Growth mode mapping and structural properties of controlled perovskite $BaTiO_3/SrTiO_3$ heterostructure

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Perovskite heteroepitaxy was investigated under various conditions using laser molecular beam epitaxy. Well-controlled $BaTiO_3/SrTiO_3$ heterostructure was studied with *in situ* reflective high energy electron diffraction and *ex situ* atomic force microscopy, x-ray diffraction, and transmission electron microscopy. The growth mode map of $BaTiO_3$ thin films was obtained as a function of substrate temperature under 600 °C for various laser repetition rates. The effective activation energy of surface migration was determined to be 0.33 eV. A mechanism of surface migration in $BaTiO_3$ heteroepitaxy was described for a basic understanding of atomic-scale controlled preparation of ferroelectric heterostructures at low temperature. © *2007 American Institute of Physics*.
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Perovskite titanates have attracted much attention for a wide variety of applications.[1–3] Understanding the surface diffusion process during film growth and controlling the growth mode are of exceeding importance for titanate films to satisfy the requirement for device applications. Unfortunately, the growth mode of perovskite titanate film is limited to the growth at high temperatures (from 800 to 1400 °C) from previous reports.[4–6] Here, we present the study of the growth mode and structure of $BaTiO_3$ (BTO) films under 600 °C.

BTO thin films were deposited by laser molecular beam epitaxy (LMBE). $SrTiO_3$ (STO) (100) single-crystal substrates with small miscut angles (<0.2°) were treated by buffered NH_4F–HF (pH ~ 4.5) solution to obtain highly smooth surface. During deposition, the chamber was kept at 10^{-5} Pa. The growth mode of BTO films was analyzed by *in situ* monitoring the high reflective energy electron diffraction (RHEED) pattern and intensity. The beam was oriented in the [100] crystal direction.

As shown in Fig. 1(a), BTO films were grown at the temperature of 550 °C with 5 Hz laser repetition rate. The RHEED patterns of the BTO films have clear bright 1×1 streaks, indicating that the films have an atomic flatness and single-phase perovskite structure. In BTO heteroepitaxy, misfit dislocations due to the difference of lattice parameter between BTO and STO were incorporated in BTO for strain relief.[7] Those misfit dislocations deteriorated the surface roughness, which led to the oscillation of RHEED intensity decayed in amplitude before the films exceeded a certain critical thickness. The oscillation amplitude increased gradually and one period of oscillation corresponds to the unit cell height of BTO, indicating the recovery of a new flat surface and the layer-by-layer growth prevails. We reduced the substrate temperature from 550 °C down in steps of 10 °C. Great attention was paid to each deposition at a given temperature, the substrate is regenerated by *in situ* annealing at 800 °C until the streaky patterns were appeared, indicating a fresh surface was obtained.[8] At 400 °C, a few RHEED intensity oscillations could be observed in Fig. 1(b). This transient behavior of the RHEED intensity and patterns represented the fact that the growth mode of BTO films had a transition from two-dimensional (2D) layer by layer to the Stranski-Krastanov (SK) growth mode, which is layer-by-layer growth plus island growth mode. When the temperature is lower than 350 °C, no RHEED intensity oscillation can be observed. The spotty patterns were measured in Fig. 1(c), which demonstrate that BTO films grow in three-

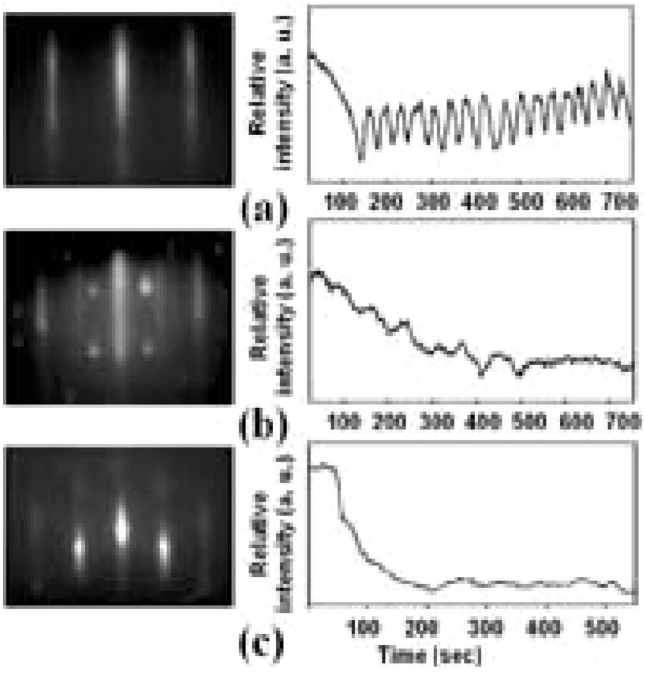

FIG. 1. Transition of growth mode at various substrate temperatures: (a) layer-by-layer growth mode at 550 °C, (b) SK growth mode at 400 °C, and (c) 3D island growth mode at 340 °C.

