Domain orientation in ultrathin (Ba,Sr)TiO₃ films measured by optical second harmonic generation

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(Received 23 May 2002; accepted 5 February 2003)

The analysis of polarization diagrams for specular and scattered second harmonic generation (SHG) was used for the structural characterization of submicron domain structures of thin (Ba,Sr)TiO₃ (BST) films. It is shown that the lack of separation of these two contributions may lead to completely wrong conclusions about the domain orientation in these films. SHG studies of the thickness dependence of domain fractions (including 180° domains) reveal the presence of ferroelectric domains in ultrathin BST films (6 nm), although no domain structure was observed by atomic force microscopy. Thus the presence of ferroelectric ordering was demonstrated in perovskite films with a thickness down to 6 nm. © 2003 American Institute of Physics.
 [DOI: 10.1063/1.1563849]

I. INTRODUCTION

Barium strontium titanate (Ba,Sr)TiO₃ (BST) thin films are being widely investigated as alternative dielectrics for non-volatile random access memory storage capacitors due to their high dielectric constant, low leakage current, small dielectric losses, lack of fatigue or ageing problems. In these devices, information is stored in the polarization state of the ferroelectric material itself. The polarization of the ferroelectric medium is proportional to the domain fraction oriented in the applied electric field direction. In a thin film geometry, the efficiency of the memory unit depends on the domain fraction oriented normal to the film (so called *c*-orientation); the presence of in-plane oriented domains or deviation of their orientation from exact *c*-orientation decreases the storage efficiency.

Also for high storage density, going to thinner films is advantageous, since reduction of the film thickness leads to a reduction of the polarization voltage and therefore to energy saving. Unfortunately a thickness reduction from the macroscopic down to the mesoscopic regimes results in a change of polarization stability, although the polarization itself can be either inhibited or enhanced.^{1–6} As the structural and polarization properties of these ultra thin films cannot readily be obtained by conventional techniques, there is a need for novel and reliable characterization techniques.

It was recently shown that for very thin ferroelectric films the nonlinear optical technique of second-harmonic generation (SHG) can give quantitative information on complex micro domain structure with a higher spatial resolution (down to 1 micron) than the standard X-Ray diffraction

(XRD) analysis.^{7–9} Following this, Gopalan *et al.*¹⁰ and Barad *et al.*^{11,12} demonstrated the use of polarization diagrams to investigate the domain structures in K₂FeO₄ and Bi₁₄Ti₃O₁₂.

However in their approaches only the coherent component of the SHG radiation is analyzed comprehensively. On the other hand, it was shown that the SHG radiation from an inhomogeneous film, with the size of inhomogeneities *D* comparable to (or smaller than) the wavelength λ_ω , generally contains both coherent and incoherent contributions,¹³ with the relative weight of the latter increasing with increasing *D*. The analysis of the incoherent component can only be omitted *a-priori* if *D* is much smaller than the wavelength λ_ω , as even with a ratio $D/\lambda_\omega \sim 0.1$ the scattered intensity is quite high.¹³

In this paper we show how a complete analysis of the polarization diagrams for specular and scattered SHG can be used for the structural characterization of the thickness dependent domain structure of ultrathin BST films. Our SHG studies reveal the presence of domains, including the fractions of 180° domains, in very thin BST films (6 nm), that were not observable by alternative methods (AFM, XRD).

II. EXPERIMENT

A. Film fabrication and structural characterization

The BST thin films were deposited on MgO(100) substrates by RF sputtering of a ceramic target. The substrate temperature was held at 800 °C during deposition at a pressure of 0.3 Torr O₂. The RF deposition of complex oxide films under a high pressure of working gas (oxygen) yields films with high crystallinity.¹⁴ The orientation, lattice constants and epitaxial nature of the films were determined by X-ray diffraction (XRD) $\Theta/2\Theta$ and ϕ scans. $\Theta-2\Theta$ XRD

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FIG. 1. Scanning electron microscopy images of BST film ($d_f = 140$ nm) before (a) and after (b) selective etching.

scans revealed only (001) (and traces of (100) for the thinnest film) type reflections and no evidence of second-phase nucleation for all of our films. The barium concentration in the films is 0.7, which gives a Curie temperature $T_C = 15^\circ\text{C}$ for bulk BST.

