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Atomic-Scale Analysis of the Terminating Layer of $BaTiO_3$ Thin Films by Laser MBE-CAICISS System

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Atomic-scale analysis of the terminating layer of the c-axis oriented $BaTiO_3$(001) films on the atomically flat $SrTiO_3$(100) substrate was performed by using a Laser MBE-CAICISS system, which has a pulsed laser molecular beam epitaxy (laser MBE) chamber equipped with an *in situ* coaxial impact collision ion scattering spectroscopy (*in situ* CAICISS). Under the optimized growth condition, the intensity oscillations were observed at the specular beam spot in the reflection high energy electron diffraction (RHEED) pattern during the deposition. One period of the intensity oscillation corresponded to the growth of 0.4 nm indicating the growth unit layer to be one molecular layer of [BaO/TiO_2]. From *in situ* CAICISS analysis, it was found that the terminating layer of the films changed from mixed (TiO_2/BaO) type to BaO atomic plane in the initial growth stage (~4 nm). The terminating layers of $BaTiO_3$(001) thin films grown on $SrTiO_3$(100) via solid phase epitaxy as well as films grown on Pt(100) (27 nm thick)/ $SrTiO_3$(100) were verified to be dominantly the BaO planes.

Key words: $BaTiO_3$ film, terminating layer, ion scattering spectroscopy, epitaxy, atomic scale analysis

1. INTRODUCTION

Oxide materials, especially perovskite-type oxides have attracted much attention as the promising matter of electronically active devices, because they exhibit various superior properties, such as superconductivity, ferroelectricity and ferromagnetism. Perovskite oxides have almost similar lattice constants of a or b axis and thermal expansion coefficients, so that it is relatively easy to combine these materials in the multilayer structure for novel oxide devices. An ideal heteroepitaxial structure should have not only a high crystallinity but also well-defined interfaces.

$BaTiO_3$ is one of the most widely investigated ferroelectric oxides with a perovskite structure having potential applications in dynamic random access memory (DRAM),[1] nonvolatile memory,[2-4] and electro-optical,[5-7] pyroelectric, and piezoelectric devices.[8] The structure of $BaTiO_3$ can be considered to consist of alternating stacks of BaO and TiO_2 atomic layer along the c-axis. Therefore, c-axis oriented $BaTiO_3$ films deposited by co-evaporation methods such as pulsed laser deposition (PLD) using ceramics targets, have BaO or TiO_2 or their mixture as the (001) terminating atomic layer. As reported previously by our group, coaxial impact collision ion scattering spectroscopy (CAICISS) is a powerful technique to analyze the atomic species and structure of the topmost atomic layers of the oxide films due to the large scattering cross section of low energy ions on these surfaces. The scattering angle of an ion beam impinging on the sample surface is very close to 180 ° in CAICISS experiments. The topmost surface atomic species and their arrangements can be ascertained from the incident and azimuthal angular dependence of the time-of-flight (TOF) spectra. Previously, we could verify the atomic species and their arrangements of the topmost surfaces for oxide films of $SrTiO_3$,[9] CeO_2,[10] Al_2O_3,[11] ZnO[12] and $(La_{0.7}\ Sr_{0.3})MnO_3$[13] by CAICISS measurements. In this paper we report the *in situ* atomic-scale CAICISS analyses of the terminating layer of epitaxial $BaTiO_3$ (001) thin films grown by Laser MBE, i.e. pulsed laser deposition in ultrahigh vacuum.[14]

2. EXPERIMENTAL

Laser MBE-CAICISS system was used to analyze the terminating layer of the c-axis oriented $BaTiO_3$ (001) films grown on $SrTiO_3$ (100) substrate as well as on Pt (100) films /$SrTiO_3$ (100) substrate. Figure 1 illustrates the Laser MBE-CAICISS system. The system is composed of four main parts; (1) an UHV deposition chamber (base pressure of $5x10^{-10}$ Torr), (2) a KrF excimer laser (wavelength: 248 nm, pulse duration: 20 ns, Lambda Physik model LPX-100), (3) *in situ* RHEED system, and (4) CAICISS system equipped with TOF analyzer and a two-axis (tilting and rotating) computer-controlled goniometer. $BaTiO_3$ films and Pt(100) epitaxial films were deposited on the well defined $SrTiO_3$(100) substrate by the Laser MBE technique. The $SrTiO_3$(100) substrate has an atomically smooth surface terminated by the TiO_2 plane consisting of one unit-cell high (0.4 nm) steps.[9, 15] A focused pulsed laser beam was impinged on a sintered $BaTiO_3$ target or Pt target to ablate film precursors. Films were deposited in either ultrahigh vacuum (UHV, ~$8x10^{-8}$ Torr at 900 ℃) or oxidizing atmosphere (by flushing the O_2 gas onto the substrate)

Table 1. Deposition conditions.

