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The Effect of the Annealing Process on Dielectric Properties of $Ba(Ti,Zr)O_3$ Thin Films Deposited by Sputtering

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$Ba(Ti,Zr)O_3$ thin films were deposited on $Pt/Ti/SiO_2/Si(100)$ substrates by RF magnetron sputtering. Films were prepared with three different annealing processes, and their dielectric properties were examined. We found that temperature coefficients of dielectric constant (TCD) of the films which were deposited (a) at 600°C, (b) at 600°C and annealed at 600°C after deposition, and (c) at room temperature and annealed at 600°C after deposition were -0.11%/K, -0.17%/K, and -0.38%/K at 25°C, respectively. These films formed by conditions (a)-(c) were composed of a perovskite crystalline structure. The mechanism of the increase in TCD was also examined, and it was proven that internal stresses of the films were strongly correlated with values of TCD. This fact provides us a clue of how to obtain high TCD values enough to be applied to uncooled infrared sensor of dielectric-bolometer mode.
Key words: $Ba(Ti,Zr)O_3$, infrared sensor, dielectric properties, ferroelectricity, sputtering

1. INTRODUCTION

Ferroelectric materials have received much attention recently because of their wide application to such uses as nonvolatile memories, piezoelectric transducers, actuators, and various sensors. Application to uncooled infrared (IR) sensor of dielectric-bolometer (DB) mode was also actively studied [1-3]. This sensor have the advantages of not needing cooling equipment meaning that it can be drastically downsized and lightweight, and of less power consumption.

Figure 1 shows cross-sectional view of an example of IR sensor of DB mode. Dielectric films were prepared between upper and lower electrodes to build capacitors, and Si substrate underlying the sensor-side capacitor was removed from the backside by an anisotropic etching, as shown in Fig. 1. When the IR ray is injected into this structure, the temperature of the sensor-side capacitor increased because of its lower heat capacity. The difference of temperature between sensor-side and reference-side capacitors can be detected by measuring the difference of capacitance, which is caused by the change of dielectric constant of the dielectric films. Therefore, it is important for dielectric films to show a high temperature coefficient of dielectric constant (TCD) at operating temperature to achieve good sensitivity. This change of dielectric constant is due to the phase transition from a ferroelectric state to a paraelectric state. As a candidate material for dielectric film, some ferroelectric thin films such as $Pb(Sc_{0.5}Ta_{0.5})O_3$ [3], $(Ba_{1-x}Sr_x)TiO_3$, $Ba(Ti_{1-x}Sn_x)O_3$ [2], which are expected to have Curie temperature (Tc) at around room temperature, have been investigated, and some methods of deposition were studied such as pulsed laser deposition, sol-gel, and metal-organic chemical vapor deposition.

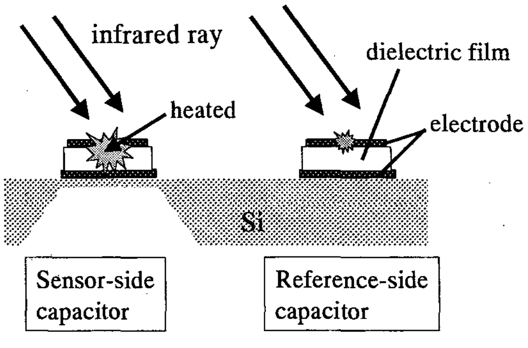

Fig 1. Cross-sectional view of an example of infrared sensor of dielectric-bolometer mode.

$Ba(Ti,Zr)O_3$ (BTZ) films are also expected to have Tc at around room temperature, with a changing ratio of Ti and Zr [4]. In this study, we performed depositions by sputtering method, which is favorable for mass-production. Films were successfully crystallized as perovskite structure, and provided excellent electrical isolation. Although there is a concern that the TCDs of thin films are smaller than those of bulk material [5], it was found that the annealing process could enlarge TCD value for thin films. The results of measurements of internal stresses of the films indicate correlation with TCD value.

