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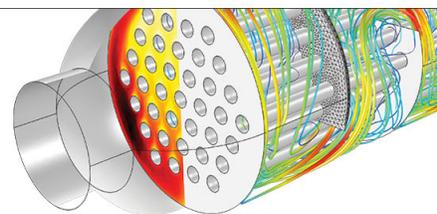
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For (001)_c oriented BaTiO₃ thin films, it has been found that epitaxial constraint can result in a dramatic increase in the temperature of a tetragonal (*T*) structural phase transition. For 2000-Å-thick films grown directly on SrTiO₃ substrates, a *T*→cubic (*C*) phase transition was found on heating at >950 K, where the lattice constant changed smoothly with temperature. It was also found for films of the same thickness that the *T*→*C* transition is nearly restored to that of bulk crystals by the use of a buffer layer, which relaxes the epitaxial constraint. These results provide evidence of an epitaxially induced high temperature structural phase transition in BaTiO₃ thin films, where the ferroelectric (internal) and structural (external) aspects of the phase transition are decoupled. © 2004 American Institute of Physics. [DOI: 10.1063/1.1812579]

The classic first order ferroelectric phase transformation is the cubic (*C*) to tetragonal (*T*) one in BaTiO₃ bulk crystals,^{1,2} which occurs near a Curie temperature of $T_C \cong 405$ K. Subsequent ferroelectric transitions occur to lower symmetry orthorhombic and rhombohedral phases with decreasing temperature. Thin films of BaTiO₃ have also been intensively investigated for applications in ferroelectric memories, integrated capacitors, and electro-optic modulators.^{3–7} Both epitaxial^{8–13} and polycrystalline¹⁴ films have been studied.

Investigations of epitaxial BaTiO₃ films from on SrTiO₃⁸ and MgO^{9–11} have reported the lack of structural phase transformations. This was evidenced by the lack of anomalies in the temperature dependence of the lattice parameters. In particular, studies by Yoneda *et al.*⁹ have found the lack of a *T*→*C* transition on heating for films of 100, 1000, and 4000 Å thickness grown on MgO—the tetragonal structure remained present at all temperatures measured upto 850 K. However, corresponding electrical property measurements revealed a maximum in the temperature dependent dielectric constant (*K*) at $T \cong 410$ K, in near agreement with that of bulk BaTiO₃ single crystals and ceramics. These results have recently been interpreted as the effect of epitaxial constraint that prevents external dimension changes of the film due to clamping, while permitting a ferroelectric phase transition with internal displacive rearrangements.¹⁵

Recently, a Landau–Ginzburg–Devonshire (LGD) thermodynamic theory has been developed by Pertsev *et al.*¹⁶ to describe the effect of epitaxial constraint on the structural phase transitions of SrTiO₃ thin films grown with differing misfits on various substrates. SrTiO₃ bulk crystals undergo a *C*→*T* transition on cooling at $T = 105$ K which is ferroelastic in nature, but not ferroelectric. Rather, it is an incipient ferroelectric. Using the LGD theory,¹⁶ the epitaxial phase diagram of (001)_c oriented SrTiO₃ as calculated for films grown on various cubic substrates. It was shown that decoupled ferroelectric and ferroelastic instabilities could be driven by epitaxial constraint, where various ferroelectric phase transitions could occur as internal atomic rearrangements within ferroelastically distorted *T* phases.

The thermodynamic investigations of constrained thin layers of SrTiO₃¹⁶ suggest that epitaxy might result in decoupled ferroelectric and ferroelastic phase transitions from prototypic cubic (*m3m*) to tetragonal symmetries in many perovskite films. However, it has yet to be shown whether there is an independent ferroelastic *T*→*C* structural phase transition in epitaxially constrained ferroelectric films at higher temperatures, or not. In this letter, we will report a high-temperature *T*→*C* phase transition (>900 K) in epitaxially constrained (001)_c oriented BaTiO₃ films grown directly on SrTiO₃ substrates. It will also be shown for films of the same thickness that the *T*→*C* phase transition temperature can be restored to that of bulk single crystals by the use of a buffer layer, which relaxes the epitaxial constraint.

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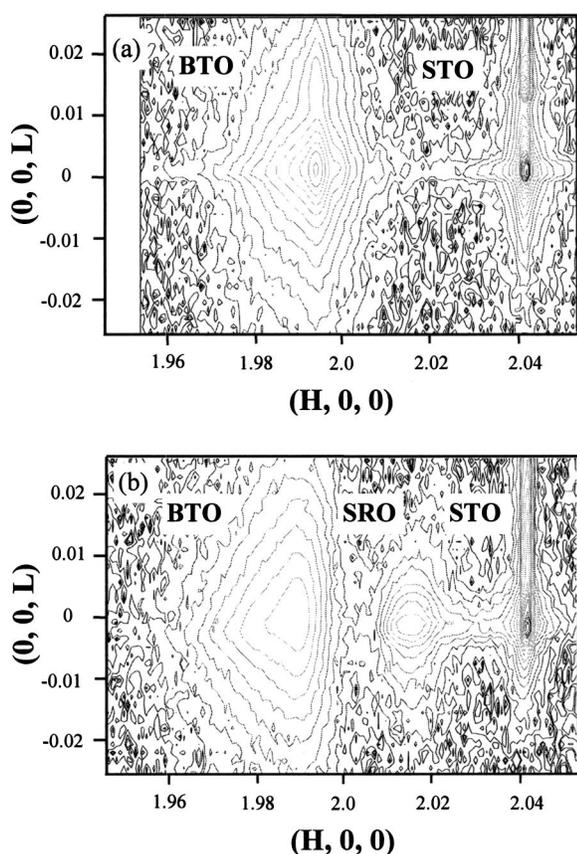


