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Crystallization and Dielectric Properties of $Ba(Zr,Ti)O_3$ Thin Films by MOD

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Thin films of $Ba(Zr,Ti)O_3$ were prepared by the metal organic decomposition (MOD) technique in order to produce a high dielectric material. A $Ba(Zr_{0.12}Ti_{0.88})O_3$ film prepared at 650℃ was polycrystalline and the grain size was smaller than $BaTiO_3$ thin films. The $Ba(Zr_{0.12}Ti_{0.88})O_3$ thin films with a thickness of approximately 120 nm exhibited a dielectric constant of 380 and loss tangent of 2.6% at the room temperature. Film leakage currents of 1.0×10^{-5} A/cm^2 were obtained at 400 kV/cm.

1. Introduction

Thin films of perovskite materials such as $BaTiO_3$, $SrTiO_3$, $(Ba,Sr)TiO_3$ and $Pb(Zr,Ti)O_3$ have been investigated as a high dielectric constant capacitor for dynamic random access memory (DRAM) or nonvolatile memory. Ceramic barium zirconium titanate $[Ba(Zr_x,Ti_{1-x})O_3]$ is a perovskite-type ferroelectric and has very high dielectric constant (10000-35000) at the curie point [1]. But there are few reports about $Ba(Zr_xTi_{1-x})O_3$ thin films. In this study, $Ba(Zr_{0.12}Ti_{0.88})O_3$ thin film were prepared by metal organic decomposition on $Pt/SiO_2/Si$ substrates and to compare with BZT films, we also prepared $BaTiO_3$ thin films by same procedure. For evaluation, we investigated the crystal structure and microstructure of the films, and measured dielectric properties.

2. Experimental Procedure

Fig.1 shows the preparation process of the $BaTiO_3$ and $Ba(Zr_{0.12},Ti_{0.88})O_3$ thin films by MOD method.

The coating solution was prepared by mixing the

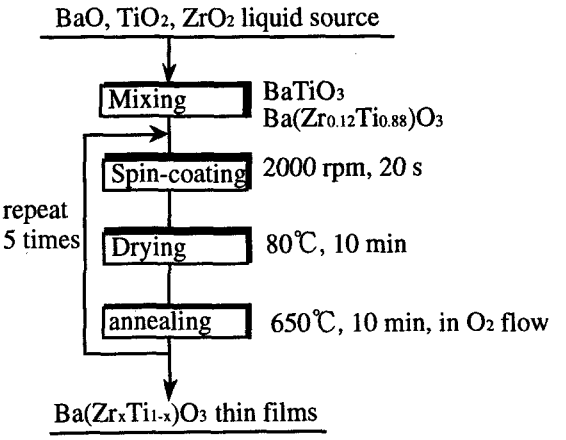

Fig.1 Flow diagram for preparation of thin film by MOD.

BaO, TiO_2 and ZrO_2 containing liquid solutions to be the compositions of $BaTiO_3$ and $Ba(Zr_{0.12},Ti_{0.88})O_3$, respectively . The solutions was spin coated at 2000 rpm for 20 s on $Pt/SiO_2/Si$ substrates. The coated films were dried at 80℃ for 10 min and annealed at 650℃ for 10 min in flowing O_2 gas. This process was repeated in order to get suitable thickness of the films.

The crystalline phase of the thin films were identified by X-ray diffraction. Films thickness, grain size and surface morphology were observed by a field-emission scanning eletron microscope (FE-SEM). Pt electrodes of 1.0 mm diameter were sputter-deposited through a mask onto the surface of the films to measure the electrical properties of the films.

The capacitance and the dielectric loss were measured at a frequency of 1kHz with a HP4194A impeadance/gain-phase analyzer, and current-voltage (I-V) characteristics were measured by a HP4140B pA meter / DC voltage source. The dielectric constant was calculated from the capacitance.

3. Result and Discussion

Fig. 2 shows XRD patterns of the $BaTiO_3$ and $Ba(Zr_{0.12}Ti_{0.88})O_3$ thin films. The XRD pattern indicates that single phase perovskite structure are obtained and each film has no preferred orientation. Fig.3 shows XRD patterns at 2θ angles from 42-48° of each film. The position of the peak at 45.34° of $BaTiO_3$ film is very close to the(200) peak at 45.4°

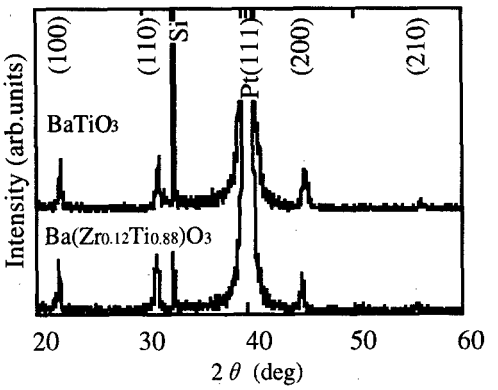

Fig.2 XRD patterns of $BaTiO_3$ and $Ba(Zr_{0.12}Ti_{0.88})O_3$ thin films.

