Nanotechnology **14** (2003) 250–253 PII: S0957-4484(03)54373-2

# Towards the limit of ferroelectric nanosized grains

**A Roelofs[1], T Schneller[1], K Szot[2] and R Waser[1,2]**

[1] Institut für Werkstoffe der Elektrotechnik, RWTH Aachen, D-52056 Aachen, Germany
[2] Elektrokeramische Materialen, Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

Received 27 September 2002, in final form 20 December 2002
Published 20 January 2003
Online at stacks.iop.org/Nano/14/250

**Abstract**

Ferroelectric random access memories are non-volatile, low voltage, high read/write speed devices which have been introduced into the market in recent years and which show the clear potential of future gigabit scale universal non-volatile memories. The ultimate limit of this concept will depend on the ferroelectric limit (synonymous superparaelectric limit), i.e. the size limit below which the ferroelectricity is quenched. While there are clear indications that 2D ferroelectric oxide films may sustain their ferroelectric polarization below 4 nm in thickness (Tybell T, Ahn C H and Triscone J M 1999 *Appl. Phys. Lett.* **75** 856), the limit will be quite different for isolated 3D nanostructures (nanograins, nanoclusters).

To investigate scaling effects of ferroelectric nanograins on Si wafers, we studied $PbTiO_3$ (PTO) and $Pb(Zr_xTi_{1-x})O_3$ grown by a self-assembly chemical solution deposition method. Preparing highly diluted precursor solutions we achieved single separated ferroelectric grains with grain sizes ranging from 200 nm down to less than 20 nm.

For grains smaller than 20 nm, no piezoresponse was observed and we suppose this could be due to the transition from the ferroelectric to the paraelectric phase which has no spontaneous polarization. Recent calculations (Zhong W L, Wang Y G, Zhang P L and Qu B D 1994 *Phys. Rev.* B **50** 698) and experiments (Jiang B, Peng J L, Zhong W L and Bursill L A 2000 *J. Appl. Phys.* **87** 3462) showed that the ferroelectricity of fine ferroelectric particles decrease with decreasing particle size. From these experiments the extrapolated critical size of PTO particles was found to be around 4.2–20 nm.

## 1. Introduction

In the growing field of applications for ferroelectric thin films it is of great importance to understand the switching behaviour of thin films in the nanoscale regime. Since ferroelectric films deposited on $Si/SiO_2/Pt$ substrates are predominantly polycrystalline, an integrated device will incorporate only a few grains as its size drops down to several 100 nm. For ferroelectric devices of a size bigger than microns the properties are defined through the integral behaviour of the grains. Although using films consisting of grains with random crystallographic orientation, having a different size and a variable remanent polarization, different devices will always show comparable performance characteristics. Nevertheless, device downscaling needs control over the film growth in order to obtain a dense well oriented film with constant grain size. Only then may the switching properties on the submicron scale be comparable (e.g. for data storage applications).

To investigate nanoscale domain mapping and switching, piezoresponse force microscopy (PFM) [4–6] is applied. Topological and ferroelectric properties of individual grains along all three dimensions are monitored. In contrast to conventional macroscopic electrical characterization using extended top electrodes, PFM may be used to study ferroelectric thin films in the early growth stage having not a complete coverage at all.

Another important question for future ferroelectric random access memories (FeRAM) is: how small can a

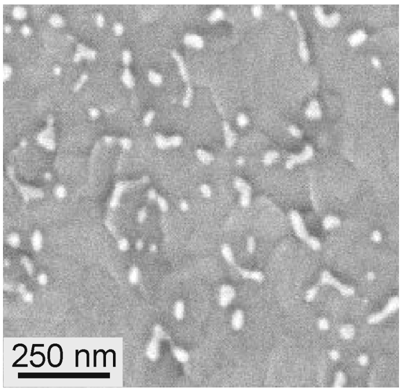


**Figure 1.** SEM image of PTO nanograins deposited onto a $Si/SiO_2/TiO_2/Pt$ substrate using a modified CSD route. Grains of different shape and sizes can be found. The grain sizes range from about 100 nm down to several 10 nm.

