

Origin of RHEED intensity oscillations during the growth of $(Y,Dy)Ba_2Cu_3O_{7-x}$ thin films

V. S. Achutharaman, N. Chandrasekhar,* Oriol T. Valls,† and A. M. Goldman

Center for the Science and Application of Superconductivity and School of Physics and Astronomy,
University of Minnesota, Minneapolis, Minnesota 55455

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We propose a mechanism for the origin of RHEED intensity oscillations during the growth of $(Y,Dy)Ba_2Cu_3O_7$ thin films. Surface relaxation and RHEED intensity recovery observed during the growth of these materials are ascribed predominantly to the diffusion of already formed $(Y,Dy)Ba_2Cu_3O_7$ units rather than to the chemical reaction of the constituents to form a unit cell. The validity of the model is demonstrated by comparing the surface step densities determined from results of Monte Carlo simulations with RHEED intensity oscillations observed during pulsed laser deposition.

The realization of structures such as planar Josephson junctions with high-temperature superconducting electrodes and the study of physical properties of ultrathin films in the limit of unit cell thickness require the fabrication of films, structures, and multilayers with atomically smooth surfaces. A comprehensive knowledge of atomistic processes,^{1,2} i.e., the growth kinetics is crucial to understanding and then controlling the evolution of the film surface morphology. The growth of films of high-temperature superconductors involves oxidation, dissociation, and recombination processes on the surface. The formation of the desired superconducting phase is controlled by the substrate temperature and oxygen partial pressure. The deposition technique governs the kinetics on the surface. Reflection high-energy electron diffraction (RHEED) intensity oscillations during the growth of $(R = Y, Dy)Ba_2Cu_3O_7$ (RBCO) on $SrTiO_3$ by molecular-beam epitaxy (MBE) and pulsed laser deposition (PLD) have been reported by a number of groups.³⁻⁷ These oscillations have been thought to be a consequence of unit cell layer-by-layer growth of these materials.³ However, it has been shown that the RHEED intensity depends inversely on the surface step density¹ and hence the intensity oscillations are *not necessarily* a signature of unit cell layer-by-layer growth. Though numerous studies relating to growth mechanisms have been reported, none of these can satisfactorily explain all of the experimental observations.⁸ Transmission electron microscopy⁹ and RHEED (Ref. 3) observations suggest that the films grow by the formation of unit cells of the correct stoichiometry, a growth mode which satisfies the requirement of charge neutrality.

Here, we propose a model for the growth of oxide superconductors by physical vapor deposition techniques, PLD and MBE, which accounts for the experimental RHEED observations. We explain the modulation of the RHEED intensity^{6,7} with the laser pulse during the growth of $YBa_2Cu_3O_{7-x}$ on $SrTiO_3$ by PLD as surface relaxation arising from the diffusion of preformed RBCO units, rather than from the chemical reaction on the surface to form a unit. The results of Monte Carlo simulations of the proposed model of growth by PLD will be presented. We will discuss the similarities and differences between PLD and MBE. We will be concerned only with the *c*-axis oriented growth of these su-

perconductors. The results of our simulations will be seen to agree with the experimental RHEED observations.

The similarity of the intensity oscillations observed during the growth of RBCO by PLD and MBE for similar growth conditions is shown in Fig. 1 and is a key observation suggesting that growth kinetics exhibit universal behavior. The surfaces of the RBCO films grown by MBE and PLD recover or relax when the growth is terminated. This is ob-

