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**In-situ observation of nanomechanical behavior arising from critical-
temperature-induced phase transformation in Ba(Zr_{0.2}Ti
0.8)O₃-0.5(Ba_{0.7}Ca_{0.3})TiO₃ thin film**

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In-situ observation of nanomechanical behavior arising from critical-temperature-induced phase transformation in Ba(Zr_{0.2}Ti_{0.8})O_{3-0.5}(Ba_{0.7}Ca_{0.3})TiO₃ thin film

Abstract

In this Letter, we use the nanoindentation technique and vary the testing temperature to above and below critical values to study the nanomechanical features of a strong Pb-free piezoelectric Ba(Zr_{0.2}Ti_{0.8})O_{3-0.5}(Ba_{0.7}Ca_{0.3})TiO₃ (BZT-0.5BCT) thin film across its piezoelectric-optimal morphotropic phase boundary. The mechanisms responsible for the Young's modulus and hardness evolution are then discussed. An X-ray diffraction method that can detect the d(110) variation associated with the change in the inclination angle ψ of the (110) plane was developed to quantify the residual stress in the BZT-0.5BCT films.

Keywords

3, 7ca0, ba0, 5, o3, 8, 2ti, zr0, ba, transformation, phase, induced, temperature, critical, arising, behavior, film, nanomechanical, thin, observation, situ, tio

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***In-situ* observation of nanomechanical behavior arising from critical-temperature-induced phase transformation in $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{-}0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ thin film**

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In this Letter, we use the nanoindentation technique and vary the testing temperature to above and below critical values to study the nanomechanical features of a strong Pb-free piezoelectric $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{-}0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (BZT-0.5BCT) thin film across its piezoelectric-optimal morphotropic phase boundary. The mechanisms responsible for the Young's modulus and hardness evolution are then discussed. An X-ray diffraction method that can detect the $d_{(110)}$ variation associated with the change in the inclination angle ψ of the (110) plane was developed to quantify the residual stress in the BZT-0.5BCT films. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818121>]

The rapid growth of the field of micro-electromechanical systems (MEMS) has generated intense research activities^{1–3} to develop techniques for the characterization of mechanical properties such as elastic modulus, hardness, interface adhesion, and residual stress for thin film materials.^{4–6} $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{-}0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (BZT-BCT) solid solution⁷ is one such promising piezoelectric system: for compositions located in proximity to the ferroelectric-ferroelectric morphotropic phase boundary (MPB), and the piezoelectric coefficient d_{33} has been reported⁷ as up to 560–620 pC/N, which is comparable with that of high-end or soft lead zirconate titanate piezoelectric transducer (PZT) ($d_{33} = 500\text{--}600$ pC/N). It seems that the MPB composition is extraordinarily “soft.” Despite the sensitive electric signal response, an understanding of the micromechanical response at the MPB composition, such as the microscale Young's modulus and the microscale hardness, especially as observed by *in-situ* nanoindentation, is still missing. Also, in one application of interest, the BZT-BCT film for use as an acoustic emission sensor, the film must be between two electrical contacts to take advantage of the piezoelectric effect when it deforms due to an incoming elastic stress wave. Therefore, it is of interest to evaluate the nanomechanical properties of BZT-BCT films on the actual layered materials being considered for use in applications. Moreover, residual stress will be produced inevitably in thin films synthesis due to the structural misfit and the thermal misfit of the thin film/substrate interface. For example, the processing from high temperature to low temperature during the deposition of the thin films can cause the thermal stress.^{8,9} Much research has

shown that residual compressive stress may cause film delamination from the substrate, and residual tensile stress may cause surface cracking in films.^{10,11} Obviously, the residual stress in a thin film has important effects on the film's service life, and the determination of residual stress in ferroelectric thin films is indispensable.

