Dielectric properties of $(Ba_{0.8}Sr_{0.2})(Zr_xTi_{1-x})O_3$ thin films grown by pulsed-laser deposition

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Abstract

Thin films of $(Ba_{0.8}Sr_{0.2})(Zr_xTi_{1-x})O_3$ ($x = 0$, 0.08, 0.18, 0.36) were grown on $Pt/TiO_2/SiO_2/Si$ substrate at temperature of 550 °C by pulsed-laser deposition. XRD patterns show that the thin films are well crystallized into perovskite structure. Electric properties of the thin films, including the dielectric constant, dielectric loss, tunability, polarization loops, and leakage current, were investigated. With an increasing of Zr content, the tunability of dielectric constant and ferroelectric polarization of the thin films decrease and the ferroelectricity disappears. Significantly, it is found that the dielectric loss and leakage current of thin films are reduced by the substitution of Ti with Zr. Furthermore, the leakage current is decreased about three-order of magnitude for an electric field of 100 kV/cm with increasing of Zr content.
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1. Introduction

As a Pb-free environmental friendly ferroelectric material, barium strontium titanate (BST) has attracted much attention. Especially, BST thin films have been investigated widely for potential application in random access memory and tunable microwave devices. Studies have shown that BST thin films have high dielectric constant, high tunability and excellent ferroelectric properties, but the exploration of BST thin films with low dielectric loss and low leakage current is still necessary for the application in devices. BST is a solid solution family composed of barium titanate and strontium titanate with the Curie temperature covering a wide range from 400 to 30 K. Usually, for the ABO_3 perovskite, substituting A and/or B sites by other ions can modify electric behavior of the material. The addition of Sr into the Ba site of barium titanate can shift the ferroelectric to paraelectric phase transition from high temperature to low temperature, resulting in a BST material with high dielectric constant at room temper-

ature. A substitution of Ti by Zr has also been found to be an effective way to decrease the Curie temperature, and exhibits several interesting features in the dielectric behavior of $BaTiO_3$ ceramics. Investigations have shown that the phase transition behavior of $Ba(Ti, Zr)O_3$ (BTZ) materials can be changed from a normal phase transition to diffusive, and further become a relaxor phase transition.[1] The modified BTZ has shown systematic variations in the dielectric, piezoelectric, and phase transition characteristics in the ceramic and single crystal forms.[2,3]

In the paraelectric phase, BTZ thin films are attractive candidates for making dynamic random access memories and tunable dielectric devices. Recently, BTZ thin films by rf magnetron and chemical solution decomposition have been reported.[4–6] Investigations on BTZ thin films have shown that BTZ thin films have highly insulator characterization, however, dependence of dielectric properties on Zr content has not been well understand. In this study, $(Ba_{0.8}Sr_{0.2})(Zr_xTi_{1-x})O_3$ thin films with various Zr content were fabricated on $Pt/TiO_2/SiO_2/Si$ substrate by pulsed laser deposition (PLD) technique, and investigation of electric properties of the thin films shows that dielectric loss and leakage current are reduced by Zr doping.

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2. Experimental

BSTZ targets were prepared by conventional solid-state reaction process, using $BaCO_3$, $SrCO_3$, TiO_2 and ZrO_2 with an analytic reagent grade of purity. Raw materials with stoichiometric composition of $(Ba_{0.8}Sr_{0.2})(Zr_xTi_{1-x})O_3$ ($x = 0$, 0.08, 0.18, 0.36) were milled, and then calcined at a temperature of 1000 °C. The calcined powders were pulverized and pressed into disk, then sintered at temperature of 1400 °C for 12 h.

Thin films of BSTZ were prepared by PLD technique by employing a XeCl excimer laser (308 nm, 20 ns and 4 Hz). The BSTZ thin films were deposited on the $Pt/TiO_2/SiO_2/Si$ substrates as bottom electrodes at 550 °C at oxygen pressure of 1 Pa. The thickness of BSTZ thin films was about 640 nm as measured by a surface profile measuring system (DEKTAK III, USA).

