Probing domain microstructure in ferroelectric Bi$_4$Ti$_3$O$_{12}$ thin films by optical second harmonic generation

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The domain microstructure in an epitaxial thin film of Bi$_4$Ti$_3$O$_{12}$ on a SrTiO$_3$(001) substrate is studied by second harmonic generation measurements. The input polarization dependence of the second harmonic signal exhibits spatial symmetries that reflect the presence of eight different domain variants present in the film. A theoretical model is presented that explains the observed symmetries and extracts quantitative information on the nonlinear optical coefficients of the material and statistics of domain variants present in the film area being probed. The following ratios of nonlinear coefficients and birefringence were determined: $d_{32}/d_{11} = -3.498\pm 0.171$, $|d_{26}/d_{12}| = 0.365\pm 0.010$, $|d_{26}/d_{11}| = 1.273\pm 0.036$, and $|n_p-n_d| = 0.101\pm 0.018$ (at 532 nm). © 2001 American Institute of Physics. [DOI: 10.1063/1.1334641]

I. INTRODUCTION

Aurivillius phases are of interest in nonvolatile memory since several of them exhibit excellent fatigue resistance during repeated polarization reversals with electric field. Bi$_4$Ti$_3$O$_{12}$ is a member of the Aurivillius phases in which the component oxide is a divalent element such as Bi$_2$O$_2$, BaTiO$_3$, SrTiO$_3$, Na$_2$O, Pb$_2$O, and several rare earth oxides, R may be Ti$_2$O$_3$, Nb$_2$O$_3$, Ta$_2$O$_5$, Mo$_2$O$_3$, W$_2$O$_5$, Ga$_2$O$_3$, Fe$_2$O$_3$, Cr$_2$O$_3$, and x can be 1 to 8. Epitaxial growth of Bi$_4$Ti$_3$O$_{12}$ films on various substrates invariably results in a complex domain microstructure, resulting from the fact that the spontaneous polarization in a monoclinic unit of Bi$_4$Ti$_3$O$_{12}$ has components along both the $a$- and $c$- crystallographic directions where $a$--$c$ forms the mirror plane (010). Both $a$ and $c$ components of the polarization can be independently reversed, thus resulting in four different classes of domain walls and 18 wall configurations. All these configurations are not readily distinguishable by conventional x-ray diffraction or transmission electron microscopy (TEM). In this article, we show how probing the second harmonic generation (SHG) response of a Bi$_4$Ti$_3$O$_{12}$ film with a complex domain microstructure can provide many of these domain distinctions in a quantitative manner.

II. FILM EPITAXY AND DOMAIN MICROSTRUCTURE

The Bi$_4$Ti$_3$O$_{12}$ thin film studied here was grown on a SrTiO$_3$(001) substrate using molecular-beam epitaxy as previously reported in detail. The lattice parameters of the cubic SrTiO$_3$(001) substrate, $a' = 3.9050$ Å closely match along its diagonals of $a'\sqrt{2}$, with the lattice parameters $a = 5.4500$ Å and $b = 5.4059$ Å of the monoclinic Bi$_4$Ti$_3$O$_{12}$. (The other lattice parameters are $c = 32.832$ Å, and $\beta$ = 90.00°.) The lattice planes $b$--$c$, $c$--$a$, and $a$--$b$ of Bi$_4$Ti$_3$O$_{12}$ are respectively denoted as (100), (010), and (001) planes. The $\theta$--2$\theta$ and $\phi$-scan x-ray diffraction spectra of the film in Fig. 1 indicate that the Bi$_4$Ti$_3$O$_{12}$ film has grown epitaxially on the underlying SrTiO$_3$ substrate. The epitaxial orientation relationship is SrTiO$_3$(001) [110]/Bi$_4$Ti$_3$O$_{12}$(001)[100]. In this configuration, there are eight possible domain configurations of the Bi$_4$Ti$_3$O$_{12}$ as shown schematically in Fig. 2. Each of the possible domains has a monoclinic unit cell, which deviates only slightly from the orthorhombic unit cell. The polarization axis forms an angle of $\sim 4.5^\circ$ from the crystallographic $a$ axis in the $a$--$c$(010) plane.

