Layer thickness and period as design parameters to tailor pyroelectric properties in ferroelectric superlattices

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Abstract

We theoretically examine the pyroelectric properties of ferroelectric-paraelectric superlattices as a function of layer thickness and configuration using non-linear thermodynamics coupled with electrostatic and electromechanical interactions between layers. We specifically study $PbZr_{0.3}Ti_{0.7}O_3/SrTiO_3$ superlattices. The pyroelectric properties of such constructs consisting of relatively thin repeating units are shown to exceed the pyroelectric response of monolithic $PbZr_{0.3}Ti_{0.7}O_3$ films. This is related to periodic internal electric fields generated due to the polarization mismatch between layers that allows tailoring of the shift in the transition temperature. Our results indicate that higher and electric field sensitive pyroresponse can be achieved from layer-by-layer engineered ferroelectric heterostructures.

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Pyroelectric effect is the generation of a current through the alteration of the average electrical dipole density of a system in response to a temperature change. [1,2] Pyroelectric materials have often been utilized in passive infrared (IR) imaging/sensing systems and energy harvesting devices.[3–5] Among those, ferroelectrics (FEs) comprise the most important group of materials in IR devices because the spontaneous polarization P_S is highly susceptible to temperature changes near the paraelectric (PE)-FE transformation temperature T_C.[6]

The integration of FEs in microelectronic circuits necessitates that such materials should be employed in thin film form. The local internal electric fields that emanate from imperfections forming during processing impact *P-E* hysteresis loops, fatigue behavior, and loss and leakage characteristics of FE films. [7–22] Despite the fact that such internal fields tend to destabilize the FE state, they may lead to interesting and highly non-linear properties in thin films. Indeed, a number of studies have focused on finding ways to tailor the changes in the phase transition characteristics of epitaxial FE films where misfit strain imposed by the substrate was used as a design parameter to bring T_C to around room temperature (RT) at which most IR devices operate.[23–25]

Another way of controlling the T_C of FEs is to fabricate graded multilayers and superlattices (SLs) with periodic interfaces.[26] Internal (depolarizing) fields form in periodic FE-PE structures with coherent interfaces that reduce the average T_C to lower temperatures. The extent of this shift, when the effect of misfit strains is isolated, has been shown to be a function of SL periodicity.[27–29] Electrical domain formation in multilayer heterostructures is one way to minimize and localize the depolarizing fields near the interfaces but this is possible only if the FE layer is above a critical thickness as demonstrated in recent studies.[30–32] Period of the repeating unit was also recently shown to be a crucial parameter in obtaining very large dielectric responses from such systems.[33] Such a finding immediately raises the question as to whether these systems can be employed in the design of devices with enhanced pyroelectric properties. A non-zero pyroresponse can only be expected in the multi-domain (MD) state in the presence of an applied bias keeping in mind that for a given strain state a FE-PE heterostructure with P normal to the film plane will have a reduced T_C compared to a FE monolayer layer sandwiched between electrodes. As such, the bias dependence of the pyroresponse (p) should be different than in single-domain (SD) films. It is well known that applying a bias to a FE layer in the MD state will lower the T_C of the system,[34] just the opposite of what happens in a SD FE under bias.[35,36] The combination of these two effects can be expected to lead to interesting pyroelectric properties in FE-PE SLs.

Here we use Landau-Ginzburg theory of phase transitions in FEs to compute the pyroelectric response of FE-PE SLs with different type and number of repeating units. Depending on the thickness of the layers and their configuration with respect to the electrodes, the FE layers can be in a MD or a SD state below the respective T_C of the heterostructure. The low lattice misfit (~1%) $PbZr_{0.2}Ti_{0.8}O_3/SrTiO_3$ (PZT/STO) system is considered for which the interlayer interfaces are coherent in carefully synthesized multilayer structures. We show that, for smaller periods of repeating units in a PZT/STO structure, there is a general tendency of the pyroresponse to become more sensitive to applied fields resulting in higher pyroelectric tunability. Furthermore, the pyroelectric properties of SLs with relatively thin repeating units can exceed the values of pseudomorphic PZT films on STO due to periodic depolarizing fields.