FIG. 1. Reciprocal space scans for $(001)_c$ oriented BaTiO_3 thin layers taken along the (HOL) zone for (a) a 2000-Å-thick BaTiO_3 films grown directly on $(001)_c$ SrTiO_3 substrate; and (b) a 2000-Å-thick BaTiO_3 films grown on a 600-Å-thick SrRuO_3 electrode (or buffer layer), which was grown on top of a $(001)_c$ SrTiO_3 substrate. The values of (HKL) are normalized to those of BaTiO_3 single crystals, i.e., $(H, K, L)_{\text{crystal}} \equiv (1, 1, 1)$. Intensity is given on a log scale.

We have grown phase-pure BaTiO_3 (BTO) thin films of 2000 Å thickness by pulsed laser deposition onto $(001)_c$ single crystal substrates of SrTiO_3 . Some of the films were grown directly on SrTiO_3 : deposited at 670 °C in an oxygen ambient of 20 mTorr at a growth rate of 0.7 Å/s. Others films were grown on top of a conducting perovskite oxide electrode. SrRuO_3 (SRO)¹⁷ was chosen as the bottom electrode due to the closest lattice mismatch with the BTO structure: films of SRO of 500 Å were deposited at 600 °C in an oxygen ambient of 100 mTorr, and followed by the BTO film deposition as described earlier. X-ray diffraction studies were performed using a Phillips MPD system. Careful investigations were performed using a high resolution x-ray diffractometer equipped with a two bounce hybrid monochromator, an open three-circle Eulerian cradle, and a doomed hot stage. A $\text{Ge}(220)$ cut crystal was used as an analyzer, which had a theta-resolution of $\sim 0.0068^\circ$ (or 0.43 arc sec). The x-ray wavelength was that of $\text{Cu}_{K\alpha}$ ($\lambda = 1.5406$ Å) and the x-ray generator was operated at 45 kV and 40 mA. The penetration depth in BaTiO_3 at this x-ray wavelength is much greater than that of the film thickness. The lattice constants of $(001)_c$ oriented BaTiO_3 films measured as a function of temperature on heating over the range of 300–1000 K. The a -lattice parameter of BaTiO_3 bulk single crystals at $T = 300$ K is $a = 3.99$ Å, and thus we use one reciprocal lattice unit as corresponding to $a^* (=b^*) = 2\pi/a$

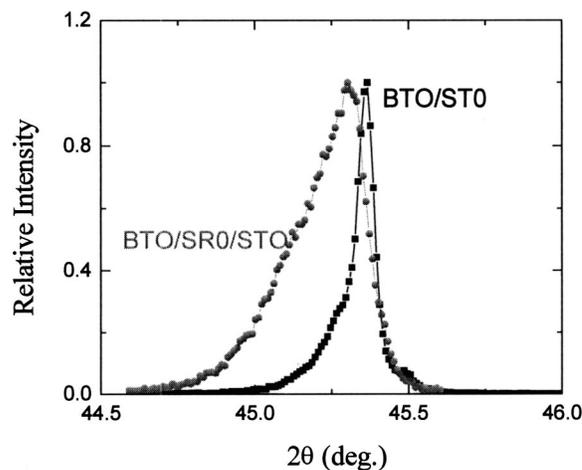


FIG. 2. Longitudinal (200) profile for a 2000-Å-thick BaTiO_3 films grown directly on $(001)_c$ SrTiO_3 substrate; and a 2000-Å-thick BaTiO_3 films grown on a 600-Å-thick SrRuO_3 electrode (or buffer layer), which was grown on top of a $(001)_c$ SrTiO_3 substrate.

$= 1.547 \text{ \AA}^{-1}$. The mesh scans presented in this letter are plotted in this reciprocal unit.

Figure 1 shows reciprocal lattice scans taken along the (HOL) zone for $(001)_c$ BaTiO_3 films (a) grown directly on SrTiO_3 ; and (b) grown on a SrRuO_3 buffer layer. The mesh scans reveal two peaks for the film grown directly on SrTiO_3 , whereas three peaks can be seen for that grown on the SrRuO_3 buffer layer. The phases corresponding to the peaks are identified in the figures. These results confirm that the SrRuO_3 buffer layer has a lattice parameter close to its bulk value ($a = 3.98$ Å), and that the BaTiO_3 layer is much better lattice matched to it than to the SrTiO_3 substrate. Accordingly, for a given thickness, films grown on a SrRuO_3 buffer layer will be significantly more elastically relaxed. It is also relevant to note that both films had a relatively small mosaic spread of $\sim 0.2^\circ$, revealing satisfactory film quality. Figure 2 shows longitudinal (200) profiles of $(001)_c$ BaTiO_3 films grown directly on SrTiO_3 , and on a SrRuO_3 buffer layer. The data reveal the coexistence of c and a domains for films grown on the buffer layer, whereas those grown directly on SrTiO_3 consisted mostly of only a domains.

