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Abstract. Epitaxial crystals of BaTiO$_3$ with thickness of 67 Å were grown on MgO substrate with a Pt electrode by the activated reactive evaporation method. The lattice parameter was characterized by x-ray diffraction. The tetragonality of the crystal was much higher than that of the bulk crystal and the growth layer was strained by the epitaxial effect. Thermal measurements were performed to clarify the phase transition of the thin crystal. A clear thermal anomaly was observed at 140 °C that suggests a phase transition of BaTiO$_3$. This is the first observation of a phase transition of such a thin crystal of BaTiO$_3$. We discuss the requirements for a phase transition in terms of the epitaxial effect.

1. Introduction

There has been considerable research focused on the growth and characterization of perovskite ABO$_3$ oxide ferroelectric materials—in particular, many studies of ferroelectric thin films have been carried out to develop dielectric integrated devices. The most typical one is BaTiO$_3$, which undergoes successive phase transitions from cubic to tetragonal, to orthorhombic and finally to a rhombohedral phase. However, it has been reported that their ferroelectricity tends to disappear or be suppressed as the film thickness decreases [1].

The phase transition is one of the most important ferroelectric properties of thin films. Depending on the film thickness, the polarization may either increase or decrease at a surface and in consequence the critical temperature of the film may be greater or less than its bulk value. Various theoretical approaches, such as Landau–Ginzburg theory, the Ising model in a transverse field and the scaling theory, have been exploited to discuss the ferroelectric instability in terms of the reduction of thickness in films by consideration of the surface effect [2–4]. However, the oversimplifications in recent theoretical analyses have resulted in some contradictions between theoretical and experimental investigations. In BaTiO$_3$ thin films, the tetragonal phase is stabilized over wide temperature ranges and the cubic–tetragonal ferroelectric phase transition disappears, while, for example, Terauchi *et al* [5] reported a temperature dependence of the lattice parameters of a lattice-matched system of BaTiO$_3$ films on SrTiO$_3$ substrate with the thicknesses 67, 230 and 1500 Å. In this system, the BaTiO$_3$ lattice remains tetragonal and no evidence of a phase transition can be observed. According

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to Ishibashi *et al* [6], the size effect of the ferroelectricity in thin films can be understood in terms of the decline of the average energy density of the polarization within the films. Ferroelectricity disappears when the thickness is reduced to the limit of critical thickness. In addition to the film thickness, the large lattice misfit strain introduced into the heteroepitaxial film was also considered to play an important role. The absence of any phase transition should be observed in ferroelectric thin films that are influenced strongly by the epitaxial effect and the size effect. In actuality, the thin films of large-lattice-mismatch systems are free from misfit strains because dislocations are generated between the growing layer and substrate. Moreover, thin films on large-mismatch substrates are hardly deposited through layer-by-layer growth. As a consequence of island growth, the roughness of the film surface is substantial and the two-dimensional size effect should not be enhanced. If the ferroelectric thin film was free from the epitaxial effect, it would show the bulk properties and the phase transition would occur.

It is necessary to control the phase transition for developing new ferroelectric devices, because most ferroelectrics show a unique property near the critical temperature (T_C) of the phase transition. Some undesirable properties at T_C should be avoided and some beneficial properties should be exploited fully for the ferroelectric devices.

We obtained clear evidence of the phase transition of $BaTiO_3$ thin film on Pt/MgO. In this paper, we characterize this film by using thermal measurements and x-ray measurements. We also discuss the requirements for the phase transition in ferroelectric thin film in terms of growth conditions.

The present work is closely connected with work on the ferroelectric field-effect transistor (FET). The structure dependence of FETs intrinsically imposed by the domains having lateral dimension much larger than the ferroelectric thickness is important. This work will give information useful in the design of nano-structured ferroelectric devices.

2. Experimental procedure

$BaTiO_3$ films were grown by a reactive evaporation method. Details of the deposition technique are given in references [7] and [8]. Essentially, this deposition method involves the coevaporation of the metal elements in an oxygen atmosphere. The deposition rate was about 2 Å s^{-1} and the substrate temperature was 700 °C. The (001)-oriented Pt single-crystal thin films (100 nm thickness) were deposited on MgO(100) substrates at 750 °C by vacuum evaporation. We also characterized a bulk $BaTiO_3$ crystal grown by the top-seeded solution growth (TSSG) method [9]. It is rectangular in shape with dimensions 3 mm × 5 mm (×1 mm thick).

