c-axis oriented epitaxial BaTiO$_3$ films on (001) Si

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c-axis oriented epitaxial films of the ferroelectric BaTiO$_3$ have been grown on (001) Si by reactive molecular-beam epitaxy. The orientation relationship between the film and substrate is (001) BaTiO$_3$||[001] Si and [100] BaTiO$_3$||[110] Si. The uniqueness of this integration is that the entire epitaxial BaTiO$_3$ film on (001) Si is c-axis oriented, unlike any reported so far in the literature. The thermal expansion incompatibility between BaTiO$_3$ and silicon is overcome by introducing a relaxed buffer layer of Ba$_2$Sr$_{1−x}$Ti$_3$O$_{12}$ between the BaTiO$_3$ film and silicon substrate. The rocking curve widths of the BaTiO$_3$ films are as narrow as 0.4°. X-ray diffraction and second harmonic generation experiments reveal the out-of-plane c-axis orientation of the epitaxial BaTiO$_3$ film. Piezoresponse atomic force microscopy is used to write ferroelectric domains with a spatial resolution of ~100 nm, corroborating the orientation of the ferroelectric film. © 2006 American Institute of Physics. [DOI: 10.1063/1.2203208]

I. INTRODUCTION

The reorientable dielectric polarization offered by a ferroelectric material is a critical element of a number of current and emerging device structures. Epitaxial ferroelectric films offer a means to constrain the possible directions in which the spontaneous polarization can exist and thus can offer significant performance advantages over randomly oriented ferroelectric films, provided they restrict the polarization to lie in directions desired for the particular application. Depending on the application of interest, polarization entirely in-plane or entirely out-of-plane is often optimal.

BaTiO$_3$ and related materials are used in many devices exploiting the dielectric,$^1$ pyroelectric,$^2$ piezoelectric,$^3$ electrostrictive,$^4$ ferroelectric,$^5$ electro-optic,$^6,7$ and nonlinear optical$^8$ characteristics of this material. The successful integration of epitaxial BaTiO$_3$ with an extensively used semiconductor such as silicon would offer functionalities (not found in conventional semiconductors) to be utilized in silicon-based semiconductor electronics.

Epitaxial BaTiO$_3$ films have been grown on silicon with a buffer layer between the film and the silicon substrate,$^9−13$ and all such reported epitaxial BaTiO$_3$ films on silicon possess an in-plane polarization. This arises for two reasons. First, the lattice mismatch $[(a_{\text{sub}}−a_{\text{film}})/a_{\text{film}}$, where $a_{\text{sub}}$ is the lattice constant of the substrate and $a_{\text{film}}$ is the lattice constant of the film]$^{14}$ between BaTiO$_3$ and (001) Si is large, −4.5% at growth temperature (~600 °C).$^{15,16}$ With such a large lattice mismatch, the resulting BaTiO$_3$ films are relaxed during growth by the introduction of misfit dislocations, even for a film thickness of only a few unit cells. Second, due to the much smaller thermal expansion coefficient of silicon as compared to BaTiO$_3$, $^{15,16}$ the relaxed BaTiO$_3$ films end up in a state of biaxial tension as they are cooled through the Curie temperature (130 °C for unstrained BaTiO$_3$).$^{17}$ To relieve this biaxial tensile strain state, the tetragonal BaTiO$_3$ films orient with their longer axis (c-axis) in the plane of the substrate and their shorter axis (a-axis) oriented out-of-plane. This results in an in-plane polarization of the BaTiO$_3$ film because the dielectric polarization lies along the c-axis of tetragonal BaTiO$_3$. Although the in-plane polarization is suitable for some applications,$^{18,19}$ there are many applications in which an out-of-plane polarization of the BaTiO$_3$ ferroelectric layer is desired. These include ferroelectric memory devices,$^{20}$ which require top and bottom electrodes, as well as a quantum computing architecture in which spin interactions in the underlying silicon are controlled by the out-of-plane polarization of an overlying ferroelectric film.$^{21}$ The
influence of strain, arising, for example, from lattice mismatch in conjunction with thermal expansion mismatch, on the orientation of the spontaneous polarization axis in thin ferroelectric films is well established.\textsuperscript{22-26} Figure 1 displays the stability of various ferroelectric phases and domain structures in (100) oriented BaTiO\textsubscript{3} thin films as a function of temperature and biaxial strain. The temperature-strain stability diagram was constructed using phase-field simulations in which an eighth-order Landau-Devonshire thermodynamic potential was employed for describing the bulk free energy of BaTiO\textsubscript{3}.\textsuperscript{25,26} From Fig. 1, it is evident that by tailoring the total strain (lattice mismatch and thermal expansion mismatch) between the film and the substrate, the resulting orientation of a BaTiO\textsubscript{3} film can be varied from a purely a-axis oriented (where the a-axis lies perpendicular to the plane of the substrate), to a mixture of c and a axes oriented, to purely c-axis oriented (where the c-axis lies perpendicular to the plane of the substrate).\textsuperscript{22,24-27} Large biaxial tensile strain results in a-axis films, while large biaxial compressive strain results in c-axis films.\textsuperscript{23,26}

