An investigation of the nanomechanical properties of 0.5Ba(Ti0.8Zr0.2)O3-0.5(Ba0.7Ca0.3)TiO3 thin films

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Abstract
For practical application, the functional piezoelectric film in microelectromechanical systems should meet the requirement of physical properties, as well as the mechanical properties. In this article, 0.5Ba(Ti0.8Zr0.2)O3-0.5(Ba0.7Ca0.3)TiO3 (0.5BZT-0.5BCT) thin films with varied properties were prepared on (100) Si substrates via a sol-gel technique at different annealing temperatures. The effects of the annealing temperature on the morphology, piezoelectricity, hardness, and elastic modulus were studied. Particular attention was paid to the surface frictional behavior of films, and the changes in the friction force can be radically explained in terms of differences in the hardness/elastic modulus ratio and the residual stress of films. And, it reveals that the higher ratio of hardness to elastic modulus and tensile residual stress can contribute to a lower friction force for 0.5BZT-0.5BCT film during sling friction.

Keywords
TiO, 5Ba, films, thin, properties, nanomechanical, investigation, TiO3, 3, 7CaO, BaO, 5, O3, 2, 8ZrO

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details
Cai, Z., Wang, Z., Wang, H., Cheng, Z., Li, B., Guo, X., Kimura, H. & Kasahara, A. (2015). An investigation of the nanomechanical properties of 0.5Ba(Ti0.8Zr0.2)O3-0.5(Ba0.7Ca0.3)TiO3 thin films. Journal of the American Ceramic Society, 98 (1), 114-118.

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This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/1299
An investigation of the nanomechanical properties of 
$(1-x)\text{BaTi}_{0.8}\text{Zr}_{0.2}\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ thin films


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BaTi$_{0.8}$Zr$_{0.2}$O$_3$-0.5(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ thin films were prepared on (100) Si substrates via a sol-gel technique at different annealing temperatures. The effects of the annealing temperature on the morphology, piezoelectricity, hardness, and elastic modulus were studied. Particular attention was paid to the frictional behavior of films, and the changes in the friction force can be radically explained in terms of differences in the hardness/elastic modulus ratio and the residual stress of films.

Keywords: BZT-BCT, annealing temperature, friction, hardness/modulus ratio

Piezoelectric thin films have been essential materials in microelectromechanical systems (MEMS), which can combine sensing, information processing, and execution in one device and have been extensively used in aviation, optoelectronics, biotechnology, and other fields [1,2]. Compared with the macroscopic engineering
world, the miniaturization and high surface-area-to-volume ratio of MEMS devices result in very high surface forces such as frictional and adhesive forces, which seriously undermine the lifetime, reliability, and performance of MEMS devices [3,4]. Common experience and scientific studies show that both a mechanical and an electrical effect contribute to high adhesion [5-7]. Therefore, it is of great importance to understand the frictional behavior at the micro-/nano-scale. A better understanding of the factors affecting the tribological behavior of MEMS devices is also expected to enable improvements in the design and operation of devices. Recently, atomic force microscopy (AFM) has been proved to be a very useful technique to study frictional behavior on the nanoscopic scale [8], making insights into the intrinsic interfacial phenomena possible.

Pb(Zr,Ti)O₃ (PZT) piezoelectric films, exhibiting an excellent piezoelectric coefficient \(d_{33}\) [9], have been widely studied for application in MEMS devices such as generators, accelerometers, and pressure sensors over the past few decades [10-12]. Due to Pb toxicity, many researchers are making efforts to develop lead-free piezoelectric materials with high performance, and among them, Ba₅Ti₀.₈Zr₀.₂O₃-x(Ba₀.₇Ca₀.₃)TiO₃ (BZT-xBCT) [13] solid solution has attracted great attention. For the composition near the morphotropic phase boundary (MPB), \(d_{33}\) can reach as high as 560-620 pC/N. BZT-BCT thin film is found to be a potential candidate to replace PZT in MEMS devices, and much work has been conducted with respect to its fabrication, phase diagram, and electrical properties [14-16]. There has been little research, however, on the nanomechanical properties of BZT-BCT films,
including their hardness \((H)\), elastic modulus \((E)\), and tribological behavior, and an understanding of the underlying factors affecting tribological properties is still lacking.

