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Investigation of BZT thin films for tunable microwave applications

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Abstract

BZT thin films have been investigated as a prospective material for tunable microwave applications. The thin films were deposited by RF magnetron sputtering from a $Ba(Zr_{0.3}Ti_{0.7})O_3$ ceramic target on MgO single crystal substrates. By means of Rutherford backscattering (RBS), scanning electron microscopy (SEM) and X-ray diffraction (XRD), the composition, thickness and crystallinity of the thin films were analyzed, respectively. Using interdigital capacitors (IDC) with Au electrodes on thin films, the dielectric constant and loss tangent were measured as a function of bias electric field (0–7 kV/mm) and temperature (-140 to $+160\,^{\circ}C$) at low frequencies up to 1 MHz. The influence of post-annealing on the tunable dielectric properties of the thin films was studied. Tunability, defined as $\tau = [\varepsilon(0) - \varepsilon(E_{max})]/\varepsilon(0)$, can be significantly increased by increasing the annealing temperature. A tunability of 76% at $E_{max} = 7$ kV/mm and a loss tangent of 0.0078 have been achieved for the sample annealed at 1100 °C, measured at 1 kHz and room temperature. In addition, BZT thin films were also characterized at microwave frequencies up to 26.5 GHz by measuring coplanar waveguide (CPW) resonators.

Keywords: $BaTiO_3$ and titanate; Dielectric properties; Films; Tunable applications

1. Introduction

Ferroelectric materials exhibit high dielectric nonlinearity (i.e. the strong dependence of dielectric constant on bias electric field) that is attractive to tunable microwave applications. To improve the performance of many tunable high-frequency devices, it is desirable to develop high-quality thin films with evident tunability and low dielectric losses.[1–3] Up to now, most of research efforts in this area are focused on investigating $Ba_xSr_{1-x}TiO_3$ (BST) system. Many attempts have been made to optimize the preparation processing, and post-annealing has been proved to be an effective method to improve the dielectric performance of the thin films.[4–6]

By taking the advantage of high dielectric constant and relatively low leakage current, extensive studies have been made to use $Ba(Zr,Ti)O_3$ (BZT) thin films for applications of dynamic random access memory (DRAM),[7] multi-chip modules (MCMs),[8] and capacitors.[9]

In recent years, we reported our investigations of BZT material as an alternative candidate of tunable dielectrics.[10–12] It was found that BZT bulk ceramics displayed diffused ferroelectric phase transition compared to BST. Much lower dielectric constant and a more diffused phase transition were observed for BZT thick films. Especially, when measuring at low frequencies, the thick films showed comparable losses and tunability with those of BST. These studies provided valuable results, which indicate the potential usefulness of BZT material in tunable microwave applications. Up to now, literatures concerning the tunable dielectric properties of BZT thin films, especially the high-frequency performances are still rare. Therefore, it is quite necessary to carry out further investigations on the aforementioned topic.

In this paper, we present a preliminary study of the tunable dielectric behavior of BZT thin films. The samples were deposited on MgO single crystal substrates from a $Ba(Zr_{0.3}Ti_{0.7})O_3$ ceramic target by RF magnetron sputtering. Microanalyses were performed to characterize the thin films, and their dielectric constants as well as loss tangents were measured at low frequencies (up to 1 MHz) and at high frequencies (up to 26.5 GHz), respectively. Particular focus was given to investigate the influence of post-annealing at different temperatures on the microstructure and dielectric properties of BZT thin films. Such an investigation may

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provide a valuable guidance for future experimental efforts to improve the performance of the material.

Table 1
Sputtering conditions of BZT thin films

Target-Substrate distance (mm)	35
Substrate temperature (°C)	650
Sputtering gas	O_2:Ar, 10 sccm:90 sccm
Total pressure of sputtering gas (mbar)	5.5×10^{-2}
Plasma power (W)	RF 150
Deposition rate (nm/min)	3.17

2. Experimental

BZT thin films were deposited on (1 0 0) MgO single crystal substrates by RF magnetron sputtering, from a sintered stoichiometric $BaZr_{0.3}Ti_{0.7}O_3$ ceramic target with a diameter of 100 mm. The sputtering conditions are listed in Table 1.