II. HETEROSTRUCTURE STRATEGY

Orientation control is achieved in this work by incorporating a buffer layer between the BaTiO\textsubscript{3} film and silicon substrate. The use of buffer layers for growing BaTiO\textsubscript{3} on Si (001) is not a new concept.\textsuperscript{9,12,28} McKee and Walker grew the BaTiO\textsubscript{3} on silicon with either buffer layers that are lattice matched to the silicon (e.g., Ba\textsubscript{0.725}Sr\textsubscript{0.275}O and Ca\textsubscript{0.64}Sr\textsubscript{0.36}O\textsubscript{3}) (Ref. 29) or compositionally graded Ba\textsubscript{a}Sr\textsubscript{1-x}TiO\textsubscript{3} buffer layers.\textsuperscript{30} The resulting films were a-axis oriented because the BaTiO\textsubscript{3} layer was sufficiently relaxed at growth temperature, and was subjected to a state of biaxial tension (from the comparatively smaller thermal expansion coefficient of the silicon substrate) as it was cooled through its Curie temperature. Nonetheless, by patterning the film into small islands, these authors succeeded in making local c-axis oriented regions (55 \textmu m or less in extent) at the outer edge of the BaTiO\textsubscript{3} islands in otherwise a-axis oriented BaTiO\textsubscript{3} films on silicon.\textsuperscript{29}

In this work, we have used buffer layers to render an entire BaTiO\textsubscript{3} film on silicon c-axis oriented, without the need for patterning into tiny islands. The important requirements of such a buffer layer are the following. First, the buffer layer should enable the epitaxial growth of a commensurate BaTiO\textsubscript{3} overlayer. The lattice mismatch between the buffer layer and the BaTiO\textsubscript{3} should be sufficiently small to enable the growth of a commensurate BaTiO\textsubscript{3} overlayer of the required thickness. Second, the biaxial compressive strain in such a commensurate BaTiO\textsubscript{3} film needs to be sufficient to overcome (by at least ~0.1% to ~0.2%) (Ref. 26) the thermal expansion mismatch-induced biaxial tensile strain (+0.4%) that arises during cooling from the growth temperature. Satisfying this criterion will result in the spontaneous polarization orienting out-of-plane as the BaTiO\textsubscript{3} film is cooled through its Curie temperature (according to Fig. 1). Third, the buffer layer thickness should greatly exceed the critical thickness for the onset of relaxation, as a completely relaxed buffer layer is desired. Finally, should the buffer layer exhibit any ferroelectric transitions, they should occur below the Curie temperature of the compressively strained BaTiO\textsubscript{3} film. A schematic of the proposed structure to stabilize a c-axis oriented BaTiO\textsubscript{3} on Si (001) is shown in Fig. 2.

III. CRITICAL THICKNESS ANALYSIS

A buffer layer satisfying these requirements is a solid solution of barium and strontium titanate (Ba\textsubscript{a}Sr\textsubscript{1-x}TiO\textsubscript{3}), with a lattice parameter that can be varied with its composition. Ba\textsubscript{a}Sr\textsubscript{1-x}TiO\textsubscript{3} with a composition of x=0.7 and a lattice...
The Poisson ratio of the film, \( \frac{\Delta H}{\Delta H_{9251}} \)

thickness at which it becomes energetically favorable for the

silicon

sor elements

equilibrium critical thickness

temperature at which these tensor elements have been

quired on top of the fully relaxed buffer layer on Si (001) for the quantum computing application of interest.

\[ \frac{\Delta H}{\Delta H_{9251}} \] is the lattice constant of cubic BaTiO\(_3\) at a growth temperature of 600 °C

\( \frac{\Delta H}{\Delta H_{9251}} \) was used as the buffer layer in this study.\(^{15,16} \)

The composition of the buffer layer and its thickness were chosen based on an analysis made using the Matthews-Blakeslee equation for the equilibrium critical thickness:

\[ \epsilon = \frac{b}{2\pi h_c} \frac{(1 - \nu \cos^2 \alpha)}{(1 + \nu) \cos \lambda} \left( \ln \left( \frac{h_c}{b} \right) + 1 \right), \]  

