Artificial Dielectric Superlattices with Broken Inversion Symmetry

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A variety of three-constituent superlattice patterns were made in atomic layer-by-layer films, with patterns breaking inversion symmetry giving effective permanent bias fields ranging up to about 200 kV/cm. Dielectric constants at room temperature were nearly 10^3, with loss tangents under 0.01. Most of the response came from discrete dipoles comprising multiple unit cells, but without any ferroelectric phase transition.

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Recently, Sai and Vanderbilt [1] predicted that in dielectric superlattices with patterns breaking inversion symmetry, using three components, the broken symmetry should produce substantial effective bias fields and hence a large second order electronic susceptibility, desirable for numerous technological purposes. Since the bias is built-in structurally, these superlattices need not have strongly temperature-dependent susceptibility, unlike other materials with large second order susceptibilities, such as ferroelectrics [2] and partially poled relaxor ferroelectrics [3], which are near phase transitions. Here we report confirmation of the predicted large bias, in superlattices with no sign of any incipient phase transitions.

In the superlattices we have studied, lattice strain differences among the constituent layers drives the formation of the bias field. Lattice strain is known to strongly influence dielectric response. Both the linear and second order electronic susceptibilities of ferroelectric $BaTiO_3$ (BTO) increase when grown under compressive strain on $SrTiO_3$ (STO) substrates [4] and in BTO/STO superlattices [4] or in patterns with net composition gradients [5]. Ferroelectric transition temperatures are also strongly affected by strain [6]. The locally asymmetrical strain provided by three-component patterns allows asymmetrical response without requiring overall gradients of strain or composition.

Our superlattices of layers of BTO, STO, and $CaTiO_3$ (CTO) were grown using atomic layer by layer molecular beam epitaxy (ALL) [7] on STO substrates at about 690 °C, with oxidation via a beam of pure ozone. During growth the specular reflection high energy electron diffraction spot was well defined and exhibited strong oscillations indicating a two dimensional growth mode. Post-growth analysis by atomic force microscopy of similar test samples showed atomically flat surfaces with terraces and unit cell high steps. X-ray diffraction analysis showed that the superlattices had the same in-plane lattice constant as the Sr substrate, so that the BTO layers were in compressive strain and the CTO layers were in tensile strain.

Denoting unit cells of CTO, STO, and BTO as C, S, and B, respectively, and starting the labeling from the bottom, the samples had supercell stacking sequences *CCSBBS*, *CCBBSS*, *CCSSBB*, *CCBBBBSS* ("*CCB4SS*"), and *CCBBBBBBSS* ("*CCB6SS*"). After a total of 120 unit-cell layers, 2 C layers were added on top. An infinitely repeated *CCSBBS* sequence has two inversion symmetry planes, but all the other sequences lack inversion symmetry. The full *CCBBSS* and *CCSSBB* sequences are inverses.

Each sample capacitor consisted of an STO substrate, a base layer of conducting $(La_{0.7}Sr_{0.3})MnO_3$(LSMO), the dielectric superlattice, an LSMO cap layer, and an Au contact layer. The films were lithographically patterned into mesa capacitors with areas from $(100\ \mu m)^2$ to $(500\ \mu m)^2$. The conducting LSMO base layer remained everywhere, shielding the substrate from the electric fields.

The real and imaginary parts of the device impedance were measured using a fixed ac drive voltage (at 77 Hz, except when noted to be at 7.7 or 770 Hz) with low amplitude (typically 20 mV, with some as low as 2.5 mV) with the current measured using a two-phase lock-in amplifier. There was no sign of nonlinearity as a function of these small ac voltages, and as discussed below the kinetic barriers were too small to give coercive effects over most of the range of T. Automated data taking recorded T, the ac voltage, current, their relative phase, and the dc voltage.

In viewing the data, it helps to keep in mind a common sense working hypothesis: that the dielectric response consists of both a simple elastic component and an anelastic one from discrete states. One expects a generic elastic response, depending weakly on temperature, electric field, and measurement frequency (T, E, and f, respectively) over the range explored. The response from discrete states separated by a barrier would be expected to freeze kinetically at low T and to saturate at large E. In a perfectly homogeneous system, the thermodynamic susceptibility of discrete dipoles would show Curie behavior $(1/T)$ at high T. In the presence of disorder that dependence will saturate at T low enough for the thermal energy scale (kT) to become small compared to any random energy asymmetries of the discrete states.

