Structural and Electric Properties of (Ba, Sr)TiO$_3$ Thin Films on Glazed Alumina Substrate

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In this study, we investigated the crystal structure of polycrystalline BST films deposited on the glazed-Al$_2$O$_3$ and α-Al$_2$O$_3$ substrates and its electrical properties. The BST films were prepared on the Pt bottom electrode/substrates by the chemical solution deposition (CSD) method. The BST films annealed at 800°C using rapid thermal annealing (RTA) were grown in random orientation on each substrate. The grain sizes were 80 nm and the average surface roughnesses Ra were approximately 3.0 nm. The dielectric constant, tanδ and tunability (at 428 kV/cm) of the Pt/BST/Pt/α-Al$_2$O$_3$ film were 476, 0.0321 and 68.6% respectively, and the Pt/BST/Pt/glazed-Al$_2$O$_3$ film also showed practical figures, 429, 0.0498 and 58.3% respectively. We confirmed that the tunability of the Pt/BST/Pt/glazed-Al$_2$O$_3$ film can be maintained at above 50% up to an environmental temperature of around 80°C. This suggests that high quality BST films to apply on tunable microwave devices can be formed on a very inexpensive glazed-Al$_2$O$_3$ substrate.

Key words: (Ba,Sr)TiO$_3$, BST film, Glazed Al$_2$O$_3$ substrate, Thermally Stimulated Current (TSC)

1. INTRODUCTION

Because (Ba$_{1-x}$Sr$_x$)TiO$_3$ (BST) films have a prominent nonlinear dielectric property through their applied electric field, their use can be expected in microwave tunable devices such as voltage-controlled oscillators, tunable filters, and phase shifters[1]. In order to improve the properties of these devices, BST films with large tunability (=(C$_{max}$-C$_{min}$)/C$_{max}$×100) and low dielectric loss are necessary. In recent years the creation of high-quality BST films by epitaxial growth on single crystal substrates such as MgO, SrTiO$_3$, LaAlO$_3$, or sapphire[2-4] has been an active area of research. However, the large costs involved have presented limitations in putting the single crystal substrates to practical use. However, most of the high frequency properties of polycrystalline-BST films deposited on Al$_2$O$_3$[5] and Si substrates[6-7] have yet to be revealed. Thus, forming high-quality BST films on these substrates is a critical issue in their practical applications. To improve the quality of polycrystalline- BST films, it will be essential to control the crystalline defects on the interface and grain boundaries. We have selected the Thermally Stimulated Current (TSC) analysis[8] for the quantitative evaluation on such crystalline defects.

In this study, we focused on the fairly reasonable substrate with the flatness improved by applying a glazing process on the polycrystalline-96%Al$_2$O$_3$ substrate. Also, we have analyzed the BST film on the chemically stable α-Al$_2$O$_3$ (Sapphire) substrate, in order to compare the properties. BST film is synthesized using the chemical solution deposition (CSD) method, and

Pt having a lattice constant close to the BST and withstanding the high temperature process, is used as the bottom electrode. In particular, since the properties of the BST film are strongly dependent on the anneal process, we have investigated its crystal structure and electrical property by changing the anneal process temperatures from 600 to 800°C.

2. EXPERIMENTAL

Pt bottom electrodes with a thickness of 100 nm were deposited on the glazed-Al$_2$O$_3$ (Kyocera-A476) and α-Al$_2$O$_3$ substrates by RF magnetron sputtering at 500°C. The BST solution (Mitsubishi Materials-Ba:Sr:Ti=60:40:100, 7wt%) was spin-coated on the Pt/glazed-Al$_2$O$_3$ substrates at 500 rpm for 5 s and subsequently at 4500 rpm for 20 s. The spin-coated films were dried at 150°C for 3 min, pyrolyzed at 350°C for 5 min in air on a hot plate. Then the films were annealed in O$_2$ at 600-800°C for 5 min by rapid thermal annealing (RTA) for crystallization. The 280 nm thick BST films were prepared by repeating this BST deposition process. Pt top electrodes with a thickness of 150 nm were deposited on the BST films by RF magnetron sputtering at room temperature. The diameter of the top electrodes was 0.27 mm. The crystalline phases of the BST films were identified by X-ray diffraction (XRD). The surface morphology and cross-sectional structure were examined with a field emission scanning electron microscope (FE-SEM) and atomic force microscope (AFM). Dielectric properties of BST films were measured at 1 MHz by using a LCR meter (HP4191A).