BZT thin films were post-annealed in air for 5 h after deposition. Three annealing temperature (T_A) levels of 650, 900 and 1100 °C were used, respectively. The heating and cooling rate was fixed to 5 °C/min for all treatments.

The composition of the BZT thin films was determined by Rutherford backscattering (RBS). The surface and cross-section microstructures as well as the thickness of the thin film were observed using scanning electron microscopy (SEM) (LEO1530). The crystallographic structure and orientation of BZT thin films were analyzed using X-ray diffraction (XRD) (Siemens D5000).

The dielectric properties (dielectric constant ε_r and loss tangent tanδ) were measured as a function of temperature (−140 to +160 °C) and bias electric field (0–7 kV/mm) at low frequencies (≤1 MHz), using an Alpha-H high-resolution dielectric analyzer (Novocontrol). To obtain the values of ε_r and tanδ, capacitance and loss measurements of interdigital capacitors (IDC) were carried out, as described in Ref. [13,6].

At microwave frequencies, BZT thin films were characterized by measuring coplanar waveguides (CPW) at room temperature. The CPW with a strip width of $w = 20\ \mu m$ and a slot width of $s = 10\ \mu m$ was fabricated on thin film using standard photolithography and plating technology. The scattering parameters of CPW on various thin films were measured up to 26.5 GHz using a HP 8510B network analyzer and an on-wafer probe station. Detailed descriptions refer to Ref. [13].

3. Results and discussion

3.1. Characterization of BZT thin films

By RBS measurements (5–10% deviation of evaluation), the composition of the thin films is determined as $BaZr_xTi_y0_{3-\delta}$ ($x = 0.26$–0.34; $y = 0.72$–0.74), which matches well with the stoichiometry of the $BaZr_{0.3}Ti_{0.7}O_3$ ceramic target.

Structural measurements were made for as-deposited and annealed BZT thin films by XRD θ–2θ scans and (0 0 2) ω-scans. Exclusive (0 0 *l*) peaks were observed in all θ–2θ patterns (not shown), revealing the films to be single-phase and epitaxial in *c*-axis orientation. One remarkable feature is found that with the increment of annealing temperature, 2θ value of (0 0 *l*) peak tends to larger angle. From XRD data, the lattice constant of the thin film normal to the substrate was precisely calculated using Nelson-Riley plots of a Debye-Scherrer method described elsewhere.[14,15] The values are 4.123 Å for as-deposited film, 4.101, 4.079 and 4.061 Å for films annealed at 650, 900 and 1100 °C, respectively. It is clear that with an increase in T_A, the lattice constant gradually becomes smaller and finally close to that of the bulk material (about 4.06 Å for $BaZr_{0.3}Ti_{0.7}O_3$, Ref. [16]). The as-deposited film has a larger lattice constant, presumably due to oxygen deficiencies.[4] The change in lattice constant after annealing is attributed to an improvement in stoichiometry with respect to O_2-content in the film and a reduction in strain.[5]

The full width at half maxima (FWHM) of (0 0 2) ω-scan curves of films annealed at different T_A is shown in Fig. 1. A decrease in FWHM can be observed with an increase in T_A, which indicates a gradual improvement of the crystallinity induced by increasing annealing temperature, i.e. the higher the T_A, the higher degree of the out-of-plane crystal perfection.

