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In-diffusion of oxygen vacancies near step edges dominates the oxidation of perovskite films

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Abstract

By a Monte Carlo simulation of the deposition process and a mean-field theory model of the surface structure, we have successfully reproduced experimental oblique-incidence optical reflectance difference signals from laser molecular beam epitaxy of Nb:SrTiO₃ on a SrTiO₃ substrate in ambient oxygen. We find that during deposition the concentration of oxygen vacancies close to step edges is larger than that on flat terraces and remains stable. We suggest that oxygen vacancies diffusing on the surface tend to accumulate near step edges due to their slow in-diffusion rate there, and that this in-diffusion dominates the oxidation of as-deposited film.

Perovskite-type oxides have been studied extensively [1–5] in the past because of their importance in basic research and thin-film applications for superconductivity, ferroelectricity, dielectricity, thermoelectricity, piezoelectricity, photoelectricity, nonlinear optics, colossal magnetoresistance, and so on. The properties of perovskite films are dependent on oxygen content [6, 7], in addition to crystallinity. However, most perovskite films deposited under pulsed laser deposition are oxygen deficient. Photoemission studies by many groups have shown that oxygen deficiency in a perovskite crystal is mostly in the form of oxygen vacancies [8, 9]; thus the dynamics of oxidation and the diffusion of oxygen vacancies have attracted considerable interest.

Our previous work has shown that the chemical potential disparity on a surface drives oxygen vacancies in as-grown oxide films to move inwards, so the films can still be oxidized in vacuum at a typical growth temperature [10]. It has also been found that the in-diffusion of surface oxygen vacancies mostly takes place at the step edges. Though both the surface

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diffusion towards step edges and the in-diffusion at the step edges of oxygen vacancies may be the limiting factor for the oxidation process of a film, it is not yet clear which diffusion dominates the oxidation process.

In this paper we present a simulation of oblique-incidence optical reflectance difference (OI-RD) signals during laser molecular beam epitaxy (MBE) of Nb:SrTiO₃ on SrTiO₃ substrate in ambient oxygen. By comparison with the experimental results we find that the concentration of oxygen vacancies near the steps is larger than that on flat terraces during film growth. We propose that the oxygen vacancies diffusing on a surface tend to accumulate near step edges due to their slow in-diffusion rate there. As a result, this in-diffusion dominates the oxidation process.

The experiments were performed in a laser MBE [11, 12] chamber with an oxygen pressure of 1.5×10^{-4} Pa. The chamber is equipped with a standard reflection high-energy electron diffraction (RHEED) apparatus and an OI-RD measurement system. The temperature of the substrate was kept at 715 °C during the deposition, and was monitored by an optical pyrometer. A sintered ceramic of stoichiometric Nb:SrTiO₃ (10 mol%) was used as the target. The OI-RD experimental setup and procedures have been described previously [13]. To recapitulate briefly, let r_{p0} and r_{s0} be the reflectivities from the bare substrate for p- and s-polarized light at the wavelength $\lambda = 632.8$ nm of a He-Ne probe laser, and r_p and r_s be the reflectivities during growth, respectively. Fractional changes in reflectivity are defined as $\Delta p = |(r_p - r_{p0})/r_{p0}|$ and $\Delta s = |(r_s - r_{s0})/r_{s0}|$. The difference, defined as $\text{Re}\{\Delta p - \Delta s\}$, is measured in the OI-RD technique.

To obtain information about the effective dielectric functions of each section of the film we simulated the OI-RD signals for the growth process. A four-medium system (including ambient, surface, bulk film, and substrate conditions) was used in our work. As shown by Kalff *et al* [14], Vrijmoeth *et al* [15], and others in scanning tunneling microscopy studies of epitaxy and ion erosion of crystalline metals, the majority of surface atoms on a growth or erosion surface are on terraces, while a minority are near step edges. In this case, to describe a more realistic system, we further divided the surface into two main parts: terraces and steps, and set ε_t and ε_s as their effective dielectric functions, respectively. Since the imaginary part of the effective dielectric function is associated with the oxygen vacancy concentration [16], these functions can reveal information about the dynamics of surface oxidation.

