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Preparation and tunability properties of $Ba(Zr_xTi_{1-x})O_3$ thin films grown by a sol–gel process

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Abstract

$Ba(Zr_xTi_{1-x})O_3$ (BZT) thin films were deposited via sol–gel process on $LaNiO_3$, as buffer layer, and Pt-coated silicon substrates. The BZT films were perovskite phase and showed a (1 0 0) preferred orientation dependent upon zirconium content. The grain size decreased and the microstructure became dense with increasing zirconium content. The addition of Zr to the $BaTiO_3$ lattice decreased the grain size of the crystallized films. The temperature dependent dielectric constant revealed that the thin films have relaxor behavior and diffuse phase transition characteristics that depend on the substitution of Zr for Ti in $BaTiO_3$. The dependence of electrical properties on film thickness has been studied, with the emphasis placed on dielectric nonlinear characteristics. $Ba(Zr_{0.35}Ti_{65})O_3$ thin films with weak temperature dependence of tunability in the temperature range from 0 to 130 °C could be attractive materials for situations in which precise control of temperature would be either impossible or too expensive.

Keywords: Sol–gel processes; Films; Perovskites; Dielectric properties; Tunability

1. Introduction

$Ba(Zr_xTi_{1-x})O_3$ ceramics and thin films have recently received renewal attention due to a high-strain level and high-piezoelectric effect in both single crystals and ceramics.[1–4] In addition, the results indicate that the system exhibits a pinched phase transition with increasing Zr concentration. It is obtained by substituting ions at the B site of the $BaTiO_3$ with Zr in compounds of the perovskite structure ABO_3. It is reported that an increase in the Zr content induces a reduction in the average grain size, decreases the dielectric constant, and maintains a leakage current low and stable. This is possible because the Zr^{4+} ion has larger ionic size (0.087 nm) than Ti^{4+}(0.068 nm).[3,4]

$Ba(Ti_{1-x}Zr_x)O_3$ materials have an orthorhombic or rhombohedral structure at room temperature.[5,6] It is expected that the enhanced dielectric performance can be also achievable at around room temperature in the ⟨1 0 0⟩ preferred orientation BZT thin films. Since $Ba(Ti_{1-x}Zr_x)O_3$ films may be applied to capacitors, tunable microwave devices, actuators, and dynamic random access memories because they are environment-friendly, it is important to investigate the tunability and effect of thickness on the dielectric properties.

In this paper, we report on $BaZr_xTi_{1-x}O_3$ thin film deposition on $LaNiO_3$, as buffer layer on Pt/Ti/SiO_2/Si substrates and analyze the relationship of composition, microstructure, and dielectric behavior of the thin films. Dielectric properties of the thin films are studied as a function of thickness, temperature, and electric field.

2. Experimental

The barium acetate [$Ba(CH_3COO)_2$], [$Zr(OC_3H_7)_4$], and [$Ti(OC_3H_7)_4$] were used as starting materials. Acetic acid was used as solvent. $Ba(CH_3COO)_2$ was heated and dissolved in acetic acid. Zirconium isopropoxide and titanium isopropoxide were mixed in a ratio according to a predetermined number ($Ba(Zr_xTi_{1-x})O_3$, $x = 0$, 0.05, 0.18, and 0.35), and then dissolved into heated glacial acetic acid. After cooling to room temperature, ethylene glycol CH_2OHCH_2OH was added to control the viscosity and cracking of films; the solution was mixed and refluxed for 1 h. Barium acetate was added in glacial acetic acid solution and heated to 120 °C to reflux for 1 h. Ba:glacial acetic acid was in a ratio equal to 1:10 mol. After cooling to room temperature, the mixed solution of $Ti(OC_3H_7)_4$,

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$Zr(OC_3H_7)_4$, and acetylacetone (AcAc $CH_3COCH_2COCH_3$) was added slowly under continuous stirring in the solution ((Ti+Zr):AcAc = 1:2 mol). Finally, 2-methoxyethanol and ethylene glycol were added to control the viscosity, cracking of films and the concentration of solution. The concentration of the final solution was adjusted to about 0.3 M. After aging the hydrolyzed solution for 24 h, thin film deposition was carried out on the $LaNiO_3$/Pt/Ti/SiO_2/Si(1 0 0) substrates by spin coating at 3000 rpm for 30 s each layer. Each spin-coated BZT layer was subsequently heat treated at 500 °C for 5 min. The coating and heat treatment procedures were repeated several times until the desired thickness was reached. A final anneal in flowing O_2 at high temperature of 700 °C for 30 min crystallize the amorphous films.

