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Ferroelectricity in ultrathin strained BaTiO₃ films: probing the size effect by ultraviolet Raman spectroscopy

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Abstract

We demonstrate a dramatic effect of film thickness on the ferroelectric phase transition temperature, T_c , in strained BaTiO₃ films grown on SrTiO₃ substrates. Using variable temperature ultraviolet Raman spectroscopy enables measuring T_c in films as thin as 1.6 nm, and film thickness variation from 1.6 to 10 nm leads to T_c tuning from 70 to about 925 K. Raman data are consistent with synchrotron x-ray scattering results, which indicate the presence of 180° domains below T_c , and thermodynamic phase-field model calculations of T_c as a function of thickness.

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Keywords:

Ferroelectrics, materials possessing a spontaneous and switchable electric polarization, which appears below the Curie temperature T_c , attract a broad interest because of a wide range of their applications, such as non-volatile memory devices or piezoelectric micro- and nanoelectromechanical systems.[1, 2] In recent years, the continuous demand for device miniaturization and advances in epitaxial technology of ferroelectric oxide materials [3, 4] have rapidly moved the the science and technology of ferroelectrics towards thin films and multilayer structures at nanometer scale. Nanoscale ferroelectrics are also fascinating objects from fundamental physics point of view, since reduction of the structural dimensions gives rise to new phenomena and properties dramatically different from those of bulk ferroelectrics.[5–7]

Understanding the basic physics of ultrathin ferroelectric films, in particular, the issue of a critical size for ferroelectricity has been the area of much research effort recently.[5–9] For a long time it was believed that ferroelectricity was suppressed in very small particles and ultrathin films [10, 11], and a spontaneous polarization could not be sustained in a material below a critical size of few tens of nanometers. Later experiments identified a ferroelectric state in much thinner films [12], and recent theoretical work [13, 14] showed the critical size to be much smaller than previously thought. Recent results on PbTiO_3 films [8, 15–17] and superlattices [18–22] provided the experimental evidence that ferroelectricity persists down to vanishingly small sizes; it can exist in superlattices containing only one-unit-cell-thick layer of ferroelectric (PbTiO_3 or BaTiO_3) embedded in much thicker non-ferroelectric SrTiO_3 . These studies revealed that the issue of critical size is very complex, and electrical and mechanical boundary conditions play an essential role in nanoscale ferroelectricity.[23, 24] In particular, mechanical strain was shown to enhance ferroelectricity in relatively thick (≥ 50 nm) BaTiO_3 films.[25]

Shrinking dimensions demand characterization techniques capable of probing the properties of nanoscale ferroelectrics. Particularly, measuring the Curie temperature T_c in such systems has been difficult, and the T_c information is missing in many reports of ferroelectricity in ultrathin films. Fong *et al.*[17] determined T_c in ultrathin PbTiO_3 films by high-resolution synchrotron x-ray scattering. A fundamental property of ferroelectrics that changes qualitatively during the phase transition is the dynamics of lattice vibrations.[10] Thus, its temperature dependence probed by Raman spectroscopy allows determining T_c . Conventional (visible) Raman measurements of oxide thin films and nanostructures are prac-

tically impossible because of the film transparency and small thickness leading to extremely weak Raman signals from thin films and the dominance of a substrate signal. We have demonstrated that ultraviolet (UV) excitation above the bandgap of ferroelectrics such as SrTiO₃ and BaTiO₃ enabled phonons of nanoscale BaTiO₃/SrTiO₃ superlattices to be observed in Raman spectra.[21] Motivated by the lack of experimental data on T_c in ultrathin films, here we focus on the size effect on T_c in strained BaTiO₃ films. We report UV Raman scattering in BaTiO₃ films as thin as 4 unit cells. Raman results, supported by synchrotron x-ray scattering and thermodynamic phase-field modeling, demonstrate tuning of T_c by over 850 K.

A series of epitaxial (001) BaTiO₃ films with thicknesses of 1.6, 2, 2.4, 4, and 10 nm (4, 5, 6, 10, and 25 unit cells) has been grown by molecular-beam epitaxy on TiO₂-terminated (001) SrTiO₃ substrates.[3, 25] The growth was monitored by reflection high energy electron diffraction. We have studied both uncapped BaTiO₃ films and films of the same thicknesses capped with 10 nm of SrTiO₃. The samples have been studied by synchrotron X-ray scattering using the Advanced Photon Source at Argonne National Laboratory. According to x-ray scattering data, all samples except for the 10 nm-thick ones were commensurate to the SrTiO₃ substrates, which implies 2.2% biaxial compressive strain in the BaTiO₃ films. In the 10 nm film, slight strain relaxation (less than 0.5% of the BaTiO₃ volume) occurred.