Figure 1(a) shows scanning electron microscopy (SEM) image of a BST film. The surface is atomically flat with rare impurities of an unknown origin. Figure 1(b) shows the same film after selective etching that allows to distinguish the domain structure of the film. Deep etched areas are positively oriented domains (dielectric polarization vector oriented towards an observer) embedded into a matrix of negatively oriented domains. Deviation of the polarization vector from the Z -axes cannot be determined by SEM.

Figure 2 shows atomic force microscopy (AFM) images of BST films of different thickness. The size of domains decreases with decreasing film thickness from $D \sim 1\ \mu$ in a 140 nm film down to $D \sim 100$ nm in a 14 nm film. For a 6 nm film AFM does not reveal a domain structure.

B. Second harmonic generation

Two types of non-linear optical experiments were performed: the dependences of the SHG intensity on the input laser wave polarization were measured (polarization diagrams) as well as the dependences on the scattering angle (scattering indicatrices). The experimental geometry for these two types of measurements is shown in Fig. 3. All these measurements were carried out at 8°C .

For the SHG measurements the output of a Ti:Sapphire laser at 760 nm with a pulse width of about 100 fs and a

repetition rate of 82 MHz was used, with an average power of 100 mW focused onto a spot of about $100\ \mu\text{m}$. The SHG signal at 380 nm in transmission was filtered by color filters and a monochromator and detected by a photomultiplier tube (PMT). Polarization of the fundamental beam could be varied by rotating a Berek compensator ($\varphi=0$ corresponds to p -polarized fundamental wave, or horizontally polarized for normal incidence), polarization of the SHG waves was chosen by Glan prisms. The angle of incidence was varied by rotating the sample around the vertical in-plane axis in the range of $\pm 12^\circ$ (restricted by the aperture of the cooling system). To study the scattering indicatrices the whole detection system could be rotated in the horizontal plane with the laser spot on the sample surface as the center of rotation, the scattering angle θ was measured with respect to the forward direction. The aperture of the detection system was 2° . For all samples the [100] axis of the MgO substrate was oriented horizontally.

Figure 4(a) shows the SHG scattering indicatrices for the 6-nm sample for normal and 10° angle of incidence for the polarization angle $\varphi=0$. The SHG radiation is completely incoherent for both normal and 10° incidence: no specular peak is observed. However for perpendicular polarization coherent radiation appears for not-normal incidence (insets in Fig. 4(a) show the polarization diagrams for appropriate points of scattering indicatrices). For thicker samples the SHG radiation is incoherent for normal incidence, but mostly coherent for 10° incidence, for which a large specular peak is observed. Scattering indicatrices (beyond the angular range of the specular radiation) are coincident for normal and 10° incidence for all samples; as an example, Fig. 4(b) shows the SHG scattering indicatrices for the 140-nm sample. Additional maxima near $\pm 20^\circ$ in both Figs. 4(a) and 4(b) correspond to speckle patterns usually observed at an inhomogeneous surface.¹⁵ Appearance of the specular peak for not-normal incidence points to a much higher unipolarity of the samples in the Z -direction.

In Fig. 5(a) one sees the SHG polarization dependences for the 140-nm sample for normal incidence (for horizontally and vertically polarized SHG wave). As no coherent SHG radiation was found for normal incidence, these dependences should be considered as *polarization diagrams for incoherent radiation*. Polarization diagrams for 10° incidence (for p - and s -polarized SHG) are shown in Fig. 5(c). In this figure for each polarization angle the incoherent radiation was subtracted from the total SHG radiation. The dependences obtained in this way are considered as *polarization diagrams for coherent radiation*.

