

IMAGING AND CONTROL OF DOMAIN STRUCTURES IN FERROELECTRIC THIN FILMS VIA SCANNING FORCE MICROSCOPY¹

Alexei Gruverman

Joint Research Center for Atom Technology—Angstrom Technology Partnership (JRCAT-ATP), Higashi 1-1-4, Tsukuba, Ibaraki 305, Japan; Present address: Sony Corporation, Yokohama Technology Center, 134 Goudo-cho, Hodogaya-ku, Yokohama 240, Japan; e-mail: alexei@src.sony.co.jp

Orlando Auciello

Argonne National Laboratory, Materials Science Division, 9700 South Cass Avenue, Argonne, Illinois 60439-4838; e-mail: orlando_auciello@qmgate.anl.gov

Hiroshi Tokumoto

JRCAT, National Institute for Advanced Interdisciplinary Research, Higashi 1-1-4, Tsukuba, Ibaraki 305, Japan; e-mail: htokumot@nair.go.jp

KEY WORDS: ferroelectric domains, nanofabrication, piezoelectricity

ABSTRACT

Scanning force microscopy (SFM) is becoming a powerful technique with great potential both for imaging and for control of domain structures in ferroelectric materials at the nanometer scale. Application of SFM to visualization of domain structures in ferroelectric thin films is described. Imaging methods of ferroelectric domains are based on the detection of surface charges in the noncontact mode of SFM and on the measurement of the piezoelectric response of a ferroelectric film to an external field applied by the tip in the SFM contact mode. This latter mode can be used for nondestructive evaluation of local ferroelectric and piezoelectric

¹The US Government has the right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper.

properties and for manipulation of domains of less than 50 nm in diameter. The effect of the film thickness and crystallinity on the imaging resolution is discussed. Scanning force microscopy is shown to be a technique well suited for nanoscale investigation of switching processes and electrical degradation effects in ferroelectric thin films.

INTRODUCTION

The science and technology of ferroelectric thin films is currently attracting worldwide attention because of the large number of applications to a new generation of novel devices, prime among them being nonvolatile ferroelectric random access memories, which have high speed and unlimited endurance (1). However, there are concerns about the long-term reliability characteristics of ferroelectric capacitors, which are at the core of memory devices. For a recording density of tens of Mbit mm⁻², the storage elements should be reduced to sub-micron dimensions, which requires substantial improvement in the understanding of properties of these materials at the nanometer scale range and implementation of new tools suitable for in situ nanoscale characterization of ferroelectric structures. Application of high-resolution techniques such as scanning force microscopy (SFM) (2–4), in conjunction with conventional electrical measurements, provides an opportunity to achieve a unique insight into the real physical processes that occur in ferroelectric thin films. One of the most important issues in the physics of ferroelectrics is the exact nature of the domain structures. Over the past few years significant progress has been made in high-resolution visualization of ferroelectric domains in bulk crystals and polycrystalline films by means of SFM (5–13). In this article, we focus on recent advances in the application of SFM to nanoscale imaging of domain structure in ferroelectric thin films, with particular emphasis on domain control via local polarization reversal and investigation of mechanisms for ferroelectric fatigue and retention loss.

PRINCIPLES OF SFM OPERATION

A number of papers and books on scanning probe methods have been published that provide an introduction to the principles of scanning force microscopy (14, 15). Thus only an outline of SFM operation is presented here. The most important part of a force microscope is a force sensor, which consists of a sharp tip mounted at the end of a soft cantilever-type spring. The forces acting on the tip after it has approached the sample surface cause a deflection of the cantilever according to Hooke's law. This deflection can be detected optically or

electrically with sub-Å accuracy and is controlled by a feedback device that regulates the vertical position of the tip over the surface. By keeping the deflection constant while scanning the sample, a three-dimensional map of the surface topography can be obtained. Scanning is realized by placing the sample on a piezoelectric scanner, which allows for lateral as well as vertical positioning of the sample relative to the tip with nanometer precision. There are two main modes of SFM operation: contact and noncontact. In the contact mode, the probing tip is in mechanical contact with the sample surface and mostly senses the repulsive short-range interatomic forces. In the noncontact mode, at a distance of 10–100 nm from the surface, the tip responds to attractive long-range forces, such as van der Waals, electrostatic, and magnetic forces. To increase the sensitivity to forces, various modulation techniques have been developed. The idea behind imaging in the noncontact mode is that the cantilever is made to oscillate near its resonant frequency. The tip-sample force interaction during scanning alters the effective spring constant of the cantilever, thereby changing its resonant frequency and its oscillation amplitude. These changes are detected using a lock-in technique, and the feedback loop adjusts the tip-sample distance so as to maintain the amplitude of oscillation constant (2, 3). In fact, the noncontact mode is more sensitive to a force gradient. The minimum detectable force gradient at room temperature is of the order of 10^{-4} – 10^{-5} N/m. Spatial resolution depends essentially on the tip-sample separation, tip geometry, and on the type of interaction being probed.

IMAGING OF FERROELECTRIC DOMAINS IN THIN FILMS

SFM-based methods of ferroelectric domain imaging make use of basic properties of ferroelectrics, namely of their piezoelectric behavior and the presence of surface charge associated with the permanent built-in electric polarization. Static surface charge, proportional to the normal component of polarization, can be detected by electrostatic force microscopy (EFM), when the microscope is operating in the noncontact (attractive) mode (3, 5). By monitoring the piezoelectric vibration of the ferroelectric sample caused by an external ac voltage, domain structure can be visualized in the SFM piezoresponse mode, when the probing tip is in contact with the sample (8, 12).

SFM Noncontact Mode

The possibility of using EFM, which was devised for imaging localized surface charges on insulators, for imaging ferroelectric domains was suggested by Quate (16). This suggestion was later realized by visualization of domain walls in ferroelectric crystals (5–7). As the tip, held at some distance from

the surface, scans over the ferroelectric sample, surface polarization charges induce an image charge Q_p in the probing tip, which results in an additional contribution to the attractive force due to Coulomb interaction. The resulting force gradient is proportional to the product of the electric field due to the polarization and the charge Q_p induced in the tip (5) and, therefore, depends only on the polarization magnitude and not the sign. This implies that the contrast of opposite 180° domains will be the same and that only domain walls will be visible due to the spatial variation of the charge density in the vicinity of a 180° domain boundary. The tip experiences a change in the force gradient when it is above the wall and the feedback loop alters the tip-sample distance to keep the gradient constant, thus producing a variation of contrast in the feedback signal image, which can be interpreted as an image of the domain wall. Image contrast depends essentially on the external bias voltage applied to the probing tip and on the tip material. By varying the bias voltage, the contrast of domain boundaries can be eliminated and contrast between opposite domains can be observed (7). A similar approach can provide a detection mechanism for previously written ferroelectric domains in thin films, as demonstrated by Ahn et al (17), where local polarization reversal in epitaxial $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3/\text{SrRuO}_3$ heterostructure was performed. In their experiment, the written structure, produced with a negative external voltage, appeared as a protrusion in the image acquired with a negative reading tip bias. Application of the positive reading bias made the same structure appear with inverted contrast, indicating the electrostatic origin of the contrast of the polarized region. The relatively large size of the lines written (of about 350 nm in width) is due to the tip-sample separation and the finite size of the tip, which broadens the image of the polarized area.