Below we present only a representative summary of the data taken over a wide range of E and T, since the full set of data cannot be compressed into viewable form in a Letter. This sample covers all the qualitative behavior of all the samples.

Figure 1 shows the real (ε') and imaginary (ε'') parts of the dielectric constant, ε, at zero dc bias, for one of the five different samples, as a function of T. Some qualitative features are shared by all the samples: $\varepsilon'(T)$ has a peak, $\varepsilon''(T)$ becomes large near the maximum of the positive slope of $\varepsilon'(T)$, and $\varepsilon''(T)$ becomes small near 300 K. (Table I lists the temperatures T_P of the peaks in $\varepsilon''(T, 77\ \mathrm{Hz})$ for the four samples for which it was determined.) In a fraction of the samples (like this one) there is another increase in $\varepsilon''(T)$ at higher T, often with strong asymmetrical dependence on dc E, but it is accompanied by dc leakage currents and thus represents some conduction mechanism. We assume the leakage comes from scattered rare defects.

The peak in ε'' in the range where ε' is a rapidly increasing function of T indicates that ε' freezes out kinetically at low T. The implied dependence of ε on f was measured in two samples from 7.7 to 770 Hz, and found to be consistent with simple Arrhenius kinetics with an attempt rate $f_A = 10^{12\pm2}$ Hz, as expected if much of ε' were from two-state systems.

In Fig. 2 $\varepsilon'(E)$ is illustrated for a symmetrical and an asymmetrical sample at several T, showing both the saturation effects expected for discrete-state systems and the desired asymmetry, mirroring the broken inversion symmetry of the superlattice. The modal effective bias fields E_P at which $\varepsilon(E)$ peaks, are listed for each sample at a few temperatures in Table I. As expected [1], $\varepsilon'(E)$ is symmetrical for only the *CCSBBS* sample, and the *CCBBSS* and *CCSSBB* showed peaks in $\varepsilon'(E)$ of opposite signs. It is surprising that E_P increases with thicker BTO layers, since one might expect the strain gradient in the BTO to be inversely proportional to that thickness.

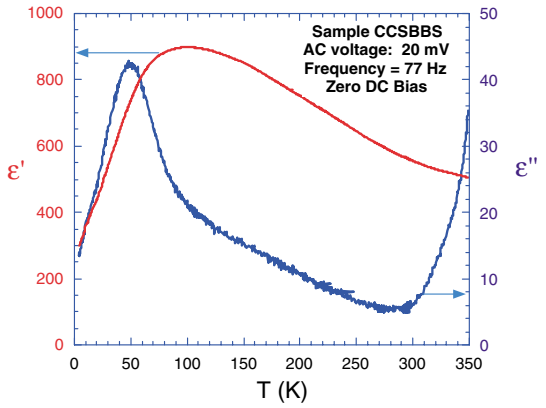

FIG. 1 (color online). ε' and ε'' vs T at zero dc bias for sample CCSBBS.

We can discern the two expected qualitatively distinct components of the dielectric response. One component has only weak T dependence, remains completely in phase over the frequency-temperature range explored, and does not saturate much over the field range explored. Table I gives approximate values ε'_E for this elastic component, obtained by eye from the wings of $\varepsilon'(E)$ at low T. The larger component, ε_D, is strongly T dependent, has a ε'' at low T, and approaches saturation at large fields, the classic symptoms of dipoles with discrete free-energy-minimizing configurations separated by an activation barrier.

The sharp peak in $\varepsilon''(T)$ indicates that there is a well-defined typical barrier height. The persistence of $\varepsilon''(T)$ far above T_P indicates a distribution of barriers, with a tail of atypically large ones. A key issue becomes whether the T dependence of ε' shows effects other than those expected for simple collections of dipoles, e.g., whether there are signs of any incipient phase transitions. For fixed thermodynamic susceptibility, purely kinetic effects with a broad spread of barrier heights give

$$\frac{d\ln\varepsilon'}{d\ln T} = \left(\frac{2}{\pi}\right)\ln\left(\frac{f_A}{f}\right)\left(\frac{\varepsilon''}{\varepsilon'}\right) \qquad (1)$$

an analog of the Dutta-Horn relation [8].

