Understanding polarization asymmetry in $PbTiO_3/SrRuO_3$ superlattices

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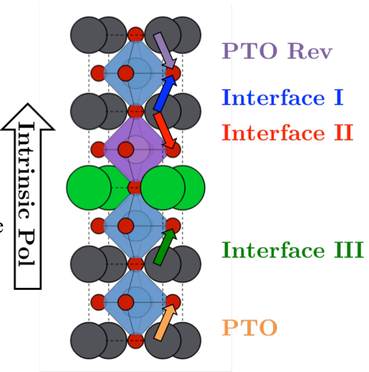
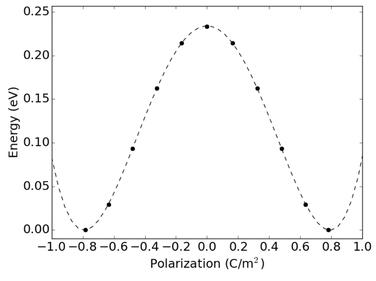
Motivation

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 ($PbTiO_3$) 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 ruthenate ($SrRuO_3$) 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.

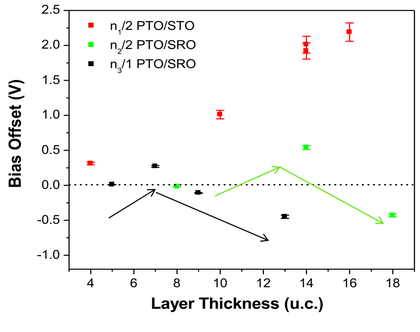
$PbTiO_3/SrRuO_3$ superlattice with asymmetrical interface, where each unit cell has a perovskite structure. The perovskite structure has a Pb/Sr ion on the edges, an O ion on the faces and a Ti/Ru ion at the center. The asymmetric interface leads to a preferred intrinsic polarization direction. In addition we show possible location of Pb-O divacancies.





Potential energy surface of bulk $PbTiO_3$. The two energy equivalent ground states correspond to up and down polarizations.

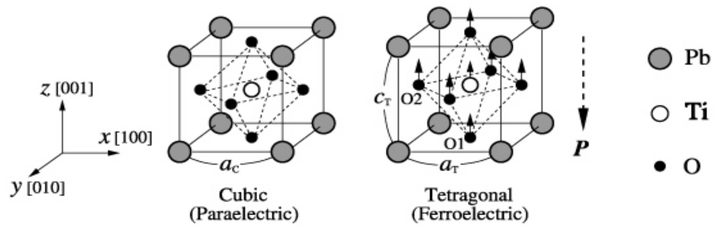
Voltage bias from dielectric measurements seen in experiments. $PbTiO_3/SrRuO_3$ systems exhibit an increasing and positive bias at low $PbTiO_3$ layer thickness and then at some critical thickness the bias becomes decreasing and.



Methods

We performed first principles calculations using density functional theory, where we simulated $PbTiO_3/SrRuO_3$ with a divacancy (a source of asymmetry) in either the interface between the $PbTiO_3$ and $SrRuO_3$ or in the center of the $PbTiO_3$ layers. It is important to note that the divacancy in Interface II can only be formed with the dipole direction opposite to the intrinsic polarization direction of the whole superlattice.

The ferroelectric state can be associated with atomic and electronic displacements, which collectively represent a polar mode. While atomic positions are already localized, the electrons can be recast from the periodic reciprocal space (Bloch) basis into the localized real space (Wannier) basis to perform the polarization calculations.



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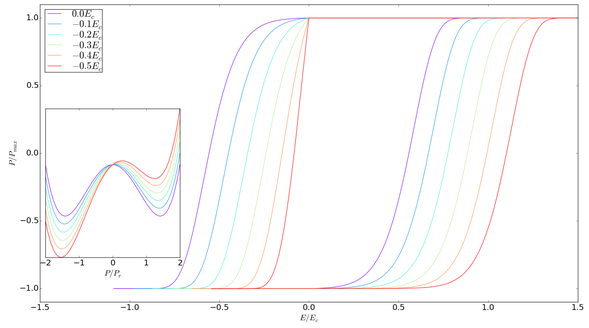
$$\mathbf{P} = \frac{e}{\Omega}\sum_n \mathbf{r}_n + \frac{e}{\Omega}\sum_I Z_I \mathbf{R}_I$$

e = Elementary charge
Ω = Volume
$\mathbf{r}_n$ = Electronic Wannier position
Z_I = Ionic charge
$\mathbf{R}_I$ = Ionic position

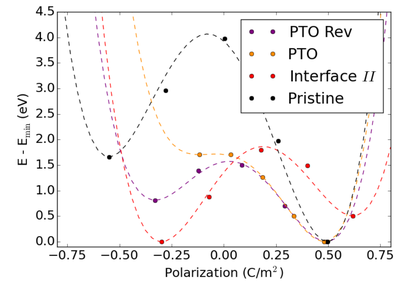
The bias that is present in experiments is observed as an offset hysteresis loop, which can be roughly translated to the energy difference between the two stable polarization states. To put this correspondence on a more mathematical footing, we performed numerical hysteresis simulations by calculating the mean first passage time of a stochastic particle on a double well potential energy surface.

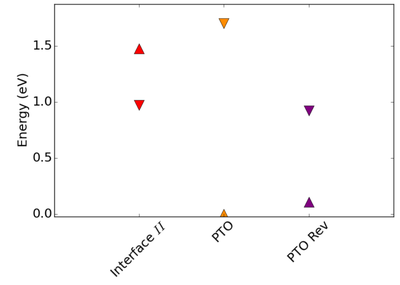


Results and Conclusion

We can summarize the behaviors of the two regimes in $PbTiO_3/SrRuO_3$ superlattices by stating that the low $PbTiO_3$ regime is dominated by inversion symmetry breaking that favors a particular polarization direction, while the high $PbTiO_3$ regime is dominated by divacancies, whose dipole moment orientations are precisely opposite to that of the intrinsic polarization direction.

Double well potential, where the intermediate points between the two local minima are calculated by interpolating the atomic positions. The dashed lines are best fits to a fourth order polynomial and each curve is plotted relative to its most stable state.





Total energy, where the up and down triangles represent positive and negative polarization of the local minima, respectively. Note that for Interface II the polarization of the ground state is flipped relative to the pristine superlattice and other locations with a divacancy.

We understand that the location and orientation of the divacancy dipole moment is determined by the interplay between the strength of the inversion breaking asymmetry, regulated by the $PbTiO_3$ thickness, screening, and the epitaxial strain, which leads to the formation of two regimes, with opposite bias. By identifying the mechanisms behind the presence of the asymmetries we are able to engineer robust superlattices by combining the phenomena that cause biases, with opposite signs, creating an implicit bias-free superlattice.