(1)

where \( \epsilon \) is the lattice misfit between the film and the substrate, \( h_c \) is the equilibrium critical thickness of the film, \( b \) is the Burgers vector of the dislocations relaxing the film, \( \nu \) is the Poisson ratio of the film, \( \alpha \) is the angle between the dislocation line and its Burgers vector, and \( \lambda \) is the angle between the slip direction and the direction in the film plane, which is perpendicular to the line of intersection of the slip plane and the interface. Knowledge of the slip system involved in producing the misfit dislocations is required to apply this model effectively. Based on the work of Suzuki et al.,\(^{35} \) the parameters \( b, \alpha, \) and \( \lambda \) in Eq. (1) are \( a(100) \) (where \( a \) is the lattice constant of cubic BaTiO\(_3\) at a growth temperature of 600 °C),\(^{15,90} \) 90°, and 45°, respectively. The Poisson ratio \( (\nu = -s_{12}/s_{11}, \) where \( s_{11} \) and \( s_{12} \) are compliance tensor elements) was taken to be 0.385 from elastic constant measurements of cubic BaTiO\(_3\) at 150 °C (the highest temperature at which these tensor elements have been reported).\(^{36} \) The critical thickness versus epitaxial strain plot obtained from Eq. (1) for BaTiO\(_3\) is shown in Fig. 3.

Assuming that Ba\(_3\)Sr\(_{1-x}\)TiO\(_3\) and BaTiO\(_3\) thin films are similar in nature, we apply the critical thickness plot in Fig. 1 to films of both materials. At a composition of \( x=0.7 \), the strain between the Ba\(_3\)Sr\(_{1-x}\)TiO\(_3\) buffer layer and silicon \( (\epsilon = -3.77\% \) at \( T_{\text{sub}}=600 \) °C\)\(^{15,16,31,32} \) implies an equilibrium critical thickness \( (h_c) \) of \( \sim 10 \) Å. While \( h_c \) is the thickness at which it becomes energetically favorable for the relaxation of the epitaxial film to begin, complete relaxation is not expected until the film is considerably thicker. This thickness is dependent on kinetic factors,\(^{33} \) but a buffer layer thickness several times thicker than the equilibrium critical thickness can be anticipated to ensure its complete relaxation (i.e., a minimum buffer layer thickness of several tens of angstroms).

The strain between such a relaxed buffer layer and an overgrown BaTiO\(_3\) film should be small enough to enable the growth of a commensurately strained BaTiO\(_3\) film of the desired thickness for the specific application. For our application, a commensurately strained BaTiO\(_3\) film of about 100 Å thick is desired (square data point in Fig. 3). At the growth temperature \((\sim 600 \) °C\), the biaxial compressive strain state in such a commensurate BaTiO\(_3\) film should be \( \epsilon = -0.7\%. \)\(^{15,16} \) Upon cooling to room temperature, this will decrease to a biaxial compressive strain of \( \epsilon = -0.3\% \) due to the thermal expansion mismatch between BaTiO\(_3\) and Si \( [\epsilon = +0.4\% \) (Ref. 38) arising from the thermal expansion mismatch].\(^{15,16} \) From Fig. 1, this small compressive strain should be sufficient to achieve purely c-axis oriented BaTiO\(_3\).

IV. GROWTH PROCEDURE

The films used in this study were grown by reactive molecular-beam epitaxy (MBE) from elemental sources in an EPI 930 MBE system modified for the growth of oxides. A complete description of the system can be found elsewhere.\(^{39–41} \) The process used to grow an epitaxial perovskite layer on (001) Si is a modification\(^{39–41} \) of the method developed by Walker and co-workers.\(^{11,29,30,42,43} \) The oxygen pressures used at various steps in the growth are based on extensive oxidation studies, which determine the minimum oxygen partial pressure necessary to oxidize the depositing species.\(^{44} \) Substrate temperatures below 550 °C are based on measurements from a thermocouple near, but not in contact with the substrate. Temperatures above 550 °C are measured using an optical pyrometer (assuming an emissivity of 0.8 for the substrate). The difference between the real temperature and the thermocouple temperature at a real temperature of 600 °C (by pyrometer) is \( \sim 75–100 \) °C and the difference decreases as the temperature is lowered. The crystallinity of the film surface was monitored in situ during growth using reflection high-energy electron diffraction (RHEED).

The BaTiO\(_3\)/Ba\(_3\)Sr\(_{1-x}\)TiO\(_3\)/Si (001) epitaxial films were grown using the following steps. Before loading into the MBE chamber, the (001) Si wafers were exposed to UV light from a mercury lamp with a quartz bulb for 15–20 min to remove surface organics by the ozone produced by the UV light. After loading into the MBE chamber, which has a base pressure of \((2–3) \times 10^{-9} \) Torr, the wafers were heated to \( \sim 980 \) °C to desorb the native SiO\(_2\) layer. RHEED then revealed a double-domain (2 \times 1) reconstruction as shown in Fig. 4(a). The substrate was then cooled to 700 °C where the clean Si surface was exposed to 1/2 monolayer\(^{45} \) (ML) of strontium (strontium flux, \( J_{\text{Sr}} \sim 1.4 \times 10^{13} \) atoms cm\(^{-2} \) s\(^{-1} \)) to form strontium silicide (SrSi\(_3\)). During this step, the RHEED pattern dynamically

![Fig. 3](Image)