In general, there could be several sources of the force gradient in the non-contact mode, such as van der Waals forces or capillary forces. As a result, the force gradient image may be a superposition of surface topographic features and the electrostatic signal. In the case of domains of irregular shape and complex surface topography, the interpretation of the images could be quite difficult. To be able to distinguish the charge signal from other possible sources of the force gradient and thereby to verify the domain structure, the EFM mode was further modified (5, 18). This new mode of imaging is sensitive to the charge only and allows determination of its sign. An ac bias voltage $U_{ac} = U_0 \sin(\omega t)$, applied between the bottom electrode and the probing tip, induces an oscillating charge $Q_e = CU_{ac}$ on the electrode, which in turn leads to the generation of an equal image charge of the opposite sign on the tip. C here is the tip-bottom electrode capacitance. Taking into account the static image charge Q_p owing to the polarization, the total charge on the tip will be $Q_t = -(Q_e + Q_p)$. The resulting electrostatic force on the tip will, therefore, consist of two terms: a capacitive term due to the applied voltage $F_{cap} = 1/2 U_{ac}^2 (\partial C / \partial z)$, where z is the tip-sample distance, and a term due to the tip-sample Coulomb interaction

$F_{Coulomb} = Q_t E_z$, where E_z is the stray electric field produced by polarization charges of the ferroelectric sample. It has been shown (18) that in the absence of net polarization ($Q_p = 0$ and $E_z = 0$), the force gradient will vary as U_{ac}^2 , and tip oscillation will be modulated at 2ω , whereas for electrically polarized samples ($Q_p \neq 0$), it will be modulated at ω . Therefore, by monitoring the ω signal with an amplifier, information about charge distribution can be obtained. The phase of this signal indicates the sign of the charge. The second harmonic signal at 2ω can be used for measurement of the dielectric constant (19, 20).

Figure 1 shows a charge image of a $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3/\text{RuO}_2$ heterostructure (PZT 53/47-RuO₂), acquired by this technique. Prior to the imaging, a small part of the film was polarized with a positive voltage and two lines were written across this area with a negative voltage. These positively and negatively polarized features appear as bright and dark areas, respectively (Figure 1). At

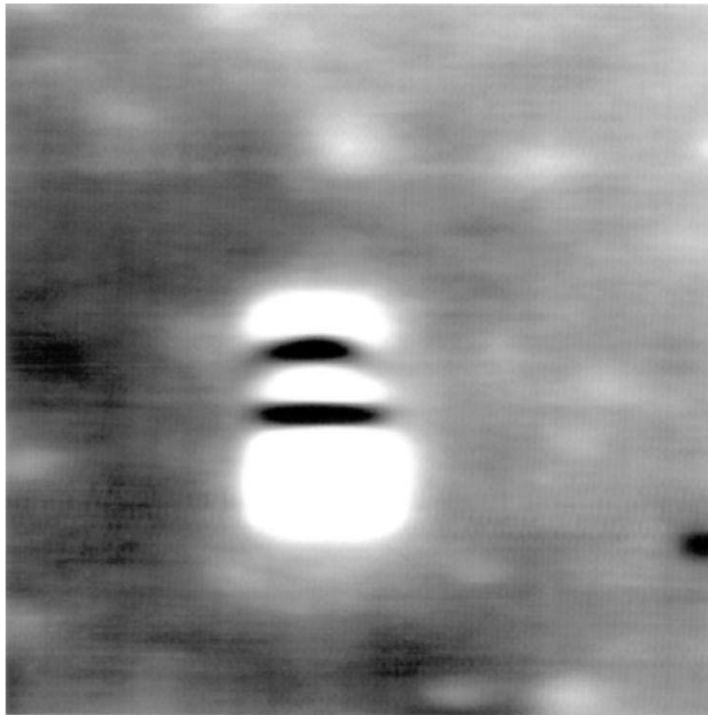


Figure 1 Charge image of a PZT 53/47-RuO₂ heterostructure. Bright and dark regions were switched by applying positive and negative 6 V dc voltage pulses, respectively. The scanning area is $10 \times 10 \mu\text{m}^2$.

the same time, the unwritten area shows only slight variation of the contrast, although, as demonstrated below, it contains an as-grown domain structure consisting of opposite domains, normal to the film surface. Within several hours the contrast of the written structure gradually fades and almost disappears. This behavior indicates that the observed contrast is from the uncompensated stray field of newly switched domains. Accumulation of charged particles from air on the film surface neutralizes polarization charges and causes a uniform contrast over the surface due to zero net charge. Therefore, although the SFM charge detection mode has the advantage of distinguishing between topographic features and the electrostatic signal, the domain contrast in this mode can be easily obscured. Another problem is that the water layer that is present on the sample surface under ambient conditions can change or even conceal the image of real domain structure. Conducting experiments in a vacuum or in an inert atmosphere can eliminate these undesirable effects and make possible detailed investigation of the spatial distribution of polarization charges and stray electric fields at ferroelectric surfaces.

SFM Contact (Piezoresponse) Mode

IMAGING MECHANISM The SFM piezoresponse mode was developed for detection of polarized regions in ferroelectric copolymer films of vinylidene fluoride and trifluoroethylene (21, 22) and later was applied for visualization of domain structure in PZT thin films (8, 12). It is based on the detection of the local electromechanical vibration of the ferroelectric sample caused by an external ac voltage. The voltage is applied through the probing tip, which is used as a movable top electrode. The modulated deflection signal from the cantilever, which oscillates together with the sample, is detected using the lock-in technique, as in the case of the noncontact imaging. However, in the piezoresponse mode the frequency of the imaging voltage should be far lower than the cantilever resonant frequency to avoid mechanical resonance of the cantilever. An external voltage with a frequency ω causes a sample vibration with the same frequency due to the converse piezoelectric effect. Vibration of the sample under the ac voltage also has a second harmonic component at 2ω due to the electrostrictive effect and dielectric constant (8). Analysis of the second harmonic signal showed that for PZT films the contribution of the latter effect dominates the influence of electrostriction (23, 24).