We consider epitaxial (001) PZT/STO SLs on a much thicker (001) STO substrate as shown schematically in Figs. 1(a) and 1(b) consisting of two types of repeating units: PZT/STO bilayer and symmetrical STO/PZT/STO multilayer. The details of the methodology are provided in Supplementary Material along with the thermodynamic parameters and materials constants entering the equations.[37]

We first focus on the values of $<|P_z|>$ and $<|P_x|>$ (P_z and P_x hereafter) where $<||>$ denotes average of the absolute value of the total polarization along the z- and x-axes as SLs often tend to stabilize into the MD state from the PE phase. The results are plotted in Figs. 2(a)-(d). In all the graphs, the temperature at which P_z vanishes under small bias or changes slope under high bias indicates the loss of stability of the PE state in the SLs during cooling. The variation of P_x that is provided in Figs. 3(a)-(d) indicate the amplitude of the polarization vector along the plane of the heterostructure. When in MD state, electrostatic considerations near the interfaces necessitate the generation of closure domains that yield a non-zero P_x at or below T_C even if the FE phase is tetragonal as in the case here due to the negative sign and magnitude of misfit near T_C. The starting temperature of strain stabilized P_x can be distinguished with sudden change in the slope of P_x. FE-PE phase transition under low bias (~0 kV/cm) occurs sharply around 700K and 500K for the 4 bilayer unit and the 4 symmetrical unit systems, respectively [Figs. 2(a) and 2(c)]. 8-unit structures have a lowered and smeared transition even under small bias regardless of the SL configuration [Figs. 2(b) and 2(d)]. For large bias (such as 140 kV/cm), we essentially see just an inclined curve for P_z in the 8-unit structures. Such a behavior is due to the fact that a SD state is possible under low-to-moderate bias values accompanied by a significant smearing of the transition. In the 4-unit bilayer and symmetrical unit structures, the transition from the PE to FE state is always into the MD configuration at zero bias. The former develops closure domains right at the transition yielding a relatively small P_x that later suddenly changes slope with cooling as the “strain stabilized” P_x appears in a range of temperatures between 450K and 550K depending on bias [see Figs. 3(a) and 3(c)]. Note that external bias “reduces” the T_C of the structures if the transition from the PE phase is into MD FE phase at zero field. In the 4-unit SL consisting of symmetrical units, the MD formation coincides with the appearance of the strain stabilized P_x components. The transition temperatures of SLs with symmetrical units have been theoretically shown to be considerably lower (more than 100 K) than that of bilayer systems and the same outcome is observed here.[33,37] However, as we shall show, the p behavior is a stronger function of repeating unit thickness than the unit type, which is an unexpected result keeping in mind the dependence of T_C on unit types. [38]

Compared to the 4-unit structures, 8-unit structures have lower T_C overall as a result of the reduced layer thicknesses in agreement with previous analytical results. [33,38–40] While the differences in the P_z with temperature for the 4-unit bilayer and symmetrical unit SLs are substantial, the 8-unit bilayer and symmetrical unit structures have identical P_z values under weak and strong bias. P_x components are nearly non-existent implying the tendency to stabilize the SD state under bias [Figs. 3(b) and 3(d)]. This is because of the proximities of the energies of the SD and MD states at such thicknesses under bias.

The dramatic variations in T_C and P_z (Fig. 2) in 4- and 8-unit SLs have a significant impact on the pyroelectric properties as shown in Fig. 4. All types of 4-unit structures display a λ-type behavior under bias with weak dependence on repeating unit type. The highest p the bilayer system is obtained near the temperature when the "strain-stabilized" P_x appears and the higher the bias, the lower the temperature at which this transition occurs. The kink in the p of the 4-unit bilayer structure in the 650-700K range corresponds to T_C. We only see this kink at T_C under bias because the PE to MD-FE state would already reveal zero pyroresponse under zero bias. Even in the case there is a finite pyroelectric response from domains with polarization in the same direction as the applied field, one may not still see a clear anomaly at T_C due to smearing effect from the field. High bias (such as 140 kV/cm) results in a SD state and the pyroelectric coefficient is relatively larger near RT [Figs. 4(a) and 4(c)]. Surprisingly, the pyroresponse curves for both 4 unit bilayer and symmetrical unit systems are similar but the bilayer unit system appears to have a slightly enhanced response around RT. This is because one of the FE layers is already in contact with the electrodes and has weaker stray fields on at least the electrode side in that layer and the same result is obtained for larger systems (see Suppl. Mat. [37]). The overall reduction in p upon occurrence of the strain stabilized P_x is due to the fact that the dependence of P_z on bias becomes also a function of the value of P_x via cross terms (see Suppl. Mat. [37]). The latter component is nearly insensitive to bias and restricts the response of P_z to changes in temperature for a given bias.