Fig. 2 shows SEM images for BZT/MgO films annealed at different temperatures. It can be observed that the surface morphology of the BZT films is affected significantly by the annealing process at temperatures higher than 650 °C. The surfaces of as-deposited (not shown) and 650 °C annealed (Fig. 2a) samples are extremely smooth and homogeneous with hardly any grains discernable. "Short sticks" distribute on the originally smooth surface for the film annealed at 900 °C (Fig. 2b), which are perpendicular to each other with the length of several hundred nanometer. More pronounced grain growth occurs for the film annealed at 1100 °C. As seen in Fig. 2c, pieces of grains stick out of the surface and incline towards different directions. Some of the pieces have a length larger than 1 μm. Though grain growth at higher T_A results

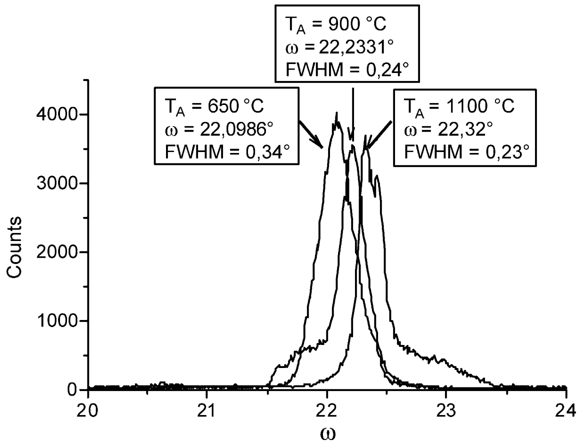

Fig. 1. (0 0 2) ω-Scan curves for BZT thin films annealed at different T_A.

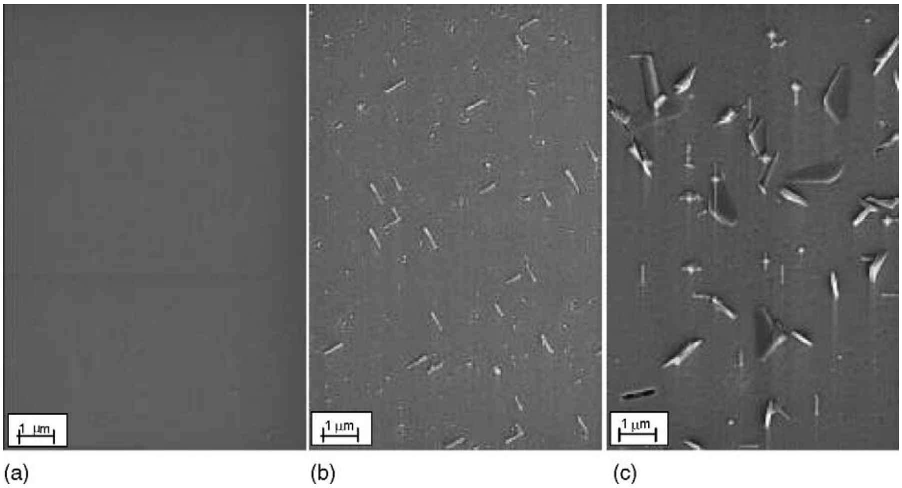

Fig. 2. SEM images for BZT thin films annealed at (a) 650 °C, (b) 900 °C and (c) 1100 °C.

in a higher surface roughness, no crack can be observed in Fig. 2(b) and (c). The reason of such abnormal grain growth upon annealing at high temperature is still not clear; one tentative explanation may be the "preferred" re-growth of some crystallites along certain axes.

To answer the question whether there exists any interaction between the BZT film material and the MgO substrate during the annealing process, mixed-powder heating investigation was proceeded. BZT and MgO powders were mixed with a weight ratio of 1:1 and calcined at 1100, 1300 and 1400 °C, respectively. XRD measurements of the calcined mixture show no new secondary-phase peak except the peaks from BZT and MgO. This may provide a convincible evidence for our assumption that the annealing only leads to the re-growth of the BZT crystallite itself, but without any reactive product arose. Further, TEM investigation is being carried out to find new proof for supporting this presumed explanation.