2. EXPERIMENTAL PROCEDURE

BTZ thin films were deposited by radio-frequency magnetron sputtering from a $Ba(Ti,Zr)O_3$ target. The deposition conditions are shown in Table I. All films were deposited on Pt: 200 nm / Ti: 20 nm / SiO_2 / Si(100) substrates, which were successively deposited by

Table I. Sputtering conditions of BTZ thin films

Substrate	Pt/Ti/SiO_2/Si(100)
Target	Ba($Ti_{0.8}$ $Zr_{0.2}$)O_3
Sputtering gases	Ar and O_2
Sputtering pressure	1.0 Pa
O2 partial pressure	20 %
Sputtering power	200 W
Deposition rate	about 10 nm/min

Table II. Conditions of annealing processes of BTZ films

	Substrate temperature Ts [°C]	Post-annealing temperature Ta [°C]
Condition (a)	500-700	-
Condition (b)	600	600-700
Condition (c)	-	500-700

magnetron sputtering on thermally oxidized Si(100) wafer. Thicknesses of BTZ films were controlled at about 600 nm, and the deposition rate was about 11 nm/min. Depositions were performed in mixed gases of argon and oxygen at 1.0Pa, while oxygen partial pressure was held at 20%. Films were prepared with three different conditions of crystallization as shown in Table II, i.e., deposited (a) at 500-700°C, (b) at 600°C and annealed at 600-700°C for 30 min after deposition, and (c) without heating during deposition and post-annealed at 500-700°C for 30 min.

Crystal structures of the deposited films were examined with an X-ray diffractometer, Rigaku RINT2500. Dielectric constants of the films were measured with an LCR meter at 1kHz and 1.0V, with varying temperature in the range of 20°C to 60°C. Leakage current was measured with a semiconductor parameter analyzer. Residual stresses of the films were estimated by X-ray peak-shift analysis, which is called the $\sin^2\psi$ method. As required values of Young's modules and Poisson ratio, we adopted 67.0 GPa and 0.30, respectively, which are introduced as values for bulk $BaTiO_3$ [6].

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis

Figure 2 shows the X-ray diffraction (XRD) patterns of prepared Ba(Ti,Zr)O_3 thin films on the conditions (a) to (c). In Fig. 2(A), all the films deposited at 500°C to 700°C exhibited cubic perovskite peaks, and dominant orientation was (111) direction. In Fig. 2(B), peaks from cubic perovskite structure were also observed, but dominant orientation was shifted from (111) direction to (100) direction. Fig. 2(C) shows the results for films annealed after deposition. The films as deposited and annealed at 500°C were found to have an amorphous structure, and the film annealed at 600°C showed tetragonal perovskite peaks. The film annealed at 700°C also had perovskite crystal peaks, but minute cracks were observed in the film after annealing.