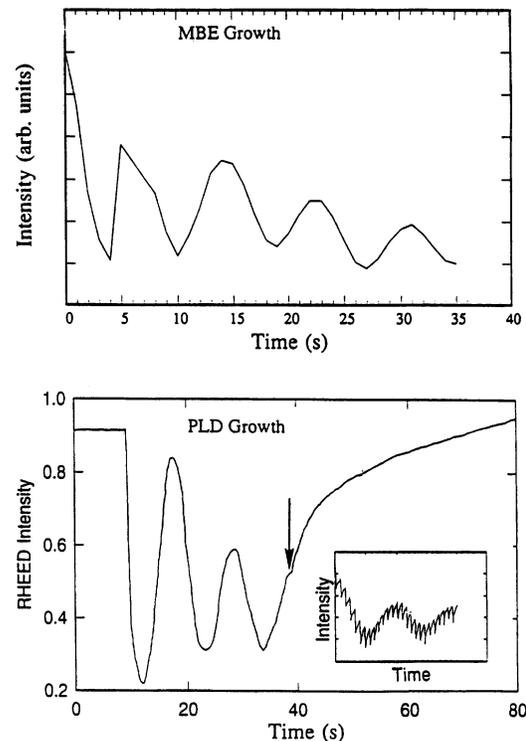


FIG. 1. Comparison of the RHEED intensity oscillations observed during the growth of RBCO by MBE (from Ref. 4) and PLD (from Ref. 7). Arrow indicates the termination of growth. Inset shows the surface relaxation observed between the pulses during PLD using a faster sampling device such as a charge-coupled device camera. Intensities are in arbitrary units and are different for the figure and the inset. Full scale on the time axis of the inset is 9.25 s.

served as an increase in the RHEED intensity upon termination of growth. This increase has to be associated with the rearrangement of material from lower coordination to higher coordination sites which would cause a *decrease* in the surface step density resulting in an *increase* of the RHEED intensity.¹ In RBCO growth, the activation energy associated with this relaxation process during MBE growth has been estimated to be about 0.85 ± 0.1 eV.¹⁰

In the case of PLD, the RHEED intensity decreases during the deposition pulse and then increases as the surface relaxes in the interval between the pulses. From the temperature dependence of the rate of relaxation between pulses, the activation energy for this process has been estimated to be 0.7 ± 0.1 eV.⁶ This surface relaxation should be similar to the growth termination surface recovery as no material is being deposited, if the RBCO units form in a time scale much shorter than the relaxation time for the process. If different processes are active during surface recovery between pulses and during growth termination, then the surface recovery after the laser pulse should display a relaxation behavior with two different time constants. However, this relaxation can be fit by a single time constant suggesting that there is only one predominant process.⁷ Further evidence for this picture comes from the fact that the activation energies obtained for relaxation between pulses⁶ (0.7 ± 0.1 eV) and after growth termination¹⁰ (0.85 ± 0.1 eV) are the same within experimental error.

Both diffusion of the unit cells of RBCO and their dissociation and reformation at a different site can lead to net mass transport on the surface. The Schottky energy for dissociation has been estimated by shell model calculations to be about 20 eV,¹¹ making the dissociation process highly improbable. In the case of ionic solids, the activation energy as well as the binding energies of ions and neutral molecules on nonpolar surfaces are low (≈ 0.2 eV) because "the corrugated electrostatic potential due to the ions decays exponentially outside the surface."¹² This has been verified by recent studies of growth of alkali halides and oxides. Epitaxial MgO and BaO films have been grown by molecular deposition at very low temperatures $\approx T_m/10$ (300 K).¹² However, the RBCO phase cannot be grown at such low temperatures as its growth is reaction controlled. The atomic diffusion coefficients are too low to promote the reaction on the surface and so are the oxygen partial pressures required for stability. The experimentally determined activation energy of 0.7–0.8 eV for RBCO appears to be very reasonable. *We are therefore led to hypothesize that diffusion of RBCO formula units is the cause of surface relaxation.*

Assuming local equilibrium, a RBCO unit can be expected to nucleate when the atomic species required for the stoichiometric compound are present within a certain critical distance.¹³ RBCO forms spontaneously as it is the lowest-energy phase and hence the free energy of formation is negative. The activation energy required for its formation can then be thought of as an effective activation energy of the various diffusion processes needed to achieve the necessary configuration. The number of diffusion jumps depends on the coverage, i.e., the number of unreacted atoms on the surface. The time required for a diffusion jump can be estimated using the equation for the hopping probability ν ,

$$\nu = \nu_0 \exp(-E/k_B T), \quad (1)$$

where ν_0 is the diffusion rate constant, T is the substrate temperature, and E is the activation energy. Taking the diffusion rate constant of the atoms to be $\nu_0 = 10^{13}$ Hz (the vibrational frequency¹), and the activation energy as 2 eV (an upper bound), this time is found to be about 1 ms at 100 K (the usual growth temperature for *c*-axis oriented films). For smaller activation energies, the time required for such a jump would be exponentially smaller. This is clearly two orders of magnitude smaller than the time between pulses (1 s) or the measured relaxation times of the intensity recovery (several hundred milliseconds⁶). The diffusion rate constant of the unit can be determined from measurements⁶ and will be shown below to be about 10^7 Hz which is about six orders of magnitude lower than that for atoms. *Hence, the relaxation process by the diffusion of units is slower even though the activation energy for diffusion of the unit is lower than that for atoms.*