3.2. Dielectric properties at low frequencies

In Fig. 3, the low-frequency dielectric constant (ε_r) and loss tangent (tanδ) are plotted as a function of the temperature for annealed BZT thin films. The sample annealed at 1100 °C exhibits distinct dielectric properties. More pronounced temperature dependence is observed in dielectric constant, which is much higher than those of the samples annealed at 900 and 650 °C. Furthermore, its temperature of maximum dielectric constant ($T_{\max}$) is shifted to around 233 K, i.e. about 60 K higher than that of the sample annealed at 900 °C. In addition, the loss tangent of the sample annealed at 1100 °C increases rapidly with decreasing temperature, while for the other two samples the losses remain at a low level.

By measuring the bias dependence of the dielectric constant, the tunability can be calculated and plotted as a function of the temperature, as shown in Fig. 4. It is noteworthy that the sample annealed at 1100 °C shows a significant high tunability of 76% at room temperature, which is much higher than that of the sample annealed at 900 °C (about 12%). The sample annealed at 650 °C shows a little tunability close to zero, which is similar to that of the as-deposited sample.

Correlating the crystal structure to the dielectric properties, the crystallinity of the thin film is improved by increasing the annealing temperature up to 1100 °C; as a consequence the dielectric constant increases. In addition, the as-deposited

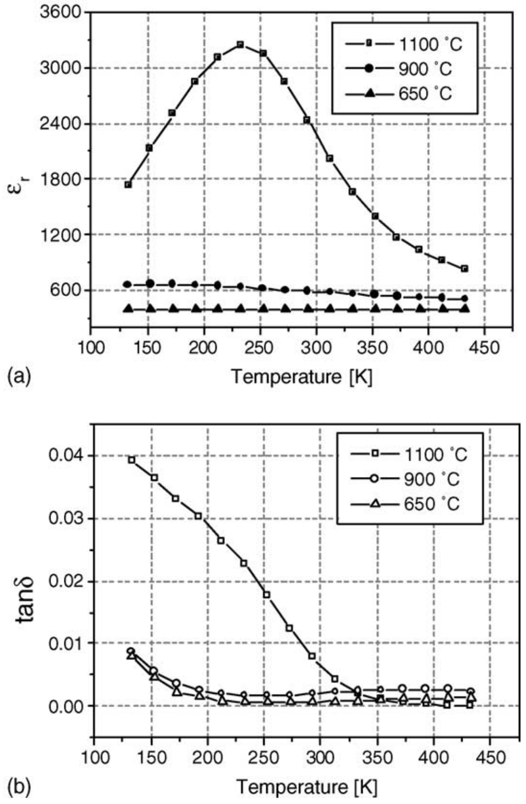

Fig. 3. Temperature dependence of (a) dielectric constant (ε_r), and (b) loss tangent (tanδ) of BZT thin films annealed at different temperatures, measured at 1 kHz.

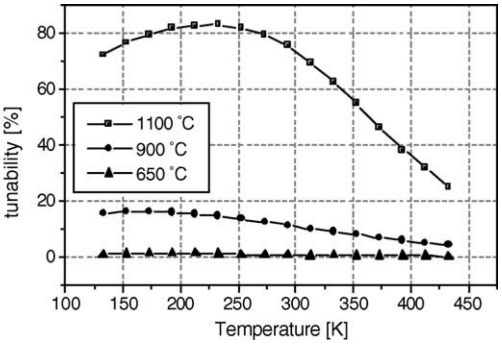

Fig. 4. Temperature dependence of tunability for BZT thin films annealed at different temperatures, measured at 1 kHz.

thin films are highly stressed, whereas the stress in the film was released after annealing, which may result in a shift of maximum dielectric constant. For the thin film with better crystallinity, higher tunability and higher losses occurred around the point of maximum dielectric constant ($T_{\max}$).

