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Dielectric properties of (Ba, Sr)TiO_3 thin films by rf magnetron sputtering

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This paper describes dielectric properties of $(Ba_{0.5}Sr_{0.5})TiO_3$ thin films prepared on Pd (100)/Mg(100) substrate using an rf magnetron sputtering technique for DRAM application. Perovskite thin films have been prepared at a gas pressure of 7 mTorr, and the crystal orientations of thin films changed with the rise of the substrate temperature. The dielectric constant has increased with increasing the substrate temperature and obtained the maximum value (~ 300) at 550 ℃. Above 550 ℃, it has slightly decreased due to porous structure. Leakage current is minimum for the film prepared at 550 ℃ .

1. INTRODUCTION

The interest in the use of the ferroelectric thin films for memory applications has increased in the recent years.[1] If they will be used as a capacitor of DRAM, films with high dielectric constants are required.[2] On the other hand, film with relatively small dielectric constants are useful for application to nonvolatile ferro-RAM. Therefore, precise control of the film composition is essential for both applications.

Among numerous ferroelectric materials, barium strontium titanate $(Ba_{1-x}Sr_x)TiO_3$ (abbreviated BST) is a promising candidate for use in DRAM's due to its high dielectric constant and no aging and fatigue effects.[3-6] In this paper, $(Ba_{0.5}Sr_{0.5})TiO_3$ thin films prepared by rf sputtering have been studied for the purpose of realizing much high dielectric constants.

2. EXPERIMENTAL

$(Ba_{0.5}Sr_{0.5})TiO_3$ thin films were prepared using a conventional rf-magnetron sputtering technique with ceramic powder target under various conditions. A palladium film (500 nm in thickness) was deposited as a bottom electrode on the polished surface of a MgO(100) substrate.

An X-ray diffraction pattern revealed that the Pd(100) plane lay parallel to the MgO(100) plane. Typical sputtering conditions are illustrated in Table 1 . The target powder was fired at 1100℃ for 3h. A gold film was sputtered for the upper electrode and fabricated into 1mm .

The chemical composition of the films was determined by the inductively coupled plasma method (ICP). Thin-film crystallogryphy was performed by X-ray diffraction (monochromatized CuKα radiation). Crystalline sizes were decided using the half-width of X-ray diffraction patterns. The typical film thickness determined by the surface profilometer was about 800 nm. The deposition rate was 4.5 nm/min. The dielectric constant (ε_r) was calculated from capacitance, for the capacitor structure of upper electrode Au/ $(Ba_{0.5}Sr_{0.5})TiO_3$ /Pd(100)/Mg(100) substrate, that was measured with a Hewlett-Packard (YHP-4194A) impedance analyzer at 1 kHz.

Table I. Sputtering conditions

Target	$(Ba_{0.5}Sr_{0.5})TiO_3$ powder
Target size	90 mm
Substrate	MgO (100)
Electrode	Pd (100)
Sputtering gas	Ar/O_2 (90/10)
Sputtering gas pressure	5–10 mTorr
Rf power	100 W
Substrate temperature	450–600 ℃
Target–substrate distance	55 mm

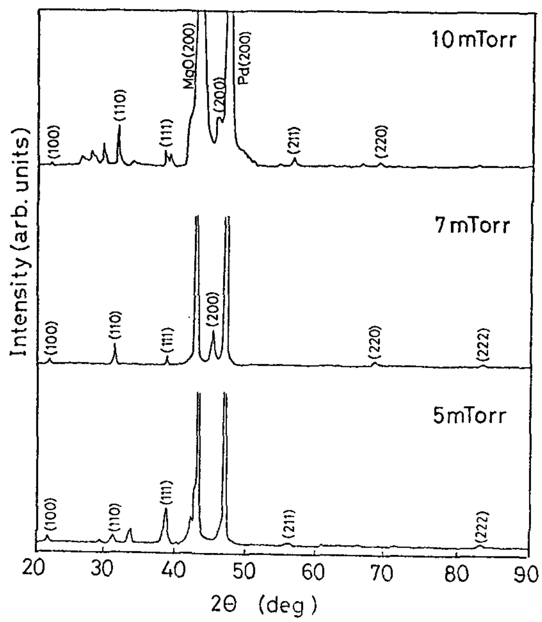

Fig. 1 X–ray diffraction pattern of BST thin films on Pd–MgO substrate with gas pressure as a parameter Substrate temperature was 500℃.

