ARTIFICIALLY LAYERED FERROELECTRIC OXIDES AND THEIR USES IN THE CONTROL OF GRAPHENE THROUGH FERROELECTRIC SWITCHING

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Outline

- Introduction to perovskite oxides, ferroelectrics, and superlattices
- Growth, fabrication, and measurement techniques
- $PbTiO_3/SrTiO_3$ superlattice system; 2DEG and photocurrent
- Surface morphology of $SrRuO_3$ during growth
- Graphene/Ferroelectric hybrid devices

- Introduction to perovskite oxides, ferroelectrics, and superlattices

What are ferroelectrics?

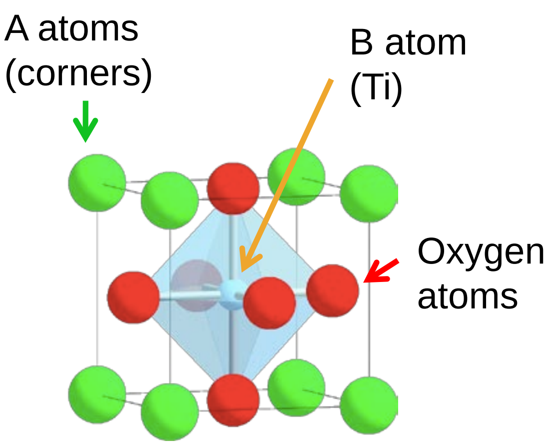
- Insulating materials with two or more discrete states of nonzero electric polarization (spontaneous polarization) in zero applied electric field which switches once an electric field is turned on.

- Ferroelectrics are both piezoelectic and pyroelectric, making them useful in many device applications such as
  - non-volatile memory
  - thermal detectors
  - piezoelectric applicators

Perovskite oxides

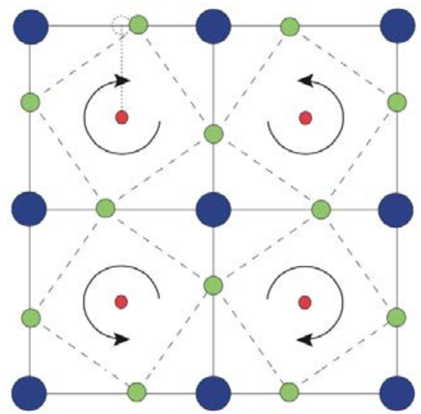
High temperature phase

ABO_3 Perovskite Structure



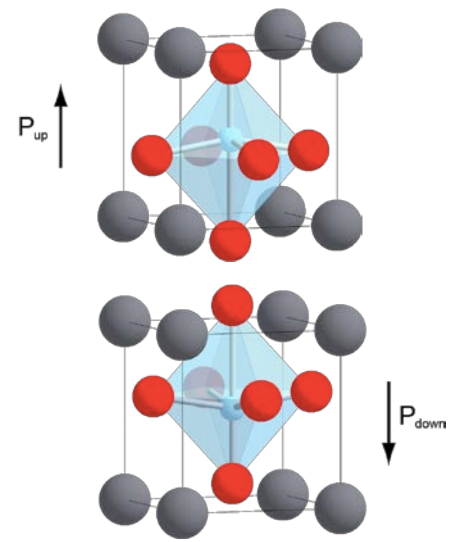
Low temperature distortions

oxygen rotation
- *A-site driven*
- *Also known as antiferrodistortion (AFD)*



Ex: $SrTiO_3$

ferroelectricity
- *B-site driven*
- *Out-of-plane*

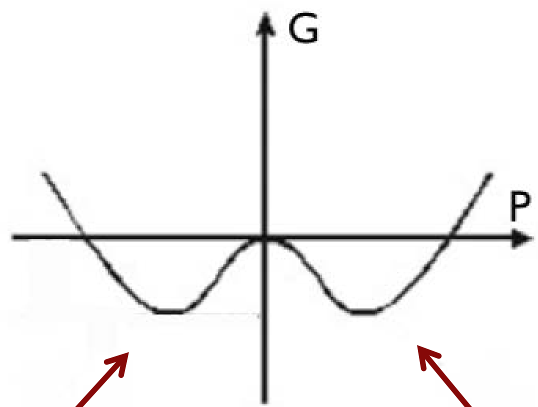


Ex: $BaTiO_3$

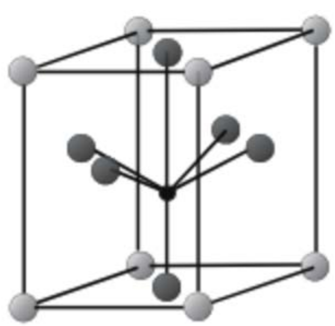
Double well potential

Landau- Ginzberg- Devonshire approximation

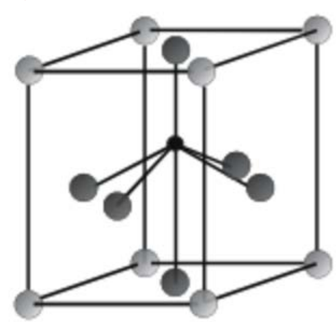
$$G = \frac{\alpha}{2}P^2 + \frac{\gamma}{4}P^4 + \frac{\delta}{6}P^6 - EP$$



Model ferroelectric energy landscape. The double well is the characteristic feature of ferroelectrics.

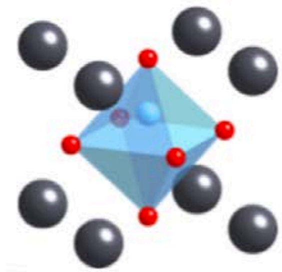


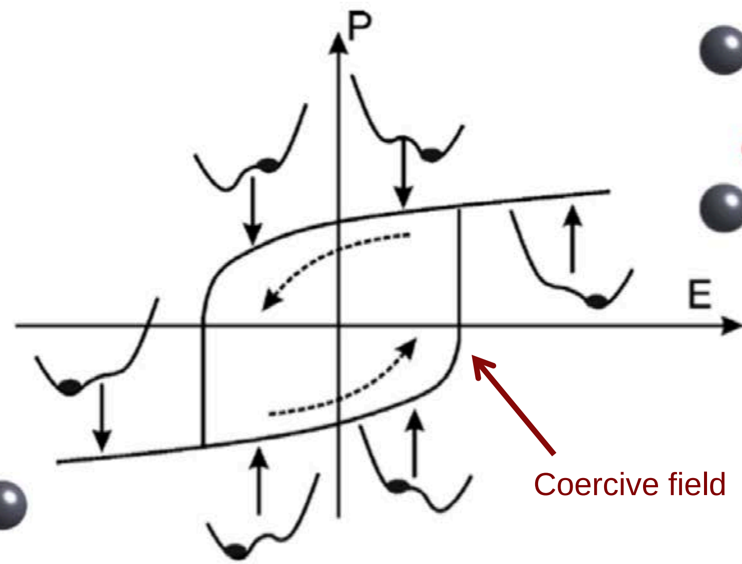
Ferroelectric phase

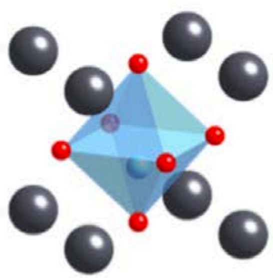


Polarization switching

- Signature property of ferroelectrics is the switchability of polarization
- Evidence of switching polarization can be seen in the P-E hysteresis loop (also the effect of E field on double well)

