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# Tuning and optimizing properties of ferroelectric films grown on a single substrate: A first-principles-based study

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A first-principles-based effective Hamiltonian is used to reveal the effects of the growth direction on properties of films made of the prototype of ferroelectric materials (namely, BaTiO<sub>3</sub>) and grown on one of the most common and available substrates (that is, SrTiO<sub>3</sub>). *Continuously* varying the growth direction from the pseudo-cubic [001] to [110] direction, via the high-symmetry [111] direction, results in: (i) an original temperature-versus-growth angle phase diagram possessing different structural states; (ii) a tuning of the Curie temperature,  $T_c$ , by more than 450K; (iii) a minimal value of  $T_c$  being *near room temperature*; and (iv) optimization of important physical responses at room temperature, such as dielectric and piezoelectric coefficients, for some specific growth directions. The origins of these features are also revealed, including the finding of a law correlating  $T_c$  with the growth direction.

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Ferroelectric materials have been intensively studied, partly because of their useful properties that can be put into use in devices [1, 2]. Among many factors that greatly affect their properties, epitaxial strain experienced by ferroelectric films grown along the [001] pseudo-cubic direction is one of the most investigated and manipulatable aspects [3–11]. For instance, it allows to induce a large electrical polarization and drastically shift the paraelectric-to-ferroelectric transition temperature [12, 13]. Epitaxial strain can even induce ferroelectricity in nominally-paraelectric compounds [6, 12, 14, 15], and results in enhanced electromechanical properties [16]. However, there is an inevitable limitation to the magnitude and sign of the epitaxial strain that (001) ferroelectric films can experience due to the facts that such strain arises from the lattice mismatch between the substrate on top of which the film is grown and the material of which the film is made, and that there are rather few available substrates. Moreover, some of these substrates are rather expensive and/or can induce high density of defects inside the films [17, 18], which may further limit their technological usefulness. Moreover, the control of the surface termination (which is crucial for optimal atomic-layer growth of epitaxial films) is only well established for rather few substrates [19, 20].

In addition to changing the film's thickness [18], another alternative way to overcome such roadblock may be to grow ferroelectric films on a single, amply available and economic substrate (such as SrTiO<sub>3</sub>), and vary the crystallographic direction of the growth axis. However, studies on the effect of the growth direction, being away from the pseudo-cubic [001] direction, on properties of ferroelectric films are scarce (see, e.g., Refs. [11, 21–24] and references therein). These studies are also limited to high-symmetry growth directions such as the pseudo-

cubic [110] or [111] directions, which may have prevented the discovery of unusual and useful effects typically associated with low-symmetry directions (as, e.g., evidenced in semiconductor physics [25]). As a result, many important questions are currently unresolved. For instance, can the *continuous* variation of the growth axis lead to novel phase diagrams exhibiting a variety of phases, and affect the magnitude but also direction of the electrical polarization? Can some particular growth directions possess enhanced physical responses, especially at room temperature (which is needed for the design of efficient miniaturized devices), and, if yes, are these directions of high-symmetry or low-symmetry? Can the Curie temperature be significantly controlled by varying the growth direction, and, if yes, is there a simple law quantifying and explaining such hypothetical useful control?

The goals of this Letter are to resolve all the aforementioned issues by investigating the effects of the growth direction on films made of the prototype BaTiO<sub>3</sub> (BTO) material grown on the SrTiO<sub>3</sub> (STO) substrate, via the effective Hamiltonian ( $H_{\text{eff}}$ ) method developed in Ref. [26, 27]. As we will see, surprises are in store.

Important degrees of freedom of this  $H_{\text{eff}}$  are the local soft modes,  $\mathbf{u}_i$ , that are centered on the Ti-sites of the 5-atom unit cell  $i$  ( $\mathbf{u}_i$  is directly proportional to the electric dipole moment of that cell, and represents the collective motion of the Ba, Ti and oxygen atoms inside the cell  $i$  [27]).  $H_{\text{eff}}$  for BTO systems contains a local mode self-energy, a long-range dipole-dipole interaction, a short-range interaction between local soft modes, an elastic energy, and interactions between local modes and strains. The analytical expressions of these terms are provided in Ref. [27]. Details about this effective Hamiltonian approach, including its demonstrated accuracy, are given in the Supplementary Material [28–34].