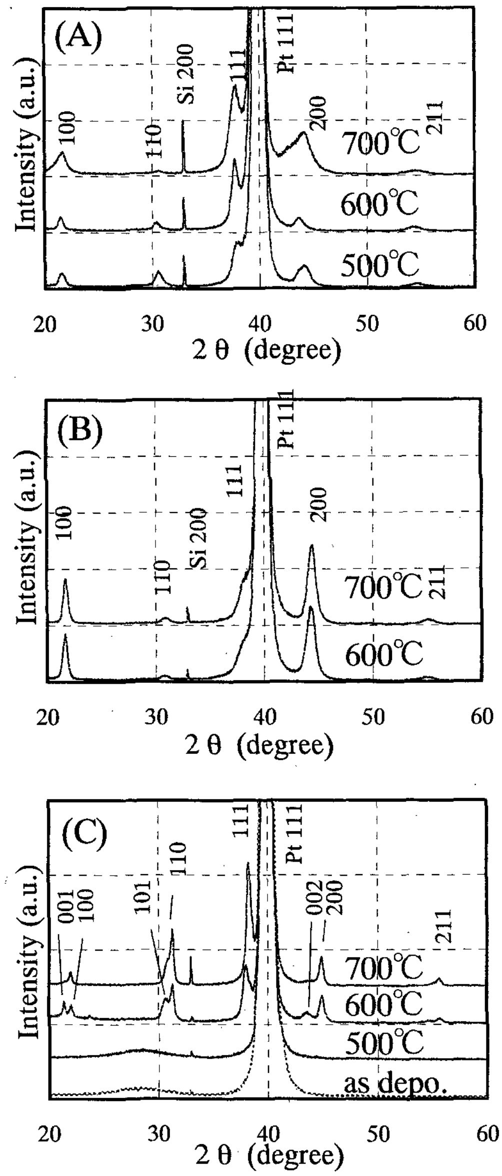

Fig 2. X-ray diffraction patterns of the films deposited on condition (A) at 500-700°C, (B) at 600°C and post-annealed at 600-700°C, and (C) at room temperature and post-annealed at 500-700°C.

3.2 Electric properties

Figure 3 shows the temperature dependence of dielectric constants of deposited films. Films deposited by condition (a) showed only a little change of dielectric constants on temperature. TCD value shows no significant increase by following annealing as shown in Fig. 3(B). On the other hand, the sample (c), crystallized from amorphous state by post-annealing, was found to indicate a larger change of permittivity on temperature. TCDs for the films deposited (a) at 600°C, (b) at 600°C and post-annealed at 600°C, and (c) at room temperature

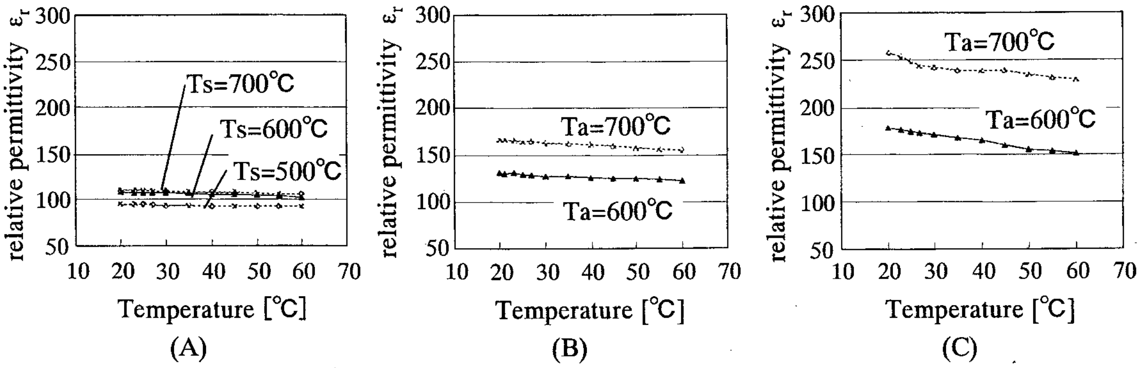

Fig 3. Temperature dependence of relative dielectric constants of BTZ films deposited on (A) condition (a) , (B) condition (b) , and (C) condition (c).