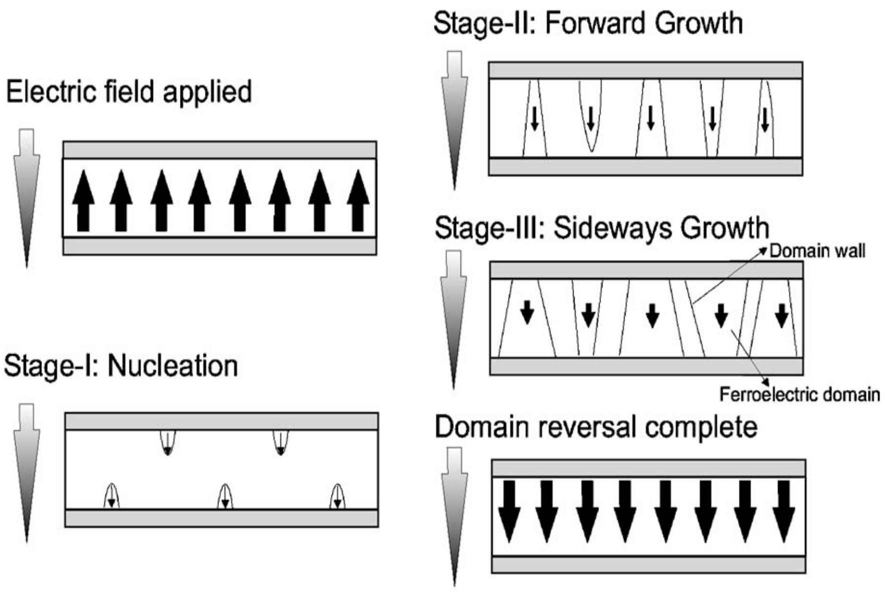






- The polarization displays hysteric behavior- producing the so-called ‘P-E hysteresis loop’ that is characteristic of ferroelectrics.

Domain switching



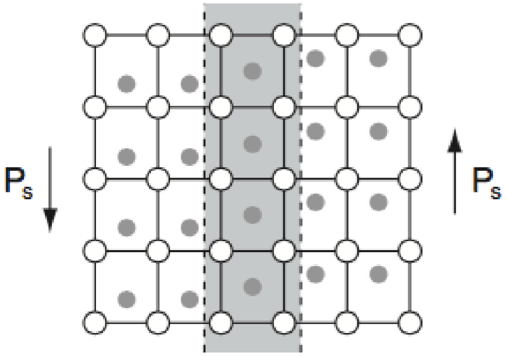
Polarization reversal is not an instantaneous process. It is preceded by

(i) Domain nucleation
(ii) Forward Growth
(iii) Sideways Growth

(Ref: 'Physics of thin-film ferroelectric oxides ', Reviews of Modern Physics Vol. 77, No. 4, M. Dawber et al. (2005))

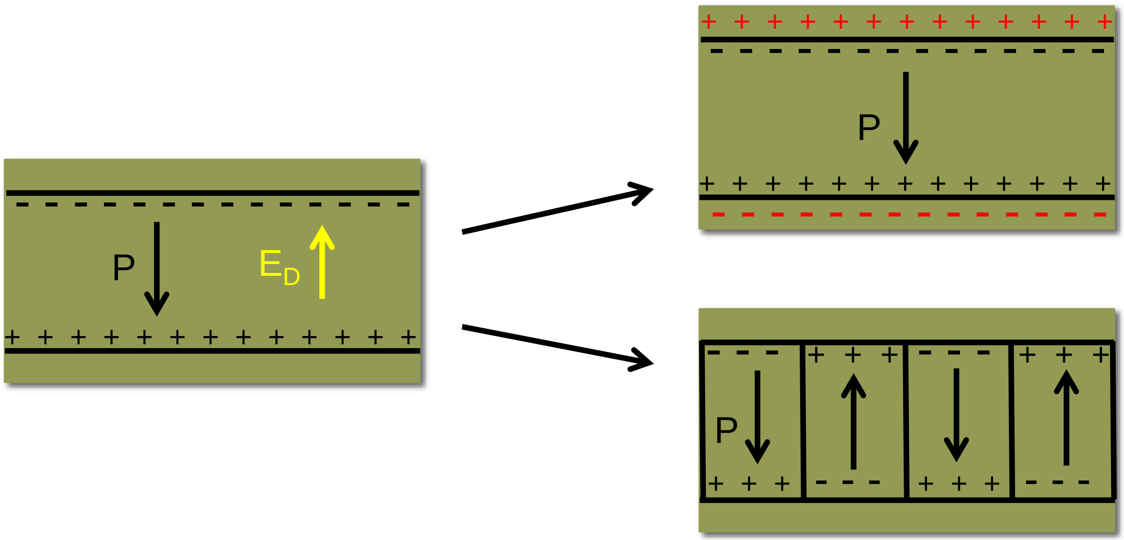
Domains

Polarization over the entire crystal is typically not uniform. Regions of uniform polarization (domains) form with different orientations to one another.



Domain walls for 180◦ domains (stripe domains) in a tetragonal perovskite ferroelectric.

Perfect screening



-Bound charges arise at the surface of a polarized dielectric material causing a depolarizing field, E_D, which is **energetically costly**

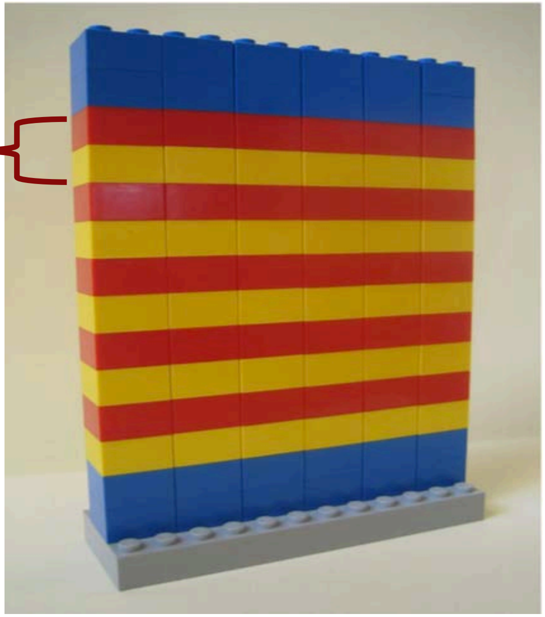
-To compensate, a polydomain configuration of periodic domains with altering polarization forms.