We describe the growth of RBCO films by the following sequence: (1) There is random deposition of material as different species (atoms or complexes) on the substrate. For PLD, with deposition rates of the order of 10^4 nm/s,⁶ deposition occurs in a very short time ($\sim \mu$ s). (2) The next step involves surface migration of the deposited species which is independent of the growth technique used. (3) The RBCO units then crystallize. Atomic rearrangements leading to the correct configurations for crystallization of *c*-axis oriented RBCO occurs due to surface migration. This process, however, depends on both the concentration and the migration of adatoms on the surface, and hence is also dependent on the growth technique. (4) Surface relaxation by diffusion of formula units occurs. This process depends on the surface topography and hence on the growth technique used.

The RHEED intensity oscillations can be understood from this picture of surface relaxation by diffusion of already formed units considered together with the standard step-edge scattering model for RHEED intensity oscillations.^{4,14} The envelope of the oscillations in the case of PLD is similar to that observed during MBE growth and is a consequence of temporal variations in surface step density. The instantaneous drop in the intensity during each pulse of PLD can be associated with random deposition and crystallization of formula units [processes (1) and (3)]. These units then diffuse from low coordination sites to higher coordination sites, thereby causing an increase in the intensity, i.e., a decrease in the step density [process (4)]. In contrast, due to the continuous nature of MBE, this feature does not appear.

We investigated the validity of this model for PLD using Monte Carlo simulations. We used a solid-on-solid model with no vacancies or overhangs. The substrate was a square lattice and we assumed the diffusing entity to be a tetragonal unit formed as the outcome of the fast processes (1) and (2) discussed above. Diffusion perpendicular to the surface was neglected as the bulk diffusion is at least an order of magnitude slower than surface diffusion. The surface migration and crystallization time is two or more orders of magnitude smaller than the duration between the pulses; therefore growth is considered as being initiated by the random deposition of units on the substrate at a rate of FA per pulse site where F is the atomic flux in atoms per unit area and A is the

area per site. Films of thickness less than a certain value (the critical thickness) are strained to match the substrate lattice constant. The critical thickness is about 150–200 Å for the case of RBCO grown on SrTiO₃ (100) substrates.¹⁵ Since the thicknesses of films simulated were much smaller than the critical thickness, the assumptions of a tetragonal unit and isotropic diffusion are justified. The diffusion of the units is modeled as a nearest-neighbor hopping process, again using Eq. (1). Here the activation energy E consists of two terms: E_s , the contribution from the underlying layer, and E_n , the contribution from each nearest neighbor on the top layer. E is given by $E = E_s + nE_n$ where n is the number of nearest neighbors for a particular site. Both the quantities E_s and E_n are “effective” activation energies only and could fluctuate locally, e.g., due to the interactions with the second-nearest neighbors. However, since only nearest-neighbor contributions are considered, the fluctuations in the activation energies are not likely to be very important.

The simulations were carried out on a 96×96 lattice with toroidal boundary conditions which we have verified to be free of finite-size effects. We consider two cases, a surface without any steps (singular surface) and a vicinal surface. The surface step density was estimated in a manner similar to the procedure used by Clarke and Vvedensky¹ who demonstrated that the RHEED intensity depends inversely on the surface step density by qualitatively reproducing the disappearance of the oscillations on vicinal surfaces during the growth of GaAs. Our previous studies on the simulation of growth of the high-temperature superconductors show that the surface step density oscillations are the cause of the RHEED intensity oscillations in these materials.¹⁶ Since we are studying heteroepitaxial growth, the steps in the substrate and film were weighted by the ratio of their heights. The steps on SrTiO₃ and RBCO thus have weights of 1 and 3, respectively. The vicinal surface comprised 3 and 6 terraces, equivalent to vicinal angles of 1.75° and 3.5°, respectively. The simulations were done as a function of the substrate temperature to facilitate comparison with the published experimental results. For each set of growth conditions, step density was evaluated from an average of three Monte Carlo runs. The step density evaluated from the simulations was converted to an intensity value using the equation

