Understanding polarization asymmetry in $PbTiO_3/SrTiO_3$ and $PbTiO_3/SrRuO_3$ superlattices

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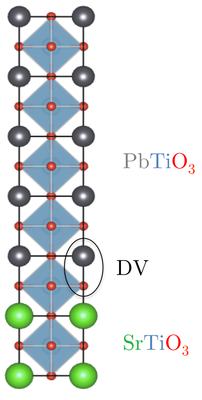
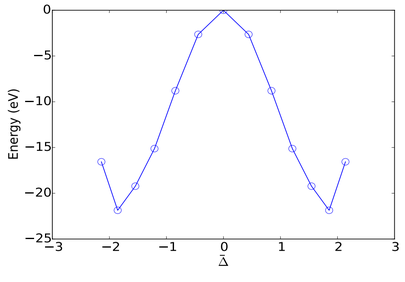
Motivation

Thin film capacitors have an encouraging outlook on being used as memory storage devices over flash memory, primarily due to their low energy consumption and write speed. Lead titanate is a suitable candidate for such devices primarily due to its large switching charge and low process temperature. Furthermore, properties of the capacitor can be enhanced when syntheized as a superlattice with one or two materials. While a superlattice constructed from lead titanate and strontium titanate has improved dielectric properties, there is an unwanted presence of a voltage bias in the dielectric measurements of uncharted origin. In this work we use first principles calculations to outline why the bias exists as a first step to developing a solution to mitigate this problem.

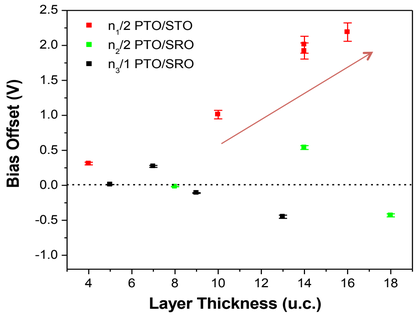


5/2 PbTiO3/SrTiO3 superlattice, where each unit cell has a perovskite structure. The perovskite structure has a Pb/Sr ion on the edges, an O ion on the faces and a Ti ion at the center.



Typical potential energy surface of an ideal PbTiO3/SrTiO3 superlattice. The two equivalent ground states correspond to up and down polarizations.

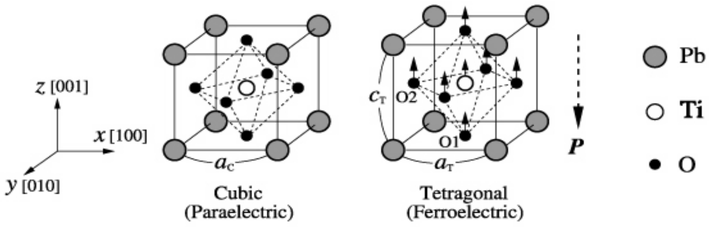
Voltage bias from dielectric measurements seen in experiments. PbTiO3/ SrTiO3 systems exhibit a larger bias with increasing PbTiO3 thickness. This behavior is absent for PbTiO3/SrRuO3 systems.



Methods

We performed first principles calculations using density functional theory, where we simulated PbTiO3/SrTiO3 with a divacancy (a source of asymmetry) in either the interface between the PbTiO3 and SrTiO3 or in the center of the PbTiO3. It is important to note that the divacancy in the interface can only be formed with only one orientation and this is the same orientation that we use when it is formed in the PbTiO3 for PbTiO3/SrTiO3. For PbTiO3/SrRuO3, we looked at both orientations due to the presence of inversion symmetry breaking at the interface. The bias that is present in experiments can be roughly translated to the energy difference between the two stable polarization states.

The ferroelectric state can be associated with atomic displacements, which collectively represent a polar mode. We can use the displacements in bulk PbTiO3 and SrTiO3 to approximate the polarization in each unit cell.



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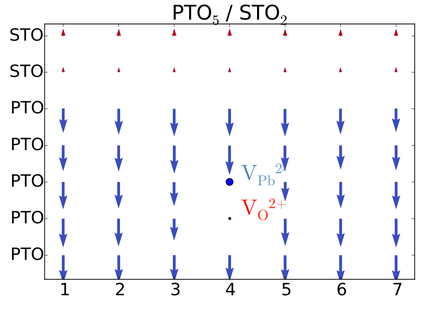
The parameter ξ corresponds to the inner product of the displacements in the superlattice, Q, with the same type of displacements in the bulk, Q_0. Therefore a value of 1 would correspond to polarization that would occur in bulk PbTiO3.

$$\xi = \frac{\mathbf{Q}\cdot\mathbf{Q}_0}{\mathbf{Q}_0^2} \qquad \mathbf{Q} = \begin{pmatrix} \Delta Pb_z \\ \Delta Ti_z \\ \Delta O_{1z} \\ \vdots \end{pmatrix}$$

The plot of ξ per √2×√2 unit cell shows that near the divacancy (represented by empty points) the polarization takes on relatively large values to screen the polarization of the dipole and smaller values in the SrTiO3 due to an energy cost associated with polarizing the dielectric.

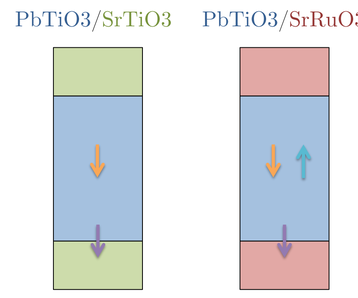


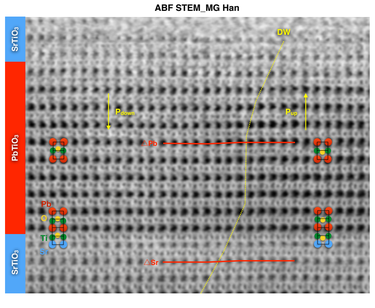
Results and Conclusion

Our results indicate that the asymmetry in polarization present due to the formation of the divacancy behaves differently in PbTiO3/SrTiO3 and PbTiO3/SrRuO3. In PbTiO3/SrTiO3 the ground state of the divacancy is almost degenerate, either forming in the PbTiO3 or at the interface. However, in PbTiO3/SrRuO3 the divacancy prefers to sit in the PbTiO3, oriented with the preferred polarization direction stemming from the inversion symmetry breaking.

Parallel (meV)	Anti-Parallel (meV)	Δ (meV)
0	**420**	**420**
44	175	131

Parallel (meV)	Anti-Parallel (meV)	Δ (meV)
883	320	-563
0	**715**	**715**
551	1263	712





This STM image gives a possible insight into why the vacancies want to form at the interface rather than the PbTiO3. When the SrTiO3 is grown on PbTiO3 structural relaxations occur to account for the epitaxial strain and thus these relaxations change the energy landscape to favor further defects such as vacancies.

In the future we plan to do both experimental and simulation work on tricolor PbTiO3/SrTiO3/SrRuO3, which should have the dielectric properties of PbTiO3/SrTiO3 and the lack of voltage bias as in PbTiO3/SrRuO3. If these properties hold for the tricolor superlattice then that would give us additional confidence in our understanding of the defects in these systems.