Raman spectra have been recorded using a Jobin Yvon T64000 triple spectrometer with a liquid-N₂-cooled multichannel CCD detector. For excitation, a 325 nm He-Cd laser line was used with a power density of 0.6 W/mm² at the sample surface, low enough to avoid any noticeable local heating.[26] Spectra have been measured over a temperature range 10–950 K using a variable temperature closed cycle He cryostat in the range 10–600 K and an evacuated hot stage for the measurements above 600 K.

Fig. 1 shows the spectra of four BaTiO₃ films at 295 K compared to that of a bare SrTiO₃ substrate. We have measured backscattering spectra in both $z(x, x)\bar{z}$ and $z(x, y)\bar{z}$ polarization configurations and found that the polarized signal dominates the spectra, while almost no signal was observed in $z(x, y)\bar{z}$ geometry. The BaTiO₃ films studied were too thin to absorb the UV light completely, and all spectra contain broad second-order Raman features of SrTiO₃ substrates in the ranges 200–500 and 600–750 cm⁻¹. [27] In the 10, 5, and 2.4 nm films, the first-order Raman peaks of BaTiO₃ are seen, indicating that the films are polar at room temperature. Thinner, 2 and 1.6 nm BaTiO₃ films become polar at low temperatures,

~ 60 – 70 K. The inset shows the 10 K spectra of the 1.6 nm film, bare substrate, and the difference spectrum, clearly indicating the presence of BaTiO₃ peaks.

For identification of the observed phonon peaks, we compared Raman spectra of the films with the spectra of bulk and thin film BaTiO₃[28–30]. The most distinct lines due to the phonons of BaTiO₃ films were observed at about 175–185, 475, and 540 cm⁻¹, and attributed to TO₁+LO₁, LO₂, and TO₃ modes of A₁ symmetry, respectively.[28, 29] According to the selection rules, the A₁(LO) modes are active in $z(x, x)\bar{z}$ geometry. The presence of the A₁(TO) modes is likely due to deviations from true backscattering along (001) direction. Higher TO₃ phonon frequency in thin films (~ 540 cm⁻¹) compared to bulk BaTiO₃ (~ 522 cm⁻¹), is likely due to the compressive strain. A peak at ~ 290 cm⁻¹ seen in the spectra of the 10 nm BaTiO₃ film corresponds to the A₁(TO₂) mode of the tetragonal BaTiO₃. [28, 30] This peak overlaps, however, with the substrate features and cannot be distinguished in thinner films, so it was not used in our analysis. BaTiO₃ phonon peaks at positions similar to the above described features are characteristic of the spectra of bulk tetragonal BaTiO₃[28, 30] and BaTiO₃/SrTiO₃ superlattices.[21] Therefore we conclude that BaTiO₃ layers are tetragonal in these strained films.

Temperature-dependent Raman spectra for the 2.4 nm-thick BaTiO₃ film are shown in Fig. 2. Other films exhibit similar temperature evolution. Bulk BaTiO₃ is cubic and paraelectric above $T_c=403$ K, becomes tetragonal and ferroelectric below T_c , and goes through additional transitions to orthorhombic at 278 K and rhombohedral at 183 K. [31] Each of the three ferroelectric phases can be identified by Raman spectra.[30] In our films, the peak positions and lineshapes remain nearly unchanged with increasing temperature (Fig. 2). Hence, the films remain in the single ferroelectric phase and the low-temperature phases characteristic for bulk BaTiO₃ are suppressed. Biaxial compressive strain in our films, which stabilizes the tetragonal c phase, is the cause for such a behavior, also observed in BaTiO₃/SrTiO₃ superlattices.[21]

Raman spectra measured as a function of temperature allow T_c to be determined, based on the fact that centrosymmetric perovskite-type crystals have no first-order Raman active modes in paraelectric phase. Above T_c the spectra contain only the broad second order substrate features. Therefore, by plotting the first-order Raman intensity as a function of temperature, T_c can be determined as the temperature where the intensity becomes zero.[21], as illustrated in the inset to Fig. 2 for two of the films studied. We used the A₁(TO₁+LO₁)

and $A_1(\text{TO}_3)$ peaks (marked in Fig.2) since they do not overlap with the second-order features. The intensities are normalized by the Bose factor $n + 1 = (1 - \exp(-\hbar\omega/kT))^{-1}$ (\hbar , k , ω , and T are the Planck's and Boltzmann's constants, the phonon frequency, and temperature, respectively), and divided by the intensity of the corresponding mode at 10 K. Both phonon peaks show similar behaviors and the dashed-dotted lines are averages of the linear fits for the intensities of these two modes. (The linear fit corresponds to a parabolic decrease of polarization with temperature as Raman intensity is proportional to the square of atomic displacement.) T_c is determined as the intersection of a dash-dotted line with the horizontal axis.