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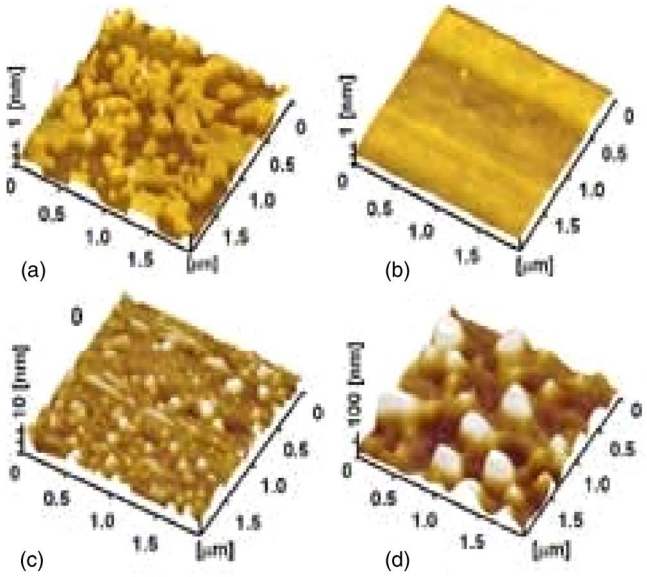

FIG. 2. (Color online) AFM images of BTO thin films grown at different growth modes: (a) the surface morphology of BTO films at the maximum of the RHEED intensity oscillation in layer-by-layer growth mode, (b) the surface morphology at the minimum of the RHEED oscillation in layer-by-layer growth mode, (c) SK growth mode, and (d) 3D island growth mode.

dimensional (3D) island growth mode. Within this scenario, because of the high particle flux and the descent of growth temperature, the surface mobility is no longer high enough to support continuous 2D layer-by-layer growth. Higher supersaturation and higher formation probability of large islands on the surface result in SK growth mode, which lead to a larger density of growing islands, and eventually more 3D islands nucleate homogeneously on the surface.

Atomic force microscopy (AFM) has been employed to reveal the surface of BTO thin films grown in different growth modes. Figures 2(a) and 2(b) were obtained at different stages of 2D growth mode. Figure 2(a) was taken when the intensity of RHEED oscillation reached the minimum value. One can see discontinuous platforms with a height of 0.4 nm, corresponding to a single molecular layer of BTO. Figure 2(b) was taken at the maximum intensity of the RHEED oscillation. It indicated that BTO layer was completely formed with flat and continuous surface. Combining Figs. 2(a) and 2(b), the layer-by-layer growth mode was well characterized and further confirmed. Figure 2(c) shows an AFM image of BTO films deposited in SK growth mode. Although smooth surface was still observed, small islands appeared on the surface. An AFM image of the film grown in 3D island growth mode was shown in Fig. 2(d). As expected, small islands aggregated on the surface and 3D islands nucleate on the surface.

To check the quality of the films, x-ray diffraction (XRD) and transmission electron microscopy (TEM) have been employed to characterize thin film which was shown in Fig. 2(b). As indicated in Fig. 3, the films show good crystalline quality and epitaxy with (h00) orientation. The TEM image also shows abrupt interface between BTO and substrate.

When the substrate temperature is fixed, BTO films were grown at various laser repetition rates, i.e., deposition rate. As shown in the inset of Fig. 4, the growth mode for BTO film has been mapped as a function of growth temperature and laser repetition rate. It is noted that when the BTO was

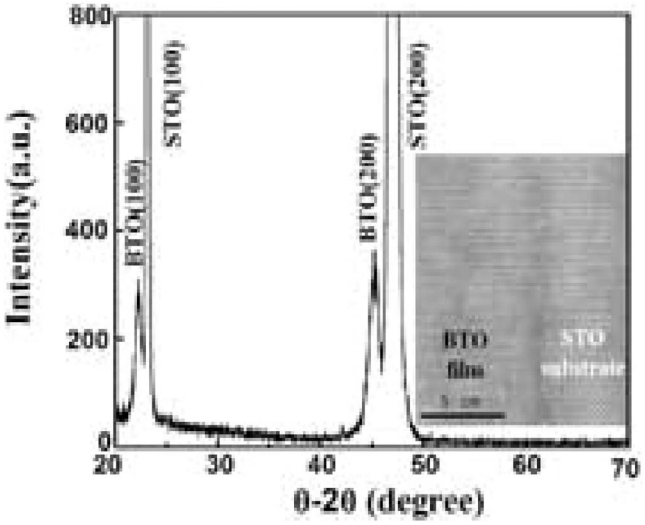

FIG. 3. Measured results of XRD for the films shown in Fig. 2(b). The inset shows TEM image.