The crystalline phase of the thin films was identified by X-ray diffraction (SIEMENS D-500 powder diffractometer). The film thickness and the surface morphology were determined by FESEM. For electrical measurements, the top gold electrode of a 200 μm square was deposited by DC-sputtering. The capacitance–voltage (*C–V*) and capacitance–temperature (*C–T*) characteristics were measured using an Agilent 4284A LCR meter. The sample's temperature was varied by using a Delta chamber.

3. Results and discussion

Fig. 1 shows the XRD patterns for the BZT thin films. It is evident that the BZT films are polycrystalline. Perovskite peaks were observed for all the films of different composition. It is evident that the BZT films were perovskite phase and had (1 0 0) preferred orientation when deposited on LNO/Pt/Ti/SiO_2/Si(1 0 0) substrate. The insert shows BZT(2 0 0) peaks in a magnified angular scale. A slight shift of the (2 0 0) plane is shown in the inset of Fig. 1. A gradual shift of 2θ angles to the low angle side with increasing Zr content in the BZT films

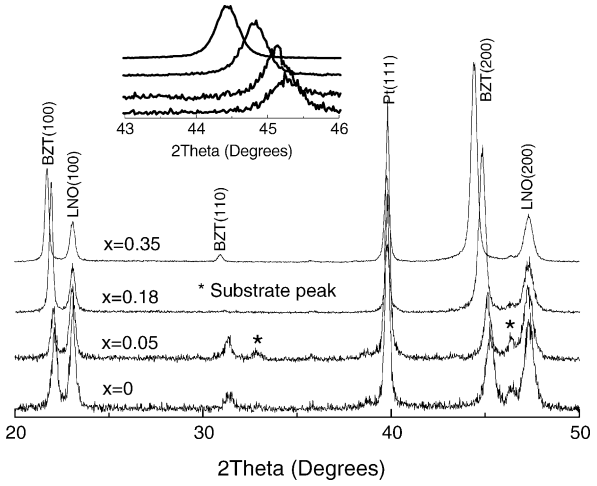

Fig. 1. XRD patterns of sol–gel deposited $BaZr_xTi_{1-x}O_3$ thin films on $LaNiO_3$/Pt/Ti/SiO_2/Si(1 0 0): (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.18$, and (d) $x = 0.35$.

reveals the expansion of perovskite lattice by the addition of the Zr in $BaTiO_3$. The grain size decreased and the microstructure became dense with increasing of zirconium content. The addition of Zr to the $BaTiO_3$ lattice decreased the grain size of the crystallized films.

The dielectric constant and dielectric loss of $x = 0.05$ and $x = 0.35$ composition thin films as a function of temperature and frequency are show in Fig. 2. With increasing zirconium content, the characteristics of diffuse phase transition were increased. With increase in Zr content to $x = 0.35$, the ferroelectric behavior of the thin films changes to a relaxor-like character. The broadening of transition together with the shift of the Curie temperature towards higher temperature in thin films of normal ferroelectrics ceramics was due to the influence of the interfaces in the films,[7] the fine grained structure,[8] and unrelaxed growth strain.[9,10]

