Reflection High-Energy Electron Diffraction Oscillations during Epitaxial Growth of High-Temperature Superconducting Oxides

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Strong intensity oscillations have been found in reflection high-energy electron diffraction during epitaxial growth of $BaTiO_3$, La_2CuO_4, and $YBa_2Cu_3O_{7-x}$ with perovskite-type structures. The oscillation period corresponds to the height of the minimum unit of each oxide that satisifies the chemical composition and electrical neutrality. The data provide a basic understanding of the epitaxial growth process of ionic oxides.

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The discovery of oscillations in reflection high-energy electron-diffraction (RHEED) specular intensity during epitaxial growth[1] has played a significant role in the understanding of the microscopic processes involved in the epitaxial growth[2,3] of metals and semiconductors. Furthermore, it has aided in the development of extremely precise control over the crystal growth of these materials on the atomic scale.[4] The RHEED oscillations are interpreted to be a consequence of the nucleation of 2D islands and their growth into a flat terrace, in a cyclic process.

Since the discovery of the high-T_c superconducting oxides, much attention has been attracted to the epitaxial film growth of these oxides for the study of basic physics as well as for wide applications. Most preparation methods, including reactive thermal evaporation, reactive sputtering, and laser ablation, are essentially codeposition of the elements. The major point of interest concerning the growth process is to find what the growth unit is: All the element atoms coexist on a substrate surface. The growth unit for single-element metals and semiconductors has been confirmed to be one atomic layer from the observation of RHEED oscillations.[2,3] However, in ionic oxide systems, the growth unit may be subject to charge neutrality and, therefore, may not be an atomic single layer.

There is one report about RHEED oscillations during the epitaxial growth of an oxide. Schlom *et al.*[5] have reported RHEED oscillations observed during the growth of Dy-Ba-Cu-O on $SrTiO_3$ by a periodical shuttering method using a molecular-beam-epitaxy (MBE) system. In their experiment the oscillation period corresponded to the shuttering period. They attributed the oscillations to microscopic responses of the surface structure due to changes in the incident flux rather than to the consequence of a layer-by-layer two-dimensional growth. As far as we know, RHEED oscillations revealing the growth unit have thus never been observed for an oxide system.

In this Letter we report on RHEED oscillations observed during the epitaxial growth of $BaTiO_3$, La_2CuO_4, and $YBa_2Cu_3O_{7-x}$ by reactive evaporation.[6] Essentially, this growth method is a coevaporation of the metal elements under an oxygen atmosphere. In previous work, we have reported on *in situ* RHEED observations during the growth of $YBa_2Cu_3O_{7-x}(001)$ on $SrTiO_3(100)$ and on MgO(100).[7] The experimental system used in the present study was the same as in Ref. 7, except for the method of oxygen activation. In this study oxygen gas was partially converted into ozone by a commercially available ozonizer (O_3 content $\leq 5\%$).[8] The typical deposition conditions were the following: The substrate temperature was 680 °C and the deposition rate was about 0.5 Å/s. The substrate was the $SrTiO_3(100)$ surface which was etched by an Ar^+-ion beam (600 V) at 650 °C before the deposition. The acceleration voltage of the incident electron beam for the RHEED observation was 20 keV. The intensity of the RHEED pattern was measured via an optical fiber using a photomultiplier.

Figure 1(a) shows RHEED oscillations observed during the epitaxial growth of $BaTiO_3(001)$ on $SrTiO_3(100)$, where the direction of the incident beam is [100]. The intensity I decreased rapidly as soon as the growth was initiated and then continuous oscillations were observed whose amplitude decreased gradually. If the growth was interrupted, the intensity increased back to initial levels and showed definite oscillations again.

In order to identify the period of the RHEED oscillations, we must compare the number of the oscillations with the film thickness on an atomic scale. One way to realize this is by the measurement of x-ray diffraction

