Probing Nanoscale Ferroelectricity by Ultraviolet Raman Spectroscopy


We demonstrated that ultraviolet Raman spectroscopy is an effective technique to measure the transition temperature ($T_c$) in ferroelectric ultrathin films and superlattices. We showed that one-unit-cell-thick BaTiO$_3$ layers in BaTiO$_3$/SrTiO$_3$ superlattices are not only ferroelectric (with $T_c$ as high as 250 K) but also polarize the quantum paraelectric SrTiO$_3$ layers adjacent to them. $T_c$ was tuned by ~500 K by varying the thicknesses of the BaTiO$_3$ and SrTiO$_3$ layers, revealing the essential roles of electrical and mechanical boundary conditions for nanoscale ferroelectricity.

Ferroelectricity at the nanoscale has emerged as fertile ground for new physical phenomena and devices (1–3). Shrinking dimensions demand characterization techniques that are capable of probing the properties of ferroelectrics in, for example, ultrathin films and superlattices. In particular, it is difficult to measure the ferroelectric phase transition temperature ($T_c$) in such systems, and the $T_c$ information is largely missing in reports of ferroelectricity in nanoscale ultrathin films and superlattices (4, 5). One fundamental property of ferroelectrics that changes qualitatively during the phase transition is the dynamics of lattice vibrations (6). Thus, its temperature dependence allows the determination of $T_c$. Although lattice dynamics in ferroelectric films (7, 8) and superlattices (9) from 150 nm to 2 μm in thickness have been investigated previously, such studies are very difficult on films thinner than ~100 nm. We report the use of ultraviolet (UV) Raman spectroscopy on BaTiO$_3$/SrTiO$_3$ superlattices with total thicknesses down to 24 nm, which enabled us to measure the $T_c$ of the BaTiO$_3$ layers in the superlattices. We found that the BaTiO$_3$ layers are ferroelectric even when their thickness is only one unit cell (0.4 nm) and that they can induce polarization in the adjacent paraelectric SrTiO$_3$ layers that are much thicker. By varying the thickness of both the BaTiO$_3$ and SrTiO$_3$ layers, $T_c$ was tuned from 250 K below to 235 K above the bulk value of BaTiO$_3$ (403 K). This result shows that under favorable electrical and mechanical boundary conditions, ferroelectricity is robust in nanoscale systems.

Conventional visible Raman spectroscopy works poorly for thin films of ferroelectrics and other wide-band-gap materials because the visible photon energy is much smaller than the band gap (10). Consequently, the absorption is extremely weak and the penetration depth is large, allowing light to travel through the film into the substrate, which generates overwhelming signals in the Raman spectra. For UV excitation, the photon energy is above the band gaps of ferroelectrics, leading to a much stronger absorption and a shorter penetration depth, preventing light from entering the substrate. UV excitation near the band gap also leads to strong resonance enhancement of Raman signals. This is demonstrated by Fig. 1, where Raman spectra of a BaTiO$_3$/SrTiO$_3$ superlattice spectrum measured with visible excitation (514.5 nm); and (3) the same superlattice measured with 351.1-nm UV excitation (red curve). The dashed black line shows the bare SrTiO$_3$ substrate spectrum measured with 351.1-nm UV excitation. Triangles show the calculated frequencies of the first folded LA doublet.arb., arbitrary.

Fig. 1. Room-temperature Raman spectra of (1) a bare SrTiO$_3$ substrate (black curve), (2) a (BaTiO$_3$/SrTiO$_3$) _25_ superlattice ($T_c = 530$ K, blue curve) measured with visible excitation (514.5 nm); and (3) the same superlattice measured with 351.1-nm UV excitation (red curve). The dashed black line shows the bare SrTiO$_3$ substrate
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measured with visible (514.5 nm) and UV (351.1 nm) excitations are shown. The substrate features dominate the 514.5-nm spectrum, but they are greatly reduced in the UV spectrum, in which peaks of superlattice phonons are clearly observed.

UV Raman spectroscopy has not been widely used for measurements of ferroelectric films because of technical difficulties such as lower throughput efficiency, insufficient dispersion, and higher stray light level of UV Raman spectrometers as compared to those operating in the visible range. Recently, room-temperature measurement of SrTiO3 films using 325-nm excitation has been reported (11). The recent progress in UV Raman instrumentation has made the measurement of ferroelectric films possible. In our experiment, a triple monochromator was used to provide high resolution and effective reduction of stray light (12). Powerful laser sources and optimized optical paths were used to improve the throughput. With these setups, we have measured Raman scattering in BaTiO3/SrTiO3 superlattices as thin as 24 nm and in (Ba0.5Sr0.5)TiO3 films that were 10 nm thick. The BaTiO3/SrTiO3 superlattices are denoted by (BTOx/STOy) × number of periods, where n and m refer to the thickness, in unit cells, of the BaTiO3 and SrTiO3 layers, respectively. They were all grown on (001) SrTiO3 substrates. Details of the sample preparation by reactive molecular-beam epitaxy (13) and structural characterization are presented in the supporting online material (12).