Figs. 4(b) and 4(d) show that p of both bilayer and symmetrical 8-unit structures are significantly higher than the 4-unit SLs. This is related to the stability and amplitude of P_z with temperature given in Figs. 2(b) and 2(d). This is an expected outcome: thinner layers are easier to convert to the SD state under bias, accompanied by a broadly smeared maxima around RT. 8-unit SLs have the highest pyroelectric properties under the lowest bias, a result just the opposite of what has been found for 4-unit SLs because thinner layers have a tendency to switch to SD state. This trend is almost independent of the total number of units (see Suppl. Mat. [37]).

We now compare the pyroresponse of the 4 and 8 unit 72 nm thick SLs with that of a SD, monolayer PZT film at RT and 500K under various values of applied bias in Fig. 5. Pyroelectric coefficient of PZT monolayer is not sensitive to applied bias. Examining Fig. 5(a), the RT response of the monolayer PZT is better than the 4-unit SLs overall but the 8-unit SL structures have an enhanced and significantly tunable pyroelectric response when the bias is not too high (< 70 kV/cm). For instance, small bias pyroelectric coefficient of 8-unit symmetrical SLs is ~55%

higher than that of a zero bias PZT monolayer reaching 0.045 μC $cm^{-2}K^{-1}$. Fig. 5(b) shows that tunability of the 4-unit and 8-unit structures tend to increase with bias but this time the monolayer PZT has a higher response at 500K. Note that this difference is not very significant and all structures (including the monolayer PZT) converge to the same value at higher temperatures as expected (not shown here). In general, regardless of the magnitude of p, the SLs appear to have better tunability than the monolayer film. We should add here that the pyroresponse enhancement observed in the 8-unit 72 nm structures (or the 16-unit 144 nm one) is identical to the effect of tensile misfit strains reducing the T_C of a short circuited monolayer uniaxial FE film: the only difference is that the SL has a reduced T_C due to periodic depolarizing fields at the FE-PE interfaces for the fixed compressive misfit strain considered here that favors at least one component of P along film normal. Smearing of p in the SL originates from the presence of domains and internal fields, unlike what one would expect from a monolayer SD FE film short circuited with ideal electrodes. For the case of a virtual misfit that allows the monolayer PZT to undergo the PE to SD state ferroelectric transition at the same temperature as the 8-unit superlattice, the former would be expected to have a larger p as the latter would be in MD state under zero bias.

In summary, our results indicate that the type of the repeating unit comprising the FE SLs and its thickness determine the magnitude of the pyroresponse. SLs consisting of thin repeating units (8-unit 72 nm thick and 16-unit 144 nm structures) have the highest pyroelectric coefficients and tunability with values exceeding that of a monolithic monolayer. The reason for this is the reduction in the T_C for structures in a MD state. Pyroresponse of FE-PE superlattices are sensitive to unit layer thickness but not so much to the repeating unit type in contrast to what one would expect in the light of previous works. [33, 38] Our results have very important implications for use of FE materials in IR devices: a higher and bias-sensitive response can be achieved from layer-by-layer engineered FE-PE structures than from monolithic films. A zero pyroresponse from a MD structure is inevitable. These systems, however, when under bias, can actually yield enhanced and tunable pyroresponse compared to an electroded monolayer film if the FE layer is periodically exposed to paraelectric layers where each layer does not exceed a thickness of a few nanometers, a highly achievable task with modern thin film processing methods.

