

## Oxidation kinetics in $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_{3-\delta}$ epitaxy on $\text{SrTiO}_3$ (001) during pulsed-laser deposition

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Using an oblique-incidence optical reflectance difference technique, we study the kinetics of  $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_{3-\delta}$  (LBMO) epitaxy on  $\text{SrTiO}_3$ (001) during pulsed-laser deposition. By monitoring the recovery of the optical response function from one-monolayer-deposited LBMO, we found that under the conditions studied, the epitaxy was rate limited by the oxidation of the as-deposited monolayer with an activation barrier of 1 eV/atom or 23 kcal/mol. The result reveals the origin of oxygen deficiency often found in manganite thin films. © 1999 American Institute of Physics. [S0003-6951(99)03723-7]

The doped manganese oxides (the manganites) have been the focus of intensive research recently due to their remarkable colossal magnetoresistance (CMR) effect.<sup>1-3</sup> For applications in magnetic sensor or memory devices, manganite materials should be made in the thin-film form. It has been known, however, that manganite thin films grown by various deposition techniques are generally oxygen deficient.<sup>4,5</sup> For some manganites, an oxygen pressure as high as 1 Torr has to be used during the deposition.<sup>6</sup> The oxygen deficiency causes magnetic inhomogeneity that in turn affects the CMR effect.<sup>7</sup> This may be improved by annealing of as-grown films in oxygen atmosphere,<sup>8</sup> although such treatment has been mostly done by trial and error. It is most desirable to understand the origin of the oxygen deficiency in terms of the kinetics of oxidation during epitaxial growth, which requires *in situ* monitoring of the film growth under high oxidant pressures. In this letter, we report an oblique-incidence optical reflectance difference study of the heteroepitaxy of  $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_{3-\delta}$  (LBMO) thin films on a flat  $\text{SrTiO}_3$  (STO) substrate. LBMO is a CMR material in which oxygen deficiency in thin films can be reduced more easily than in other CMR systems such as  $(\text{Nd}, \text{Sr})\text{MnO}_3$ .<sup>1</sup> Through *in situ* monitoring of the oxidation process, we were able to reveal the kinetics of oxidation of LBMO monolayer films.

In the oblique-incidence optical reflectance difference measurement, we monitor the evolution of the optical reflectivity difference between the *s*- and *p*-polarized light after the deposition of one monolayer (ML) of LBMO on STO (001). We determine the “relaxation” or “recovery” time constant of the epitaxial layer as a function of the substrate temperature (750–850 °C) and the oxygen pressure (0.3–0.6 Torr). This technique has recently been applied by Zhu and co-

workers in homoepitaxy on STO (001) in an ozone environment.<sup>9</sup> Complimentary to the reflection high-energy electron-diffraction (RHEED) technique, the optical technique is effective under high ambient pressure as well as vacuum conditions. In addition to probing the structural change during the epitaxy, the optical reflectance difference signal also detects the change in the electronic or chemical state of the epitaxy.<sup>9</sup>

Monolayer thin films are deposited in a pulsed-laser deposition chamber with a base pressure of  $1 \times 10^{-6}$  Torr. A 10 mm × 3 mm × 1 mm STO (001) single crystal with a miscut angle of 0.1° is used as the substrate. They were preannealed in oxygen flow at 1100 °C for 4 h. Surface imaging using scanning tunneling microscopy shows that the surface exhibits terraces predominantly 0.4 nm (one unit cell) in height with widths of ~300 nm, indicating a miscut angle of <0.08°. A small portion of the surface displays 0.2 nm steps. All terraces are atomically flat with a surface corrugation less than 0.1 nm. Such a high-quality surface is found to be essential for the following study. The target is a ceramic pellet of stoichiometric  $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$ . The 248 nm pulsed laser is operated at a repetition rate of 5 Hz. The target–substrate distance is about 10 cm. The deposition rate is calibrated to be 1.4 Å/s or 0.3 ML/s at around 0.3 Torr of pure oxygen. It takes 14 laser pulses or roughly 3 s at 5 Hz to deposit one monolayer (i.e., one unit cell thick) of LBMO.