The crystal structure of the $BaTiO_3$ crystals was investigated using x-ray diffraction. Data collection was performed in the 2θ range of 35° to 55° (around the 002 and 200 reflections of the $BaTiO_3$ crystals) using a double-axis diffractometer and Cu Kα radiation monochromatized by a pyrolytic 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 $BaTiO_3$ crystals.

3. Results and discussion

The x-ray diffraction profile of the bulk $BaTiO_3$ crystal at room temperature is shown in figure 1. The strong splitting 200 and 002 peaks of $BaTiO_3$ signify that the bulk crystal is in the tetragonal phase and it has a domain structure. From these peaks, the lattice parameters along the *a*- and *c*-axes in the tetragonal phase were calculated to be 4.03 Å and 3.99 Å,
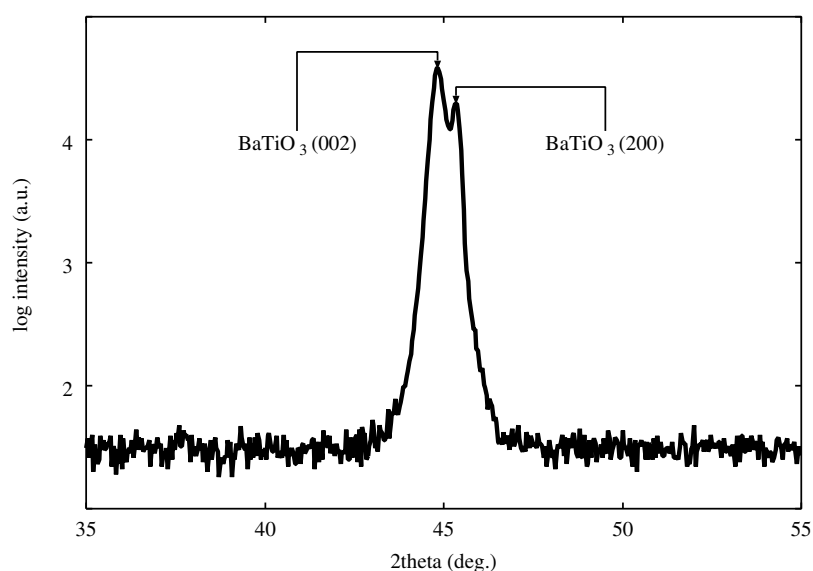
Figure 1. The x-ray diffraction pattern of bulk BaTiO₃ crystal around the 002 and 200 reflections.

respectively. The scattering profile of 1000 Å thick BaTiO₃ thin film along the [001] direction (growth direction) is shown in figure 2(a). Only a 002 reflection of BaTiO₃ film is observed between the strong Pt and MgO peaks. In order to determine the lattice parameter along the [100] direction in the growth plane, the epitaxial BaTiO₃ films were investigated under grazing-incidence x-ray diffraction conditions. The scanning profile around the (200) reflection is shown in figure 2(b). The lattice parameter of the film is found to be $c = 4.05$ Å. The lattice parameter along the a-axis was measured by the glancing-incidence x-ray diffraction (GIXD) method, which involved scanning along the [100] direction in the growth plane, and it was found that $a = 4.01$ Å. Note that the lattice parameters of bulk MgO and Pt at room temperature are 4.21 Å and 3.91 Å, respectively. We also performed x-ray diffraction studies on the other BaTiO₃ films with thicknesses 67, 100, 500 and 4000 Å. The thickness dependence of the BaTiO₃ films on Pt/MgO substrates is shown in figure 3. The lattice parameters of 67 Å and 100 Å thick BaTiO₃ crystals were highly strained by the epitaxial effect. In the growth plane, the lattice parameter a is squeezed to match the lattice parameter of Pt. The lattice parameter c is elongated along the growth plane to maintain the Poisson ratio. Similar expansions were observed in BaTiO₃ films on SrTiO₃ substrates [1]. On the other hand, the lattice parameters of the films with thickness above 500 Å were nearly equal to those for the bulk. These films were free from epitaxial strain because dislocations should be generated near the interface. Although the lattice mismatch in the growth plane with Pt is exactly equal to that for SrTiO₃ substrates, the epitaxial effect is not enhanced in Pt/MgO substrates like in SrTiO₃ substrates. It is considered that the surface roughness of a Pt electrode is larger than that of a SrTiO₃ substrate and that the epitaxial effect cannot be enhanced because of dislocations or misfit transitions [10]. Therefore, in BaTiO₃ films on Pt/MgO substrates, the epitaxial effect in the phase transition should be investigated by using 67 Å thick film.

