Ferroelectric and anti-ferroelectric coupling in superlattices of paraelectric perovskites at room temperature

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Results from dielectric and structural measurements on epitaxial SrTiO$_3$/BaZrO$_3$ superlattices reveal properties that cannot be explained simply in terms of those measured on single films of the constituent materials. For large superlattice periodicities (20/20 and 38/38 structures, i.e. samples in which each SrTiO$_3$ and BaZrO$_3$ layer are 20 or 38 unit cells thick, respectively), the capacitance-voltage curves indicate room-temperature ferroelectricity. For smaller periodicities (7/7 and 15/15), anti-ferroelectric-type behavior is observed, suggesting strong coupling between individual polar layers. This is consistent with recent second-harmonic generation results [A.Q. Jiang et al., J. Appl. Phys. 93, 1180 (2003)] of ordering in SrTiO$_3$/BaTiO$_3$ superlattices. However, both constituents of the structures investigated here are paraelectric. Strain-induced room-temperature ferroelectricity in SrTiO$_3$ and distance-dependent coupling between these layers are proposed as mechanisms leading to the observed behavior.

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The periodic stacking of epitaxial perovskite films, and thus the formation of artificial superlattice structures, allows us to intimately couple dissimilar materials and to observe emerging physical properties that are not necessarily a simple combination of those found in the constituent materials. Motivated both by the technological interest in ferroelectrics for device applications and the quite good understanding of these materials' intriguing properties, structures consisting of paraelectric and ferroelectric layers have received considerable attention. Here we report on the observation of ferroelectric and antiferroelectric properties in structures consisting entirely of paraelectric constituents, and show that the data are compatible with an interpretation of strain-induced ferroelectricity at room temperature and spacing-dependent coupling between such layer.

Periodic heterostructures consisting of paraelectric and ferroelectric perovskite titanate or niobate layers have been studied in detail before [1-5]. In the case of KTaO$_3$/KNbO$_3$ superlattices, for example, it was observed that below a critical layer spacing, the structural phase transition occurs at the same temperature as that of the alloy [6,7], but the local structure remains distinctively different from that of the solid-solution [8]. Furthermore, dielectric measurements show evidence of anti-ferroelectricity in 1/1 superlattices [9].

SrTiO$_3$ is typically described as a quantum paraelectric, i.e. a material in which ferroelectricity would occur at low temperature if it were not for the quantum fluctuations. The lattice is easily be distorted by impurities (such as Ca or Ba on the Sr-site), leading to local polar clusters or ferroelectric states. In addition, the dielectric constant is strongly pressure-sensitive [10-12], and a transition to a ferroelectric state at low temperature can be induced by uniaxial stress [13,14].

More recently, a careful treatment of SrTiO$_3$ films in the presence of misfit strains (resulting from film/substrate interactions) in the framework of the Landau-Ginsburg-Devonshire theory has led to a rather complete description of ferroelectricity in these layers [15]. Room-temperature ferroelectricity is predicted for large strains of about 0.015 but has not been confirmed experimentally.

Epitaxial superlattices provide the ideal platform to probe the effects of such large misfit strains on SrTiO$_3$. According to a recent report [16], second-harmonic generation data show that SrTiO$_3$ exhibits a polar state at room temperature in SrTiO$_3$/BaTiO$_3$ superlattices if the SrTiO$_3$ layer thickness falls below 30 unit cells (i.e. 30/30 superlattices). Interestingly, “antidipole patterns” are observed in superlattices with unit cells below 10/10, corresponding to anti-ferroelectric ordering of the structure.
Dielectric measurements can shed light onto the properties of such materials; however, these experiments probe the entire structure, and the properties of a material that is not ferroelectric in its relaxed state may be partially or completely masked by the ferroelectric constituent of the superlattice. In order to circumvent this difficulty, we performed dielectric measurements on superlattices of SrTiO$_3$ and BaZrO$_3$. Both of these materials are cubic (Pm$ar{3}$m) and paraelectric at room temperature. Our data are consistent with an interpretation (motivated by the above-mentioned study of the related SrTiO$_3$/BaTiO$_3$ structures) of a polar state in SrTiO$_3$ (and/or in BaZrO$_3$) having long-range (inter-layer) order of ferroelectric or anti-ferroelectric nature depending on the stacking periodicity (ferroelectricity for (20/20) and (38/38) structures, anti-ferroelectricity for (15/15) and (7/7) structures).

