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## Phase transition of BaTiO<sub>3</sub> thin films

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### Abstract

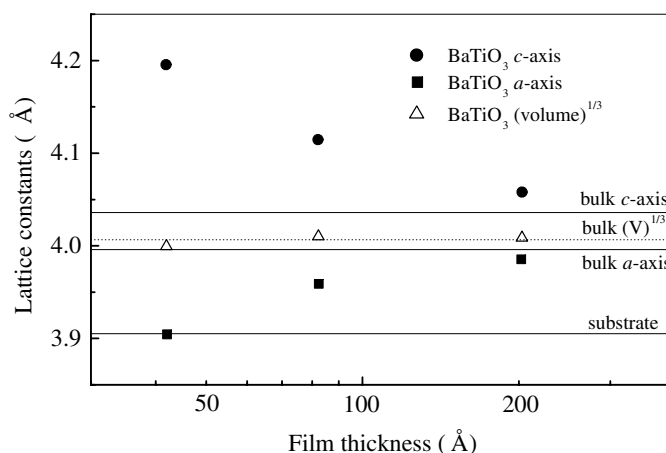
The phase transition of ferroelectrics is one of their most important bulk-nature attributes. In well-epitaxial ferroelectric thin films, the crystal structures are highly strained and the ferroelectric phase transitions tend to disappear because of an epitaxial effect. We investigated the epitaxial effect by structural analysis and clarified the growth conditions of BaTiO<sub>3</sub> films that show their bulk nature. As a result, epitaxial crystals of BaTiO<sub>3</sub> with a thickness of 67 Å were grown on a MgO substrate with a Pt electrode by the activated reactive evaporation method. A clear thermal anomaly was observed at 140 °C that suggests the phase transition of BaTiO<sub>3</sub>.

### 1. Introduction

Oxide perovskites show a variety of interesting properties, such as ferroelectricity, piezoelectricity, electro-optic effects and high- $T_C$  superconductivity. Barium titanate, BaTiO<sub>3</sub>, is a typical ferroelectric material used in many practical applications in the forms of ceramic and single crystals. It undergoes three successive phase transitions as the temperature is lowered: first from the prototype cubic perovskite to tetragonal at 403 K ( $T_C$ ), then to orthorhombic at 278 K and finally to a trigonal phase below about 183 K. Ferroelectricity has been observed in the three low-temperature phases.

Recently extensive attention has been paid to ferroelectric thin films, because they are promising materials for functional thin film devices such as surface acoustic wave devices, pyroelectric sensors, electro-optic modulators, ferroelectric memory devices and ferroelectric integrated devices. Many attempts have been made to prepare BaTiO<sub>3</sub> films by electron-beam evaporation and r.f. sputtering methods [3–5]. These as-grown films were usually polycrystalline and did not show any dielectric anomaly in the neighbourhood near 403 K ( $T_C$ ). Thick films of about 1 μm show an anomaly at  $T_C$ . This suggested that the ferroelectric phase

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**Figure 1.** Lattice parameters  $c$  and  $a$ , and  $V^{1/3}$  as a function of the film thickness for BaTiO<sub>3</sub> ultrathin films at room temperature. The lattice parameters of BaTiO<sub>3</sub> and SrTiO<sub>3</sub> bulk are given by the solid lines.

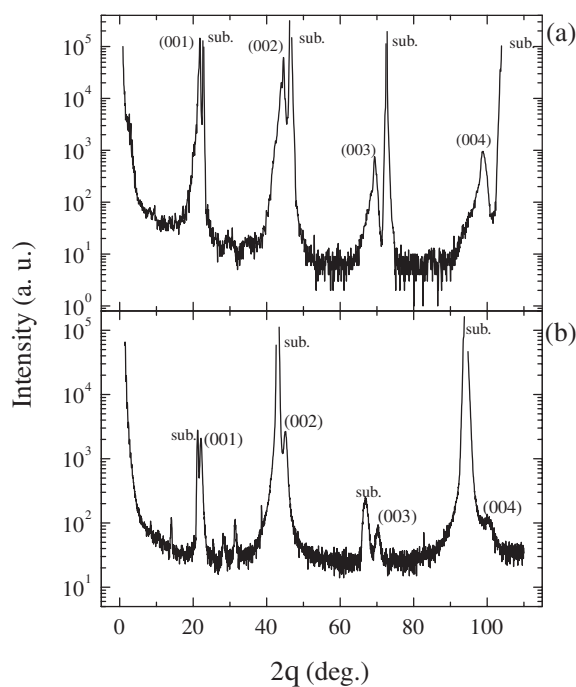
was unstable for thin films below about 0.1  $\mu\text{m}$ . However, Slack and Burfoot showed that thin films of about 0.004  $\mu\text{m}$  thick showed ferroelectric switching behaviour in flash-evaporated BaTiO<sub>3</sub> films [1]. Tomashpolski *et al* found that vacuum-deposited films showed a sharp dielectric anomaly near 403 K even in the film with 0.023  $\mu\text{m}$  thickness [2]; this anomaly disappeared for films with 0.01 mm. There are still many discrepancies in experimental properties that have not been studied yet.