**Fig. 3.** (Color online) Theoretical equilibrium critical thickness estimated using Matthews-Blakeslee analysis [Eq. (1)] for a BaTiO\(_3\) film at 600 °C, as a function of the in-plane epitaxial strain in the film. The square data point indicates the typical thickness of the strained BaTiO\(_3\) film required on top of the fully relaxed buffer layer on Si (001) for the quantum computing application of interest.
reflects the changes in the silicide layer through a series of reconstructions. The RHEED pattern of 1/2 ML SrSi$_x$ has a 2× reconstruction, as shown in Fig. 4(b). This silicide template has been shown to be comparatively robust to oxygen exposure and to resist the formation of amorphous SiO$_2$. The substrate was then cooled to 100 °C for the deposition of a 1/2 ML of Ba$_{0.7}$Sr$_{0.3}$ metal with $J_{Ba} \sim 3.3 \times 10^{13}$ and $J_{Sr} \sim 1.4 \times 10^{13}$ atoms cm$^{-2}$ s$^{-1}$. Oxygen was then introduced to a background pressure of $4 \times 10^{-8}$ Torr during which an additional 2.5 ML of Ba$_{0.7}$Sr$_{0.3}$ was deposited to form a total of 3 ML of epitaxial Ba$_{0.7}$Sr$_{0.3}$O (the underlying 1/2 ML of Ba$_{0.7}$Sr$_{0.3}$ also gets oxidized during this step). The 3-ML-thick epitaxial Ba$_{0.7}$Sr$_{0.3}$O film so formed is commensurately strained with the substrate, as revealed by the spots on an arc in the RHEED pattern in Fig. 4(c). This was followed by the deposition of 2 ML of titanium ($J_{Ti} \sim 4 \times 10^{13}$ atoms cm$^{-2}$ s$^{-1}$) in a background oxygen partial pressure of $2 \times 10^{-7}$ Torr to form 2 ML of amorphous TiO$_2$. The wafer was then heated in UHV (1–2 $\times 10^{-9}$ Torr) to $\sim 550$ °C to enable the recrystallization of the perovskite Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ through a topotactic reaction that occurs as the 2 MLs of TiO$_2$ diffuse into the underlying 3 MLs of Ba$_{0.7}$Sr$_{0.3}$O to form 2 unit cells of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$. The RHEED pattern of the recrystallized epitaxial Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ is shown in Figs. 4(e) and 4(f), along the [110] and [100] azimuths of silicon, respectively. The streaky nature of the RHEED pattern of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ in Fig. 4(e) indicates that the layer is partially relaxed even for a thickness of 2 unit cells. Further growth of the remaining buffer layer of epitaxial Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ was achieved by shuttered growth (involving the supply of alternate monolayer

FIG. 4. RHEED patterns along the [110] azimuth of Si from different stages of growth of the 100 Å BaTiO$_3$/300 Å Ba$_{0.7}$Sr$_{0.3}$TiO$_3$/001 Si heterostructure. (a) 2× reconstructed silicon surface after desorbing the SiO$_2$ at 980 °C, (b) after the deposition of 1/2 ML Sr to form SrSi$_x$ at 700 °C, (c) after the deposition of 3 ML of Ba$_{0.7}$Sr$_{0.3}$O at $\sim 100$ °C, and (d) after the deposition of 2 ML of amorphous TiO$_2$ at $\sim 100$ °C. (e) and (f) RHEED patterns after recrystallization of 2 unit cells of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$, viewed along the [110] and [100] azimuths of silicon, respectively. (g) and (h) RHEED patterns after the growth of a 300-Å-thick Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer along the [110] and [100] azimuths of silicon, respectively. (i) and (j) RHEED patterns along the [110] and [100] azimuths of silicon, respectively, following the growth of the 100 Å of BaTiO$_3$ completing the heterostructure.
of-plane lattice parameters of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ and BaTiO$_3$ buffer layer along the $[110]$ and $[100]$ azimuths of silicon are shown in Figs. 4(g) and 4(h), respectively.

It can be seen from Fig. 3 that the equilibrium critical thickness (energetically favorable thickness for the onset of relaxation) for the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer on silicon is $\sim$ 10 Å. Though the results shown here are for a buffer layer thickness of 300 Å, we have investigated different buffer layer thicknesses from 40 to 300 Å. Based on the x-ray diffraction (XRD) analyses of these films (details discussed below in the XRD section), it can be inferred qualitatively that the minimum thickness of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer for complete relaxation is $\sim$ 100 Å. Complete relaxation of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer is necessary to strain a commensurate overlying BaTiO$_3$ film sufficiently to make it pure c-axis oriented after cooling to room temperature.

On top of the 300-Å-thick Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer, a 100-Å-thick BaTiO$_3$ layer was grown using the same growth temperature and oxygen partial pressure as the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer. The RHEED patterns of the 100-Å-thick BaTiO$_3$ film in Figs. 4(i) and 4(j) were obtained along the $[110]$ and $[100]$ azimuths of silicon, respectively.

