Microstructure and Dielectric Properties of Barium Titanate Film Prepared by MOCVD

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Barium titanate (BaTiO3) films have attracted much attention for the application of dynamic random access memories and electro-optic devices due to excellent dielectric and optical properties. Several methods such as rf-magnetron sputtering, reactive evaporation, laser deposition, chemical solution deposition, sol-gel, and metal-organic chemical vapor deposition (MOCVD) have been applied to prepare BaTiO3 films. BaTiO3 films generally consisted of fine grains ranging from several tens to hundreds of nanometers in size, whose dielectric constant might change from several tens to thousands decreasing with decreasing the grain size. However, the relationship between dielectric properties and microstructure of BaTiO3 films has not been well understood.

MOCVD is advantageous to control the microstructure of films by changing deposition conditions. Many papers have been published on the preparation of BaTiO3 films by MOCVD, and reported that the dielectric properties were significantly affected by deposition conditions and microstructure.

In the MOCVD process, many deposition conditions such as partial pressure of source gases, deposition temperature and total pressure should be controlled to obtain high-quality BaTiO3 films. In published papers, however, the effect of oxygen partial pressure on the dielectric properties has not been reported. We have prepared BaTiO3 films by MOCVD. This paper reports the effect of oxygen partial pressure (P O2 ) on the microstructure and dielectric properties of the BaTiO3 films.

1. Introduction

Barium titanate (BaTiO3) films were prepared on (100)Pt/(100)MgO substrates by metal-organic chemical vapor deposition (MOCVD). The effects of deposition temperature (T dep ) and O2 partial pressure (P O2 ) on the microstructure and dielectric properties of the films were investigated. The BaTiO3 films prepared at T dep = 873 K showed a randomly orientated granular structure, while those prepared at T dep = 973 K showed a significant (001) orientation with a columnar structure. The grain size was strongly affected by P O2 and showed the maximum at P O2 = 66 to 93 Pa. The dielectric constant increased from 93 to 640 with increasing grain size from 20 to 130 nm, showing a broad peak at 350 to 380 K.

2. Experimental Procedure

A horizontal hot-wall type CVD furnace was used to prepare films. The detailed experimental setup was reported elsewhere. Bis-dipivaloylmethanato-barium (Ba(DPM)2) and bis-isoproxy-bis-dipivaloylmethanato-titanium (Ti(O-i-C3H7)2(DPM)2) as Ba and Ti sources were vaporized at 503 to 523 K and 333 to 373 K, respectively. The source vapors were separately transported to the reaction chamber with Ar gas whose flow rate was 0.75 \( \times \) 10^{-6} m^3.s^{-1}. O2 gas was introduced as an oxidant and mixed with source vapors near the substrate. The O2 gas flow rate (FR O2 ) was changed from 0 to 1.0 \( \times \) 10^{-6} m^3.s^{-1} to control P O2 from 0 to 160 Pa. The total gas flow rate was kept at 2.5 \( \times \) 10^{-6} m^3.s^{-1}, and the total pressure in the reaction chamber was fixed at 400 Pa. The deposition temperatures (T dep ) were 873 and 973 K. The deposition time was 3.6 ks at most. In order to measure the dielectric properties, Pt films were prepared on the (100)MgO substrates as a bottom electrode by dc sputtering, where the (100)Pt || (100)MgO relation was observed. Pt films were prepared again on the BaTiO3 films as a top electrode (0.5 mm in diameter).

The phase and preferred orientation were examined by X-ray diffraction (XRD: Rigaku RAD-C). The thickness was measured by a thickness tester (Taylor Hobson, Talystep). The surface and cross-sectional morphologies were observed by scanning electron microscopy (SEM: JOEL JSM-5400F). Dielectric properties were measured by impedance spectroscopy (Solartron 1260 and 1294) in the frequency (f) range from 10^{-1} to 10^6 Hz.

