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Microwave dielectric properties of the $(Ba_xSr_{1-x})TiO_3$ thin films on alumina substrate

Peng Qi, Ji-wei Zhai *, Xi Yao

Functional Materials Research Laboratory, Tongji University, Shanghai 200092, China

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Abstract

Barium strontium titanate, $(Ba_xSr_{1-x})TiO_3$ (BST) thin films have been prepared on alumina substrate by sol–gel technique. The X-ray patterns analysis indicated that the thin films are perovskite and polycrystalline structure. The interdigital electrode with 140 nm thickness Au/Ti was fabricated on the film with the finger length of 80 μm, width of 10 μm and gaps of 5 μm. The temperature dependence of dielectric constant of the BST thin films in the range from −50 °C to 50 °C was measured at 1 MHz. The dielectric properties of the BST thin films were measured by HP 8510C vector network analyzer from 50 MHz to 20 GHz.

Keywords: B. Thin films; B. Interdigital electrode; C. Microwave properties; $(Ba_xSr_{1-x})TiO_3$

1. Introduction

In recent years, a great attention has been paid to electric field tunable dielectric materials due to their potential applications in tunable microwave devices. Barium strontium titanate $(Ba_xSr_{1-x})TiO_3$ provides a continuous solid solution of $BaTiO_3$ and $SrTiO_3$ over the whole concentration region. The Curie temperature (T_c) of BST increases linearly with increasing Ba content. The strong field dependent dielectric constant of BST makes it attractive for tunable microwave devices.

In order to match circuits containing the high dielectric constant components with conventional microwave circuits, thin film technology of the ferroelectrics was suggested such as sputtering [1], pulsed laser deposition [2], and chemical vapor deposition [3]. Meanwhile, the different dielectric properties of films are obtained. Among these methods, the sol–gel method has some advantages over others, for example, a precise control of the composition, lower processing temperature, low cost and the ability to deposit large area film on different substrates.

From now on, many study works had been reported on the dielectric properties of the BST films in the range of low frequency (kHz to MHz), however, many of the films are expected to be used in microwave frequency. Therefore, in this present study, $(Ba_{0.4}Sr_{0.6})TiO_3$(BST40), $(Ba_{0.5}Sr_{0.5})TiO_3$(BST50), $(Ba_{0.6}Sr_{0.4})TiO_3$(BST60) thin films were derived on alumina substrate by sol–gel technique. The microwave dielectric properties of BST films are investigated.

2. Experimental

Barium acetate $[Ba(CH_3COO)_2]$, strontium acetate $[Sr(CH_3COO)_2]$ and tetra-n-butyl titanate $[Ti(OC_4H_9)_4]$ were used as starting materials. Glacial acetic acid (CH_3COOH), and acetylacetone ($CH_3COCH_2COCH_3$) were used as solvent and polymerizing agents, respectively. Barium acetate and strontium acetate were mixed according to a predetermined ratio and then added in the glacial acetic acid solution and heated to 100 °C for 10 min.Then the solution was mixed with the solution of tetra-n-butyl titanate and acetylacetone under constant stirring. Finally, glacial acetic acid was added to control viscosity and the concentration of solution. The concentration of the final solution was adjusted to 0.3 M. The BST films were prepared by spin-coating at 3000 rpm for 20 s. Each layer was dried at 200 °C for 60 s, and prefired at 500 °C for 10 min to remove residual organics. The films with thickness of 800 nm were achieved by repeated spin-coating and heating treatment. Finally, the samples were heated to 950 °C for 3 h to crystalline the films.

* Corresponding author. Tel.: +86 21 65980544; fax: +86 21 65985179.
E-mail address: apzhai@tongji.edu.cn (J.-w. Zhai).