Leakage current was measured by means of electrometer.

3. RESULTS AND DISCUSSION

3.1. Crystal structure of the films

The crystal structures of the films were sensitive to the gas pressure and substrate temperature as shown in Figs. 1 and 2.

Figure 1 shows that thin films with a mixture of pyrochlore, perovskite and another structures were obtained at the lowest and highest pressure, and those having a perovskite structure were stably obtained at a gas pressure of 7 mTorr at 500℃. The orientations of the BST films were also affected by the substrate temperature. Figure 2 shows the orientations of BST films on Pd(100)/MgO (100) as a function of temperature. Below 525℃, (100)–oriented BST films were obtained. Cubic BST films were obtained in the temperature range of 525–575℃ and (111)–oriented BST films were obtained above 600℃. These results indicate that the epitaxial temperature for obtaining (100)–oriented BST film is below 525℃.

The lattice mismatch does not explain the change of orientation because the lattice mismatches between Pd and BST for those directions are almost the same.

Figure 3 shows that lattice constants of BST films decrease with increasing substrate temperature and approach that of bulk materials (0.399nm) at 600℃.

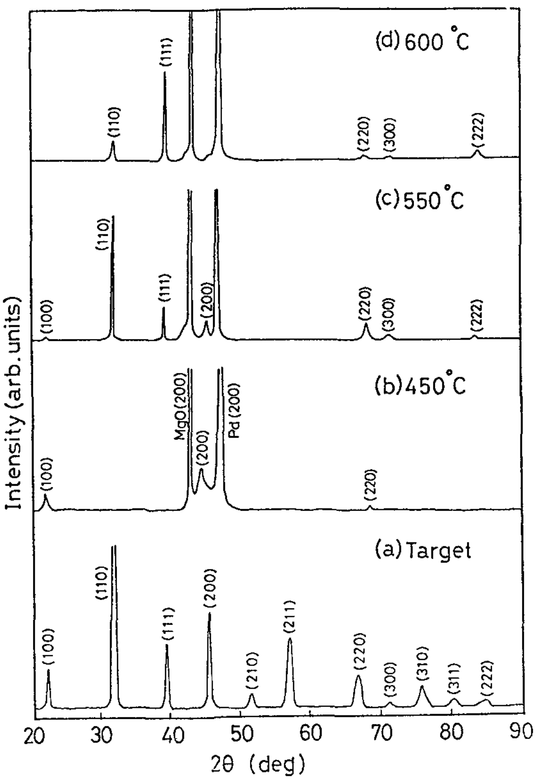

Fig. 2 X-ray diffraction pattern of BST thin films on Pd/MgO substrate with substrate temperature as a parameter
Gas pressure was 7 mTorr.

Crystalline sizes of the BST films increase monotonically with increasing substrate temperature from 25 nm at 450℃ to 60 nm at 600℃ .

The film composition, including both (Ba+Sr)/Ti and (Ba/Sr) ratio, was almost the same as that of the target composition.

3.2. Electrical properties

To measure the dielectric properties, electrodes of Au(1mmϕ) were deposited on 800nm-thick films. The dielectric constant ε_r was measured at 1 kHz applying at electrical field of 25V/cm, by an impedance analyzer.

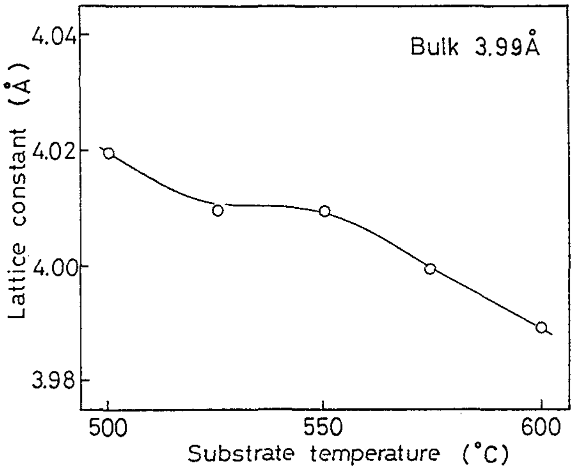

Fig. 3 Lattice constant vs substrate temperature for BST thin films deposited on Pd/MgO substrate.
Gas pressure was 7 mTorr.