Our original plan was that the Pt/MgO substrate be used as the bottom electrode and the phase transition be clarified by dielectric measurements. However, the 67 Å thick film has pinholes and a film capacitor cannot be made with it. Moreover, the structural analysis by x-ray diffraction could hardly be performed, because the reflection from the 67 Å thick
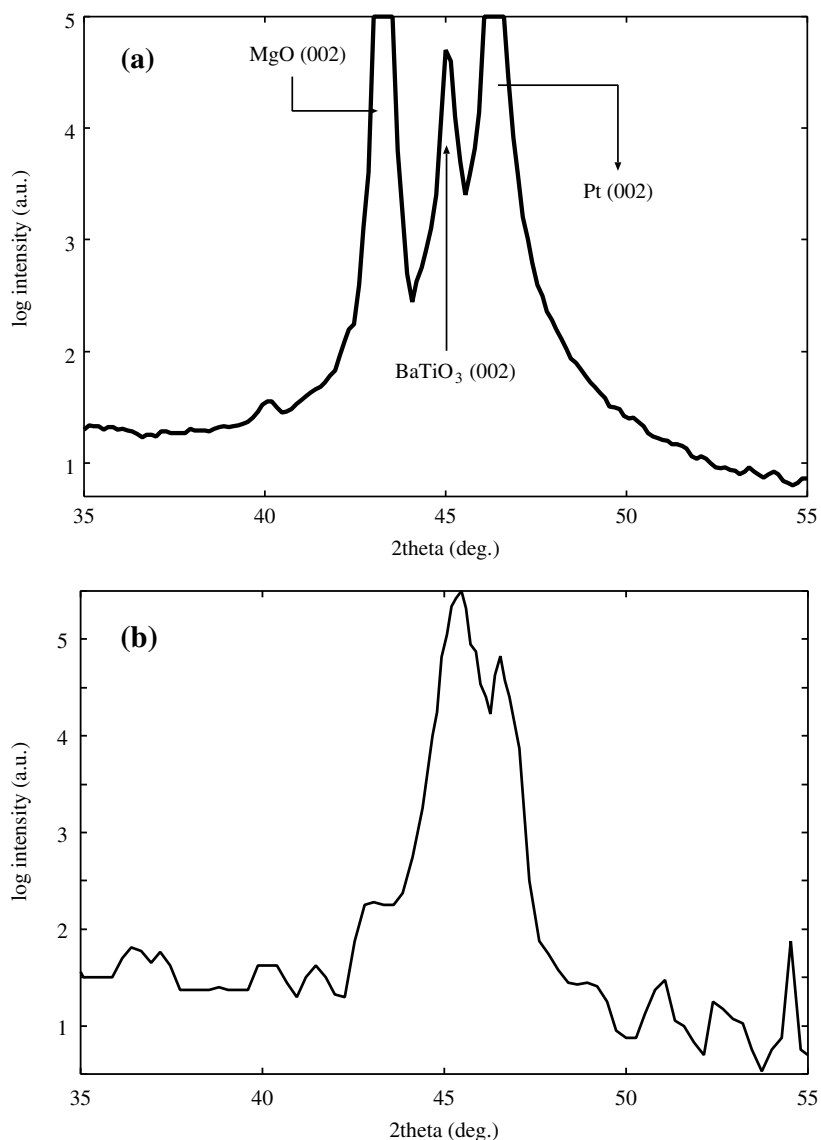
Figure 2. (a) The x-ray diffraction pattern of a 1000 Å thick BaTiO$_3$ thin film on a Pt/MgO substrate around the 002 reflection obtained using the conventional geometry. The BaTiO$_3$ reflection was observed between the reflections for the MgO substrate and Pt electrode. (b) The x-ray diffraction pattern of a 1000 Å thick BaTiO$_3$ thin film on a Pt/MgO substrate around the 200 reflection obtained under grazing-incidence x-ray diffraction conditions.

BaTiO$_3$ crystal was so broad and weak that the structural change at the phase transition was difficult to observe by x-ray measurement. Thus, we tried to clarify the phase transition of the 67 Å thick BaTiO$_3$ film by thermal measurements.