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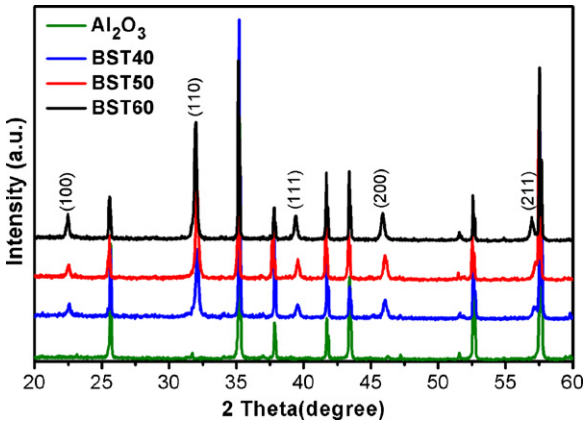

Fig. 1. XRD patterns of the $(Ba_xSr_{1-x})TiO_3$ ($x = 0.4, 0.5, 0.6$)films on alumina substrate.

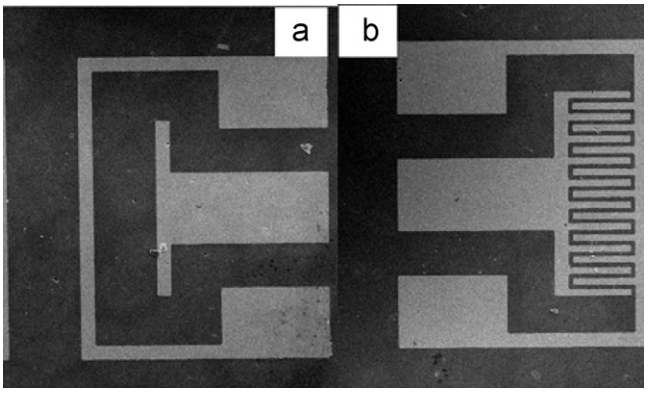

Fig. 3. The electrode figure for measuring the microwave dielectric property of the BST films. (a) For calibration and (b) for measurement.

X-ray diffraction (XRD, Bruker D8 Advanced, Germany) analysis was performed to identify phase structure of the BST films. The interdigital electrode with thickness of Au 100 nm/Ti 40 nm was fabricated on the film with the finger length of 80 μm, width of 10 μm and gaps of 5 μm. The surface morphology of the film was determined by FESEM (FEI Quanta 200 FEG). The microwave dielectric property of the BST thin film was measured HP 8510C vector network analyzer from 50 MHz to 20 GHz.

3. Results and discussion

Fig. 1 shows the XRD patterns of different Ba contents of the BST films on the alumina substrates annealed at 950 °C for 3 h. All the films exhibit a good crystalline quality and a pure perovskite phase. With increasing Ba content, the (2 0 0) peak of BST is evidently shifted towards a lower angle. This shift is due to the radius of the Ba^{2+} (1.61 Å) larger than that of Sr^{2+} (1.28 Å), which leads to the lattice parameter of the BST film becoming larger, so the peak of the BST will shift to lower angle.

The microstructures of the BST films with different Ba contents deposited on alumina substrate are shown in Fig. 2. Some small voids between crystalline grains of the BST40 films on the alumina substrate are observed by the FESEM, whereas the surface morphology of BST thin film is relatively dense and the grains became larger with increasing Ba content. Because there are large amounts of organic solvent in the sol–gels, the films should experience shrinkage and internal stress as a result of removal of these materials during the heat treatment. The perfect sintering temperature of Barium titanate and strontium titanate are 1200 °C and 1400 °C for bulk ceramics, respectively [4,5]. Crystallization may also be earlier with higher Ba content, it may result in a larger grain size for the same heat treatment. The photograph of the measurement setup using the interdigital capacitor which was prepared on the films is shown in Fig. 3.

The temperature dependence of dielectric constant of the BST thin films ranging from −50 °C to 50 °C is shown in Fig. 4. The dielectric constant of the films can be transformed using the following formula [6]:

$$\varepsilon = \varepsilon_s + \frac{C - K(1+\varepsilon_s)}{K[1 - \exp(-4.6h/g + w)]} \quad (1)$$

where $\varepsilon_s = 10$ is the dielectric constant of alumina substrate, $h = 800$ nm is the film's thickness, and $g = 10$ μm and $w = 5$ μm are the width of gap and finger. K is the constant which is related to the width of the gap and finger can be defined as

$$K = 6.5\left(\frac{g}{g+w}\right)^2 + 1.08\frac{g}{g+w} + 2.37 \quad (2)$$

C is the capacitance per unit finger length per electrode section of width and equal to $C_a/(LN)$ where C_a is the measured

