

Interface and Surface Structures of BaTiO₃ Thin Film Grown On SrTiO₃ by an MBE Method

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BaTiO₃(BT) thin films were grown on SrTiO₃(ST) substrates by an MBE method using an oxygen radical source. The interface and surface structures of the BT thin films were evaluated by XRD, RHEED, TEM, AFM, XPS and CAICISS. The BT thin films were oriented for their *c*-axis to be perpendicular to the substrate surfaces. The lattice constants of the BT thin films varied with the distance from BT/ST interface. Step structure was observed for the ST and BT surfaces before and after the thin film growth by AFM. XPS analysis indicated that adsorbed oxygen was enriched on the BaO-terminated surface in comparison with the TiO₂-terminated surface.

1. Introduction

In general, oxide thin films are grown onto different materials with different lattice constants. However, it is well known that such inevitable lattice misfit causes huge stress at the interface and, as a result, interfacial dislocations or atomic distortions are introduced in the interfacial region. Recently, dielectric properties of BaTiO₃(BT)/SrTiO₃(ST) multilayered thin films deposited by laser ablation method were found to change as a function of lattice deformation¹. Thus, the relationship between hetero-interface formation process and stress relaxation mechanism is necessary to design and control electrical property of oxide thin film. In near future, controlling a stress relaxation will be key technology to enhance the electrical property.

In the present paper, BT thin films were grown on the ST substrates and their interface and surface structures were studied in order to elucidate the lattice relaxation.

2. Experimentals

An MBE system was composed of a high-vacuum growth chamber (~10⁻³Pa) equipped with Knudsen cells(K-cells) for Ti and Ba metal sources. Oxygen radicals were supplied by a helicon plasma gun which can effectively generate oxygen radicals.

As-polished ST substrates with (001) mirror planes (0.5wt% Nb-doped, 10 × 10 × 0.5mm³; Shinkosha Co.) were cleaned and annealed at 1000°C for 1 hour in O₂ atmosphere. After this treatment, step structure could be observed on the substrate surface. In order to eliminate carbon on the substrate surface, the substrates were heated at 930°C in the MBE chamber for 1 hour at 3 × 10⁻³Pa under oxygen radical irradiation.

BT thin films were grown on substrates at 650~700°C by the alternate deposition of Ba and Ti metals. Shutter control of Ba and Ti K-cells was carried out by monitoring a RHEED oscillation. The K-cell's temperature was kept at 480~500°C for Ba and at 1390~1400°C for Ti. The helicon

plasma gun was excited at 13.56MHz with a power of 200W.

Surface structures of ST substrates and BT thin films were observed by AFM (Nanoscope IIIa, Digital Instruments Co.), RHEED(ULVAC Co.Ltd.: 20kV, incident angle 4°) and CAICISS (Shimadzu Co.: 3keV He⁺). A cross-sectional view of the BT/ST interface was observed by TEM (JEM-2000EX, JEOL Co.Ltd.) with 200keV accelerating voltage. XRD patterns were obtained using Cu-K α radiation (20kV, 10mA: RINT2000, Rigaku Co.Ltd.). XPS spectra were measured with Mg-K α excitation (1253.6eV: Microlab 320-D, VG Scientific Ltd.) under a pressure of 3×10^{-7} Pa without exposing the specimen to air.

3. Results and Discussion

3.1. Lattice mismatch and RHEED oscillation

The BT thin film indicated streaky RHEED patterns. The growth direction of the BT thin film was *c*-axis and its *a*-value was calculated from the RHEED patterns to be $a=0.397\text{nm}$ which was smaller than *a*-axis of bulk BT ($a=0.3994\text{nm}$). Since the *a*-value of the ST substrate is $a=0.3905\text{nm}$, the lattice mismatch of the BT thin film against the ST substrate was estimated to be +1.66%. The lattice mismatch of bulk BT against bulk ST is +2.28%. Therefore, it is found that the BT lattice shrank to relax the lattice mismatch.