For the optical reflectance measurement, we use a 2 mW linearly polarized He–He laser as a source. The optical setup is essentially the same as that reported in Ref. 9. We use a photoelastic modulator (PEM-90, Hinds Instruments) to change the polarization from *s* to *p* polarization at a rate of  $\omega = 50$  kHz. The polarization modulated He–Ne laser beam is incident on the STO (001) substrate at an angle of 65°. The reflected beam passes through a linear polarizer with the transmission axis at an angle of  $\theta$  from the *s* polarization. The amplitude of the reflected light intensity that varies at  $2\omega$  (100 kHz) has been shown to be  $I(2\Omega)$

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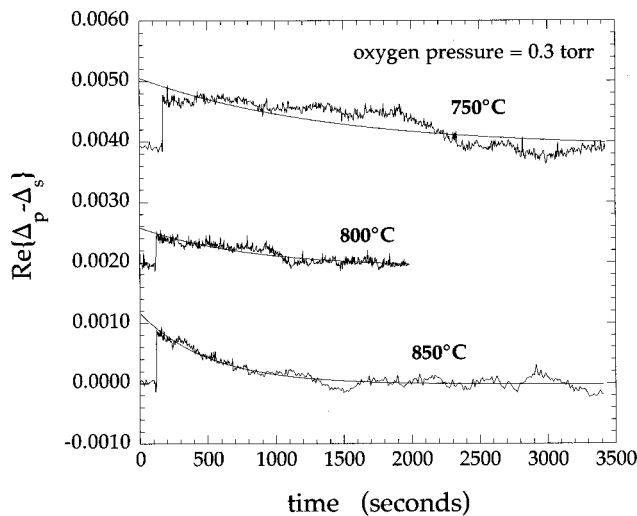


FIG. 1. Optical reflectance difference signal  $\text{Re}\{\Delta_p - \Delta_s\}$  vs time before and after the deposition of 1 ML of LBMO at an oxygen pressure of 0.3 Torr. The data were taken at three different temperatures. The smooth solid lines are calculated with a rate constant  $\kappa(T, P_{O_2}) = \alpha_0 \exp(-E_a/k_B T) P_{O_2}$  with  $\alpha_0 = 180 \text{ Torr}^{-1} \text{ s}^{-1}$  and  $E_a = 1.0 \text{ eV/atom}$  (or 23 kcal/mol).

$= 0.24 I_{\text{inc}} (|r_p \sin \theta|^2 - |r_s \cos \theta|^2)$ . Before deposition, we adjust  $\theta$  so that  $|r_{p0} \sin \theta|^2 - |r_{s0} \cos \theta|^2 = 0$ . The subsequent change in  $I(2\Omega)$ , in response to the deposition and epitaxy, is given by

$$I(2\Omega) = 0.48 I_{\text{inc}} |r_{p0} \sin \theta|^2 \text{Re}\{\Delta_p - \Delta_s\}. \quad (1)$$

Here, we define  $\Delta_p \equiv (r_p - r_{p0})/r_{p0}$  and  $\Delta_s \equiv (r_s - r_{s0})/r_{s0}$ .  $I(2\Omega)$  is detected with a photodiode and the resultant photocurrent is measured with a EG&G digital lock-in amplifier. We separately measure  $I_{\text{inc}} |r_{p0} \sin \theta|^2$ . From the two measurements we deduce  $\text{Re}\{\Delta_p - \Delta_s\}$ . At the He-Ne wavelength of 633 nm, the STO (001) substrate is transparent and has an index of refraction of 2.38. Bulk LBMO is opaque and its optical dielectric constant  $\epsilon = \epsilon' + i\epsilon''$  is expected to be complex. It can be shown that the leading contribution to  $\text{Re}\{\Delta_p - \Delta_s\}$  by a thin LBMO overlayer on a transparent STO substrate comes from  $\epsilon''$ .<sup>9,10</sup> Experimentally, we effectively monitor how the  $\epsilon''$  of a LBMO monolayer at the optical frequency of the He-Ne laser evolves with time during and after the pulsed-laser deposition. The optical  $\epsilon''$  is a function of both the atomic arrangement and electronic (or chemical) state of the LBMO layer. It has a contribution from the ac conductivity of the LBMO monolayer and the latter is related to the low frequency or dc conductivity of the layer.

