Effect of oxygen partial pressure on structure and dielectric property of BaTi$_2$O$_5$ films prepared by laser ablation

Wang Chuanbin, Tu Rong, Goto Takashi

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Effect of Oxygen Partial Pressure on Structure and Dielectric Property of BaTi$_2$O$_5$ Films Prepared by Laser Ablation

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BaTi$_2$O$_5$ ferroelectric films were prepared on MgO (100) substrates by laser ablation at various oxygen partial pressures ($P_{O_2}$). The effect of $P_{O_2}$ on the orientation, composition, surface morphology and dielectric property of the films was investigated. The molar ratio of Ti to Ba was independent of $P_{O_2}$, almost in agreement with the stoichiometric composition of BaTi$_2$O$_5$. The BaTi$_2$O$_5$ films showed the orientation of (710) and (020) depending on $P_{O_2}$. At $P_{O_2} = 12.5$ Pa, (020) oriented BaTi$_2$O$_5$ film with an elongated granular and perpendicularly crossing texture was epitaxially grown on MgO (100) substrates. The BaTi$_2$O$_5$ film prepared at $P_{O_2} = 12.5$ Pa exhibited a sharp permittivity maximum ($\varepsilon' \approx 2000$) at 750 K. [doi:10.2320/matertrans.48.625]

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Keywords: BaTi$_2$O$_5$ films, laser ablation, structure, permittivity

1. Introduction

Thin ferroelectric films with perovskite structure have attracted much attention due to the applications in high density dynamic random access memories (DRAM), volatile ferroelectric random access memories (FRAM) and optoelectronic devices.\(^{1,2}\) In particular, BaTiO$_3$ (BTO), PbTiO$_3$ (PTO) and PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) films have been extensively studied for their high dielectric constant and significant ferroelectricity.\(^{3-7}\) However, these materials have drawbacks of too low Curie temperature for BTO ($T_c \approx 410$ K) and environmentally unfriendly element (Pb) contained in PTO and PZT. Therefore, many researches have been conducted to develop a new lead-free material having a high $T_c$. Recently, a TiO$_2$-rich compound in the BaO-TiO$_2$ system, BaTi$_2$O$_5$, was found to be ferroelectric by our group\(^{8,9}\) and Akishige et al.\(^{10}\) Single crystalline BaTi$_2$O$_5$ prepared by floating zone and flux methods exhibited a significant permittivity peak at $T_c \approx 750$ K along the monoclinic b-direction. However, no research on BaTi$_2$O$_5$ films has been reported in spite of their potential applications as ferroelectric actuators and devices.

In order to obtain highly oriented ferroelectric BaTi$_2$O$_5$ films, the appropriate film deposition processing should be chosen to control the film structure and property. Many deposition techniques have been developed to obtain films, for example, sputtering,\(^{11}\) metal-organic chemical vapor deposition (MOCVD),\(^{12}\) sol-gel processing\(^{13,14}\) and laser ablation.\(^{15,16}\) The oxygen partial pressure can be a dominant deposition parameter, obviously affecting the oxygen deficiency, deposition rate and other characteristics of oxide films in those film processes. Since the laser ablation can be conducted in wide-ranged oxygen pressures, the preferred orientation of BaTi$_2$O$_5$ films may be controlled by adjusting oxygen partial pressure using laser ablation. It has been reported that the preferred orientation in the laser ablated BaTiO$_3$ films\(^{15}\) changed from (001) to (100) with increasing oxygen partial pressure. In the present study, BaTi$_2$O$_5$ films were prepared by laser ablation, and the effect of oxygen partial pressure on the preferred orientation as well as composition, surface morphology and dielectric property was investigated.

2. Experimental

BaTi$_2$O$_5$ films were deposited on MgO (100) single crystal plate ($10 \times 10 \times H$ 0.5 mm) by laser ablation (TSLM-1000). A Q-switch pulsed Nd : YAG laser with a wavelength of 355 nm was used. The laser beam was introduced into a deposition chamber at an angle of 45$^\circ$ and focused on a rotating target. A hot-pressed BaTi$_2$O$_5$ pellet with a relative density of 96% was used as a target. MgO (100) substrate was placed parallel to the target at a distance of 50 mm. The chamber was evacuated to a high vacuum ($1 \times 10^{-6}$ Pa) and then the deposition was carried out under different oxygen partial pressures ($P_{O_2}$) up to 20 Pa for 2 h. The substrate temperature ($T_{sub}$) was fixed at 973 K because BaTi$_2$O$_5$ phase was not obtained below 973 K. Table 1 summarizes the deposition parameters for preparing BaTi$_2$O$_5$ films.