3. Results and Discussion

Figure 1 shows the effect of P O2 on the XRD patterns of BaTiO3 films prepared at T dep = 873 and 973 K. When O2 gas was not introduced into the chamber, the films were amorphous and black-colored due to a carbon residue. The films prepared at P O2 \( \geq \) 13 Pa were transparent and all XRD peaks were identified to BaTiO3. To understand the effect of P O2 on the carbon residue in the deposits, the equilibrium compositions of solid phases in the Ba–Ti–C–H–O–Ar system were calculated as shown in Fig. 2. Detailed procedure of the calculation was reported elsewhere. 17 solid species (BaTiO3, Ba2TiO4, BaCO3, etc.) and 20 gas species (O2, CO2, H2O, etc.) were considered in the calculation. The equilibrium state is calculated from minimizing the total Gibbs free energy un-
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Fig. 1 XRD patterns of BaTiO$_3$ films prepared at (a) $T_{\text{dep}} = 873$ K and (b) $T_{\text{dep}} = 973$ K.

Fig. 2 Calculated solid phases as functions of $T_{\text{dep}}$ and $P_{\text{O}_2}$. ($P_{\text{tot}} = 400$ Pa, $(\text{Ba(DPM)}_2 + \text{Ti(O-i-C}_3\text{H}_7)_2(\text{DPM})_2)/(\text{Ar + O}_2) = 1/2.5 \times 10^4$).

Fig. 3 Surface morphology of BaTiO$_3$ films prepared at $T_{\text{dep}} = 973$ K and (a) $P_{\text{O}_2} = 13$ Pa, (b) $P_{\text{O}_2} = 93$ Pa and (c) $P_{\text{O}_2} = 160$ Pa.

under the mass conservation conditions. Ba and Ti source contents were assumed as the same as the experimental condition (i.e., $(\text{Ba(DPM)}_2 + \text{Ti(O-i-C}_3\text{H}_7)_2(\text{DPM})_2)/(\text{Ar + O}_2) = 1/2.5 \times 10^4$). The carbon phase might be calculated to remain in the BaTiO$_3$ phase at $P_{\text{O}_2} = 0.17$–0.2 Pa. Since $P_{\text{O}_2}$ in the experiments was more than 13 Pa, the O$_2$ content could be enough to oxidize the carbonates in metal-organic sources, and no residue carbon might be deposited.

The BaTiO$_3$ films prepared at $T_{\text{dep}} = 873$ K showed no preferred orientation, or XRD peaks were too small to be identified. The lattice parameter of films prepared at $T_{\text{dep}} = 873$ K and $P_{\text{O}_2} = 13$ to 120 Pa was 0.401 nm in a cubic expression. The BaTiO$_3$ films prepared at $T_{\text{dep}} = 973$ K showed a significant (001) orientation. The lattice parameter calculated from the (001) diffractions was 0.402 nm which was close to that of BaTiO$_3$ sintered body ($c = 0.404$ nm).

Several paper reported that (001) oriented films were prepared on (100)Pt/(100)MgO substrates by sputtering, reactive evaporation and laser deposition. They explained that the (001) orientation might be caused of the close lattice parameters between BaTiO$_3$ ($a = 0.399$ nm, $c = 0.404$ nm) and Pt ($0.392$ nm) and MgO ($0.421$ nm). This might be cause the (001) orientation at $T_{\text{dep}} = 973$ K in this study.

Figure 3 shows the effect of $P_{\text{O}_2}$ on the surface morphology of the films prepared at $T_{\text{dep}} = 973$ K. The grain size of the films prepared at $T_{\text{dep}} = 973$ K and $P_{\text{O}_2} = 13$ Pa was about 40 nm, and increased with increasing $P_{\text{O}_2}$. Figure 4 shows the relationship between $P_{\text{O}_2}$ and the grain size of the films. The grain size of the films prepared at $T_{\text{dep}} = 973$ K showed the maximum of 130 nm at $P_{\text{O}_2} = 66$ Pa, and was almost constant about 100 nm at $P_{\text{O}_2} > 90$ Pa. At $T_{\text{dep}} = 873$ K, the grain size showed the maximum of 70 nm at $P_{\text{O}_2} = 93$ Pa, and it decreased with increasing $P_{\text{O}_2}$. Figure 5 shows the cross-sections of the films prepared at $P_{\text{O}_2} = 93$ Pa. The BaTiO$_3$ film prepared at $T_{\text{dep}} = 873$ K (Fig. 5(a)) had a granular structure, and that prepared at $T_{\text{dep}} = 973$ K a columnar struc-
tecture. In the CVD process, the morphology of deposits often changes from a granular to a columnar microstructure with increasing $T_{\text{dep}}$ due to significant grain growth at high temperatures.\(^{17}\) The morphology shown in Fig. 5 was in agreement with the general trend of CVD process.