The I-V properties were determined using a pA meter (Advantest-R834A).

3. RESULTS AND DISCUSSION

3.1 Crystal structure of the BST films

Fig.1 shows XRD patterns of the BST films deposited on the glazed-Al_2O_3 and α-Al_2O_3 substrates. The BST film formulated a single perovskite phase by the anneal process over 600°C. However, while the Pt bottom electrode showed a single orientation to (111) on both substrates, the BST films grew with random orientation without reflecting the impact of Pt electrode. For the glazed-Al_2O_3 substrate, diffraction peaks of the Al_2O_3 substrate were not observed since its glazed layer was thick (50 μm).

Fig.2 shows the surface morphology of those BST films. While the grain size of the BST films had increased according to the anneal process temperatures, the surface roughness also showed an increasing trend. The average grain sizes for respective samples are 40, 80 and 80 nm for BST/Pt/glazed-Al_2O_3 film (600°C), BST/Pt/glazed-Al_2O_3 film (800°C), and BST/Pt/α-Al_2O_3 film (800°C). The average surface roughness Ra was 1.47, 3.00, and 3.00nm respectively, and the grain showed a similar tendency of growth on both substrates. From the SEM observation results of respective samples indicating there are no pinholes or microcracks, we have confirmed the flatness is in a good condition.
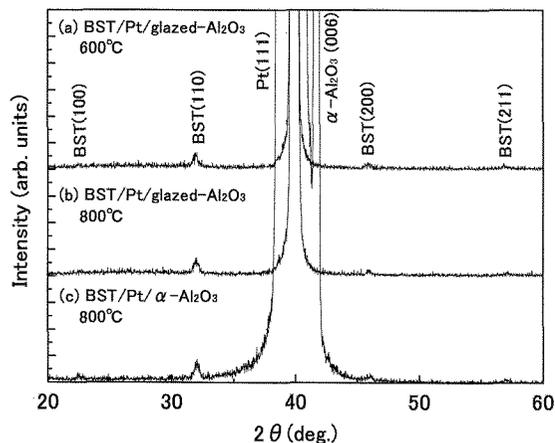

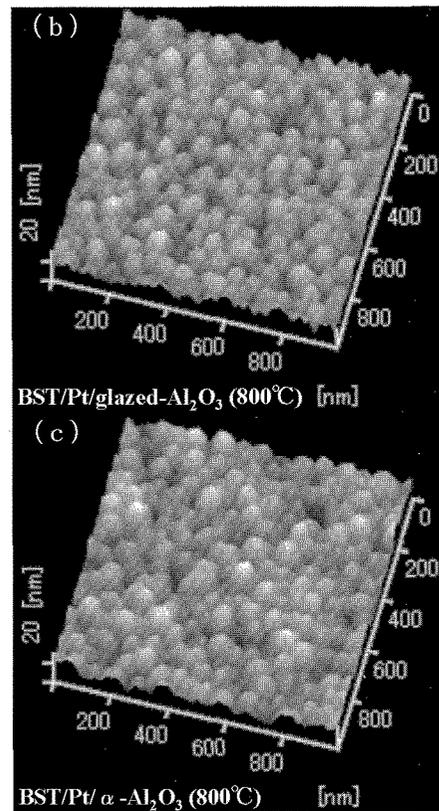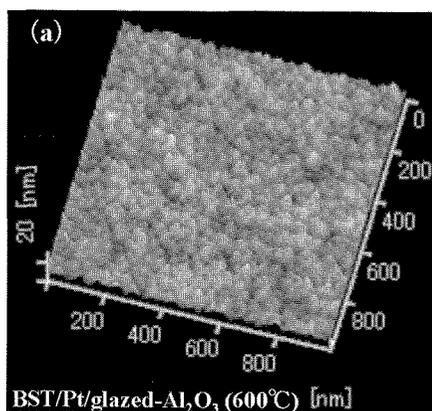Fig.1 X-ray diffraction patterns of BST films on Pt/glazed-Al_2O_3 and Pt/α-Al_2O_3 substrates.

