# Laser Molecular Beam Epitaxy Growth of $BaTiO_3$ in Seven Thousands of Unit-Cell Layers *

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(Received 28 July 2005)

*$BaTiO_3$ thin films in seven thousands of unit-cell layers have been successfully fabricated on $SrTiO_3$ (001) substrates by laser molecular beam epitaxy. The fine streak pattern and the undamping intensity oscillation of reflection high-energy electron diffraction indicate that the $BaTiO_3$ film was layer-by-layer epitaxial growth. The measurements of scanning electron microscopy and atomic force microscopy show that surfaces of the $BaTiO_3$ thin film are atomically smooth. The measurements of x-ray diffraction and transmission electron microscopy, as well as selected-area electron diffraction reveal that the $BaTiO_3$ thin film is a c-oriented epitaxial crystalline structure.*

*PACS: 77.84.−s, 68.55.Jk, 81.15.Fg*

Perovskite oxide materials have attracted a great deal of attention because of their remarkable dielectric, piezoelectric, ferroelectric, optical, pyroelectric, electro-optic, superconducting, colossal magnetoresistance and so on.[1−6] Many studies have focused on the growth of these oxide thin films, since it is essential to acquire the high-quality epitaxial films with good crystallinity and smooth surfaces for realizing the mechanisms and applications. For many years, perovskite oxide films have been fabricated by many methods such as metalorganic chemical-vapour deposition (MOCVD),[7] magnetron sputtering,[8] sogel processing,[9] reactive vaporization,[10] pulsed laser deposition (PLD)[11] and laser molecular-beam epitaxy (laser MBE).[12,13] The fabrication of artificial crystalline materials through layer-by-layer epitaxial growth with full control over the composition and structure at the atomic level has become one of the most exciting areas of research in condensed matter physics and material sciences. We have successfully fabricated more than ten kinds of oxide thin films and their heterostructures by laser MBE. More than 1000 cycles of intensity oscillation of reflection high-energy electron diffraction (RHEED) could be observed during the epitaxial growth of oxide thin films.[13,14] With the increasing film thickness, it is not easy to obtain high-quality films due to the lattice parameter misfits of different materials and interfacial stress as well as dislocations. Recently, Lee *et al.*[15] reported the three-component superlattices grown up to 1 $\mu$m in thickness on $SrTiO_3$ (001).

In this Letter, seven thousands unit-cell layers (∼2.8 $\mu$m) $BaTiO_3$ films were epitaxially grown on $SrTiO_3$ (001) substrates by laser MBE. The $BaTiO_3$ film was examined *in-situ* using RHEED, and was also characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). To our best knowledge, it is the first time to epitaxially grow perovskite oxide of seven thousands of unit-cell layers (thickness is more than 2 $\mu$m).

In order to obtain high-quality epitaxial growth, before deposition, the $SrTiO_3$ substrate was annealed at 680°C for 30 min under the background pressure of $2 \times 10^{-6}$ Pa to clean up the surface. Then a focused pulse laser beam (308 nm, duration 20 ns, energy density $\sim 1\,\mathrm{J\cdot cm^{-2}}$, repetition rate 2 Hz) was impinged onto a ceramics $BaTiO_3$ target. During deposition, the substrate temperature and oxygen pressure were maintained at 620°C and $2 \times 10^{-4}$ Pa, respectively. The deposition rate was one cell layer per 33 pulses. The $BaTiO_3$ film in seven thousands of unit-cell layers was layer-by-layer epitaxially grown on a $SrTiO_3$ substrate.

The *in-situ* and real-time RHEED provides useful information of the surface structure, morphology and growth modes. The RHEED intensity oscillations enable us to control the exact number of deposited molecular layers. Figure 1 shows the RHEED intensity oscillations of the specular spot at the beginning of the $BaTiO_3$ growth, and the RHEED patterns of the $BaTiO_3$ film along the [110] and [100] directions on the $SrTiO_3$ (001) substrate are given in the insets of Fig. 1. The sharp and bright RHEED patterns as

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* Supported by the National Natural Science Foundation of China under Grant No 10334070, and the National Key Basic Research and Development Programme of China under Grant No 2004CB619004.

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well as steady and undamping RHEED intensity oscillations could be observed during the $BaTiO_3$ film growth, indicating that the $BaTiO_3$ film was perfectly layer-by-layer epitaxial growth.

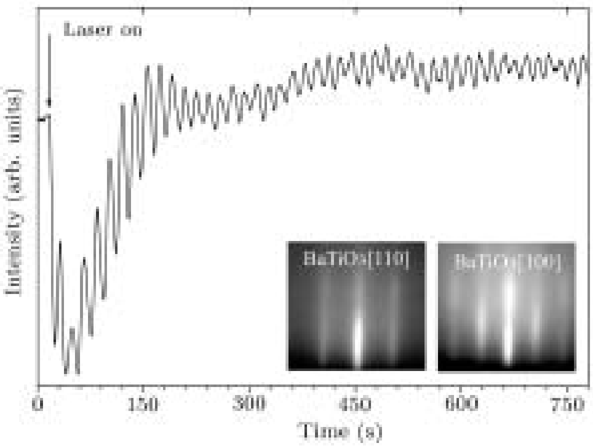

**Fig. 1.** RHEED intensity oscillation monitored at the specular beam spot at the beginning of the $BaTiO_3$ film growth. The inset displays the RHEED patterns of the film along the [110] and [100] directions.