Figure 1 shows the RHEED oscillation observed along the $\langle 100 \rangle$ direction during the growth of BT thin film. When a K-cell's shutter for Ba was

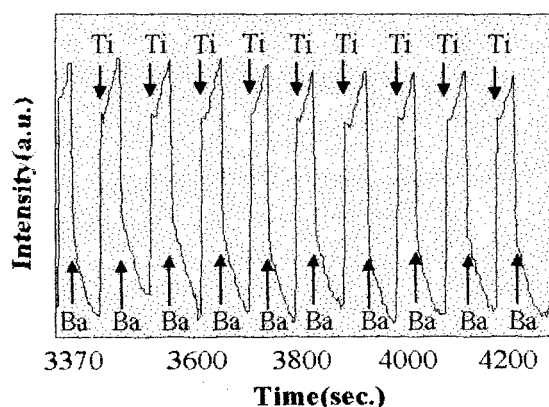


Fig.1 RHEED oscillation observed during thin film growth of BaTiO₃/SrTiO₃

opened, the RHEED intensity decreased and reached a minimal value. On the other hand, when a K-cell's shutter for Ti was opened, the RHEED intensity increased and reached a maximal value. Only with such shutter control could the BT thin film grow continuously. In addition, it is worth to note that the RHEED oscillation could be observed only when the BaO layer was stacked at the beginning. The film thickness was estimated to be $d=16\text{nm}$ which corresponded to 40 BT unit cells.

3.2. Interfacial structure and lattice deformation

Figure 2 shows the cross-sectional TEM images of BT/ST. Top figure is BT thin film, middle one is BT/ST interface, and bottom one is ST substrate. It is seen that the *c*-axis elongates near the interface, and the BT lattice fits very well to the ST lattice. This

result indicates that the BT thin film was epitaxially grown. In the present work, misfit dislocation could not be detected.

The intense peaks were assigned to the ST substrate and the weak peaks to the tetragonal BT: (001) and (002) peaks on the θ -2 θ XRD pattern of the BT thin film. From the XRD pattern, the lattice constant *c* of the BT film was calculated to be $c=0.4149\text{nm}$. This value is larger than that of bulk BT ($c=0.4038\text{nm}$): that is, the unit cell of the BT thin film elongates along the *c*-axis though it is compressed within the *a*-*b* plane.

The *a*- and *b*-axes of the BT film have shrunk to reduce the lattice mismatch with the ST substrate. As a result, the elongate lattice deformation is induced along the *c*-axis, presumably in order to relax the compressive distortion produced in the *a*-*b* plane.

Table 1 shows the relationship between the lattice constants and the film thickness. The *a*-value increases with the film thickness, while the *c*-value decreases with the thickness. The 40-layered BT has the lattice constants close to the bulk BT. From the TEM image of a cross-sectional BT/ST interface, it is found that the BT lattices fit the ST lattices very well. Therefore, the lattice distortion gradually relaxes far from the interface with increasing the film thickness.

3.3. Surface structure of thin film

According to AFM observation, it is found that the surface of the BT film has a step structure, which is apparently similar to the ST substrate. This

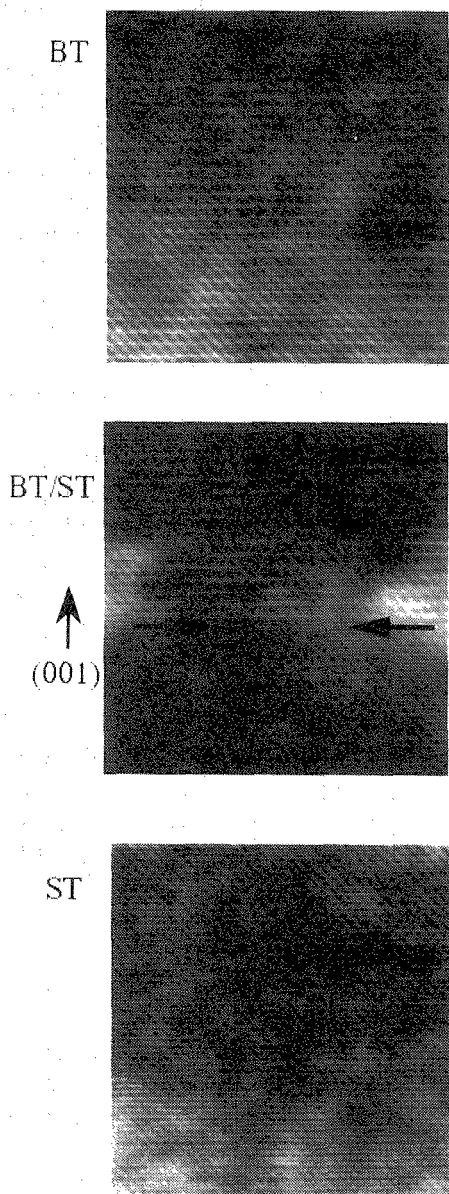


Fig.2 TEM images of BT/ST

Table 1 Relationship between lattice constants of BaTiO₃ (BT) thin film grown on SrTiO₃ and the film thickness

	Thickness (nm)	c value (nm)	a value (nm)
Bulk SrTiO ₃		0.3905	0.3905
20 layers BT	8	0.4208	0.391
40 layers BT	16	0.4149	0.397
Bulk BaTiO ₃		0.4038	0.3994

suggests that the BT crystal grew layer by layer.