Crystalline phase and structure of the BSTZ thin films were analyzed by X-ray diffraction (XRD) employing Cu $K\alpha$ radiation (40 kV, 50 mA). For dielectric measurements, Pt top electrodes with a diameter of 0.2 mm were deposited through a shadow mask onto the BSTZ thin films at pressure of 1×10^{-3} Pa at room temperature. The dielectric constant and dielectric loss of the metal-insulator-metal (MIM) capacitor of the BSTZ thin films were measured at 1 MHz using HIOKI 3532 LCR HiTESTER with an oscillating voltage of 50 mV. Polarizations and leakage current were measured using a RT6000 ferroelectric analyzer.

3. Results and discussion

XRD patterns of BSTZ thin films are shown in Fig. 1a for the thin films BSTZ with $x = 0$, 0.08, 0.18 and 0.36, noted as Zr0, Zr8, Zr18 and Zr36, respectively. As revealed from the XRD patterns, all peaks, indexed in Fig. 1a, correspond to a perovskite phase, which indicates all BSTZ thin films formed in single phase. Moreover, it is observed that the diffraction peaks shift to a lower angle with increasing of Zr content. This is clearly shown in Fig. 1b for the (1 1 1) diffraction peak of BSTZ thin films. Such a kind of peak shift to lower diffraction angle indicates an increase in the lattice parameter. Due to the fact that ionic radius of Zr^{4+} (0.72 Å) is lager than that of the Ti^{4+} (0.605 Å),[7] the substitution of Ti^{4+} by Zr^{4+} can increase the lattice parameter of the thin film, which is also evidenced in the XRD patterns of target ceramics. In addition, the diffraction peak of the thin films is shift to lower angle, when compared to the correspondingly peak in ceramics. This suggests there is a larger lattice parameter in the thin film than that of target material for the same composition. The lattice parameter of thin films is usually lager than that of the bulk materials, because of non-equilibrium and highly distorted interface exists in the thin films deposited in vacuum.

Capacitance–voltage (C–V) relationships of the BSTZ thin films are shown in Fig. 2a, and the corresponding dielectric loss shown in Fig. 2b. At zero electric field, both the dielec-
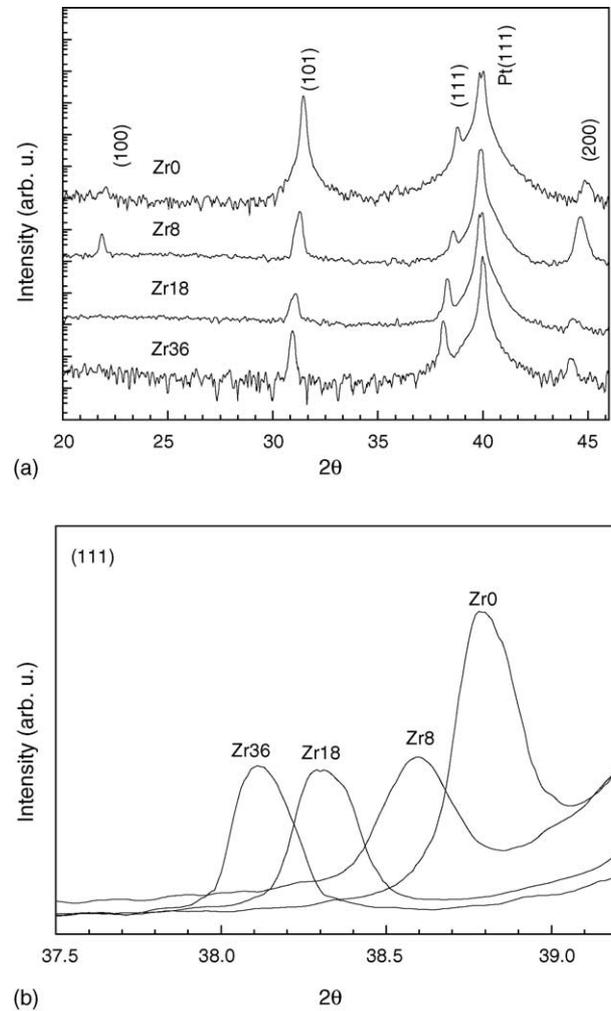

