Journal of the European Ceramic Society 21 (2001) 2131–2134

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Scanning nonlinear dielectric microscopy with nanometer resolution

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Received 4 September 2000; received in revised form 2 November 2000; accepted 5 November 2000

Abstract

A very high-resolution scanning nonlinear dielectric microscope (SNDM) with nanometer resolution was developed for the observation of ferroelectric polarization. We demonstrate that the resolution of the microscope is of a nanometer order by measurement of the c–c domain wall of a $BaTiO_3$ single crystal and of the domains in PZT thin film. Especially in a film measurement, the resolution was sub-nanometer . Next, we also demonstrate that the resolution of SNDM is higher than that of a conventional piezo-response imaging. Finally, we conducted a fundamental study on the writing of a domain inversion dot in PZT thin film and succeeded to have a very small domain dots of the size 25 nm. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: $BaTiO_3$ and titanates; Ferroelectric properties; PZT; Scanning nonlinear dielectric microscopy

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1. Introduction

Recently, ferroelectric materials, especially in thin film form, have attracted the attention of many researchers. They are investigated for application in nonvolatile memory using the switchable dielectric polarization of ferroelectric material. To characterize such ferroelectric materials, a high-resolution tool is required for observing the microscopic distribution of remanent (or spontaneous) polarization of ferroelectric materials. With this background, we have proposed and developed a new purely electrical method for imaging the state of the polarizations in ferroelectric and piezoelectric material and a crystal anisotropy of them. It involves the measurement of point-to-point variations of the nonlinear dielectric constant of a specimen and is termed "scanning nonlinear dielectric microscopy (SNDM)".[1–4] This is the first successful, purely electrical, method for observing the ferroelectric polarization distribution without the influence of the shielding effect from free charges. To date, the resolution of this microscope has been improved down to the nanometer.

In this paper, at first we briefly describe the theory for detecting polarization and the technique for the nonlinear dielectric response. Next, we report the results of the imaging of the ferroelectric domains in $BaTiO_3$ single crystals and PZT thin films using SNDM with nanometer resolution. Especially in a measurement of PZT thin film, it was confirmed that the resolution was sub-nanometer. We also describe the theoretical resolution of SNDM. Moreover, we demonstrate that the resolution of SNDM is higher than that of a conventional piezo-response imaging by using scanning force microscopy (SFM) technique. Finally, we conducted a fundamental study on the writing of domain inversion dot in PZT thin film and succeeded to have very small domain dots of size 25 nm.

2. Nonlinear dielectric imaging with nanometer resolution

First, we briefly describe the theory for detecting polarization. Precise descriptions of the principle of the microscope have been reported elsewhere (see Refs. 2 and 3).

Fig. 1 shows the system setup of the SNDM using the LC lumped constant resonator probe.[3] In the figure, $C_s(t)$ denotes the capacitance of the specimen under the center conductor of the probe (the needle). $C_s(t)$ is a function of time because of the nonlinear dielectric response under an applied alternating electric field $E_{p3}(=E_p\cos\omega_p t, f_p=5\text{ kHz})$. The ratio of the alternating

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PII: S0955-2219(01)00187-X

variation of capacitance $\Delta C_s(t)$ to the static value of capacitance C_{s0} without time dependence is given as[2]

$$\frac{\Delta C_S(t)}{C_{S0}} = \frac{\varepsilon_{333}}{\varepsilon_{33}} E_P \cos\omega_P t + \frac{\varepsilon_{3333}}{4\varepsilon_{33}} E_P^2 \cos 2\omega_P t \quad (1)$$

where ε_{33} is a linear dielectric constant and ε_{333} and ε_{3333} are nonlinear dielectric constants. The even rank tensor, including the linear dielectric constant ε_{33}, does not change with 180° rotation of the polarization. On the other hand, the lowest order of the nonlinear dielectric constant ε_{333} is a third-rank tensor, similar to the piezoelectric constant, so that there is no ε_{333} in a material with a center of symmetry, and the sign of ε_{333} changes in accordance with the inversion of the spontaneous polarization.