In this paper, BZT-0.5BCT thin films were fabricated on (100) Si substrate through the sol-gel technique. After deposition, the thin films were annealed at different temperatures. Their microstructure was investigated, as well as their piezoelectric and nanomechanical properties. Particular attention was paid to the evolution of the tribological properties with sintering temperature in the BZT-0.5BCT films, which can be fully explained in terms of the differences in residual stress and the \(H/E\) ratio of the films.

The fabrication of the BZT-0.5BCT thin film coating was based on our previous research and is presented in detail elsewhere [17]. The films were then annealed under four different temperatures: 650\(^\circ\)C, 700\(^\circ\)C, 750\(^\circ\)C, and 800\(^\circ\)C. The thickness of these films is approximately 800 nm, as measured by field emission scanning electron microscopy (not shown). The phase structure of all the samples was determined by X-ray diffraction (XRD) using a Rigaku Rint 2200 V powder diffractometer with graphite monochromatized Cu K\(\alpha\) radiation \((\lambda = 0.15405\) nm\), at a scanning rate of 1\(^\circ\)/min. The surface morphology of the crystallized microstructure of the BZT-0.5BCT films was observed by atomic force microscopy (AFM) (Nano Cute SII). The measurements of local piezoelectric displacement were carried out by keeping the scanning probe microscope (SPM) tip fixed on the grain of interest with a DC voltage from -40 to 40 V to record the piezoresponse signal. The nanomechanical properties,
including elastic modulus ($E$) and hardness ($H$), were measured via a Micro Materials NanoTest instrument with a Berkovich diamond indenter. To minimize the error, every sample was measured in a 5×5 matrix. The tribological properties were measured through force-distance curves in the friction mode of the lateral force microscope (LFM) in contact mode, and the applied force was small, in the range of 0–20 nN.

The XRD patterns for BZT-0.5BCT films annealed at different temperatures are shown in Fig. 1. Compared with the films annealed at temperatures of 650$^\circ$C and 800$^\circ$C, the BZT-0.5BCT films annealed at 700$^\circ$C and 750$^\circ$C consist of single perovskite phase and have better crystallinity than the other samples, as evidenced by a sharpening of the diffraction peaks. At 650$^\circ$C, crystallization is not complete, with pyrochlore phase and perovskite phase coexisting in the film. When the post-annealing temperature was raised to 800$^\circ$C, very small amounts of impurities appeared in the film. This is mainly because the higher annealing temperature (800$^\circ$C) could provide enough energy for Ca and Zr to diffuse from the pervoskite structure to react with oxygen.

The inset in Fig. 2(a) contains a typical AFM image of the BZT-0.5BCT thin film annealed at 800$^\circ$C. It is obvious that the film exhibits a smooth surface and dense microstructure with homogeneous grain size. Fig. 2(a) summarizes the root mean square (RMS) roughness value and grain size dependence on the annealing temperature. As the post-annealing temperature increases from 700$^\circ$C to 800$^\circ$C, the average grain size increases from 38 to 59 nm, while the RMS surface roughness decreases from 7.10 to 3.31 nm. In the BZT-0.5BCT film sintering process, diffusion
is the main means of mass transfer and is controlled by the vacancy concentration gradient. G. C. Kuczynski [18] proposed the neck stress model, as shown in Fig. 2(b). When two spherical particles come into contact with each other, the stress in the neck surface, $\sigma_p$, is tensile, while the stress in the center of contact for the particles, $\sigma_2$, is compressive. It has been calculated that [19] the formation energy for a vacancy in the tensile stress areas is lower than in the compressive ones, resulting in a higher vacancy density in the neck surface than at the contact center. Therefore, the vacancy diffusion would run from the neck surface to the contact center, while the atoms diffuse along the opposite direction. The main sources for the atoms include the surface, and intracell and grain boundaries, and the corresponding diffusion paths are shown in Fig. 2(b). With the filling in of the neck and migration of structural units in contact areas, the pore shrinks, and the particles approach each other. As a result, the porosity decreases, and grains are developed at elevated temperatures. The higher the temperature is, the higher the self-diffusion coefficient will be. Hence, the grain size increases, and the roughness decreases with increasing annealing temperature, which is consistent with the AFM results.