Epitaxial films and superlattices were grown onto LaAlO$_3$ substrates by pulsed laser deposition (PLD) under standard growth conditions (KrF radiation, 2 J/cm$^2$ at 10 Hz, 200 mTorr oxygen background, and substrates mounted with silver paint to a plate kept at 780 $^\circ$C). Single-phase ceramic targets were used, and all films were grown with a total thickness of 500 nm.

The superlattices were first characterized by x-ray diffraction. As shown in Fig. 1, satellite peaks are clearly observed in normal $\theta$-2$\theta$ scans (using a Rigaku 2-circle diffractometer) and allow us to determine the periodicity of the structure accurately. Profilometry measurements on single BaZrO$_3$ and SrTiO$_3$ films indicate that the growth rates are identical ($\pm$ 5%) for the two materials; thus the thickness of each constituent layer is half of the superlattice periodicity.

For the samples with larger periodicity, x-ray diffraction allowed us to determine the in-plane and out-of-plane lattice parameters of both constituents. Out-of-plane measurements were made with a four-circle diffractometer, using Cu K$\alpha$ radiation, and a sagitally-focusing focusing graphite monochromator. Reflections were broad, indicating that the layers were incoherent. Measuring the Bragg angle for the (110), (200), (220), (101), (211), (112), and (202) peaks on a (20/20) superlattice shows that the films are strongly strained. Table I shows the results for each material’s lattice parameter.

| Material    | Bulk $a_0$ (Å) | Film in-plane $a$ (Å) | Film normal $c$ (Å) | Intrins (cubic) film lattice para. $\bar{a}$ | In-plane strain $\varepsilon_{xx} = (a - \bar{a})/\bar{a}$ | Normal strain $\varepsilon_{zz} = (c - \bar{a})/\bar{a}$ |
|-------------|----------------|----------------------|---------------------|---------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| SrTiO$_3$   | 3.905          | 3.955                | 3.918               | 3.934 (v=232) 3.932 (v=5)                  | 5.9$\times$10$^{-3}$ (v=232) 3.1$\times$10$^{-3}$ (v=5) | -3.5$\times$10$^{-3}$ (v=232) -6.2$\times$10$^{-3}$ (v=5) |
| BaZrO$_3$   | 4.193          | 4.161                | 4.212               | 4.178 (v=232) 4.193 (v=5)                  | -7.6$\times$10$^{-3}$ (v=232) -4.1$\times$10$^{-3}$ (v=5) | 4.6$\times$10$^{-3}$ (v=232) 8.2$\times$10$^{-3}$ (v=5) |
| LaAlO$_3$   | 3.788          |                      |                     |                                              |                                                 |                                                 |

Table I. Observed lattice parameters of SrTiO$_3$ and BaZrO$_3$ in a (20/20) superlattice on LaAlO$_3$. The intrinsic film lattice parameter (relaxed cell volume) and the strain values are given for the bulk SrTiO$_3$ Poisson’s ratio ($\nu$ = 0.232) and for the limiting case of an incompressible solid ($\nu$ = 0.5).
leaving a stress inhomogeneity of 1.8% FWHM. This indicates that the material near the interface may be under more strain than the middle of each layer.

For the samples with smaller periodicity (7/7 and 15/15), it was impossible to determine the in-plane and out-of-plane lattice parameters of the constituents independently. We can, however, safely assume that strain values obtained for the 20/20 structure represents a lower limit for the actual values present in the 7/7 and 15/15 structures.

From the data in Table I, the strain in each of the layers can be obtained. First, the intrinsic relaxed (cubic) lattice parameter of the SrTiO$_3$ and BaZrO$_3$ layers is calculated as

$$\hat{a} = \frac{(1 - \nu)c + 2\nu a}{1 + \nu}$$

where $\nu$ is Poisson’s ratio. For an incompressible solid, $\nu = 0.5$; for bulk SrTiO$_3$, $\nu = 0.232$ [17]. The Poisson’s ratios for thin films of SrTiO$_3$ and BaZrO$_3$ are not known, however, the in-plane strain, $\varepsilon_{xx} = (a - \hat{a})/\hat{a}$, and the out-of-plane (or normal) strain, $\varepsilon_z = (c - \hat{a})/\hat{a}$, can be calculated for different values of $\nu$ and are found to be in the range of a fraction of a percent, as shown in Table I.

Not surprisingly, the films’ intrinsic lattice parameter differs from that of the bulk value, as often observed for PLD-grown films due to a high density of point defects.