Here, we use this  $H_{\text{eff}}$  numerical technique in Monte-Carlo (MC) simulations. Three-dimensionally periodic  $12 \times 12 \times 12$  supercells (8,640 atoms) are employed to get well-converged results (Note that the use of such periodicities imply that, as commonly done in many previous calculations (see, e.g., Refs. [3, 5, 35]), the effect of the surface on the films' properties is neglected. This is because we are presently interested by the "sole" combined effects of the strain and growth direction on these properties). Two different coordinate systems are used here: (1) the "usual" (xyz) system for which the x-, y- and z-axis lie along the pseudo-cubic [100], [010], [001] directions, respectively; and (2) another coordinate system ( $x'y'z'$ ) for which the  $z'$ -axis corresponds to the growth direction of the film and for which the  $x'$ -,  $y'$ - and  $z'$ -axes are practically chosen to be along the pseudo-cubic  $[\bar{1}10]$ ,  $[m\bar{m}n]$ , and  $[h\bar{h}k]$  directions, respectively, with  $m = -\cos(\theta)/\sqrt{2}$ ,  $n = \sin(\theta)$ ,  $h = \sin(\theta)/\sqrt{2}$  and  $k = \cos(\theta)$ , where  $\theta$  is the angle between the  $z'$ - and  $z$ -axes and will be referred to as the growth angle afterwards. Note that we are going to continuously rotate the growth direction from the pseudo-cubic [001] to [110], via [111], directions in this study, implying that  $\theta$  will vary between 0 and 90 degrees. The mimicking of finite-temperature properties of BTO films that are *epitaxially* grown along the  $z'$ -axis is accomplished by imposing the following conditions for the homogeneous strain tensor (in Voigt notation):  $\eta_{1'} = \eta_{2'} = (a_{\text{sub}} - a_{\text{lat}})/a_{\text{lat}} = \delta$  and  $\eta_{6'} = 0$ , while  $\eta_{3'}$ ,  $\eta_{4'}$  and  $\eta_{5'}$  can fully relax during the simulations. Here, the prime ' is used to denote properties computed in the ( $x'y'z'$ ) coordinate system and  $a_{\text{sub}}$  is the in-plane lattice constant of the substrate.  $a_{\text{lat}}$  is the lattice parameter of the BTO paraelectric bulk at the Curie temperature,  $T_c$ .  $\delta$  is the resulting misfit strain experienced by the epitaxial films. In the present study, we select  $\delta$  to correspond to the growth of the BTO films on the well-known and used STO substrate, therefore yielding  $\delta = -2.2\%$ . Note that the growth, along different direction, of BTO films on STO substrate can be experimentally achieved by using high index planes or different facets of the STO substrate. Technically, for each chosen growth angle  $\theta$ , we cool down the system from high to low temperature with a 5K step, using 500,000 MC sweeps. The correlation functions of Refs. [36, 37] are also employed to compute the dielectric susceptibility and piezoelectric coefficients. Note that the interface between BTO and STO, beyond the strain effect that is taken into account in our simulations, is known to have rather minor effects on properties of BTO films, especially if these films have a thickness being large enough (but smaller than the critical thickness associated with the full strain relaxation of the films) [23, 38]. Its effect beyond the mediation of the strain is thus neglected here. Note that also several studies (see, e.g., Refs. [6, 13, 16]) demonstrated that (for a given growth direction) one of the most important aspects of ferroelectric thin films is the amount of strain

experienced by these films and arising from the lattice mismatch between the materials forming the film and the substrate. In other words, effects, such as surface reconstruction, film's thickness or precise morphology or stoichiometry of the substrate, have typically much less consequence on physical properties of these films than this epitaxial strain.

Figure 1a shows the predicted temperature-*versus*-growth angle phase diagram for BTO films grown on a STO substrate. When  $\theta$  is equal to  $0^\circ$ , these films undergo a phase transition from the paraelectric  $p$  to ferroelectric  $c$  state (that has a polarization lying along the pseudo-cubic [001] direction) [3] at  $\simeq 755\text{K}$ . Such predictions are qualitatively consistent with the previous work of Refs. [3, 8, 21] on (001) BTO epitaxial films. Note, however, that the experimental study of Ref. [21] gives  $\simeq 700\text{K}$  for the Curie temperature of (001) BTO films grown on STO substrates. This discrepancy of around 50K between these experimental data and our calculations may originate from a weak strain relaxation of the (001) BTO films grown in Ref. [21], as consistent with Fig. 1b of Ref. [21] indicating a strain gradient and with our numerical finding that slightly varying  $\delta$  from  $-2.2\%$  to  $-1.9\%$  results in a predicted  $T_c$  of 705K for (001) BTO films. This discrepancy can also originate from the presence of defects in the grown films, or from the effective Hamiltonian method used here that neglects the finite thickness of the films. Moreover, Figure 1a also indicates that, when the growth angle becomes near  $90^\circ$ , the BTO films now experience a paraelectric-to-ferroelectric phase transition at a much smaller Curie temperature (namely, around 395K) leading to another ferroelectric state, that is the so-called  $aa$  phase [3] for which the polarization lies along the pseudo-cubic [110] direction. These latter predictions are in-line with those reported for (110) BTO films under compressive epitaxial strain [11]. Interestingly, Figure 1a further reports that the minimal value of  $T_c$  occurs when the growth direction of the film lies along the high symmetric [111] pseudo-cubic direction (which corresponds to  $\theta = 54.7^\circ$ ). In that case, the Curie temperature is around 295K, which can be, e.g., put into use to design devices having large dielectric tunability near room temperature (see, e.g., Ref. [39] and references therein). It is therefore remarkable that  $T_c$  can be considerably varied and controlled when playing with the growth direction:  $T_c$  greatly decreases by nearly 460K when the growth direction rotates from the pseudo-cubic [001] to [111] directions, while  $T_c$  slightly increases by around 100K when the growth direction then rotates from the pseudo-cubic [111] to [110] directions. It is important to realize that such tuning is continuous and involves the *same* (experimentally available) STO substrate, which is thus much promising than trying to alter  $T_c$  by growing (001)-films on substrates having different misfit strains (since the values of strain offered by available substrates are discrete and limited, and since grow-