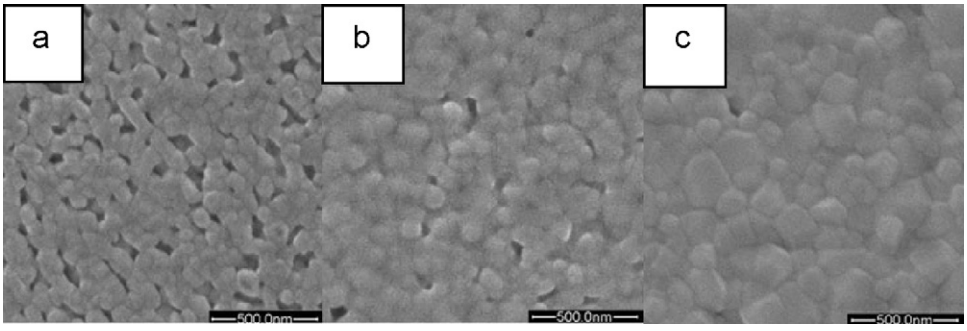

Fig. 2. FESEM images of the $(Ba_xSr_{1-x})TiO_3$ ($x = 0.4, 0.5, 0.6$) films on alumina substrate.

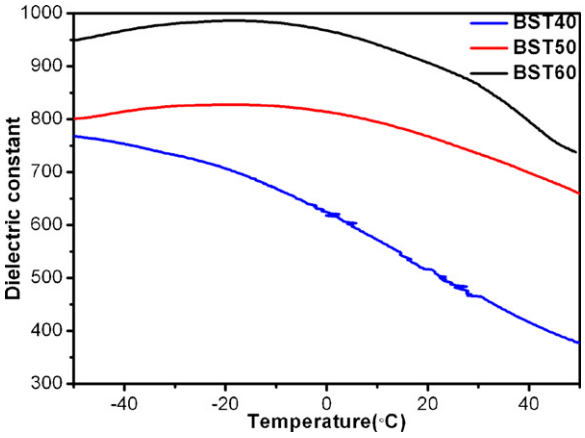

Fig. 4. Temperature dependence of the dielectric constant of the (Ba_xSr_{1-x})-)TiO_3 ($x = 0.4$, 0.5, 0.6) films at 1 MHz.

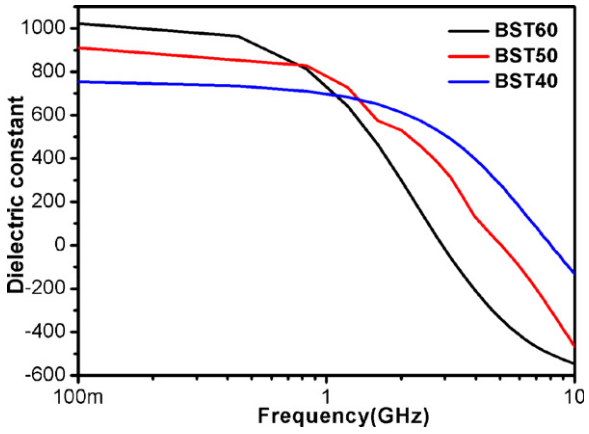

Fig. 5. The dielectric constant vs. frequencies of the $(Ba_xSr_{1-x})TiO_3$ ($x = 0.4$, 0.5, 0.6) films on the alumina substrate at room temperature.