Curve 3 in Fig. 1 is typical of the UV Raman spectra of BaTiO3/SrTiO3 superlattices below Tc, exhibiting strong first-order (single-phonon) peaks as labeled in the figure. Weak second-order (two-phonon) features from the SrTiO3 substrate can be seen between 600 and 700 cm−1 and as a background in the range from 200 to 500 cm−1. The phonon mode assignment was made by comparison with the spectra of SrTiO3 and BaTiO3 single crystals (12) and with the help of first-principles calculations. The lines at about 290 cm−1 have similar positions and shapes to the TO2 modes of A1 symmetry of the tetragonal-phase BaTiO3 (14, 15); thus, they are assigned to the BaTiO3 layers. The line at about 180 cm−1 corresponds closely to the TO2 line in the electric field-induced Raman spectrum of SrTiO3 crystals (16). It is not from the SrTiO3 substrate, because the first-order Raman lines are symmetry-forbidden in bulk SrTiO3 (17). Although the TO2 mode of A1 symmetry of BaTiO3 is at about the same position (177 cm−1), it has markedly different relative intensity and shape (14) from the 180-cm−1 line. Therefore, we attribute this line to the TO2 phonon in the SrTiO3 layers. The LO3 and TO4 modes involve both SrTiO3 and BaTiO3 layers and extend through the superlattice. A doublet of folded longitudinal acoustic (LA) phonons due to the superlattice periodicity (18) is also observed. The two triangles indicate the predicted first-doublet frequencies by an elastic continuum model (19). The observation of the LA phonon folding suggests that these superlattices possess the requisite structural quality for acoustic Bragg mirrors and cavities used for coherent phonon generation (20, 21).

Bulk crystalline BaTiO3 is cubic and paraelectric above Tc = 403 K, becomes tetragonal and ferroelectric below Tc, and goes through additional transitions to orthorhombic at 278 K and rhombohedral at 183 K (22). Bulk crystalline SrTiO3 is paraelectric at all temperatures because of quantum fluctuations (23). The temperature evolution of Raman spectra for two superlattice samples is shown in Fig. 2A (BTO2/STO13) × 20 and Fig. 2B (BTO5/STO4) × 10. The shapes and positions of the BaTiO3 lines at low temperatures are characteristic of BaTiO3 in the tetragonal phase (12, 14, 15), indicating that the BaTiO3 layers are tetragonal and ferroelectric below Tc. The presence of the first-order Raman lines of SrTiO3 shows that the SrTiO3 layers are polar because the first-order lines are symmetry-forbidden in nonpolar......
SrTiO$_3$ (17). The intensities of the first-order superlattice phonons decrease as the temperature increases and disappear at $T_c$. Above $T_c$ the spectra contain only the second-order features, as expected from the symmetry selection rules. When the BaTiO$_3$ layers are paraelectric, the induced polarization in the SrTiO$_3$ layers also disappears.

By plotting the first-order Raman intensity as a function of temperature, we can accurately determine $T_c$ as the temperature where the intensity becomes zero. For this purpose, the TO$_2$ and TO$_3$ phonon lines are the most suitable because they do not overlap with the second-order features. The results, with the phonon intensities normalized by the Bose factor $n + 1 = \{1 - \exp[-(\hbar \omega/kT)]\}^{-1}$ (where $\hbar$ is Planck's constant, $k$ is phonon frequency, $T$ is Boltzmann's constant, and $T$ is temperature) and by the intensities at $7 \, K$, are presented for four superlattices: (BTO$_2$/STO$_4$)$_m$ and (BTO$_3$/STO$_4$)$_n$ in Fig. 3A and (BTO$_3$/STO$_4$)$_n$ and (BTO$_2$/STO$_4$)$_m$ (strain partially relaxed) in Fig. 3B. Both TO$_2$ and TO$_3$ phonons show similar behaviors, and the dashed-dotted lines are linear fits to the average of the two modes. The linear fit corresponds to a parabolic decrease of polarization with temperature, because Raman intensity is proportional to the square of atomic displacement. The intersection of the dashed-dotted line with the horizontal axis is taken as the $T_c$ of the sample.