ferroelectric capacitor be and still have a stable switchable remanent polarization? Up to now there are some calculations predicting a transition from the ferroelectric phase to a paraelectric phase if the grain size becomes small enough [2]. (The estimated transition size for lead titanate (PTO), finite in three dimensions, calculated by Wang *et al* is 7.4 nm [7].) The required cell charge $Q_S$ decreases along with the minimum feature size $F$ of the FeRAM because of a decrease of the bit line capacity and improvement of the sense amplifier sensitivity (not shown here) [8]. Due to the fact that the polarization $P_r$ is area-independent under ideal conditions and is expected to decrease only slightly on real chips, this leads to a significant reduction in the capacitor area $A_S$. This is in contrast to the required capacitor area for DRAMs which is independent of $F$ because of the expected reduction in the operating voltage [9]. Together with the cell charge, this leads to an almost constant dielectric capacitance and, hence, to an almost constant capacitor area for DRAM. As a consequence, the DRAM cell required 3D folding of the capacitor area onto the cell area at relatively large feature size. This is much relaxed for FeRAM, for which the requirement to step into 3D starts at feature sizes below 130 nm (4 Mb generation). The geometry of the ferroelectric material and the ferroelectric limit will determine the scaling at future, very low feature sizes. The aspect of the ferroelectric limit for nanosized ferroelectric material is addressed by this paper.

## 2. Experiment

In this work we apply a bottom-up approach. A chemical solution deposition (CSD) method for the preparation of PTO [10] thin films is modified to achieve separated single PTO grains in the size ranging from 200 nm to less than 20 nm (this is yet to be published). This method opens up the way to study intrinsic size effects of several ferroelectric materials using an easy deposition method without the need of sophisticated structuring methods.

Operation in the PFM mode allows simultaneous recording of at least three different items of information: sample topography, out-of-plane polarization (OPP) and in-plane-polarization (IPP) along the $x$-scan direction (via lever torsion). A conducting p-doped silicon tip, serving as movable

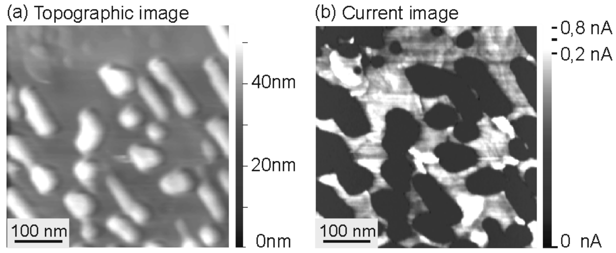


**Figure 2.** Current image of PTO nanograins deposited on a polycrystalline platinum bottom electrode. The sample was scanned in contact mode using a metallic coated tip and a dc voltage of 50 mV was applied while monitoring the local current. Clearly the large platinum grains can be distinguished from the small PTO grains.

top electrode, was used both for domain visualization (by applying an imaging ac voltage well below the coercive voltage of the PTO film).

Monitoring the inverse piezoelectric effect and separating both the $x$ (in-plane) and $z$ (out-of-plane) signals enables us to determine the projection of the polarization onto the $x$–$z$ plane. Please note that a polarization along the $y$-direction causes a small lifting of the cantilever leading to a overlap with the $z$ signal. Nevertheless, careful calibration on single crystalline standard samples allows full disentangling [11]. The domain imaging method is described in more detail elsewhere [12].

The PTO nanograins were deposited onto $Si/SiO_2/TiO_2/Pt$ substrates. An anhydrous lead acetate based precursor solution [13, 14] was spin coated onto the substrate and dried for 2 min on a hot plate at 350 °C. Crystallization was initiated by a rapid thermal annealing process at 700 °C for 10 min, resulting in separated single PTO grains. The separated PTO grains have no predominant crystallographic orientation as proven by x-ray diffraction experiments. Figure 1 shows a scanning electron microscope (SEM) image of a sample with grain sizes in the range of 10–100 nm. Scanning the sample in contact mode and applying a dc voltage between the platinum bottom electrode and the conductive cantilever monitoring the local electrical current (figure 2) enabled us to ensure that even the smallest grains that do not show piezoresponse are at least dielectric. This rules out the possibility of these grains being platinum hillocks.

Nanoscale inspection of the ferroelectric grains was carried out using a modified scanning force microscope [15] from JOEL$^{TM}$. Comparable experimental setups can be found elsewhere [16–18].

In figure 3 the piezoresponse image of a relatively dense PTO film is shown. The domain configuration in the different grains mostly show simple equidistant stripes of width ranging from 12 to about 80 nm. Analysing the IPP- and the OPP-image simultaneously, show that these stripes are representing 90° domains. For example, within the circle in figure 3(a) (OPP-image) we see black and grey stripes in the grain. The black region indicates the projection of the polarization onto the $z$-axis which points out of the plane of the paper. The grey stripes demonstrate that the polarization in these regions is lying in the $x$–$y$-plane and therefore not leading to any piezoresponse signal in the $z$-direction. (This information is enough to know that these neighbouring domains form 90° domain walls.) Taking into account that the domains will

