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Preparation and Properties of $Ba(Zr,Ti)O_3$ Thin Films by Chemical Solution Deposition

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Perovskite $Ba(Zr,Ti)O_3$ (BZT) is a representative dielectric material for capacitor applications and its properties can be controlled by Zr/Ti ratios. In this study, BZT thin films have been fabricated by the chemical solution deposition method. Perovskite BZT thin films were successfully synthesized above 650°C on $Pt/TiO_x/SiO_2/Si$ substrates. Among BZT thin films with various Zr/Ti ratios, BZT (Zr:Ti=20:80) thin films showed the homogeneous and smooth surface morphology and the most excellent dielectric properties. The dielectric constant of the BZT (Zr:Ti=20:80) thin film was found to be approximately 900 with dielectric loss tangent less than 5% at 10 kHz and room temperature. The BZT (Zr:Ti=20:80) thin films also exhibited the small temperature dependency of dielectric constant with low loss values over wide temperature range.

Keywords: $Ba(Zr,Ti)O_3$, chemical solution deposition, thin film, surface morphology, dielectric properties

1. INTRODUCTION

Recently, the miniaturization, high performance and high integration of electronic components such as multilayer ceramic capacitor (MLCC), etc., are strongly demanded.[1] Among various electronic components, MLCC is one of the most important electronic components and expected to achieve the smaller size with thinner internal layers and larger numbers of layers. Therefore, in the case of MLCC, direct fabrication of dielectric and conductive thin multilayers on Si-based integrated circuit is required for the future applications in the semiconductor device. In order to realize such a device, the appropriate fabrication process of thin films should be developed.

The chemical solution deposition (CSD) method is one of the methods for the fabrication of thin films.[2,3] This method has several advantages, such as good homogeneity, precise control of chemical composition, lower processing temperature and low equipment cost.

For the integrated capacitor devices, the selection of the suitable material of dielectric layer is very important, therefore, the dielectric material is required to have excellent dielectric properties with small temperature dependence. Of course, the fabrication of thin films with high quality is also needed.

Barium titanate ($BaTiO_3$) is a typical ferroelectric perovskite material that shows a large dielectric constant at Curie temperature at around 120°C. However, the optimization of its dielectric properties should be done for capacitor applications. Barium zirconate titanate ($Ba(Zr,Ti)O_3$, BZT) is a representative lead-free dielectric material and its properties can be controlled by Zr/Ti compositions.[4-6] BZT is reported to exhibit a very large dielectric constant by the pinching effect, which occurs when the phase transitions (rhombohedral ⇄ orthorhombic ⇄ tetragonal) are concentrated.[7]

In this study, BZT is selected as a dielectric material and the fabrication of BZT thin films is performed by CSD. The effect of Zr/Ti ratio on the surface morphology and dielectric properties of synthesized thin films was mainly investigated.

2. EXPERIMENTAL

Figure 1 shows the experimental procedure for preparing BZT precursor solutions and thin films. Barium metal, zirconium tetra-isopropoxide and titanium tetra-isopropoxide were selected as starting materials. 2-methoxyethanol was dried over molecular sieves and distilled prior to use. At first, Ba metal was dissolved in absolute 2-methoxyethanol and refluxed for 18 h. $Zr(O^iPr)_4$ and $Ti(O^iPr)_4$ corresponding to each composition [$Ba(Zr,Ti)O_3$, Zr:Ti=5:95, 15:85, 20:80, 30:70] were also dissolved in absolute 2-methoxyethanol and refluxed for 18 h. Then, these solutions were mixed and refluxed again to react alkoxides. The procedure was conducted in a dry N_2 atmosphere. This solution was concentrated to approximately 0.2 mol/l by removal of the solvent by vacuum evaporation.

BZT precursor films were fabricated using the precursor solution by spin-coating on $Pt/TiO_x/SiO_2/Si$ substrates. Precursor films were dried at 150°C for 5min,

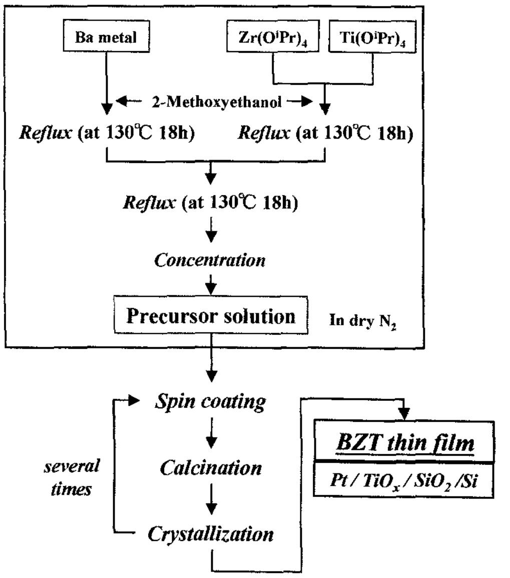

Fig.1 Experimental procedure for preparing $Ba(Zr,Ti)O_3$ thin films

then, heat-treated at various temperatures to obtain crystalline BZT thin films. Film thickness was adjusted to 350 nm by repeating the coating / heating cycle.