In Figs. 1 and 2, we display  $\text{Re}\{\Delta_p - \Delta_s\}$  during and after depositing 1 ML of LBMO on STO (001) at 750, 800, and 850 °C. The data shown in Fig. 1 are obtained at an oxygen pressure of 0.3 Torr, and that in Fig. 2 at 0.61 Torr. For the purpose of display, we have vertically separated the curves obtained at different temperatures. As a result, only the changes in  $\text{Re}\{\Delta_p - \Delta_s\}$  after the deposition of a LBMO monolayer are meaningful. Before each deposition, we monitor  $\text{Re}\{\Delta_p - \Delta_s\}$  from the substrate under the same oxygen pressure and the substrate temperature. The signal remains unchanged. It means that the subsequent change in  $\text{Re}\{\Delta_p - \Delta_s\}$  comes ONLY from the deposited monolayer of LBMO. In the experiment, we continue to deposit up to 25 ML of LBMO, one monolayer at a time. We find that the

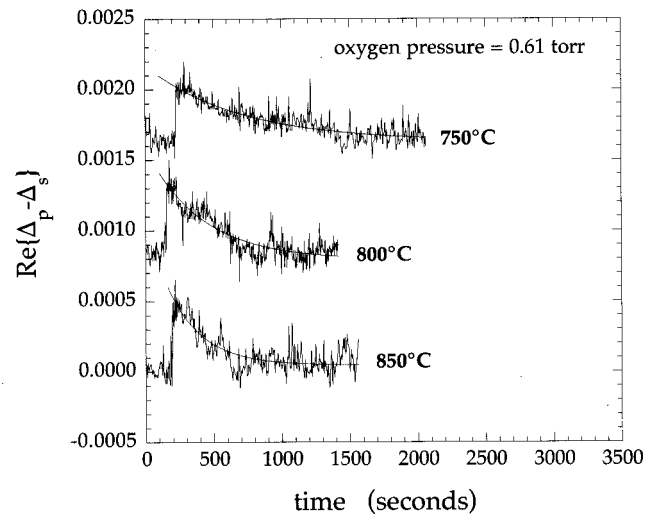


FIG. 2. Optical reflectance difference signal  $\text{Re}\{\Delta_p - \Delta_s\}$  vs time before and after the deposition of 1 ML of LBMO at an oxygen pressure of 0.61 Torr. The data were taken at three different temperatures. The smooth solid lines are calculated with a rate constant  $\kappa(T, P_{O_2}) = \alpha_0 \exp(-E_a/k_B T) P_{O_2}$  with  $\alpha_0 = 180 \text{ Torr}^{-1} \text{ s}^{-1}$  and  $E_a = 1.0 \text{ eV/atom}$  (or 23 kcal/mol).

optical signal in response to the deposition and the recovery of each monolayer behaves essentially the same. This indicates that the termination of each unit cell prior to deposition of a subsequent LBMO layer is roughly the same. At the rate of 0.3 ML/s, the deposition of one monolayer of LBMO causes  $\text{Re}\{\Delta_p - \Delta_s\}$  to jump by roughly 0.005 in all cases. Afterward,  $\text{Re}\{\Delta_p - \Delta_s\}$  restores to its equilibrium value. This process continues for minutes or even up to an hour. The rate of recovery is temperature dependent: it is larger at higher temperatures, indicating that the recovery is a thermally activated process. Most interestingly, the rate of recovery is also dependent upon the ambient oxygen pressure. At a fixed temperature the recovery rate increases linearly with the oxygen pressure. This suggests that the observed recovery is primarily the result of oxidation of the LBMO monolayer rather than the structural regrowth or the surface diffusion of LBMO molecules, which are not expected to depend upon the oxygen pressure. This observation is consistent with the x-ray scattering and ion channeling measurements of thick LBMO films grown at the same pulsed-laser deposition conditions as used in this experiment. These measurements indicate that the films grow epitaxially on STO (001) with high-quality crystalline structures. The monolayer film is, however, oxygen deficient and it is being oxidized over the subsequent minutes or up to one hour.

We now examine the kinetics of the oxidation reaction quantitatively. Let  $\Delta N(t)$  be the surface density of the oxygen deficiency sometime after the deposition. Since the structural regrowth of the LBMO monolayer has already completed,  $\text{Re}\{\Delta_p - \Delta_s\}$  comes only from the oxygen deficiency and thus varies linearly with  $\Delta N(t)$ , namely,  $\text{Re}\{\Delta_p - \Delta_s\} \propto \Delta N(t)$ . As a result of continuing oxidation,  $\Delta N(t)$  is expected to decay at a rate

$$\frac{d(\Delta N)}{dt} = -\kappa(T, P_{O_2}) \Delta N. \quad (2)$$

The rate constant for the oxidation is expected to vary linearly with ambient oxygen pressure so that  $\kappa(T, P_{O_2}) = \alpha(T)P_{O_2}$ . Consequently, we expect