Phase transition is one of the typical bulk-nature attributes of ferroelectrics. In ferroelectric thin films with large internal lattice strain, the ferroelectric phase transition tends to disappear because of the epitaxial effect [6–9]. In contrast, films with the ferroelectric phase transition are free from the epitaxial effect and the lattice parameters are nearly equal to those of the bulk. We found it possible to release the internal strain from the epitaxial effect and investigated the effectiveness of some releasing methods by structure analysis. As a result, we have successfully observed the ferroelectric phase transition of a 66 Å thick BaTiO<sub>3</sub> ultrathin film.

We tried to control the epitaxial effect of BaTiO<sub>3</sub> films by controlling thickness, mismatch between growth layer and substrates and roughness of substrates.

## 2. Experimental

The BaTiO<sub>3</sub> ultrathin films were grown by alternate deposition using a molecular beam epitaxy (MBE) chamber. In this growth method [10], the BaO layers and TiO<sub>2</sub> layers were deposited alternately. After 1 unit BaO and TiO<sub>2</sub> layer growth, 1 monolayer (ML) BaTiO<sub>3</sub> layer was grown. The deposition rate was about 1 unit (4 Å)/70 s. The substrate temperature was kept at 700 °C during the growth. The phase, crystallographic orientation and crystalline quality of the grown films were analysed by a variety of x-ray diffraction techniques. The  $2\theta/\theta$  scan, conventional and glancing-incidence x-ray diffraction (GIXD) measurements were carried out using Cu K $\alpha$  radiation (40 kV, 240 mA) monochromatized by a graphite crystal. Differential scanning calorimeter (DSC, Rigaku Model DSC8230D, Japan) analysis in the temperature range of 30 to 200 °C was performed in order to characterize the thermal anomalies of the BaTiO<sub>3</sub> ultrathin films.

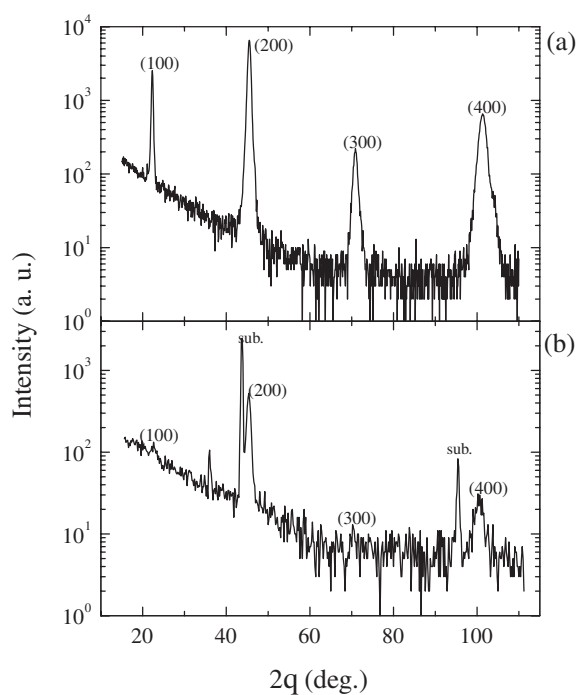


**Figure 2.** X-ray diffraction patterns of 50 ML thickness BaTiO<sub>3</sub> on (a) a SrTiO<sub>3</sub> substrate and (b) a MgO substrate. The scanning direction was along the [001] direction of the substrate crystal axis (along the growth direction).

