Piezoelectric Force Microscopy Study of Domain Structure In High Tc Ferroelectric Films

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Nowadays the piezoelectric force microscopy (PFM) technique has become an ideal and unique technique to study ferroelectric materials, through which the local piezoresponse induced ferroelectric domain configurations and their evolution as applied ac electric field can be observed at the nanoscale level. An introduction to principles for studying ferroelectric domain structure by PFM has been provided, and several results on domain structure and piezoelectric response in high Curie temperature ferroelectric thin films had been introduced.

Keywords piezoelectric force microscopy; ferroelectric; thin films; local piezoresponse; domain structure

1. Introduction

(1-x)BiScO3-xPbTiO3 (BSPT) thin films are recognized as promising high Curie temperature (Tc) ferroelectrics for applications in MEMs, memory devices, etc, in high temperature environment.[1-4] Morphotropic phase boundary (MPB) BSPT exhibits a high Tc 450 °C (100°C higher than PZT) and comparable properties to those of relaxor-PbTiO3 meeting the requirements for high temperature applications in automotive and aerospace industry, etc.

However, there is a lack of understanding on the microscopic mechanism of polarization behavior in high-Tc ferroelectric films. Piezoelectric force microscopy (PFM) has become the ideal tool to directly observe the switching behaviour and evaluate local polarization reversal in ferroelectric thin films at the microscopic level, and is an important complement for macroscopic studies. Along with the local piezoelectric measurements and domain visualization, the PFM technique allows for a direct matching of local properties to the microstructures, as both of them can be imaged simultaneously.

This chapter presents the recent development of high-Tc ferroelectric films, the basic principle of PFM, and some investigation results in local domain structures and polarization behaviors in BSPT thin films.

2. Background of BSPT high Curie temperature ferroelectric films

Perovskite type ABO3 oxide materials, such as Pb(Zr1−xTix)O3 (x~0.48) (PZT) system, form the backbone of the ferroelectrics industry. These materials have come into widespread use in applications that range in sophistication from medical ultrasound and underwater sonar systems[5-9].

Recent developments in regard to relaxor-based single crystal piezoelectrics, such as Pb(Zn1/3Nb2/3)O3–PbTiO3 (PZNT) and Pb(Mg1/3Nb2/3)O3–PbTiO3 (PMNT) have shown superior performance characteristics compared to Pb(Zr,Ti)O3 (PZT) polycrystalline ceramics[10-13]. Particularly, their ultrahigh piezoelectric and electromechanical coupling factors in the <001> direction can reach to d33>2000pC/N and k33≈94%, which have attracted tremendous interests and still make many researches about them very hot. The enhanced piezoelectric activity of PZNT and PMNT, however, comes with the sacrifice of the temperature stability of the properties, being limited to their relatively low Curie temperatures (Tc≈178 °C), and further restricted by their lower ferroelectric phase transition temperatures (Tα-r≈120 °C). In some important applications, especially in the automotive and aerospace industries, the need for actuation and sensing over a broad temperature range is essential. Therefore, the low Curie temperature and relatively low ferroelectric phase transition temperatures (rhombohedral to tetragonal phase) of PZNT and PMNT systems limit their implementation in many fields. On the other hand, the temperature stability of the electrical properties, as well as good ferroelectric or piezoelectric activity, is important for device applications. So, ferroelectrics with high transition temperatures (Tc) are attractive [14-17].

Many relaxor-PbTiO3 ferroelectrics, such as Pb(In1/2Nb1/2)O3-PbTiO3(PINT), Pb(Yb1/2Nb1/2)O3-PbTiO3 (PYNT), BiScO3-PbTiO3 (BSPT) systems, have Curie temperatures as high as that of PZTs’s or about 100°C higher than that of PZTs, and hold excellent properties, which can overcome the shortage of PZNT and PMNT crystals, and meet the requirements in applications as next generation materials for actuators in automobiles and aerospace sensors.

Based on the perovskite formula ABO3 and the geometrical packing of charge spheres, a concept of tolerance factor (t) was proposed as

\[ t = \frac{r_a + r_e}{\sqrt{2} (r_b + r_e)} \]
where $r_a$, $r_b$, and $r_0$ stand for the respect ionic radii[5, 6]. The ideal tolerance factor for a perovskite material is equal to 1. Based on the tolerance trends in perovskite ferroelectrics, a relationship between tolerance factor ($t$) and Curie temperature ($T_c$) was proposed, namely, tolerance factor can be used to estimate the changes of Curie temperature with different perovskite systems[5-7].