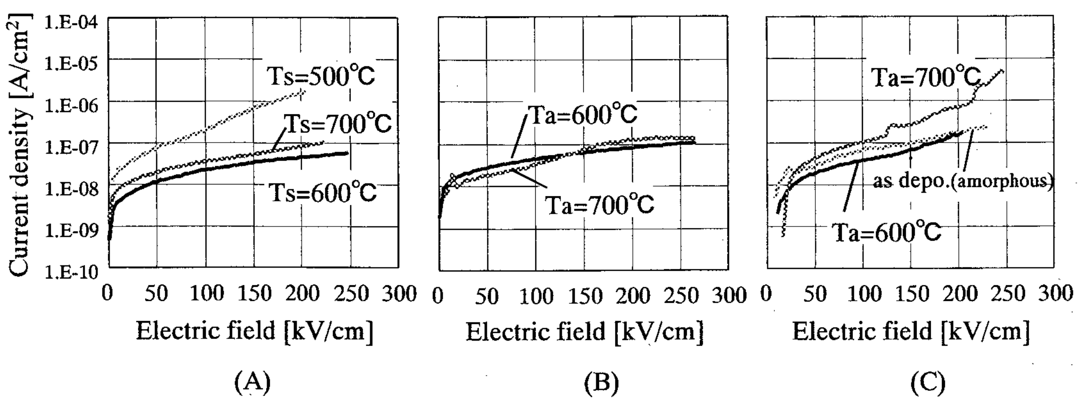

Fig 4. Current density of BTZ films deposited on (A) condition (a) , (B) condition (b), and (C) condition (c).

and post-annealed at 600°C were determined to be –0.11%/K, -0.17%/K, and -0.38%/K at 25°C, respectively. In Fig. 3, the dielectric constants of all films show monotonic decrease with increasing temperature, though the gradient is different. This fact suggests that Tc of the films was below 20°C. To make it possible to detect infrared ray from a human body, TCD value is expected to be more than 1%/K at room temperature. The TCD values obtained were still small for high-sensitive detection of infrared ray from a human body, but we think further optimization of the annealing process and composition of films such as Ti/Zr ratio, which means optimization of Tc of thin films, would successfully enlarge the TCD.

Figure 4 shows dependence of current density on electric field for BTZ films deposited on conditions (a)-(c). This figure shows that leakage currents for all the films were small enough to be used for the dielectric film of the capacitance.

3.3 Internal stress measurement

To investigate the mechanism of improvement in TCD for condition (c), we examined the residual stresses of BTZ films. The results are shown in Table III. Minute cracks were observed in the film deposited on condition (c) post-annealed at 700°C; therefore we prepared two different films similarly deposited on condition (c) post-annealed at 600°C, to increase the sample number. It was revealed that internal stresses of films deposited on conditions (a) and (b) had relatively large compressive stress. On the other hand, films deposited on condition (c) had relatively small tensile stresses.

Table III. Residual stresses of the deposited films

Condition	Ts [°C]	Ta [°C]	TCDat25°C [%/K]	Stress [GPa]
(a)	500	-	-0.11	-1.6
(a)	600	-	-0.11	-2.1
(a)	700	-	-0.14	-1.7
(b)	600	600	0.01	-1.8
(b)	600	700	-0.11	-1.7
(c)	-	600	-0.38	+0.7
(c)	-	600	-0.36	+0.8

The reason for the differences in internal stresses of the films was considered as follows: films deposited with heating substrates were compressed at the interface between the dielectric film and the Pt film, when the substrates were cooled to room temperature, due to the difference of coefficient of thermal expansion between Pt film and the dielectric film. For films deposited at room temperature, the compressive force mentioned above was not attached, and tensile force was applied because of the shrinking of dielectric films when transforming from the amorphous state to the crystalline state by post-annealing.

These results suggest to us that the internal stresses correlate with the values of TCD. As a reason for the increase in TCD value, we believe that small stress or tensile stress of films make it possible to achieve more obvious phase transition from the ferroelectric state to the paraelectric state, which leads to an increase in TCD. The detailed mechanism is under investigation.

4. CONCLUSIONS

$Ba(Ti,Zr)O_3$ thin films were deposited on $Pt/Ti/SiO_2/Si(100)$ substrates by RF magnetron sputtering. Films were deposited with different annealing processes, and were successfully crystallized as perovskite structure. It was proven that the TCD of the film annealed at 600°C after deposition from amorphous state was –0.38%/K at 25°C, which was higher than that of the film crystallized with heating substrate at 600°C, -0.11%/K. It was proven that the TCDs could be improved by post-annealing from amorphous state after deposition. Leakage currents of both films were small enough to be used for the dielectric film of the capacitor.

Films crystallized from amorphous state were found to have relatively small tensile stresses, while all films deposited with heating had large compressive stresses. We believe that the internal stress is an important factor in deciding the value of TCD. This sheds light on achieving high TCD values of dielectric films in future investigations.

5. REFERENCES

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