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Prepartion and Characterization of Barium Zirconate Titanate Thin Films

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Abstract

We investigated the structural and electrical properties of the $Ba(Zr_xTi_{1-x})O_3$ (BZT) thin films with a mole fraction of x=0.2 and thickness 150 nm for the application in MLCC (Multilayer Ceramic Capacitor). BZT films were prepared on $Pt/SiO_2/Si$ substrate at various substrate temperatures by the RF-magnetron sputtering system. When the substrate temperature was above 500 ℃, we could obtain multi-crystalline BZT films oriented at (110), (111), and (200) directions. The crystallization of the film and high dielectric constant were observed with the increase of substrate temperature. Capacitance of the film deposited at high temperature is more sensitive to the applied voltage than that of the film deposited at low temperature. This paper reports surface morphology, dielectric constant, dissipation factor, and C-V characteristics for BZT films deposited at three different temperatures. The BZT film deposited at 400 ℃ shows stable electrical properties but a little small dielectric constant for MLCC application.

1. INTRODUCTION

Ferroelectric perovskite thin films such as $(Ba_{1-x}Sr_x)TiO_3$ (BST)[1-3], $Ba(Zr_xTi_{1-x})O_3$ (BZT)[4,5], $Pb(Zr_{1-x}Ti_x)O_3$ (PZT)[6], etc., have been studied for areas requiring high permittivity, such as cell capacitors for Giga-bit Dynamic Random Access Memory (DRAM), Multilayer Ceramic Capacitor (MLCC), Ferroelectric Random Access Memory (FeRAM), etc. It is well known that Zr, like Sr, is an effective substituent in $BaTiO_3$ to decrease and shift the Curie temperature below room temperature[7]. Moreover, the Zr^{4+} ion is chemically more stable than the Ti^{4+} and has a larger ionic size to expand the perovskite lattice. Therefore, the substitution of Ti with Zr would depress the conduction by electronic hopping between Ti^{4+} and Ti^{3+} and it would also decrease the leakage current of the $BaTiO_3$ film system. It is reported that an increase in the Zr content induces a reduction in the average grain size, decreases the dielectric constant (ε_r), and maintains a low and stable leakage current[5]. This is possible because, Zr^{4+}ion has lager ionic size (0.087 nm) than Ti^{4+} (0.068 nm). Previously, BST thin films were used as the high permittivity material, however in this study we used BZT thin films whose characteristics are controlled by substitution of Ti with Zr. In com-

pounds of perovskite structure ABO_3, BZT is obtained by substituting ion of B site of the $BaTiO_3$ with Zr instead of substitution of A site with Sr in ABO_3 compounds with perovskite structure. Zr to Ti ratio is very important in $Ba(Zr_xTi_{1-x})O_3$ system and a 0.2/0.8 mole fraction is known to show very good bulk properties[8]. Thus BZT thin films have good properties at high frequencies and can be applied as a storage capacitor for the next generation of DRAM and a dielectric material for MLCC. However, they have been studied extensively. In this study we deposited $Ba(Zr_{0.2}Ti_{0.8})O_3$ thin film by RF-magnetron sputtering and examined the feasibility of the next generation high efficient insulating thin film.

2. EXPERIMENTS

The BZT thin films were deposited on a 2×2 cm Pt (150 nm)/SiO_2 (400 nm)/Si substrate by RF-magnetron sputtering method using a 2 inch $Ba(Zr_{0.2}Ti_{0.8})O_3$ target. To remove the impurities in the chamber, the pressure inside the chamber was maintained at 2×10^{-6} Torr for 1 hour. A pre-sputtering was carried out for 10 minutes with a RF power of 80 W in Ar ambient in order to remove defects on the target and to obtain stable plasma. Then, oxygen was admitted into the chamber. During the deposition, Ar to O_2 ratio was maintained at a ratio of 4:1 (Ar=12 sccm, O_2 = 3 sccm) and the substrate temperature was fixed at three different values, viz., 400, 500, and 600 ℃. The deposition conditions are shown in Table.

The top metal (Pd) was deposited for electrical measurements by thermal evaporation using a 0.2 mm diameter shadow mask and the area of top electrode was measured by optical microscope.

Table 1. Deposition conditions in BZT films preparation

Sputtering parameter	Conditions
Target	Sintered BZT ceramic target
Substrate	Pt/SiO_2/Si
Target-Substrate distance	65mm
Ar to O_2 ratio	4:1
Base pressure	2.0×10^{-6} Torr
Working pressure	5.0×10^{-3} Torr
Deposition time	1 hour
RF Power	80 W
Substrate temperature	400, 500, 600 ℃