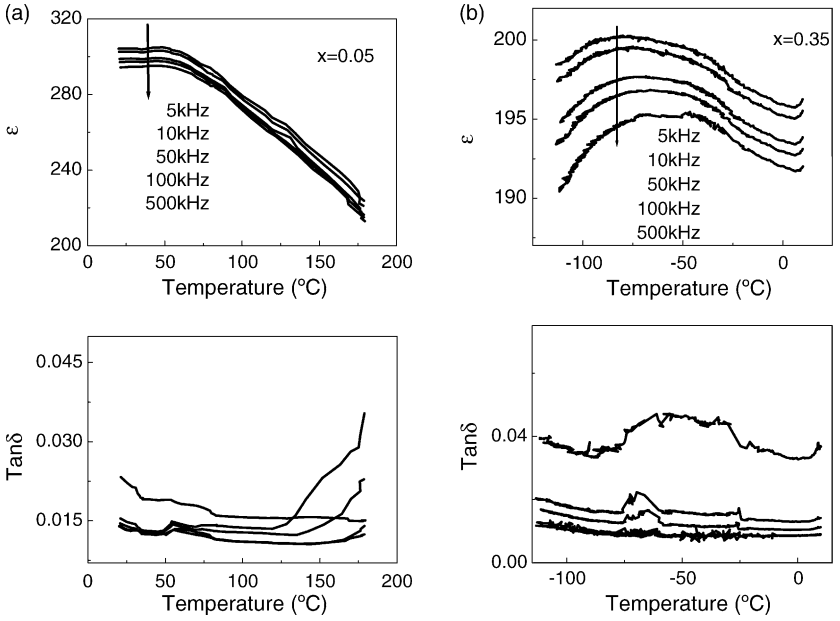

Fig. 2. The dielectric constant and dielectric loss of $BaZr_xTi_{1-x}O_3$ thin films: (a) $x = 0.05$ and (b) $x = 0.35$, as a function of temperature and frequency.

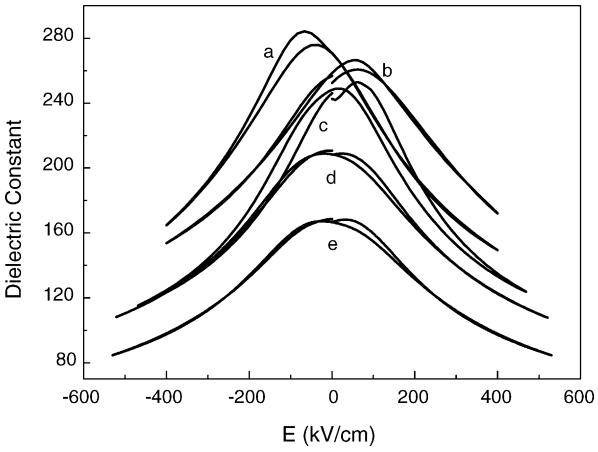

Fig. 3. ϵ–E characteristics of $BaZr_{0.35}Ti_{0.65}O_3$ thin films for different thickness: (a) 150 nm, (b) 200 nm, (c) 320 nm, (d) 480 nm, and (e) 660 nm (measurement frequency 100 kHz).

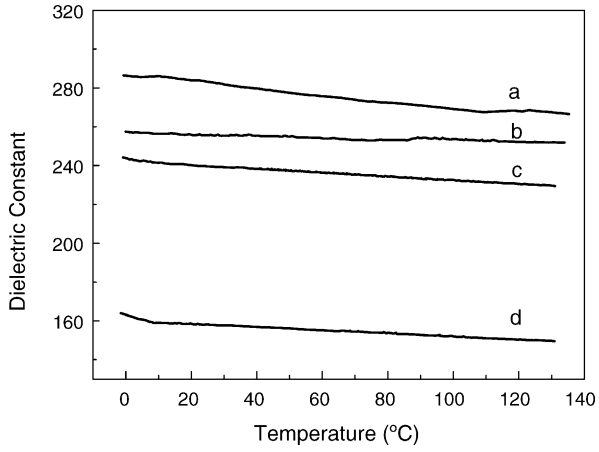

Fig. 4. The dielectric constant and dielectric loss of $BaZr_{0.35}Ti_{0.65}O_3$ thin films for different thickness: (a) 150 nm, (b) 200 nm, (c) 320 nm, and (d) 660 nm, as a function of temperature (measurement frequency 100 kHz).

Fig. 3 shows the room temperature dielectric constant versus electric field characteristics as a function of BZT film thickness. Dielectric constant and dielectric loss of the films was measured at 100 kHz, with an AC field of 0.4 kV/cm superimposed on a slowly varying DC bias field. The DC bias was stepped through 0.2 V intervals and held 1 s prior to capacitance measurement. The loss tangent measurements as a function of bias voltage gave curves of similar shape to the tuning curves. Losses for all samples were less than 2% at room temperature and zero bias. The zero-field dielectric constant decreased systematically with increasing film thickness, while at higher fields, the dielectric constant was also thickness dependent, not consistent with previous observations.[8,11] We will discuss this phenomenon in another paper.