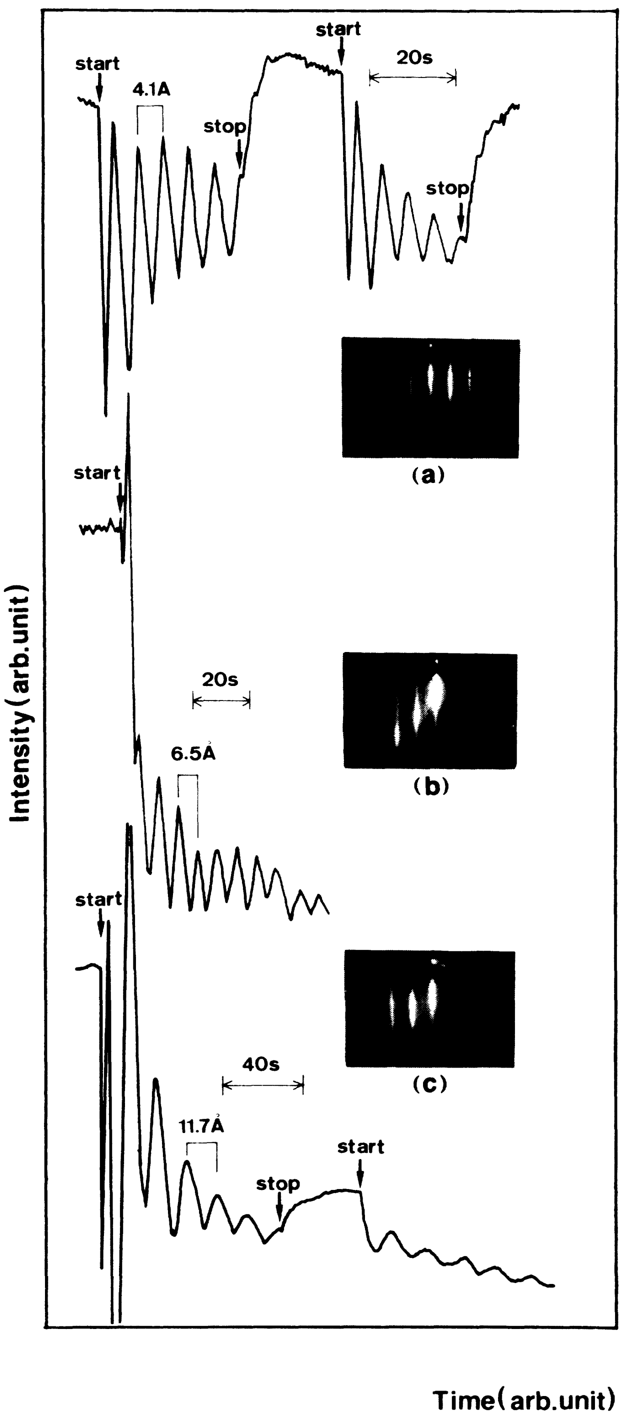

FIG. 1. RHEED intensity oscillations of the specular beam during epitaxial growth for (a) $BaTiO_3(001)$, (b) $La_2CuO_4(001)$, and (c) $YBa_2Cu_3O_{7-x}(001)$ on $SrTiO_3(100)$. The acceleration voltage of the incident beam is 20 keV and the incident angle is 1.9° (off-Bragg condition); [100] azimuth. The starting and ending points of the growth are indicated by the arrows. $T_s = 680\,^\circ C$. Insets: The RHEED patterns observed during the growth of each oxide.

from the ultrathin films.

In general, the intensity of x-ray diffraction is described by

$$I = I_e F^2 G^2 , \tag{1}$$

where $I_e = (c/8\pi)\langle E_0^2 \rangle (e^2/mc^2R)^2(1+\cos^2 2\theta)/2$, F is a structure factor, and the Laue function G^2 for a one-dimensional system is given as

$$G^2 = \sin^2(\pi N x)/\sin^2(\pi x) , \tag{2}$$

where x is the Miller index and N is the number of the unit cells in a crystal.[9] In the plane of the crystal N is large and G^2 has finite values only when x is integer. However, along the direction of the thickness where N is small, G^2 has $N-2$ submaximum points of finite intensity between the peaks of $(00l)$ and $(00l+1)$. Also, $N-1$ minimum points appear when $x = l+1/N, l+2/N, \ldots, l+(N-1)/N$ (l is integer). The thickness L of the ultrathin film can be determined from the angles of the minimum points of G^2 by

$$L = \tfrac{1}{2}\lambda/(\sin\theta_n - \sin\theta_{n-1}) , \tag{3}$$

where θ_n and θ_{n-1} are the angles of the nth and $(n-1)$th minimum points, respectively.[9]

Figure 2(a) shows an x-ray-diffraction pattern scanned along the [001] direction for a $BaTiO_3(001)$ film, the growth of which was finished at the sixteenth peak position of the RHEED oscillations. The submaximum peaks of the Laue function are seen around the fundamental peaks of (001) and (002). The thickness is determined from Eq. (3) to be 67.0 Å. The thickness can also be determined from Scherrer's formula[10] using the full width at half maximum (FWHM) value of the (002) peak ($\Delta 2\theta = 1.44°$) to be 66.0 Å, neglecting instrumentation broadening. These values are in good agreement with 16 times the lattice spacing c_0 which is determined from the (002) peak position to be 4.14 Å. The RHEED oscillation period thus precisely corresponds to the height of one unit cell of $BaTiO_3$, i.e., the thickness of two atomic layers—one each of (BaO) and (TiO_2).