capacitance, $L = 80$ μm is the length for interdigital fingers, and $N = 18$ is the number of gaps for interdigital capacitor. So the result is

$$\varepsilon = 925 * C_m(F\,p) - 35 \tag{3}$$

The T_c of the BST40, BST50, BST60 films on the alumina substrate are below −50 °C, −30 °C, and −20 °C, respectively. The dielectric constant of the BST films became larger with increasing Ba content due to the grain size of BST films. As the grain size increases, the maximum of dielectric constant increases [7], this behavior is agreed with Fig. 2. All the BST thin films show a broad peak at Curie temperature. The main cause of the suppression of the dielectric constant peak is that the grain sizes of the BST film are much smaller than their counterparts of bulk ceramics and the grain boundary increases [8]. The ferroelectric and paraelectric phases coexist in the temperature range of diffusion phase transition. Phase transitions show such a broad dielectric constant maximum and large deviation from the Curie-Weiss [9]. With increasing Ba content, the T_c will shift to higher temperature. This is accordant with others' work [10]. The Curie peaks shift to a lower temperature compared to their counterparts of bulk ceramics [11]. This is due to the strain induced by the lattice misfit or difference in thermal expansion between the film and the substrate. In general, if there is a tensile stress along the in-plane direction inside the film, the T_c of the BST films is likely to shift towards the high temperature. Conversely, a compressive stress may lower the T_c of the films [12]. As a result, the properties of the films can be markedly different than the intrinsic properties of the corresponding unstrained bulk materials. The compressive stress will occur induced by the lattice misfit and difference in thermal expansion between the BST film and the alumina substrate, so the T_c of the BST thin films shift towards the low temperature. This is consistent with the report of Wang et al. [13].

Fig. 5 shows the dielectric property of the BST film in microwave range. The *S*-parameters of the IDC and the pad pattern were converted to the *Y*-parameters (admittance-parameters) [14]. The capacitance C of the whole IDC can be obtained using the following equations:

$$C = \frac{\mathrm{Im}\{Y\}}{\omega} \tag{4}$$

ω stands for angular frequency. The capacitance was converted to dielectric constant by Eq. (3). In order to estimate whether this method is accurate or not, the IDC was directly fabricated on the alumina substrate whose dielectric constant is about 10 from 1 MHz to 10 GHz. The dielectric constant of the alumina is about 12 by above method. The dielectric constant of the BST60, BST50, BST40 films are about 1050, 900, 760 at 100 MHz. The dielectric constant of the films gradually decreased in low frequency. Because the trapped charges, space charges, lots of dipole and domains have contributions to the dielectric constant of the BST films. But some of them cannot switch with increasing the frequency. The dielectric constant of the BST films sharply decreases with increasing the frequency. This is due to the self-resonance of the parasitic inductance and capacitance. The IDC on the BST films can be modeled with the equivalent LCR circuit. This model does not take into account parasitic inductances and resistances. But the electromagnetic filed also propagates through the substrate, so the capacitance of IDC is the sum of BST thin film and the substrate. The capacitance of the substrate is more significant at higher frequency. The capacitance of BST will bigger when eliminating the parasitic capacitance [15]. The resonant frequency is:

$$f = \frac{1}{\sqrt{2\pi LC}} \tag{5}$$

The L is the parasitic inductance and C is the capacitance of the IDC. With increasing the dielectric constant of the BST films, the capacitance of the IDC will increase from Eq. (2), so the resonant frequency will shift to low frequency. The dielectric constant of the films will increase with increasing Ba content, the resonant frequencies are 2 GHz, 0.8 GHz and 0.4 GHz with BST40, BST50 and BST60 films, respectively. This measurement matches the conclusion very well. Over the resonant frequency, the dielectric constant of the BST films sharply decreases. The dielectric constant of BST60 is below zero at about 3 GHz. This is not the intrinsic dielectric property of the

BST films, but induced by the inductance and capacitance. The same condition had been reported by Kakemoto et al. [16]. The capacitance of the IDC relates to the width of the gaps and the finger [17]. So the resonant frequency can be shifted by changing the length of the finger and the width of the gaps.

4. Conclusions

BST thin films have been prepared on alumina substrate by sol–gel technique, and the IDC structures were fabricated on the films. All the BST thin films show a broad peak in dielectric constant curves at Curie temperature and the Curie peaks shift to a lower temperature compared to their counterparts of bulk ceramics. This is due to the compressive stress in the films. The microwave properties of the BST films were measured through the *S*-parameters of the IDC. Then it is converted to the dielectric constant of the films. The dielectric constant sharply decreases with increasing the frequency due to the self-resonance of the parasitic inductance and capacitance.

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