Fig.2 AFM images of BST films on Pt/glazed-Al_2O_3 and Pt/α-Al_2O_3 substrates.

3.2 Electrical property of the BST films

Fig.3 shows the C-V property at 1 MHz of the BST films. Since the effect of the anneal process gives a significant impact on the dielectric property, the dielectric constant of Pt/BST/Pt/glazed-Al_2O_3 film, tanδ and tunability (at 428 kV/cm) showed 294, 0.0436, 44.9% respectively at 600°C, and 429, 0.0498, 58.3% respectively at 800°C. Also, Pt/BST/Pt/α-Al_2O_3 film (800°C) showed 476, 0.0321, 68.6% respectively. This implies that the dielectric constant and tunability increase the more the grain size of the BST film grows. For Pt/BST/Pt/α-Al_2O_3 film (800°C), it was slightly influenced by the bottom electrode Pt (111) and its BST(111) increased. Hence, it is expected that its dielectric property was better than other samples.
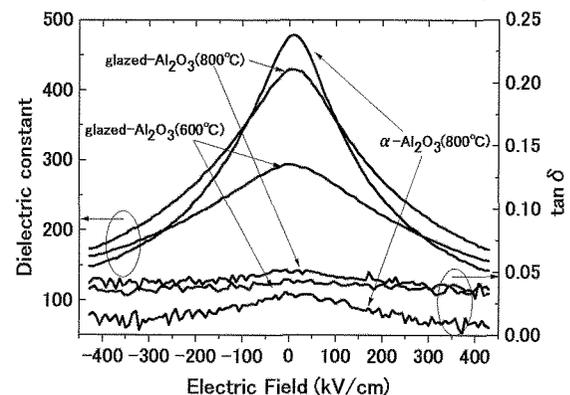

Fig.3   ε -V properties of BST films at 1 MHz.

Fig.4 shows the I-V property of the BST films. The difference of the leakage current property at the positive pole is considered to be dependent on the interface condition of the BST film and bottom electrode Pt. In particular, Pt/BST/Pt/glazed-Al₂O₃ film (800°C) showed the tendency to decline in the electrical insulating within the low electric field region. This is assumed to be due to deterioration of the interface condition, caused by a diffusion of glass components in the glazed layer into the bottom electrode Pt. The glass transition temperature and the softening temperature of this glazed layer are 685°C and 870°C respectively. Accordingly, when conducing the crystallization annealing at 800°C, an improvement in the electrical insulating can be expected by depositing TEOS (tetraethyl orthosilane) between the bottom electrode Pt and the glazed layer as an interlayer insulating film. For Pt/BST/Pt/glazed-Al₂O₃ film (600°C), since the surface roughness Ra is fairly flat (1.47 nm), it can be considered that the leakage current is kept in the low electric field region. Pt/BST/Pt/α-Al₂O₃ film (800°C) also showed a significant increase in the leakage current for the property at the negative pole. This is considered to be caused due to absence of post anneal process after the formulation of the top electrode, which resulted in the poor adherence between the top electrode Pt and the BST interface and nonuniformity in the interface condition.
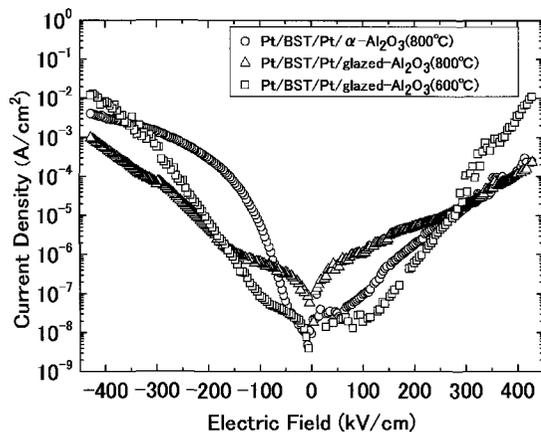