The crystal structure was examined by X-ray diffraction ($\theta$/$\theta$ scan) and pole figure ($\phi$ scan) with Cu K$_\alpha$ radiation (Rigaku, RAD-2C). The surface morphology was observed by a field emission scanning electron microscope (JEOL, SM-71010). The three-dimensional tapping mode AFM image over a scanning area of $2 \times 2 \mu$m was taken by an atomic force microscope (TOYO, NANO SCOPE III) to measure the surface roughness. Electron probe X-ray micro-

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<th>Table 1</th>
<th>Deposition parameters for BaTi$_2$O$_5$ film prepared by laser ablation.</th>
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<td>Deposition conditions</td>
<td>Parameters</td>
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<tr>
<td>Laser</td>
<td>Wave length: 355 nm</td>
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<tr>
<td></td>
<td>Repetition rate: 10 Hz</td>
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<td></td>
<td>Pulse duration: 15 ns</td>
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<tr>
<td></td>
<td>Energy density: $2 \times 10^4$ J/m$^2$</td>
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<tr>
<td>Target</td>
<td>BaTi$_2$O$_5$ pellet ($\phi$ 20 mm × H 3 mm)</td>
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<tr>
<td>Substrate</td>
<td>MgO (100) wafer ($10 \times 10 \times H$ 0.5 mm)</td>
</tr>
<tr>
<td>Substrate temperature ($T_{sub}$)</td>
<td>973 K</td>
</tr>
<tr>
<td>Oxygen partial pressure ($P_{O_2}$)</td>
<td>$10^{-6}$–20 Pa</td>
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<tr>
<td>Distance between target and substrate</td>
<td>50 mm</td>
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analyzer (JEOL, JXA-8621MX) was used to determine the composition, where seven spots were measured for each sample. The permittivity was measured by using an AC impedance analyzer (HP 4194) at a frequency of 100 kHz and in flowing Ar from room temperature to 973 K. DC sputtered Pt thin film (400 nm) and painted silver paste were used as bottom and top electrodes, respectively.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of BaTi$_2$O$_5$ films deposited at $P_{O_2} = 10^{-6}$ to 20 Pa. Below $P_{O_2} = 20$ Pa, the peaks from BaTi$_2$O$_5$ were identified, showing a (710) or (020) orientation. The BaTi$_2$O$_5$ films prepared at $P_{O_2} = 10^{-6}$ to 7.5 Pa had a single peak indexed to (710). The full widths at half maximum (FWHM) of the (710) peak for $P_{O_2} = 10^{-6}$ and 7.5 Pa were 1.23$^0$ and 1.14$^0$, respectively. At $P_{O_2}$ = 10-15 Pa, the preferred orientation of BaTi$_2$O$_5$ was (710) and/or (020), depending on the $P_{O_2}$. No BaTi$_2$O$_5$ phase was identified at $P_{O_2} = 20$ Pa.

The preferred orientation of the BaTi$_2$O$_5$ films was evaluated by using an orientation factor $TC_{(020)}$ given by eq. (1).

$$TC_{(020)} = I_{(020)}/[I_{(020)} + I_{(710)}]$$

where, $I_{(020)}$ and $I_{(710)}$ are the intensities of (020) and (710) peaks of BaTi$_2$O$_5$, respectively.

Figure 2 depicts the relationship between $P_{O_2}$ and $TC_{(020)}$ of the BaTi$_2$O$_5$ films. $TC_{(020)}$ showed the highest value of 1.0 at $P_{O_2} = 12.5$ Pa, implying that the film was completely oriented to (020). For BaTi$_2$O$_5$ crystals, the (020) plane should be one of the most stable planes.$^{8,9}$ The (710) plane is slanted from the (020) plane and would have higher energy than the (020) plane. At a too low $P_{O_2}$ ($P_{O_2} < 10$ Pa), the ablated species would have excess kinetic energy on the substrate surface, forming a less stable plane, i.e., (710) plane. On the other hand, at a too high $P_{O_2}$, the ablated species would not have enough mobility to settle down at the stable plane$^{17,18}$ because they would lose the kinetic energy due to much collision in a gas phase. As a result, the films showed the (710) preferred orientation at $P_{O_2} = 15$ and 17.5 Pa; furthermore, no BaTi$_2$O$_5$ crystal phase can be obtained at $P_{O_2} = 20$ Pa. In the present study, the appropriate $P_{O_2}$ to form the stable (020) plane could be 10 to 12.5 Pa.