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FIGURE CAPTIONS

Figure 1 (Color online) Schematics of epitaxial PZT/STO SLs on STO substrates. The total thickness *L* is 72 nm for (a) bilayer and (b) symmetric configurations. Number of repeating units considered here is 4 and 8 in each configuration.

Figure 2 (Color online) Field dependent average absolute out-of-plane plane polarizations of 72nm-thick epitaxial PZT/STO SLs on STO substrate as a function of temperature for a bilayer configuration with (a) 4 and (b) 8 repeating units. (c) and (d) show P_z of 4- and 8-unit symmetrical SLs, respectively. The insets in (a) and (c) are the position dependent polarization maps of the corresponding heterostructures near T_C (~700 K for bilayer and ~500 K for symmetrical). The maximum P_Z values on insets are 0.01 C/m^2.

Figure 3 (Color online) Field dependent average absolute in-plane polarizations of 72 nm-thick epitaxial PZT/STO SLs on STO substrate as a function of temperature for a bilayer configuration with (a) 4- and (b) 8 repeating units. (c) and (d) show P_x of 4 and 8-unit symmetrical SLs, respectively.

Figure 4 (Color online) Field dependent average out-of-plane pyroelectric coefficients of 72 nm-thick epitaxial PZT/STO SLs on STO substrate as a function of temperature for a bilayer configuration with (a) 4 and (b) 8 repeating units. (c) and (d) show the pyroresponse of 4- and 8-unit symmetrical SLs, respectively.

Figure 5 (Color online) Field dependent average out-of-plane pyroelectric coefficients of 72 nm-thick epitaxial PZT/STO SLs on STO substrate at (a) room temperature (300K) and (b) 500K. Pyroresponse of a pseudomorphic, SD PZT monolayer on STO are also indicated in both figures for comparison.

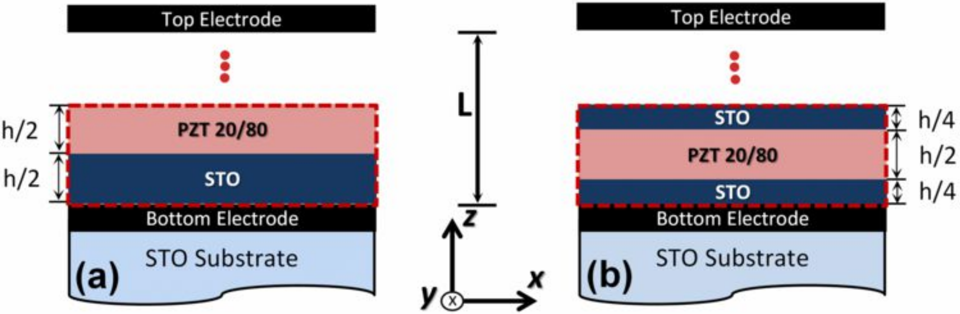

Top Electrode
h/2
PZT 20/80
h/2
STO
Bottom Electrode
STO Substrate
(a)
L
z
x
y
Top Electrode
STO
h/4
PZT 20/80
h/2
STO
h/4
Bottom Electrode
STO Substrate
(b)