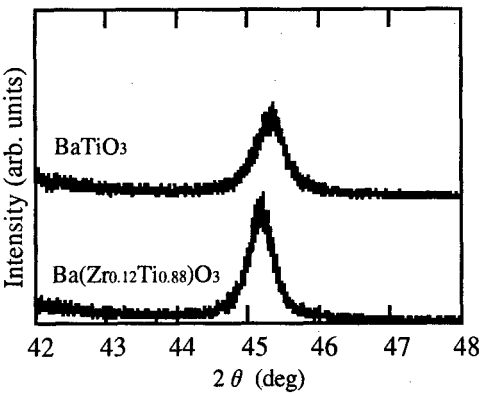

Fig.3 XRD patterns of $BaTiO_3$ and $Ba(Zr_{0.12}Ti_{0.88})O_3$ thin films measured at 2θ angle from 42 to 48° .

of tetragonal $BaTiO_3$ reffered by Hayashi et al.[2]. The peak shifts to lower angle by substituting $BaZrO_3$ which means that the lattice constant become larger. The obvious (002) peak of the tetragonal phase was not observed in each film.

In Fig. 4, FE-SEM micrographs of the thin films at (a)$BaTiO_3$, (b)$Ba(Zr_{0.12}Ti_{0.88})O_3$ are shown. Thickness of the each films are about 120 nm. The grain size of the films decrease with increasing the

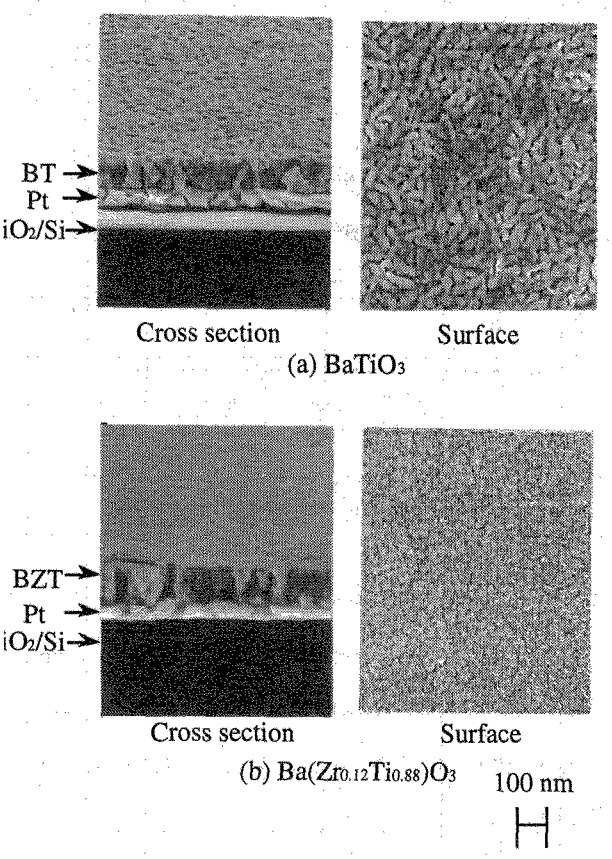

Fig.4 FE-SEM micrographs of the thin films prepared at 650℃ of (a) $BaTiO_3$, (b) $Ba(Zr_{0.12}Ti_{0.88})O_3$.

substitution of $BaZrO_3$. Well-defined grain boundaries are observed and the average grain size is 50 nm with subgrain of about 10-20 nm on $BaTiO_3$ thin film. On the other hand, very fine grain and very smooth surface are obtained on $Ba(Zr_{0.12}Ti_{0.88})O_3$ thin film. This result indicates that substituting $BaZrO_3$ inhibits grain growth and promotes densification.