ing high-quality films on substrates other than STO can be rather challenging), as now typically done.

We also found that, for temperatures just below  $T_c$  and when the growth angle varies between  $\simeq 2^\circ$  and  $54.7^\circ$  (respectively, between  $54.7^\circ$  and  $\simeq 87^\circ$ ), the stable state is  $r_c$  (respectively,  $r_{aa}$ ) which is a ferroelectric state for which the x- and y- components of the polarization are non-null, equal to each other and larger (respectively, smaller) than the non-zero z-component of the polarization [8]. Note that, at precisely  $\theta = 54.7^\circ$  (i.e., when the growth direction is along the pseudo-cubic [111] axis), the ferroelectric phase for temperatures smaller than the Curie temperature is such as the three Cartesian components of its polarization in the (xyz) coordinate system are equal to each other and non-vanishing. The polarization therefore lies along the [111] axis, which coincides with the growth direction, and the resulting state has a rhombohedral symmetry, as consistent with Ref. [22].

Furthermore, Figures 1b and 1c display the Cartesian components of the supercell average of the local modes (which is directly proportional to the spontaneous electrical polarization) in the xyz and x'y'z' frames, respectively, with respect to the growth angle at 295K for the investigated BTO systems. In particular, Fig. 1c reveals that the z'-component of the polarization ( $P_{z'}$ ) dominates for all growth directions. As a result, the occurrence of the different crystallographic phases existing when varying the growth direction mostly stems from the fact that, as a response to the compressive strain experienced by the film, the polarization rotates with the growth angle in order to lie along a direction that is close to the growth axis. Note, however, that in some cases (especially when  $\theta$  is close to  $35^\circ$ ) the spontaneous polarization of the film is tilted away from, rather than perfectly aligned with, the growth direction, as evidenced by the non-negligible y'-component of the polarization ( $P_{y'}$ ) revealed by Fig. 1c. Figures 1d and 1e provide similar data than Figs. 1b and 1c, respectively, but for the low temperature of 5K rather than 295K. Some differences exist between the polarization at these two different temperatures. For instance,  $P_{y'}$  does not vanish at 5K when  $\theta$  is equal to  $90^\circ$  (see Fig. 1e), unlike the case for  $T=295K$  (cf Fig. 1c). As a result and as consistent with Figure 1a, a phase transition occurs *at low temperature* when the growth angle is larger than  $\simeq 87^\circ$ : in that situation,  $aa$  evolves into  $r_{aa}$  via the formation of a z-component of the polarization. Note that this latter transition can be prevented from occurring if one studies larger magnitude of the compressive strain than the one presently investigated, as consistent with Ref. [11].

Let us now investigate how the growth direction affects the  $\chi$  dielectric and  $d$  piezoelectric tensors *near room temperature*. Such information is provided in Figures 2a and 2b, respectively, as computed within the (x'y'z') basis at 295K. One can see that some components of the dielectric tensor (namely,  $\chi'_{33}$  and  $\chi'_{22}$ ) and some piezo-