The shape of the ϵ–E curves change and depend on the thickness. The ϵ–E characteristics are noticeably different in the positive and negative voltage region, especially for the thinner films. This asymmetry of the ϵ–E characteristic is due to the film/substrate interface effects, consistent with previous reports.[12,13]

It is revealed that the BZT possesses high tunability even in the paraelectric phase. The dielectric constant tunability of the films can be expressed as $(\epsilon(0) - \epsilon(E))/\epsilon(0)$. The tunability of $BaZr_{0.35}Ti_{0.65}O_3$ films for different thickness is about 42%, at an applied field of 400 kV/cm and measurement frequency of 100 kHz. These values are comparable to those of polycrystalline BST thin films.[14] The existence of polar-clusters and their coarsening with increasing temperature may be one of the reasons for the tunability of dielectric constant in BZT thin films.[15]

The dielectric constant and dielectric loss of $x = 0.35$ composition thin films as a function of temperature and thickness are show in Fig. 4. The data reveal a relatively flat profile, in the range of temperature from 0 to 130 °C, for $BaZr_{0.35}Ti_{0.65}O_3$ films having different thickness. As expected, there is no steep change occurring in this range of temperature due to parelectric state.

Fig. 5 shows the temperature dependence of dielectric constant as a function of externally applied DC voltage for the

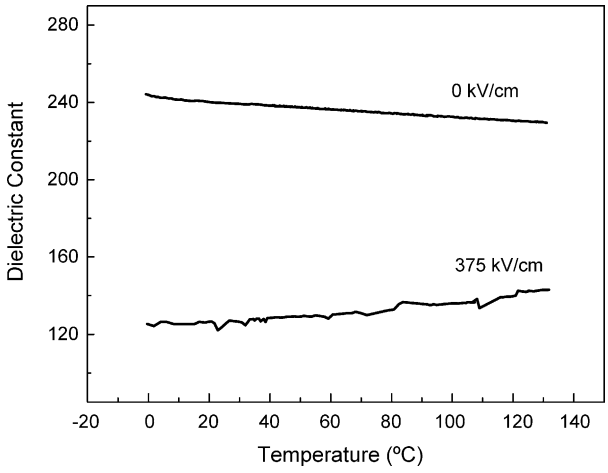

Fig. 5. Temperature dependence of the measured dielectric constant at zero-field and 375 kV/cm for the thickness of 320 nm sample (measurement frequency 100 kHz).

$Ba(Zr_{0.35}Ti_{65})O_3$ thin films, measured at 100 kHz. All show a relatively flat profile under different DC bias field in the temperature range of 0–130 °C. The change of dielectric constant versus DC bias field is quite appreciable, indicating a high tunability over a wide temperature range.

Generally, ferroelectric material is tunable in only a narrow temperature range near a phase transition. $BaZr_{0.35}Ti_{0.65}O_3$ thin film with weak temperature dependence of tunability could make attractive materials for situations in which precise control of temperature would be either impossible or too expensive.

4. Conclusions

The $Ba(Zr_xTi_{1-x})O_3$ ($x = 0$, 0.05, 0.15, and 0.35) thin films were deposited via sol–gel process on $LaNiO_3$-coated silicon substrates. The films were of single perovskite phase and had (1 0 0) preferred orientation. The temperature dependent dielectric measurements revealed that the thin films have relaxor behavior and diffuse phase transition characteristics dependent upon zirconium content. It was revealed that the

$BaZr_{0.35}Ti_{0.65}O_3$ possess high tunability even in the paraelectric phase. The tunability of $BaZr_{0.35}Ti_{0.65}O_3$ films for different thickness is about 42%, at an applied field of 400 kV/cm and measurement frequency of 100 kHz. The zero-field dielectric constant decreased systematically with increasing film thickness. Generally, ferroelectric material is tunable in only a narrow temperature range near a phase transition. $BaZr_{0.35}Ti_{0.65}O_3$ thin film with weak temperature dependence of tunability could be attractive materials for situations in which precise control of temperature would be either impossible or too expensive.

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