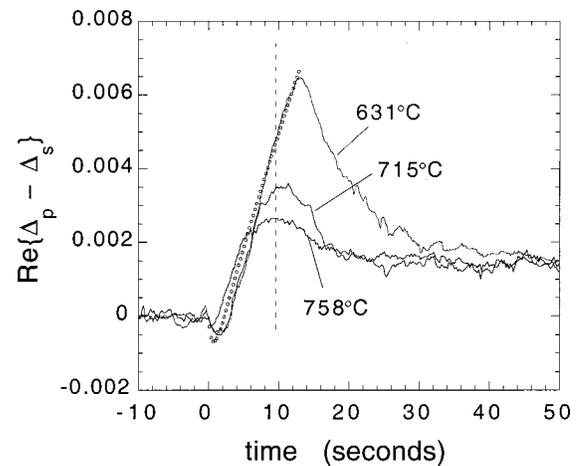


FIG. 3. $\text{Re}\{\Delta_p - \Delta_s\}$ from the surface of a $\text{SrTiO}_3(100)$ substrate during one cycle of interrupted deposition of Nb:SrTiO_3 in an *oxygen-free* ambient. Measurement is performed in the temperature range from 630 to 758 °C. The dotted line marks the completion of deposition of 1 ML. Open circles are calculated $\text{Re}\{\Delta_p - \Delta_s\}$ using the complex refractive index for oxygen-deficient Nb:SrTiO_3 .

consistent with the RHEED observation of incomplete recrystallization immediately after the deposition. The increasingly large drop in $\text{Re}\{\Delta_p - \Delta_s\}$ is associated with the buildup of roughness due to insufficient mass transport during the growth.

In an *oxygen-free* ambient and above 630 °C, the reflectivity difference signal $\text{Re}\{\Delta_p - \Delta_s\}$ behaves differently, as shown in Fig. 3. It goes through a smaller dip initially and then rises up to a level markedly higher than the equilibrium value of 0.0016 at the completion of monolayer deposition. The optical signal decreases afterward and reaches the equilibrium value after a period of time. We note that in this temperature range the RHEED intensity recovers as soon as the monolayer deposition is complete (see Fig. 1). This means that the overshoot in the optical signal must result from the chemical composition of the unit cell. In the present case it has to be caused by the oxygen deficiency in the Nb:STO unit cells for lack of ambient oxygen during deposition. We have separately measured the complex refractive index, $n_{\text{Nb:STO}}^{\text{O-deficient}} = 3.00 + i0.263$, for 10 mol % Nb:STO that was grown in an *oxygen-free* ambient in a layer-by-layer mode.¹⁶ Using this value and assuming that the as-deposited monolayer of Nb:SrTiO_3 forms a smooth, compact film, we found the calculated $\text{Re}\{\Delta_p - \Delta_s\}$ (shown in the open circles in Fig. 3) to reproduce both qualitatively and quantitatively the experimental result taken at 631 °C. At this temperature oxidation during the deposition has not had a significant influence.

The continuing evolution of the optical reflectance difference signal to the equilibrium value of 0.0016 indicates that *the Nb:STO monolayer is being oxidized to the correct oxygen stoichiometry even in the absence of ambient oxygen*. This means that *the $\text{SrTiO}_3(001)$ substrate has been supplying the needed oxygen at temperatures above 631 °C*. The temperature dependence of the rate at which the optical signal reaches the equilibrium reflects the “apparent” kinetics of oxygen transport from the bulk $\text{SrTiO}_3(001)$ substrate to the surface. We found that the kinetics is not simply dominated by the bulk diffusion of oxygen atoms or oxygen va-

cancies. In fact, the time that it takes the optical signal to reach the equilibrium value increases if we increase the time interval between two successive interrupted deposition cycles. A longer time interval should produce a smoother growth surface with less structural defects, and particularly, step edges. This suggests that a smoother surface inhibits the overall transport of oxygen vacancies or oxygen atoms in the topmost monolayer into and out of the substrate.

It has been shown recently by Moos and co-workers¹⁷ that at temperatures below 800 °C singly ionized oxygen vacancies ($V_{\dot{O}}$) form in the bulk of SrTiO₃, presumably in TiO₂ planes.¹⁴ Between 630 and 800 °C, the rate of diffusion for oxygen vacancies has been reported to be 2–3 orders of magnitude larger than that for oxygen atoms.¹⁸ We should then expect the transport of oxygen vacancies instead of oxygen atoms to dominate the kinetics of oxygen supply to the as-deposited monolayer. Between 760 and 630 °C (relevant to Fig. 3), the equilibrium concentration of oxygen vacancies in a stoichiometric SrTiO₃ is estimated to be around $[V_{\dot{O}}] \sim 10^{17} \text{ cm}^{-3}$ or $[V_{\dot{O}}]d_0^3 \sim 10^{-5}$ (extrapolated from Table 1 of Ref. 17). When a monolayer of Nb:SrTiO₃ is deposited on SrTiO₃(001) under the pulsed-laser-deposition condition, it has a much higher volume concentration of oxygen vacancies (by at least three orders of magnitude) than that in the bulk, as evidenced by a large change (more than 10%) in the complex refractive index. The chemical potential difference resulting from the large difference in volume concentration drives the oxygen vacancies in the as-deposited monolayer into the bulk. Since the optical penetration depth into stoichiometric Nb:SrTiO₃ at the He–Ne laser wavelength is 1.4 μm and oxygen vacancies traverse 3–30 μm in a SrTiO₃ crystal in a time period of 10 s between 760 and 630 °C,^{18,19} the oxygen vacancy transport is sufficiently fast to restore the oxygen stoichiometry in the deposited monolayer, as shown in Fig. 3.

Segregation of materials to the surface of a solid at elevated temperatures through creation of bulk vacancies and their diffusion toward the surface have been reported previously. McCarty and co-workers recently studied the surface morphology of NiAl(110) as a function of temperature using low-energy electron microscopy (LEEM).²⁰ These authors observed that at above 776 °C the NiAl islands on the surface expand *in the absence of external supply of materials*. They concluded that extra NiAl units for the expansion of the two-dimensional NiAl islands come from the NiAl substrate through formation of vacancies and the subsequent diffusion of the NiAl unit towards (or that of vacancies away from) the surface. The process is driven by the chemical potential difference, which depends on the temperature. They also found that the rates of bulk vacancy creation (resulting in extra NiAl units) are controlled by atomic steps rather than terrace sites on the NiAl(011) surface. We believe that similar processes likely have taken place in the heteroepitaxy of

Nb:SrTiO₃ on SrTiO₃(001) at temperatures above 630 °C. Our observation that oxidation through in-diffusion of oxygen vacancies is slowed down when the time interval between two successive deposition cycles increases shows that the defects and step edges serve as passageways for oxygen vacancies to transport into the bulk.

In conclusion, oxidation of epitaxially grown perovskite-oxide thin film on SrTiO₃(001) is significantly influenced by the segregation of oxygen atoms from the bulk through transport of oxygen vacancies from the surface into the bulk at temperatures above 630 °C. Defects and step edges may have a large effect on the oxygen vacancy transport to and from the surface layer. We are currently investigating the step-edge effect more quantitatively using LEEM.

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