Raman data show that T_c varies in a very broad range as a function of film thickness, being as high as 925 K for the 10-nm BaTiO_3 films. Even the 10 nm-thick films are still nearly fully strained (less than 0.5% of film volume is relaxed, as follows from x-ray scattering data). Fig. 3 summarizes the results of the T_c determination for all the samples as a function of BaTiO_3 film thickness. Even the films containing only four monolayers of BaTiO_3 , are ferroelectric with $T_c \sim 70$ K. T_c increases dramatically with increasing BaTiO_3 thickness, provided that the films remain fully (or nearly fully) strained.

Synchrotron x-ray scattering results indicate the presence of 180° domains in the 2.4, 4.0, and 10 nm-thick BaTiO_3 films capped with 10 nm SrTiO_3 . Similar to the results obtained for PbTiO_3 films,[8, 32] diffuse intensity induced by the periodic nature of the ferroelectric 180° domains appears in the scattering around the BaTiO_3 Bragg peaks, as illustrated by the in-plane reciprocal space map for the 10-nm-thick capped film (Fig. 4). While the diffuse intensity was absent at 950 K, it was present at 870 K and below, yielding a T_c value consistent with Raman results. Similar diffuse scattering was observed for the 4 and 2.4 nm capped samples at room temperature. Results on the 2 and 1.6 nm films, however, provided no evidence for diffuse scattering, suggesting that T_c is below room temperature for these films, also consistent with T_c 's obtained from Raman data (Fig. 3).

From the reciprocal space maps, the 180° domain period can be determined as the inverse distance from the center to the diffuse intensity maximum along the $\langle 110 \rangle$ direction. For 10 nm sample (Fig. 4), the period is ~ 6.3 nm. The domain size decreases with film thickness and increases with cooling. While the satellites were not clearly observed for the uncapped BaTiO_3 samples, this may be due to the existence of non-periodic domains or domain periods larger than observable by the experimental resolution (~ 80 nm). Raman spectra and their

temperature evolution for uncapped and capped BaTiO₃ films show almost no difference in terms of the shape and relative intensity of phonon peaks. The values of T_c are pretty close for capped and uncapped films of the same BaTiO₃ thickness, being slightly higher for capped films.

Observed T_c for the 10-nm films (925 K) approaches the value obtained from the phase diagram calculated without considering the finite thickness effect [33] at the relevant strain, -2.2% (~ 1000 K). For thinner films the size effect becomes significant and causes a dramatic decrease in T_c (Fig. 3). Using the phase-field method, we have calculated T_c of BaTiO₃ films clamped to SrTiO₃ substrates as a function of film thickness. The time-dependent Ginzburg-Landau equations (see Eq. 1 in ref. [33]) have been used, considering surface polarization extrapolation and open circuit electrostatic boundary conditions, corresponding to our case of the films with no electrodes. The bulk Landau energy coefficients, elastic stiffness, and electrostrictive coefficients have been chosen the same as those listed by Li *et al.* [33, 34] The result, shown in Fig. 3, agrees very well with experimental data. Simulations also show the films to consist of 180° tetragonal domains with polarizations pointing up and down normal to the film plane; the domain width increases with the film thickness (at 295 K: $\sim 2-3$, $5-6$, and 10 nm for 4 , 8 and 12 nm-thick films, respectively), in reasonable agreement with x-ray scattering results.

Fong *et al.* [17] observed a different behavior in synchrotron x-ray scattering study of ultrathin tetragonal PbTiO₃ films: relatively small suppression of T_c (even for the 1.2 nm film), and no 180° domains formed. The difference can be explained by the fact that the PbTiO₃ films studied by Fong *et al.* were grown on conducting SrRuO₃ layers and with surfaces exposed to a vapor environment of MOCVD chamber (including oxygen). Therefore, there were free charges available at both interfaces to compensate the depolarizing field. Our BaTiO₃ films neither have conducting layers at the bottom interfaces nor free ions in the environment of the top surface, so the size (depolarizing field) effect is more pronounced here.