Fig.4 I-V properties of BST films.

Fig.5 shows the temperature dependency of the dielectric constant for the BST films. Pt/BST/Pt/α-Al₂O₃ film (800°C) and Pt/BST/Pt/glazed-Al₂O₃ film (800°C), both holding high dielectric constant in the room temperature, showed a large variation. Their temperature coefficient of relative dielectric constant were − 0.60%/K and − 0.48%/K respectively. Also, Pt/BST/Pt/glazed-Al₂O₃film (600°C) showed the lower value, − 0.28%/K. Curie temperatures for all the samples existed broadly around −60°C, which were shifted to the lower side, compared with bulk ceramics. The impact of a problem concerning the composition ratio of the BST film and the bottom electrode/substrate stress on the property, is considered to be a reason for this shift. Next, the temperature dependency of tunability is shown in Fig.6 When applying the BST film to the tunable microwave device, 50% of tunability is required. Tunability of

Pt/BST/Pt/glazed-Al₂O₃ film (800°C) remained 50% up to the ambient temperature of around 80°C in the case where the applied electric field was 428 kV/cm (12 V). This implies that it is possible to form a high-quality BST film to be applied for the tunable microwave devices, on the fairly reasonable glazed-Al₂O₃ substrate.
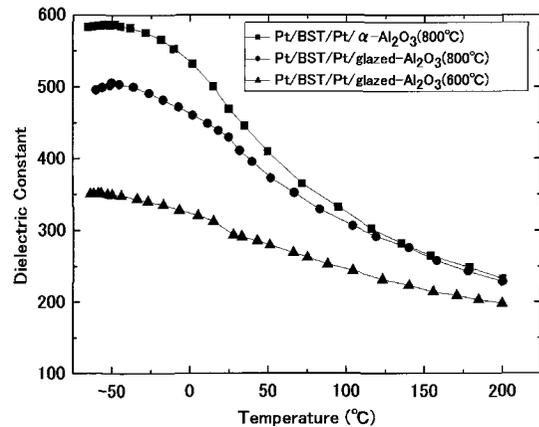

Fig.5 Temperature dependence of dielectric constant of BST films.
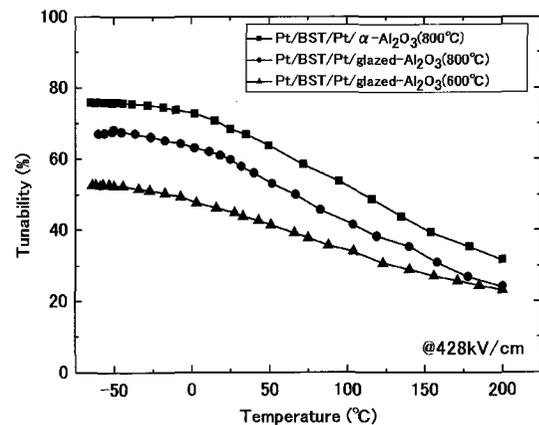

Fig.6 Temperature dependence of dielectric tunability of BST films.