The XRD $\theta-2\theta$ scan pattern of the $BaTiO_3$ film is shown in Fig. 2. Except for $BaTiO_3$ $(00h)$ and $SrTiO_3$ $(00h)$ peaks, no other peaks can be observed. The XRD $\omega$ rocking curve from $BaTiO_3$ (002) diffraction peak is shown in the inset of Fig. 2, and displays a narrower full-width at half-maximum (FWHM) of 0.313°. The XRD results reveal that the $BaTiO_3$ film is the $c$-oriented epitaxial crystalline structure.

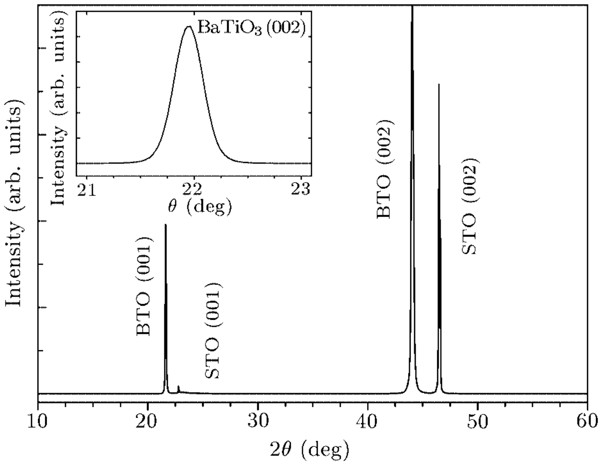

**Fig. 2.** XRD $\theta-2\theta$ scan of the $BaTiO_3$ film grown on the $SrTiO_3$ (001) substrate. The inset shows the $\omega$ rocking curve for the $BaTiO_3$ (002) peak of the film.

Figure 3 displays a low magnification cross-sectional TEM image of the $BaTiO_3$ film grown on the $SrTiO_3$ substrate. The interface of $BaTiO_3$ and $SrTiO_3$ is very clear and smooth. The $BaTiO_3$ film thickness, obtained from the TEM image, is in excellent agreement with that calculated from the number of RHEED oscillation periods as recorded during the epitaxial growth. The selected area electron diffraction (SAED) pattern in the inset of Fig. 3 shows that the $BaTiO_3$ film is perfectly oriented, and the epitaxial crystalline orientations of $BaTiO_3$ (001) and $BaTiO_3$ [100] can be obtained on $SrTiO_3$ (001) and $SrTiO_3$ [100], respectively.

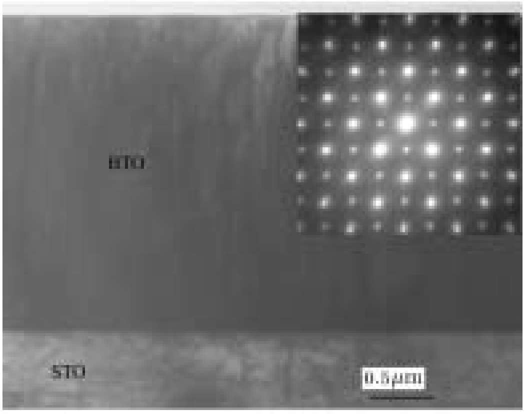

**Fig. 3.** Low magnification cross-sectional TEM image of a $BaTiO_3$ film grown on a $SrTiO_3$ substrate with the corresponding SAED pattern.

The surface morphology of the $BaTiO_3$ film was examined by SEM and AFM. Figure 4 shows a typical SEM image (100 μm×100 μm), and Fig. 5(a) is a two-dimensional (2D) AFM image (500 nm× 500 nm) of the surface of the $BaTiO_3$ film. Figure 5(b) is the height profile along the horizontal line of 2D image in Fig. 5(a). The rms surface roughness is 0.254 nm. Figures 4 and 5 show that the film surface is atomic-scale smooth after $BaTiO_3$ growing several thousands of unit-cell layers.

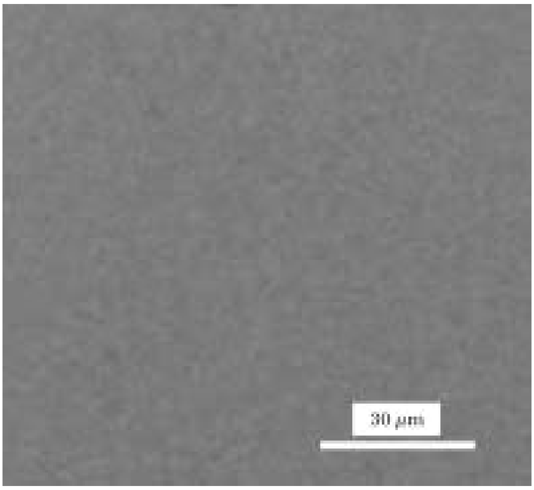

**Fig. 4.** SEM image of the surface morphology of the $BaTiO_3$ film.

The chemical analysis of the $BaTiO_3$ film was performed by an x-ray photoelectron spectroscope (XPS), and the XPS spectra were measured with a