Comparing our results with other calculations of the phase diagrams of ultrathin BaTiO₃ films for ideal short-circuit electrical conditions,[35, 36], films with imperfect-screening metal electrodes [35], and under open-circuit conditions [37], we found a good agreement with the latter calculations. (The T_c value for 2.4 -nm BaTiO₃ films is 370 K from our Raman data and ~ 380 K from Fig. 3 of Ref.[37], extrapolated to -2.2% strain). Calculations assuming

unscreened [37] or incompletely screened [38]) depolarizing field also predict the existence of 180° domains, which we have observed in capped BaTiO₃ films.

In summary, ultraviolet Raman spectroscopy was applied to study ultrathin BaTiO₃ films, commensurately grown on SrTiO₃ substrates. Raman scattering from BaTiO₃ films as thin as 1.6 nm has been observed, indicating the spontaneous polarization. Variable-temperature Raman spectroscopy demonstrates that interplay between strain and film thickness allows tuning the Curie temperature in a very broad range. T_c as high as ~ 925 K was observed in 10-nm films, which is over 500 K above the bulk BaTiO₃ value. Raman data are consistent with synchrotron x-ray scattering results. The measured T_c values agree well with thermodynamic phase field model calculations for 2.2% compressively strained BaTiO₃ under open circuit boundary conditions.

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FIGURE CAPTIONS

FIG. 1: (Color online) Room temperature Raman spectra of four BaTiO₃ ultrathin films on SrTiO₃ substrates compared to the spectrum of a bare substrate. Arrows mark the phonon peaks of the BaTiO₃ films. The inset shows Raman spectra of 1.6 nm-thick BaTiO₃ film and SrTiO₃ substrate measured at 10 K, and the difference between the two spectra.

FIG. 2: (Color online) Temperature evolution of Raman spectra of a 2.4 nm-thick BaTiO₃ film on a SrTiO₃ substrate. Arrows mark the phonon peaks of the film used for T_c determination. The inset shows the temperature dependencies of normalized Raman intensities of the peaks at ~ 180 and 540 cm^{-1} ($A_1(\text{TO}_1+\text{LO}_1)$ and $A_1(\text{TO}_3)$ phonons, respectively), for 2.4 and 10 nm-thick BaTiO₃ films capped with 10 nm SrTiO₃. The dashed-dotted lines are fits to a linear temperature dependence.

FIG. 3: (Color online) T_c as a function of the BaTiO₃ layer thickness, as determined from Raman data for all films studied (symbols). The dashed-dotted line is a result of the phase-field model calculation with open circuit boundary conditions.

FIG. 4: (Color) In-plane reciprocal space map around the BaTiO₃ 303 peak at 500 K for a 10-nm-thick BaTiO₃ film capped with 10 nm of SrTiO₃. A redder hue indicates higher intensity (log scale). The reciprocal lattice units (rlu) are in terms of the SrTiO₃ substrate.

