NANOSCALE INVESTIGATION OF POLARIZATION RETENTION LOSS IN FERROELECTRIC THIN FILMS VIA SCANNING FORCE MICROSCOPY*

A. Gruverman[1], S. A. Prakash[2], S. Aggarwal[2], R. Ramesh[2], O. Auciello[3], and H. Tokumoto[1]

[1]Joint Research Center for Atom Technology
Tsukuba, Ibaraki 305, Japan

[2]University of Maryland
Dept. of Materials Engineering
College Park, MD 20742

[3]Argonne National Laboratory
Materials Science Division
Argonne, IL 60439

January 1998

Invited paper to be presented at the Materials Research Society, Boston, MA, December 1-5, 1997.

*We wish to acknowledge support from NEDO at NIAIR-Japan, NSF-MRSEC at UMCP and the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

DISCLAIMER

NANOSCALE INVESTIGATION OF POLARIZATION RETENTION LOSS IN FERROELECTRIC THIN FILMS VIA SCANNING FORCE MICROSCOPY

A. GRUVERMAN*[1], S.A. PRAKASH**, S. AGGARWAL**, R. RAMESH**, O. AUCIELLO***, H. TOKUMOTO****

*Joint Research Center for Atom Technology (JRCAT), Tsukuba, Ibaraki 305, JAPAN

**Dept. of Materials Engineering, University of Maryland, College Park, MD 20742

***Argonne National Laboratory, Materials Science Division, Argonne, IL 60439-4838

****JRCAT-NAIR, Tsukuba, Ibaraki 305, JAPAN.

ABSTRACT

Scanning force microscopy (SFM) was applied to direct nanoscale investigation of the mechanism of retention loss in ferroelectric thin films. Experiments were conducted by performing local polarization reversal within an individual grain with subsequent imaging of a resulting domain structure at various time intervals. A conductive SFM tip was used for domain switching and imaging in the SFM piezoresponse mode.

INTRODUCTION

Commercial application of ferroelectric films is hindered by the degradation effects which limit the lifetime and reliability of ferroelectric-based devices [1]. 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 under and in the absence of an external field. In this respect, application of high resolution techniques such as scanning force microscopy (SFM) in conjunction with conventional electrical measurements may provide an opportunity to achieve a unique insight into the real physical processes which occur in ferroelectric thin films. Recently, it was shown that SFM is a well-suited technique both for imaging and for control of domain structures in ferroelectric thin films at the nanometer scale [2-5]. In this article, we report on SFM studies of the mechanism of polarization retention loss in ferroelectric films via the direct observation of their domain structures.

EXPERIMENT

The principle of domain observation in the SFM piezoresponse mode was described in detail elsewhere [2,4]. In brief, it is based on the detection of the local electromechanical vibration of the ferroelectric sample caused by an external ac voltage applied through the conductive tip. The voltage with a frequency ω, causes a film vibration with the same frequency due to the converse piezoelectric effect. The modulated deflection signal from the cantilever is detected using the lock-in technique. The phase of the vibration signal depends on the sign of the piezoelectric coefficient and polarization direction. This means that regions with opposite orientation of polarization should appear as regions of different contrast in the piezoresponse image.

RESULTS

Figures 1(a) and (b) show simultaneously acquired topographic and piezoresponse images of a $Pb(Zr_{0.2}Ti_{0.8})O_3$ film deposited on the $La_{0.5}Sr_{0.5}CoO_3$/Pt/TiN/Si substrate (PZT/LSCO film) by

[1]Present address: Sony Corporation, Yokohama Research Center, 134 Goudo-cho, Hodogaya-ku, Yokohama 240-0005, Japan; e-mail: alexei@src.sony.co.jp

A. Gruverman 1 6

laser ablation. The topographic image reveals the crystallite structure with clearly resolved morphological features. On the corresponding piezoresponse image, areas with opposite piezoelectric constants and polarities appear as bright and dark regions. Variation of contrast in the piezoresponse image reflects the perplexing arrangement of domains in the film. From comparison of surface morphology with the piezoresponse image a strong effect of the film crystallinity on the domain arrangement can be seen: often domains are limited by the grain boundaries. This is in contrast with the data, reported in [5], where almost no correlation was found between domain and crystallite structures in a sol-gel $Pb(Zr_{0.53}Ti_{0.47})O_3$ film on the RuO_2 electrode. A problem of microstructure-domain correlation in ferroelectric thin films is one of the important issues which can be addressed using SFM. From phase monitoring of the film vibration, it was concluded that in the dark areas of the piezoresponse image (Fig. 1(b)) polarization vector is oriented upwards (negative polarization state), while in the bright regions it is oriented downwards (positive polarization state). Possible reasons for the gray contrast in the piezoresponse image are discussed elsewhere [5].