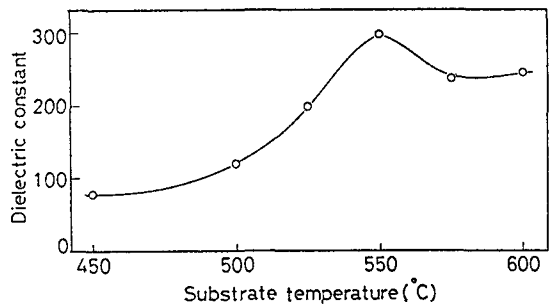

Fig. 4 Dielectric constant vs substrate temperature for BST thin films deposited on Pd/MgO substrate.
Gas pressure was 7 mTorr.

For DRAM application, it is necessary to realize high dielectric constant ε_r . Figure 4 shows variation of ε_r value with the substrate temperature using the target powder fired at 1100℃ for 3 h. The ε_r value showed a maximum of 300 at 550℃ in which crystal orientation was changeable. It decreased to around 250 at 600℃. The maximum value of 300 is near the reported value of 320.[4]

The ε_r value did not increase markedly for $(Ba_{0.5}Sr_{0.5})TiO_3$ thin films compared with bulk materials, even when the substrate temperature was increased to 600℃. It is assumed that ε_r value depends on firing temperature of target powder and has the maximum value at 900℃.[4] In this experiment, firing temperature of target powder is fixed at 1100℃. This condition may have to be changed. However, the main reason for smaller ε_r value is due to porous structure of BST thin films at higher substrate temperature. The SEM image reveals that the film at 600℃ has a coarse surface and porous structure. The leakage current characteristics at varous substrate are shown in Fig. 5. It was found from Fig. 5 that the minimum leakage current was obtained for the film prepared at 550℃.

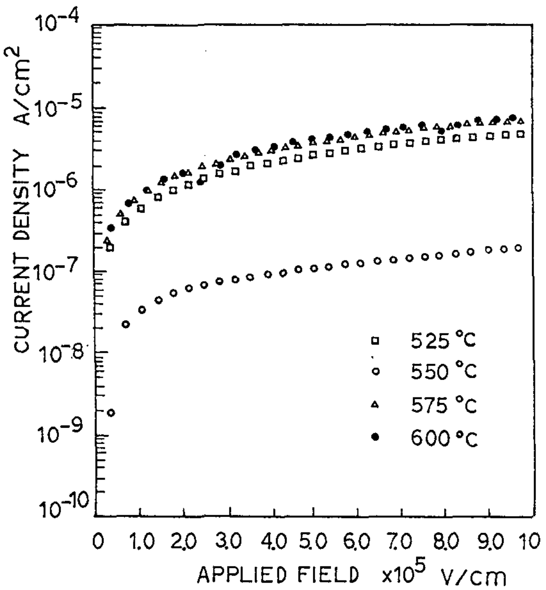

Fig. 5 Leakage current of a $(Ba,Sr)TiO_3$ thin films at various substrate temperature.

4. CONCLUSION

The $(Ba_{0.5}Sr_{0.5})TiO_3$ thin films with perovskite-type structure were prepared on Pd(100)/MgO(100)substrates by rf magnetron sputtering system at a gas pressure of 7 mTorr. The crystal structure were prepared on Pd(100)/MgO(100) substrates by rf magnetron sputtering system at a gas pressure of 7 mTorr. The crystal structure of thin films changed from (100)-oriented to (111)-oriented structure depending on the substrate temperature.

The chemical composition ((Ba+Sr)/Ti and (Ba/Sr) ratio) of the thin films was almost the same as that of the target composition. The ε_r value of thin films chaged with the substrate temperature and a maximum value of ~300 was obtained at 550℃. Furthermore, the minimum leakage current was obtained for the film prepared at 550℃.

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