Figure 1

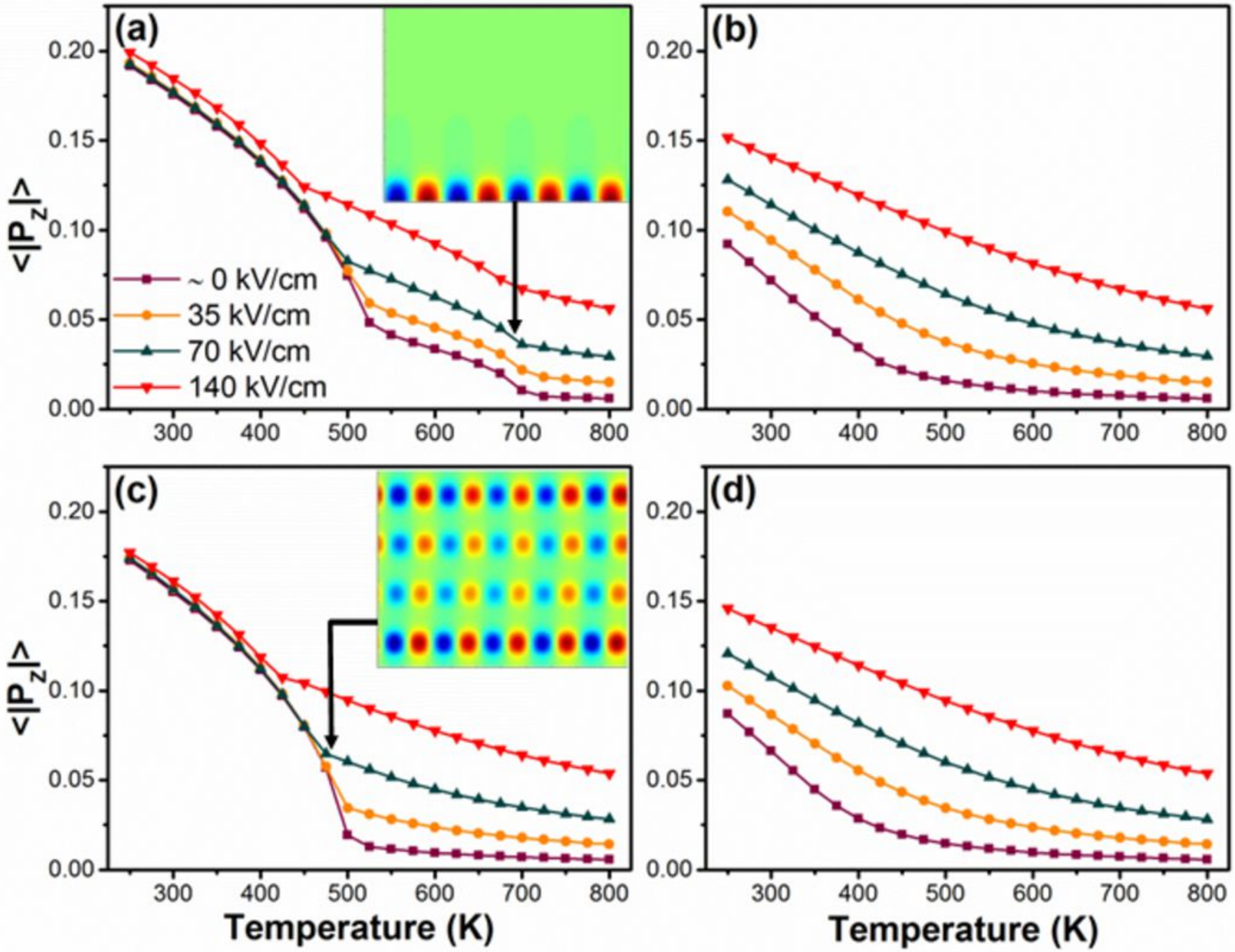
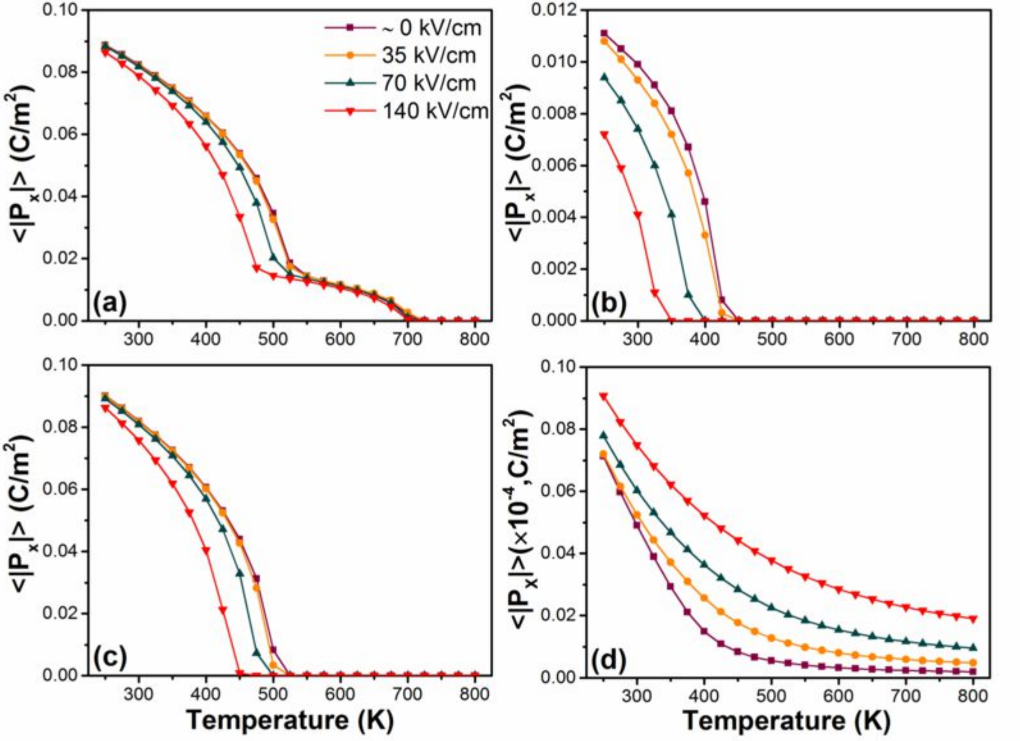