### 3. Results and discussion

#### 3.1. Thickness dependence of BaTiO<sub>3</sub> thin films

Figure 1 shows the lattice parameters  $c$  and  $a$ , and  $V^{1/3}$  at room temperature as a function of the film thickness. The lattice parameters  $c$  along the growth direction were determined from the  $2\theta/\theta$  scan spectra of the conventional geometries, and the lattice parameters  $a$  in the growth plane were determined from the GIXD conditions. Note that the lattice parameters of bulk ferroelectric BaTiO<sub>3</sub> crystal are  $a = 3.99 \text{ \AA}$  and  $c = 4.04 \text{ \AA}$  at room temperature. The lattice parameter  $a$  of the 10 ML thick film is exactly the same as that of the SrTiO<sub>3</sub> substrate and the lattice parameter  $c$  of the 10 ML thick film is elongated along the growth direction. Although the lattice parameters were highly strained by the epitaxial effect, the volume of the film was nearly equal to that of the bulk crystal. A similar behaviour was observed for the 20 ML thick BaTiO<sub>3</sub> film. The tetragonality of the 10 ML and 20 ML thick films was larger than that of bulk BaTiO<sub>3</sub>, but the volumes of these films were nearly equal to that of bulk BaTiO<sub>3</sub>. In the 50 ML thick film, the crystal structure was slightly distorted from that of bulk BaTiO<sub>3</sub>; the volume of the 50 ML thick film was also nearly equal to that of bulk BaTiO<sub>3</sub>. This fact indicates that the transformation of the BaTiO<sub>3</sub> thin films was in agreement with the Poisson ratio of the bulk. In other words, the internal strain caused by the substrate effect increases as the film thickness decreases and the BaTiO<sub>3</sub> crystal deforms. Therefore, one way to release the internal strain from the BaTiO<sub>3</sub> film is increasing the film thickness.



**Figure 3.** X-ray diffraction patterns of 50 ML thickness BaTiO<sub>3</sub> on (a) a SrTiO<sub>3</sub> substrate and (b) a MgO substrate. The scanning direction was along the [1 0 0] direction of the substrate crystal axis (in the growth plane).

### 3.2. Substrate dependence of BaTiO<sub>3</sub> thin films

The lattice mismatch between the growing layer and the substrate is one important growth condition, but the relation between the mismatch and epitaxial effect is very complicated. In the case of the BaTiO<sub>3</sub> film on the SrTiO<sub>3</sub> substrate, the magnitude of the mismatch between the substrate and bulk BaTiO<sub>3</sub> *a*-axis was smaller than that between the substrate and bulk BaTiO<sub>3</sub> *c*-axis. It was reasonable that the *a*-axis of the BaTiO<sub>3</sub> films agreed with the SrTiO<sub>3</sub> substrates in the growth plane and that the *c*-axis was oriented along the growth direction. On the other hand, the magnitude of mismatch between the MgO substrate and bulk BaTiO<sub>3</sub> *c*-axis was smaller than that between the MgO substrate and bulk BaTiO<sub>3</sub> *a*-axis. If the epitaxial relation depended only on the lattice matched condition, the *c*-axis of the BaTiO<sub>3</sub> films should have agreed with the MgO substrates in the growth plane and the *a*-axis should have been oriented along the growth direction. In reality, however, the *a*-axis of the BaTiO<sub>3</sub> films agreed with the MgO substrates in the growth plane and the *c*-axis was oriented along the growth direction, similar to the case of the SrTiO<sub>3</sub> substrate, as shown in figures 2 and 3. Therefore, the growth of BaTiO<sub>3</sub> films on MgO substrates is carried out through a tight growth condition. The difference in the growth condition is reflected in the crystal quality of the BaTiO<sub>3</sub> films.