The domain structure can be visualized by monitoring the first harmonic signal (piezoresponse signal). The phase of the piezoresponse signal depends on the sign of the piezoelectric coefficient (and therefore on the polarization direction) and reverses when the coefficient is opposite. This means that regions with opposite orientation of polarization, vibrating in counter phase with respect to each other under the applied ac field, should appear as regions of

different contrast in the piezoresponse image. Figure 2 shows simultaneously obtained topographic and piezoresponse images of the PZT 53/47-RuO₂ sol-gel film, the same as shown in Figure 1. Because the X-ray diffraction pattern of the film showed only (001) peaks, it is reasonable to conclude that protrusions (bright areas) and depressions (dark areas) seen in the piezoresponse image represent regions with opposite d_{33} piezoelectric constants and antiparallel polarization vectors normal to the film surface. By monitoring the phase of the

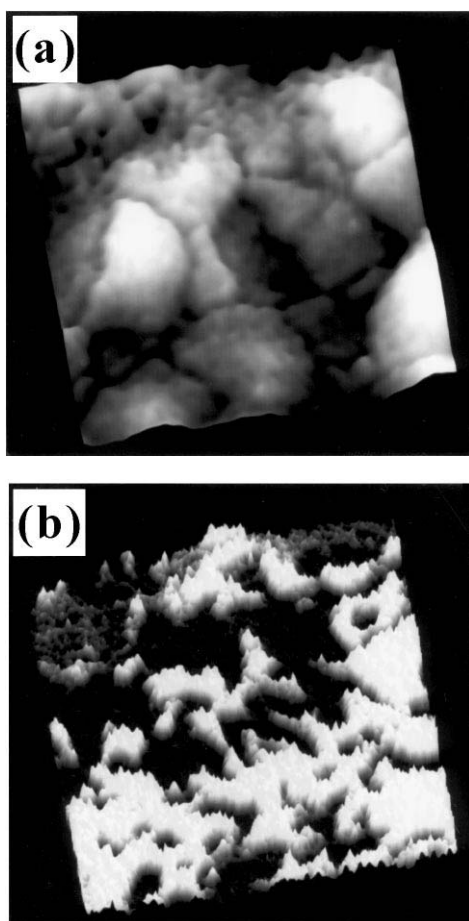


Figure 2 Simultaneously obtained topographic (a) and piezoresponse (b) images of a PZT 53/47-RuO₂ film. Bright and dark regions on the piezoresponse image correspond to positive and negative domains, respectively. The scanning area is $1250 \times 1250 \text{ nm}^2$.

piezoresponse signal it was determined that bright regions in Figure 2*b*, which vibrate in phase with the ac imaging voltage, represent positive domains (polarization is toward the bottom electrode), whereas dark regions correspond to negative domains with the polarization vector oriented upward. Note that these regions have not been detected in the charge image in Figure 1, where adsorbed charges completely screened polarization charges and hid the as-grown domain structure. In contrast, because of the imaging mechanism, the piezoresponse mode is not susceptible to contrast deterioration due to screening effects.

The vibration amplitude measured with a lock-in amplifier provides information about the value of the piezoelectric coefficient. An amplitude of less than 1 Å can be detected in SFM, which provides a vertical sensitivity of about $5 \times 10^{-12} \text{ m V}^{-1}$ for an applied voltage of 10 V. Such a high vertical sensitivity makes this method nondestructive because in thin films with high piezoelectric constants, the imaging voltage can be reduced to a value lower than the coercive voltage, and as a result, the imaging process will have no effect on the existing domain configuration. However, it might be problematic to apply this technique to materials with low piezoelectric constants. Because only a change in the sample thickness is detected in the piezoresponse mode, it also allows one to avoid the effect of surface roughness on domain contrast and makes possible imaging of a domain structure even underneath a rough surface dielectric layer, although at the expense of the lateral resolution (25). Although the probing tip under the applied voltage generates a highly nonuniform electric field and, therefore, the piezoresponse mode seems to be more applicable to thin films than to bulk samples, with use of this method, 180° domains have been imaged in single crystals of barium titanate and lithium niobate (25).

INTERPRETATION OF THE PIEZORESPONSE IMAGES A piezoresponse image of a well-oriented thin film can be easily understood, provided the film is fully characterized prior to the SFM measurements. In a *c*-oriented film, dark and bright regions correspond to opposite domains with the polarization vector normal to the film plane (Figure 2). Generally, however, piezoresponse images present a much more complex variation of contrast that reflects the perplexing arrangement of domains in the ferroelectric films. This is illustrated by Figure 3, which shows topographic and piezoresponse images of an as-deposited PZT 20/80 film on a LaSrCoO/Pt/TiN/Si substrate (PZT 20/80-LSCO). The topographic image reveals the crystallite structure of the film with clearly resolved morphological features. The corresponding piezoresponse image shows regions of bright, dark, and gray contrast. From comparison of crystallite structure with the piezoresponse image, a strong effect of the film crystallinity on the domain arrangement can be seen: quite often domains are limited by the grain boundaries. This contrasts with the data presented in Figure 2, which show almost no

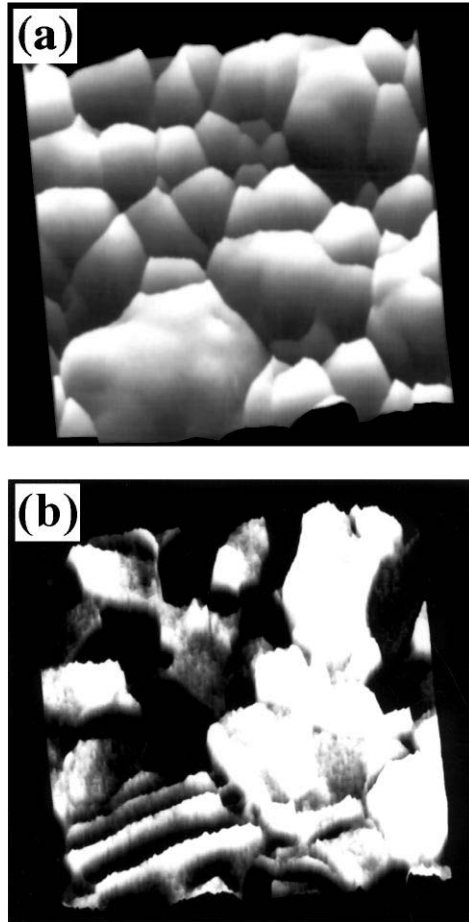


Figure 3 Simultaneously obtained topographic (a) and piezoresponse (b) images of a PZT 20/80-LSCO film. The scanning area is $600 \times 600 \text{ nm}^2$.

correlation between domain and crystallite structures in the PZT 53/47-RuO₂ film. A problem of microstructure-domain correlation in ferroelectric thin films is one of the important issues that can be addressed using SFM.

There are several possible reasons for the gray piezoresponse contrast:

1. There may be several randomly polarized grains stacked in the direction normal to the film plane (Figure 4a). The piezoresponse signal detected in the SFM piezoresponse mode is integrated over the entire range of the film

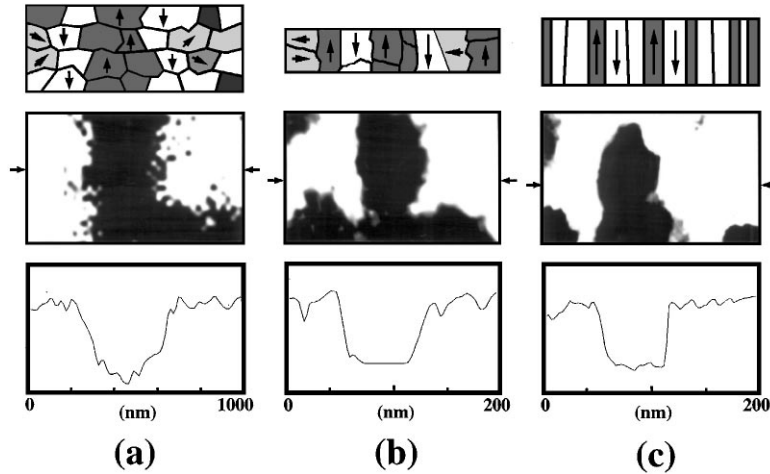


Figure 4 Schematic diagrams showing possible film microstructures, piezoresponse images and corresponding cross-sectional plots illustrating different SFM imaging resolutions: (a) relatively thick film; (b) relatively thin film; (c) columnar film. Cross sections were taken along the lines marked by arrows in the piezoresponse images.

thickness, and its amplitude and the phase provide information about the integral strain induced along the film thickness and about the direction of the polarization, respectively. The applied electric field compresses grains with a given direction of polarization and expands grains with opposite polarization. If all grains in the direction normal to the film surface are polarized randomly, the integral piezoelectric response will be equal to zero because the expansion of one grain with polarization component along the external field will be compensated by the compression of another grain with polarization component opposite to the applied field. As a result, gray contrast will be observed in the piezoresponse image. This situation is likely to occur in films with grains that are relatively small compared with the film thickness (12).