From the empiric analysis, $\text{BiMe}_3\text{O}_5$-$\text{PbTiO}_3$ perovskites with decreasing values ($t$) were suggested to confirm the premise that $T_c$ increases with decreasing tolerance factor. It is evident that solid solution of $\text{BiScO}_3$ ($t=0.907$), $\text{BiInO}_3$ ($t=0.884$), or $\text{BiYbO}_3$ ($t=0.857$) with $\text{PbTiO}_3$ would exhibit MPBs with $T_c$ were significantly greater than PZT ($t=0.96, T_c=386^\circ C$) [5]. So, solid solutions with $\text{BiMe}_3\text{O}_5$-$\text{PbTiO}_3$ have small tolerance factors and are proving to give new high temperature ferroelectric solid solutions. Although, the $T_c$ of $\text{BiInO}_3$-$\text{PbTiO}_3$ and $\text{BiYbO}_3$-$\text{PbTiO}_3$ systems may reach to 560 $^\circ C$ and 700 $^\circ C$, respectively, however, the instability of the perovskite phase in these two materials prevent them from being easily synthesized. The $(1-x)\text{BiScO}_3$-$x\text{PbTiO}_3$ solid solution system has demonstrated the potential for producing piezoelectrics with higher piezoelectric activity, higher in-use temperatures, better phase stability, and lower temperature-property dependence than other present-day stable ferroelectric materials, with the perovskite or any other crystal structure[5-8]. So in this work, we focus the $(1-x)\text{BiScO}_3$-$x\text{PbTiO}_3$ system, exhibiting a MPBs and having a $T_c$ greater than 450$^\circ C$.

The phase diagram of BS-PT system indicates that, at room temperature, the rhombohedral symmetry lies in the region of $50<x<62$ mole% $\text{PbTiO}_3$ (PT), the tetragonal phase lies in the range $x>65$ mole% PT. In the solid-solution range $62<x<65$ mole% PT, there exists a morphotropic phase boundary (MPB) phase[1]. Near the MPB compositions, BSPT system exhibits very good electric properties comparable to those of $\text{PbTiO}_3$-based ferroelectrics, for instance, a $P_f$ of $32 \mu C/cm^2$ and a piezoelectric coefficient, $d_{33}$ on the order of 500 pC/N were observed in BSPT bulk materials. All these observations have been the driving force for the continuous research on BSPT system (ceramics and crystals), since its discovery by Randall et al., in 2001[18]. The justification for further investigating on BSPT films are also related with the current interest in thin films to meet the miniaturization requirements of microelectronics industry.

Only a few works on high-$T_c$ BSPT thin films have been reported. T. Yoshimura et al fabricated 1-$\mu$m thick epitaxial films of rhombohedral (001) $(1-x)\text{BiScO}_3$-$x\text{PbTiO}_3$ (with $x=0.60$ and 0.50) on (100) $\text{SrRuO}_3$/La$\alpha$O$\beta$ substrates by pulsed laser deposition.[19, 20] A room temperature permittivity of about 850 and dielectric losses of 0.08, well-saturated hysteresis loops with remanant polarization of 36-42 $\mu C/cm^2$ and coercive field of 65-75 kV/cm were observed. H. Wen et al prepared (100)-oriented tetragonal $(1-x)\text{BiScO}_3$-$x\text{PbTiO}_3$ ($x=66$) thin films by aqueous sol-gel method.[21] Room temperature dielectric constant and dielectric losses achieved values of 1200 and 0.09, respectively. These authors also reported saturated hysteresis loops with remanant polarization of 33$\mu C/cm^2$ but with very high coercive fields of around 220 kV/cm. In their subsequent works,[22-25] variations on the ferroelectric properties of thin films with the same composition were reported, in which high coercive field values were always presented.

In our works, MPB 0.37$\text{BiScO}_3$-$0.63\text{PbTiO}_3$ systems (here abbreviated as BSPT (37/63)) are selected to investigate. Sol-gel spin coating technique was applied to deposit BSPT (37/63) thin films. The spin rate ranges form 3000 to 5000 rpm, and the spin time is 30 seconds. BSPT (37/63) films were firstly dried on a hot-stage at the temperature about 350$^\circ C$ for 5 minutes, then pyrolyzed at 650$^\circ C$ for 10 minutes. Subsequently, these films were converted to perovskite BSPT (37/63) ferroelectric thin films by a conventional thermal annealing (CPA) process, at the crystallization temperature of 750$^\circ C$ for 2 hours. Their domain structure and electrical properties are evaluated through the PFM technique.