$$I = 1 - \frac{1}{3N^2} \sum_{ij} (h_{i,j} - h_{i,j+1}) \cos \phi + (h_{i,j} - h_{i+1,j}) \sin \phi,$$

where N is the size of the lattice, ϕ depends on the azimuth ($\phi = 0$ for [100] azimuth and $\phi = 90$ for [010] azimuth), and h is the height of a lattice site (i, j) . The factor of 3 arises because of the weighting of the steps as explained earlier.

The values of E_s , ν_0 , and E_n need to be assigned to proceed with the simulations. The diffusion parameters cannot be determined from first principles. Hence, we will follow here the only procedure¹ to our knowledge used in the past for their estimation. We assume that the experimentally measured activation energy^{6,10} is dominated by E_s since it is difficult to separate out the *a priori* contributions from E_s and E_n . The validity of this assumption will be established below. As discussed before, since the surface relaxation process is due to the diffusion of RBCO units, the activation energy measured for surface relaxation should be equal to

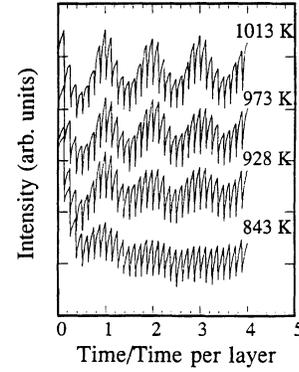


FIG. 2. Temporal variation of the simulated RHEED intensities for different substrate temperatures. Deposition rate, 1.5 Å/s; pulse rate, 1 Hz. Compare with Fig. 1 of Ref. 6.

that for the diffusion of RBCO units. Thus, we take $E_s = 0.85$ eV which is obtained from the surface relaxation measurements.^{6,10} The surface diffusion coefficient at a particular growth temperature can be determined from the transition to the “step-flow” growth mode (evident from the disappearance of RHEED intensity oscillations) during the growth of RBCO on vicinal SrTiO₃ substrates.^{6,7} Using Einstein’s relation, $L^2 = Dt$ where L and t are the terrace width and the surface diffusion time, respectively, the diffusion coefficient D can be determined to be of the order of 10^{-12} cm²/s at 720 °C.⁶ Taking $D(720 \text{ °C}) = 1.0 \times 10^{-12}$ cm²/s, jump distance $a = 3.9$ Å, and $D \approx a^2 \nu$ we obtain the diffusion rate of the units, $\nu_0 = 1.33 \times 10^7$ s⁻¹. Finally, E_n is determined by the best fit to experimental observations as discussed below in connection with Fig. 2. It is found to be 0.25 ± 0.05 eV, consistent with the assumption made in the determination of E_s . Only E_n is adjustable, all other parameters, i.e., are taken from independent experiments.^{6,10} These values could be optimized with the availability of more experimental data.

In Fig. 2, the RHEED intensities obtained from the simulations on a flat surface are plotted as a function of deposition time (in terms of time per unit cell layer). Growth parameters identical to those of the experiment⁶ were chosen so that the comparison could be made: an overall deposition rate of 1.5 Å/s, a pulse rate of 1 Hz, and temperatures of 1013, 973, 928, and 843 K were used. The simulations were done for different values of E_n until the damping of the simulated oscillations agreed with the experiments, for each of the substrate temperatures considered and thus E_n was determined. For low values of E_n (< 0.1 eV), the oscillations are very pronounced and showed no damping at all. For higher values of E_n (> 0.4 eV), the oscillations were drastically damped and were very different compared to the experimental observations. By comparing these results to those reported in Fig. 1 of Ref. 6, it can be seen that the features observed in the experiment are clearly reproduced. The decrease in the intensity during each laser pulse, the surface relaxation between each pulse, and the overall shape of the surface step density oscillations agree extremely well with the experimental RHEED intensity oscillations. The damping of the oscillations also agrees very well with the experimental observations during the MBE growth of these materials.