The temperature dependence of polarization from a phase-field model calculation (24) is plotted in Fig. 3, C and D, for the same samples as in Fig. 3, A and B. The model assumes that the BaTiO$_3$ and SrTiO$_3$ layers in the superlattices have their respective bulk elastic and thermodynamic properties. The in-plane lattice constant is commensurately constrained to the SrTiO$_3$ substrate except for the partially relaxed case, and the top surface is stress-free. The surface depolarization field is ignored and a short-circuit electrostatic boundary condition is employed. A computational cell of 64 nm along the two in-plane directions and one unit cell along the growth direction was employed. The corresponding three-dimensional (3D) time-dependent Ginzburg-Landau equations are then numerically solved using the perturbation method with semi-implicit Fourier-spectral algorithms (25). The result reveals a spontaneous polarization along the growth direction with multiple 180° domains in the BaTiO$_3$ layers, which induces polarization in the adjacent SrTiO$_3$ layers, whose magnitude and distribution vary with the thickness and domain size of the BaTiO$_3$ layers. The spontaneous polarization in the BaTiO$_3$ layers becomes zero at $T_c$, and the predicted $T_c$ values agree with those from the Raman data. This is remarkable considering that no fitting parameters from the Raman experiments are used in the calculations.

In Fig. 4, $T_c$ determined by the Raman data, x-ray diffraction (XRD), and the phase-field model are shown as a function of the BaTiO$_3$ thickness. The XRD measurement provides an additional confirmation of the Raman results, where a change in the temperature dependence of the out-of-plane lattice constant can be taken as an indication of $T_c$ (12). The figure shows that the BaTiO$_3$ layers in the superlattices are ferroelectric even when their thickness is only one unit cell, with a $T_c$ as high as 250 K. $T_c$ increases with increasing $n$ as the dipole-dipole interaction in BiTiO$_3$ layers becomes stronger, whereas large $m$ suppresses $T_c$ by reducing the coupling between the BaTiO$_3$ layers. By changing the values of $n$ and $m$, we were able to tune $T_c$ from 151 to 638 K; that is, from 250 K below to 235 K above the bulk value of BaTiO$_3$. The higher-than-bulk $T_c$ is due to the strain in the BaTiO$_3$ layers, just as strain enhances $T_c$ in single-layer ferroelectric films (26, 27). When the strain is partially relaxed in sample (BTO$_3$/STO$_4$)$_m$, $T_c$ drops almost to the bulk BaTiO$_3$ value. Although the 3D phase-field model allowing domain formation provides a good description of the Raman data, simulations assuming a single domain in the BaTiO$_3$ layers yield significantly lower $T_c$ for $m = 13$, demonstrating the importance of domain formation in theoretical calculations (28).

We now can conclude that ferroelectricity can be very strong in one-unit-cell-thick BaTiO$_3$ layers ($T_c \sim 250 \, K$ for $n/m = 1/4$). The electrical boundary condition plays a critical role. With the highly polarizable SrTiO$_3$ in contact with the BaTiO$_3$ layers, the critical thickness is reduced to a single unit cell. Meanwhile, the mechanical boundary condition imposed by the SrTiO$_3$ substrate leads to strain in the BaTiO$_3$ layers and thus to enhanced ferroelectricity. The interplay between the electrical and mechanical boundary conditions enables the tuning of $T_c$ by nearly 500 K.

References and Notes
12. See supporting material on Science Online for details.
29. We thank L. Bergman for her help in the early stage of this work. This work was partially supported by the U.S. Department of Energy (DOE) under grant no. DE-FG02-01ER45907 (X.X.X.), by the Office of Naval Research under grant nos. N00014-03-1-0721 (D.G.S.), N00014-03-1-0543 (P0005 (A.F.), N00014-05-1-0559 (C.B.E.), N00014-03-1-0561 (K.M.R.), and N00014-03-1-0365 (K.M.R.), by NASA under grant no. NAG3-16184 (R.S.K.); by NSF under grant nos. DMR-0507146 (D.G.S.), DMR-0241835 (L.Q.C., X.X.X.), DMR-0122285 (L.Q.C.), DMR-0213623 (L.Q.C.), DMR-0313764 (C.B.E.), ECS-0210449 (C.B.E.), and DMR-0315633 (X.P.F.); and by a Guggenheim fellowship (L.Q.C.). The work was supported by the Laboratory-Directed Research and Development Program under DOE.

Supporting Online Material
www.sciencemag.org/cgi/content/full/313/5793/1614/DC1
Materials and Methods
Figs. S1 to S6
References
22 May 2006; accepted 31 July 2006
10.1126/science.1130306