This LC resonator is connected to the oscillator tuned to the resonance frequency of the resonator. The above mentioned electrical parts (i.e. needle, ring, inductance and oscillator) are assembled into a small probe for the SNDM. The oscillating frequency of the probe (or oscillator) (around 1.3 GHz) is modulated by the change of capacitance $\Delta C_s(t)$ due to the nonlinear dielectric response under the applied electric field. As a result, the probe (oscillator) produces a frequency modulated (FM) signal. By detecting this FM signal using the FM demodulator and lock-in amplifier, we obtain a voltage signal proportional to the capacitance variation. Thus we can detect the nonlinear dielectric constant just under the needle and can obtain the fine resolution determined by the diameter of the pointed end of the needle and the linear dielectric constant of specimens. The theoretical resolution of SNDM is precisely described in the same special issue of this *Journal of the European Ceramic Society*.[6]

For this study, the needle of the lumped constant resonator probe was fabricated using electrolytic polishing of a tungsten wire or a metal coated conductive cantilever. The radius of curvature of the tip was 1 μm–25 nm. To check the performance of the new SNDM, first, we measured the macroscopic domains in a multidomain $BaTiO_3$ single crystal. Fig. 2 shows the two-dimensional image of the so-called 90° a–c domain which is obtained by a coarse scanning over a large area. The sign of the nonlinear dielectric constant ε_{333} of the +c-domain is negative, whereas it is positive in the-c-domain. Moreover the magnitude of $\varepsilon_{111} = \varepsilon_{222}$ is zero in the a-domain, because $BaTiO_3$ belongs to tetragonal system at room temperature. Thus, we can easily distinguish the type of the domains.

Next, we measured the c–c domain boundary of the $BaTiO_3$ crystal, whose domain wall thickness was considered to be within a few lattice spacings, by the high resolution mode of SNDM. At first, we identified the c–c domain boundary using macroscopic two-dimensional scanning [Fig. 3(a)]. Then one-dimensional scanning was used just on the domain boundary along the direction perpendicular to the boundary. The results are shown in Fig. 3(b). If we define the domain wall thickness of this crystal by the clearly distinguishable distance between the +c and −c-domains, it was 9 nm.

To demonstrate that this microscopy is also useful for the domain measurement of thin films, we measured a PZT thin film. Fig. 4 shows the SNDM (a) and AFM (b) images taken from a same location of PZT thin film deposited on a $SrTiO_3$ (STO) substrate using metal organic chemical vapor deposition. From Fig. 4(b), it is apparent that the film is polycrystalline and that each grain in the film is composed of a several domains [from Fig. 4(a)]. From X-ray diffraction analysis, this PZT film belongs to the tetragonal phase and diffraction

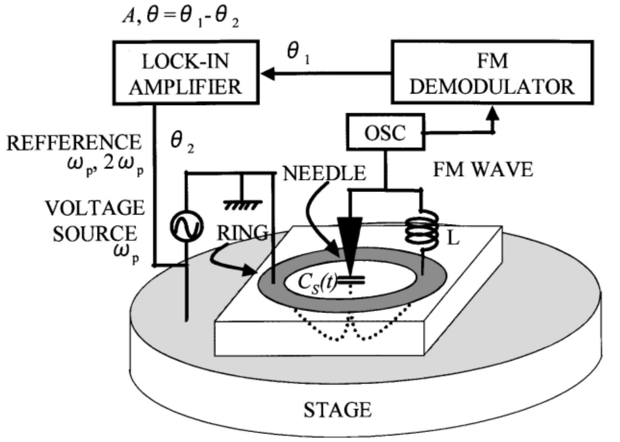

Fig. 1. Schematic diagram of SNDM.