Recently, 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 [2-5]. 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. In our experiment, the probing tip was positioned at the center of negatively polarized grain 1 in Fig. 1(a), and after a 6 V, 200 ms voltage pulse was applied to this grain, the piezoresponse image was acquired again. From Fig. 1(c), it can be seen that the grain, about 100 nm in size, exhibits a reversed contrast compared to that in Fig. 1(b), which is an indication of 180° polarization reversal occurring under the dc voltage.

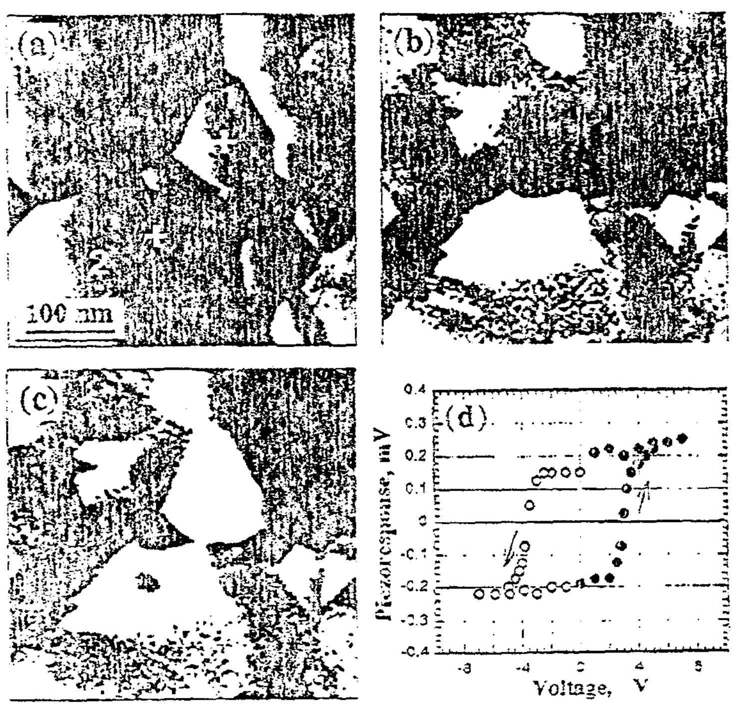

Figure 1. Nanoscale domain switching in a PZT/LSCO film: (a) topographic image of the film with the white crosses indicating positions of the SFM tip during dc voltage application; (b, c) corresponding piezoresponse images acquired before and after dc poling, respectively; (d) piezoelectric hysteresis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

It should be emphasized that the size of a reversed domain depends essentially on the parameters of the switching voltage pulse [4]. By varying the pulse width, partial switching of the grain can be accomplished: application of a shorter 6V, 50 ms voltage pulse to grain 2 (Fig. 1(a)) resulted in producing of a reversed domain as small as 30 nm in diameter, which appears as a dark spot in the piezoresponse image of grain 2 (Fig. 1(c)). 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. From comparison of Figs. 1(b) and 1(c), please note that the imaging process itself does not affect the existing domain structure as the other grains are still in their original polarization states. This fact supports the statement that the SFM piezoresponse mode can be used as a nondestructive method for domain visualization in ferroelectric films. Measurement of the piezoresponse signal as a function of a dc poling voltage applied to grain 1 showed its clear ferroelectric hysteresis behaviour (Fig. 1(d)) which is another evidence for the nanoscale ferroelectric switching occurring in the film.

One of the most serious degradation effects in ferroelectric films is the spontaneous reversal of polarization leading to a progressive loss of remnant polarization [7,8]. This phenomenon, referred to as a retention loss, limits the functionality of the ferroelectric capacitor as a memory storage element. Direct observation of time evolution of domain structure allows one to clarify the mechanism of retention loss in ferroelectric films.