Figure 3 shows the two sides of Eq. (1) for the *CCB4SS* sample, on which we have the cleanest data over the widest range of T. Three regimes appear. The kinetic prediction and the T dependence agree only qualitatively below T_P, as expected since $\varepsilon''(T)$ indicates that distribution of barriers has a sharp peak at the low end, rather than a broad tail. From about 70 to 230 K, the agreement is good. At higher T, where ε'' is quite small (i.e., kinetics are not important), ε' becomes a decreasing function of T, as expected if thermodynamic factors become relevant, giving a crossover to Curie behavior. Other samples behaved qualitatively similarly.

The crossover to a regime dominated by thermodynamic rather than kinetic factors allows us to address whether the discrete dipoles consist of individual unit cells or more extended clusters. If the material were entirely microscopically homogeneous, the individual dipole moments, p, could be determined via the simple thermodynamic result $p = \varepsilon_D kT/4\pi P$, where ε_D is measured at the peak of $\varepsilon(E)$ and P is the saturation polarization of this component of the response. The marked asymmetries of the $\varepsilon(E)$ around their peaks require that there be a distribution of local effective bias fields, which would also explain the nonkinetic part of the deviation of the peak ε from Curie behavior. P can be determined by integrating $\varepsilon'_D(E)$ out to saturation, obviously requiring some approximate extrapolation of the $\varepsilon'(E)$ data. We find P ranging from 15 to 40 $\mu\mathrm{C/cm}^2$, depending on the sample. In the range for which kinetic freezing is not important, we find no significant dependence of this

TABLE I. Values for some of the key parameters of several samples are shown. Quantities for which only bounds are given are ones for which the thermodynamic derivatives were likely to have been significantly affected by kinetic freezing. The values of ε_E were estimated by eye from the low-T data, as were the error bars. The value of ε'_E for the *CCBBSS* sample was not independently determined but assumed to be the same as for the *CCSSBB* sample. For W we used 1.1 times the half-width at half-maximum of $\varepsilon'(E)$. P, p, and V were calculated from the other quantities, as described in the text. Despite the approximations used, we believe that these calculated numbers are accurate to about 20%.

Sample	ε'_E	T_p (K)	T (K)	E_P (kV/cm)	ε' at E_P	W (kV/cm)	$-d\ln\varepsilon'_D/d\ln T$	P (μC/cm^2)	p (10^{-26} C · cm)	V (10^{-22} cm^3)
CCSBBS	120 ± 20	50	200	0	752	330	> 0.3	22	<1.4	<7
			300	0	560	480	0.8	22	1.0	5
CCB4SS	70 ± 10	70	370	−180	635	430	0.6	22	1.5	7
			320	−70	845	360	> 0.3	25	<2.1	<8
CCB6SS	90 ± 10	45	280	−158	980	470		41		
			360	−140	930	500	0.3	37	1.8	5
CCBBSS	180 ± ?	···	200	−80	1090	265	1	21	1.0	5
			260	−70	900	360	1	25	1.0	4
			280	−60	850	370	1	22	1.0	5
			320	−45	750	~470	~1	20	0.9	5
CCSSBB	180 ± 20	75	280	+53	805	290	0.8	16	1.5	9

saturation P on T, although the crude technique would not pick up effects less than some 20%.

At low T, when the width of the inhomogeneous broadening exceeds the thermal broadening (kT/p), the Curie behavior of the individual dipoles is obscured. Both the width and the height of the thermodynamic $\varepsilon'(E)$ would then saturate, leaving only kinetic T dependence, as found. No large T-dependence of the distributions of p and E_0 are required to fit the results. There is no sign of the most important possible effect, growth of p as T is lowered, and hence no indication of even incipient ferroelectricity.

The T dependence of the peak in $\varepsilon'_D(E)$ provides a crude but useful estimate of the magnitude of p. For a fixed collection of dipoles and a fixed functional form of $\varepsilon'_D(E)$ this peak value is inversely proportional to the width of the $\varepsilon'_D(E)$ curve. Making the approximation that the width of $\varepsilon'_D(E)$ results from adding in quadrature a fixed inhomogeneous width and the thermal width, we can extract the approximate thermal width, kT/p, and hence obtain $p = kT/W(-d\ln\varepsilon_D/d\ln T)^{1/2}$, where W is the actual width of $\varepsilon'_D(E)$. Making the approximation that the saturation polarization is spatially uniform gives the volume V occupied by each discrete dipole: $V = p/P$.