2. There could be *a* domains and domains with the polarization vector deviating from the direction normal to the film plane (Figures 4*a, b*). The piezoelectric signal from these domains should be weaker than from *c* domains, and in the SFM piezoresponse images they should be represented by regions with contrast intermediate between dark and bright. X-ray diffraction analysis showed that there are fractional amounts of (001)-, (100)-, and (101)-oriented grains in the film. Therefore, taking into account the PZT

20/80-LSCO film thickness of $0.2 \mu\text{m}$, it is reasonable to assume that gray regions in the piezoresponse images in Figure 3 represent domains with the polarization vector deviating from the direction normal to the film plane.

3. There may be an amorphous or a nonferroelectric structure that does not exhibit piezoelectric properties. For example, a film area without distinct crystallite structure in the upper part of Figure 2a corresponds to a gray region with zero piezoelectric signal in Figure 2b. Confirmation of this hypothesis may require localized diffraction analysis to verify that the particular gray area is indeed amorphous.
4. Polarization reversal may occur under the action of the imaging ac field and with the same frequency. This will result in a decrease of the first harmonic (piezoelectric) component of the integral response and an increase in the second harmonic component. Whether this effect is taking place can be checked by comparison of several subsequent piezoresponse images and by simultaneous acquisition of second harmonic images.

IMAGING RESOLUTION A problem of particular importance is the spatial resolution capability of the SFM piezoresponse mode. The resolution in this mode can be defined as the width of the transition region between regions of opposite polarizations normal to the film surface. Generally, in the case of thin films, there are two main factors involved: (1) the size of the probing tip and (2) the microstructure of the ferroelectric sample.

1. In the piezoresponse mode, the SFM tip is in contact with the sample and senses the electromechanical response of the sample. Therefore, the lateral resolution depends mainly on the tip-sample contact area. In addition, due to the high dielectric constant of the ferroelectric samples, the field generated by the tip in a thin film is effectively concentrated underneath the contact area. The actual contact area, which is a function of the tip radius and depends also on the tip and sample material properties, would be extremely difficult to measure precisely. For a loading force of 3 nN and a Si_3N_4 tip of radius 20 nm, the contact area is estimated to be of the order of several nanometers in diameter (26). This is the lower limit for the lateral resolution of the piezoresponse mode. Increase in the loading force results in a larger contact area and suppresses the piezoelectric response (27), which leads to deterioration of the resolution and also the contrast.
2. The effect of the film structure on the lateral resolution of the SFM piezoresponse mode was studied by imaging domain structures in predominantly

c-oriented films with different microstructures and thicknesses. A resolution of about 80 nm was achieved in the polycrystalline 0.8 μm thick PZT 53/47 film (12), whereas in a thinner PZT 53/47 film of 0.18 μm thickness, opposite domains were imaged with a resolution of about 15 nm. On the other hand, in films with columnar structure, a spatial resolution of about 10 nm was found to be independent of the film thickness within the range of 0.1 to 0.3 μm . These data are consistent with the results obtained by Franke et al (8), who reported that a resolution of better than 10 nm was achieved in a 0.6 μm thick PZT film with columnar structure. In monocrystalline films of 0.2 and 0.4 μm thickness, domain structure was also imaged with a lateral resolution of about 10 nm.

The effect of the film microstructure on the lateral resolution can be explained in the following way. Fabrication of relatively thick PZT films by the sol-gel method involves multiple layer depositions accompanied by heat treatment. Therefore, in the 0.8 μm thick PZT film there could be several grains stacked in the direction normal to the film plane (Figure 4*a*). In this case, a sharp 180° domain boundary extending through the film thickness could not be observed as all grains underneath the tip are likely to be polarized differently. As a result, the piezoresponse image of the transition region between two oppositely polarized regions will be diffuse. In addition, even a slight deviation of the polarization vector from the normal direction in a relatively thick film severely affects the imaging resolution. In the relatively thin 0.18 μm PZT film with large grains, one can assume that the film thickness equals the size of individual crystallites and, therefore, domain walls could extend the entire distance between film surfaces (Figure 4*b*). This case is equivalent to the case of a monocrystalline film, where the resolution is mainly determined by the tip radius, rather than by the sample thickness. The high resolution of the piezoresponse image can be similarly explained for films with a columnar structure, where the situation of uniformly polarized crystallites could be easily realized (Figure 4*c*). The regular shape of the grain boundaries normal to the film surface results in a slightly improved domain structure resolution, close to the ultimate resolution of the piezoresponse mode.

As is discussed in the next section, a fine domain structure can be produced by applying an external voltage to the probing tip. However, film thickness has its effect on the writing resolution as well. An electric field generated in the film increasingly spreads with increasing thickness, which leads to deterioration of the writing resolution. The smallest domain written in the 0.8 μm thick PZT film was about 200 nm in diameter (12), whereas in the much thinner PZT films (of about 0.2 μm), written domains of less than 50 nm in diameter have been observed (11).

SFM CONTROL OF FERROELECTRIC DOMAINS IN THIN FILMS

Nanoscale Switching

It has been demonstrated that a conductive probing tip in the contact mode can be used not only for domain visualization but also for modification of the original domain structure (8, 11, 12, 25). By applying a small dc voltage between the tip and bottom electrode an electric field of several hundred kilovolts per centimeter can be generated, which is high enough to induce local polarization reversal in most ferroelectrics. A tip with an apex radius R positioned at distance d from the surface generates a nonuniform electric field, and its normal component at the sample surface, E_z , can be estimated as a function of distance x from the tip axis as $E_z = 2RUd/(d^2 + x^2)^{3/2}$, where U is the applied voltage. This field decreases as $1/\epsilon z^2$ in the polar direction z as the domain expands into the crystal. Therefore, even in the case of thin films, the lateral size of written domains will be larger than the actual tip-sample contact area. However, polarization reversal can be limited to an area of less than a hundred nanometers in diameter which is small enough to observe switching within an individual grain.