Figure 3 shows the various domain walls that can arise from a combination of these domain variants. In particular, referring to the pseudo-orthorhombic planes of Bi$_4$Ti$_3$O$_{12}$, the four main types of domain walls can exist: (I) Nearly-90° domain walls along the (110) planes, (II) domain walls separating variants with opposite $a$ component of polarization. These walls are either neutral (001) planes or charged (100) planes. (III) Domain walls separating variants with opposite $c$ component of polarization. These walls are either neutral (100) planes or charged (001) planes and (IV) 180° domain walls parallel to the (010) planes and separating domains with opposite sense of both $a$ and $c$ components of polarization. Dark-field TEM image formed using a weak (210) reflection in the [001] zone axis reveals a network of 90° domain walls as shown in Fig. 4. The black and white contrasts in image represent domain variants separated by 90° domain walls. These walls separate domains with their $a$ axis along the SrTiO$_{3}$[110] or along the SrTiO$_{3}$[110] directions. The

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average lateral size of such domains is \( \sim 100-200 \) nm.

Based on the above discussion, we define four classes of domain variants \( X^+, X^-, Y^+, \) and \( Y^- \) according to whether the \( a \) component of polarization points in the \( \text{SrTiO}_3 [110], [\bar{1}10], [1\bar{1}0], \) or \( [\bar{1}10] \) directions, or alternatively \((+x, -x, +y, -y)\) directions in Fig. 2, respectively. In the following sections, we describe how the \( X^+, X^-, Y^+, \) and \( Y^- \) domains can be distinguished by second harmonic generation measurements in normal incidence to the substrate.

III. SECOND HARMONIC GENERATION MEASUREMENTS

A. Experimental procedure

A schematic description of the experimental setup is shown in Fig. 5. The fundamental beam from a 10 Hz \( Q\)-switched Nd:YAG laser (\( \lambda = 1064 \) nm) is passed through a series of beam splitters to cut its intensity to approximately 10 mW. The beam is then propagated through a polarizer, half-wave plate, focusing lens (\( f = 500 \) mm) and a long-wave pass filter to absorb any residual second harmonic light. The half-wave plate is situated on a computer controlled rotating stepper motor to allow the continuous change of the polarization at the input. The sample is placed 50 mm in front of the focal point of the focusing lens, where the beam diameter is approximately 1.2 mm, and the energy density is below the damage threshold. The sample is held with the thin film at the backside of the sample. The output beam is passed...
through a short-wave pass filter to absorb the fundamental light at 1064 nm and the second harmonic signal at 532 nm is analyzed with a polarizer aligned either along the \( x \) axis (\( \text{SrTiO}_3[110] \)) or \( y \) axis (\( \text{SrTiO}_3[1\bar{1}0] \)). The beam is then propagated to the photomultiplier tube (PMT) and its intensity is lowered using neutral density filters if needed. The signal from the PMT is fed to a gated integrator and a boxcar averager. The averaged output is read to the computer via an analog-to-digital converter.

The measurement starts with the light polarization parallel to the \( \text{Bi}_4\text{Ti}_3\text{O}_{12} \) thin film [010] and with the analyzer either parallel or perpendicular to that direction. (The \( \text{SrTiO}_3 \) substrate is cubic, and it was confirmed that it does not result in any second harmonic response.) The incident polarization is changed by rotating the half-wave plate while keeping the analyzer fixed. The measurement is made once with the analyzer along the \( x \) axis and once along the \( y \) axis. A typical polar–plot pair of the SHG intensity as a function of input polarization angle for the two different output polarizations of the 532 nm light is shown in Fig. 6. The experimental data is shown as circles, while the solid line is a fit obtained from the theoretical model described as follows. These plots provide information on the specific distribution of domains in the area probed. In general, a different area on the film gives slightly different polar plots, however, all these plots can be analyzed within the theoretical framework described in the following section.

**B. Theoretical model**

In order to describe the expected SHG intensity from the thin film \( I^{2\omega} \), the net polarization at the second harmonic frequency \( P^{2\omega} \), should be calculated along a global coordinate system \( (x, y, z) \) of the substrate (shown in the schematic of Fig. 2). Referring first to the monoclinic unit cell coordinates \( (a, b, c) \) of \( \text{Bi}_4\text{Ti}_3\text{O}_{12} \), the second harmonic polarization components are given by

\[
\begin{bmatrix}
P_a^{(2\omega)} \\
P_b^{(2\omega)} \\
P_c^{(2\omega)}
\end{bmatrix} = \begin{bmatrix}
d_{11} & d_{12} & d_{13} & 0 & d_{15} & 0 \\
0 & 0 & 0 & d_{24} & 0 & d_{26} \\
d_{31} & d_{32} & d_{33} & 0 & d_{35} & 0
\end{bmatrix}
\begin{bmatrix}
E_a^2 \\
E_b^2 \\
E_c^2 \\
2E_bE_c \\
2E_aE_c \\
2E_aE_b
\end{bmatrix}.
\]

Here, the electric fields \( E_a \), \( E_b \), and \( E_c \) are the electric fields of the incident light at the optical frequency \( \omega \) inside the thin film and \( d_{ij} \) are the nonlinear coefficients, where the subscripts \( i,j = (1, 2, \text{ and } 3) \) correspond, respectively, to the coordinates \( (a, b, \text{ and } c) \) of the unit cell. The superscripts \( (\omega) \) and \( (2\omega) \) are simply labels referring to the frequency of the incident electric fields, \( E^\omega \), and the nonlinear polarizations \( P^{2\omega} \).