Fig. 3(a) presents the typical piezoelectric response dependence of the applied voltage for the BZT-0.5BCT film annealed at 800°C. As can be seen, a well-shaped displacement-voltage ($D$-$V$) “butterfly” loop is obtained with a maximum displacement of 3.11 nm at 34 V. Because of the unexpected shift of the intersection of the $D$-$V$ loop, the $d_{33}$ can be calculated according to the modified law of the converse piezoelectric effect:
where $D_0$ and $V_0$ are the piezoelectric deformation and voltage at the intersection, respectively. The piezoelectric hysteresis loop ($d_{33}$-$V$) is determined from the $D$-$V$ curve by Eq. (1), and the local effective piezoelectric coefficient $d_{33}$ is estimated to be approximately 112 pm/V at 10 V. This is comparable to the piezoelectric response of PZT thin films (125 pm/V) [20]. Fig. 3(b) summarizes the $d_{33}$ dependence on the annealing temperature, and it can be seen that the $d_{33}$ increases as the post-annealing temperature increases. The piezoelectricity for the 650°C film is poor because of the presence of a non-ferroelectric pyrochlore phase, while for nanocrystalline films, the trend in $d_{33}$ with annealing temperature can be explained by the grain boundary (GB) effect. It is well known that [21] GBs are non-ferroelectric and could provide possible sites for space-charge “pinning”. The thus-formed space-charge layer would hinder polarization in the film by its space-charge field, in other words, reduce the piezoelectricity of the film [22]. Therefore, it is reasonable to observe a larger piezoelectric coefficient in the film annealed at high temperature.

The variations of $E$ and $H$ with annealing temperature are given in Fig. 4(a). It is clear that $E$ and $H$ improve with higher annealing temperature, but then drop a little in the film annealed at 800°C. For the ionic BZT-BCT material, the bonding is delocalized, and the mechanical properties are greatly influenced by extrinsic factors such as impurities, precipitates, grain boundaries, and the like [23]. It has been recognized [24] that at the intersection between two boundaries (e.g., the grain boundary and phase boundary), stress becomes concentrated, and
hence, the stiffness will be reduced because cracks are easier to generate near these areas. Belova et al. [25] have derived that the effective diffusivity for atoms increases with increased volume fraction of grain boundaries for nanocrystalline materials. Therefore, less grain boundaries in films annealed at higher temperature will lead to fewer stress concentrations and less plastic deformation, which will result in improvement of the elastic modulus and hardness. Also, the slight drop in both $H$ and $E$ – for the film annealed at 800°C can be attributed to the formation of small amounts of impurities, as indicated by XRD (shown in Fig. 1), which can accelerate the plastic deformation process because of the high energy around impurities.

The frictional behavior of the BZT-0.5BCT films annealed at different temperatures is summarized in Fig. 4(b). It is obvious that the friction force was not zero when the applied force was zero. In general, the relationship between the friction force and the normal load for nanocrystalline films can be expressed as follows:

$$F = F_0 + f F_n^\beta$$

(2)