The RHEED oscillations observed during the epitaxial growth of GaAs and Si, etc., under the layer-by-layer growth condition are interpreted by the single-scattering theory[11] to be a consequence of the repetition of the formation of 2D nuclei and growth to a flat terrace. One significant experimental fact which supports this growth model is that the intensity of the oscillations is different when observed under in-phase (Bragg) and out-of-phase conditions. In an in-phase condition, where the electrons are insensitive to surface steps, intensity oscillations are much weaker.[1] We have confirmed that the intensity oscillations during the growth of $BaTiO_3$ also become weaker when the incident beam angle is near the in-phase Bragg condition. This result supports the conclusion that the oscillations of Fig. 1(a) are attributed to

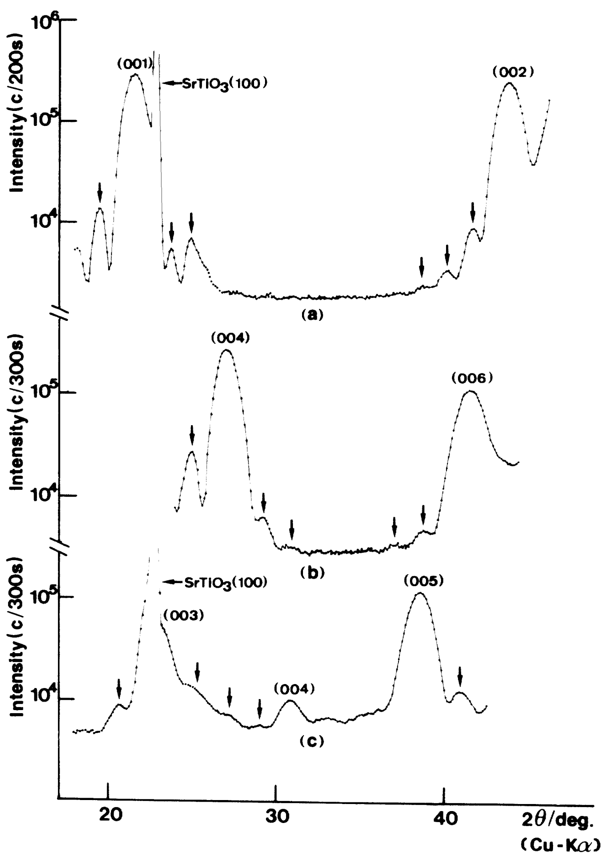

FIG. 2. X-ray-diffraction patterns scanned along the [001] direction of (a) $BaTiO_3(001)$ film, (b) $La_2CuO_4(001)$ film, and (c) $YBa_2Cu_3O_{7-x}$ film of which growth was finished at the sixteenth, tenth, and fifth peak positions of the RHEED oscillations, respectively. The peaks indicated by the arrows are those of the Laue function.

