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Stress-induced polarization-graded ferroelectrics

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Polarization-graded ferroelectrics and their electrically active embodiments, graded ferroelectric devices and transpacitors, have been formed from a variety of material systems, both by grading the composition of the ferroelectric and by imposing temperature gradients normal to the electrode surfaces. In this letter, we show how these same devices can be formed from homogeneous ferroelectric films of lead strontium titanate by imposing stress gradients on the material normal to their electrode surfaces. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1498506]

Polarization-graded ferroelectrics and their associated active structures, graded-ferroelectric devices (GFDs) and transpacitors, have been characterized as the dielectric analogues of semiconductor diode junctions and transistors.[1,2] Such devices are usually formed from planar, capacitive-like structures by establishing a gradient in electric polarization normal to the electrode surfaces. Most recently, the gain characteristics of transpacitor charge amplifiers have been measured. In this latter configuration, it was found that the gain factors are remarkably similar to transistor current amplifiers.[2]

It is well known that the ferroelectric spontaneous polarization, P_s is a function of material composition, c; temperature, T; and stress, σ; i.e., $P_s = P_s(c, T, \sigma)$.[3,4] Consequently, it has been possible to form GFDs from a variety of material systems, both by grading the composition of the ferroelectric and by imposing temperature gradients normal to the electrode surfaces.[5–12] The latter, temperature-based, experiments convincingly demonstrate that extraneous artifacts, such as asymmetric electrical contacts and space charge regions near the electrode surfaces, are not the origin of the observed aberrant ("up" and "down") hysteretic characteristics of these devices.[5]

The above findings are fully consistent with theoretical analysis, which has anticipated such behavior.[4,6,13] However, prior theory has gone further than the existing body of experiments, predicting that GFDs and transpacitors can be formed by imposing stress gradients on homogeneous materials.[4] It is, therefore, this experimental omission that this letter aims to address. In particular, we show that homogenous ferroelectric structures in the presence of a gradient in stress give rise to polarization-graded structures, which in turn yield the unconventional hysteresis seen in GFDs and transpacitors.

Lead strontium titanate (PST) thin films, ~4 μm thick, were deposited on 0.02-cm-thick platinum foil substrates by metalorganic decomposition. Metal oxide precursors consisting of titanium (IV) 2-ethylhexoxide, lead (II) neodecanoate, and strontium neodeconoate were combined in proper proportions, then diluted with xylene to yield a single precursor solution. Films of $Pb_{0.4}Sr_{0.6}TiO_3-PST$ (with a composition determined by x-ray photospectroscopy) were prepared by depositing the metalorganic precursor solution onto platinum substrates through spin coating; 4000 rpm for 15 s. After each coat, the metalorganics were pyrolized in a muffle furnace at 550 °C for 1 min in air, whereby the organics decompose into their metal oxide constituents. Multiple coatings were made to obtain the desired film thickness. Final annealing of the sample was carried out at 950 °C for 60 min in air. Scanning electron microscopy revealed that the films had grains ~0.2–0.3 μm in diameter. X-ray diffraction analysis clearly indicated a perovskite crystal structure (tetragonal) at room temperature.

From substrate bow measurement it was determined that the PST films (as formed) were under compression (see Fig. 1). The radius of curvature was determined from the bow

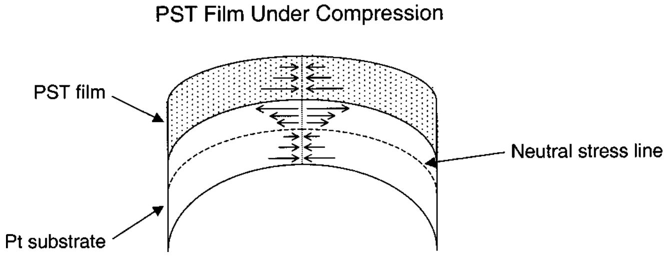

FIG. 1. As formed, the PST films are in compression with a stress gradient normal to the platinum substrate (not to scale).