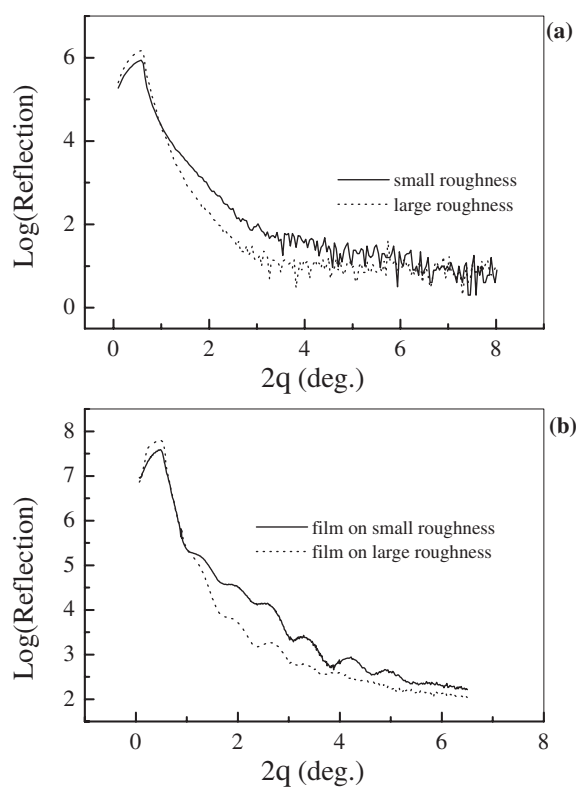
In the large mismatch system, the lattice strain is released rapidly at the interface and the lattice parameter of the growing layer is close to the bulk value. In the small lattice mismatch system, dislocations were hardly ever generated near the interface and the lattice strain remained. Therefore, the BaTiO<sub>3</sub> film on the MgO substrate tends to show bulk properties, compared to that on the SrTiO<sub>3</sub> substrate. The results are summarized in tables 1 and 2.

**Table 1.** Lattice parameters of *c*-axis (growth direction).

Bulk BaTiO <sub>3</sub> <i>c</i> -axis	4.034 Å
BaTiO <sub>3</sub> film on SrTiO <sub>3</sub> substrate	4.061 Å
SrTiO <sub>3</sub> substrate	3.904 Å
BaTiO <sub>3</sub> film on MgO substrate	4.021 Å
MgO substrate	4.211 Å

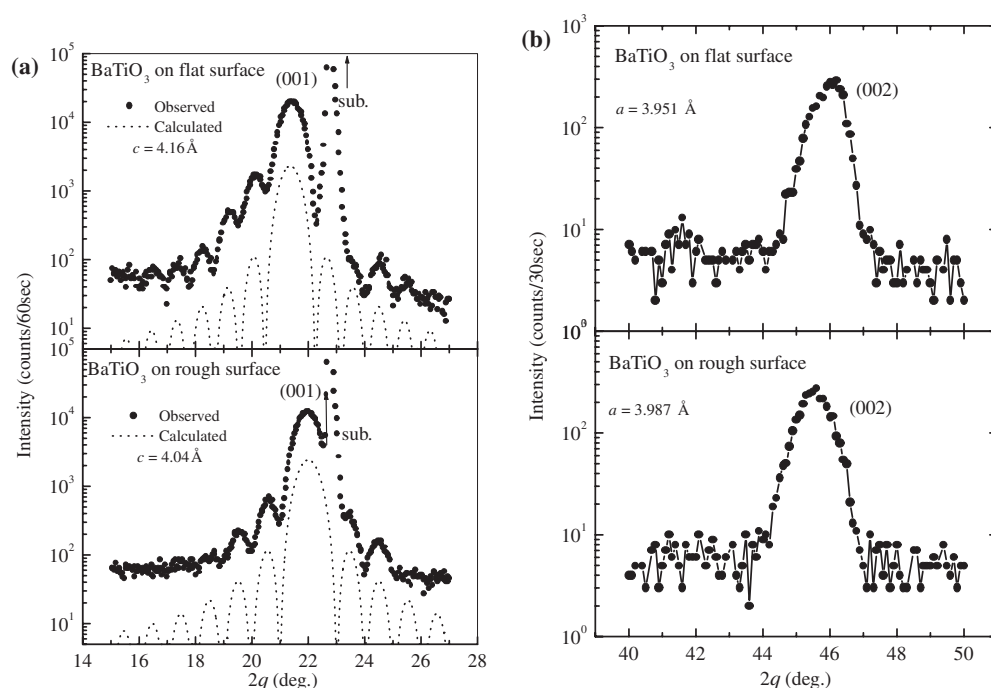
**Table 2.** Lattice parameters of *a*-axis (in-plane).

Bulk BaTiO <sub>3</sub> <i>c</i> -axis	3.993 Å
BaTiO <sub>3</sub> film on SrTiO <sub>3</sub> substrate	3.988 Å
SrTiO <sub>3</sub> substrate	3.905 Å
BaTiO <sub>3</sub> film on MgO substrate	4.008 Å
MgO substrate	4.211 Å

**Figure 4.** Small angle x-ray diffraction profiles of (a) small and large roughness SrTiO<sub>3</sub> substrate, and (b) 10 ML thick BaTiO<sub>3</sub> films on small and large roughness SrTiO<sub>3</sub> (001) substrate.