Film	$BaTiO_3$(001)	$BaTiO_3$(001)	Pt(100)	$BaTiO_3$(001)
Substrate	$SrTiO_3$(100)	$SrTiO_3$(100)	$SrTiO_3$(100)	Pt(100)/ $SrTiO_3$
Deposition temperature	700 ℃	R. T. (20 ℃)	900 ℃	800 ℃
Oxygen pressure	1 x 10^{-6} Torr	1 x 10^{-6} Torr	UHV	1 x 10^{-4} Torr
Laser energy density	2 J/cm^2	2 J/cm^2	2 J/cm^2	2 J/cm^2
Laser frequency	2 Hz	2 Hz	10 Hz	2 Hz
Post-annealing for solid phase epitaxy	—	800 ℃, 30 min.	—	—

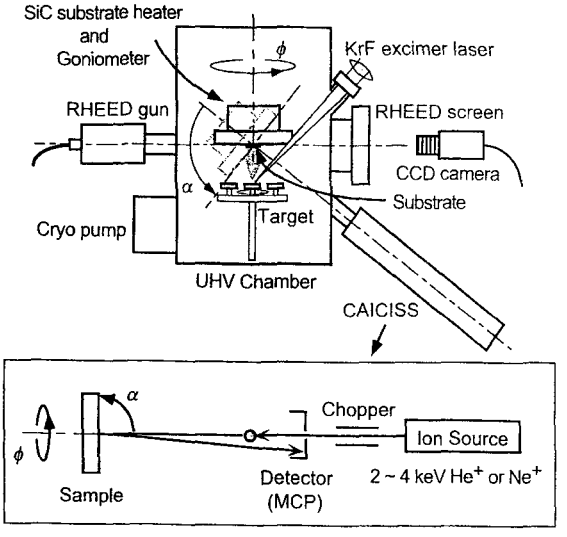

Fig. 1. Laser MBE-CAICISS system.

conditions as summarized in Table 1. $BaTiO_3$ film as-deposited on $SrTiO_3$(100) at room temperature (R. T.) was amorphous and became the c-axis oriented epitaxial film after post-annealing at 800 ℃ for 30 minutes in 1x10^{-6} Torr O_2 atmosphere. *In situ* monitoring of the RHEED pattern and intensity at the specular beam spot was performed using an incident electron beam of 25 keV and a CCD camera connected to an image processor and a personal computer.

The *in situ* CAICISS measurements were carried out at 300 ℃ in ultra high vacuum (less than 5 x 10^{-9} Torr). The He^+ ion beam (2 keV) was chopped into pulses of 150 ns duration at a 100 kHz repetition rate. The ion beam was focused into a 2-mm-diam spot on the sample surface. The time-averaged current of the incident ion beam was about 100 pA. The backscattered ions and neutral species were detected by multichannel plates at a distance of 530 mm from the specimen to obtain the TOF spectra. The film structure was characterized by X-ray diffraction (XRD). The composition of the $BaTiO_3$ film was analyzed by inductively coupled plasma (ICP) spectrometry. The surface morphology of the specimens was observed with an atomic force microscope (AFM, SII SPI-3700) in air.

3. RESULTS AND DISCUSSION

Figure 2 shows the typical RHEED intensity oscillations observed during the growth of the $BaTiO_3$ film on the $SrTiO_3$(100) substrate at 700 ℃. The period of RHEED intensity oscillations corresponded to the growth of 0.4 nm thick film. The surface morphology of the resultant film exhibited atomic terraces and steps structure. The step height was ~0.4 nm, which is close to the c-axis lattice constant of $BaTiO_3$. These results indicate the unit-cell [BaO/TiO_2] layer-by-layer growth of the $BaTiO_3$ film on the $SrTiO_3$ substrate. From the XRD measurements, the $BaTiO_3$ film (80 nm) on $SrTiO_3$(100) substrate grown under the present conditions was found to have a c-axis orientation with c = 0.406 nm. The full width at half-maximum (FWHM) of the (001) peak was 0.06°. From the ICP spectrometry analyses of $BaTiO_3$ films, the ratio of Ti to Ba was evaluated to be between 1.02 and 1.05.