The crystallographic phases of thin films were identified by X-ray diffraction (XRD) analysis using CuKα radiation with a monohromator. The surface morphology of thin films was observed using an atomic force microscope (AFM). The dielectric properties of thin films were measured using a Pt top electrode with diameter of 0.2 mm deposited by DC sputtering onto the surface of the films followed by annealing at 300°C for 30 min. The Pt layer of the $Pt/TiO_x/SiO_2/Si$ substrate was used as a bottom electrode. The electrical properties of the thin films were evaluated using an impedance gain-phase analyzer and a wafer cryostat from −190°C to 190°C under vacuum.

3. RESULTS AND DISCUSSION

3.1 Fabrication of BZT thin films

Figure 2 illustrates the XRD profiles of $Ba(Zr_xTi_{1-x})O_3$ (BZT) thin films with various Zr/Ti ratios crystallized at 700°C. Synthesized BZT thin films were crystallized to the single phase of perovskite BZT. It is turns out from Fig. 2 that the 211 diffraction peak sifted to lower 2θ angle with increasing Zr content. This result indicates that the increase in lattice parameter is due to the substitution by larger zirconium ion (ionic radius of 0.72Å) for titanium site (ionic radius of 0.61Å).

3.2 Surface morphology of BZT thin films

Figure 3 shows the AFM images of BZT thin films prepared at 700°C on $Pt/TiO_x/SiO_2/Si$ substrates. As can be seen from the AFM images in Fig. 3, grain size of the synthesized BZT thin films decreased and surface morphology became homogeneous and dense with increasing zirconium content. The effect of Zr substitution to $BaTiO_3$ on the surface morphology was clearly observed. The BZT thin films with an optimum amount of Zr exhibited good surface morphology as shown in Fig. 3 (c). This fact is important to apply this BZT thin film in the layer-structured capacitor devices by laminating with electrode thin layers.

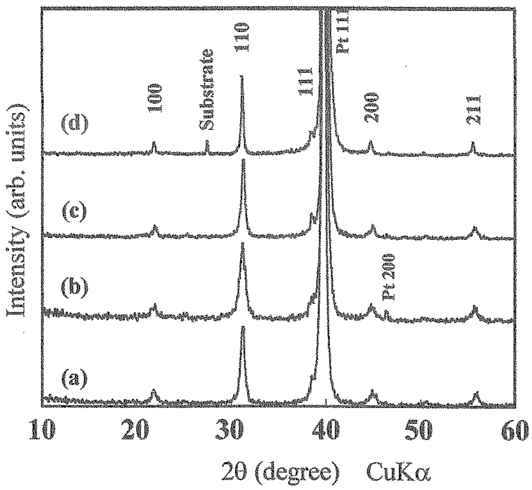

Fig.2 XRD profiles of $Ba(Zr,Ti)O_3$ thin films crystallized at 700°C on $Pt/TiO_x/SiO_2/Si$ substrates (a) Zr:Ti=5:95, (b) 15:85, (c) 20:80 and (d) 30:70

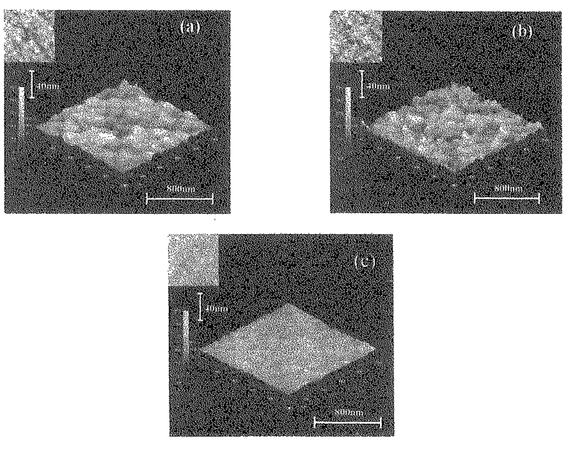

Fig.3 AFM images of $Ba(Zr,Ti)O_3$ thin films prepared at 700°C. (a) Zr:Ti=5:95, (b) 15:85 and (c) 20:80

3.3 Dielectric properties of BZT thin films

Figure 4 shows the frequency dependences of dielectric constant and loss of BZT thin films prepared at 700°C with various Zr/Ti ratios. The measurement was done at room temperature. With an increase of zirconium content from 5 to 20mol%, dielectric constant increased whereas dielectric loss decreased. This result is due to the improvement of surface morphology described in the previous section as well as the optimization of Zr content of BZT. The most excellent dielectric properties appeared at Zr:Ti=20:80 as shown in Fig. 4. The lower dielectric constant of BZT (Zr:Ti=30:70) thin films is considered to be due to the smaller grain size than BZT (Zr:Ti=20:80) thin films and existence of the Curie temperature below 0°C.