Figures 5a and b show simultaneously acquired topographic and piezoreponse images of the PZT 20/80-LSCO film. To further characterize the film at the nanometer scale, the piezoreponse signal was measured as a function of a poling voltage. The probing tip was positioned at the center of negatively polarized grain 1 where the 200 ms voltage pulses were applied. After each pulse, the piezoreponse signal was measured by applying a small ac voltage to the same point. The piezoreponse images of the grain under investigation was acquired after half of the piezoelectric hysteresis loop was measured. In Figure 5c, it can be seen that this grain, about 100 nm in size, exhibits a reversed contrast compared with that in Figure 5b. The reversing of the contrast as well as the change in the sign of the piezoreponse signal occurs under positive voltage (+ applied to the tip), suggesting that the grain was originally in the negative polarization state (polarization upward), which is consistent with the previous conclusion made from phase monitoring of the film vibration. Contrast reversal, along with the clear ferroelectric hysteresis behavior of the piezoreponse signal (Figure 5d), is solid proof of 180° polarization reversal occurring under the applied voltage. Note that the imaging process itself does not affect the existing domain structure because the adjacent grains are still in their original polarization states. This fact supports the statement that the SFM piezoreponse mode can be used as a nondestructive method for domain visualization.

The size of the reversed domain depends essentially on the parameters of the switching voltage pulse (12). By varying the pulse width, partial switching of the grain can be accomplished: application of a shorter 6 V, 50 ms voltage

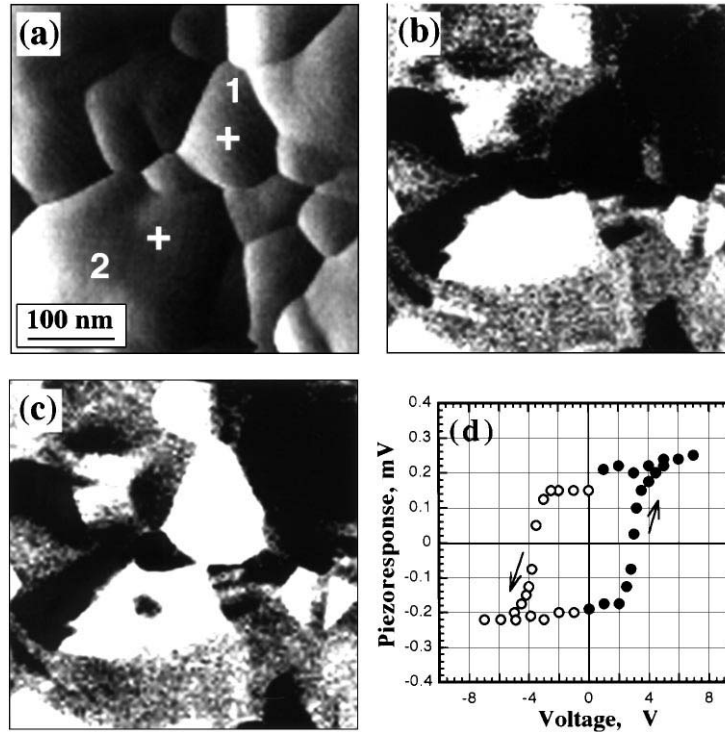


Figure 5 Nanoscale domain switching in a PZT 20/80-LSCO film: (a) topographic image of the film with the white crosses indicating positions of the SFM tip during dc voltage application; (b, c) corresponding piezoresponse images acquired before and after dc poling, respectively; (d) piezoelectric hysteresis loop measured in grain 1.

pulse to grain 2 (Figure 5a) resulted in writing of a reversed domain as small as 30 nm in diameter, which appears as a dark spot in the piezoresponse image of grain 2 (Figure 5c). SFM ability to induce and detect switching in such a small area can provide an insight into the process of domain transformations within an individual grain and can help to explore the correlation between the macroscopic switching characteristics of ferroelectric capacitors and elementary switching mechanisms.

Domain Dynamics in Thin Films

It is likely that SFM can make a significant contribution to long-standing questions on the switching mechanism in thin films. It is commonly assumed that

this mechanism involves three elementary processes: domain nucleation at the polar surface, domain forward growth to the opposite surface, and sidewise domain expansion (1). However, until recently direct observation of domain dynamics seemed impossible. SFM provides a unique opportunity for in situ investigation of domain structure evolution at the nanometer scale. By applying a series of voltage pulses of various widths and acquiring piezoresponse images after every pulse, a consistent picture of the time-dependent behavior of domain structure in thin films at the nanometer scale can be obtained. A problem here is poor time resolution, because acquisition of an SFM image requires a time period of the order of minutes. Therefore, investigation of domain dynamics is possible in a quasi-static regime. Although there is an essential difference between switching in a real ferroelectric capacitor and in SFM experiments, local polarization reversal induced by the biased SFM tip imitates the growth of an individual domain in the capacitor during switching and can be used to measure directly the wall velocity, its interactions with defects, and other features of domain wall motion. Some qualitative experiments that demonstrate the capabilities of SFM in investigating domain dynamics have already been performed using ferroelectric crystals (7, 28, 29).

Experiments on investigation of domain growth within an individual grain were performed using the PZT 53/47-RuO₂ film (30). The tip was positioned at a certain point and voltage pulses of successively increasing width were applied to this point. After each pulse the resulting domain structure was imaged using the SFM piezoresponse mode. Figure 6 shows a topographic image of the film with a large grain in its center and a sequence of corresponding piezoresponse images showing domain sidewise growth as a result of the periodic local voltage application (the tip position during dc poling is marked by the cross in Figure 6a). The motion of the domain wall is decelerated by the grain boundary but not stopped. Under a pulse of sufficiently long duration and high amplitude, a growing domain propagates through the grain boundary by forming a lump that extends along the grain boundary and merges with domains in the neighboring grain. Subsequently, this lump bulges out and, as a result, the growing domain extends into the next grain. This result is reproducible. Although this result might seem unexpected, it is supported by inferences made by Scott et al (31) based on experimental data on the electrode size dependence of switching time in PZT capacitors (32) and on Ishibashi's nucleation model of switching (33, 34). Based on their numerical values of nucleation rate and domain wall speed for PZT films, it was shown (31) that the only way to explain the electrode size effect on switching time is to assume that domain walls in PZT films move through grain boundaries. It has to be noted that the wall velocity measured in SFM is several orders of magnitude lower than that estimated from the integral