(a)
(b)
(c)
(d)
$<|P_z|>$
Temperature (K)
~ 0 kV/cm
35 kV/cm
70 kV/cm
140 kV/cm
0.00
0.05
0.10
0.15
0.20
300
400
500
600
700
800

Figure 2



(a)
(b)
(c)
(d)
~ 0 kV/cm
35 kV/cm
70 kV/cm
140 kV/cm
<|P_x|> (C/m^2)
<|P_x|>(×10^-4, C/m^2)
Temperature (K)
0.00
0.02
0.04
0.06
0.08
0.10
0.000
0.002
0.004
0.006
0.008
0.010
0.012
300
400
500
600
700
800

Figure 3

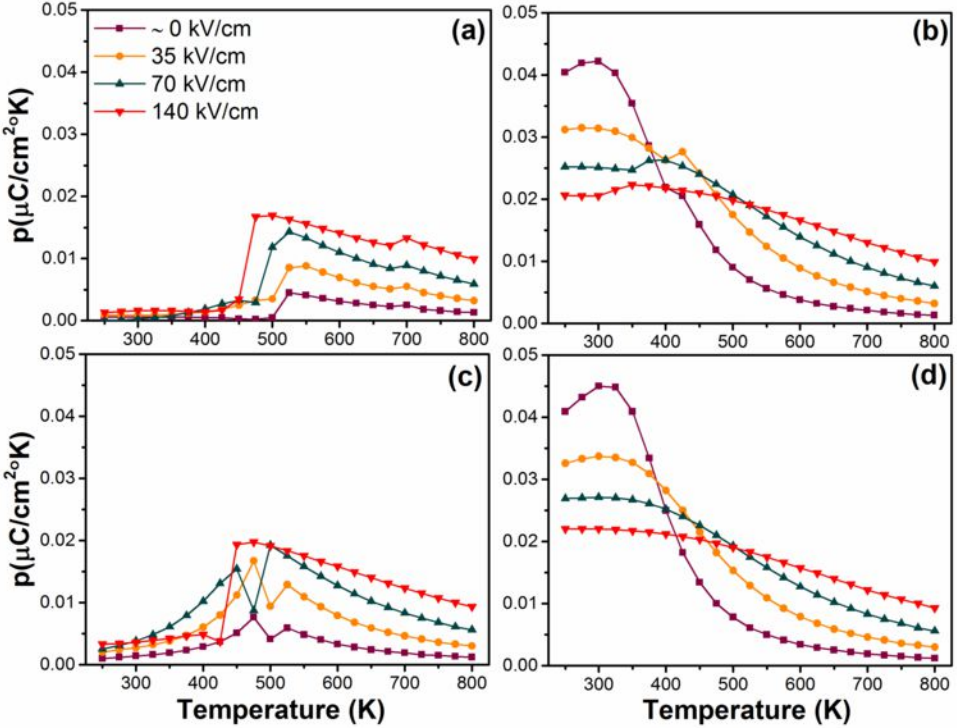