A complete structural analysis was then done using longitudinal (200) and (202) profiles for both types of films. Figure 3 shows the lattice parameters as a function of temperature for films grown (a) directly on the substrate; and (b) on the buffer layer. Comparisons of data in the figure will reveal a dramatic difference in the $T \rightarrow C$ phase transition temperature on heating between these two types of films. For 2000-Å-thick films grown on SrTiO_3 substrates, the $T \rightarrow C$ phase transition occurred on heating near 950 K (maybe slightly deviated due to fitness error). However, for an identical 2000-Å-thick film grown on SrRuO_3 buffer layers, the $T \rightarrow C$ phase transition occurred near 470 K—which is close to $T_C = 405$ K of bulk BaTiO_3 single crystals.^{1,2} These results provide evidence of an epitaxially induced high temperature structural phase transition in BaTiO_3 thin films, which is relaxed by growth of an identical film on a SrRuO_3 buffer layer.

It is also important to note several other features in Fig. 3. First, the a -lattice parameter for both films exhibited no indications of a phase transition. Rather, the lattice parameters changed gradually with temperature, similar to a simple

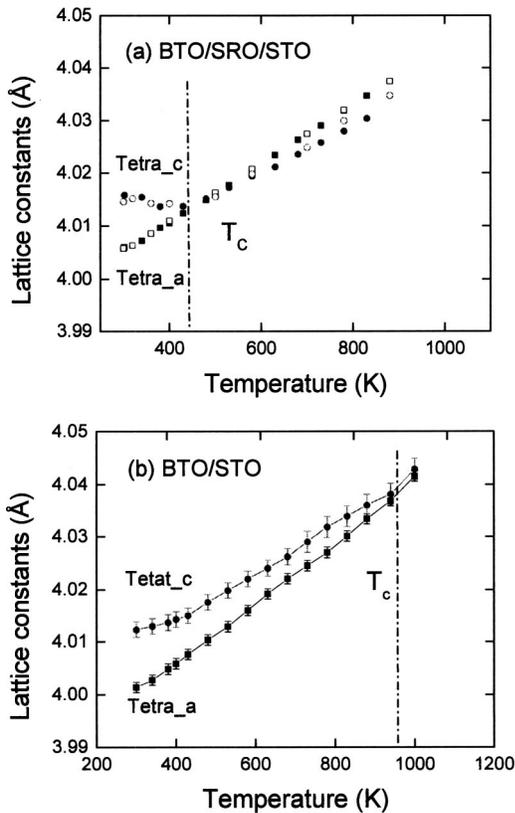


FIG. 3. Temperature dependent lattice parameters for (a) a 2000-Å-thick BaTiO₃ films grown directly on (001)_c SrTiO₃ substrate; and (b) a 2000-Å-thick BaTiO₃ films grown on a 600-Å-thick SrRuO₃ electrode (or buffer layer), which was grown on top of a (001)_c SrTiO₃ substrate. Solid circles and squares represent increasing temperature and open circles and squares represent decreasing temperature.

thermal expansion. This is because any changes in the a -lattice parameter with temperature must be invariant with respect to corresponding ones in the substrate or buffer layer. Second, the c/a ratio is nearly equal for both films at 300 K: in fact, for both types of films, the relative changes in c/a with temperature below 470 K were gradual and of similar magnitude. These results suggest that the ferroelectric phase transformation temperature is nearly the same for both films, as T_C is generally expected to be proportional to c/a .¹ This is also supported by previous dielectric and structural studies of (001)_c BaTiO₃ thin films grown on Pt/MgO that demonstrated the lack of a $T \rightarrow C$ phase transition, in spite of a maximum in the dielectric constant at 470 K.⁹ Our structural

data for the films grown directly on the SrTiO₃ substrate are qualitatively similar—except we clearly show that a $T \rightarrow C$ phase transition occurs near 950 K. In our case, for films grown directly on the substrate, the ferroelectric (internal) and structural (external) aspects of the phase transition must clearly be decoupled.

In summary, 2000-Å-thick BaTiO₃ films grown directly on (001)_c SrTiO₃ substrates have a tetragonal structure until a temperature greater than 900 K. However, an identical film of the same thickness grown on a 500-Å-thick SrRuO₃ buffer layer on top of the substrate undergoes a $T \rightarrow C$ transition at 470 K, in close proximity to $T_C=405$ K of bulk BaTiO₃ crystals. These results provide evidence of an epitaxially induced high temperature structural phase transition in BaTiO₃ thin films, where the ferroelectric (internal) and structural (external) aspects of the phase transition are decoupled.

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