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profile to be 2.61 m with a maximum displacement of ~17 μm along the film–substrate normal. The film compression arises from the difference in thermal expansion coefficients of the film and the substrate (11.8×10^{-6} and $\sim11\times10^{-6}$ °C, for Pt and PST, respectively) as the film is cooled from the annealing temperature.[14] Therefore, as formed, the PST films have a built-in stress gradient normal to the platinum substrate, with a stress maximum at the film substrate (Fig. 1); a point which will be of significance later in the letter when we discuss the electrical hysteresis of the material in the absence of an externally imposed stress gradient.

Gold/chromium (~40-nm-thick chromium followed by ~300 nm of gold) electrodes were deposited upon the PST surface in the form of circular dots (~0.02 cm^2) using electron beam evaporation. The platinum substrate served as the counter and reference electrode contact when the devices were inserted into a Sawyer–Tower circuit.[15] All such characterization was done at room temperature with 10 V peak, 10 kHz sine wave excitation. The low voltage PST "capacitance" was ~3 nF.

The lead strontium titanate (PST) system is remarkably similar to the barium strontium titanate (BST) system in that the Curie temperature for the cubic to tetragonal transition can be adjusted over an exceedingly large temperature range by adjusting the lead to strontium ratio. With a Pb:Sr ratio of 4:6 the Curie temperature of the PST thin-film material is slightly below room temperature. In Fig. 2(a) we plot the relative permittivity (normalized to vacuum) as a function of temperature. Note the broad peak centered around 15 °C. Full conversion from the tetragonal to cubic phase (with increasing temperature) is not abrupt, and we find that measurable hysteresis persists to nearly 150 °C, see Fig. 2(b).

To form GFDs from the homogeneous PST films, a gradient in the polarization was established between the electrode surfaces through the imposition of a stress gradient normal to the growth surface of the film. To accomplish this task in a well-defined geometry, the substrate and brass thermal heat sink were sandwiched between two electrically insulated blocks with the bend point along the diameter of one of the gold/chromium electrical contacts as shown in Fig. 3(a). Because the platinum substrate is very much thicker than the PST film, the neutral stress line for the bilayer should lie within the platinum when a bend angle θ is imposed.[16] Consequently, the PST as a whole remains in compression (only for small θ); though, superimposed on this compressional stress field there is a gradient in stress (either tensile or compressional) due to the externally applied force as shown in Fig. 3(b). To obtain a reliable measure of θ, we sandwiched the platinum substrate extending beyond the clamped region between two electrical quality fiberboards to serve as an 82.5 mm lever arm. The end deflection of the lever arm was measured using a modified micrometer mechanism capable of ±0.1 mm resolution. Theta, the deviation angle, could thus be measured as the arctangent of the deflection/lever arm ratio with a ±0.07° uncertainty.