- As a result, the bound surface charge vanishes on average and the magnitude of the local depolarizing fields is greatly reduced.

Ferroelectric superlattices

Interesting properties arise in a superlattice system for many reasons, including size and strain effects in the individual layers, competition between the properties of the constituent materials, and interactions at the interfaces.

Bilayer



The thickness of a bilayer is called the **bilayer wavelength (Λ)**

A **ferroelectric superlattice** is a structure created by repeatedly stacking ultrathin layers of materials on top of a substrate, all of which have a similar crystal structure, allowing coherent epitaxial growth.

Novel material systems can be engineered by altering the composition and/or thickness of the layers, allowing for the tuning of the material properties.

- Growth, fabrication, and measurement techniques

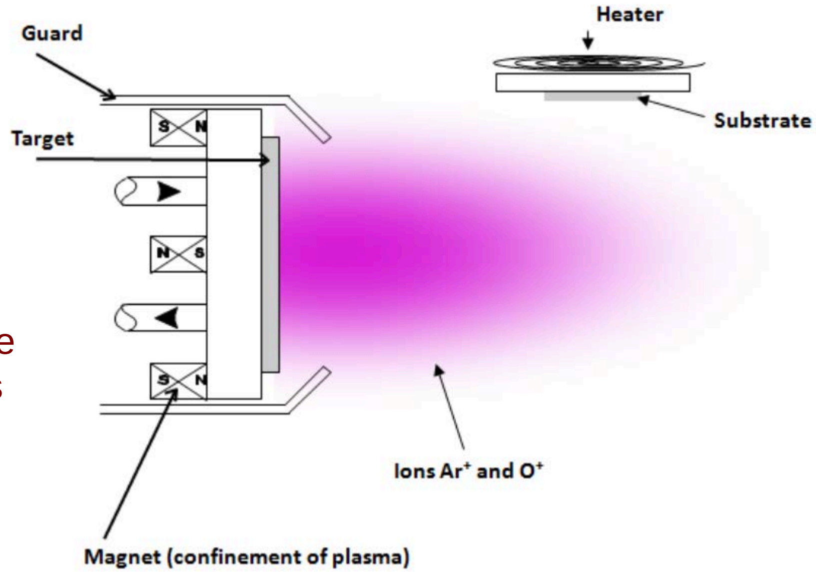
Growth

Off-axis RF Magnetron Sputter Deposition Chamber at Stony Brook

Sputter deposition:

- A type of physical vapor deposition
- Uses Ar ions in order to eject particles from a target of the desired material

The sputtering chamber is electrically grounded and therefore acts as an anode with the gun as a cathode, and so the electric field is then much higher near the sputter gun, which causes the Ar ions to accelerate towards the target.



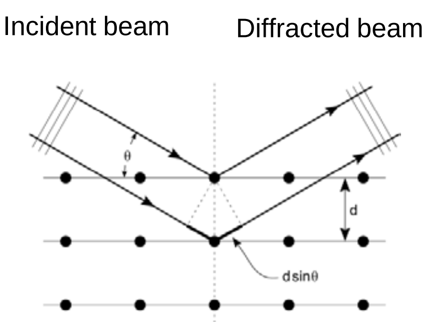
The sputter system in our lab is a custom designed vacuum chamber that allows for up to 6 different materials to be grown without breaking vacuum.

X-ray Diffraction

X-ray diffraction (XRD) methods are used to study the crystal structure of these superlattice systems to find properties such as

- lattice parameters
- crystal quality
- film thickness
- evidence of ferroelectric domains.

The diffraction pattern resulting from the periodic structure of the ions in a crystal can be expressed as Bragg's law:

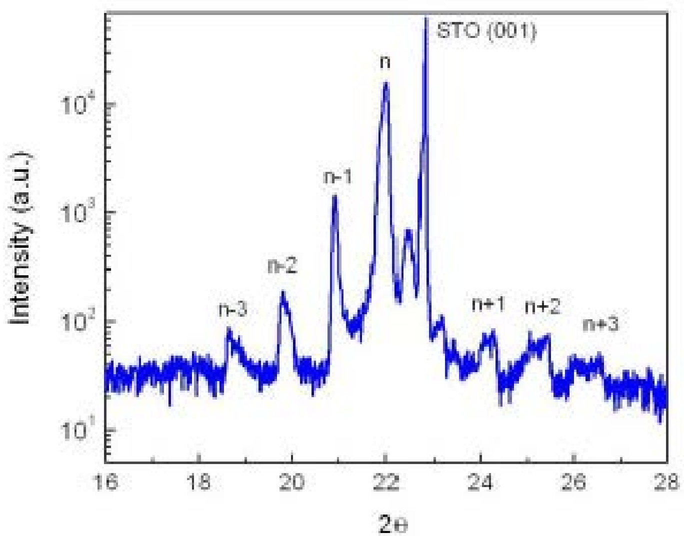


$$n\lambda = 2d\sin\theta$$

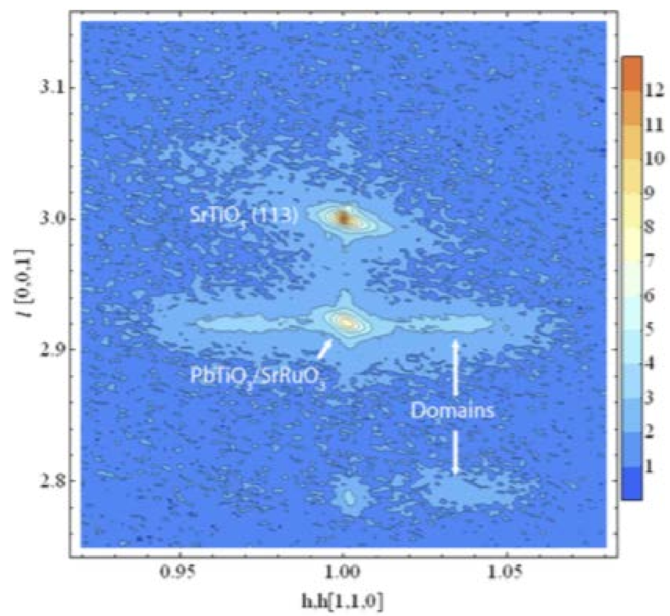
Λ is the new periodicity of the system, so Bragg's condition changes to:

$$2\Lambda\sin\theta_n = n\,\lambda$$

The peaks resulting from the 2θ - ω scan can be used to find characteristics about the superlattice.