3. Introduction for Piezoelectric force microscopy (PFM)

3.1 The Atomic Force Microscope

After the invention of the scanning tunneling microscope (STM) in 1981,[26] the investigation of local properties with atomic-scale resolution became possible. As STM was limited to conductive surfaces, the atomic force microscopy (AFM) was then developed to measure sample topography by employing a tip and force sensor to detect repulsive forces.[27] Till now, many additional techniques have been developed to probe other forces (and hence various film properties) on the nanometer scale (nanoscale), such as piezoresponse force microscopy (PFM) [28] and magnetic force microscopy (MFM).[29]

An AFM primarily has several components: the first, a micro-fabricated cantilever, which serves as a force sensor, a device to detect cantilever deflection, and the second, a scanner which scans either the cantilever or sample stage and adjusts tip-sample distance. The cantilevers are usually made of Si or other materials, and are coated on the backside with metal to increase reflectivity. At the end of the other side of the cantilever is a sharp probe tip that contacts the sample. A laser and position sensitive photodetector (PSPD) are used to detect cantilever deflection. In AFM, a laser beam is reflected off the backside of a cantilever and directed onto the PSPD, through which can detect the changes of cantilever deflection. The third component is either a tip-scanning or sample-scanning mechanism.

The two main working mode for imaging surface topography in AFM are contact and non-contact modes. In contact mode, the tip is in contact with the sample, and an image is generated by measuring either the tip deflection in constant
height mode or the voltage applied to the scanner in constant force mode. In non-contact mode, the tip is kept at a
distance of tens to hundreds of Ångstroms from the sample driven (made to oscillate) near its resonance frequency. By
detecting the oscillation amplitude of the tip (or feedback required to keep the frequency or tip-sample separation
constant), an image of the surface topography can be generated.

3.2 PFM Experimental Setup

PFM is a contact mode imaging technique,[28, 30] the setup schematic is shown in Figure 1. A modulation or driving
voltage is applied between the conductive tip and a back electrode, creating an alternating electric field that causes the
piezoelectric response to expand and contract at the modulation frequency, and causes the tip to deflect. The tip
deflection at the modulation frequency is measured using a standard lock-in technique. The modulation frequency is
kept above the AFM feedback loop response frequency to avoid a cross talk between surface topography and measured
piezoresponse, and below the resonant frequency of the cantilever to eliminate resonance between oscillations of the
cantilever and the sample. Thus if the tip deflection is due entirely to the sample deformation as a result of the converse
piezoelectric effect, we can measure the piezoresponse of the sample through measuring the deflection.

There are two main approaches to PFM depending on the homogeneity of the applied field. Firstly, when a
homogeneous electric field is applied, we can measure the effective longitudinal piezoelectric constant, $d_{33}$. When a top
electrode is larger than the tip-sample contact area, a homogeneous field is generally generated to excite piezoelectric
oscillations. In this case, the piezoelectrically excited region is large compared to tip radius, and when such a top
electrode is present, the sample is often referred to as a capacitor, allows standard polarization, capacitance, and current
measurements to be performed. The other approach is to detect the piezoelectric response generated on a bare surface
by the conductive tip. This method is advantageous because it allows one to study the material directly; a correlation
can be obtained between the film microstructure and the piezoresponse or the domain configuration. This approach also
exhibits high-resolution features, makes it possible to investigate individual domains and to switch (e.g. cause
polarization reversal) individual ferroelectric domains and grains. Furthermore, it may be possible to investigate the
microscopic mechanism of switching and domain wall motion.

This PFM system can measure both piezoresponse phase and magnitude, as well as measure local piezoelectric
hysteresis loops, allowing us to image spatial variations in piezoelectric properties and to measure ferroelectric
properties at individual points.

3.3 Piezoelectric Measurements in PFM

The measurement of the piezoelectric constant using PFM can be accomplished in a point by point mode, using the
values on the digital readout of the lock-in amplifier or by analyzing the PFM magnitude image.

3.3.1 Determining the Piezoelectric Constant From the Lock-In [30]

This measurement is performed by lowering the tip (with the AFM scanner) and measuring the tip deflection (with the
photodiode) while the tip is in contact with the surface. The scanner must first be calibrated with a known step height in
order to calibrate the photodiode signal to a known scanner displacement, and the conversion constant must be
measured again anytime the laser position is changed or the cantilever is replaced. The 10kHz component of voltage
signal is measured by the lock-in amplifier, which can be converted to a distance using a calibration procedure.
With zero strain and tensor notation dropped for simplicity, the total strain of the film under an applied field, can be considered as:

\[ S = \frac{\Delta t}{t} = dE + \gamma E^2, \]

where \( t \) is the film thickness and \( \Delta t \) is the change in film thickness.