We assume the fundamental wave is a plane-wave propagating along the \( z \) direction and incident normal to the film. This assumption has been found to be quite good when comparing the predicted nonlinear coefficients from the model with known nonlinear coefficients of reference samples.\(^6\) This, we believe, is due to the fact that the incident gaussian beam is very weakly focused (beam divergence \( \sim 0.01 \text{ rad} \)), and the sample is placed close to the focal point where the beam incident on the sample is large (1.2 mm). Further, due to the large index, \( n \), of the film, any external

![FIG. 6. Polar plots of the SHG intensity \( I^{2\omega}(\lambda = 532 \text{ nm}) \) as a function of input polarization angle, \( \theta(\lambda = 1064 \text{ nm}) \) for the output polarization of the SHG light along (a) \( \text{SrTiO}_3[1\bar{1}0] \) (y axis), and (b) \( \text{SrTiO}_3[110] \) (x axis). The experimental data is shown as circles, while the solid line is a fit obtained based on Eq. (5) derived from the theoretical model presented in the article. Inset shows the details around the origin.](image-url)
Consider light passing through the film thickness in an area along the measurement, the output analyzer is fixed either across the film. The film thickness fraction $t_X$ of the film, the second harmonic intensity from the film, can now be written as

$$P_X^y = \left( \int_0^{A^x} (r^{X^+} - r^{X^-}) dA_X \right) P_X^{y^+},$$

where the superscript $2\omega$ has been dropped for convenience, and the nonlinear polarizations are henceforth understood to be at this frequency. The integral expression inside the bracket in Eq. (2) is defined as $\Delta A_X$. In words, $\Delta A_X$ is the net thickness fraction of $X^+$ domains with respect to $X^-$ domains, i.e., the relative thickness fraction of domains with the $a$ component of their polarization along SrTiO$_3$ [110] versus [1̅1̅0] directions. This expression also implicitly includes areas of exclusive $X^+$ (with $t^{X^+} = 1$) and $X^-$ (with $t^{X^-} = 1$) domains, which are separated by charged domain walls of type II perpendicular to the substrate plane, or are spatially separated by $Y^+$ and $Y^-$ domains though 90° domain walls of Type I. This analysis, therefore, assumes complete phase correlation, which implies that the second harmonic response of all dominant variants are phase correlated. This assumption is justified in our present case since the domain sizes of $X^+$ and $X^-$ variants are of the order of 100–200 nm in the film growth plane, which is less than the wavelength of light (see Fig. 4). Using similar arguments, we can also write the net nonlinear response from $Y^+$ and $Y^-$ domains as

$$P_Y^x = \left( \int_0^{A^y} (r^{Y^+} - r^{Y^-}) dA_Y \right) P_Y^{x^+},$$

where $A_Y$ represents the total area fraction of the probed film area composed of $Y^+$ and $Y^-$ domains. The integral expression inside the bracket in Eq. (3) is defined as $\Delta A_Y$, which is the net thickness fraction of $Y^+$ domains with respect to $Y^-$ domains, i.e., the relative thickness fraction of domains with the $a$ component of their polarization along SrTiO$_3$ [1̅1̅0] versus [1̅1̅0] directions. The total nonlinear polarization from the film can now be written as

$$P_{x,y} = \Delta A_X P_{x,y}^X + \Delta A_Y P_{x,y}^Y e^{i\Gamma}.$$

The phase shift $\Gamma$ is the difference in phase of the nonlinear polarizations arising from $X^{(+/-)}$ and $Y^{(+/-)}$ domains, and is given by $\Gamma = 2\omega c(n_b^{2\omega} - n_a^{2\omega})t$, where $n_b$ and $n_a$ are the refractive indices of Bi$_4$Ti$_3$O$_{12}$ at the SHG frequency, along the crystallographic $b$ and $a$ axes, respectively, and $t$ is the film thickness. The second harmonic intensity from the film, $I_{2\omega}^x^y P_{2\omega}^x (P_{2\omega}^x)^*$, can now be calculated:

$$I_{j}^{2\omega} = K_{ij} (\sin^2 \theta + K_{ij} \cos^2 \theta)^2 + K_{ij} \sin^2 2\theta + K_{ij} (\sin^2 \theta + K_{ij} \cos^2 \theta) \sin 2\theta,$$

where $K_{ij}$ are the piezoelectric coefficients of Bi$_4$Ti$_3$O$_{12}$.
where \( j = x \) or \( y \) denotes the polarization direction, and \( K_{ij} \) are the phenomenological fitting parameters. Using Table I, we can show the following relations between these parameters and the physical quantities:

\[
\frac{d_{12}}{d_{11}} = K_{2,x} = (K_{2,y})^{-1},
\]

\[
\frac{d_{26}}{d_{12}} = \left(\frac{K_{3,x}}{K_{1,x}(K_{2,x})^2} \right) \left(\frac{K_{3,y}}{K_{1,y}}\right),
\]

\[
\frac{d_{26}}{d_{11}} = \left(\frac{K_{3,y}}{K_{1,y}(K_{2,y})^2} \right) \left(\frac{K_{3,x}}{K_{1,x}}\right).
\]

The fitting coefficients \( K_{ij} \) can be determined from the experimental measurements. Equations (6) and (8) can be used to determine two independent ratios; \( d_{12}/d_{11} \) and \( d_{26}/d_{11} \). Equation (7) then provides a consistency check for the ratio \( d_{26}/d_{12} \). The phase shift \( \Gamma \) can be determined from Eq. (9), which in turn can be used to determine the material birefringence \( \Delta n = (n_2^a - n_1^a) \). Note that the parameters \( d_{12}/d_{11}, d_{26}/d_{11} \), and \( \Delta n \) are intrinsic material properties, and can be determined independent of the domain microstructure, i.e., the relative area fractions of the eight different types of domain variants. Equation (10) provides new microstructural information, \( \Delta A_x / \Delta A_y \), in the area probed.

**IV. RESULTS AND DISCUSSION**

In Fig. 6, the theoretical model for the second harmonic signal intensity (\( I_2^z \) and \( I_2^z \)), derived in Eq. (5), is fitted (solid line) to the experimental data (circles) by using nonlinear least-square fitting. The fitting of experimental polar plots is facilitated by the following guidelines: the first term in Eq. (5) gives rise to a two-lobed structure, while the second term to a four-lobed structure. The third term, is a cross term which produces a phase shift, causing a rotation of the lobes. Thus \( K_1 \) increases the structure of the two-lobed structure, and \( K_3 \) of the four-lobed structure. The phase shift depends on \( K_4 \) and the constant \( K_2 \) is the ratio of the magnitude of the intensity along the \( y \) axis (\( \theta = 0^\circ \)) to that along the \( x \) axis (\( \theta = 90^\circ \)). Since \( K_2 \) is related only to the \( d_{ij} \) coefficients, this ratio is a pure material property, independent of the domain statistics. Since \( K_1 \) and \( K_3 \) are related to \( \Delta A_z \) and \( \Delta A_y \), as the ratio of \( \Delta A_x / \Delta A_y \) increases, the polar plot becomes increasingly two-lobed for output polarization along the \( x \) axis and increasingly four lobed for output polarization along the \( y \) axis.

From the phenomenological fitting parameters to these measurements, the following ratios were calculated for the nonlinear coefficients: \( d_{12}/d_{11} = -3.498 \pm 0.171, \) \( d_{26}/d_{12} = 0.365 \pm 0.010, \) and \( d_{26}/d_{11} = 1.273 \pm 0.036. \) Note that from Eq. (6), we have also determined without ambiguity, that the signs of \( d_{12} \) and \( d_{11} \) are opposite, as indicated by the negative sign of the ratio \( d_{12}/d_{11} \). The linear birefringence was determined to be: \( |\Delta n^2| = 0.101 \pm 0.018, \) and the ratio of the net area fraction was calculated to be: \( \Delta A_x / \Delta A_y = 0.833 \pm 0.024. \) Assuming equal probability of all domain variants, this ratio would on the average be expected to be equal to 1. However, in probing the local area of \( \sim 0.36\pi \) \( \times 100 \) mm\(^2\), one sensitively detects the local deviation of the \( \Delta A_x / \Delta A_y \) from 1. On moving the beam to different locations, the shapes of the polar plots change, and the corresponding \( \Delta A_x / \Delta A_y \) ratio changes as well, varying by \( \pm 15\% \sim 20\% \) about the value of 1.