Figures 4 and 5 show the results of differential scanning calorimeter (DSC) analysis of the bulk BaTiO$_3$ crystal and 67 Å thick BaTiO$_3$ thin film, respectively. The sharp endtherm in figure 4 shows that in bulk crystal the cubic–tetragonal phase transition occurred at 125 °C. Clear evidence of a phase transition was also observed at 140 °C for the 67 Å thick BaTiO$_3$
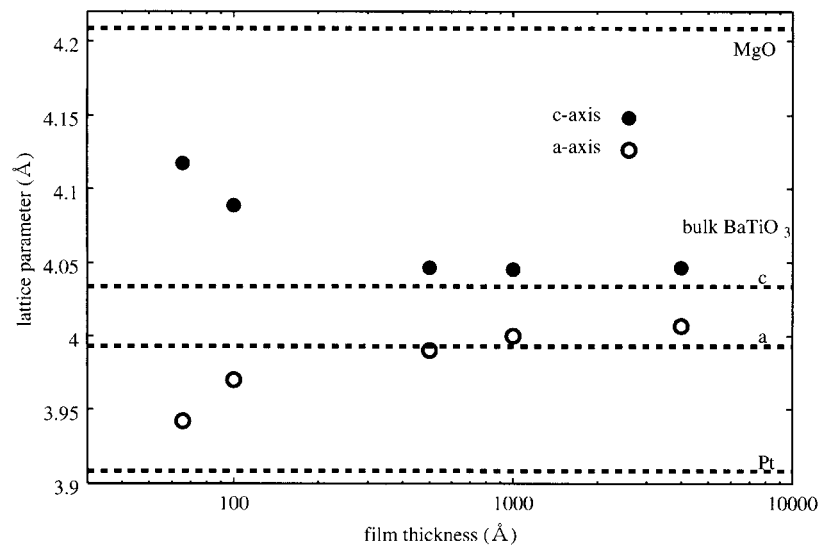
Figure 3. Lattice parameters a and c as functions of the film thickness in $BaTiO_3$ films at room temperature. The parameters of bulk $BaTiO_3$, Pt and MgO are indicated by broken lines.
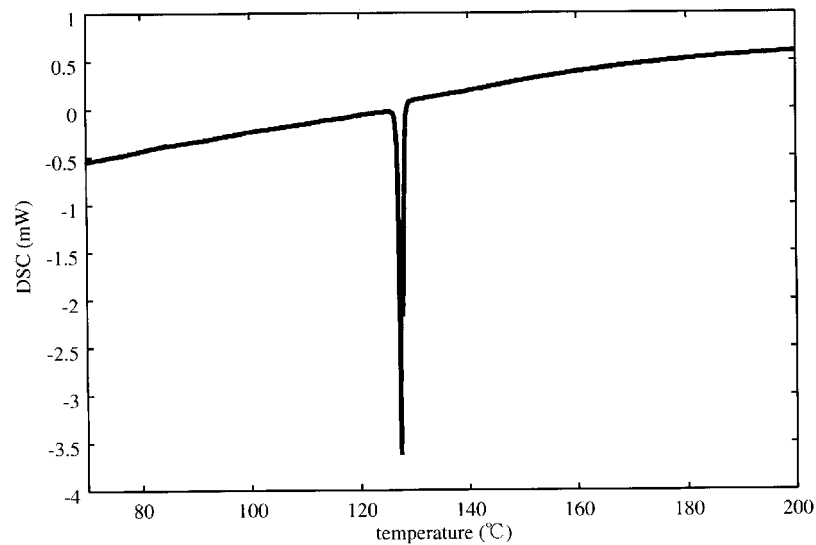
Figure 4. The differential scanning calorimetry curve for bulk $BaTiO_3$ crystal.

film. The DSC signal from the film was so weak that the background of the DSC curve was noisy, as shown in figure 5. The broad endtherm 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. This is the first observation of a phase transition in such a thin crystal of $BaTiO_3$.