Reciprocal Space Map
(113) of PTO/SRO



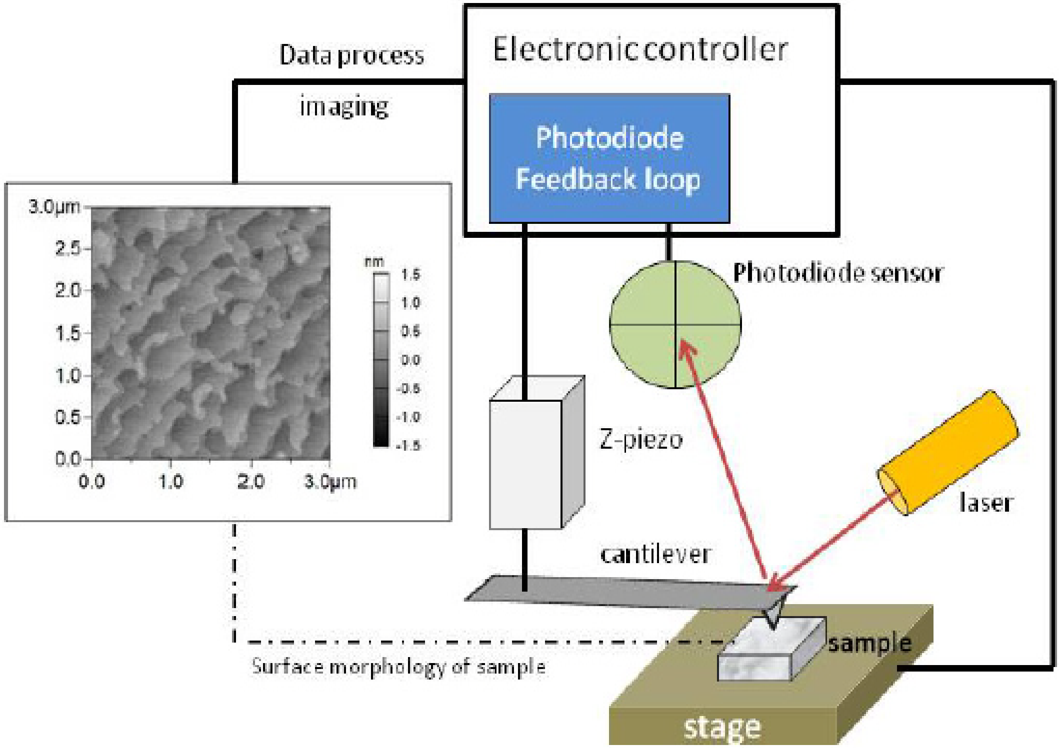
Reciprocal space maps can be used to determine:

- if a sample has coherently grown on a substrate
- determine lattice parameters
- examine samples for the presence of ferroelectric domains.

$$\text{Domain periodicity} = \frac{a}{\Delta h\sqrt{2}}$$

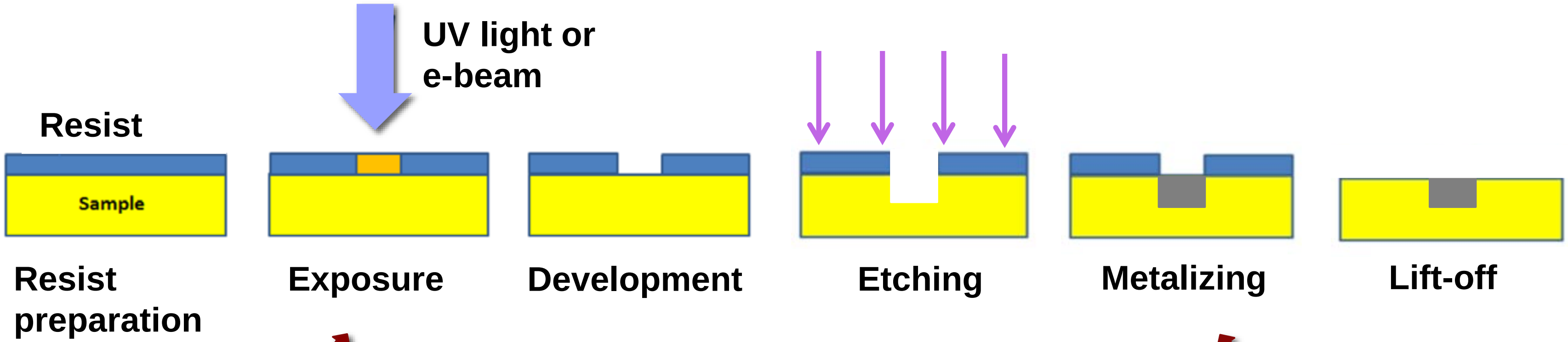
Atomic Force Microscopy (AFM)

The topography mode of the AFM can show the surface roughness of the substrate and sample.



Other AFM techniques I use include Piezoforce Microscopy and Contact Mode Force Microscopy.