III. THEORETICAL CONSIDERATION

The ferroelectric films we studied are in a polydomain state. According to the XRD results, the c -axes is the preferable orientation of the domains. However traces of in-plane oriented domains can be found as well as deviations from exact c -axes orientation (within 1 degree). We therefore consider two models of the film structure. In the first model, which we call the mixture model (MM), all types of X , Y and Z -oriented domains are present. In the second model, called

FIG. 2. Atomic force microscopy images of BST films of different thickness.

the deviation model (DM), only near- c -oriented domains are considered with a deviation from exact c -orientation. Experimental data were fitted using both models, and on the base of the results of the fitting procedure the preferable model was chosen.

It is important to note, that the SHG technique is sensitive for very small deviations of the domains from a pure c -orientation as for normal incidence a 4 mm symmetry (001) surface gives zero SHG signal. However, *any* deviation from the (001) orientation will yield a nonzero SHG signal. Therefore it is not possible to conclude *a priori* which factor is dominant: small deviations from the (001) orientation or the presence of in-plane oriented domains. Ferroelectric films with the same symmetry and analogous structure were studied in Ref. 16, in which it was shown that the mostly anisotropic SHG signal originates from the deviation of the film surface from the exact c -orientation.

Details of the described model structures are shown in Fig. 6. In the MM (Fig. 6(a)) the fractions of domains with dielectric (DE) polarization vector oriented parallel and antiparallel to one of three main crystallographic axes of the

substrate are denoted as F_I^+ and F_I^- ($I=X, Y$ or Z). The differences of the fractions of positively and negatively oriented domains are denoted as $\Delta F_I = F_I^+ - F_I^-$ and determine the relative contributions to the SHG field of the specular signal. For the incoherent part we need to define the contributions of the total fraction of domains oriented along the corresponding axes by $F_I = F_I^+ + F_I^-$.

In the DM (Fig. 6(b)) the DE polarization in each domain is oriented with a deviation from the exact z -orientation. The deviation angles along X and Y axes are θ_X and θ_Y respectively, the domain fractions are denoted in the same way as in the MM model. The deviation angle distribution is supposed to be random within $0 < \theta < \theta_\alpha$ ($\alpha=X, Y$).

The ferroelectric phase of BST is described by the 4 mm point group symmetry. For this symmetry there are 3 nonzero tensor elements: $\chi_{xxz} = \chi_1$, $\chi_{zxx} = \chi_2$ and $\chi_{zzz} = \chi_3$; positively and negatively oriented domains give SHG fields with opposite signs. As for coherent radiation the superposition of SHG fields from individual domains yields the total SHG field, only the relative factors ΔF_X , ΔF_Y and ΔF_Z are es-

sential. If “+” and “-” domains are compensated the SHG coherent signal equals zero. For incoherent radiation, intensities rather than fields are summed up in the total signal, and the sign of the field does not play a role. For MM the SHG fields for $X(E_{FX})$ and $Y(E_{FY})$ oriented domains for normal incidence (Z -oriented domains do not contribute to SHG at normal incidence for this symmetry) are given by:

$$E_{FX} = f_{\omega}^2 f_{2\omega} \cdot d_f \cdot \begin{cases} \chi_3 \cos^2 \varphi + \chi_2 \sin^2 \varphi, & p\text{-out} \\ \chi_1 \sin 2\varphi, & s\text{-out} \end{cases} \quad (1a)$$

$$E_{FY} = f_{\omega}^2 f_{2\omega} \cdot d_f \cdot \begin{cases} \chi_1 \sin 2\varphi, & p\text{-out} \\ \chi_2 \cos^2 \varphi + \chi_3 \sin^2 \varphi, & s\text{-out} \end{cases} \quad (1b)$$

where f_{ω} and $f_{2\omega}$ are Fresnel factor for fundamental and SHG waves, d_f is the film thickness (approximation $nd_f \ll \lambda$ is used, n is the refractive index of the film, for the Fresnel factors birefringence is not taken into account).