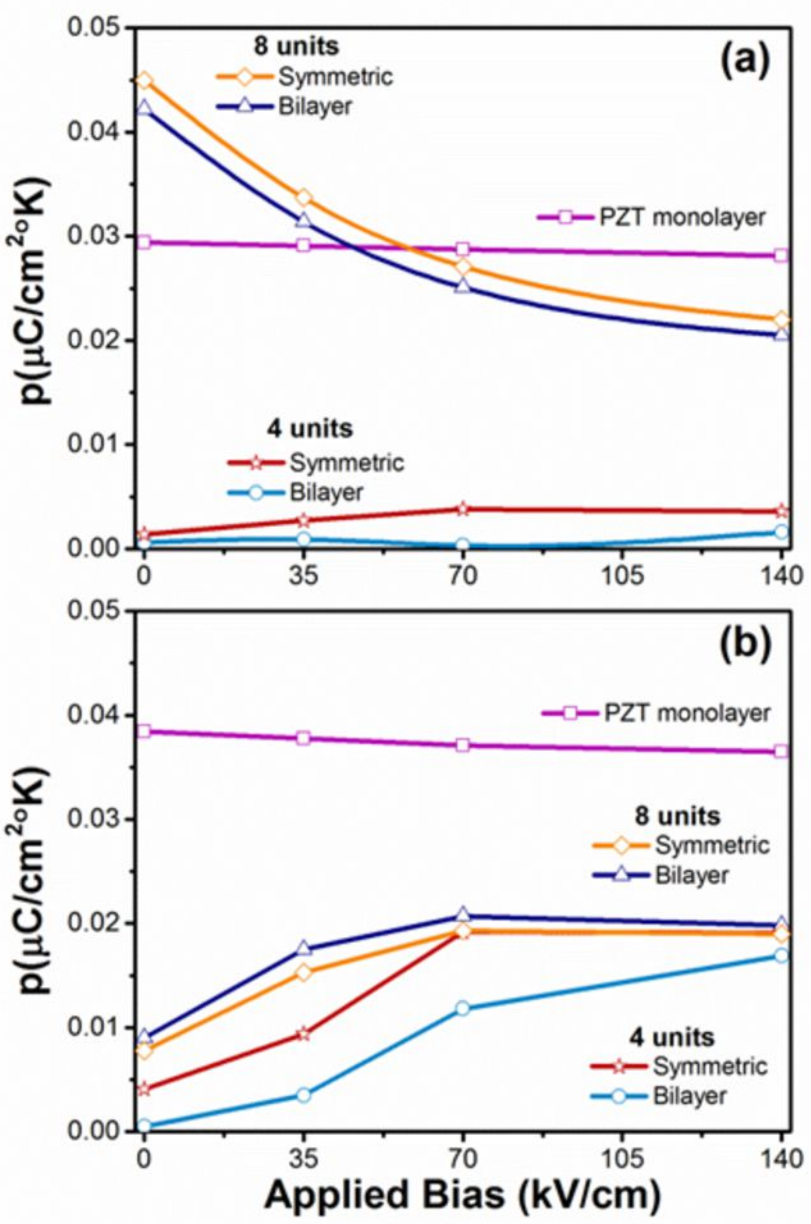

(a)
(b)
(c)
(d)
~ 0 kV/cm
35 kV/cm
70 kV/cm
140 kV/cm
p(μC/cm²°K)
0.00
0.01
0.02
0.03
0.04
0.05
300
400
500
600
700
800
Temperature (K)

Figure 4



p(µC/cm^2°K)
8 units
Symmetric
Bilayer
PZT monolayer
(a)
4 units
Symmetric
Bilayer
0.05
0.04
0.03
0.02
0.01
0.00
0
35
70
105
140
(b)
PZT monolayer
8 units
Symmetric
Bilayer
4 units
Symmetric
Bilayer
Applied Bias (kV/cm)

Figure 5