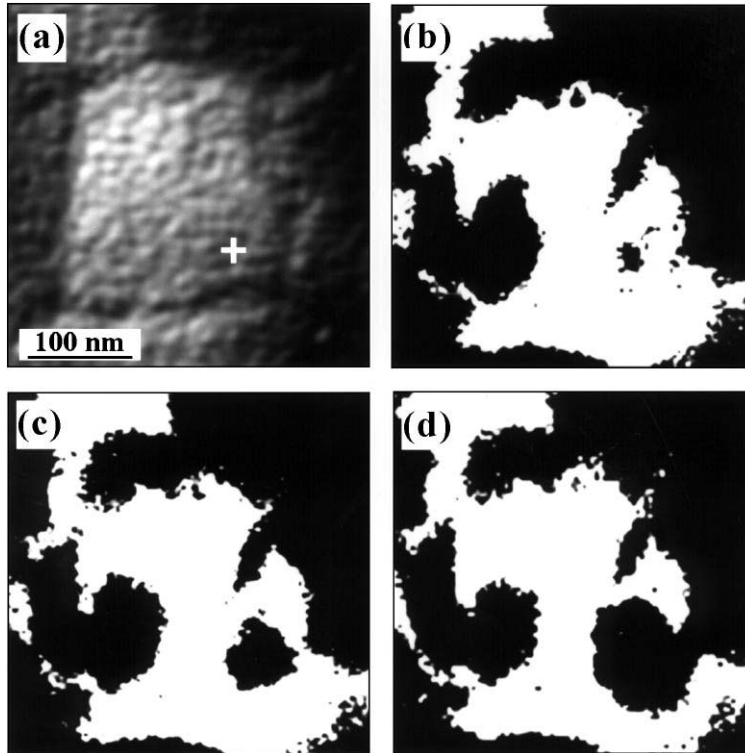


Figure 6 Domain dynamics observed in a PZT 53/47-RuO₂ film: (a) topographic image with the white cross indicating the tip position during dc voltage application; (b, c, d) piezoresponse images showing domain sidewise growth and apparent domain expansion into a neighboring grain; (b) original domain structure; (c, d) domain structures after application of the 8 V voltage pulses. Pulse duration: (c) 50 ms; (d) 150 ms.

switching measurements. A reason for this discrepancy could be the large time constant of the tip-sample contact. The reason for the tendency to switch along the grain boundary is not clear and needs further study.

SFM Studies of Degradation Effects in Thin Films

Commercial application of ferroelectric films is hindered by the degradation effects that limit the lifetime and reliability of ferroelectric-based devices (1, 35). Numerous efforts have been undertaken to better understand the physical mechanisms of these effects and reduce degradation properties of ferroelectric layers. However, these macroscopic studies focus on controlling integral parameters of ferroelectric capacitors and do not provide information on the exact nature of

complex domain configurations and their evolution in the presence or absence of an external field. In this respect, the SFM imaging method is a well-suited tool for investigation of degradation effects via the direct observation of domain structure, which is naturally linked to the polarization state of a ferroelectric film.

RETENTION LOSS One of the degradation effects is the spontaneous reversal of polarization leading to a progressive loss of remnant polarization (36, 37). This phenomenon, referred to as a retention loss, limits the functionality of the ferroelectric capacitor as a memory storage element. An important factor influencing the retention characteristics of the ferroelectric capacitor is the effect of grain boundaries and other internal interfaces. This effect was studied by carrying out local switching in different areas of an individual grain: namely, in the center of the grain and near its edge. The tip was put at the positions marked by crosses in the topographic images in Figures 7*a* and 7*d*, and a single voltage pulse was applied to each of these areas. The pulse width was chosen so as to induce partial switching of the grain. Subsequently, piezoresponse images of the grain were recorded at various time intervals, thus providing information about time evolution of the domain structure after the switching. When partial switching is induced well within the grain by applying the pulse to the grain center (Figure 7*a*), the reversed domain, less than 30 nm in size, is unstable and reverts back to the initial polarization direction within 10 min (Figures 7*b,c*).

This spontaneous back-switching can be attributed to the presence of an internal bias created by the trapped charge carriers, which makes the original domain configuration advantageous over the switched one. It should be noted that a reversed domain in the grain center disappeared within 10 min regardless of the number of SFM snapshots taken during this period, i.e. the imaging process has almost no effect on the characteristic time of domain back-switching, which suggests that the imaging voltage does not enhance the polarization decay. On the other hand, when the tip is moved closer to the grain boundary, the reversed domain generated (Figure 7*e*) is stabilized by the boundary, such that it does not switch back to its original state for at least 1 h (Figure 7*f*). This effect provides direct evidence for the role played by grain boundaries in stabilizing the switched polarization state. Further studies are imperative to clarify the mechanism of domain stabilization and to deconvolve the effects of the grain boundaries and the domain boundaries on retention characteristics.

SFM also allows direct observation of the retention loss when the entire grain is polarized. Upon application of a wider voltage pulse to the center of the grain (Figure 8*a*), it was fully switched to the opposite polarity, indicated by a change in grain contrast (Figures 8*b,c*). In this case, despite the stabilizing effect of the grain boundaries, the spontaneous back-switching is also observed, although

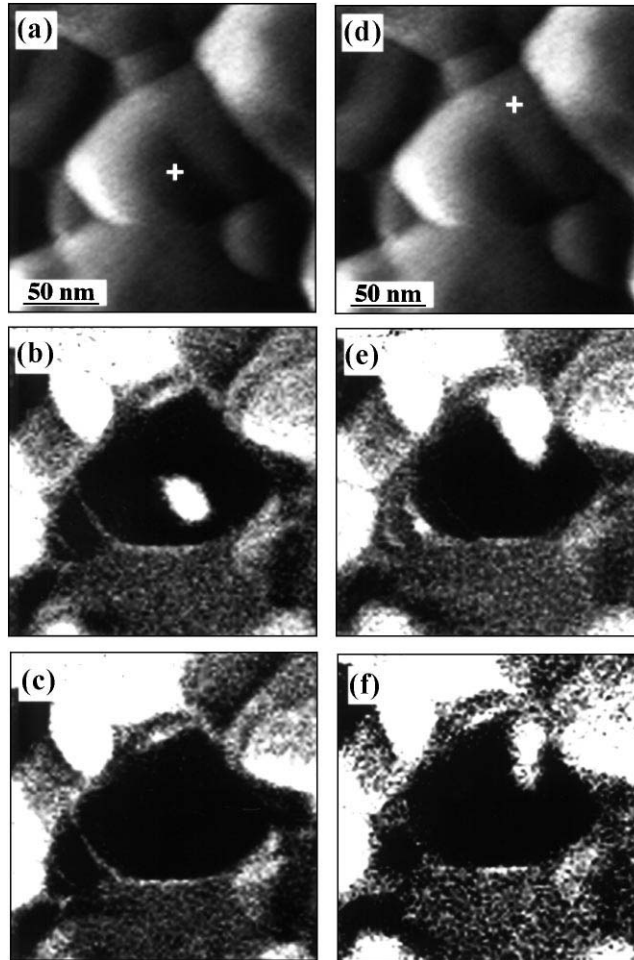


Figure 7 Retention experiments illustrating the role of grain boundaries in stabilizing the switched polarization state. Piezoresponse images were obtained at different time intervals on different grain locations in a PZT 20/80-LSCO film. Grain center: (a) topographic image with the white cross indicating the tip position during dc voltage application in the grain center; (b) immediately after dc poling (6 V, 50 ms); (c) 9 min after poling; Grain edge: (d) topographic image with the white cross indicating the tip position during dc voltage application near the grain edge; (e) immediately after dc poling (6 V, 50 ms); (f) 40 min after poling.