VG ESCALAB MK Ⅱ system, using Al $K_\alpha$ radiation (1486.6 eV) under a pressure of $2 \times 10^{-7}$ Pa in Fig. 6. The energy scale of the spectrometer was calibrated with pure Cu $2p_{3/2}$ and Au $4f_{7/2}$ samples. The XPS spectra were referenced to the C 1*s* line of the residual carbon setting at 285.0 eV. In addition to C from Fig. 6, no other contaminant was detected on the surfaces of the sample. High resolution spectra of Ba 3*d*, Ti 2*p* and O 1*s* photoelectron peaks were also obtained. It can be seen from the XPS spectra of Ba 3*d* that there exists one electronic state of Ba $3d_{5/2}$ in the detectable surface region with a binding energy of 779.1 eV. Compared to the work reported by Mukhopadhyay *et al.*,[16] two components in the XPS spectrum of Ba $3d_{5/2}$ in $BaTiO_3$ ceramic, i.e. $\alpha$ (779.0 eV) and $\beta$ (780.6 eV), were observed in this work. The Ba $3d_{5/2}$ state of our observation corresponds to the $\alpha$ state, which is associated with the bulk perovskite structure. The $\alpha$ state was also observed for $BaTiO_3$ powder (778.9 eV) by the wet chemical process.[17] The Ti $2p_{3/2}$ peak located at a binding energy of 458.3 eV and the Ti $2p_{1/2}$ peak at 464.2 eV. The Ti $2p_{3/2}$ binding energy has been reported at 458.4 eV for single crystals,[18] and 458.3 eV for sintered $BaTiO_3$ ceramics.[17] The O 1*s* peak exhibits one main peak, centred at 529.6 eV, which is reported to be 529.9 eV in Ref. [17]. It is clear that our results for the elemental chemical states are in good agreement with $BaTiO_3$ bulk materials and films.

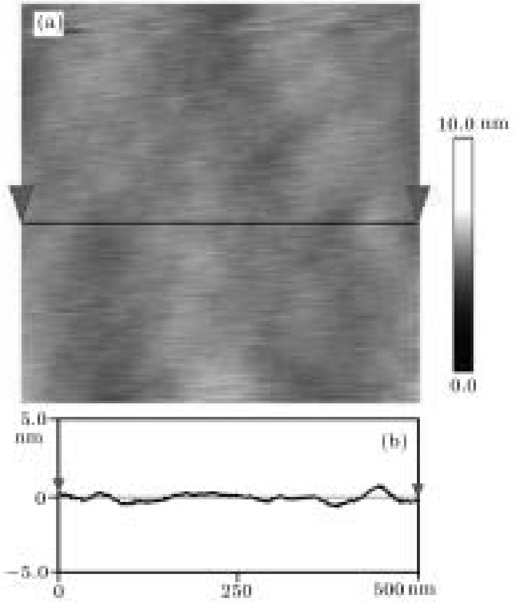

**Fig. 5.** AFM image: (a) 2D image of $BaTiO_3$ film (500 nm×500 nm), and (b) the height profile along the horizontal line of this 2D image. The rms surface roughness value is 0.254 nm.

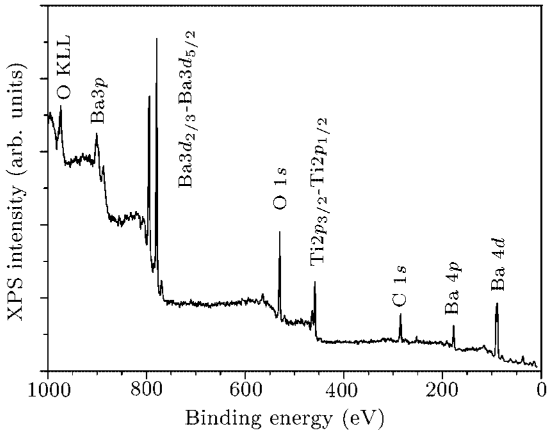

**Fig. 6.** The XPS spectrum of the $BaTiO_3$ film.

In conclusion, $BaTiO_3$ thin films in seven thousands of unit-cell layers have been successfully fabricated on $SrTiO_3$ (001) substrates by laser MBE. The measurements by *in-situ* RHEED and *ex-situ* XRD, AFM, SEM, TEM, SAED, and XPS demonstrate that the $BaTiO_3$ film is nearly perfect layer-by-layer epitaxial growth in the *c*-oriented epitaxial crystalline structure. The surface and interface of the $BaTiO_3$ thin film are atomically smooth. The thickness of the $BaTiO_3$ thin film is controlled in atomic scale. Our experimental results have fully proven that the laser molecular beam epitaxy is a very useful method to fabricate the films of high melting point ceramics and multicomponent solid controlled in atomic scale.

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