Fig. 1. XRD patterns of the BSTZ thin films with various Zr content (a). Shift of (1 1 1) diffraction peak of BZT thin films to lower diffraction angle with the increase in Zr content (b).

tric constant and dielectric loss of the thin films decreases with increasing of Zr content. The decrease of dielectric constant and loss is related to the transition of materials from the ferroelectric to paraelectric phase with addition of Zr. As it is well know, at room temperature, that BSTZ with $x = 0$ is in tetragonal phase and the BTSZ with $x = 0.36$ is in cubic phase. Furthermore, with increasing of bias electric field, the dielectric constant and dielectric loss decrease. Such a kind of decrease of dielectric loss with increasing electric field is related to pinning effect of domain or movable charge defects. The characterization of dielectric constant depending on the bias dc voltage provides a useful foreground in tunable devices. Tunability of dielectric constant of the thin films defined as $[\varepsilon_r(0) - \varepsilon_r(E)]/\varepsilon_r(0)$ can be calculated from the C–V relationships. The tunability of the thin films at the electric field of 330 kV/cm decreases with increasing Zr content.

The dependences of dielectric constant and tunability on the Zr content have been reported in the reference.[8] The mechanism of the relationship between dielectric constant
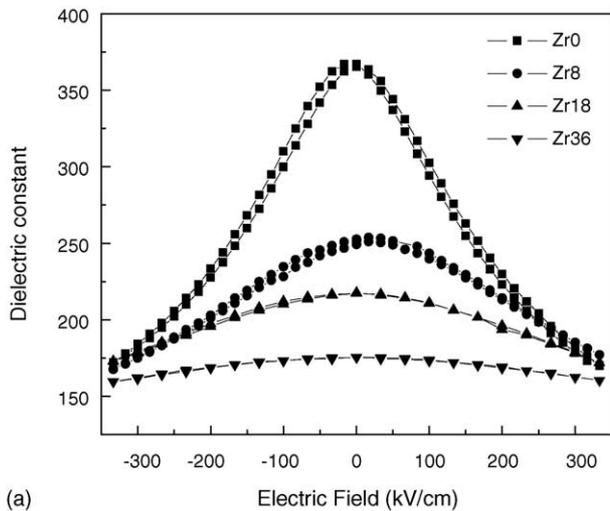
(a)
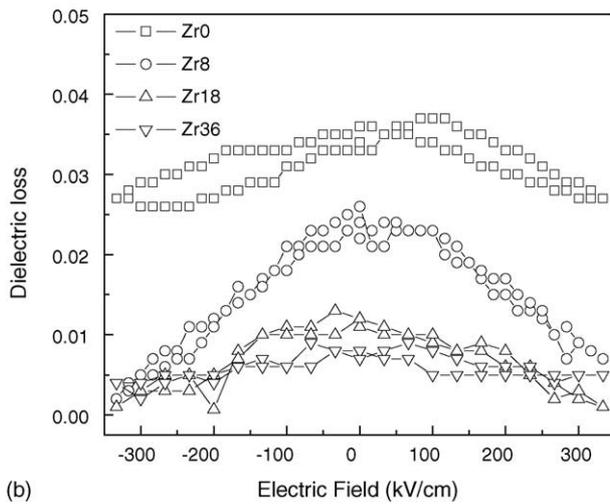
(b)

Fig. 2. Capacitance–voltage (*C–V*) relationships (a) and corresponding dielectric loss (b) of the BSTZ thin films.

and external bias dc field is not well understood yet. According Johnson's formula derived from Helmhotz free energy,[9] the tunability is directly proportion to the dielectric constant of the material, which is well demonstrated in our results. From Fig. 2, it is observed that both dielectric constant and loss for the thin film with $x = 0$ show hysteresis behavior, and that of other thin films have no obvious hysteresis behavior. The hysteresis behavior of the BSTZ thin films could result from the ferroelectricity of the thin film, which is evidenced by the polarization measurement shown later.