V. X-RAY DIFFRACTION

The structural quality of the film was assessed ex situ using a four-circle x-ray diffractometer with a Cu $K\alpha$ source ($\lambda \sim$ 1.54 Å). Figure 5(a) shows a $\theta$-2$\theta$ scan of the 100 Å BaTiO$_3$/300 Å Ba$_{0.7}$Sr$_{0.3}$TiO$_3$/Si(001) film in which the 00$\ell$ peaks of the BaTiO$_3$ and Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (indistinguishable at low angles because of the small difference in lattice parameters) are labeled. The good structural quality of the film is revealed by the narrow rocking curve (ω-scan) full width at half maximum (FWHM) of 0.38° of the 002 peak. The out-of-plane lattice parameters of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ and BaTiO$_3$ film obtained from a scan of the 004 peaks [shown in Fig. 5(b)], are 3.960±0.001 and 4.025±0.003 Å (error bars based on a Gaussian fit), respectively, indicating that the entire BaTiO$_3$ film is c-axis oriented. A φ-scan of the 111 Ba$_{0.7}$Sr$_{0.3}$TiO$_3$/BaTiO$_3$ peak (FWHM in φ of 1.65°), in Fig. 5(c) reveals the epitaxial nature of the buffer layer and film. The epitaxial relationship of the film to the substrate is (001) BaTiO$_3$||[001] Si and [100] BaTiO$_3$||[110] Si.

The out-of-plane lattice constant of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ and BaTiO$_3$ layers obtained using the 004 peak positions can be used to assess qualitatively the extent of relaxation of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer and the in-plane strain state of the BaTiO$_3$ layer. Using such an analysis on heterostructures with 80–100 Å-thick BaTiO$_3$ layers on top of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layers with thickness varying from 40–300 Å on Si (001), we estimate that the thickness of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer should be at least 100 Å for its complete relaxation. The x-ray 004 peaks of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ and BaTiO$_3$ as a function of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer thickness are shown in Fig. 6. For a buffer layer thickness of 40 Å, the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ and BaTiO$_3$ peaks overlap, indicating that the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ layer is not completely relaxed and therefore, resulting in an a-axis oriented BaTiO$_3$ film. A double peak is barely discernable for a Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer thickness of 60 Å and gets more pronounced for thickness $\geq$ 100 Å. The positions of the 004 BaTiO$_3$ peak at a $2\theta$ value of $\sim$ 99.6° and the 400 Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer peak at $\sim$ 102.1° for buffer layer thicknesses of 100 and 300 Å indicate that the buffer layer is completely relaxed (no change in
lattice constant with increase in buffer layer thickness), which is an important part of our strategy to orient the c-axis of the tetragonal BaTiO$_3$ film out of plane.

The in-plane lattice constants were also measured to see if the BaTiO$_3$ film was commensurate with the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer and to ascertain if the buffer layer itself is fully relaxed. This was accomplished by measuring the in-plane 200 peaks of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ and BaTiO$_3$ layers by grazing-incidence diffraction on a synchrotron (the UNICAT beamline on the Advance Photon Source). These measurements indicated the 100-Å-thick BaTiO$_3$ film to be commensurate with the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer and the buffer layer to be completely relaxed from the silicon substrate for thickness $> 100$ Å. In Fig. 7, the in-plane 200 scan from a 200-Å-thick Ba$_{0.7}$Sr$_{0.3}$TiO$_3$/Si (001) is compared with the scan from a 100 Å BaTiO$_3$/300 Å Ba$_{0.7}$Sr$_{0.3}$TiO$_3$/Si (001) heterostructure. The peaks from both samples lie at the same 2θ value and have the same FWHM, showing the BaTiO$_3$ overlayer to be commensurate with the fully relaxed Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ buffer layer. The in-plane lattice constant of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ and BaTiO$_3$ obtained from the synchrotron data is 3.9996±0.0005 Å. The Si 220 peak (marked by * at 2θ=42.057°) is shown along with the film peak to illustrate that the buffer layer is completely relaxed from the substrate.

VI. SECOND HARMONIC GENERATION

The x-ray diffraction studies reveal that the BaTiO$_3$, in the 100 Å BaTiO$_3$/300 Å Ba$_{0.7}$Sr$_{0.3}$TiO$_3$/Si (001) oxide film heterostructure, is predominantly c-axis oriented. This conclusion was further corroborated by optical second harmonic generation (SHG) measurements. SHG involves the conversion of light at frequency $\omega$ into optical signal at a frequency of $2\omega$ by the nonlinear material (BaTiO$_3$ film). The conversion process occurs by the creation of a nonlinear polarization $P_{2\omega} = d_{ijk}E_{\omega}E_{\omega}^*E_{\omega}^*$, by light of frequency $\omega$ through the third order nonlinear tensor $d_{ijk}$ (nonlinear optical coefficients). Each of the subscripts $i, j, k$ refer to any one of the crystal physics axes of the material, 1, 2, 3. Both BaTiO$_3$ and Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ have the point group symmetry of 4mm, where the four-fold rotation axis is also generally labeled as c, 3, and z axis. By symmetry considerations, the ferroelectric polarization, $P_z$ in this point group can lie only along this four-fold axis, which is conventionally labeled as crystal physics axis 3. Additionally, by Neummann’s law, only the nonlinear coefficients, $d_{15}, d_{23}, d_{31}=d_{32},$ and $d_{33}$ are nonzero, where the abbreviated Voigt notation of $jk\rightarrow i$ is used.