To the best of our knowledge, the nonlinear \( d_{ij} \) coefficients for single crystal Bi\(_2\)Ti\(_3\)O\(_{12}\) have not been reported in the literature before. However, the optical birefringence \( \Delta n^2 = (n_2^a - n_1^a) \) has been reported in the literature for Bi\(_2\)Ti\(_3\)O\(_{12}\) single crystals as \( \Delta n^2 \sim 0.111 \pm 0.035, \) which agrees well with our calculated value.

Knowledge of at least one nonlinear coefficient out of \( d_{26}, d_{11}, \) and \( d_{12} \) can yield the other two coefficients, using the aforementioned relations given. The absolute values of \( \Delta A_x \) and \( \Delta A_y \) can also be found by performing SHG intensity reference measurements on a well known crystal. The reference crystal used here was a \( \z \)-cut single crystal single domain LiTaO\(_3\) crystal, 0.52 mm thick for which \( d_{22}^{22} = 4.4 \times 10^{-12} \) \( \text{mV/m} \). The Maker fringes were measured for this crystal by measuring the intensity of the second harmonic intensity as a function of incidence angle for a transverse electric (TE) polarized incident light. The Maker fringes measurement is shown in Fig. 7. The reference intensity value was calculated using the nonlinear coefficient \( d_{22} \) and the maximum intensity of the envelope of fringes at normal incidence. Following the derivation given in Ref. 12, we then find the nonlinear coefficient of the film in a specific geometry as:
Here, the indices \( f \) and \( r \) represent the film and reference respectively, \( P^{2\omega} \) is the measured SHG intensity, \( n^{2\omega} \) and \( n^\omega \) represent the indices of refraction at the SHG wavelength and at the fundamental wavelength, respectively, \( l_f \) and \( l_r \) are the thickness of film and reference crystal, respectively, \( l_c \) is the coherence length and \( T \) is the transmittance given by \( T = 1/(1 + n^\omega) \). Referring to Eq. (5), the intensity of the SHG from the film at an incidence angle of \( \theta = 0^\circ \) yields \( I_x(\theta = 0^\circ) \propto (\Delta A_x d_{12})^2 \) and \( I_y(\theta = 0^\circ) \propto (\Delta A_y d_{11})^2 \). Similarly, \( I_x(\theta = 90^\circ) \propto (\Delta A_x d_{11})^2 \) and \( I_y(\theta = 90^\circ) \propto (\Delta A_y d_{12})^2 \). On comparison with the reference signal according to Eq. (11), and assuming bulk refractive indices from Ref. 7, we can determine \( (\Delta A_x d_{11})^2 = 5.15 \times 10^{-3} \text{ (pm/V)}^2 \) and \( (\Delta A_y d_{12})^2 = 7.46 \times 10^{-3} \text{ (pm/V)}^2 \). However, the absolute values of \( \Delta A_x \) and \( \Delta A_y \) can only be determined from the knowledge of at least one of the coefficients \( d_{11}, d_{12}, \) and \( d_{26} \), which are currently undetermined.

V. CONCLUSIONS

This work has presented second harmonic generation measurements along with theoretical modeling of the response from a composite domain microstructure in a Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} thin film on a SrTiO\textsubscript{3} substrate. The treatment yields quantitative information on basic material properties, such as the ratios of nonlinear optical coefficients, and optical birefringence, as well as microstructural information specific to the area probed, such as relative fractions of different domain variants in the film. The following nonlinear coefficients and birefringence were determined: \( d_{12}/d_{11} = -3.498 \pm 0.171, \quad |d_{26}/d_{12}| = 0.365 \pm 0.010, \quad |d_{26}/d_{11}| = 1.273 \pm 0.036, \quad \text{and} \quad |n_{b} - n_{a}| = 0.101 \pm 0.018 \) (at 532 nm). The relative thickness fractions \( \Delta A_x/\Delta A_y \), representing the ratio of the net fraction of \( a \) component of polarization in the \( x \) to that in \( y \) directions could be determined sensitively in the probed area (see Eqs. (2) and (3) for definitions).

The technique of SHG measurements presented here to probe materials structure is quite general. Since the property is a third rank tensor, it is very sensitive to the point group symmetry of the material. In particular, it arises from a lack of center of inversion symmetry, and therefore surfaces, interfaces, and materials with point groups without inversion symmetry would give rise to second harmonic response. Under nonphase matched conditions, the technique probes material surfaces down to a depth of approximately the coherence length. Films which are thinner than coherence length, \( l_c \) (typically \( l_c \sim \text{micrometers in ferroelectrics} \) can therefore be studied without phase matching considerations. A simple theoretical analysis of the information is possible in this case with the knowledge of all the possible structural variants and wall configurations that separate them. We are currently employing this technique to probe dynamic changes in the domain microstructure that occur under external electric fields and by varying the temperature.

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