CAICISS measurement showed that experimental result is in good accordance with simulated spectra; the BaO- and TiO₂-layers have normal atomic configuration, indicating that the BaTiO₃ film by grew layer-by-layer mechanism.

Figure 3 shows the XPS spectra of oxygen core-level, O_{1s}. The solid line was observed for the TiO₂-terminated surface and the broken line for the BaO-terminated surface. Two oxygen peaks were detected, as shown in Fig.3. The peak observed around 533eV is ascribed to adsorbed oxygen and that around 530eV to lattice oxygen. From the spectra, it is found that the BaO- and TiO₂-terminated surfaces have different compositions: that is, a small amount of oxygen is adsorbed on the TiO₂ surface while a large amount of oxygen is adsorbed on the BaO surface.

Kang et al.² have calculated the electronic structure of BT surface by a DV-X α cluster method. According to their result, when an oxygen atom arrives at the TiO₂ surface, an antibonding orbital is occupied by electrons, which cause the chemical bond of Ti-O unstable. This means that the oxygen cannot easily adsorb on the TiO₂-terminated surface of BT; in fact, the amount of adsorbed oxygen is low on the TiO₂ surface as shown in Fig.3. In comparison with the TiO₂ surface, the amount of the adsorbed oxygen is very high on the BaO surface; this suggests that the oxygen can chemically adsorb on the BaO surface, probably onto a Ba ion.

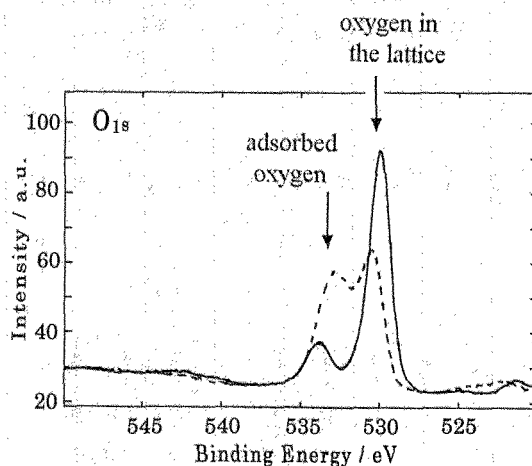


Fig.3 XPS spectra of oxygen core-level O_{1s}
solid line: TiO₂ terminated surface
broken line: BaO terminated surface

3.4. Growth mechanism of BT thin film

Based on the RHEED and XPS results, the growth mechanism of BT thin film is proposed as follows. When the Ti K-cell is opened, the TiO_2 layer grows. Then Ti metal enters probably between the adsorbed oxygens on the BaO surface. Thus, as shown in Fig.1, the RHEED intensity increases corresponding to the result that the final TiO_2 surface is flat without adsorbed oxygen.

In the next step, the BaO layer grows on the flat TiO_2 surface. When Ba and O come on the surface, BaO layer grows. Then, oxygen, probably neutral oxygen, adsorbs on the BaO layer. Because of oxygen adsorbed on the BaO-terminated surface, the RHEED intensity shown in Fig.1 is considered to decrease with the growth of BaO layer.

The adsorbed oxygen is important for the BaTiO_3 thin film growth, since the BT film can grow only when the BaO layer is stacked at the beginning. The adsorbed oxygen probably acts as surfactant for the growth of TiO_2 layer.

4. Conclusions

According to TEM observations, the BT thin film grew epitaxially on the ST substrate. The BT thin

film was tetragonal and oriented in the [001] direction. The lattice constant a of the BT thin film shrank while its c -axis elongated. The shrinkage of the a -axis resulted from a lattice mismatch between the BT film and the ST substrate. The lattice elongation along the c -axis presumably took place to reduce the compressive stress generated in the a - b plane of the BT film. According to XPS analysis, a large amount of oxygen was adsorbed on the BaO surface while only a small amount of oxygen was adsorbed on the TiO_2 surface. The result of DV- $X\alpha$ calculation on BT surface which Kang et al. has reported supported the oxygen adsorption behavior. It was considered that the chemically adsorbed oxygen played an important role in the BT film growth.

References

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