Recent progress in *in situ* atomic force microscopy (AFM) now enables the direct observation of mechanical behavior in ceramics,^{12–14} semiconductors,¹⁵ and even in metallic materials.¹⁶ Using *in situ* AFM nanoindentation, we can subject the specimen to an arbitrary temperature and dynamically observe the deformation processes, even at the microscopic scale.^{17,18} As an excellent tool in determining the mechanical properties of ferroelectric materials, the nanoindentation technique is capable of providing information on aspects such as hardness and elastic properties.^{19–21} In addition, nanoindentation is ideal for measuring the mechanical properties of thin films. It is well known that, if the substrate is harder than the film, the substrate influence can be negligible when the penetration depth of the indenter is less than $\sim 10\%$ of the film thickness.²² To measure the residual stresses in BZT-BCT thin film, several techniques, including the nanoindentation fracture method,⁵ X-ray diffraction (XRD),⁶ and Raman spectroscopy,²³ were used.

In this Letter, BZT-BCT near the MPB composition was fabricated by the sol-gel method, and its structure and ferroelectric properties were studied. The residual stress in the BZT-BCT ferroelectric thin film was evaluated by the conventional XRD diffraction method. We used the high temperature nanoindentation technique to observe the Young's modulus and hardness evolution across the temperature-induced MPB in BZT-0.5BCT thin film. The dependence of Young's modulus, E , and hardness, H , on temperature is

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addressed, and discussion of the underlying mechanisms is presented based on the linear thermal expansion coefficient (LTEC) dependence on the temperature.

The BZT-0.5BCT film was prepared via a sol-gel method on Pt(111)/Ti/SiO₂/Si(100) substrate by annealing at 850 °C according to a previously described procedure,²⁴ and the film thickness was $\sim 1 \mu\text{m}$. The phase structure of the BZT-xBCT thin film was characterized by using XRD in a Bruker AXS D8 DISCOVER with Cu K_α radiation ($\lambda = 1.5405 \text{ \AA}$). Fig. 1(a) presents the XRD pattern of the as-deposited BZT-BCT thin film. It is evident that the film is of perovskite polycrystalline phase without any impurities. To calculate the average value of strain within the BZT-BCT film, the (110) diffraction peaks at $\sim 31.8^\circ$ in 2θ were measured by varying the angle (ψ) between the diffraction vector and the surface normal. The BZT-BCT (110) lattice spacing, d_{110} , was determined by a Lorentzian fit of the diffraction peak centers. It is reasonable to assume that the stress state in the sample is isotropic, biaxial in the plane of the film, and zero for all other components of the stress tensor. In this context, the d value is a function of the tilt angle of the grains. According to the elasticity theory in solids, the relationship between the plane spacing and the tilt angle can be expressed as follows:²⁵

$$\sigma = \frac{E}{(1 + \nu)\sin^2 \psi} \left(\frac{d_i - d_n}{d_n} \right), \quad (1)$$

FIG. 1. (a) XRD pattern of BZT-0.5BCT thin film, (b) XRD spectra of (110) planes for different X-ray tilt angles ψ , and (c) dependence with linear fitting of the value of $(d_i - d_n)/d_n$ against $\sin^2 \psi$ for the BZT-BCT thin film.

where E is the Young's modulus, ν is the Poisson's ratio, d_n and d_i are, respectively, the spacing of the planes parallel to the surface and of the planes whose normals are inclined at an angle of ψ . Diffraction patterns were collected at five values of ψ : 0° , 20.7° , 30° , 37.8° , and 45° as shown in Fig. 1(b). The (110) reflection around $2\theta = 31.8^\circ$ was used for the stress analysis. To decrease the error, it was measured five times for each angle. From fitting the experimental data to Eq. (1) [Fig. 1(c)], the residual stress obtained is about 1.66 GPa, which is slightly higher than for other ferroelectric films.²⁶

For characterization of the ferroelectric properties of the BZT-BCT film, circular Pt top electrodes 0.1 mm in diameter were deposited on the film surface by magnetron sputtering. P - E hysteresis loops were measured using a Premier II test system (Radiant Technologies), as shown in Fig. 2. The remnant polarization (P_r) values and the coercive field (V_c) were $10 \mu\text{C}/\text{cm}^2$ and 5 V, respectively, which were slightly lower than our previous results.²⁴