The thickness, the cross-sectional view, and the surface morphology of BZT thin film were analyzed by surface profiler (Tencor Alpha-Step 500), scanning electron microscopy (Hitachi S-2150), and atomic forces microscopy (Digital Instrument nanoscope 3A), respectively. In addition, XRD (Mac Science M18XHF-SRA) was applied to analyze the crystallinity of the film. Dielectric properties of the BZT thin film with MIM structure were measured using a multi-frequency LCR meter (HP 4274A) and the dielectric constants were calculated.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra of the BZT target and BZT thin films deposited at the substrate temperatures of 400 to 600 ℃. The spectra for the as-deposited film show highly polycrystalline perovskite BZT peaks at (111) and (200) directions. The BZT film deposited at 400 ℃ shows weak BZT peaks at (110) and (200) directions, but X-ray diffraction intensity increases at higher deposition temperatures (500 and 600 ℃). This is due to the increase of crystallinity at higher temperature. No other secondary phases are observed in the spectra. Also, the Pt peak intensity increases

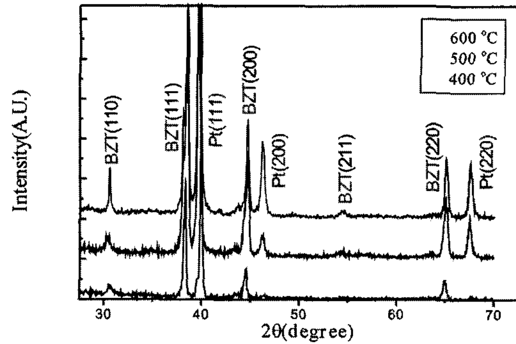

Fig. 1 XRD patterns of the BZT thin films deposited at different substrate temperatures

at higher temperature and this is because of the substrate temperature effect on the lower electrode (Pt), and this is just like an annealing effect.

Figure 2 shows the surface morphology of BZT thin films deposited at different temperatures analysed using SEM and AFM. From AFM measurement, the surface roughness of the films was observed to be 0.845, 1.655, and 6.614 nm at 400, 500, and 600 ℃, respectively. The roughness is a very important factor because the interface be-

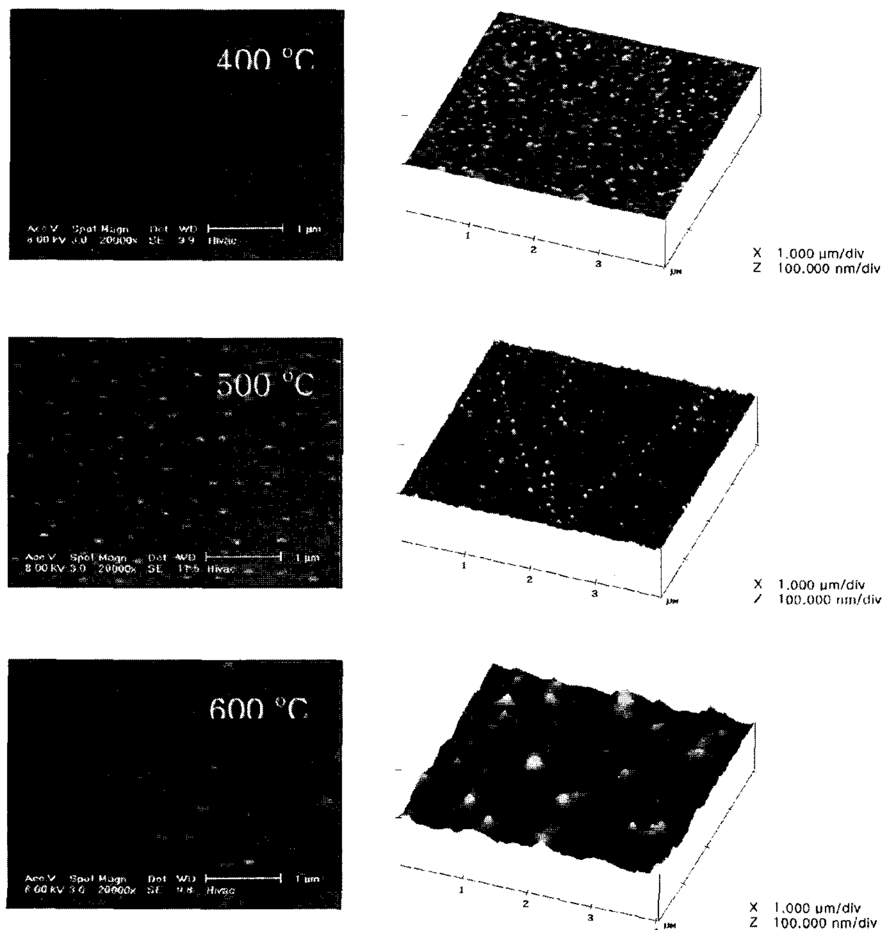

Fig. 2 (a) SEM and (b) AFM images of the BZT thin films deposited at different temperatures

tween an electrode and a dielectric material is a significant matter for multilayer system. The BZT film deposited at 400 ℃ shows amorphous-like aspect while crystalline sizes of the BZT film deposited at 500 ℃ are 0.005~0.15 μm and they are locally grown. Also, the film deposited at 600 ℃ shows crystalline size over 0.1~0.3 μm. One can see that higher the substrate temperatures, larger and denser are the grains. This result is agreement with the XRD results and the crystallity of BZT thin film is improved by the deposition temperature, which results from the increase of atom mobility at higher temperature.

