Microstructure and Dielectric Properties of BaO-Bi$_2$O$_3$-TiO$_2$ System Films Prepared by MOCVD

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(1 − y)BaTiO$_3$ (BT) − yBi$_2$O$_3$Ti$_2$O$_7$ (BIT) films in the composition range up to y = 0.05 were prepared on (100) MgO substrates by metalorganic chemical vapor deposition (MOCVD). The effect of composition on the microstructure, morphology and dielectric properties of the films was investigated. At y < 0.03, the BIT-doped BT films were obtained, and the grain size of films increased with increasing y. BaBi$_2$Ti$_2$O$_7$ phase was identified at y = 0.03. The BIT-doped BT film of y = 0.01 exhibited the maximum dielectric constant of 1010 that was twice as great as that of BT film. The high dielectric constant might be resulted from the increase in grain size. The remanent polarization (2P$_r$) and the coercive field (2E$_c$) of the BIT-doped BT film of y = 0.01 were 0.7 × 10$^{-2}$ C$ \cdot$ m$^{-2}$ and 6.0 × 10$^5$ V$ \cdot$ m$^{-1}$, respectively. [Received August 12, 2003; Accepted December 24, 2003]

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1. Introduction

Since barium titanate (BaTiO$_3$, BT) is a Pb-free ferroelectric perovskite compound having a high dielectric constant and excellent piezoelectric properties, BT films are expected for many applications, such as nonvolatile ferroelectric random access memories (FeRAMs). However, the performance of BT films may be insufficient particularly due to so-called size effect (i.e., degradation of ferroelectric property with decreasing thickness or crystal size) and a sharp temperature dependence of dielectric constant around the Curie temperature.$^{1,2}$ Therefore, the electric properties of BT have been modified by doping foreign elements or fabricating solid solution with other perovskite compounds, such as SrTiO$_3$,$^{3,4}$ and BaZrO$_3$.$^5$

Bismuth titanate (Bi$_2$Ti$_3$O$_{12}$, BIT) is also a Pb-free ferroelectric perovskite-related compound that possesses a high Curie-temperature ($T_c = 948$ K) and high spontaneous polarization.$^4$ It was reported that the solid solution range between BIT and BT could be y=0.04 at most in the (1−y)BT−yBIT bulk materials,$^5$ and the solid solution increased the density of sintered bodies.$^6$ The $T_c$ of BT−BIT solid solutions decreased with increasing y, and exhibited relaxor-type behavior at y=0.04.$^5$

So far, no paper has been reported on the BT−BIT system films. In the present study, (1 − y)BT−yBIT system films were prepared by MOCVD, and the effects of BIT doping on the microstructure and dielectric properties of the films were investigated.

2. Experimental procedure

A horizontal hot-wall type CVD chamber was employed to prepare the films. Bis-dipivaloylmethanato-barium (Ba (dpm)$_2$) and tri-phenyl-bismuth (Bi(Ph)$_3$) precursors were used as source materials. The precursor vapors were transported to the reaction chamber with Ar gas, and mixed with O$_2$ gas around the substrate. The deposition temperature ($T_{dep}$) and the total pressure were fixed at 973 K and 400 Pa, respectively. MgO(100) single crystals were used as substrates. Pt films 100 nm in thickness were deposited by dc sputtering on (100) MgO substrates, and a (100)/Pt/(100) MgO relation was confirmed. The films were deposited on the Pt-coated MgO substrate.

The phase and preferred orientation were examined by X-ray diffraction (XRD: Rigaku RAD-C) and a pole-figure method. The tetragonality of the films was studied by Raman spectroscopy (Tokyo instruments Nanofinder). The composition was investigated by electron probe X-ray microanalysis (EPMA: JXA-8621) and X-ray fluorescence spectroscopy (XRF: Kevek model 920). The surface and cross-sectional microstructures were observed by scanning electron microscopy (SEM: JOEL JSM-5400F). The thickness was measured by a thickness tester (Rank-Taylor Hobson Talystep). For the measurement of electrical properties, Pt top electrodes 100 nm in thickness were deposited at room temperature by dc sputtering. Dielectric constant ($\varepsilon'$) and loss tangent ($\tan \delta$) were measured by impedance spectroscopy (Solartron 1260, Solartron 1294) in the frequency range of 0.1 to 10$^6$ Hz and ac electric field ($E_{ac}$) range of 0.15 × 10$^5$ to 15 × 10$^5$ V$ \cdot$ m$^{-1}$. The polarization ($P$)−electric field ($E$) relationship was studied by a ferroelectric testing system (Toyo Technica FCE-1).