Device Fabrication



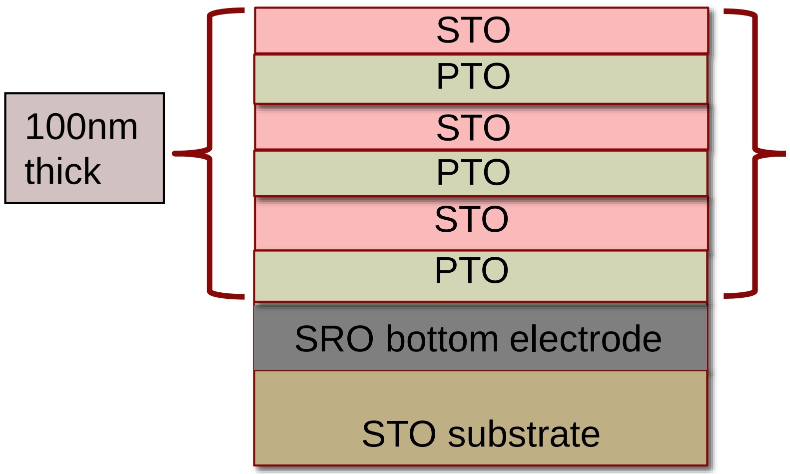
e-beam
lithography system

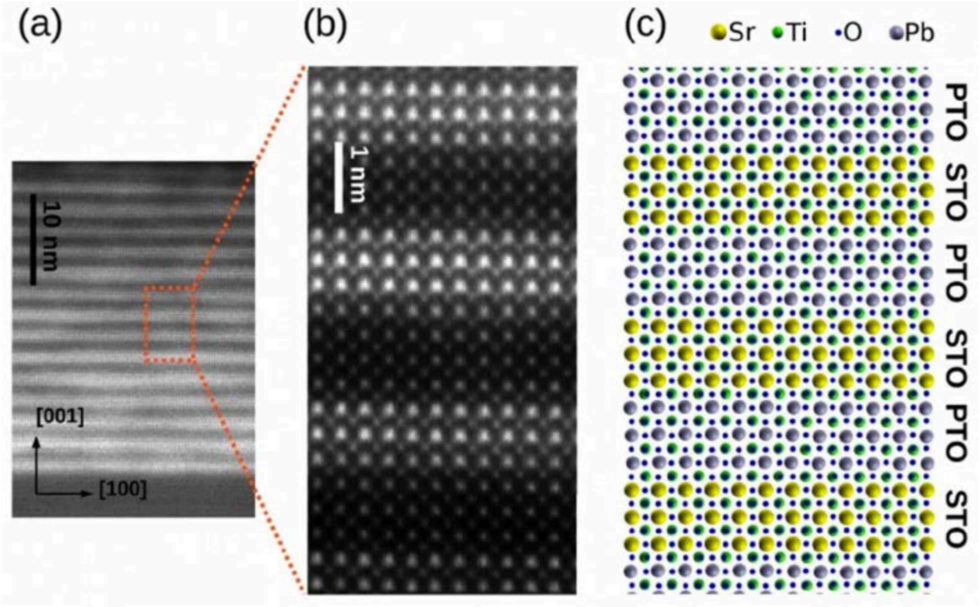
Plasma etcher

Evaporation
deposition chamber
for metallization

- PTO/STO superlattice system; 2DEG and photocurrent

PTO/STO superlattice system



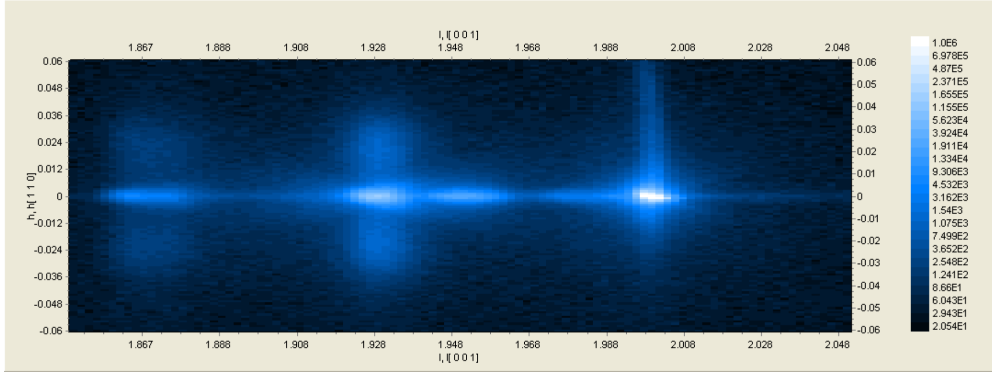


Two coupling regimes:

- Strong coupling (STO layer < 3 u.c.); polarization continuous layer-to-layer
- Weak coupling (STO layer > 3 u.c.); layers are decoupled and PTO layers act like thin films

(https://wikiar2011.bsc.es/index.php5/Strain_tunning_of_ferroelectric-antiferrodistortive_coupling_in_PbTiO3/SrTiO3_superlattices', Barcelona Supercomputing Center)

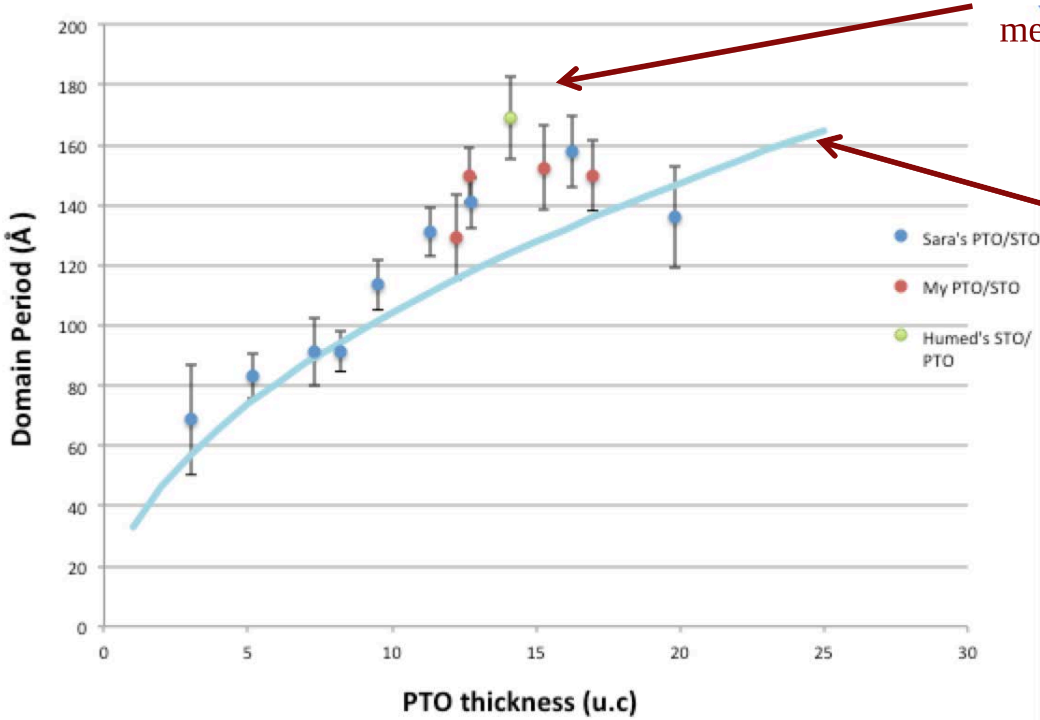
Domain sizes in (n/3) PTO/STO superlattices



So far we know that for (n/3) PTO/STO superlattices:

- Polarization is continuous throughout the layers
- Compressive strain on PTO causes out-of plane 180° domain structure

But how does the domain size scale with PTO layer thickness?

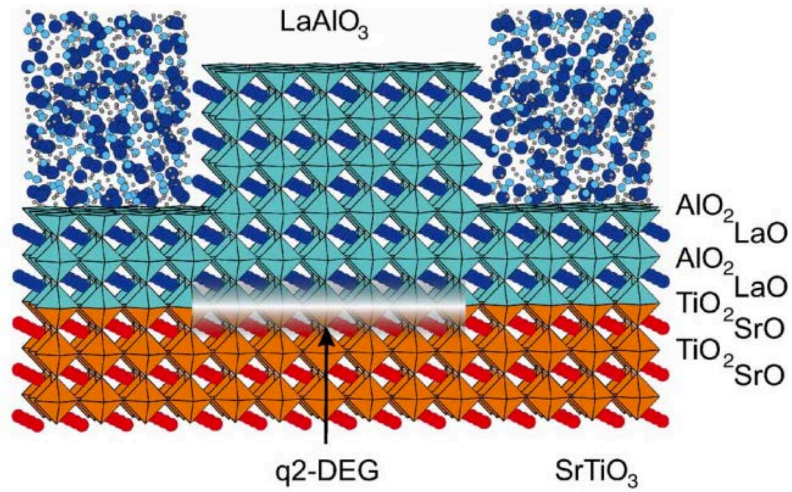


Competition of screening mechanisms?