We employed the Monte Carlo method to simulate the deposition process [17, 18], and characterized the film structure with the mean-field theory proposed by Zhu [19]. In the simulation, the unit cell is treated as a cubic growth unit, whose mobility and nearest-neighbour bonding of units are isotropic (the solid-on-solid model) [20]. The simulation was carried out on a 60×60 flat lattice with periodic boundary conditions. The growth kinetics was described as two processes: the deposition of units onto the substrate at random sites, and subsequent migration of surface units. According to the nature of pulsed laser deposition, unit cells were assumed to impinge onto the substrate batch by batch rather than one by one [17, 18]. The migration was taken as a nearest-neighbour hopping process at a rate $K_T = K_0 \exp(-E_D/k_B T)$, where T is the substrate temperature, $K_0 = 2k_B T/h$, k_B is Boltzmann's constant, h is Planck's constant, and E_D is the hopping barrier. The barrier of a unit with n lateral nearest neighbours is given by $E_D = E_S + nE_N$, where E_S is the contribution from the unit below the migrating one, and E_N is the contribution from each nearest neighbour ($n = 0, \dots, 4$). The activation energy associated with the surface relaxation process during SrTiO₃ epitaxial film growth was estimated to be 0.5 eV by Lee *et al* [21] and about 3.5 eV by Lippmaa *et al* [22]. While no accurate values of E_S and E_N for Nb:SrTiO₃ have been reported, in our calculation we assume E_S and E_N to have reasonable values of 1.1 and 0.05 eV (the error of the absolute value does not change the qualitative results), respectively. With a temperature

of $T = 715^\circ\text{C}$, the deposition rate is calibrated to be 36 pulses for one unit-cell layer (each pulse introduces 100 unit cells).

At the same time, we collected statistics of numbers of step edge atoms and terrace atoms on the surface to obtain their coverage, and calculated the reflectivity for s- and p-polarized light as the sum of the contributions from all units:

$$r_{s(p)} = \sum_{j=0} r_{s(p)}^{(t)}(d_j) \theta_{j,t} \exp[-i4\pi(d_j - \langle d \rangle) \cos \phi_{\text{inc}}/\lambda] + \sum_{j=0} r_{s(p)}^{(\text{step})}(d_j) \theta_{j,\text{step}} \exp[-i4\pi(d_j - \langle d \rangle) \cos \phi_{\text{inc}}/\lambda], \quad (1)$$

where $\theta_{i,t}$ is the coverage of the j th ‘coalesced’ terrace atoms at a distance $d_j = jd_0$ away from the top surface, $\theta_{i,\text{step}}$ the corresponding coverage of step edge atoms, d_0 the thickness of one monolayer in the direction normal to the substrate, d_j the height of each unit, $\langle d \rangle$ the average thickness of the bulk film, ϕ_{inc} the incident angle, and $\theta_{\text{step}} = \sum_{i=0} \theta_{i,\text{step}}$ the total coverage of step edge atoms. Here $r_{s(p)}^{(t)}(d_j)$ is the reflectivity of one unit for s(p)-polarized light from a four-medium system that consists of vacuum, a monolayer of surface atoms (step edge atoms or terrace atoms), a layer of bulk-phase film, and substrate. Also the surface RMS (root mean square) roughness could be simulated with

$$\sigma_s = \text{RMS} = \sqrt{\sum_{i,j} (h_{i,j} - h_{\text{ave}})^2 / L}, \quad (2)$$

where h_{ave} is the average height of all the units on the surface, L is the number of the lattice sites, and $h_{i,j}$ is the height of the units at the lattice site (i, j) . By comparing our simulated OI-RD results with the experimental signals we can then derive information about the effective dielectric functions of the film system during growth. As the growth period is much less than the annealing time, it is assumed that the effective dielectric functions of each part of the film system remain constant during growth. It should be noted that in this paper we focus only on the imaginary part of the effective dielectric functions. Information from the real part of the effective dielectric functions is ignored.

The experimental RHEED and OI-RD signals obtained in monolayer growth are shown in figures 1(a) and (b), respectively. A remarkable characteristic of the monolayer OI-RD signal is that there is a small tip at the beginning of the deposition, and its minimum appears nearly at the same time when the surface is roughest, judging from the corresponding RHEED data. The RHEED and OI-RD signals both correspond to a monolayer growth. Further experimental results show that a small tip is frequently found in experiments [6, 10, 17] and the intensities of these small tips vary with experimental conditions. These tips usually appeared when the film was growing under oxygen ambient, but they seldom appeared in oxygen-free ambient. To clarify the origin of the tip we simulated the OI-RD signal during growth. We found that the tip is associated with two initial conditions: the surface roughness and the difference between the imaginary parts of the effective dielectric functions of step edge atoms and terrace atoms $\delta\varepsilon = \text{Im}(\varepsilon_s - \varepsilon_t)$.