If we apply a modulation voltage \( V = V_0 \sin(\omega t) \), and assume that \( E = V/t \), the sample thickness change is given by

\[ \Delta t = \frac{V}{2t} + \frac{dV_0}{2t} \sin(\omega t) + \frac{V}{2t} \sin(2\omega t - \frac{\pi}{2}). \]

If the tip deflection is due to the sample deformation, the amplitude of the 10 kHz component of the change in thickness is

\[ \Delta h_{10kHz} = dV_0 = \alpha V_{LI}. \]

Assuming the modulation voltage is in V RMS, where the photodiode conversion constant is \( \alpha \) [Å/mV], and the lock-in voltage output is \( V_{LI} \) [mV RMS], the piezoelectric constant (d) is related to the lock-in output voltage by

\[ d = \alpha \left( \frac{V_{LI}}{V_0} \right) \text{ [Å/V]}. \]

where \( V_0 \) is in units of V RMS.

### 3.3.2 Image ferroelectric domains by PFM

PFM can be used to monitor the phase of the tip oscillation with respect to the modulation voltage in order to image ferroelectric domains. One of the main advantages of PFM is that it is a nondestructive technique for measuring domain structure. In ferroelectrics, the piezoresponse is directly related to the polarization direction. Through monitoring the phase of the piezoresponse, it is possible to determine the orientation of ferroelectric domains. The sign of the piezoelectric constant and the polarity of non-ferroelectric materials can also be determined from the piezoelectric sign convention.

### 4. PFM studies in BSPT high-Tc ferroelectric films

#### 4.1 Investigation of the evolution of micro domain structure by PFM

The PFM technique for the imaging of polarized regions was applied for the visualization of domain structure of ferroelectric films, which is based on the detection of local electromechanical vibrations of ferroelectric sample caused by an external ac field applied between the conducting tip and a counter electrode (Fig. 1). The deflection signal of the cantilever that oscillates together with the surface of the sample is detected using two lock-in amplifiers and is imaged along with the regular topographic signal in the contact mode.

As described above, the domain structure is visualized by monitoring the first harmonics of the deflection signal. The amplitude is proportional to the local longitudinal piezoelectric coefficient \( d_{33} \) and the phase \( \phi \) reflects the polarization direction (about 0° if the field is parallel to polarization and about 180° if it is antiparallel). If the signal with phase is imaged (\( d_{33} \cos \phi \)), the contrast depends on both the amplitude of \( d_{33} \) and polarization direction. The bright areas on this image depict polarization directed towards the bottom electrode and dark areas correspond to the domains of opposite direction. The applied voltage has to be high enough in order to cause the measurable signal, but it should be sufficiently small to prevent local switching and domain wall motion.

A modified commercial atomic force microscope (Multimode, Nanoscope IIIA, Digital Instruments) was used in the experiment. A conductive Pt-coated Si tip–cantilever (NSG01/Pt, NT-MDT) system was used for the application of external voltages and for vibration detection. Ferroelectric films were excited by an external ac voltage \( V_{ac} \) applied between the PFM tip and the bottom electrode, and the deflection signal from the cantilever was detected by a lock-in amplifier. A topographic image of the film surface was taken simultaneously with the domain image. In the experiments, the films were scanned with the different voltages applied to the tip over the area of 2×2 μm².

#### 4.2 micro-scale ferroelectric domain in BSPT thin films on Pt electrodes

Fig. 2 shows the images of topography and domain structure of unseeded BSPT films on Pt electrode taken from PFM. From the two-dimensional morphology image, The BSPT/Pt film shows dense grained microstructure. The average grain size is about 150 nm, the surface roughness is about 9 nm.
Piezoelectric domain images acquired simultaneously with the topography of BSPT/Pt films are also shown in Fig. 2. These images were respectively taken under conditions by applying a small ac voltage (0-0.9 V peak-to-peak, 50 kHz) between the grounded tip and the bottom electrode. The comparison of the topographic and piezoresponse images of the BSPT films allows us to establish an apparent correlation between the surface morphology (grain size) and domain structure. It is observed that the ac field induced ferroelectric domains exhibit a size of 100-150 nm, which is comparable to the grain size.