From the $d_{ij}$ tensor, one can generally conclude that for fundamental light ($\omega$) propagating along the c-axis of BaTiO$_3$ or Ba$_{0.7}$Sr$_{0.3}$TiO$_3$, no SHG signal will be created in the direction of fundamental light propagation. A schematic of the reflection geometry used in the SHG experiments is shown in Fig. 8(a). One can therefore conclude that for light propagating perpendicular to the film surface, ($\varphi=\varphi_o=0^\circ$), a film consisting of only c domains will not give rise to any SHG signal, while any signal observed will arise from a net contribution from the four types of $a$ domains only. This fact alone does not allow us to distinguish the domain structure of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ from the BaTiO$_3$ layers, since both have the same point group symmetry, and any SHG signal observed cannot be attributed to one or the other layer alone. Theory predicts, however, that the variation of the SHG intensity generated from purely $c$ and $a$ domains is given as

$$I^c_{2\alpha} = K_{3c}(K_{1c}\cos^2\theta + K_{2c}\sin^2\theta)^2, \quad (c \text{ domains}),$$

$$I^a_{2\alpha} = K_{4a}(K_{1a}\cos^2\theta + K_{2a}\sin^2\theta + K_{3a}\sin2\theta)^2, \quad (a \text{ domains}),$$

where $K_{ia}$ ($i=1, 2, 3,$ and 4) and $K_{ic}$ ($i=1, 2,$ and 3) are constants that depend on nonlinear coefficients ($d_{15}, d_{31},$ and
d_{33}), and the incidence angle $\varphi_i$ through their dependence on linear Fresnel factors ($t_s$, $t_r$, and $t_f$) and nonlinear Fresnel factors ($f_s$, $f_r$, and $f_f$) describing the refraction of fundamental beam and second harmonic beam, respectively 54 (see Appendix for exact functional forms).

Calculated plots of $F_{2\omega}^{(\varphi_f)}$ and $F_{\omega}^{(\varphi_f)}$ for BaTiO$_3$ thin films are shown in Fig. 8(b). One clearly observes that for pure c domains, the SHG intensity, $F_{2\omega}^{(\varphi_f)}$, increases with a power law dependence on the incidence angle $\varphi_i$. On the other hand, the $F_{\omega}^{(\varphi_f)}$ arising from the $a$ domains shows little change with increasing angle, $\varphi_i$. With these predictions in hand, SHG experiments were performed as follows: a fundamental wavelength ($\lambda_0$) of 800 nm is incident with the geometry shown in Fig. 8(a), giving rise to SHG signal at a wavelength ($\lambda_{2\omega}$) of 400 nm. The incidence polarization is set to $p$ polarized ($\theta=0^\circ$) and the detected SHG polarization is also $p$ polarized. The same oxide heterostructures characterized by RHEED and x-ray diffraction measurements (Figs. 4, 5, and 7) were investigated by SHG: 200 Å Ba$_{0.5}$Sr$_{0.5}$TiO$_3$/Si(001) and 100 Å BaTiO$_3$/300 Å Ba$_{0.5}$Sr$_{0.5}$TiO$_3$/Si(001). The experimental results, shown as data points, are overlayed with the theoretical predictions, shown as a continuous line, in Fig. 8(b). Excellent agreement between experiment and theory indicates that the 200 Å Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ film on Si (001) is comprised of predominantly $a$ domains, and the 100 Å BaTiO$_3$ film on 300 Å Ba$_{0.5}$Sr$_{0.5}$TiO$_3$/Si(001) is comprised of predominantly $c$ domains, corroborating the x-ray diffraction studies.

**VII. PIEZORESPONSE ATOMIC-FORCE MICROSCOPY**

To further confirm the direction of film polarization as well as to check the ferroelectric nature of the BaTiO$_3$ films, experiments were performed to control the out-of-plane orientation of the spontaneous polarization using piezoelectric response (piezoresponse) atomic-force microscopy (AFM). 55–58 In this technique, an AFM is operated in contact mode while applying a small ac voltage (typically $V_{ac} = 0.07$ V$_{rms}$) to a conductive cantilever. The electric field between the probe and the doped silicon substrate produces a small thickness change in the ferroelectric film, which is detected using a lock-in amplifier. Images of the piezoelectric response are obtained by scanning the sample over the conductive tip of the AFM cantilever. Piezoresponse measurements in noncontact mode for domain imaging and patterning have also been demonstrated. 57–60

Experiments were performed using a Pt/Ti coated silicon cantilevers (Olympus AC-240TM) having a typical tip radius of 15 nm and a resonance frequency of 70 kHz in air. The frequency of the ac signal applied to the cantilever during scans was determined from a resonance curve obtained while in contact with the sample, prior to the start of patterning.