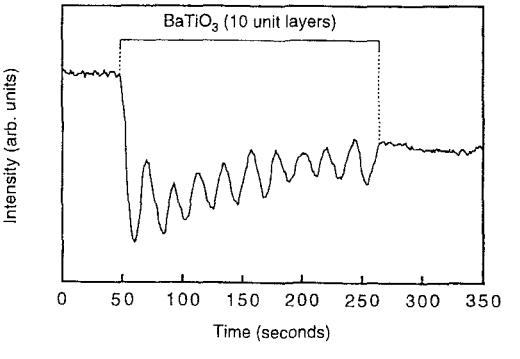

Fig. 2. RHEED intensity oscillations during the growth of $BaTiO_3$ film on $SrTiO_3$(100) substrate at 700 ℃.

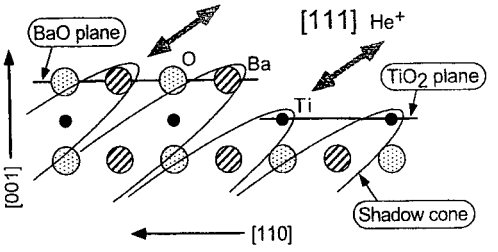

Fig. 3. Schematic cross-sectional geometry of $BaTiO_3$(001) along [110] direction.

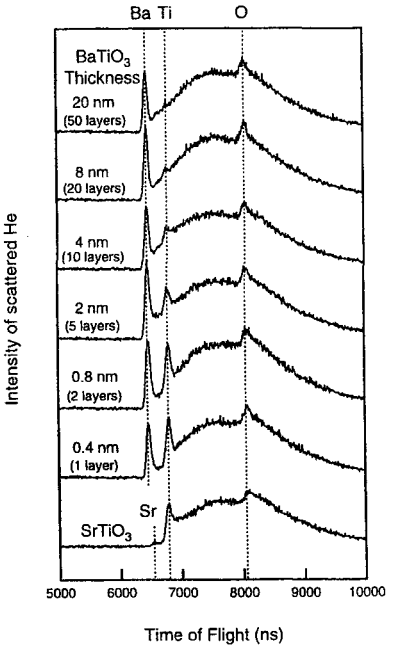

Fig. 4. CAICISS-TOF spectra of $BaTiO_3$ films (0.4 ~ 20 nm) on $SrTiO_3$(001) at [111] direction.

In order to examine the terminating atomic plane of the $BaTiO_3$(001) film, CAICISS spectra were taken at [111] direction on $BaTiO_3$(001) surface. As shown in Fig. 3, if the topmost layer on the $BaTiO_3$(001) is terminated with TiO_2 atomic plane, both Ti and O atoms can be "seen", but Ba atoms cannot be "seen", because Ba atoms in the second layer are located in "shadow-cones" formed by the topmost Ti atoms. "Shadow-cone" means the shadow area behind the atom confronted with an incident ion beam. In this shadow-cone no incident ion can penetrate, so the signal of atoms in the shadow-cone is not detected. In the same way, if the topmost layer on the $BaTiO_3$(001) is terminated with BaO atomic plane, both Ba and O atoms can be "seen" but Ti atoms cannot be "seen".

Figure 4 shows the CAICISS-TOF spectra taken at [111] direction for the $BaTiO_3$(001) films grown on $SrTiO_3$(100) substrate by monitoring the corresponding RHEED oscillations as presented earlier (in Fig. 2). These TOF spectra were acquired as follows. After the $BaTiO_3$(001) film was deposited while observing the RHEED intensity oscillations at 700 ℃, the substrate temperature was cooled down to 300 ℃ and then CAICISS measurements were conducted in UHV. CAICISS measurements were carried out in between the consecutive deposition runs of $BaTiO_3$. The TOF peaks observed at 6460, 6560, 6810 and 8050 ns correspond to the head-on collisions of He^+ ion with Ba, Sr, Ti and O atoms, respectively. As for the $SrTiO_3$ substrate, dominant Ti peak is clearly observed indicating termination of the topmost surface of the substrate with the TiO_2 plane. During the film growth, with the increasing film thickness, the Ba signal increase and the Ti signal decrease. The Ti signal disappears for the film with thickness of about 20 unit-cell layers (~8nm). This implies that the topmost layer consisted of mixed BaO/TiO_2 atomic planes at the initial growth stage and the terminating layer changed to BaO single atomic plane with film growth. Taking into account of the ICP results on the film compositions as mentioned above, it is difficult to consider that excess Ba segregation on the surface would have occurred. Since the TOF spectra did not show any change on annealing at 900 ℃, the topmost BaO layer is stable at high temperatures.