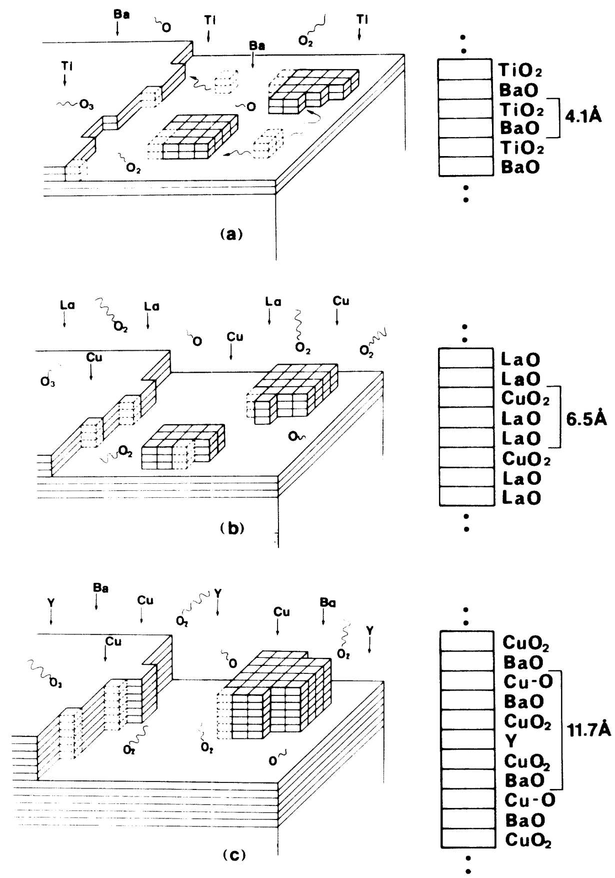

FIG. 3. Schematical illustrations for the deposition and growth process of (a) $BaTiO_3(001)$, (b) $La_2CuO_4(001)$, and (c) $YBa_2Cu_3O_{7-x}(001)$ on $SrTiO_3(100)$. Insets: The stacking sequences of the atomic layers in each crystal, with the growth units indicated. Note that the stacking sequences in the growth units shown in the figures have no specific meaning; the top layer cannot be specified.

the two-dimensional layer-by-layer growth mode.

As mentioned already, the intensity recovered and the oscillation amplitude increased after the growth was interrupted. This recovery of the intensity is commonly observed in the growth of GaAs by MBE. It is interpreted to be due to an increase in the mean terrace width of the surface and, hence, a reduction in the surface step density by the migration of surface adatoms to the flat terrace edge. From the remarkable recovery of the RHEED intensity, it is assumed that the migration of surface adatoms occurs easily in the $BaTiO_3$ system. Figure 3(a) shows a schematical illustration of a deposition-and-growth process model for $BaTiO_3$.

Figures 1(b) and 1(c) show RHEED oscillations observed during the growth of $La_2CuO_4(001)$ on $SrTiO_3(100)$ and $YBa_2Cu_3O_{7-x}(001)$ on $SrTiO_3(100)$. In the first place, we must note that an abrupt increase of the RHEED intensity is observed in both cases as soon as the growth is initiated. An initial transient increase of the RHEED intensity is well known in the MBE growth of GaAs.[12,13] It was revealed that the transient behavior strongly depended on the diffraction conditions, i.e., the angle and the azimuth of the incident beam. The initial transient behavior has been explained to be caused by an initial smoothing of steps already present on the substrate surface[12] or a reconstruction of the substrate surface.[13] Anyway, as the period to the first peak from growth initiation is very short compared with those of the subsequent regular oscillations, we can distinguish between the first peak and others.

Figure 2(b) shows an x-ray-diffraction pattern for a $La_2CuO_4(001)$ film whose growth was finished at the tenth peak position of the RHEED oscillations. In the numbering of the oscillation peaks, we neglected the initial transient peak. For this film, the thickness was determined from the Laue function and Sherrer's formula [$\Delta 2\theta(004) = 1.40°$] to be 66.0 and 65.0 Å, respectively. From this result, one period of the RHEED oscillations was determined to be 6.5 Å. For La_2CuO_4, the chemical repetition unit consists of three atomic layers (LaO), (LaO), and (CuO_2), as shown in the inset of Fig.

3(b), and this unit is stacked on itself with the relation $a/2+b/2$ shifted in the (001) plane. The lattice spacing of this unit along the [001] direction is determined to be 6.50 Å from the (006) peak position, and this value is in good agreement with one period of the RHEED oscillations.

Finally, Fig. 2(c) shows an x-ray-diffraction pattern for the film of $YBa_2Cu_3O_{7-x}$ where the growth was finished at the fifth peak position. In the numbering of the RHEED oscillation peaks, we also neglected the initial transient peak. As shown in the inset of Fig. 3(c), a unit cell of $YBa_2Cu_3O_{7-x}$ consists of six atomic layers along the c axis, the length of which is determined to be 11.7 Å from the (005) peak position. The thickness of this film was determined to be 58.9 and 59.0 Å using the Laue function and Scherrer's formula [$\Delta 2\theta(005) = 1.57°$]. These values are in good agreement with 5 times the lattice spacing c_0. This result revealed that one period of the RHEED oscillations observed during the growth of $YBa_2Cu_3O_{7-x}(001)$ corresponded to the height of the unit cell. Such a long period of the RHEED oscillations was first observed in this system. We have confirmed that the intensity oscillations during the growth of $YBa_2Cu_3O_{7-x}$ become weaker in the in-phase condition. This indicates that the growth of $YBa_2Cu_3O_{7-x}$ also occurs in the two-dimensional growth mode.

The present results have significance for an understanding of the epitaxial growth of ionic oxides. The observed period in the RHEED oscillations indicates that the 2D nuclei of $YBa_2Cu_3O_{7-x}$, La_2CuO_4, and $BaTiO_3$ all have the height of one minimum unit needed to satisfy the chemical composition and electrical neutrality. That is, the chemical and neutral unit is the unit of crystal growth of ionic materials. The deposition-and-growth process models for $La_2CuO_4(001)$ and $YBa_2Cu_3O_{7-x}(001)$ are schematically shown in Figs. 3(b) and 3(c).