### 3.3. Roughness dependence of BaTiO<sub>3</sub> films

In the previous section, we discussed that the growing BaTiO<sub>3</sub> film released the epitaxial strain with the large lattice mismatched substrates. On the analogy of the large mismatched system, the surface roughness should also play a similar role in the film growth. We performed the

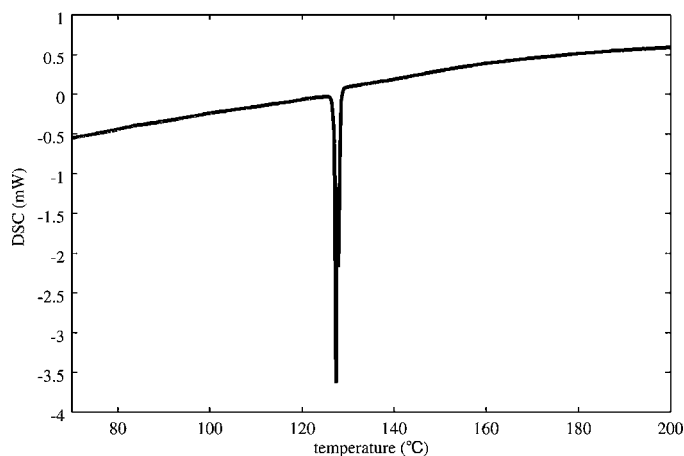


**Figure 5.** X-ray diffraction profiles of the 10 ML thick BaTiO<sub>3</sub> (a) around the (001) reflection on small and large roughness SrTiO<sub>3</sub> (001) substrates, and (b) around the (200) reflection on small and large roughness SrTiO<sub>3</sub> (001) substrates. The dotted curves of (a) are the calculated intensity of Laue oscillation in 10 ML thick BaTiO<sub>3</sub>.

growth of BaTiO<sub>3</sub> thin films using a small surface roughness SrTiO<sub>3</sub> substrate and a larger one. The roughness of these substrates was evaluated by small angle x-ray diffraction, as shown in figure 4(a). The surface roughness of the flat substrate was 2.0 Å and that of rough substrate was 9.9 Å. After the 10 ML thick BaTiO<sub>3</sub> deposition, they were evaluated again by small angle x-ray diffraction, as shown in figure 4(b). The total roughness of the 10 ML thick BaTiO<sub>3</sub> films on flat and rough substrates was 4.0 Å and 6.1 Å, respectively. Figures 5(a) and (b) show comparisons of x-ray diffraction profiles around (001) and (200) reflection, respectively. Although the Laue oscillations were observed in these patterns of figure 5(a) with the same period, the fundamental (001) peak of a large roughness substrate was shifted to a higher angle than that of a small roughness substrate, as shown in figure 5(a). On the other hand, the (200) peak of BaTiO<sub>3</sub> film on a rough substrate shifted to a lower angle than that on a flat substrate. The lattice parameter of the *c*-axis on the large roughness substrate is shorter towards the bulk value than that on the flat substrate and the lattice parameter of the *a*-axis on the large roughness substrate is longer towards the bulk value than that on the flat substrate, suggesting that the BaTiO<sub>3</sub> film on the large roughness substrate is not highly distorted but in a relaxed state due to the generation of the misfit dislocations at the interface. On the large roughness surface of the substrate, the surface has many steps. The more steps lie on the surface, the more misfit dislocations are generated. As a result, the BaTiO<sub>3</sub> film on the large roughness substrate is relaxed and freed from the epitaxial effect, because of the high dislocation density. By using the large roughness substrate, relaxed and bulk-nature BaTiO<sub>3</sub> thin films can be grown.