Kittel power law for ferroelectrics: to minimize the total energy in ferroelectric thin films, a stripe domain configuration forms where the domain width is proportional to the square root of the film thickness

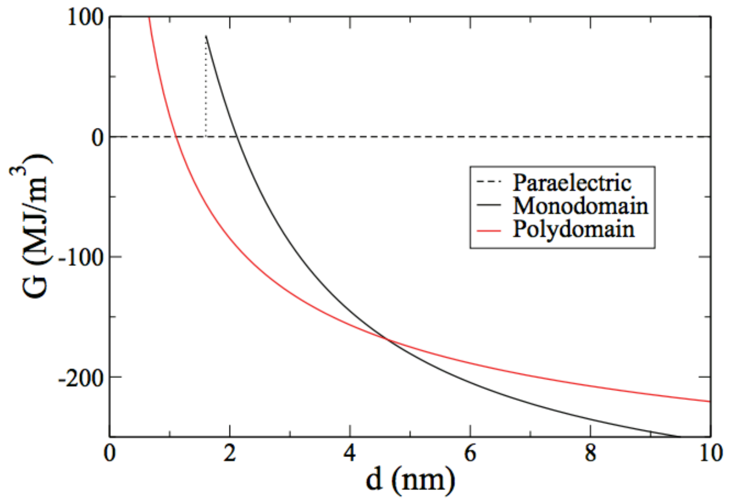
2DEGs at oxide interfaces

Above a critical thickness of lanthanum aluminate (LAO) there is a formation of 2D electron gas at the heterointerface of LAO/STO which makes the interface superconducting.



The polar discontinuity is energetically costly and to compensate, electrons accumulate at the interface to screen the discontinuity via electronic reconstruction.

Theorists use Landau model to investigate whether a monodomain state can be stabilized at PTO/STO interface by means of electronic reconstruction. Confirm that ferroelectricity can be used to induce the formation of 2DEGs at the interface with nonpolar substrates.

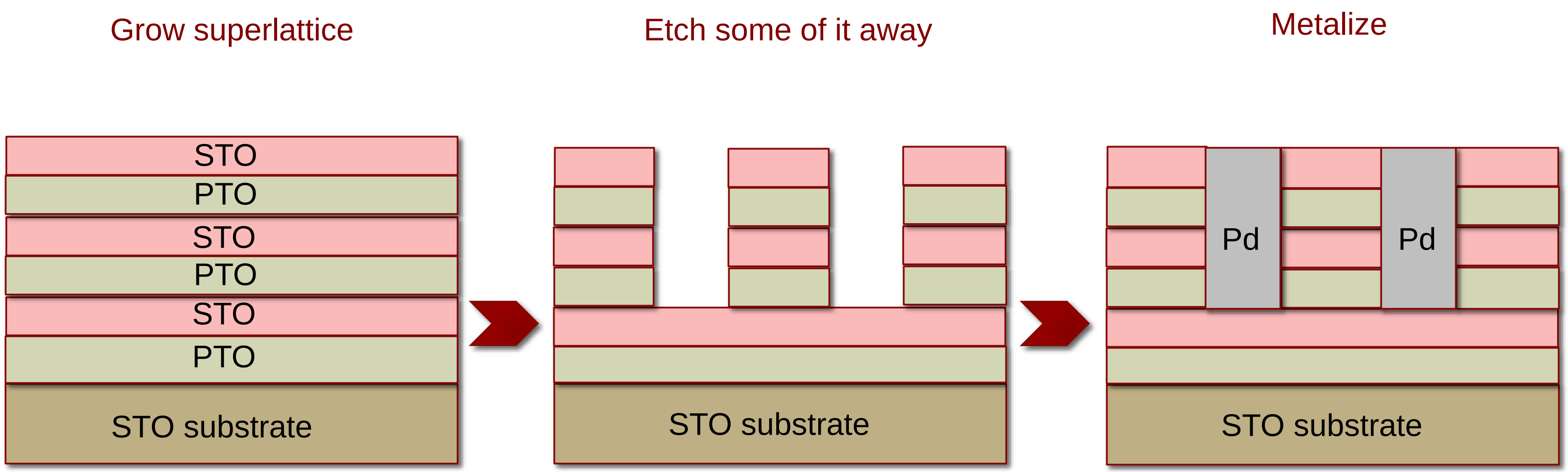


Investigating the relative stability of the two phases by comparing the thickness evolution of the energy, they arrive at the conclusion that ferroelectric monodomain polarization can exist

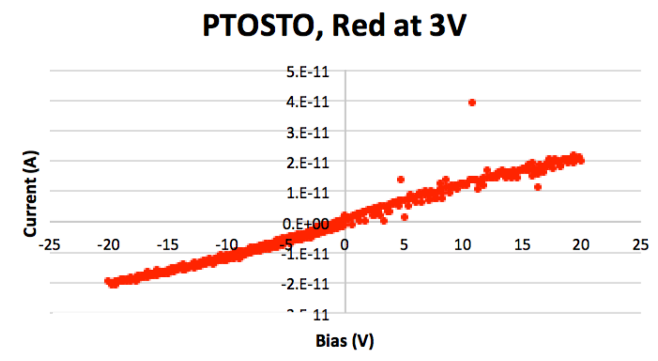
(Ref: 'A high-mobility electron gas at the LaAlO3/SrTiO3 heterointerface.', Ohtomo, A., and H. Y. Hwang, Nature 427.6973 (2004): 423-426.''Microlithography of electron gases formed at interfaces in oxide heterosctructures', C. W. Schneiderat al., APL 89, 122101 (2006))

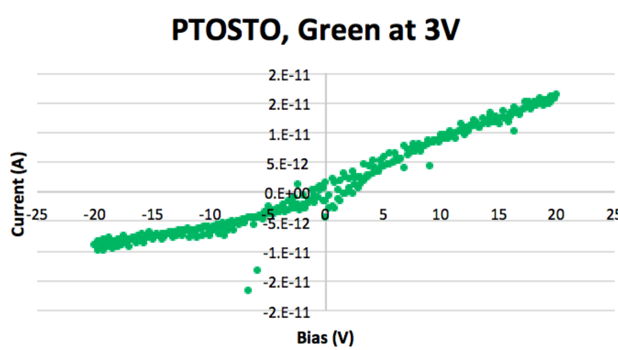
(Ref: 'Model of two-dimensional electron gas formation at ferroelectric interfaces', Aguado-Puente et al., Phys. Rev. B 92, 035438 (2015) and 'Two dimensional electron gas at the PTO/STO interface: An ab initio study, Binglun Yin et al., Phys. Rev. B 92,115406 (2015))