A significant problem is derived from this result. There should exist a definite stacking sequence of atomic layers in the growth unit, and therefore, the top atomic layer in the growth unit should always be the same. In the present stage, we cannot specify the metallic element of the top atomic layer in the growth unit, and it still remains as an extremely important problem for the understanding of the epitaxial growth of ionic oxides.

The discovery of RHEED oscillations during the growth of oxides provides a means for the material design of new superlattice oxides. Recently, superlattices composed of a few unit cells of $YBa_2Cu_3O_{7-x}$ and those of other 1:2:3 compounds, e.g., $PrBa_2Cu_3O_{7-x}$,[14] have been fabricated in order to study the two-dimensional nature of superconductivity. The present results suggest that artificial materials can be designed if we combine growth units which satisfy electrical neutrality.

In conclusion, we have observed for the first time RHEED oscillations during the epitaxial growth of oxides caused by layer-by-layer (unit-by-unit) growth and have found that one period of the RHEED oscillations corresponds to the height of the minimum unit which satisfies the chemical composition and the electrical neutrality of the oxide. The data provide a basic understanding of the epitaxial growth mechanism of oxides. Finally, we believe that the formation of superlattices composed of different kinds of oxides by monitoring the RHEED oscillations brings a hopeful new field of study.

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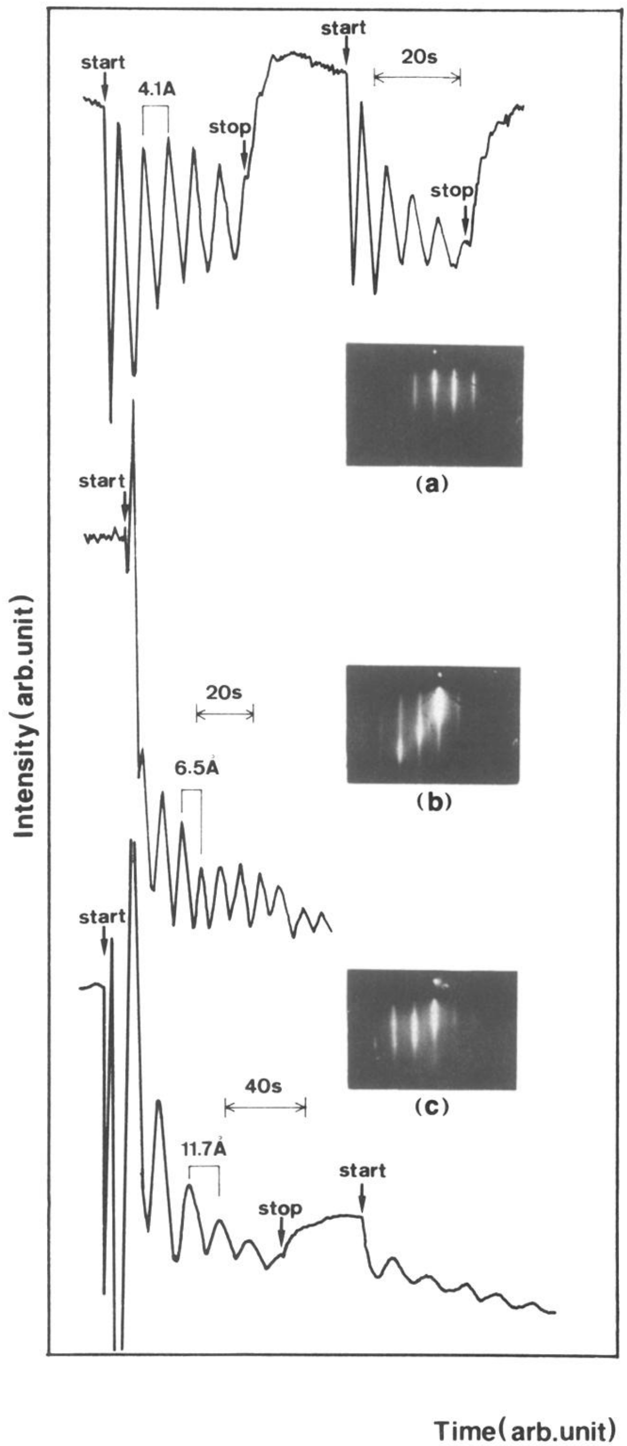

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