For dielectric measurements, interdigital (co-planar) Au/Cr electrode structures were deposited onto the film surfaces, and the measurements were performed at 10 kHz. The finger spacing of these electrodes was 10 $\mu$m; thus a bias voltage of 1V corresponds to an electric field of 1 kV/cm. Measurements were performed either at room temperature or by immersing the entire structure in liquid nitrogen.

Figure 2 shows room-temperature dielectric data for various structures. The data in (a) and (b) are obtained for reference films of BaZrO$_3$ and SrTiO$_3$. As expected, little variation is observed in the capacitance (and thus the dielectric constant) as function of applied dc voltage. The superlattices, in contrast, exhibit an interesting electric-field dependence. Clearly, their behavior cannot be understood as a simple combination of the BaZrO$_3$ and SrTiO$_3$ properties, despite the fact that the in-plane measurement geometry would allow us to view the sample as a parallel-combination of individual BaZrO$_3$ and SrTiO$_3$ layers. For the samples with the smallest periodicity (but with the same total sample thickness of 500 nm), the capacitance curves exhibit a local minimum at 0 kV/cm, and two symmetrically placed maxima at a value that depends on the periodicity. For larger structures, such as shown in Fig. 2(e) (and also in Fig. 3, see below), a conventional (hysteretic) butterfly-loop is observed. This type of curve is typically associated with ferroelectric structures. Note that here, however, neither of the two constituent materials of the superlattice is independently ferroelectric.

Figure 3 shows the capacitance vs. voltage data for a 500 nm thick film consisting of 16 pairs of SrTiO$_3$ and BaZrO$_3$, each layer being approximately 38 unit cells thick. Ferroelectric-type behavior is observed both at room temperature and at 77 K.

The temperature-dependence of the out-of-plane film lattice parameter was recorded from room temperature to 650 °C by x-ray diffraction (data not shown). Quite surprisingly, no anomaly is observed, i.e. the thermal expansion is linear over the entire range with a scatter of about 4 · 10$^{-5}$. Thus, if a structural transition were present in this temperature range (similar to our earlier work on KTaO$_3$/KNbO$_3$ [6]), it would clearly be detected. It is important to point out, however, that the (c-a)/a distortions in the KTaO$_3$/KNbO$_3$ change by only about 30% at the transition, and that the distortion observed here ((c-a)/a $\approx$ 9 · 10$^{-5}$) is comparable in magnitude to that observed in KTaO$_3$/KNbO$_3$ even in the high-temperature phase ((c-a)/a $\approx$ 6 · 10$^{-5}$).

Capacitance vs. voltage (C(V)) curves are, by definition, the derivative (with respect to the electric field) of polarization vs. field (P(E)) loops (in our case with the dc field swept at a very low rate of about 10$^{-2}$

![FIG. 2. Capacitance-voltage curves obtained using coplanar (inter-digital) electrodes on various films on LaAlO$_3$ substrates at room temperature. (a) and (b) show the data for single reference films of BaZrO$_3$ and SrTiO$_3$, respectively. In (c), (d), and (e), the data is presented for superlattices in which the BaZrO$_3$ and SrTiO$_3$ are 7, 15, and 20 unit cells thick, respectively. Total film thickness for all samples is 500 nm.](image-url)
reduces the energy associated with the dipolar long-range elastic (short-range) interactions, domain formation associated with long-range ferroelectric ordering. In electric dipolar interaction leads to a large energy from energy arguments. In fact, the long-range nature of ferroelectric layers in a superlattice may be understood long-range correlation or order ferroelectrically. and thickness, these ferroelectric slabs either show no thickness of 15 or fewer unit cells. For larger layer spacing polar order of anti-ferroelectric nature for spacing and size in a ferroelectric layer scales as \( \propto \) case of ferromagnetic films [19], the equilibrium configuration is no longer determined by the properties of the individual layers in a superlattice but by the total material within a domain.

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ferroelectricity in SrTiO$_3$ and spacing-dependent coupling between the layers are proposed as mechanisms leading to this behavior. For large superlattice periodicities (20/20 and 38/38 structures), these ferroelectric layers appear to act as independent ferroelectric slabs or exhibit long-range ferroelectric ordering. For smaller periodicities (7/7 and 15/15), anti-ferroelectric coupling between these polar layers is observed, consistent with energy considerations for long-range electrostatic interactions and domain formation.

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