Table 1 shows dielectric constant and tan δ of the $BaTiO_3$ and $Ba(Zr_{0.12}Ti_{0.88})O_3$ thin films. The dielectric constants are similar but the dielectric loss decreased slightly by substituting $BaZrO_3$. The dielectric constant and tan δ of the the $BaTiO_3$ and $Ba(Zr_{0.12}Ti_{0.88})O_3$ thin films as a function temperature are shown in Fig. 5. The dielec constant and tan δ are relatively constant until 6 at which point a maximum value are observed. maximum point of the $BaTiO_3$ and $Ba(Zr_{0.12}Ti_{0.8}$ is 74℃ and 70℃ respctively. The dielectric cos and tan δ then decrease with increasing temperat It seems that the ferroelectric to paraelectric pl transition of these films occures at 63℃. Hayash al. found that $BaTiO_3$ thin films prepared by sol process has a tetragonal symmetry at rc

Table 1 Dielectric constant and tan δ of the $BaTiO_3$ and $Ba(Zr_{0.12}Ti_{0.88})O_3$ thin films at room temperature.

composition	dielectric constant	tan δ (%)
$BaTiO_3$	370	3.4
$Ba(Zr_{0.12}Ti_{0.88})O_3$	380	2.6

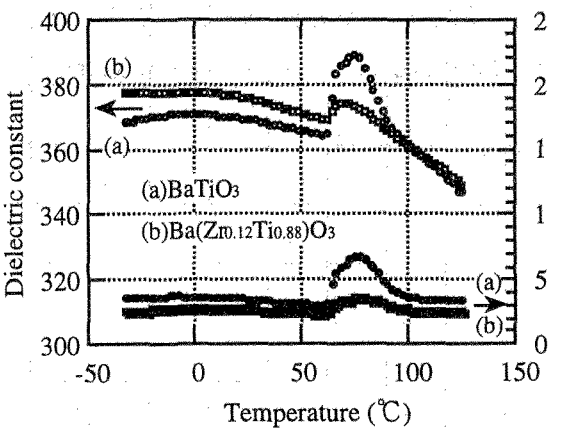

Fig. 5 Temperature dependence of dielectric constant and tan δ at (a)$BaTiO_3$, (b)$Ba(Zr_{0.12}Ti_{0.88})O_3$.

temperature, and the film is very similar to that at 100℃ of the bulk sample by the Raman spctroscopy [2]. This indicates that the transition temperature of the film is lower than that of a bulk of $BaTiO_3$ which shows the currie point at 120℃ . Futhermore, the transition temperature are not greatly effected by the substitution of $BaZrO_3$ to the $BaTiO_3$ film. It seems that the films are affected more by the substrate than by the composition.

The current-voltage(I-V) characteristics of the $BaTiO_3$ and $Ba(Zr_{0.12}Ti_{0.88})O_3$ thin films are shown in Fig.6. Substitution of the 12 mol % of the $BaZrO_3$ decreased the leakage current from 1.2×10^{-4}A/cm^2 to 1.0×10^{-5} A/cm^2 at 400 kV/cm. It seems that this is due to differeces in grain size and surface morphology of the films.

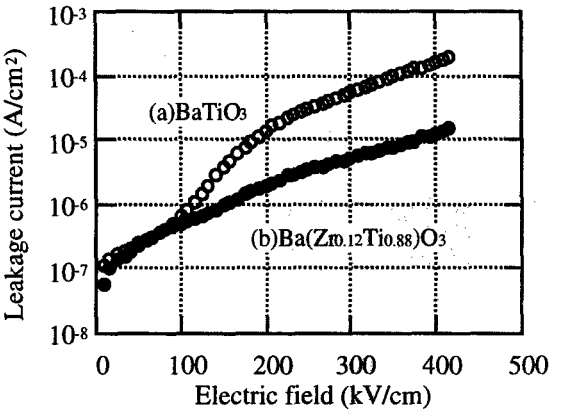

Fig.6 The current-voltage (I-V) characteristics of thin films of (a)$BaTiO_3$, (b)$Ba(Zr_{0.12}Ti_{0.88})O_3$

4.Conclusion

Thin films of $Ba(Zr_{0.12}Ti_{0.88})O_3$ were prepared by the MOD technique and compared with $BaTiO_3$ films. The BZT thin film prepared at 650℃ are polycrystalline, and the grain size is smaller than $BaTiO_3$ film. A dielecteic constant of 380 and loss tangent of 2.6 % were obtained at the room temperature. A leakage current of the $Ba(Zr_{0.12}Ti_{0.88})O_3$ thin films of 1.0×10^{-5} A/cm^2 was measured at 400 kV/cm.

1)D.Henning, A.Schnell and G.Simon: J. Am. Ceram. Soc., 65, 539-544 (1982).

2)T.Hayashi, N.Oji and H.Maiwa: Jpn. J. Appl. Phys 33, 5277-5280 (1994).