The simulated OI-RD results for growth with different surface roughnesses are shown in figure 2(a). Curve 1 corresponds to the smoothest surface with σ_s of 0.005 nm, curve 2 corresponds to σ_s of 0.034 nm, and curve 3 to the roughest surface with σ_s of 0.067 nm. Figure 2(b) displays the corresponding simulated θ_{step} . It is clear that when the initial θ_{step} is large, which means a rougher surface, the OI-RD tip appears earlier and its intensity is smaller. Only when the surface is very flat do the OI-RD and θ_{step} both come to an extremum at nearly the same time. The simulated OI-RD signals for growth with different $\delta\varepsilon$ and all with ideal flat surfaces are displayed in figure 3. The values of $\delta\varepsilon$ corresponding to curves A–E in figure 3

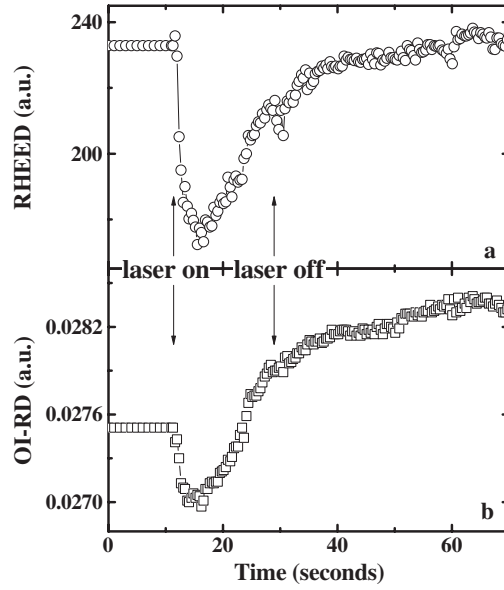


Figure 1. Signal intensity versus time during intermittent deposition of one Nb:SrTiO₃ monolayer on SrTiO₃(001) in ambient oxygen at 715 °C from (a) RHEED and (b) OI-RD experimental measurements.

are 0.0, 1.7, 2.2, 2.7, and 3.2, respectively. Curve A does not have a tip. Among the curves which have tips, curve B corresponds to the smallest $\delta\varepsilon$, and curve E to the largest $\delta\varepsilon$. We see here that when $\delta\varepsilon$ is larger the OI-RD tip appears later and its intensity is larger. The inset shows the intensity of the small tip as a function of the difference $\delta\varepsilon$. It is evident that the intensity of the small tip has a near linear dependence on $\delta\varepsilon$ over a large range. Returning to the experiment results, this may mean that the oxygen ambient during growth caused a larger difference ($\delta\varepsilon$) between the imaginary parts of the dielectric functions of atoms on terraces and step edges. Moreover, further simulation shows that when $\delta\varepsilon = 0$, no matter what the initial surface roughness is, the tip does not appear.

We have thus found from the simulation that the intensity of the OI-RD tip is roughly proportional to $\Delta\theta_{\text{step}}$ and $\delta\varepsilon$, where $\Delta\theta_{\text{step}} = (\theta_{\text{step}})_{\text{max}} - (\theta_{\text{step}})_{\text{initial}}$, $(\theta_{\text{step}})_{\text{max}}$ is the maximum coverage of step edge atoms during growth, and $(\theta_{\text{step}})_{\text{initial}}$ the coverage of step edge atoms before deposition. What may be more important is that we found $\delta\varepsilon > 0$ is a necessary condition for the appearance of the tip.