The shift of T_C towards higher temperatures should be due to the epitaxial strain. The tetragonality of 67 Å thick $BaTiO_3$ film is much higher than that of bulk crystal. The large degree of tetragonality should stabilize the tetragonal phase and T_C for the film should be
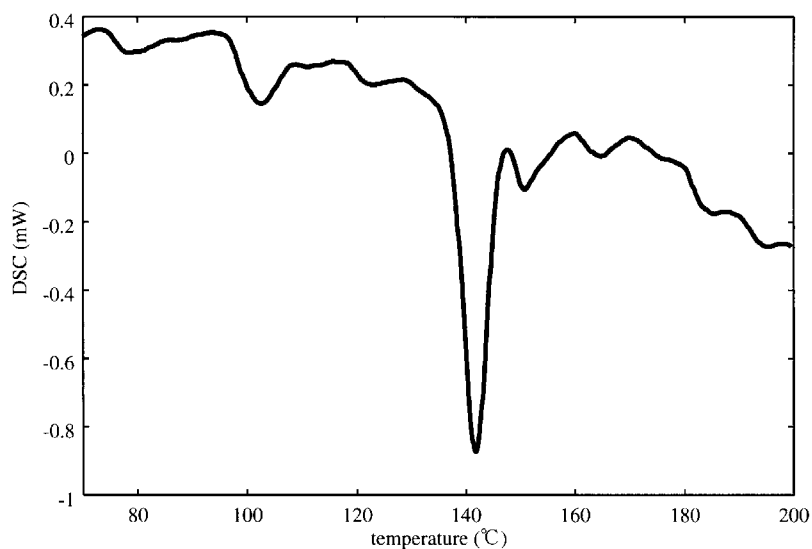
Figure 5. The differential scanning calorimetry curve for the 67 Å thick $BaTiO_3$ film.

shifted toward higher temperature. In $BaTiO_3$ films on Pt/MgO substrates, the epitaxial effect is enhanced more strongly near the interface than those far from the growth-layer/substrate boundary, because the tetragonality decreases as the film thickness increases. The $BaTiO_3$ films with a thickness above 1000 Å should show no shift of T_C, because they are similar as regards tetragonality to the bulk crystal. In other words, control of the transition temperature can be achieved by controlling the internal lattice strain using the epitaxial effect. This conclusion is supported by the results for Pb(Zr, Ti)O_3 (PZT) films on MgO substrates [11]. T_C for the PZT-on-MgO system is also close to the bulk transition temperature, as the tetragonality is close to the bulk value. There are many ways of controlling the phase transitions of ferroelectrics by growing strained thin films. Firm control of the growth conditions including the lattice mismatch and the surface roughness of the substrates is necessary to obtain ferroelectric thin films that are strongly affected by the epitaxial effect. For example, for the lattice-matched system of a $SrTiO_3$ substrate with a flat surface, the epitaxial strain would remain in a thick film and the tetragonal phase would be stabilized at a higher temperature. The epitaxial effect of our $BaTiO_3$ films is weakened because of the rough substrate surface, compared to the case for lattice-matched $BaTiO_3$ films on flat $SrTiO_3$ substrates for which no phase transition is shown up to 600 °C [12].

There are some theoretical and experimental [13] data which contradicted our work. Our work was carried out using an ultra-thin film. The lateral critical thicknesses calculated in reference [2] and reference [3] are larger than that of our $BaTiO_3$ film. At the surface, the local field that stabilizes the polarized state may become smaller on decreasing the film thickness. However, this prediction may not hold good below the calculated critical thickness. Additionally, the thermal analysis was performed without a top electrode. The boundary condition may be seen as arising from an intrinsic variation of material parameters near a surface. So the disagreement between the theoretical and our experimental data seems still controversial. While the surfaces of ferroelectric films are covered by electrodes, the surface charges will be fully compensated. Even without covering surface electrodes, the bending of the surface energy band could also partially screen the polarization [14], offsetting the

depolarization field. The size effect in ferroelectric thin films could be attributed to the influence of a depolarizing field. Nevertheless, it has been found quite difficult to confirm the influence of a depolarizing field experimentally. Our work will contribute to clarifying the size effects on ferroelectric thin films without top electrodes.

4. Conclusions

The phase transition and phase stability of BaTiO₃ films on Pt/MgO substrates were studied by means of x-ray diffraction and thermal measurement. The highly strained film with a thickness of 67 Å showed a clear phase transition at 140 °C. This is the first observation of a phase transition of such a thin crystal of BaTiO₃. Because the Pt electrode surface was rougher than conventional substrates, the dislocations were generated near the interface and the substrate effect was weakened in the growing layer. However, the phase transition of the BaTiO₃ film was influenced by a small epitaxial effect. The transition temperature was 10 °C higher than that of the bulk crystal. This was because the tetragonality of the 67 Å thick BaTiO₃ crystal was higher than that of the bulk and the tetragonal phase was stabilized over a wide temperature range.

Acknowledgment

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