The hardness and elastic modulus of the BZT-0.5BCT film were measured using a Micro Materials NanoTest with a Berkovich diamond indenter at different temperatures, room temperature (RT), and 60, 95, and 120 °C. Nanoindentation has been proven to be a powerful technique for characterization of the mechanical response of nanoscale materials. The surface and substrate effects are negligible if the nanoindentation tests are performed at certain penetration depths less than one tenth of the film thickness. In our indentation tests, the indentation depth was about 100 nm, that is, about one tenth of the BZT-0.5BCT film thickness. Each indentation test consisted of loading, holding the indenter at peak load for 5 s, and unloading completely. Fig. 3(a) shows the load-displacement curves at different temperatures, and the variations of elastic modulus and hardness with temperature are given in Fig. 3(b). Young's modulus was found to decrease from 151.2 GPa at RT to 131.91 GPa at 60 °C, and then increase to 156.97 GPa at 120 °C. Fig. 4 shows the statistical distribution of the Young's modulus of the BZT-BCT film, which follows a Gaussian distribution. The similar trends between the hardness and the modulus suggest that the underlying deformations are fundamentally same: hardness is regarded as the resistance to

FIG. 2. Hysteresis loops for BZT-0.5BCT film.

FIG. 3. (a) Typical load-displacement indentation curves for BZT-0.5BCT thin film under different temperatures. (b) Variation of Young's modulus and hardness as a function of temperature.

plastic deformation and Young's modulus reflects the elastic deformation behavior.

To reveal the underlying mechanism for the unusual behavior of the mechanical properties mentioned above, thermomechanical analysis (TMA 402 F3, NETZSCH, Germany) was performed in air atmosphere to investigate the thermomechanical behavior of the BZT-0.5BCT film. The temperature was scanned from room temperature to 200 °C at a heating rate of 5 °C/min. The change in the linear expansion coefficient with temperature of the BZT-BCT film is shown in Fig. 5. The linear thermal expansion coefficient is found to substantially increase with temperature and peak at 70 °C, above which it surprisingly decreases up to 100 °C. This result implies that phase transformations take place at 70 and 100 °C. According to the phase-diagram⁷ for

FIG. 5. Variation of linear expansion coefficient with temperature in BZT-BCT film. Dashed lines indicate T_{MPB} and T_C .

the BZT-BCT system, the two pseudo-binaries, BZT and BCT, exhibit symmetry-lowering transitions from high-temperature paraelectric cubic phase (*C*) to low-temperature ferroelectric rhombohedral (*R*) and tetragonal (*T*) phases with spontaneous polarizations P_S aligned along the [111] and [100] directions, respectively. The MPB is located in the transition region between *R* and *T*. Therefore, 70 and 100 °C may be regarded as the MPB temperature and the Curie temperature (T_C), respectively. The difference between the phase transformation temperatures observed in our film sample and ones reported⁷ is possibly attributable to deviation in the composition. The thermomechanical behavior of the sample can effectively explain the temperature dependence of the Young's modulus and the hardness. When the temperature is lower than 60 °C, the atomic distance will increase with rising temperature due to thermal expansion and weaken the interatomic force, resulting in the decrease of the Young's modulus and hardness. Thereafter, their increase with temperature is mainly due to the *R*-phase to *T*-phase transformation around 70 °C, and the *T*-phase to *C*-phase transformation around 100 °C. During these structural transformations, the structure become more compact, and the interatomic force is further strengthened, as the cubic phase is the most compact among the three crystal structures. The more compact the crystal structure is, the higher the interatomic bonding energy, and the higher the hardness and Young's modulus.

In summary, the BZT-BCT polycrystalline film was deposited on Pt/Ti/SiO₂/Si substrate by the sol-gel process. An XRD method, which was based on the detection of the variation in the $d_{(110)}$ value versus the inclination angle ψ of the plane (110), was developed to effectively determine the residual stress in the BZT-BCT film. Results show that the film has relatively large residual stress of 1.66 GPa. The nanomechanical properties were studied using *in-situ* AFM nanoindentation and varying the temperature across its piezoelectric-optimal MPB. The Young's modulus E and hardness H both first decrease with rising temperature up to 60 °C and then substantially increase. The enhancement of the interatomic bonding energy due to phase transformation may explain this unusual mechanical behavior in BZT-BCT film.

FIG. 4. Distribution of Young's modulus for BZT-BCT film at (a) RT, (b) 60 °C, (c) 95 °C, and (d) 120 °C.

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