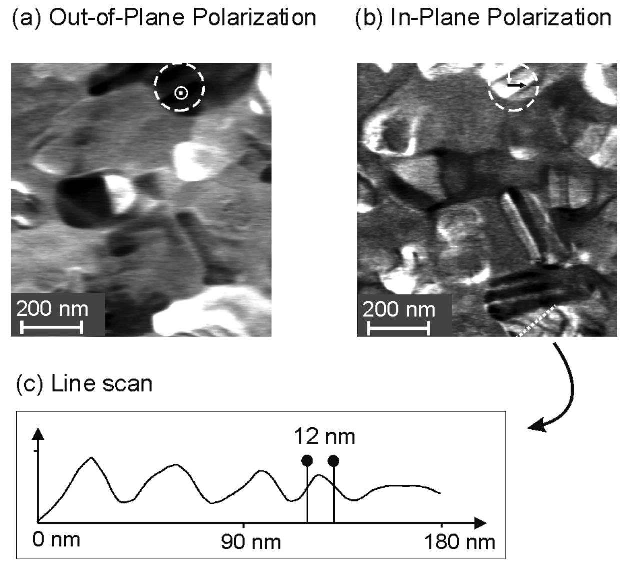


**Figure 3.** Piezoresponse image of a dense PTO film prepared by a standard CSD method with a non-diluted precursor solution. In (a) the OPP is shown. The grain in the upper part of the image marked with a circle consists of 90° domains. Black indicates that the projection of the polarization onto the $z$-axis is pointing into the positive $z$-direction. Black in the in-plane image (b) signifies that the projection of the polarization onto the $x$-axis points into the negative $x$-direction. In the lower part of the image (b) a line scan over the grain marked with an arrow exhibits the excellent resolution of the PFM, clearly showing domains with a width of 12 nm.

have a 'head-to-tail' configuration (for non-charged domain walls) leads to the conclusion that the polarization in the grey stripes of this grain will point into the negative $y$-direction. This analysis can be done for each grain and it is found that these stripes indicate domains with 90° domain walls. The line scan over the grain marked with an arrow in the IPP-image in figure 3(b) shows the excellent resolution of the measurement. Domains with a width of 12 nm can clearly be distinguished.

## 3. Results and discussion

The most fascinating finding is represented in figure 4. The topographic image clearly shows nine PTO grains of which two (marked with the white circle) do not lead to a piezoresponse signal as shown in the piezoresponse images, see figure 4(b). The grain size can be estimated in the line scan to ≈18 nm. We believe that at this grain-size the transition from the ferroelectric to the paraelectric phase could take place. Tybell *et al* reported on PFM measurements on epitaxial thin films down to 4 nm, which seems to contradict our results. This could be explained either by the different stress induced through the different substrate they are using, making the ferroelectric phase stable for thinner films, or may be due to the fact that they shrink the ferroelectric only in one dimension and not in all three as in this approach. If ferroelectricity is viewed as a collective phenomenon with a spontaneous polarization resulting from the alignment of localized dipoles within a correlation volume [19], it would be important to shrink all three.

Theoretical studies [2] predict a phase transition for PTO from the tetragonal phase (ferroelectric phase) to a cubic

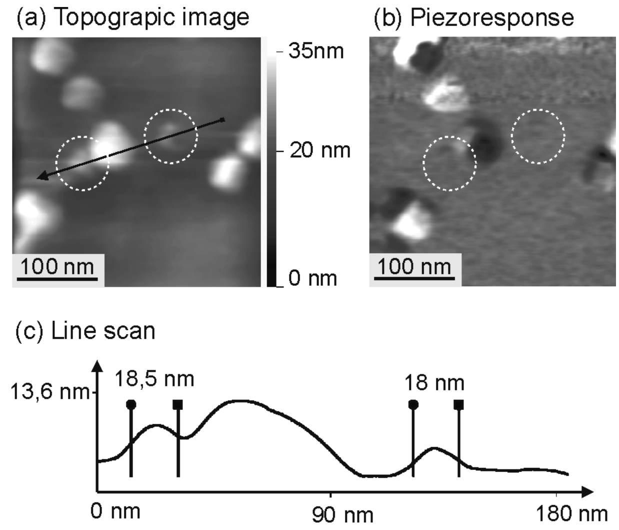


**Figure 4.** The topographic image (a) shows 11 PTO grains of sizes between 100 nm down to 20 nm indicated by the circles. In the line scan over the grain denoted with an arrow, shown at the bottom, the size of the grains can be determined. In the PFM images (b) in-plane and (c) out-of-plane piezoresponse, the grain of the size of 20 nm is not visible, leading to the assumption they do not have any permanent polarization.