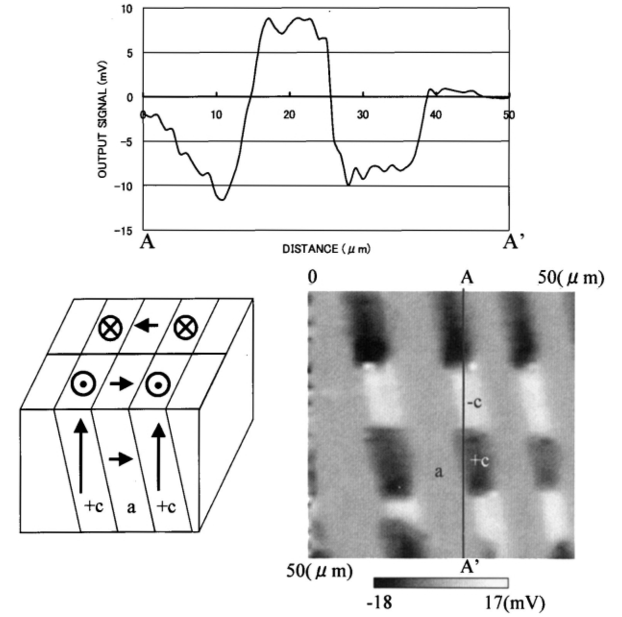

Fig. 2. A two-dimensional image of the 90° a–c domain in a $BaTiO_3$ single crystal and the cross-sectional (one-dimensional) image along the line A–A′.

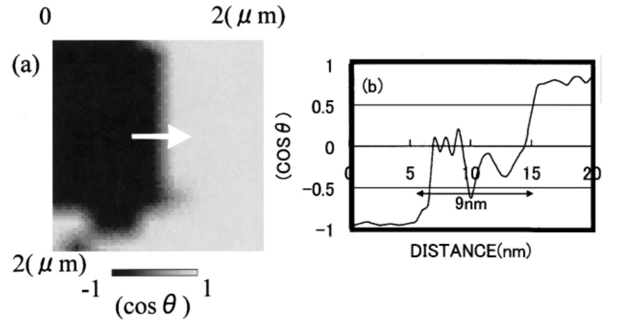

Fig. 3. (a) A two-dimensional image of the 180° c–c domain boundary in a $BaTiO_3$ single crystal. (b) A one-dimensional phase (cos θ) image of the 180° c–c domain boundary.

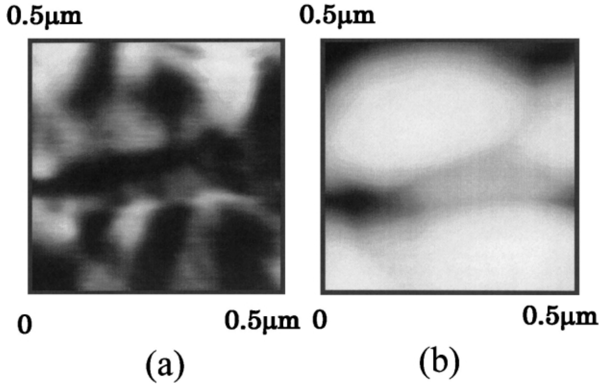

Fig. 4. Images of a PZT film on a $SrTiO_3$ substrate. (a) Domain patterns by SNDM, (b) surface morphology by AFM.