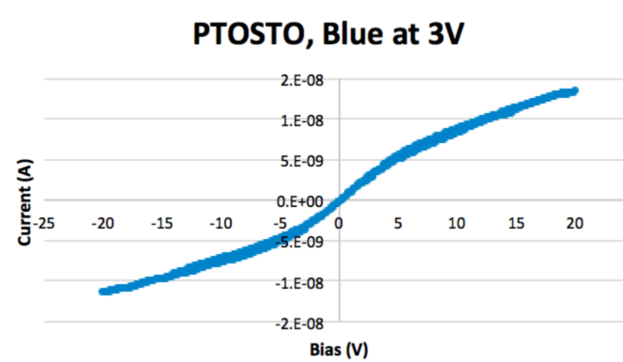
Probing the PTO/STO interface



Photocurrent in PTO/STO



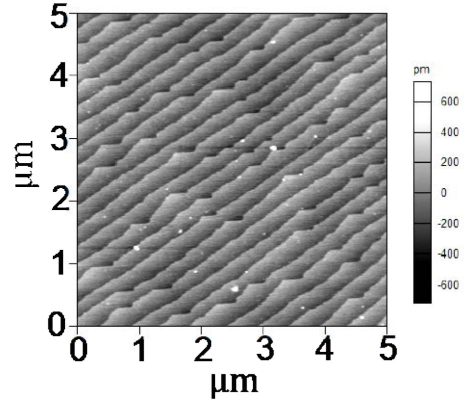


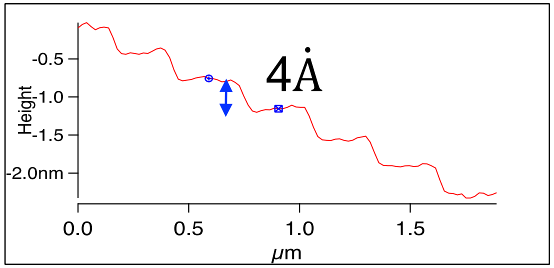


- Evolution of the surface morphology of $SrRuO_3$ during growth

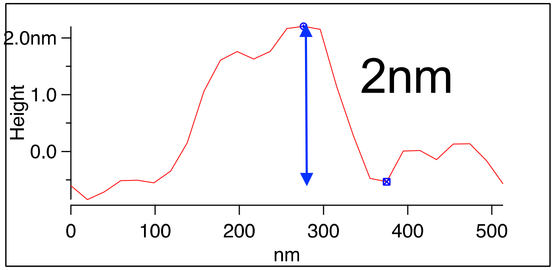
$SrRuO_3$ surface: a key step in heterostructure synthesis

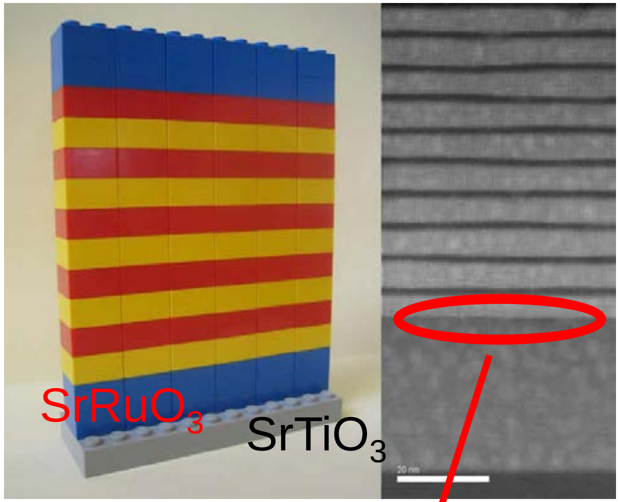
Typical $SrTiO_3$ surface

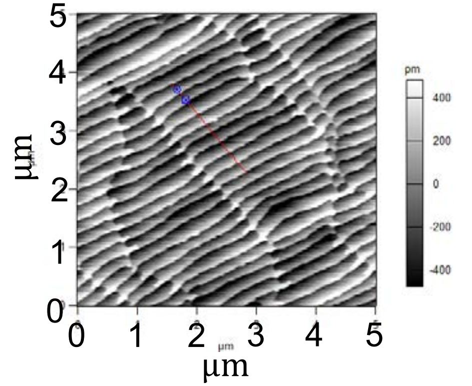




8Å

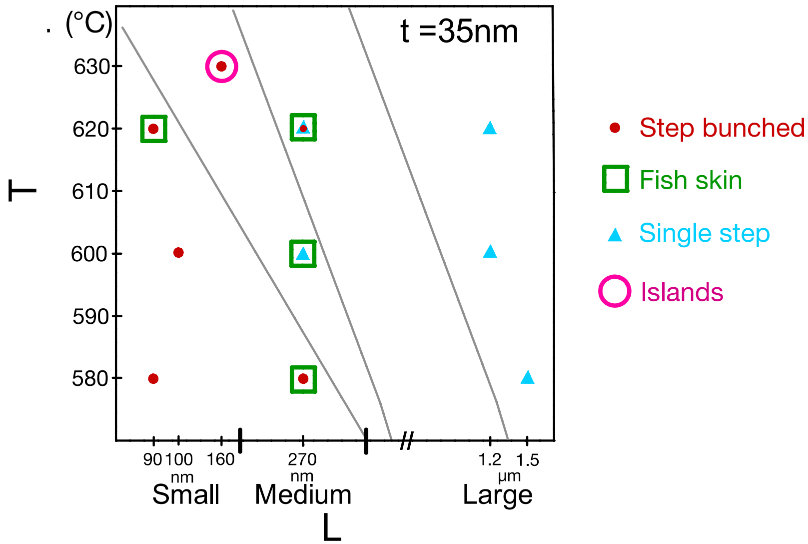


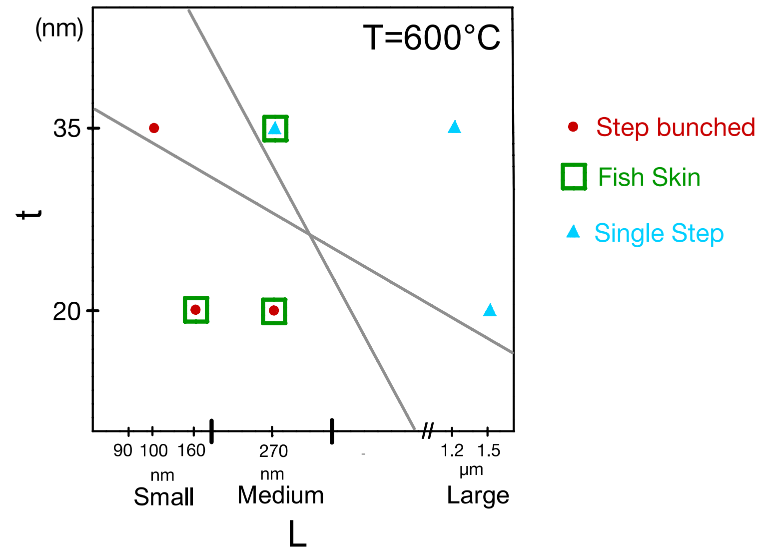


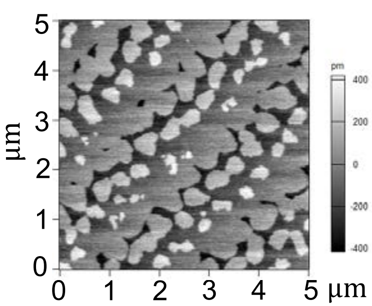


GOAL: Systematic study of $SrRuO_3$ film morphology to control the growth regime and step bunching