Capacitance-Voltage (C-V) characteristics (at a frequency of 1 MHz) of MIM structure (Pd/BZT/Pt) is shown in figure 3. The results are similar to that of BST[2] and PZT[6] systems. The films deposited at 400 and 500 ℃ show paraelectric nature. BZT film deposited at 400 ℃ has constant capacitance value to the applied voltage while specimens deposited at 500 and 600 ℃ are sensitive to the applied voltage. The thin film deposited at 500 ℃ shows the symmetrical C-V characteristics about 0 V and the capacitance decreases when the applied voltage is increased beyond 0 V. This is because of the space charge region which developed between the electrode and the dielectric material[9]. The ratio of capacitance (C) to maximum capacitance (C_{max}) is found to be 0.936 for the film deposited at 600 ℃, and they are asymmetric about 0 V. Also, the C-V graph has two peaks, which is a result of the ferroelectric properties and has a switching voltage of about 2 V. These results are due to the strong ferroelectric properties of the BZT thin films and the crystallization of the film is proceeded.

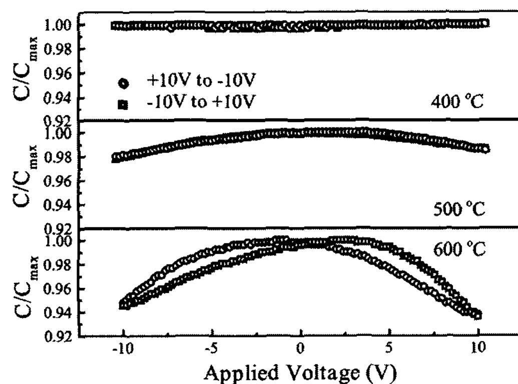

Fig. 3 C-V characteristics of the MIM capacitor with BZT thin films deposited at different temperatures, which were measured at the frequency of 1MHz

Figure 4 gives the variation of the dielectric constant (ε_r) and dissipation factor (tanδ) as a function of applied frequency. The BZT films have high dielectric constants even without annealing. The BZT film has the dielectric constant of 100, 150, and 250 at 400, 500, and 600 ℃, respectively. The dielectric constant increases with the increase of deposition temperature, but it has almost constant value without regard to the measuring frequency. Therefore, it could be concluded that, as seen from XRD and SEM results, the dielectric constants increase as the film crystallization is progressed. The dissipation factor shows

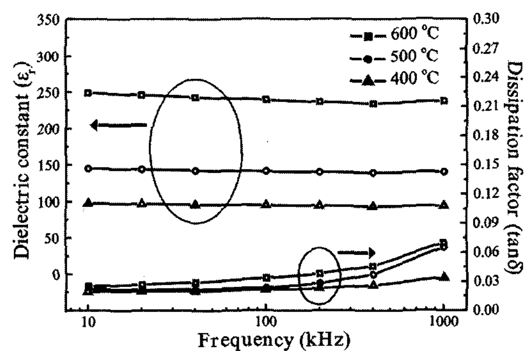

Fig. 4 Dielectric properties with the frequency of BZT thin films deposited at different temperatures

a little change from 0.019 (at 10 kHz) to 0.033 (at 1 MHz) in the thin film deposited at 400 ℃. On the other hand, $\tan\delta$ of the film deposited at 500 ℃ changes from 0.022 to 0.065 and changes from 0.025 to 0.07 for the film deposited at 600 ℃ at same frequency region. The dissipation factor changes more at 500 and 600 ℃ than at 400 ℃. It is known that the increase of dissipation factor is due to extrinsic resonance behavior[10]. However, the dissipation factor above 200 kHz is higher in the films deposited at 500 and 600 ℃ compared with that of films deposited at 400 ℃. This may be due to the defects (vacancy, movable ion, leaky grain boundary[2], etc.) that developed in the structure of the film with the increase of crystallization. Hence, it is inferred that the defects causes the dielectric loss with the increase of the measuring frequency.

4. CONCLUSIONS

In this study, BZT thin films with a thickness of 150 nm are deposited by RF magnetron sputtering method on to $Pt/SiO_2/Si$ substrates kept at different temperatures (400, 500, and 600 ℃). The dielectric constant at the frequency of 10 kHz was measured as 100, 150 and 250 for the films deposited at 400, 500, and at 600 ℃ respectively. As the deposition temperature increases, the dielectric constant increases and the crystallity of the film improves. In XRD analysis, it is seen that, as the deposition temperature increases, BZT peaks oriented at (110) and (200) directions increase and all specimens show high (111) BZT peak without annealing. C-V characteristics of BZT film deposited at higher temperature is influenced by applied voltage, whereas the BZT film deposited at low temperature is not influenced. As the applied frequency increases, the dissipation factor increases due to the defects in the structure of the film. However, the applied frequency does not influence the dielectric constant.

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