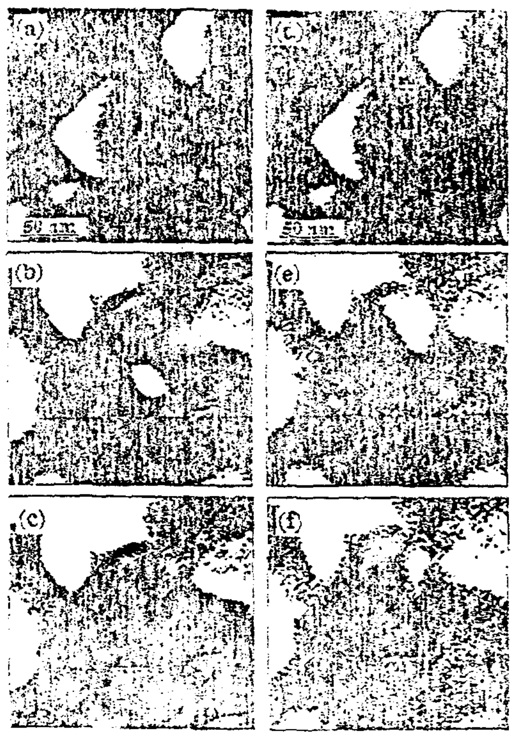

Figure 2. Retention experiments illustrating the role of grain boundaries in stabilizing the switched polarization state. Piezoresponse images were obtained at different time intervals on different grain locations in a PZT/LSCO film. Grain center: (a) topographic image with the white cross indicating 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.

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 accomplishing 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 Figs. 2(a) and 2(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 (Fig. 2(a)), the reversed domain, less than 30 nm in size, is unstable and reverts back to the initial polarization direction within 10 minutes (Figs. 2(b, c)). This spontaneous backswitching 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 minutes 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 there (Fig. 2(e)) is stabilized by the boundary, such that it does not switch back to its original state for at least 1 hour (Fig. 2(f)). This effect is a 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.

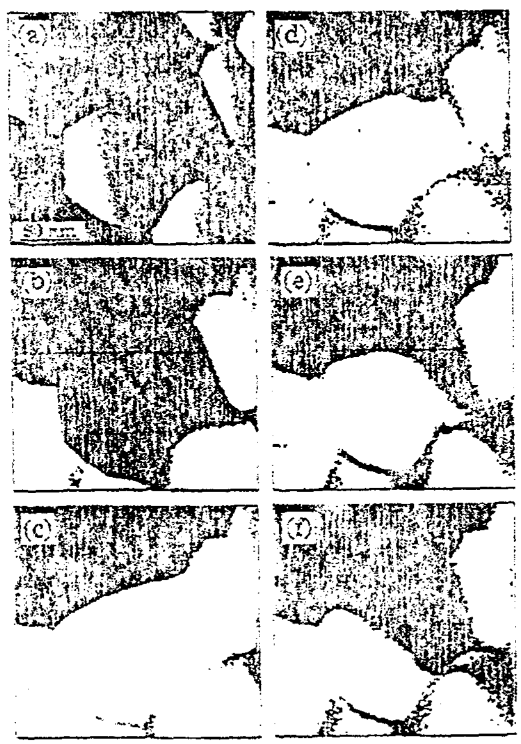

Figure 3. Retention loss dynamics observed in a PZT/LSCO film: (a) topographic image with the white cross indicating the tip position during dc voltage application; (b) original domain structure; (c) domain structure immediately after dc poling (6 V, 200 ms); (d-f) domain structures appearing after the removal of a dc field and acquired at different time intervals: (d) 4 hours after poling; (e) 90 hours after poling; (f) 140 hours after poling.

REFERENCES

1. J.F. Scott and C.A. Paz de Araujo, Science **246**, 1400 (1989).
2. K. Franke, J. Besold, W. Haessler and C. Seegebarth, Surf. Sci. Lett. **302**, L283 (1994).
3. T. Hidaka, T. Maruyama, M. Saitoh, N. Mikoshiba, M. Shimizu, et al., Appl. Phys. Lett. **68**, 2358 (1996).
4. A.L. Gruverman, O. Auciello and H. Tokumoto, J. Vac. Sci. Technol. **B14**, 602 (1996).
5. A.L. Gruverman, O. Auciello, R. Ramesh and H. Tokumoto, Nanotechnology **8**, No 3A, A38 (1997).
6. A.L. Gruverman, O. Auciello and H. Tokumoto, Appl. Phys. Lett. **69**, 3191 (1996).
7. J.F. Scott, C.A. Paz de Araujo, H.B. Meadows, L.D. McMillan, A. Shawabkeh, J. Appl. Phys. **66**, 1444 (1989)
8. R. Nasby, J. Schwank, M. Rodgers, S. Miller, Integrated Ferroelectrics **2**, 91 (1992).
9. R.V. Chamberlain, G. Mozurkewich, R. Orbach, Phys. Rev. Lett. **52**, 867 (1984).

A. Gruverman

6 6