3.3 TSC property of the BST films

Fig.7 shows the TSC property of Pt/BST/Pt/glazed-Al₂O₃ films. As for the measuring condition of the TSC, the trapping voltage when carrier injecting the sample into the trapsite was set at 0.5 V. The applied collecting voltage was 5 mV and the temperature rising rate was 2 K/min during measurement. Furthermore, background noise was eliminated by deducting the current when the temperature was falling from the current when the temperature was rising to carry out the analysis. From the findings of this TSC measurement of Pt/BST/Pt/glazed-Al₂O₃film (600°C), we were able to verify a clear peak somewhere around 120°C. First of all, it is likely that the peak of around 120°C is associated with the Curie temperature Tc of BaTiO₃. This is likely to be due to the BaTiO₃ phase being deposited ahead in a low anneal temperature of 600°C since the melting point for BaTiO₃ and SrTiO₃ was 1612°C and 2353°C respectively. This suggests that the pyroelectric current of the BaTiO₃ phase which is present in minute amounts

within the BST film was observed in the peak of around 120°C. However, uniform BST films without different phases were formed and the peak of around 120°C extinguished in the sample annealed at 800°C. Here, we confirmed that true TSC has a peak of around 260°C by optimizing the measuring condition. We will continue to analyze this peak and deliberate about the crystalline defects of BST film in detail.
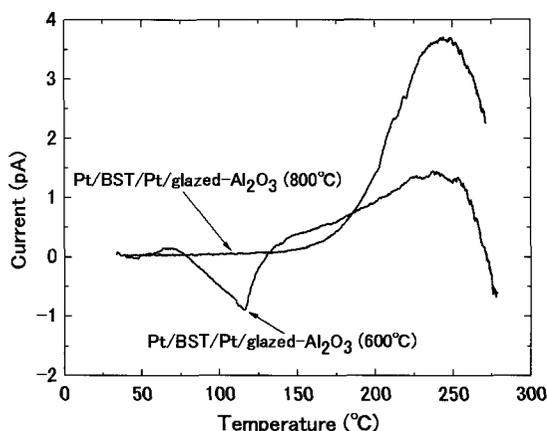

Fig.7 TSC properties of Pt/BST/Pt/glazed-Al₂O₃ films.

4. CONCLUSIONS

In this study, we investigated the crystal structure of polycrystalline BST films deposited on the glazed-Al₂O₃ and α-Al₂O₃ substrates and its electrical property. The BST films were prepared on the Pt bottom electrode/substrates by the chemical solution deposition method. The BST films annealed at 800°C using RTA which were grown in random orientation on each substrate. The grain sizes were 80 nm and the average surface roughness Ra was approximately 3.0 nm. The dielectric constant, tanδ and tunability (at 428 kV/cm) of the Pt/BST/Pt/α-Al₂O₃ film (800°C) were 476, 0.0321 and 68.6% respectively, and the Pt/BST/Pt/glazed-Al₂O₃ film (800°C) also showed practical figures, 429, 0.0498 and 58.3% respectively. We confirmed that the tunability of the Pt/BST/Pt/glazed-Al₂O₃ film (800°C) can be maintained at above 50% up to an environmental temperature of around 80°C. This suggests that high quality BST films to apply on tunable microwave devices can be formed on a very inexpensive glazed-Al₂O₃ substrate. However, the dielectric property and tunability of the Pt/BST/Pt/glazed-Al₂O₃ film (600°C) showed a lesser figure of 294 and 44.9%. This is likely to be due to the smallness of the grainsize at 40 nm. Moreover, from the TSC analysis of the Pt/BST/Pt/glazed-Al₂O₃ film (600°C), we confirmed a clear peak at around 120°C. This was probably the result of polyelectric current of the BaTiO₃ phase present in minute amounts within the BST film being observed. For an assessment technique of materails to be able to verify the presence of quantitative crytalline defects as well as different phases such as these is very effective. We will need to carry out further detailed analysis of the crystalline defects of BST films in the future.

6. REFERENCES

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