Figure 5 shows CAICISS-TOF spectra for the [111] direction of $BaTiO_3$(001) films crystallized epitaxially by thermal annealing (at 800 ℃) of the amorphous films deposited on $SrTiO_3$(001) at room temperature. These TOF spectra are similar in shape to those of the films deposited at high temperatures as shown in Fig. 4. This observation suggests that the parameter controlling the terminating layer is related not to the deposition temperature but is most likely related to the film thickness. It might be concerned with stress relaxation

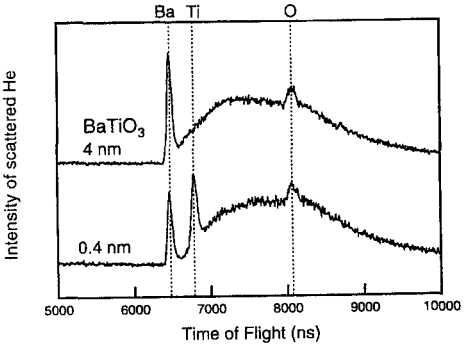

Fig. 5. CAICISS-TOF spectra of 0.4 and 4 nm thick $BaTiO_3$(001) films crystallized epitaxially by thermal annealing of the amorphous films deposited on SrTiO3 substrates at R. T. ([111] direction).

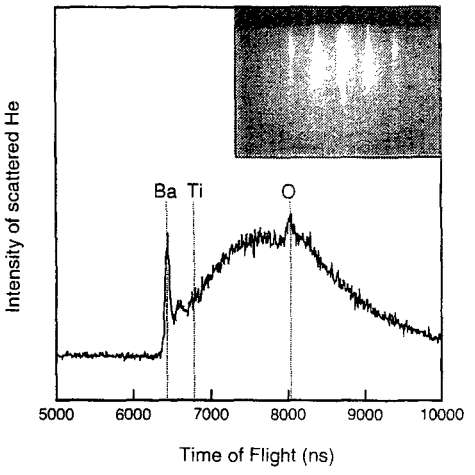

Fig. 6. The [111] direction CAICISS-TOF spectrum of the $BaTiO_3$(001) (32 nm thick) /Pt (27 nm thick) /$SrTiO_3$(100) substrate. Inset shows the RHEED pattern.

during film growth. The theoretical critical thickness for stress relaxation in the $BaTiO_3$ film on $SrTiO_3$(100) system is calculated by forces acting on the misfit dislocations. Using the Matthews' formula,[16] the critical thickness in the present system is estimated to be about 3 nm.[17] From Figs. 4 and 5, the remarkable decrease of Ti signal can be seen in the thickness range of 2 to 4 nm. Some growth imperfections such as dislocations or intergrowth might exist in the early growth stage of $BaTiO_3$(001) film resulting in the change of the terminating layer. Further investigations in order to clarify the detailed mechanism of the initial growth are in progress.

From the viewpoint of technological applications, it is of interest to examine the terminating layer of $BaTiO_3$(001) films grown on Pt which is often used as the electrode in ferroelectric devices. $BaTiO_3$(001) thin films grown on Pt(100) (27 nm thick)/$SrTiO_3$(100) substrate were subjected to CAICISS analysis. Figure 6 shows the [111] direction CAICISS-TOF spectrum for the surface of [$BaTiO_3$ (001) (32 nm thick)/ Pt (100) (27 nm thick)/$SrTiO_3$(100) substrate]. The inset in Fig. 6 is the RHEED pattern of this $BaTiO_3$ film. Only the Ba signal was observed. It indicates that the terminating layer of $BaTiO_3$(001) films epitaxially grown on Pt(100) is BaO plane as also observed for the films grown on $SrTiO_3$(100) substrate.

4. CONCLUSION

Atomic-scale analysis of the terminating layer of $BaTiO_3$(001) films grown on $SrTiO_3$(100) substrate and Pt(100) (27 nm thick)/$SrTiO_3$(100) substrate was performed by using the Laser MBE-CAICISS system. The topmost surface of $BaTiO_3$(001) films with thickness over 4 nm was found to be dominantly terminated with BaO plane. It is noticed that the $BaTiO_3$ (001) film (4 nm) on $SrTiO_3$ (100) prepared through solid phase epitaxy (by thermal annealing of an amorphous film) was also terminated with BaO atomic plane.

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