Fig. 3 shows the polarization versus electric field of the BSTZ thin films. The thin film with $x = 0$ exhibits a hysteresis loop, which indicates ferroelectric behavior, and the other thin films exhibits linear relationships between the polarization and electric field. For the single crystal BTZ, with the increasing of Zr content, the phase transition temperature T_C (cubic to tetragonal) decreases, both T_2 (tetragonal to orthorhombic) and T_3 (orthorhombic to rhombohedral) in-
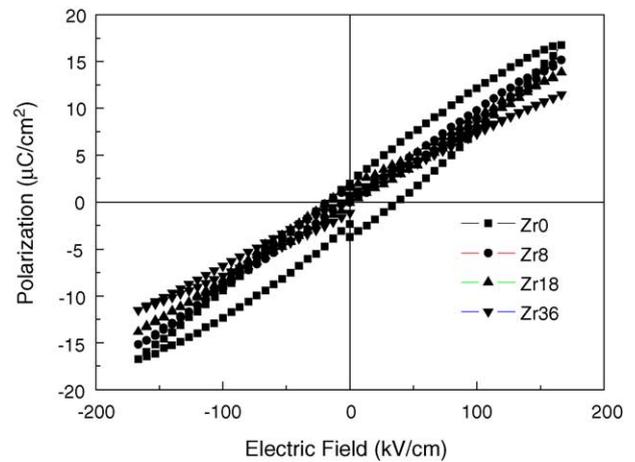

Fig. 3. Polarization hysteresis loops for different BSTZ thin films.

crease. When the content of Zr is larger than a critical value, all these three-phase transitions merge, and T_C decreases with increase of Zr content.[10] In our case, with the substitution of Ti with Zr, the BSTZ thin films exhibit a paraelectric behavior because of the decrease of phase transition temperature T_C.

The leakage current of the BSTZ thin films is measured at room temperature as shown in Fig. 4. The leakage current of the BSTZ thin films reduces significantly with increasing of Zr content. For example, the leakage current is reduced about three-order of magnitude in BSTZ with $x = 0.36$ comparing $x = 0$ at the electric field of 100 kV/cm. This can understood as follows. The electron transport by hopping between Ti^{4+} and Ti^{3+} is one of the major paths of leakage current in barium titanate. The valence of Zr^{4+} is chemically more stable than that of Ti^{4+}, and Zr^{4+} ion also has a lager ionic size inducing of increasing of the perovskite lattice. The conduction by electron hopping between Ti^{4+} and Ti^{3+} can be depressed by the substitution of Ti with Zr, because Zr^{4+} would block the path between two adjacent Ti
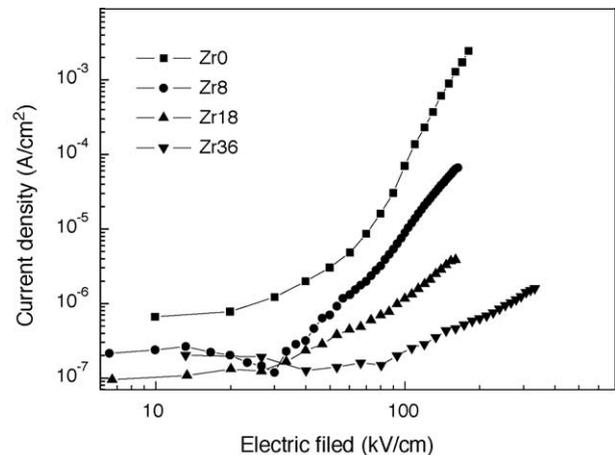

Fig. 4. Current density vs. electric field of BSTZ thin films at room temperature.

ions and enlarge hopping distance. Therefore, both the reduction of leakage current and dielectric loss with increasing of Zr content in BSTZ thin films can ascribed to the depressed probability of the electron hopping between Ti^{4+} and Ti^{3+}.

4. Conclusion

BSTZ thin films with various Zr content have been successfully fabricated by pulsed-laser deposition. The lattice parameters of BSTZ thin films increase with increasing of Zr content. Investigation of dielectric properties shows that the BSTZ thin films have a low dielectric loss and leakage current with reduced dielectric constant and tunability. The measurement of ferroelectric properties indicates that the materials are transformed from the ferroelectric phase to paraelectric phase after the substitution of Ti by Zr. The improved dielectric loss and leakage current will be significant for the use of the environmental friendly material in devices.

Acknowledgements

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