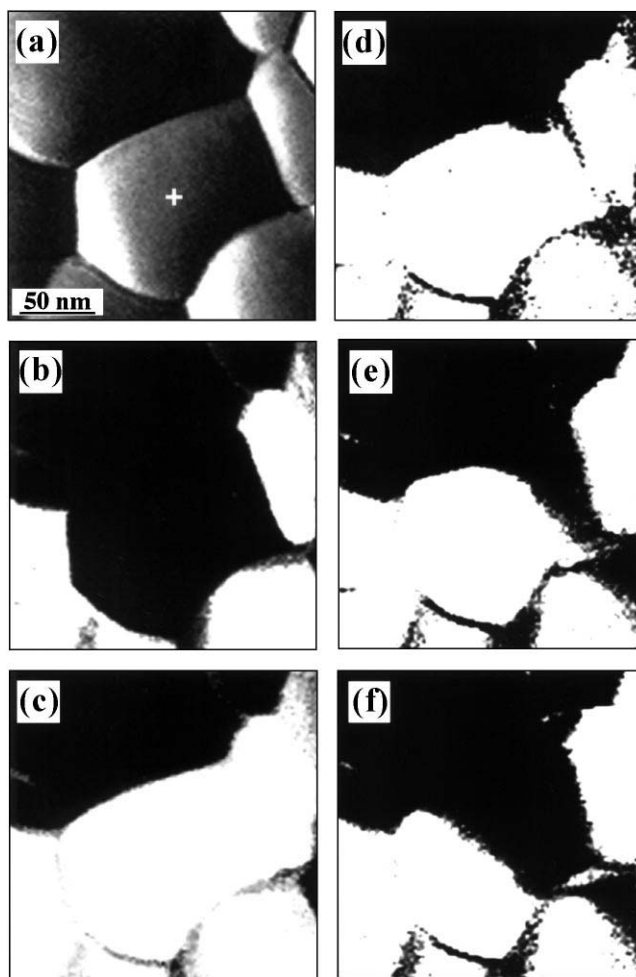


Figure 8 Retention loss dynamics observed in a PZT 20/80-LSCO film: (a) topographic image with the white cross indicating the tip position during dc voltage application; (b) original domain structure; (c) domain structure immediately after dc poling (6 V, 200 ms); (d–f) domain structures appearing after the removal of a dc field and acquired at different time intervals: (d) 4 h after poling; (e) 90 h after poling; (f) 140 h after poling.

it occurs within a much longer period of time. The piezoresponse images in Figures 8*d–f* show a gradual change in the domain structure of the switched grain, occurring after the removal of a dc field. As illustrated in Figure 8*d*, the first stages of the backward switching were detected 4 h after the pulse application. Once the reversal begins, it proceeds through the sidewise expansion of the reversed portion of the grain (Figures 8*e, f*). The most interesting factor is that the reversal begins along the grain boundary bordering a grain having a polarization state, which coincides with the original state of the switched grain, suggesting that the electrostatic interaction across the grain boundary initiates the backward switching. The time dependence of the size of the reversed fraction of the grain can be fitted to a power law dependence with an exponent of 0.68. The data suggest that the spontaneous reversal may proceed via a random walk-type mechanism similar to that postulated for magnetization reversal in spin-glass (38).

FATIGUE Another important degradation phenomenon to be considered in connection with the reliability problems is ferroelectric fatigue, or the decrease of switchable polarization with repeated polarization reversals. This effect is attributed to the pinning of domain walls by defects and by trapped electronic charge, which inhibits domain switching (1, 39–41). Recently, the possibility of direct studies of fatigue effects in ferroelectric films by means of SFM was demonstrated (42). To induce the repeated polarization switching and to simulate the fatigue process using SFM, a part of a PZT film on the Pt electrode, which is known to undergo severe fatigue upon repeated switching, was scanned for several hours with the tip held under an applied ac voltage, with amplitude higher than the coercive voltage. Periodically, the fatigue process was interrupted and a dc voltage was applied through the scanning tip to a square of $2 \times 2 \mu\text{m}^2$ to check the reversibility of domains in the fatigue area. This area was subsequently imaged using the SFM piezoresponse mode. The resulting piezoresponse images, which correspond to the different stages of the fatigue process, are shown in Figure 9. A bright square in the center of a piezoresponse image represents an area switched by the external dc voltage, whereas dark areas inside the bright square represent crystallites of opposite polarity that have not been switched. An increase in the area occupied by unswitchable crystallites is consistent with the fatigue behavior observed in ferroelectric capacitors, which indicates that SFM can induce ferroelectric fatigue at the sub-micrometer scale. This result is also direct experimental proof that the degradation of switching characteristics upon repeated switching is indeed caused by strong domain pinning and formation of unswitchable polarization in the film grains (39–41). However, further experiments are necessary to elucidate the physical mechanism for domain pinning.

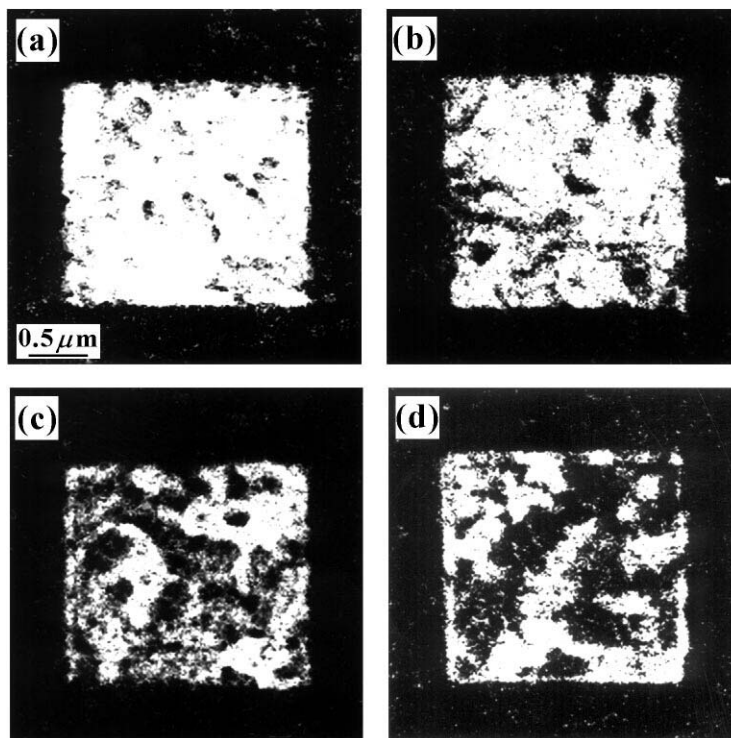


Figure 9 Piezoresponse images of the PZT/Pt heterostructure: (a) as-deposited and fatigued by applying 10 V, 20 kHz ac voltage through the scanning tip for (b) 1 h, (c) for 2 h, (d) for 4 h. The coercive voltage of the corresponding capacitor is about 1.5 V. The bright square of $2 \times 2 \text{ nm}^2$, produced by moving the SFM tip while applying a negative 15 V dc voltage, represents negatively polarized regions. Unswitchable crystallites appear as dark areas inside the white square region.

CONCLUDING REMARKS

Application of scanning force microscopy provides a unique opportunity for in situ nanoscale investigation of domain structure in ferroelectric thin films. SFM imaging methods for ferroelectric domains are based on the detection of surface charges associated with permanent built-in polarization and on the measurement of the piezoelectric response of a ferroelectric film to an applied ac field. The SFM charge imaging method might be more useful for domain visualization in soft thin films or in films with low piezoelectric activity. However, piezoresponse imaging has significant advantages over charge imaging of domains, such as high spatial resolution and insensitivity to screening effects.