**Table 3.** Lattice parameters of 66 Å BaTiO<sub>3</sub> film on Pt–MgO.

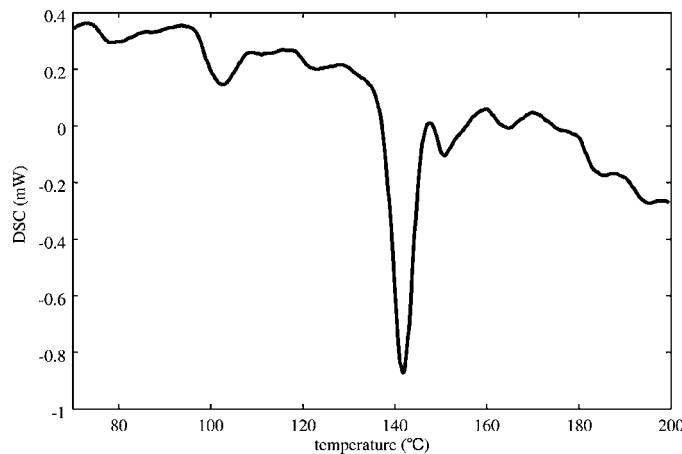
Growth direction	BaTiO <sub>3</sub> (0 0 1)//Pt(0 0 1)//MgO(0 0 1)
Bulk <i>c</i> -axis of Pt	3.99 Å
<i>c</i> -axis of BaTiO <sub>3</sub> film	4.12 Å
In-plane	BaTiO <sub>3</sub> [1 0 0]//Pt[1 0 0]//MgO[1 0 0]
Bulk <i>a</i> -axis of Pt	3.99 Å
<i>a</i> -axis of BaTiO <sub>3</sub> film	3.95 Å

**Figure 6.** Differential scanning calorimetry curve of bulk BaTiO<sub>3</sub> crystal.

### 3.4. Phase transition of BaTiO<sub>3</sub> film

Judging from the above, the BaTiO<sub>3</sub> thin films which are free from the epitaxial effect show characteristics of bulk nature. Here is another example of a BaTiO<sub>3</sub> film that releases the epitaxial effect. By using the MgO substrate with a deposited Pt layer (Pt–MgO substrate), the roughness of the substrate becomes larger than cleaved MgO substrates. We tested the Pt–MgO substrate and investigated the phase transition of BaTiO<sub>3</sub> thin films. Epitaxial BaTiO<sub>3</sub> thin films with thickness of 67 Å were grown on the Pt–MgO substrate. The lattice parameter was characterized by x-ray diffraction. The structural properties are summarized in table 3. The tetragonality of the crystal was rather higher than that of the bulk crystal. Thermal measurements were performed to clarify the phase transition of the thin crystal. Figures 6 and 7 show the results of differential scanning calorimeter (DSC) analysis of the bulk BaTiO<sub>3</sub> crystal and 67 Å thick BaTiO<sub>3</sub> thin film on Pt–MgO substrate, respectively. The sharp peak in figure 6 shows that in bulk crystal the cubic–tetragonal phase transition occurred at 125 °C. Clear evidence of the phase transition was also observed at 140 °C for the 67 Å thick BaTiO<sub>3</sub> film. Note that this peak was not observed in the Pt–MgO substrate without deposited film. The DSC signal from the film was so weak that the background of the DSC curve was noisy. The broad peak at 100 °C indicates the boiling point of water. The critical temperature ( $T_C$ ) of the thin film is higher than that of bulk crystal. There are many ways of controlling the phase transitions of ferroelectrics by growing strained thin films. Careful control of the growth conditions including the lattice mismatch and the surface roughness of the substrates is





**Figure 7.** Differential scanning calorimetry curve of the 67 Å thick BaTiO<sub>3</sub> film.

necessary to obtain ferroelectric thin films that are strongly affected by the epitaxial effect. For example, for the lattice-matched system of a SrTiO<sub>3</sub> substrate with a flat surface, the epitaxial strain remains in a thick film and the tetragonal phase is stabilized at a higher temperature, with no phase transitions up to 600 °C [10].

#### 4. Conclusion

The bulk nature of phase transition in ferroelectric thin films was studied by means of structural and thermal measurement. In order to present the bulk nature, the growth conditions of film thickness, lattice mismatch and surface roughness were controlled. BaTiO<sub>3</sub> films with thicknesses above 200 Å, BaTiO<sub>3</sub> films of large mismatched systems or BaTiO<sub>3</sub> films on large roughness substrates, are released from the epitaxial effect and their lattice parameters are nearly equal to those of the bulk BaTiO<sub>3</sub> crystal. The 67 Å thick BaTiO<sub>3</sub> thin film is typical of those showing the bulk nature of the ferroelectric phase transition.

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