with $F$: the measured friction force between the film and probe; $F_n$: the applied normal load; $F_0$: the friction force when the applied load is zero; $f$: the friction coefficient, which reflects the growth rate of the friction force with increasing normal load; and $\beta$: a fitting exponent. When the fitting exponent $\beta$ is set to 1, the degree of fitting is optimal. That is, $F$ presents a linear relationship with $F_n$, as can be seen in Fig. 4(b). Obviously, although the 700°C film has highest RMS value, its friction force is the lowest. Tribological interactions are known to be extremely complex,
depending on morphology, roughness, tribochemical reactions, and structural rearrangement because of local temperature spikes, all of which have great effects on the tribological properties [26]. In this experiment, all of the samples were measured under constant surrounding temperature and humidity, using a certain AFM tip; therefore, no structural rearrangement was expected to occur, and the tribochemical reactions were supposed to be similar for all the films, as the amounts of atoms which compose the films are very much the same. Friction is a typical non-equilibrium process, which is energy-dissipative by converting the mechanical energy into thermal energy. That is, the mechanical properties of a sample have a great effect on its frictional behavior. Researchers [27, 28] have discovered that nanostructured materials with a high ratio of hardness to elastic modulus ($H/E$) can exhibit improved wear properties. Therefore, it is acceptable to take the ratio of $H/E$ to evaluate the friction behavior of the BZT-BCT thin films. The $H/E$ values for the different films are summarized in Fig. 4(c). It clearly observed that the 650°C film has the lowest ratio while the 700°C film has the highest ratio, corresponding to the highest and lowest friction force, respectively, as seen in Fig. 4(b). The results suggest that a low ratio of $H/E$ can lead to a high friction force and, to some extent, poor wear properties, which is in accordance with Reference [27]. Detailed observations showed that the 800°C film is abnormal compared with others, because its ratio of $H/E$ is bigger than for the 750°C film, but it is accompanied by a lower friction force. Another mechanical factor that can influence the tribological behavior of films certainly exists. Reports have shown that the residual tensile stress retained in the film can reduce the
adhesion force [29]. In order to have a better understanding of the influence of the residual stress on the tribological behavior, small-angle X-ray diffraction, as described elsewhere [30], was used to measure the residual stress in the films, and the results are summarized in Table 1. These results show that the residual stress is tensile and increases with annealing temperature for the 700, 750, and 800°C films, but for the film annealed at 650°C, the stress is compressive and about 313 MPa. This may be attributed to the interaction between the thermal stress and the lattice stress, resulting in the conversion from tensile to compressive stress [31]. Comparing the different residual stresses in the films, it is easy to identify that the tensile stress could reduce the friction force and that higher tensile stress reduces it more, which may be related to the stress relaxation, however, the underlying mechanism is still under investigation.

In summary, BZT-BCT thin films were prepared via the sol-gel process and annealed under different temperatures. For these nanocrystalline films, the piezoelectricity is mainly dependent on the grain size, while the mechanical properties are more sensitive to impurities and the tribological behavior is largely affected by the residual stress and the ratio of the hardness to the elastic modulus, that is, greater tensile stress and a higher $H/E$ ratio can result in a lower friction force.

This work is financially sponsored in part by National Basic Research Program of China (Grant No. 2012CB619401), Natural Science Foundation of China (Grants No. 51002029 and 11134004). Z. X. Cheng thanks Australia Research Council for support through a Future Fellowship.


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Table and Figure Captions

Table 1. Residual stress in films annealed at different temperatures.

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>650°C</th>
<th>700°C</th>
<th>750°C</th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual Stress</td>
<td>-313MPa</td>
<td>0.515GPa</td>
<td>1.459GPa</td>
<td>2.275GPa</td>
</tr>
</tbody>
</table>

“-” indicates that the residual stress is compressive.

Fig. 1. XRD patterns of BZT-BCT films annealed at different temperatures. (Inset: 650°C-annealed film with strong impurity phase peak.)

Fig. 2. (a) Roughness and average grain size dependence of annealing temperature (inset: AFM image of film annealed at 800°C). (b) The neck stress model and different diffusion paths for atoms during the annealing process. I: from surface to neck, II: from grain interior to neck, III: from grain boundary to neck.

Fig. 3. (a) Typical local piezoelectric response versus applied voltage for the BZT-BCT film annealed at 800°C. (b) $d_{33}$ value of the films as a function of annealing temperature.

Fig. 4. (a) Dependences of the hardness and Young’s modulus on the post-annealing temperature of different samples. (b) Friction vs. normal-load curve. (c) Ratio of the hardness to the elastic modulus of the BZT-0.5BCT films.
Fig. 1
Fig. 2
Fig. 3

(a) Displacement (nm) vs. Applied Voltage (V)

(b) $d_{33}$ (pmV) vs. Temperature (°C)

Fig. 3
Fig. 4