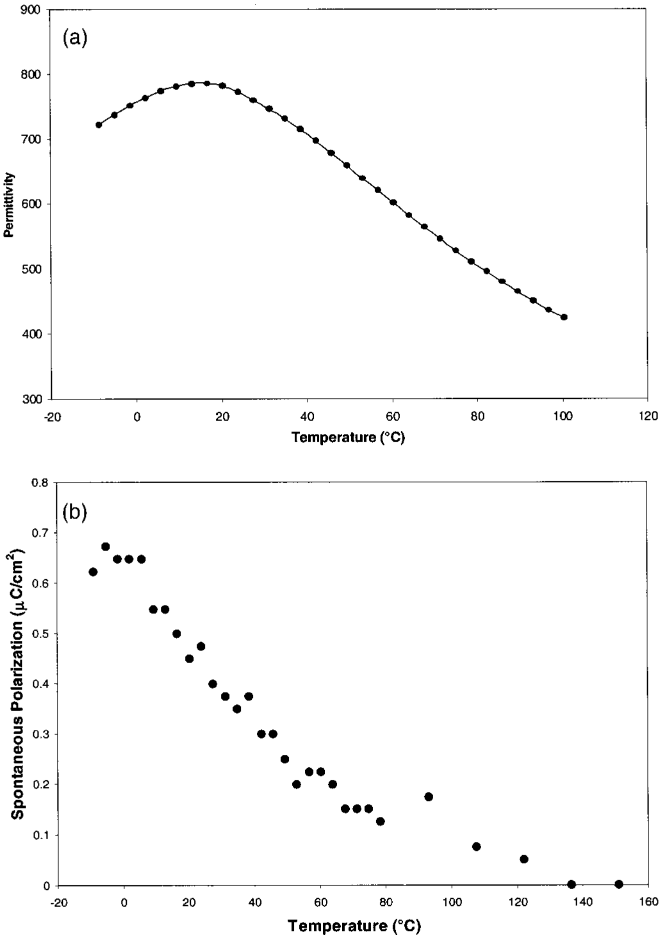

FIG. 2. (a) Relative permittivity (normalized to vacuum) as a function of temperature for a ~4-μm-thick $Pb_{0.4}Sr_{0.6}TiO_3$–PST film deposited on a platinum substrate. (b) Spontaneous polarization as a function of temperature for the same PST film.

Two types of GFD structures have been demonstrated, "up" and "down."[6–12] This terminology arises from the fact that, unlike conventional ferroelectric materials, GFDs yield asymmetric ferroelectric charge–voltage ($Q-V$) or polarization-electric field ($P-E$) hysteresis plots, which are translated along the charge axis, up or down, when the GFD is placed in a Sawyer–Tower circuit and excited with a periodic alternating electric field.[6–12]

Because the measured hysteresis offsets were quite small, the traditional Sawyer–Tower circuit required modification to reliably obtain reproducible results with high precision and low uncertainty. In particular, the voltage across the PST film was measured using a dual input Tektronix 7A22 differential amplifier plug-in unit into a Tektronix 7904 oscilloscope, so that only the voltage across the sample was recorded. The plus and minus spontaneous polarization values, as measured across the series 50 nF capacitor, were limited to three significant digits with a net difference between the two readings limited to ±1 mV uncertainty. Thus, the very stable and reproducible offset measurements were accurate to within ±0.00024 μC/cm^2.

While we had some concern that thermal drift would obscure the effects due to the imposed stress gradients, it appears that the placement of the brass heat sink in contact with the platinum substrate was sufficient to ensure the stability of the measurement against thermal drift. Indeed, the stability of the system was such that no measurable deviation from a recorded offset would occur during an overnight measurement hiatus.

In Fig. 4 we plot the offset, ΔP, as a function of bend

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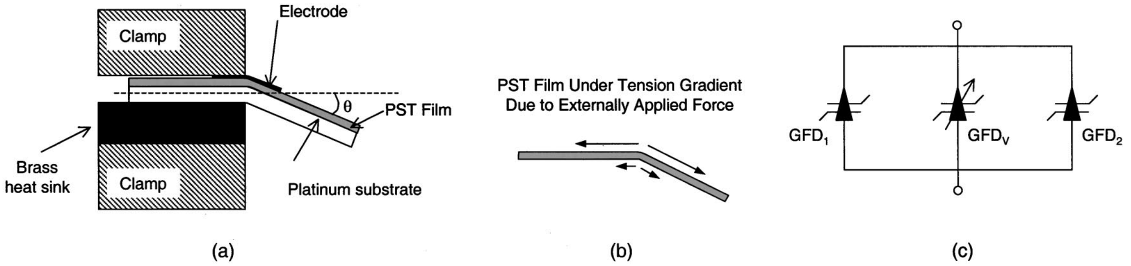