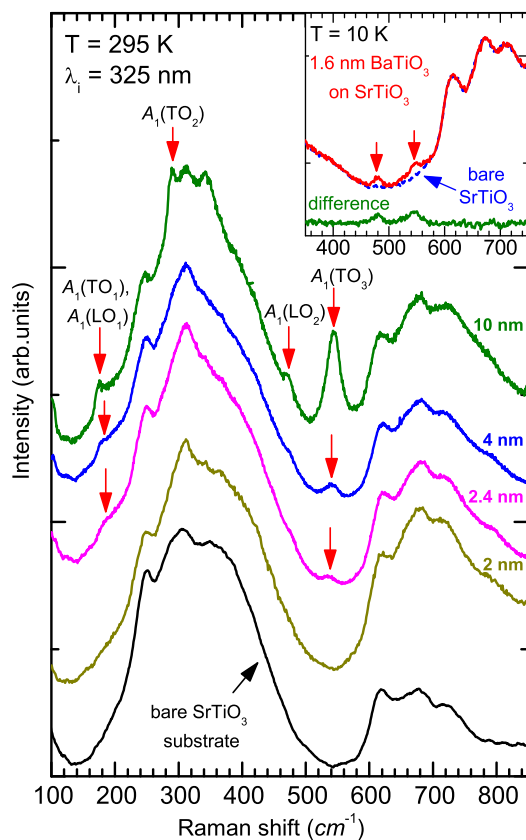


Figure 1
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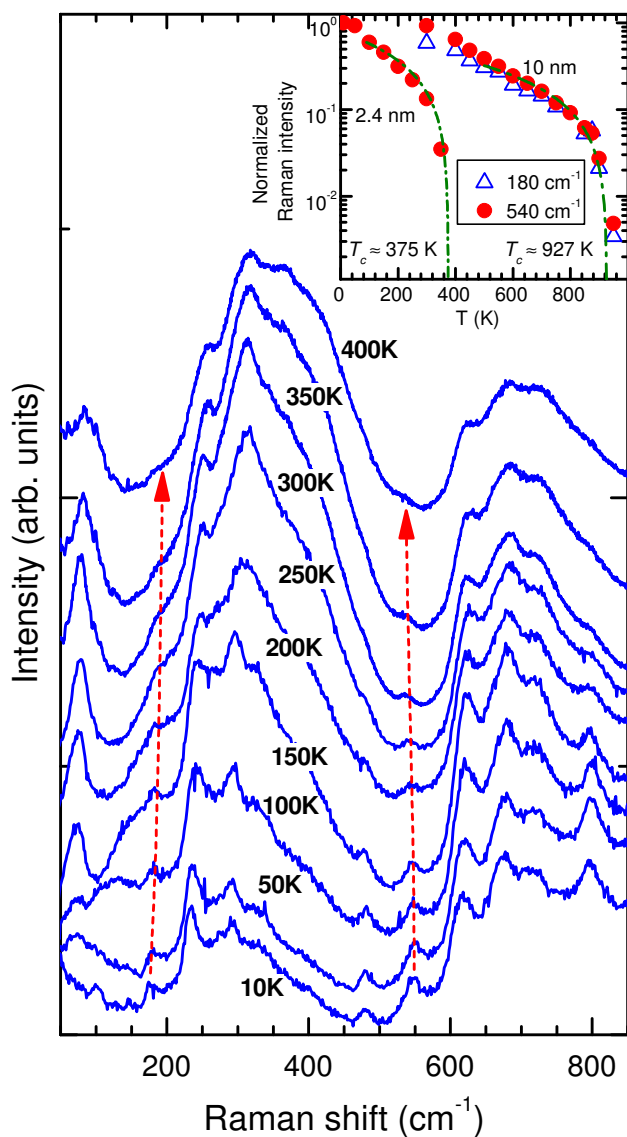


Figure 2
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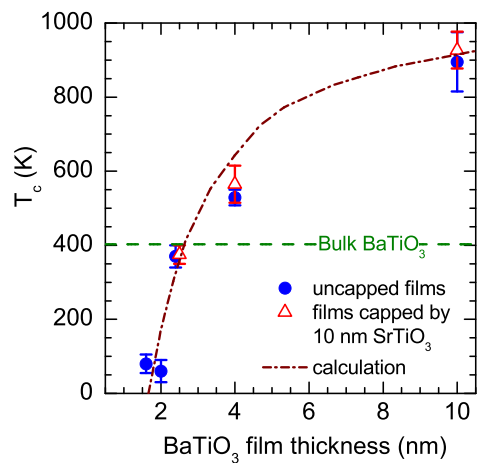


Figure 3
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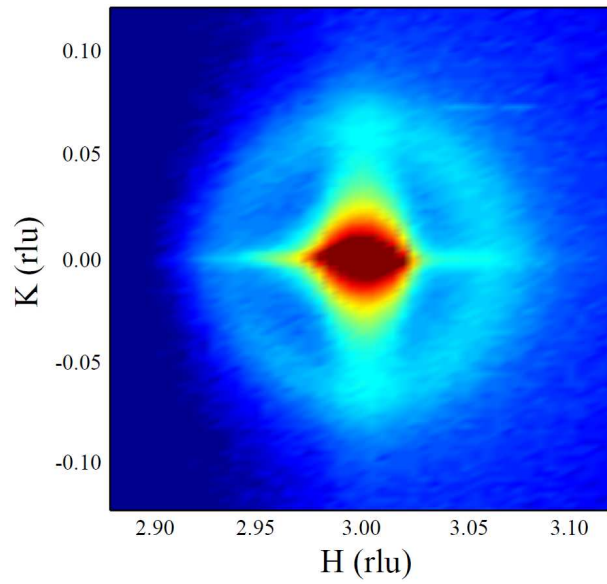


Figure 4

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