The imaging resolution of the SFM piezoresponse mode depends on the film thickness and microstructure, but it still provides domain imaging with resolution of less than 100 nm. Its ultimate resolution is tip radius-limited and can be as good as several nanometers. SFM is emerging as a powerful technique for reliable control of domain structure at the nanometer scale level and for investigation of switching processes and electrical degradation effects in ferroelectric thin films. The SFM ability to manipulate domains smaller than 50 nm shows its potential as a data storage technique with a record density of tens of Gbits cm⁻².

In recent years tremendous progress has been made in ferroelectric film processing, yet various aspects of domain arrangement and domain dynamics in ferroelectric thin films are still to be addressed. Scanning force microscopy, via the direct imaging of domain structure, provides a unique insight into the real physical processes occurring in ferroelectric thin films, and there is no doubt that further quantitative SFM studies of ferroelectric films will substantially improve understanding of the basic properties of these materials.

ACKNOWLEDGMENTS

We thank Dr. H Yokoyama at the Electrotechnical Laboratory for acquiring charge images of PZT films. The authors are grateful to Profs. R Ramesh and A Prakash at the University of Maryland for supplying PZT films. This work was partly supported by the New Energy and Industrial Technology Development Organization (NEDO), Japan; and by the Department of Energy (DOE), USA.

Visit the *Annual Reviews* home page at
<http://www.AnnualReviews.org>.

Literature Cited

1. Scott JF, Paz de Araujo CA. 1989. *Science* 246:1400-5
2. Binnig G, Quate CF, Gerber Ch. 1986. *Phys. Rev. Lett.* 56:930-33
3. Martin Y, Williams CC, Wickramasinghe HK. 1987. *J. Appl. Phys.* 61:4723-29
4. Sarid D, Elings V. 1991. *J. Vac. Sci. Technol. B* 9:431-37
5. Saurenbach F, Terris BD. 1990. *Appl. Phys. Lett.* 56:1703-5
6. Luthi R, Haefke H, Meyer KP, Meyer E, Howald L, Guntherodt HJ. 1993. *J. Appl. Phys.* 74:7461-71
7. Luthi R, Haefke H, Gutmannsbauer W, Meyer E, Howald L, Guntherodt HJ. 1994. *J. Vac. Sci. Technol. B* 12:2451-55
8. Franke K, Besold J, Haessler W, Seegebarth C. 1994. *Surf. Sci. Lett.* 302:L283-87
9. Bluhm H, Wadas A, Wiesendanger R, Roshko A, Aust JA, Nam D. 1997. *Appl. Phys. Lett.* 71:146-48
10. Eng LM, Friedrich M, Fousek J, Gunter P. 1996. *J. Vac. Sci. Technol. B* 14:1191-96
11. Hidaka T, Maruyama T, Saitoh M, Mikoshiba N, Shimizu M, et al. 1996. *Appl. Phys. Lett.* 68:2358-59
12. Gruverman AL, Auciello O, Tokumoto H. 1996. *J. Vac. Sci. Technol. B* 14:602-5
13. Correia A, Massanell J, Garcia N, Levanyuk AP, Zlatkin A, Przeslawski J. 1996. *Appl. Phys. Lett.* 68:2796-98
14. Sarid D. 1991. *Scanning Force Microscopy with Applications to Electric, Magnetic and Atomic Forces*. New York/Oxford: Oxford Univ. Press
15. Wiesendanger R. 1994. *Scanning Probe Microscopy and Spectroscopy: Methods*

- and Applications. Cambridge: Cambridge Univ. Press
16. Quate CF. 1989. *Proc. NATO Advanced Study Institute on Basic Concepts and Applications of Scanning Tunneling Microscopy, Erice, Italy*, pp. 281–97. Dordrecht/Boston/London: Kluwer
 17. Ahn CH, Tybell T, Antognazza L, Char K, Hammond RH, et al. 1997. *Science* 276: 1100–3
 18. Terris BD, Stern JE, Rugar D, Mamin HJ. 1989. *Phys. Rev. Lett.* 63:2669–72
 19. Martin Y, Abraham DW, Wickramasinghe HK. 1988. *Appl. Phys. Lett.* 52:1103–5
 20. Yokoyama H, Inoue T. 1994. *Thin Solid Films* 242:33–39
 21. Guthner P, Dransfeld K. 1992. *Appl. Phys. Lett.* 61:1137–39
 22. Birk H, Glatz-Reichenbach J, Li-Jie, Schreck E, Dransfeld K. 1990. *J. Vac. Sci. Technol. B* 9:1162–65
 23. Franke K, Weihnacht M. 1995. *Ferroelect. Lett.* 19:25–34
 24. Franke K. 1995. *Ferroelect. Lett.* 19:35–43
 25. Gruverman AL, Auciello O, Hatano J, Tokumoto H. 1996. *Ferroelectrics* 184:11–20
 26. Burnham NA, Colton JR. 1993. Force microscopy. In *Scanning Tunneling Microscopy and Spectroscopy: Theory, Techniques and Applications*, ed. DA Bonnell, pp. 191–249. New York/Weinheim/Cambridge: VCH
 27. Zavala G, Fendler JH, Trolier-McKinstry SE. 1997. *J. Appl. Phys.* 81:7480–85
 28. Haefke H, Luthi R, Meyer KP, Guntherodt HJ. 1994. *Ferroelectrics* 151:143–49
 29. Gruverman AL, Hatano J, Tokumoto H. 1997. *Jpn. J. Appl. Phys.* 36:2207–11
 30. Gruverman AL, Auciello O, Tokumoto H. 1997. *Ferroelect. Rev.* In press
 31. Scott JF, Paz de Araujo CA, Melnick BM. 1994. *J. Alloys Compounds* 211:451–54
 32. Hase T, Shiosaki T. 1991. *Jpn. J. Appl. Phys.* 30:2159–62
 33. Ishibashi Y. 1986. *Jpn. J. Appl. Phys.* 24: 126–31 (Suppl.)
 34. Ishibashi Y, Takagi Y. 1971. *J. Phys. Soc. Jpn.* 31:506–10
 35. Warren WL, Dimos D, Waser RM. 1996. *MRS Bull.* 21:40–45
 36. Scott JF, Paz de Araujo CA, Meadows HB, McMillan LD, Shawabkeh A. 1989. *J. Appl. Phys.* 66:1444–49
 37. Nasby R, Schwank J, Rodgers M, Miller S. 1992. *Integrated Ferroelect.* 2:91–104
 38. Chamberlain RV, Mozurkewich G, Orbach R. 1984. *Phys. Rev. Lett.* 52:867–70.
 39. Scott JF, Pouligny B. 1988. *J. Appl. Phys.* 64:1547–51
 40. Warren WL, Dimos D, Tuttle BA, Pike GE, Schwartz RW, et al. 1995. *J. Appl. Phys.* 77:6695–702
 41. Mihara T, Watanabe H, Paz de Araujo CA. 1994. *Jpn. J. Appl. Phys.* 33:5281–86
 42. Gruverman AL, Auciello O, Tokumoto H. 1996. *Appl. Phys. Lett.* 69:3191–93