Table I gives T_{P_r}, P, p, and V. In all cases V exceeds the unit cell size of the homogeneous parent compounds by almost an order of magnitude, raising the question of what sets this unusual correlation volume.

Two-state polarization configurations are to be expected as remnants of the ferroelectric behavior of the BTO layers, projected onto the single axis along which we can apply a field [1]. However, the theoretical analysis to date seems to have implicitly assumed that the multiple minima in systems of a few unit cells arranged along the superlattice direction correspond to ferroelectricity [1]. In effect, that assumes that the lateral coupling between unit cells is not drastically reduced from that in the parent ferroelectric compound. Experimentally, even though the polarization coherence volumes easily exceed a unit

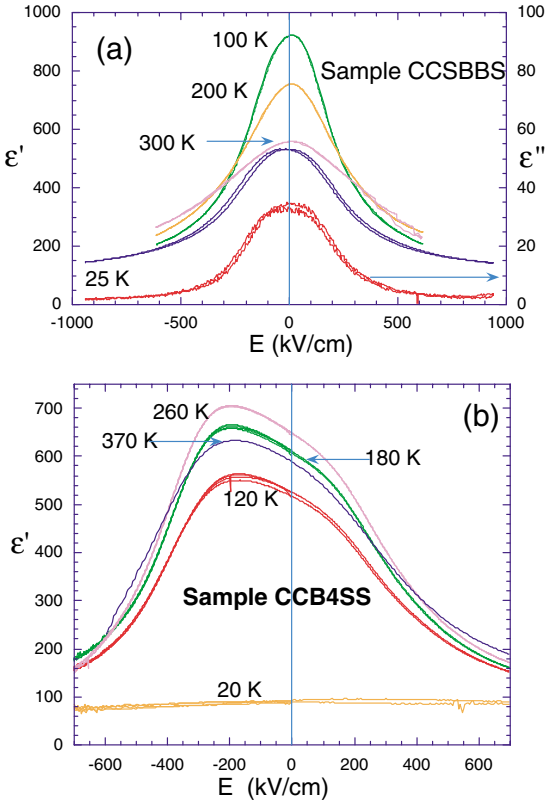

FIG. 2 (color online). (a) ε' vs E for sample *CCSBBS* is shown at several T, along with ε'' vs E at 25 K. (b) ε' vs E is shown at several T for one of the asymmetrical samples, *CCB4SS*.

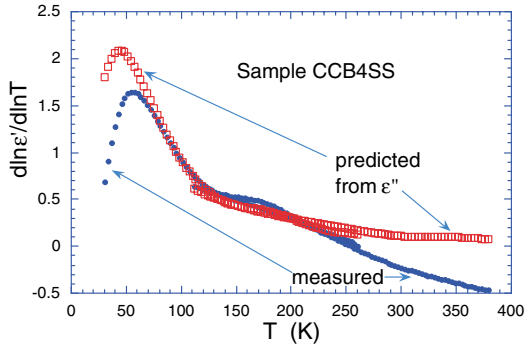

FIG. 3 (color online). The derivative $d\ln\varepsilon'/d\ln T$ (at zero dc bias) is shown for sample *CCB4SS* (circles). The squares show the right-hand side of Eq. (1), based on ε'', with a fixed $f_A = 10^{12}$ Hz, and no adjustable parameters. There are two overlapping data sets for each, from runs with different T ranges. Each data set was fit with a ninth-order polynomial before differentiation, to reduce the point-by-point scatter.

cell, the absence of any indication of growing moments or super-Arrhenius behavior at low T indicates that the superlattice structure is suppressing the long-range ferroelectricity of the BTO. This behavior contrasts with that of BTO-STO superlattices, which are ferroelectric [5] even though the corresponding bulk compound is paraelectric.

In summary, three-component artificial superlattices of ferroelectric and nonferroelectric titanates show predicted [1] asymmetrical $\varepsilon'(E)$, reflecting the broken inversion symmetry of the superlattices. The large dielectric response, including the nonlinear part at low E, comes from discrete dipoles. Their local bias fields and barrier heights are somewhat heterogeneous, presumably due to material disorder at the interfaces between layers with different constituents. The dipoles consist of several unit cells, but do not grow at low T, raising the question of how the superlattice (and perhaps the disorder) determines their size.

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