Domain patterning was accomplished programmatically, by selectively offsetting and biasing the AFM tip within the original scan region. Regular 3 × 3 grids of square, 400 nm domains, offset from one another by 700 nm, were written over 2.5 × 2.5 $\mu$m$^2$ regions of the 100 Å BaTiO$_3$/300 Å Ba$_{0.5}$Sr$_{0.5}$TiO$_3$/Si(001) sample. To normalize the background response of the film, the 2.5 × 2.5 $\mu$m$^2$ region was initially prepoled while scanning under a dc bias at ~2 V. Following the prepoiling, the 400 nm domains were written at 5 Hz, and the resulting domain pattern was imaged (256 × 256 points) using piezoresponse over the 2.5 × 2.5 $\mu$m$^2$ region centered on the pattern at 0.4 Hz. Figure 9 shows the piezoresponse for a set of domains written into this film (the same film characterized in Figs. 4–8) at a dc bias of +2 V on the AFM tip. The line profile indicates the sharpness of the domain boundaries obtained. Subsequent experiments have confirmed the reversibility of the film polarization induced in this manner; out-of-plane oriented domains may be patterned controllably, erased, and reestablished in the same region of the 100 Å BaTiO$_3$/300 Å Ba$_{0.5}$Sr$_{0.5}$TiO$_3$/Si(001) ferroelectric heterostructure.
FIG. 9. (Color online) Ferroelectric domain patterns written on the same 100 Å BaTiO3/300 Å Ba0.7Sr0.3TiO3/Si (001) heterostructure whose RHEED and x-ray diffraction results are shown in Fig. 4–7 using piezores-ponse AFM, corroborating the c-axis orientation of the BaTiO3 film.

VIII. CONCLUSIONS

Using a relaxed Ba0.7Sr0.3TiO3 buffer layer, c-axis oriented epitaxial BaTiO3 has been grown on (001) Si. X-ray measurements of the out-of-plane and in-plane lattice parameters validate a structural strategy that uses biaxial compressive epitaxial strain on a BaTiO3 film to override the biaxial tensile strain from thermal expansion mismatch between the film and the substrate and, therefore, orient the c-axis of the BaTiO3 film out of plane. SHG experiments on these heterostructures corroborate the presence of predominantly c-axis domains in the BaTiO3 film. The out-of-plane spontaneous polarization in these films has been patterned with an AFM tip. These structures are an important enabler for devices on silicon requiring a ferroelectric layer with an out-of-plane spontaneous polarization.

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APPENDIX

The constants $K_{ic}$ and $K_{ia}$ in Eqs. (2) and (3) are given by

$$K_{ic} = \left[-2d_{15}\alpha_{c} f_{x} + (d_{31}\alpha_{c}^{2} + d_{33}\alpha_{c}^{2}) f_{z}\right],$$

$$K_{ia} = (d_{31}\alpha_{c}^{2} f_{z}),$$

$$K_{ia} = \left[\frac{8\pi^{2}d \sin \varphi_{i}^{2w}}{\lambda^{2} n_{i} \sin \left(\varphi_{i}^{2w} + \varphi_{i}^{2w}\right)}\right]^{2} \delta_{2c/-c} ,$$

$$K_{1a} = \delta_{X+i-} \frac{d_{33}\alpha_{c}^{2} + d_{31}\alpha_{c} f_{x} - (2d_{15}\alpha_{c} f_{z})}{d_{33}\alpha_{c}^{2} + d_{31}\alpha_{c} f_{x} - (2d_{15}\alpha_{c} f_{z})} ,$$

$$K_{2a} = \delta_{Y+i-} \frac{d_{31}\alpha_{c} f_{x}}{d_{33}\alpha_{c}^{2} + d_{31}\alpha_{c} f_{x} - (2d_{15}\alpha_{c} f_{z})} ,$$

$$K_{3a} = \delta_{Y+i-} \frac{d_{15}\alpha_{c} f_{x} - \alpha_{f} f_{z}}{d_{33}\alpha_{c}^{2} + d_{31}\alpha_{c} f_{x} - (2d_{15}\alpha_{c} f_{z})} ,$$

and

$$K_{4a} = \left[\frac{8\pi^{2}d \sin \varphi_{i}^{2w}}{\lambda^{2} n_{i} \sin \left(\varphi_{i}^{2w} + \varphi_{i}^{2w}\right)}\right]^{2} \delta_{2c/-c} .$$

where, within a two-dimensional microstructure approximation, $\delta_{2c/-c}$ represents the difference in the area fraction of +c domains to −c domains, $\delta_{X+i-}$ represents the difference in the area fraction of +X domains to −X domains, and $\delta_{Y+i-}$ represents the difference in the area fraction of +Y domains to −Y domains. The coefficients $\alpha_{c}$, $\alpha_{x}$, and $\alpha_{y}$ have a linear relationship with the linear Fresnel factors ($t_{x}$, $t_{y}$, and $t_{z}$).