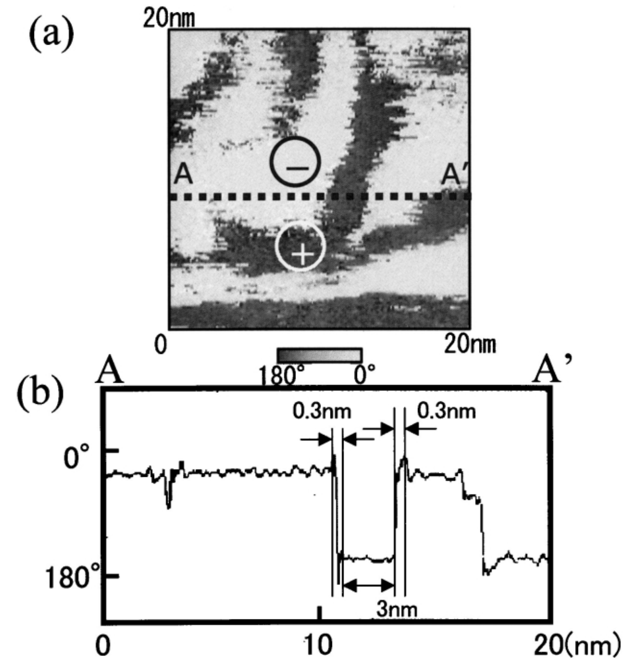

Fig. 5. Nano-scale ferroelectric domain on PZT thin film, (a) domain image, (b) cross-sectional (one-dimensional) image along the line A–A′.

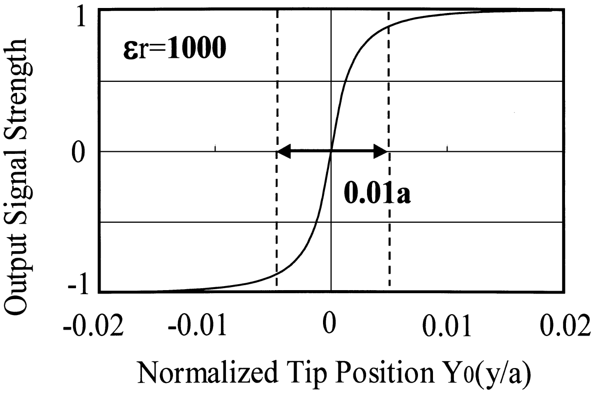

Fig. 6. Theoretical images of the 180° c–c domain boundary.

peaks corresponding to both the c-axis and a-axis were observed. Moreover, in Fig. 4(a), the observed signals were partially of zero amplitude, and partially positive. Thus, the images show that we succeeded in observing 90° a–c domain distributions in a single grain of the film.

This image of the film was taken from a relatively large area. Therefore, we also tried to observe very small domains in the same PZT film on STO substrate but in a different location of the film by seeking very small c–c domain distribution. The results are shown in Fig. 5. The bright area and the dark area correspond to the negative polarization and the positive polarization, respectively. It shows that we can successfully observe a nano-scale 180° c–c domain structure. Fig. 5(b) shows a cross-sectional image taken along line A–A′ in Fig. 5(a). As shown in this figure, we measured the c–c domain with the width of 3 nm. Moreover, we found that the resolution of the microscope is less than 0.3 nm.

To clarify the reason why such high resolution can be easily obtained, even if a relatively thick needle is used for the probe, we show the calculated results of the one-dimensional image of 180° c–c domain boundary lying at $y=0$ (we chose y direction as the scanning direction). The details of the model of this calculation have been precisely reported elsewhere (see Refs. 5 and 6). Fig. 6 shows the calculated results where Y_0 is the tip position normalized with respect to the tip radius a. The resolution of the SNDM image heavily depends on the dielectric constant of the specimen. For example, for the case of $\varepsilon_{33}/\varepsilon_0=1000$ and $a=10$ nm, an atomic scale image will be able to be taken by SNDM.