electric coefficients (e.g.,  $d'_{33}$  and  $d'_{24}$ ) peak and adopt rather large values when  $\theta$  is close to  $54.7^\circ$ . For instance,  $\chi'_{33}$  is larger than 10,000 and  $d'_{24}$  is bigger than 200 pC/N when  $\theta = 54.7^\circ$ . Such behaviors are very promising to design efficient miniaturized devices, and originate from the facts that (i)  $T_c$  is minimal and around room temperature when the growth direction is along the pseudo-cubic [111] direction (see Fig. 1a) – which results in the peaks of  $\chi'_{33}$  and  $d'_{33}$  at 295K when  $\theta = 54.7^\circ$ ; and (ii)  $P_{y'}$  only vanishes when  $\theta$  is precisely  $54.7^\circ$  for growth directions lying around the pseudo-cubic [111] direction (see Fig. 1c) – which leads to enhanced  $\chi'_{22}$  and  $d'_{24}$ . Figures 2a and 2b further reveal that  $\chi'_{11}$  has a rather large “tail” (i.e., values larger than 700) while  $d'_{15}$  continuously increases to reach a magnitude as large as 500 pC/N, when the growth angle is increased above  $54.7^\circ$  and up to  $90^\circ$  near room temperature. Such technologically-relevant and striking features arise from the easiness of the spontaneous polarization to rotate within the (x', z') plane via, e.g., the application of external electric field or stress [40, 41]. Such easiness is consistent with the fact that Ref. [11] predicted that (110) BTO films experiencing a misfit strain of around -2.2% lie, at 295K, near the edge of a phase transition towards the  $ab$  phase, for which the polarization vector is in-between our x'- and z'-directions, that is in-between the pseudo-cubic  $[\bar{1}10]$  and  $[110]$  directions.

Let us now try to understand the behavior of  $T_c$  shown in Fig. 1a, since it is associated with useful physical properties. For that and as detailed in the Supplemental material [42, 43], the analytical expression of the internal energy provided by the effective Hamiltonian of BTO systems, as well as the values of its parameters, allows to derive the following dependence of the Curie temperature:

$$T_c \simeq \frac{M}{\alpha_e + \gamma_e(\sin(\theta)^2 - \frac{3}{4}\sin(\theta)^4)} + N \quad , \quad (1)$$

where  $M$  and  $N$  are positive coefficients that only weakly depend on  $\theta$ . The  $\alpha_e$  and  $\gamma_e$  coefficients of Eq. (1) are found to be positive and negative, respectively, and almost independent of  $\theta$  for the BTO system. Figure 1a shows that neglecting the dependence of  $M$  and  $N$  on  $\theta$  results in rather good fit of the numerical data. Such function provided by Eq. (1) therefore allows to understand how and why  $T_c$  depends on the growth direction. In particular, this function leads to a  $T_c$  that is minimal when  $\sin^2(\theta)$  is  $2/3$ , that precisely corresponds to the [111] direction – as consistent with our Monte-Carlo results.

Interestingly, we also performed similar calculations on  $\text{PbTiO}_3$  (PTO) films grown under -1.6% strain (not shown here). Although PTO is rather different from BTO (as, e.g., evidenced by the fact that PTO bulk only experiences a single phase transition with temperature, with the resulting ground state being tetragonal rather than rhombohedral), general features of  $T_c$  depicted in



Fig. 1a also apply to the temperature-*versus*-growth angle phase diagram of PTO films. Examples are: (1)  $T_c$  greatly reduces as the growth angle increases from  $0^\circ$  to  $54.7^\circ$ , and increases as  $\theta$  increases from  $54.7^\circ$  to  $90^\circ$ ; and (2) Equation (1) fits rather well the Monte-Carlo data obtained for  $T_c$ . It therefore appears that the directional minimum of  $T_c$  at the pseudo-cubic [111] direction, as well as Eq. (1), are general features of ferroelectric systems. Knowing such general features may now be taken advantage of, in order to design materials with optimized responses.

In summary, we have examined properties of BTO films grown on a single substrate made of STO and along various growth directions rotating from [001] to [110], via [111], using an effective Hamiltonian method [26, 27]. Several interesting features are found, ranging from the novel phase diagram given in Fig. 1a to the optimization of properties reported in Figs 2, via the derivation of the simple law given by Eq. (1). We therefore hope that these predictions will be observed soon and (along with their explanations) help to deepen our knowledge of ferroelectric and functional materials as well as of nanoscience.

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Figure Captions.

Figure 1 (Color online): Structural properties of BTO films grown on a STO substrate as a function of the growth angle. Panel (a) reports the temperature-*versus*-growth angle phase diagram, while Panels (b) and (c) display the components of the supercell average of the local mode in the (xyz) and (x'y'z') coordinate frame, respectively, at 295K. Panels (d) and (e) provide similar data than Panels (b) and (c), respectively, but for a temperature of 295K. The solid red line in Panel (a) represent

the fitting of  $T_c$  by Equation (1), with the parameters of this fitting being:  $M = 1022.83$ ,  $N = 1754.88$ ,  $\alpha_e = 1.04$ , when assuming  $\gamma_e = -1.00$ .

Figure 2 (Color online): Physical responses of BTO films grown on a STO substrate as a function of the growth angle, at a temperature of 295K and within the (x'y'z') coordinate frame. Panel (a) reports the  $\chi'_{11}$  and  $\chi'_{22}$  components of the dielectric susceptibility, with its inset giving  $\chi'_{33}$ . Panel (b) displays the  $d'_{33}$ ,  $d'_{15}$  and  $d'_{24}$  piezoelectric coefficients.