For DM SH field is more complicated and is expressed in terms of appropriate deviation angles:

$$E_{FX} = f_{\omega}^2 f_{2\omega} \cdot d_f \cdot \sin \theta_x \begin{cases} \chi_2 \sin^2 \varphi + \cos^2 \varphi ((2\chi_1 + \chi_2) \cos \theta_x^2 + \chi_3 \sin \theta_x^2), & p\text{-out} \\ \chi_1 \sin 2\varphi, & s\text{-out} \end{cases} \quad (2a)$$

$$E_{FY} = f_{\omega}^2 f_{2\omega} \cdot d_f \cdot \sin \theta_y \begin{cases} \chi_1 \sin 2\varphi, & p\text{-out} \\ \chi_2 \cos^2 \varphi + \sin^2 \varphi ((2\chi_1 + \chi_2) \cos \theta_y^2 + \chi_3 \sin \theta_y^2), & s\text{-out} \end{cases} \quad (2b)$$

The polarization diagrams for coherent $I_{\text{coh}}^{2\omega}$ and incoherent $I_{\text{incoh}}^{2\omega}$ radiation are described respectively by the following equations:

$$\begin{aligned} I_{\text{coh}}^{2\omega} &= (\Delta F_X E_{FX} + \Delta F_Y E_{FY}) (\Delta F_X E_{FX} + \Delta F_Y E_{FY})^* \\ &= \Delta F_X^2 E_{\Delta X}^2 + \Delta F_Y^2 E_{\Delta Y}^2 + 2\Delta F_X \Delta F_Y E_{\Delta X} E_{\Delta Y} \cos \gamma \end{aligned} \quad (3)$$

$$I_{\text{incoh}}^{2\omega} = F_X E_{\Delta X} \cdot E_{\Delta X}^* + F_Y E_{\Delta Y} \cdot E_{\Delta Y}^* = F_X E_{\Delta X}^2 + F_Y E_{\Delta Y}^2 \quad (4)$$

where $\gamma = 2\omega/c(n_X^{2\omega} - n_Y^{2\omega})$ is the phase difference between the SHG waves from X - and Y -oriented domains. Note, that Eqs. (1–3) can be easily transformed into the equation used in the works of Gopalan.¹⁰ For incoherent component one should keep in mind that the same domains give both coherent and incoherent radiation, because of their intrinsic

nonlinear-optical inhomogeneity,¹³ this is why the total SHG intensity is a superposition of coherent and incoherent component.^{17,18}

Analogous expressions can be obtained for non-normal incidence. In those equations Z -oriented domains are represented by ΔF_Z (for coherent radiation) and F_Z (for incoherent radiation). However, whereas for normal incidence Fresnel factors are equal for X - and Y -oriented domains ($f_x = f_y = f$) and therefore can be considered in Eq. (1–2) as scaling factors), for non-normal incidence the Fresnel factors are different, giving rather complicated expressions for the polarization dependences that are not presented here.

FIG. 3. Experimental geometry: for polarization measurements Berek compensator (BC) is rotated; the angle of incidence is changed by rotating the sample; Glan prism is used as analyzer (A), and PMT can be rotated to receive transmitted or scattered SH radiation.

FIG. 4. SHG scattering indicatrices for normal and 10° incidence for $d_f = 6$ nm (a) and $d_f = 140$ nm (b). Insets in (a) show the polarization diagrams for transmitted and scattered radiation for both angles of incidence, arrows point to the scattering angle at which the polarization diagrams were measured.

FIG. 5. SHG polarization diagrams for BST film with $d_f = 140$ nm for incoherent radiation ((a) and (b), normal incidence) and coherent radiation ((c), 10° incidence, SHG intensity after incoherent contribution being subtracted). Lines are fits to data using MM ((a) incoherent radiation; (c) coherent radiation) and DM (b), incoherent radiation. Filled circles correspond to p -polarized SHG wave, open circles correspond to s -polarized SHG wave.