FIG. 3. (a) Experimental arrangement for imposing a stress gradient in the central region of the PST capacitor structure. Note that θ is negative as depicted (*externally applied tension*). (b) Stress distribution due to bending action only, ignoring built-in compression. (c) Equivalent circuit of (b).

angle, θ. Some features of Fig. 4 are worthy of special note. (1) There is an observable, positive, net offset even in the absence of an externally imposed stress gradient, i.e., $\theta=0$. (2) The variation in offset is nearly symmetric for positive and negative θ, though film compression (positive θ) has less effect on the observed offset than when tension (negative θ) is externally applied to the film. (3) The offset, ΔP, changes by only $\sim\pm10\%$ as the bend angle varies from $-10°$ to $+10°$.

To understand these results, recall that substrate bow measurements indicated that, as formed, the PST films are under compression. Thus, there exists a stress gradient across the film even in the absence of an *externally* applied stress gradient (see Fig. 1). Therefore, it is not surprising that a polarization offset is observed even for the $\theta=0$ state. This result is consistent with previous work on barium strontium titanate films deposited by molecular beam epitaxy upon single crystal strontium titanate.[8] There it was found that the presence of a substrate-imposed stress gradient was the primary factor in determining the direction and magnitude of the polarization offset; the presence of a compositional gradient in Ba:Sr ratio normal to the substrate only modified the primary effect.[8]

To complete our analysis of the results of Fig. 4 it is important to understand the experimental setup as depicted in Fig. 3(a). Recall that the film/substrate bilayer was clamped along *a line* that traversed the major diameter of the gold/chromium top electrode. Thus, even though the entire electrode area is quite small ($\sim$0.020 cm^2) the *stress-changed* area (*arising from* θ) of the PST capacitor is much smaller than the entire sample area—as represented by the electrode area. We, therefore, depict the applied stress gradient experiment schematically as shown in Fig. 3(c). Here, GFD$_1$ and GFD$_2$ represent the GFDs that are formed due to the compressional stress gradient across the PST film imposed by the difference in expansion of the platinum and PST ceramic when the perovskite phase of the PST is formed. These GFDs remain essentially unchanged as θ is varied. GFD$_v$, however, represents a variable GFD whose stress gradient varies with bend angle, θ. Of course, by construction, the three GFDs are electrically in parallel.

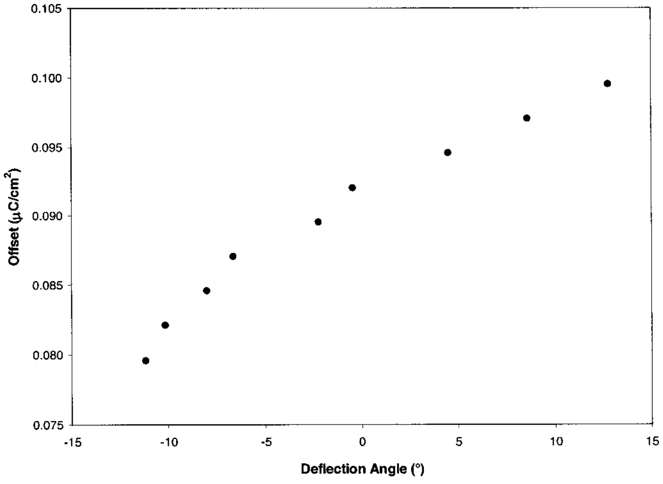

FIG. 4. Hysteresis offset, ΔP, as a function of bend angle θ.

Our understanding of Fig. 4 now becomes clearer from the above discussion. One would: (1) Expect a hysteresis offset for $\theta=0$ due to the compressional stress in the as-formed PST films. (2) Expect some degree of symmetry for $\pm\theta$ as the "built-in" and externally imposed stress gradients are mostly uncoupled. (3) Expect the externally imposed stress gradient to produce a small variation in ΔP due to the fact that the θ effected zone of the PST sample is only a small fraction of the overall electrode area.

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