3. Comparison between SNDM imaging and piezoelectric imaging

Another frequently reported high-resolution tool for observing ferroelectric domains is piezoelectric response imaging using SFM. From the viewpoint of resolution for ferroelectric domains, SNDM will surpass

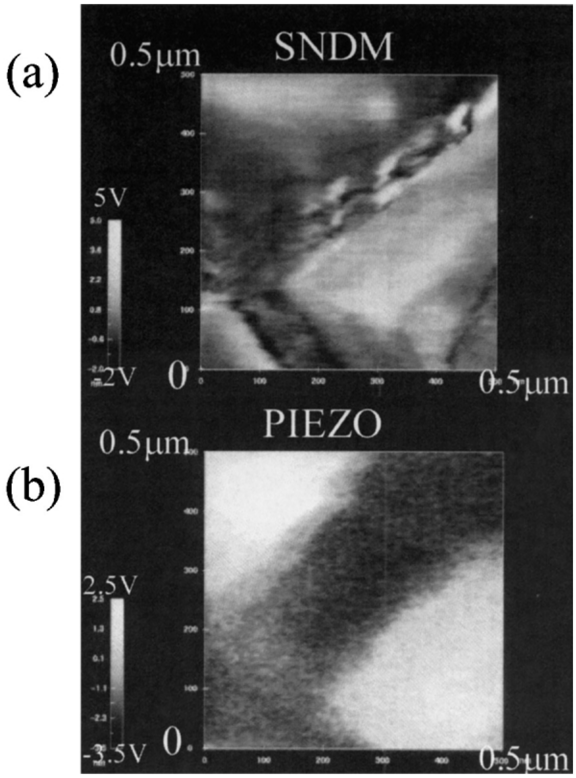

Fig. 7. Simultaneously taken images of a PZT film on a $SrTiO_3$ substrate. (a) Domain patterns by SNDM, (b) domain patterns by SFM (piezo-imaging).

the piezo-response imaging because SNDM measures the nonlinear response of a dielectric material which is proportional to the square of the electric field, whereas the piezoelectric response is linearly proportional to the electric field. The concentration of the distribution of the square of the electric field in the specimen just under the tip is much higher than that of the linear electric field. Thus, SNDM can resolve smaller domains than that measured by piezo-imaging technique. To prove this fact experimentally, we also performed the simultaneous measurements of the same location of the above-mentioned PZT film sample by using SNDM- and piezo-imaging. The results are shown in Fig. 7. These images were taken just under the same conditions using the same metal coated cantilever. From the images, we can understand that the resolution of SNDM is higher than that of conventional piezo-response imaging using SFM
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4. Ferroelectric recording on PZT thin film by SNDM

Finally, to check the performance of the SNDM system as a ferroelectric recording system, we wrote a domain inversion dot in a PZT thin film. First, we sought an area with negative polarity and then formed inversion dots by applying a pulsed voltage of 10 V between the needle (tip) and the metal stage with intervals of 15.6 nm using the same SNDM system as shown in Fig. 1. The pulse duration was 250 μs. The result is shown in Fig. 8. Although in some places domains were not inverted, we succeeded in some places to produce very small inverted domain dots with smallest dimension 25 nm.

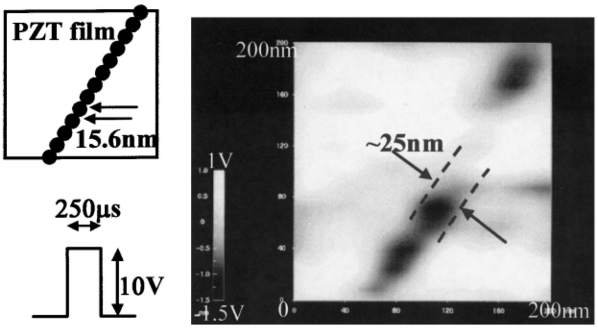

Fig. 8. Ferroelectric recording on PZT thin film by SNDM.

5. Conclusions

From the measurement of the ferroelectric domains, we have experimentally demonstrated that the newly developed scanning nonlinear dielectric microscope has nanometer resolution. Especially in a film measurement, the resolution was sub-nanometer. Next, we demonstrated that the resolution of SNDM is higher than that of a conventional piezo-response imaging. Finally, we conducted a fundamental study on the writing of domain inversion dots in a PZT thin film and succeeded to produce small inverted domain dots with the size of 25 nm.

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