3. Results and discussion

Figure 1 shows the XRD pattern of (1−y)BT−yBIT films prepared at $T_{dep}$=973 K on Pt-coated MgO substrates. The film of y=0.00 was highly crystallized showing a significant (001) orientation, and the lattice parameter of the film calculated from (001) planes was 0.402 nm. The BIT-doped BT films were obtained in the range of 0 < y ≤ 0.03. BaBi$_2$Ti$_2$O$_7$ was identified at y=0.03. It was reported that the solid solution between BT and BIT for sintered bulk bodies was ranged from

![Fig. 1. XRD patterns of (1−y)BaTiO$_3$−yBi$_2$O$_3$Ti$_2$O$_7$ films prepared at $T_{dep}$=973 K on Pt-coated (100)MgO substrates. (a) y=0, (b) y=0.01 and (c) y=0.03]
0 to 0.04.\(^5\) The solid solution range of the present study was close to that of sintered bodies.

Figure 2 illustrates the X-ray pole figure of (101) plane for the BT (\(y=0\)) film. The BT film had a following epitaxial relationship, i.e., \(\langle 001\rangle BT/\langle 100\rangle Pt/\langle 100\rangle MgO, \langle 100\rangle BT/\langle 100\rangle Pt/\langle 100\rangle MgO, \langle 001\rangle BT/\langle 100\rangle Pt/\langle 100\rangle MgO, \langle 100\rangle BT/\langle 100\rangle Pt/\langle 100\rangle MgO\). The epitaxial growth could be related to close lattice parameters between BT (0.3994 nm), Pt (0.3923 nm) and MgO (0.4213 nm).

Figure 3 shows Raman spectra of \((1-y)\)BT-yBIT films. Three broad peaks at 270, 520 and 720 cm\(^{-1}\) and a sharp peak at 305 cm\(^{-1}\) were observed in the BT film (Fig. 3(a)). These Raman spectra were in agreement with those of sintered bulk BT.\(^8\)\(^-\)\(^9\) The intensity of each peak decreased with increasing \(y\). The Raman peak of BT at 305 cm\(^{-1}\) is generally employed to identify tetragonal BT phase.\(^8\)\(^-\)\(^9\) In the present study, the peak of 305 cm\(^{-1}\) was observed in the \(y\) range from 0 to 0.03, indicating the formation of tetragonal structure.

The surface microstructure of \((1-y)\)BT-yBIT films are depicted in Fig. 4. The BT film (\(y=0\)) consisted of fine grains about 100 nm in diameter. The grain size of films increased with increasing \(y\) from 0 to 0.03. This suggests that the solid solution of BT in BT accelerated the grain growth.

Figure 5 shows the effect of \(y\) on \(\varepsilon'\) and \(\tan \delta\) of \((1-y)\)BT-yBIT films at 100 kHz and 298 K. The \(\varepsilon'\) significantly changed from 494 to 1010 with increasing \(y\) from 0 to 0.01, and showed the maximum at \(y=0.01\). The \(\tan \delta\) was almost independent of \(y\).

Figure 6 shows the temperature dependence of \(\varepsilon'\) and \(\tan \delta\) for \((1-y)\)BT-yBIT films at 100 kHz. The \(\varepsilon'\) exhibited a broad peak, and the temperature of the maximum \(\varepsilon'\) (\(T_{\text{max}}\)) decreased from 380 to 340 with increasing \(y\) from 0 to 0.05. The \(\tan \delta\) decreased with increasing temperature at temperatures below 450 K. The \(\varepsilon'\) values for the films of \(y=0.01\) and 0.02 were greater than those of \(y=0\) at temperatures from 298 to 523 K. It is well-known that the \(\varepsilon'\) of BT would increase with increasing grain size.\(^1\)\(^-\)\(^4\)\(^-\)\(^12\) As shown in Fig. 4, the significant grain growth was observed for the films of \(y=0.01\) to 0.03. This could cause the increase in \(\varepsilon'\) values.
Fig. 5. Effect of $y$ on $\varepsilon'$ and $\tan \delta$ for $(1-y)\text{BaTiO}_3-y\text{Bi}_2\text{Ti}_3\text{O}_{12}$ films at 298 K and 100 kHz.

Fig. 6. Temperature dependence of $\varepsilon'$ (a) and $\tan \delta$ (b) for $(1-y)\text{BaTiO}_3-y\text{Bi}_2\text{Ti}_3\text{O}_{12}$ films at 100 kHz.

4. Summary

$(1-y)\text{BT}-y\text{BIT}$ $(y=0$ to 0.05) films were prepared on Pt-coated MgO substrates by MOCVD. The effects of solid solution between BT and BIT on the microstructure and dielectric properties of films were investigated. The BIT-doped BT films were obtained in the range up to $y=0.03$. The grain size of the films increased with increasing $y$ from 0 to 0.03. The dielectric constant showed the maximum value of 1010 at $y=0.01$. This value was twice as great as that of BT film. The increase in dielectric constants might be resulted from the increase in grain size of the films. The $2P_c$ and $2E_c$ for the BIT-doped BT film of $y=0.01$ were $7 \times 10^{-2}$ C·m$^{-2}$ and $6.0 \times 10^5$ V·m$^{-1}$, respectively.

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References