Figure 3 shows the effect of $P_{O_2}$ on molar ratio of Ti to Ba in BaTi$_2$O$_5$ films. The ratios were around 2.0 to 2.1, almost in agreement with the stoichiometric composition of BaTi$_2$O$_5$.

Figure 4 shows the effect of $P_{O_2}$ on the surface morphology of the BaTi$_2$O$_5$ films. At $P_{O_2} = 5$ Pa, small BaTi$_2$O$_5$ grains in a spherical shape were observed (Fig. 4(a)). The higher the $P_{O_2}$, the more numbers the grains. At higher $P_{O_2}$, the BaTi$_2$O$_5$ grains were elongated. At $P_{O_2} = 12.5$ Pa, (020) oriented BaTi$_2$O$_5$ films with dense and elongated texture were obtained (Fig. 4(c)). Each grain was about 100 nm in length and 50 nm in width, and crossed rectangularly.
At $P_{O_2} = 15$ Pa, the texture of the elongated grains was disordered, where the (710) peak became the main peak (Fig. 1(f)).

Figure 5 demonstrates the X-ray pole figure of the (020) oriented BaTi$_2$O$_5$ film prepared at $P_{O_2} = 12.5$ Pa, where the $\phi$ of BaTi$_2$O$_5$ (022) was scanned. Four diffraction spots were identified at $\alpha = 23^\circ$, which was in agreement with the angle between BaTi$_2$O$_5$ (020) and (022). Since BaTi$_2$O$_5$ (022) is a two-fold symmetry, the four poles could indicate the two sets of two poles from BaTi$_2$O$_5$ (022) and (022) rotating 90$^\circ$. The (020) oriented BaTi$_2$O$_5$ film had the rectangularly crossed texture (Fig. 4(c)), which could cause the four poles as schematically illustrated in Fig. 6. It is generally known that the lattice mismatch should be less than 1% for epitaxial growth. Since the a-axis length of BaTi$_2$O$_5$ is 0.39% greater than that of MgO, BaTi$_2$O$_5$ (020) can be epitaxially grown on MgO (100) substrate.

The effect of $P_{O_2}$ on the surface roughness (root mean square roughness, RMS) of BaTi$_2$O$_5$ films is illustrated in Fig. 7. The RMS increased from 3.2 to 6.7 nm with increasing $P_{O_2}$ from 5 to 15 Pa. At lower $P_{O_2}$, the ablated species can arrive at substrate with a high kinetic energy due to less collision with ambient species. This would lead to the high mobility of atoms and thus smooth surface at low $P_{O_2}$.

Figure 8 shows the effect of temperature on the permittivity of BaTi$_2$O$_5$ films prepared at $P_{O_2} = 5$ and 12.5 Pa having a weak (710) and a strong (020) orientation, respectively. The (710) oriented BaTi$_2$O$_5$ film prepared at $P_{O_2} = 5$ Pa exhibited small permittivity from room temperature to 973 K, because the ferroelectricity of BaTi$_2$O$_5$ can be only observed in the b-direction. On the contrary, the (020) oriented BaTi$_2$O$_5$ film obtained at $P_{O_2} = 12.5$ Pa had a significant peak of permittivity ($\varepsilon' \approx 2000$) at the Curie temperature ($T_c$) of BaTi$_2$O$_5$ ($\approx 750$ K).
4. Summary

BaTi$_2$O$_5$ films were prepared on MgO (100) substrates by laser ablation at various oxygen partial pressures ($P_{O_2}$). The orientation of BaTi$_2$O$_5$ films changed from (710) to (020) depending on $P_{O_2}$. The surface roughness increased with increasing $P_{O_2}$. The molar ratio of Ti to Ba was almost 2.0 independent of $P_{O_2}$. The optimum $P_{O_2}$ to obtain ferroelectric BaTi$_2$O$_5$ film was 12.5 Pa at $T_{\text{sub}} = 973$ K. The (020) oriented BaTi$_2$O$_5$ film with a dense and elongated texture was epitaxially grown on MgO (100) substrates. The BaTi$_2$O$_5$ film prepared at $P_{O_2} = 12.5$ Pa exhibited a sharp permittivity maximum ($\varepsilon' \approx 2000$) at 750 K.

Acknowledgements

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