IV. RESULTS AND DISCUSSION

For normal incidence, for which in our experiments only incoherent radiation was found, the experimental polarization diagrams were analyzed using Eq. (4). For the MM, 3 fitting parameters were used: the ratios of nonlinear susceptibilities χ_2/χ_1 and χ_3/χ_1 , and the ratio of the fractions of X - and Y -oriented domains: F_X/F_Y . The same scaling factor was used for all samples, therefore the thickness dependence of F_X/F_Y can be obtained. For the DM, 4 fitting parameters were used: the same ratios of nonlinear susceptibilities and the deviation angles θ_X and θ_Y .

We used simultaneous fits for p -out and s -out SHG polarization. The results of this fitting procedure for the sample with $d_f = 140$ nm are shown in Fig. 5 ((a) for MM and (b) for DM respectively). Fitting parameters are presented in Table 1. For all samples the χ^2 is better for MM and also

TABLE I. Fitting parameters in the mixed and deviation models.

	$d_f = 6$ nm	$d_f = 14$ nm	$d_f = 49$ nm	$d_f = 70$ nm	$d_f = 140$ nm
MM					
χ_2/χ_1	4.4	21	30	2.1	1.2
χ_3/χ_1	+3.9	-0.7	-0.5	-1.2	-0.9
Chi-squared, 10^3	0.2	1.3	2	1	1
DM					
χ_2/χ_1	14	7	0.6	2.7	1.2
χ_3/χ_1	90	197	1160	170	7
M_x (degrees)	10.5	12.2	5.5	3.4	5.4
M_y (degrees)	7.5	6.1	4.9	4.5	6.5
Chi-squared, 10^3	0.5	7	9	2	2

FIG. 6. Model structure of polydomain film: (a) mixed model, (b) deviation model.

yielded very reasonable values of the in-plane domain fractions. In contrast, with DM very high values for the ratio χ_3/χ_1 were obtained, that were never found for any ferroelectric crystal. Additionally, the deviation angle obtained in this way exceeds the value measured by XRD (which is $<1^\circ$ for all samples). These results strongly support the choice of the MM for the further analysis. Note, that if the polarization diagram for a single output polarization was fitted, the value of chi-squared can be reduced by more than one order of magnitude. However, we consider the simultaneous fits as being more reliable.

For 10° incidence, both coherent and scattered radiation contribute to the total SHG radiation. To obtain the coherent SHG radiation, necessary for calculating the differences in the domain fractions, we subtract the scattered radiation (extrapolated from the scattering diagram to the zero scattered angle, see Fig. 4) from the total SHG radiation. The polarization diagrams obtained in this way for the sample with $d_f = 140$ nm are presented in Fig. 5(c). Using the nonlinear susceptibility values calculated from the SHG results at normal incidence, one can fit these data by Eq. 3 with 2 new fitting parameters: $\Delta F_X/\Delta F_Z$ and $\Delta F_Y/\Delta F_Z$.

The thickness dependences of these parameters within MM are presented in Fig. 7. The nonlinear susceptibility tensor components measured with respect to χ_1 reveal an extremum around 50 nm. The total fractions of X - and Y -oriented domains (normalized for the value of F_X for $d_f = 140$ nm) have a minimum around 50 nm and increase strongly for the thinnest film with $d_f = 6$ nm; $F_X \approx F_Y$ for thick films. The absolute value of the domain difference (ΔF_Z for $d_f = 140$ nm is taken as unity) increases with decreasing film thickness.

Qualitatively the obtained results are in agreement with the thickness dependence of the film parameters measured independently. When the film thickness is decreased, the out-of-plane lattice constant passes a maximum around 50 nm and then decreases substantially (see Fig. 7(d)).