In the piezoelectric image, domains with opposite polarities exhibit different contrast. Dark regions (negative domains) correspond to domains with polarization oriented towards the substrate, and bright regions (positive domains) to domains with polarization oriented to the film surface. Since the PFM technique is sensitive only to the component of polarization normal to the film surface, grains with in-plane polarization (with vanishing out-of-plane polarization) will exhibit an intermediate grey contrast. The gray contrast regions can also be attributed to the incomplete 180° switching and/or the formation of 90° domains. With the applied ac voltages increase from 0 V to 0.9 V, the population of the positive and negative domains increase, and the contrast of the ferroelectric domain become more clearly.

4.3 Local Fatigue Characterization by PFM in PbTiO3 seeded BSPT films

It is well known that ferroelectric thin films deposited on Pt metal electrodes exhibit serious fatigue of the ferroelectric response, denoted by the reduction of the switchable polarization as a function of the switching cycles, affecting their performance and limiting their utilization. To overcome this problem, one potential effective approach is to introduce a seed layer between the Pt electrode and ferroelectric films. The major objective of this work is to study the effect of PbTiO₃ (PT) seed layer on the micro-scale switching performance and local fatigue behaviour of MPB 0.37BiScO₃-0.63PbTiO₃ (BSPT) thin films. The local characterization of piezoelectric force microscopy (PFM) on the domain degradation were conducted, as sown in Fig. 3 and Fig. 4.

We found that the PT seed layer improves the film quality and the ferroelectric properties of BSPT thin films deposited on Pt electrodes. At the macroscopic level, the seeded BSPT films show no ferroelectric fatigue till more than 10⁷ switching cycles, while the identical ferroelectric films on bare Pt exhibit obvious fatigue behaviour just at 10⁷ cycles, which indicates that the introduction of a PT seed layer improves the switching reliability of BSPT thin films on Pt electrode. At the microscopic level, after switching for 1.5×10⁸ cycles, the unseeded BSPT thin films exhibit an evident degradation of the out-of-plane domain images with increasing the switching cycles. In comparison, the domain configuration in the seeded BSPT thin films do not apparently degrad or disappear. These microscopic level observations clearly imply that the use of PT seed layer improves the polarization switching and fatigue behavior of BSPT films.
4.4 Local Piezoelectric Measurements of BSPT thin films on LaNiO₃

To study the effect of LNO electrode on enhancing the piezoelectric performance of BSPT thin films in light of the microscopic viewpoint, we investigated the local piezoelectric response by the method of piezo-force response microscopy (PFM). Figure 5 (a) and (c) show the topography images of BSPT/Pt and BSPT/LNO films, which indicate an average grain size less than 100 nm in BSPT/LNO films. In the piezoresponse images shown in Figure 5 (b) and (d), domains with opposite polarization exhibit different contrast. Dark regions (negative domains) correspond to domains with polarization oriented towards the substrate, and the polarization in bright regions (positive domains) pointed to the surface of the film.[31] Figure 6 shows the local piezoelectric hysteresis loops (piezoloops) of BSPT/Pt and BSPT/LNO measured on a fixed point inside a bright domain (as shown in the cross points in Figure 5 (b) and (d)). From these loops one can observe that under the applied voltage of 10 V, the maximum relative $d_{33}$ value of BSPT/LNO is much higher than that of BSPT/Pt. This indicates BSPT/LNO exhibit a better local and micro piezoelectric properties than BSPT/Pt.

The piezoelectric constant $d_{33}$ is affected by many factors such as the film orientation and residual stress. Firstly, this result is in agreement with that the introduction of LNO oxide conductor layer between BSPT film and Pt electrode not only improves the crystalline degree but also enhances remarkably the (100) orientation degree of the ferroelectric films, and further enhances significantly the piezoelectric properties.

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**Figure 5** (color on-line only) the topography and domain structure images of BSPT/Pt and BSPT/LNO films
5. Summary

In this article, an introduction to principles for studying ferroelectric domain structure by piezoelectric force microscopy (PFM) has been provided, and several results on domain structure and piezoelectric response in BSPT high Curie temperature ferroelectric thin films had been introduced. PFM has become a unique technique to characterize ferroelectric materials. By this technique, the piezoresponse induced ferroelectric domain configurations of BSPT films and their evolution as applied ac electric field was observed at the nanoscale level. These local piezoresponse behaviors will correlate with the macroscopically measured piezoelectric properties of BSPT films.

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