Figure 6 shows the effect of $P_{\text{O}_2}$ on the deposition rates of BaTiO$_3$ films. The deposition rates at $T_{\text{dep}} = 873$ K were 0.16 to 0.21 nm·s$^{-1}$ almost independent of $P_{\text{O}_2}$, while those at $T_{\text{dep}} = 973$ K showed the maximum of 0.22 nm·s$^{-1}$ at $P_{\text{O}_2} = 70$ Pa. The deposition rates of BaTiO$_3$ films by MOCVD on literatures\(^{11–15}\) have ranged from 0.02 to 0.4 nm which were close to those of this study.

Figure 7 shows the frequency dependence of relative dielectric constant ($\varepsilon'$) and loss tangent (tan $\delta$) of the BaTiO$_3$ film prepared at $T_{\text{dep}} = 873$ K and $P_{\text{O}_2} = 13$ Pa. The $\varepsilon'$ and tan $\delta$ at 298 K were almost constant in the frequency range from $10^{-1}$ to $10^6$ Hz, but those at 523 K increased significantly with decreasing frequency below $10^4$ Hz. This apparent increase of $\varepsilon'$ at the low frequency region might be caused of the effect of d.c. conduction. The $\varepsilon'$ and tan $\delta$ slightly increased at more than $10^4$ Hz. This may be caused of the effect of inductance component of the measurement cell which becomes significant at high frequencies.\(^{18,19}\) The $\varepsilon'$ and tan $\delta$ at $10^4$ to $10^5$ Hz should be the intrinsic value of BaTiO$_3$ films. Figure 8 shows the temperature dependence of $\varepsilon'$ of BaTiO$_3$ films at $10^5$ Hz. The $\varepsilon'$ showed broad peaks at 350 to 380 K close to the Curie temperature of BaTiO$_3$ ($T_C = 393$ K). The $\varepsilon'$ values were smaller than those of bulk sintered bodies,\(^{20}\) and the temperature dependence of $\varepsilon'$ became less significant with decreasing $\varepsilon'$. The $\varepsilon'$ values of the films prepared at $P_{\text{O}_2} = 40$ Pa were greater than those prepared at $P_{\text{O}_2} = 13$ and 160 Pa.

It is known that the tetragonal ferroelectric phase of BaTiO$_3$ would change to a cubic paraelectric phase with decreasing grain size.\(^{20–23}\) The critical grain size disappearing the ferroelectricity of BaTiO$_3$ was reported to be 25 to 120 nm.\(^{20–23}\) The small $\varepsilon'$ values and the weak temperature dependence of $\varepsilon'$ shown in Fig. 8 might be caused of the small grain size of BaTiO$_3$ films.

Figure 9 shows the effect of $P_{\text{O}_2}$ on $\varepsilon'$ and tan $\delta$ of BaTiO$_3$ films at $10^5$ Hz and 298 K. The $\varepsilon'$ of films prepared at $T_{\text{dep}} = 873$ and 973 K showed the maximum of 535 and 640
at $P_{O_2}$ = 93 and 66 Pa, respectively. The $\tan \delta$ of BaTiO$_3$ films were 0.01 to 0.02 close to those of BaTiO$_3$ films prepared by a sol-gel method.\textsuperscript{9) Figure 10 shows the relationship between grain size and $\varepsilon'$ at 298 K. The $\varepsilon'$ clearly increased with increasing grain size. The trend at $T_{dep}$ = 973 K was slightly different from that at $T_{dep}$ = 873 K. It is reported that the $\varepsilon'$ to the (001) direction of BaTiO$_3$ is smaller than those to other direction.\textsuperscript{24) Since the films prepared at $T_{dep}$ = 973 K had the significant (001) orientation, the different trend between $T_{dep}$ = 873 K and 973 K could be caused of the effect of preferred orientation.