3.3. Dielectric properties at high frequencies

The high-frequency performance of BZT thin films annealed at 900 °C was gained from CPW measurements up to 26.5 GHz and at room temperature. The results are given in Fig. 5. A distinct decrease in ε_r and in τ, whereas a slight increase in tanδ with increasing frequency can be observed. A tunability of about 8.5 % is achieved at 8.25 GHz, based upon an applied E-field strength of 10 kV/mm. However, this value of tunability is not kept as the frequency increasing. It decreases to 3–4% when frequency reaching 26.5 GHz. In addition, in comparison with the value at low frequencies, the loss tangent of BZT at high frequencies is noticeably increased by a factor of about 100, i.e. higher than 20%. A similar level of such high tanδ values was also found in HF measurements for BZT thick films.[10]

In our recent work, the microwave measurements were made for BST thin films prepared using the same processing described in this paper. The results indicated that the BST thin films possessed more stable dielectric constant of about 300, higher and stable tunability of about 14%, and lower losses of <7%. Comparing with these values, the BZT thin films prepared in current study do display the disadvantages of dielectric properties in GHz-region.

By far, the dielectric properties of annealed BZT thin films have been characterized. At low frequencies, the thin films exhibit appropriate ε_r, tanδ and τ, which are comparable with those of the BST thin films.[6] However, at high frequencies, the properties of BZT thin films is indeed unsatisfactory, especially their high dielectric losses which are not applicable for tunable microwave applications in practice. Currently, work is in progress, which attempts to improve the dielectric performance of BZT thin films at high frequencies.

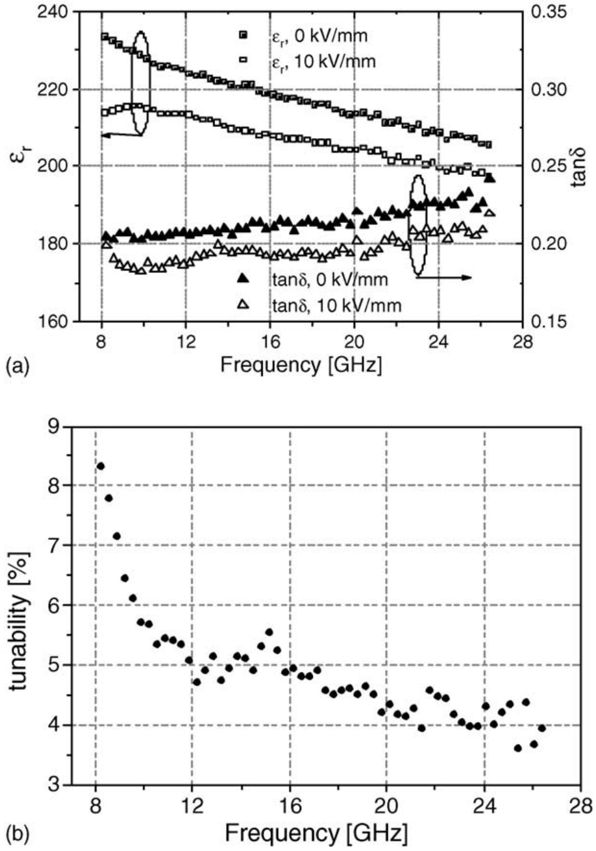

Fig. 5. Frequency dependence of (a) dielectric constant (ε_r) and loss tangent (tanδ), and (b) tunability of BZT thin film annealed at 900 °C, measured in GHz-region, at room temperature.

4. Summary

The effects of post-annealing on the microstructure and dielectric properties of RF sputtered BZT thin films were investigated. In low frequency region, tunability can be significantly increased by increasing the annealing temperature. A tunability of 76% at $E_{\max} = 7$ kV/mm and a loss tangent of 0.0078 have been achieved for a sample annealed at 1100 °C. The improvement of the crystallinity and the release of the stress after annealing are deemed to be the dominant factors, which affect the dielectric properties. By CPW measurements, a tunability of 8.5% was achieved at 8.25 GHz for BZT thin film annealed at 900 °C, upon an applied E-field of 10 kV/mm. Distinctly high tanδ values of more than 20% were observed in the GHz-region. Further study has to be done to improve their HF performance.

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