Since $\delta\varepsilon > 0$, $\text{Im}(\varepsilon_s)$ must be larger than $\text{Im}(\varepsilon_t)$. The imaginary part of the effective dielectric function is associated with the oxygen vacancy concentration [16]; thus the concentration of oxygen vacancies near step edges is larger than that on terraces. It is known that diffusion of oxygen vacancies both on the surface and into the film exists during film growth, and our previous work has shown that the in-diffusion of surface oxygen vacancies mostly takes place at step edges [10]. Hence, if the diffusion rate of oxygen vacancies towards step edges is less than that into the film, oxygen vacancies would not accumulate near step edges. However, the simulation demonstrates that most of the oxygen vacancies accumulate close to step edges and their concentration changes little during growth. We suggest that, though the step edges act as a route for oxygen vacancies on the surface to move into the film, due to their low in-diffusion rate their concentration does not decrease markedly. Our

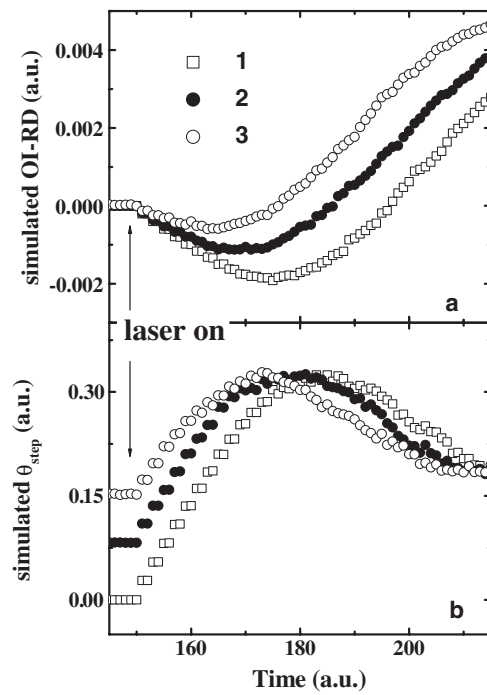


Figure 2. (a) Three different simulated OI-RD signals as a function of time for growth with different initial surface roughnesses. (b) The corresponding simulated variation of θ_{step} . Curves 1–3 indicate increasing surface roughness.

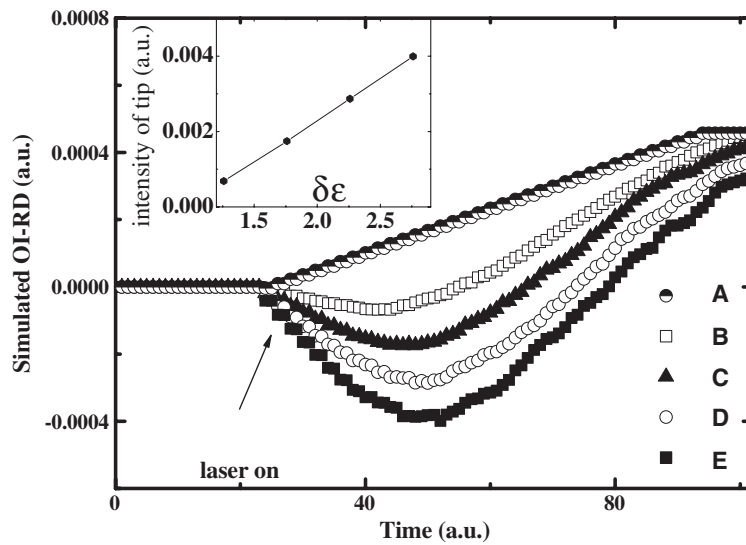


Figure 3. Five different simulated OI-RD signals as a function of time for growth with different $\delta\epsilon$. The inset shows the tip intensity as a function of the difference $\delta\epsilon$.

conclusion is that the in-diffusion rate of oxygen vacancies is limited by step edges. No matter how large the surface diffusion rate is, the oxidation process is dominated by the in-diffusion of oxygen vacancies near step edges.

To summarize, we have found that the step edges play an important role in the oxidation of perovskite films. Through comparison of simulated OI-RD results for the growth process with experimental data, the imaginary part of the effective dielectric function of step edge atoms is found to be larger than that of terrace atoms during the growth, which indicates that the concentration of oxygen vacancies near step edges is larger than that of flat terraces. We further conclude that the in-diffusion of oxygen vacancies is limited by step edges so that the oxygen vacancies on the surface tend to accumulate near these edges. As a result, the in-diffusion of oxygen vacancies dominates the oxidation process. Further study of OI-RD signals of thin-film growth with different temperatures and oxygen pressures is expected to reveal more details about the dynamics of film growth.

Acknowledgments

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