grown at 300 °C for 1 Hz, the streaky patterns still existed and clear oscillations were observed. Below 300 °C, RHEED patterns had disappeared. As a result, we consider 300 °C as the lowest crystalline temperature of BTO films in layer-by-layer growth. It suggests that the surface mobility of adatoms during growth plays an important role in determining the growth mode. Furthermore, the mobility of adatoms depended on the growth temperature and deposition rate. A faster deposition rate and the lower temperature represent a larger influx of adatoms, a higher degree of supersaturation and a shorter diffusion length, which leads to a larger density of growing islands. Accordingly, effective diffusion of the particles is hindered and islands aggregated on the surface gradually. Consequently, the growth mode of BTO films changed from 2D layer-by-layer mode to SK mode, and eventually 3D island mode. The RHEED oscillation data from five depositions performed with a laser repetition rate of 1 Hz at various temperatures have been obtained from the growth mode map. Pure layer by layer of 2D growth mode

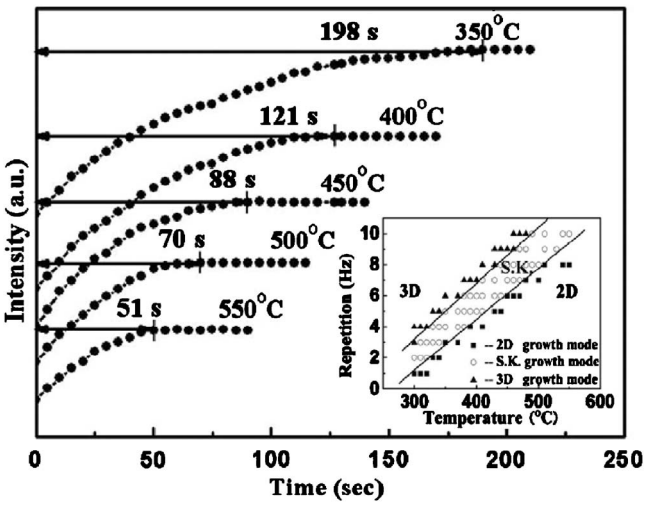

FIG. 4. Partial recovery of the RHEED intensity after a laser pulse from five depositions performed with a laser repetition rate of 1 Hz at various temperatures in layer-by-layer growth mode. The inset shows growth mode map of BTO films as a function of substrate temperature for various laser repetition rates at which the RHEED patterns changed their appearance.

was measured. Partial recoveries to the five depositions of the RHEED intensity after a laser pulse were showed in Fig. 4. The recovery during various periods can be understood in terms of slow surface migration, which has been observed by high-temperature scanning tunneling microscopy.[9] At each temperature, single-pulse depositions were performed and the specular spot intensity recovery was analyzed by fitting with a single exponential. Figure 4 was further analyzed by measuring the amplitudes of the slow oscillations and the exponential recovery peaks. The Arrhenius plot indicates that the activation energy (E_a) of the surface diffusion process was 0.33 ± 0.01 eV. In comparison with other deposition methods such as sputtering and evaporation, the particles (atoms and cluster of atoms) in LMBE arrive at the substrate with higher incident energy and migrate with higher kinetic energy.[10,11] In general, we assume that the activation energy, which corresponds to the diffusion barrier of a unit cell, i.e., the energy required to remove a unit cell from an unstable site to another site,[12] can be supplied by the particles' kinetic energy on the surface and heating temperature-induced thermal energy. In LMBE process, the atomic rain to the surface in the growth of perovskite oxide film by laser induced deposition is dominated by small particles of unit cells rather than the element atoms or ions. The raindrops can be in the form of multiple ABO_3 unit cells before they arrive at the substrate surfaces, especially when the laser energy is high and the distance between target and substrate is long in our case. The formation of unit cell droplet can significantly reduce the system energy during the kinetic process, which may help to reach the final stable state with a minimum value of self-free-energy. The diffusion barriers for a perovskite unit cell migrate on an atomically flat surface are much lower than a semiconductor atom on a semiconductor surface.[13–15] The low activation energy will benefit the unit cell to migrate and find the lowest energy site to stay and form crystalline film.[16]

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