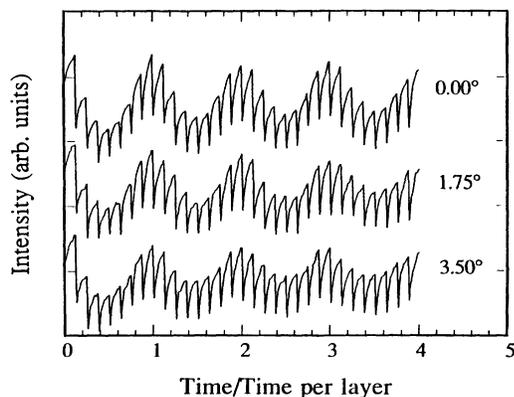


FIG. 3. Temporal variation of the simulated RHEED intensities for different substrate misorientations. Deposition rate, 1.5 Å/s; pulse rate, 1 Hz; temperature, 740 °C. Compare with Fig. 3 of Ref. 6. The amplitude of the oscillations for a vicinal angle of 3.5° is about 50% of that for the flat substrate (0.0°).

As the temperature is reduced, the amplitude of the intensity oscillations decreases. More quantitative comparisons are not possible for this relatively simple model of growth, since we have neglected the occurrence of simultaneous nucleation and growth of *a*-axis and *c*-axis oriented regions which are known to occur at lower substrate temperatures.¹⁷

The simulated RHEED intensities as a function of the misorientation angle are shown in Fig. 3. It can be seen that the amplitude of the intensity oscillations is gradually reduced as the vicinal angle is increased, in accordance with the experimental observations (Fig. 3 of Ref. 6) suggesting a transition to a “step-flow” growth mode. For a vicinal angle of 3.5°, the oscillations in the simulations do not vanish completely as in the case of the experiment. Since the surface step densities were evaluated in the simulations without making any estimation of the relative scattering amplitudes of substrate steps and film steps, we ascribe the discrepancy to diffraction effects.

We now consider the effect of changes in deposition parameters. Frey *et al.*⁷ have also observed surface relaxation between pulses using different growth conditions: an overall deposition rate of 3.4 Å/s, a pulse rate of 4 Hz, and a deposition temperature of 740 °C. Figure 4 compares the results obtained by Frey *et al.*⁷ to our simulation. The simulated intensity matches the experimental intensity except for the

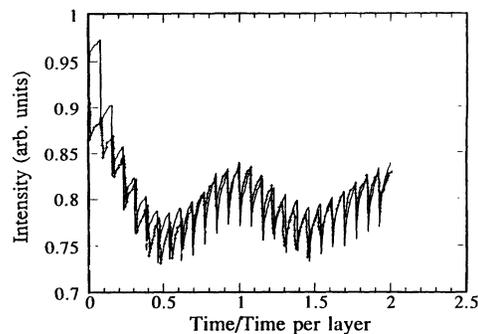


FIG. 4. Comparison of simulated (solid line) and experimental RHEED intensities (dotted) (Ref. 7). Deposition rate, 3.4 Å/s; pulse rate, 4 Hz; temperature, 740 °C. Details given in text.

first few laser pulses. Commercially available substrates are only within 0.5° of the preferred orientation, causing the surface to have steps. In the case of the simulations, we assume a perfectly flat surface without any steps which explains the higher value of the simulated intensity during the first few laser pulses. As the roughness to step density increases with more material deposition, the effect of the initial substrate steps becomes less important. The terrace width is much higher than that required to induce a transition to a “step-flow” growth mode and the substrate steps merely reduce the initial intensity in the case of experimental observations.

In conclusion, we have shown that the epitaxial growth of high-temperature superconducting oxides can be understood in terms of a relatively simple model: random deposition of atoms and/or complexes, surface migration of species for reaction, and diffusion of formula units to higher coordination sites. We have also argued that surface relaxation in these materials is due to the diffusion of charge neutral units and not due to chemical reaction on the surface. The agreement of experimental results with the Monte Carlo simulations is consistent with both the proposed growth model and the fact that RHEED intensity oscillations are due to surface step density oscillations.

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*Present address: Physics Department, Indian Institute of Science, Bangalore 560 012, India.

[†]Also at Minnesota Supercomputer Institute, University of Minnesota, Minneapolis, Minnesota 55455.

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