$$\Delta N(t) = \Delta N_0 \exp[-\alpha(T)P_{O_2}t]. \quad (3)$$

Generally, the oxidation reaction is also expected to be thermally activated with

$$\alpha(T) = \alpha_0 \exp(-E_a/k_B T). \quad (4)$$

If such a simple oxidation reaction model adequately describes our experimental observation, we should expect one set of kinetics parameters to describe all six curves shown in Figs. 1 and 2. This is indeed the case. The solid lines in Figs. 1 and 2 are calculated with  $\alpha_0 = 180 \text{ Torr}^{-1} \text{ s}^{-1}$  and  $E_a = 1.0 \text{ eV/atom}$  (or  $23 \text{ kcal/mol}$ ). They fit the experimental data very well. We should note that the value of the activation energy barrier is effectively determined from the oxidation rates measured at three temperatures that are not very far separated. The good agreement with the experimental data on the other hand indicates that the value of  $E_a = 1.0 \text{ eV/atom}$  is a good approximation in the present study. We note that the recovery of the measured  $\text{Re}\{\Delta_p - \Delta_{sf}\}$  has, in fact, two consecutive parts. This means that either the details of the optical response to the oxidation or the oxidation reaction itself is more complex than our simple model. Our present measurements do not have enough signal-to-noise ratio and the dynamic range to separately determine the rate parameters for each part. However, the key feature of the experimental observation is described well by the simple physical picture that the oxidation is the rate-limiting kinetics step in the epitaxy of LBMO on STO (001) in the investigated parameter range.

In most *in situ* deposition of oxide films, the films are grown at an elevated temperature in an oxidant pressure high enough to ensure the phase stability (from  $10^{-5}$  Torr ozone to  $\sim 1$  Torr pure oxygen), and further oxygenation is achieved during the postdeposition cooling in  $\sim 1$  atm oxygen.<sup>11</sup> Our result shows that for manganites, the oxidation kinetics during the growth are much different from other metal oxides: the oxidation of the deposited film takes much longer time. For example, the recovery of  $\text{Re}\{\Delta_p - \Delta_{sf}\}$ , indicative of the oxidation process, is much faster in the growth of STO on STO (001) (less than 20 s under the same condition).<sup>12</sup> The activation energies  $E_a$  are about the same for LBMO and STO, but  $\alpha_0$  is much smaller in LBMO than in STO. To understand the difference, knowledge on the nature of the oxidation reaction and defect chemistry specific to each system is needed. As a result, the as-grown LBMO films are highly oxygen deficient and the oxygen deficiency cannot be easily removed by the postdeposition cooling.

We now briefly remark on the findings of our present work in the light of an earlier work by Ju and co-workers on the dc conductivity of LBMO as a function of oxygen content.<sup>7</sup> These authors found that the dc conductivity increases as the oxygen deficiency in a bulk sample of  $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_{3-\delta}$  (LBMO) decreases from  $\delta = 0.2$  to 0.01 in the temperature range from 0 to 400 K. Their result is consistent with our present optical reflectance difference measurement. The optical reflectance difference signal measures the changes in  $\epsilon''$ , and thus, in ac conductivity of the

deposited LBMO monolayer. We expect such changes to be proportional to the oxygen deficiency. Immediately after the deposition, the as-grown LBMO monolayer has an initial oxygen deficiency that is reflected by the initial change in  $\text{Re}\{\Delta_p - \Delta_{sf}\}$ . The oxygen content and in turn the  $\epsilon''$  (including the ac conductivity) of the LBMO monolayer subsequently restore to their respective equilibrium values as a result of the reaction with the ambient oxygen. The restoration is reflected by the recovery or decay of the optical reflectance difference signal  $\text{Re}\{\Delta_p - \Delta_{sf}\}$  back to its equilibrium value.

In conclusion, we have shown that the oblique-incidence optical reflectance difference technique is a simple and effective means for monitoring in real time the kinetics of thin-film epitaxy under high ambient pressure. In addition to the sensitivity to the atomic arrangement, the optical reflectance difference signal is also sensitive to the evolution of the electronic or chemical state of an epitaxial film. The latter is important for studying oxide epitaxy as the oxidation state may continue to change after the crystalline structure of the film is completed. In the case of LBMO epitaxy on STO (001), our study shows both qualitatively and quantitatively that the oxidation reaction is the rate-limiting step of the growth under the commonly used pulsed-laser deposition conditions. The kinetics parameters obtained in our experiment are important for devising the growth strategy to make fully oxygenated LBMO epitaxial films.

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