Table 1 summarized the reported deposition conditions and properties of BaTiO$_3$ films. The dielectric properties, particularly $\varepsilon'$, of BaTiO$_3$ films were strongly affected by preparation methods and deposition conditions. Figure 11 shows the relationship between grain size and $\varepsilon'$ of BaTiO$_3$ prepared by several methods. The $\varepsilon'$ of BaTiO$_3$ bulk sintered bodies showed the maximum at the grain size of 800 to 1000 nm.\textsuperscript{20) There is the general trend that the $\varepsilon'$ decreases with decreasing grain size in the region less than 700 nm. The relationship between $\varepsilon'$ and grain size in this study was in agreement with the general trend.

Figure 12 shows the relationship between leakage current density ($J$) and electric field ($E$) at 298 K. The BaTiO$_3$ films showed significant low leakage current density below 1 MV/m$^{-1}$. Above the critical electric field ($E_{crit}$), $J$ increased exponentially with increasing $E$ indicating non-ohmic conduction. The $E_{crit}$ of films prepared at $T_{dep}$ = 873 K showed greater $E_{crit}$ than those prepared at $T_{dep}$ = 973 K. Tsai et al. reported that the $E_{crit}$ of (Ba, Sr)TiO$_3$ films increased with decreasing grain size.\textsuperscript{25) The smaller grain size means more numbers of grain boundary in the films. They assumed that the grain boundary could be more insulative.

<table>
<thead>
<tr>
<th>Method</th>
<th>Substrate</th>
<th>$T_{dep}$/K</th>
<th>Orientation</th>
<th>Thickness /nm</th>
<th>Grain size /nm</th>
<th>$\varepsilon'$</th>
<th>Ref.</th>
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<td>210–2000</td>
<td>50–180</td>
<td>750–2500</td>
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<td>(001)</td>
<td>20–800</td>
<td>100–700</td>
<td>350</td>
<td>5)</td>
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<td>1073</td>
<td>(001)</td>
<td>950</td>
<td>100</td>
<td>350</td>
<td>6)</td>
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<td>random</td>
<td>200</td>
<td>30–170</td>
<td>250–850</td>
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<td>973–1123</td>
<td>random</td>
<td>1600</td>
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<td>random</td>
<td>600</td>
<td>200</td>
<td>300</td>
<td>15)</td>
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</table>

MOCVD: (100)Pt/(100)MgO | 873 | random | 520–750 | 20–66 | 96–555 | This study |

CSD: chemical solution deposition, PE-MOCVD: plasma enhanced MOCVD
BaTiO₃ films were prepared on (100)Pt/(100)MgO substrates by MOCVD. The BaTiO₃ films prepared at $T_{\text{dep}} = 873$ K showed a randomly oriented granular structure. The grain size of films prepared at $T_{\text{dep}} = 873$ K increased with increasing $P_{O_2}$ and showed the maximum of 65 nm at $P_{O_2} = 93$ Pa. The BaTiO₃ films prepared at $T_{\text{dep}} = 973$ K showed a significant (001) orientation with a columnar structure. The grain size of films prepared at $T_{\text{dep}} = 973$ K showed the maximum of 130 nm at $P_{O_2} = 66$ Pa. The $\varepsilon'$ increased from 93 to 640 with increasing grain size from 20 to 130 nm. The films prepared at $T_{\text{dep}} = 973$ K had larger grain sizes and slightly smaller $\varepsilon'$ than those prepared at $T_{\text{dep}} = 873$ K. The smaller $\varepsilon'$ might be associated with the significant (001) orientation of the films prepared at $T_{\text{dep}} = 973$ K. The $\varepsilon'$ of films showed broad peaks at 350 to 380 K. The films prepared at $T_{\text{dep}} = 873$ K had smaller leakage current density than those prepared at $T_{\text{dep}} = 973$ K.

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