$$\alpha_{c} = t_{c} \cos \varphi_{i}^{2w}, \quad \alpha_{x} = t_{x}, \quad \alpha_{y} = t_{y} \sin \varphi_{i}^{2w} .$$

The linear and nonlinear Fresnel factors are given by

$$\begin{align*}
\begin{bmatrix} t_{x} \\ t_{y} \\ t_{z} \end{bmatrix} &= \frac{2 \sin \varphi_{i}^{2w}}{\sin(\varphi_{i}^{2w} + \varphi_{i}^{2w})} \begin{bmatrix} \cos \varphi_{i}^{2w}/(\cos(\varphi_{i}^{2w} - \varphi_{i}^{2w})) \\ \cos \varphi_{i}^{2w}/(\cos(\varphi_{i}^{2w} - \varphi_{i}^{2w})) \\ (1/n_{i}^{2})(\cos \varphi_{i}^{2w}/(\cos(\varphi_{i}^{2w} - \varphi_{i}^{2w})) \end{bmatrix},
\end{align*}$$

and

$$\begin{align*}
\begin{bmatrix} f_{x} \\ f_{y} \\ f_{z} \end{bmatrix} &= \begin{bmatrix} -\cos \varphi_{i}^{2w}/(\cos(\varphi_{i}^{2w} - \varphi_{i}^{2w})) \\ 1 \\ (n_{i}^{2}/n_{m}^{2})^{2}(\sin \varphi_{i}^{2w}/(\cos(\varphi_{i}^{2w} - \varphi_{i}^{2w})) \end{bmatrix}.
\end{align*}$$

To simplify the SHG analysis, a single layer film of BaTiO3 of thickness $d$ on silicon was assumed in the above derivations. The interface index contrast between BaTiO3 ($n_{i}=2.32$ and $n_{m}=2.366$ at a wavelength of 800 nm) (Ref. 61) and Ba0.7Sr0.3TiO3 ($n_{i}=2.358$ (Ref. 62) at a wavelength of 800 nm, based on linear interpolation between the $n_{m}$ values of BaTiO3 and SrTiO3 (Ref. 63) is small and hence neglected. The refractive index of silicon is obtained from the Landolt-Börnstein tables.64 Similarly, due to the lack of availability of data, the differences in the nonlinear coefficients $d_{ij}$ between BaTiO3 and Ba0.7Sr0.3TiO3 are neglected. Nonlinear coefficients of $d_{15} = 13.6$, $d_{31} = -14.4$, and $d_{33} = -5.5$ pm/V were used for BaTiO3.65,66 Since the final aim of the work is not the absolute SHG intensity, but the variation of the SHG intensity with the incidence angle, $\varphi_{i}$, these assumptions were found to be acceptable for this study. As shown above, the net SHG intensity is also dependent on the relative area fractions of antiparallel domains in the probe region, which experimentally varies considerably from film to film, and with the location of the probe area within the
film. Hence the absolute SHG intensity is not relevant to this study. Therefore, the SHG intensity from Eqs. (2) and (3) are scaled accordingly to fit the experimental intensities in Fig. 8(b) to highlight the change in the functional form with increasing incident angle away from normal incidence ($\phi = 0^\circ$).

24It is not possible to distinguish whether the structural distortion of Ba$_{0.55}$Sr$_{0.55}$TiO$_3$ buffer layer is due to thermal expansion mismatch induced tensile strain or due to strain-induced paraelectric-ferroelectric (or cubic-tetragonal) phase transition. Therefore, pseudocubic indexing of the Ba$_{0.55}$Sr$_{0.55}$TiO$_3$ buffer layer is used throughout this manuscript.
25The in-plane lattice spacing and therefore the lattice constant of the film and substrate spacings of the substrate are obtained from the synchrotron data using the following equation, $d_{	ext{film}}=d_{	ext{sub}}\sin\theta_{\text{lab}}/\sin\theta_{\text{inc}}$ (variation of Bragg’s law) and the known lattice spacings of the substrate. In our case, $d_{	ext{film}}$ and $d_{	ext{lab}}$ are the lattice spacings of the film and substrate (silicon, respectively), and $\theta_{\text{lab}}$ and $\theta_{\text{inc}}$ are the Bragg peak positions (established using a Gaussian fit of the synchrotron data) of the film peak and substrate reference peak (Si 220), respectively.
34In bulk, Ba$_{0.55}$Sr$_{0.55}$TiO$_3$ is cubic at room temperature and hence has isotropic refractive index.