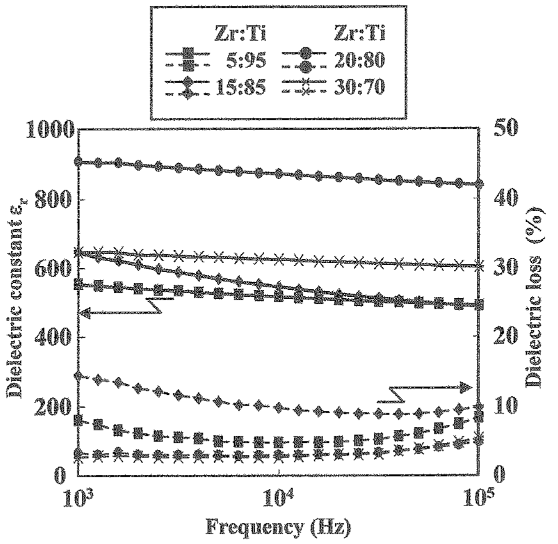

Fig.4 Frequency dependence of dielectric properties of $Ba(Zr,Ti)O_3$ thin films prepared at 700°C on $Pt/TiO_x/SiO_2/Si$ substrates [Measured at room temp.]

Furthermore, the measurement of temperature dependence of dielectric properties was performed for the BZT (Zr:Ti=20:80) thin film. Figure 5 shows the temperature dependences of dielectric constant and loss of BZT thin film of Zr:Ti=20:80 prepared at 700°C. It is clear from Fig. 5 that the BZT (Zr:Ti=20:80) film has small temperature dependency of dielectric constant (above 800) with low loss values less than 5% over wide temperature range. The maximum of dielectric constant for the BZT film was found to be between 0°C and a room temperature. The ε-T curves of the film were broadened and the values of dielectric constant were much smaller than those of BZT bulk ceramics.[4] This is mainly due to the small grain size (about 100 nm confirmed by AFM) of the BZT (Zr:Ti=20:80) thin film. The appropriate dielectric properties for thin film capacitor applications were confirmed when the Zr content was 20 mol% of $Ba(Zr,Ti)O_3$. The density of capacitance for the conventional ceramic capacitor is known to be 15 ~20 μF/mm^3. The calculated value of current BZT thin film capacitor is about 30 μF/mm^3. Multilayered thin film capacitor devices can be realized by achieving the alternative by stacked structure of the BZT thin film and the conductive thin film (ex. $LaNiO_3$ thin film) layers.

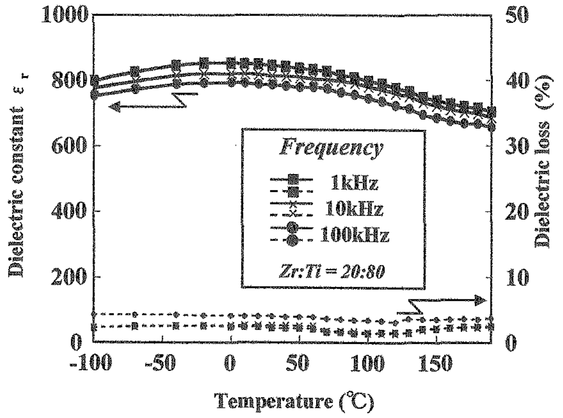

Fig.5 Temperature dependence of dielectric properties of Ba(Zr, Ti)O_3 (Zr:Ti=20:80) thin film prepared at 700°C

4. CONCLUSION

Perovskite BZT thin films were successfully synthesized using the chemical solution deposition (CSD) process. BZT precursor solution was prepared through the selection of appropriate starting materials and a solvent. BZT precursor thin films were found to crystallize in the perovskite single phase above 650°C. BZT thin films with homogeneous and smooth surface morphology were fabricated by optimizing the Zr/Ti ratio. Dielectric constant of BZT thin films had small temperature dependency with high dielectric constant and low loss over wide temperature range when Zr content was set at Zr:Ti=20:80. The maximum of dielectric constant of BZT (Zr:Ti=20:80) thin film appeared between 0°C and room temperature.

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