(non-ferroelectric) phase, called a paraelectric phase if the size of a PTO cell becomes smaller than several nanometres. Furthermore, it can be seen that the domain configuration for single ferroelectric grains become simpler with the reduction in grain size. For grains in the range of about 40–50 nm we often find only two domains, and if the grain size becomes smaller than 40 nm we find monodomain grains.

## 4. Conclusion

In conclusion, we presented a simple bottom up approach to achieve separated ferroelectric PTO grains down to 20 nm. It was found that the domain configuration was strongly dependent on the size of the grains. For dense PTO films the grains are dominated by 90° domain walls whereas 180° domain walls govern the separated grains. Grains that were smaller then 20 nm did not show any piezoresponse, which led us to the conclusion that this could be the limiting size for the ferroelectric phase.

## Acknowledgments

This work has been supported in part by the Volkswagen Stiftung and the HGF project *Piccolo*.

## References


[1] Tybell T, Ahn C H and Triscone J M 1999 *Appl. Phys. Lett.* **75** 856

[2] Zhong W L, Wang Y G, Zhang P L and Qu B D 1994 *Phys. Rev.* B **50** 698
Wang C L and Smith S P 1995 *J. Phys.: Condens. Matter* **7** 7163
Li S, Eastman J A, Vetrone J M, Foster C M, Newnham R E and Cross L E 1997 *Japan. J. Appl. Phys.* 1 **36** 5169

[3] Jiang B, Peng J L, Zhong W L and Bursill L A 2000 *J. Appl. Phys.* **87** 3462
Zhong W L *et al* 1993 *J. Phys.: Condens. Matter* **5** 2619
Ishikawa K, Ishikawa K, Nomura T, Okada N and Takada K 1996 *Japan. J. Appl. Phys.* 1 **35** 5196

Chattopadhaya S, Ayyub P, Palkar V R and Multani M 1995 *Phys. Rev.* B **52** 13177

[4] Abplanalp M, Eng L M and Günter P 1998 *Appl. Phys.* A **66** S231

[5] Roelofs A, Schlaphof F, Trogisch S, Böttger U, Waser R and Eng L M 2000 *Appl. Phys. Lett.* **77** 3444

[6] Roelofs A, Pertsev N A, Waser R, Schlaphof F, Eng L M, Ganpule C, Nagarajan V and Ramesh R 2002 *Appl. Phys. Lett.* **80** 1424

[7] Wang Y G, Zhong W L and Zhang P L 1995 *Phys. Rev.* B **51** 17235

[8] Böttger U and Summerfelt S 2003 *Nanoelectronics and Information Technology* ed R Waser (New York: Wiley) at press

[9] International Technology Roadmap for Semiconductors (ITRS), 2001 http://public.itrs.net/Files/2001ITRS/Home.htm

[10] Bolten D, Hoffmann M, Hasenkox U, Lohse O and Waser R 1999 *Ferroelectrics* **225** 117

[11] Eng L M, Güntherodt H J, Schneider G A, Köpke U and Muñoz Saldaña J 1999 *Appl. Phys. Lett.* **74** 233

[12] Eng L M, Abplanalp M and Günter P 1998 *Appl. Phys.* A **66** S679

[13] Nouwen R, Mullens J, Franco D, Yperman J and Van Poucke L C 1996 *Vib. Spectrosc.* **10** 291

[14] Wouters D J, Norga G J and Maes H E 1999 *Mater. Res. Soc. Symp. Proc.* **541** 381

[15] Binnig G and Rohrer H 1982 *Helv. Phys. Acta* **55** 726

[16] Franke K, Besold J, Haessler W and Seegebarth C 1994 *Surf. Sci. Lett.* **302** L283
Hidaka T, Maruyama T, Sakai I, Saitoh M, Wills L A, Hiskes R, Dicarolis S A, Amano J and Foster C M 1997 *Integr. Ferroelectr.* **17** 319
Auciello O, Gruverman A, Tokumoto H, Prakash A S, Aggarwal S and Ramesh R 1998 *MRS Bull.* **23** 33

[17] Gruverman A, Auciello O and Tokumoto H 1998 *Annu. Rev. Mater. Sci.* **28** 101
Gruverman A, Kholkin A, Kingon A and Tokumoto H 2001 *Appl. Phys. Lett.* **78** 2751

[18] Ganpule C S, Nagarajan V, Li H, Ogale A S, Steinhauer D E, Aggarwall S, Williams E and Ramesh R 2000 *Appl. Phys. Lett.* **77** 292

[19] Lines M E and Glass A M 1977 *Principles and Applications of Ferroelectrics and Related Materials* (Oxford: Oxford University Press)