Though there is no direct correlation between the lattice constant and the nonlinear susceptibility it might appear indirectly through the local polarization (dipole momentum) and relaxation constants ζ . It was shown in Ref. 19 that the

FIG. 7. Thickness dependence of BST film parameters obtained from SHG measurements: (a) the ratios of nonlinear susceptibility tensor components χ_2/χ_1 and χ_3/χ_1 ; insets: dependences of the same ratios on the damping constant ζ and local polarization P_0 (according to Ref. 19); (b) total fractions of in-plane domains (normalized on F_x for $d_f = 140$ nm); (c) fractions of non-compensated domains (normalized on ΔF_z for $d_f = 140$ nm); (d) thickness dependence of lattice constant; horizontal line corresponds to the out-of-plane lattice constant of bulk BST crystal.

increase of local polarization P_0 influences the value of χ_3/χ_1 . This dependence is not monotonic, for specific value of P_0 the absolute value of χ_3/χ_1 increases sharply and then passes zero (see insets in Fig. 7(a) for qualitative picture). The ratio χ_2/χ_1 depends only on relaxation constants ζ . It is quite reasonable to assume that the increase of the lattice constant leads to a “loosening” of the lattice, that according to Ref. 19 results in an increase of χ_2/χ_1 ratio.

Further theoretical investigations as well as independent measurements of the film parameters (constants of Landau expansion for free energy, damping constants, etc.) are required for a more quantitative description of the thickness dependence of nonlinear susceptibility tensor components.

The analysis of the domain fraction is more straightforward. Decreasing the film thickness leads to a relative increase of the total in-plane fractions of in-plane oriented domains. From the present measurements we are not able to estimate the total fraction of c -oriented domains, more de-

FIG. 8. Dependence of remnant polarization on the film thickness.

tailed study of the angle of incidence is required for such estimation, which is in progress now. The fraction of in-plane noncompensated domains increases slightly with decreasing film thickness. More drastic changes are observed for c -oriented non-compensated domains: ΔF_z increases 5 times and changes sign for the thinnest sample. The absence of coherent radiation for normal incidence and its appearance for not-normal incidence indicates that X - and Y -oriented domains are quite compensated in comparison with Z -oriented domains. The increase of unipolarity with decreasing film thickness was observed also by TEM measurements (etching technique). In the film plane the net-projection difference is more than an order of magnitude lower than for the z -direction.

However with the thickness decrease, the fraction of non-compensated domains (both in-plane and c -axis-oriented) increases. These results are in agreement with dielectric measurements showing an increase of unipolarity of BST films with thickness decrease (Fig. 8).

It is important to note that the accuracy of our present measurements (for two angles of incidence only) is not enough for reasonable calculations of the full fraction of z -oriented domains F_z . In order to obtain this value and to increase the accuracy of the ratios of $\Delta F_x/\Delta F_z$ and $\Delta F_y/\Delta F_z$, the dependences of scattered and coherent radiation on the angle of incidence (known as Maker fringes for coherent radiation) should be measured (in progress now).

V. CONCLUSIONS

In conclusion we have shown how the nonlinear optical technique of second harmonic generation can be used to study the domain structure of very thin ferroelectric films. In contrast to earlier studies we show that for these thin films it is essential to investigate both the coherent and incoherent parts of the SHG response. This generalized approach can be applied for any type of thin films with a domain structure, and is not restricted to the limit $D/\lambda_\omega < 0.1$.

We applied the technique to characterize the domain structure of ferroelectric thin films and found a good agreement with the data obtained independently, where possible. Moreover, the sensitivity of the method allows us to go beyond the sensitivity of conventional *in-situ* techniques and show the presence of domains for the film thickness close to the theoretically predicted limit. In particular, we found for very thin BST films a maximum of the nonlinear susceptibility tensor component χ_{zzz} around 50 nm, coinciding with the

thickness dependence of the lattice constant and an increase of the unipolarity of the films with decreasing film thickness. According to the SHG measurements a domain structure exists for thin films down to 6 nm, while in AFM images it only becomes visible above 14 nm.

ACKNOWLEDGMENTS

This work is supported partly by the Dutch Science Foundation (Grant No NWO 1604-1999), INTAS (Grant INTAS-0100075), the EU network SILC and the Russian Foundation of Basic Research (Grant No 00-02-16557).

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