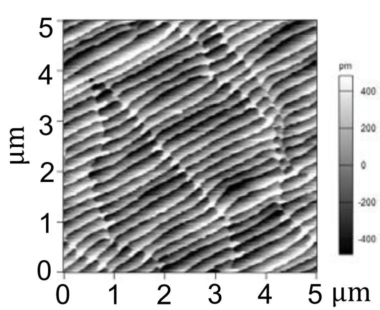
Temperature and thickness dependence of film morphology



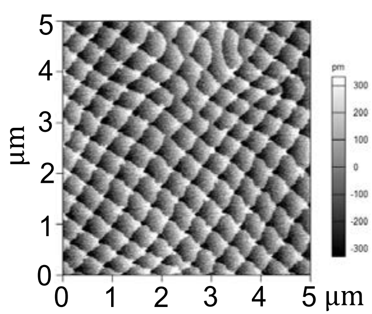




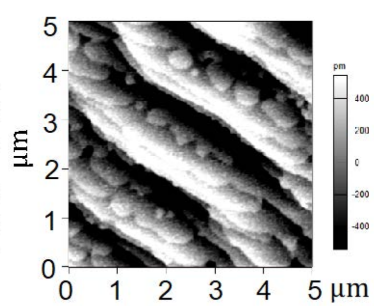
Single step



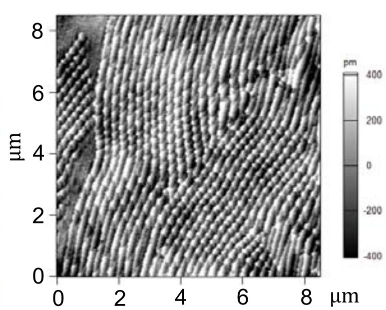
Step bunched



Fish-Skin



Islands

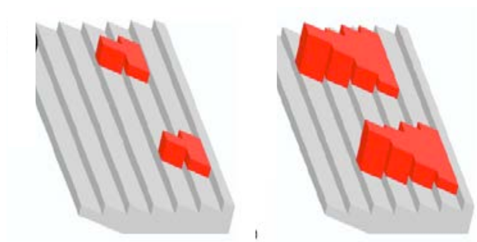


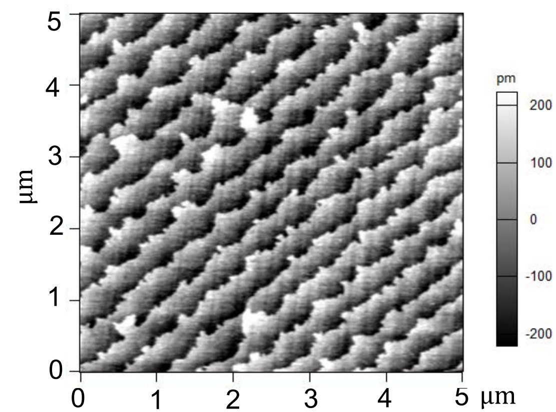
Mixed growth regime

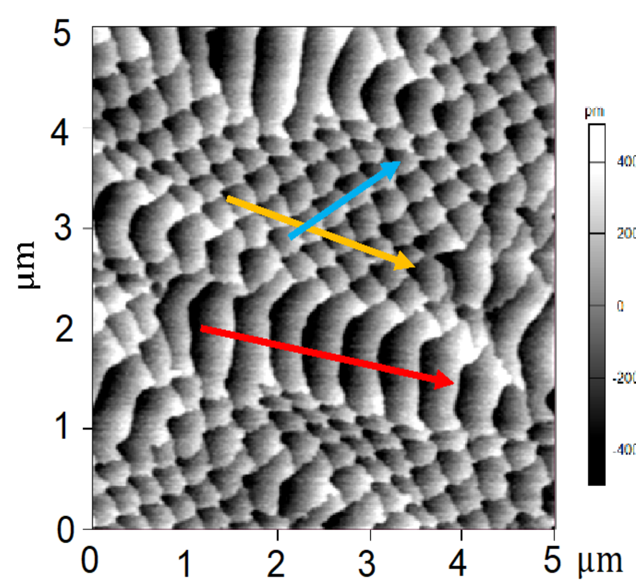
A. Gura et al., *Phys. Rev. B,* Submitted.

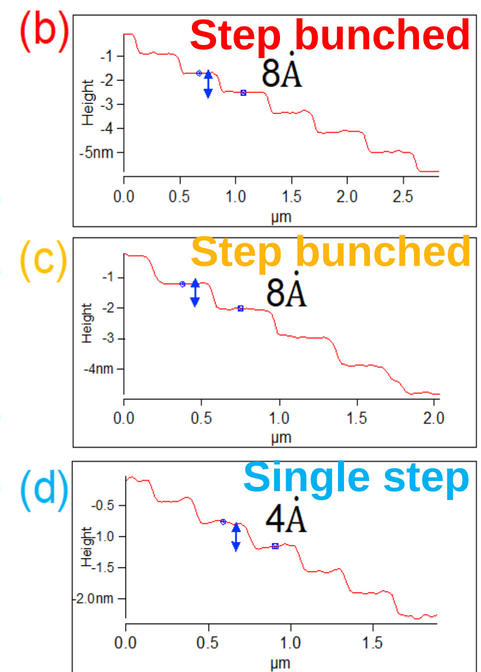
Fish-skin structure as a result of 2D islands merging

- 2D flat triangular islands nucleate at step edges
- Islands grow laterally along the steps
- Merging → **Fish-skin.**
- Growth proceeds perpendicularly to step edges → **Step bunching.**
- Step bunched steps cover several single-unit steps of the substrate





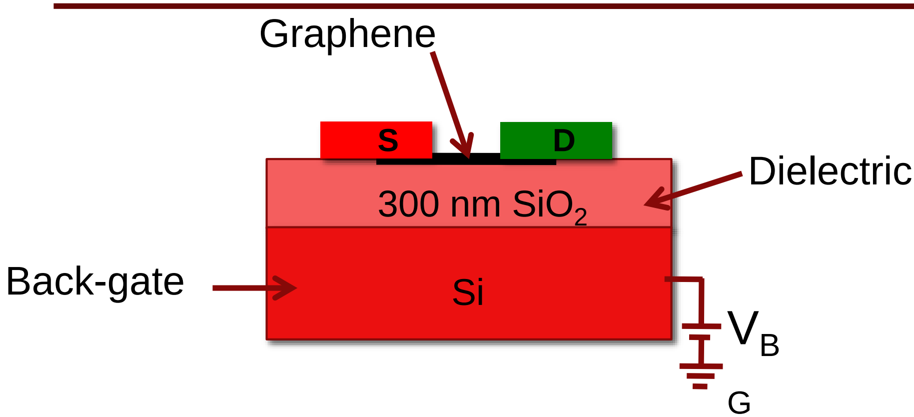




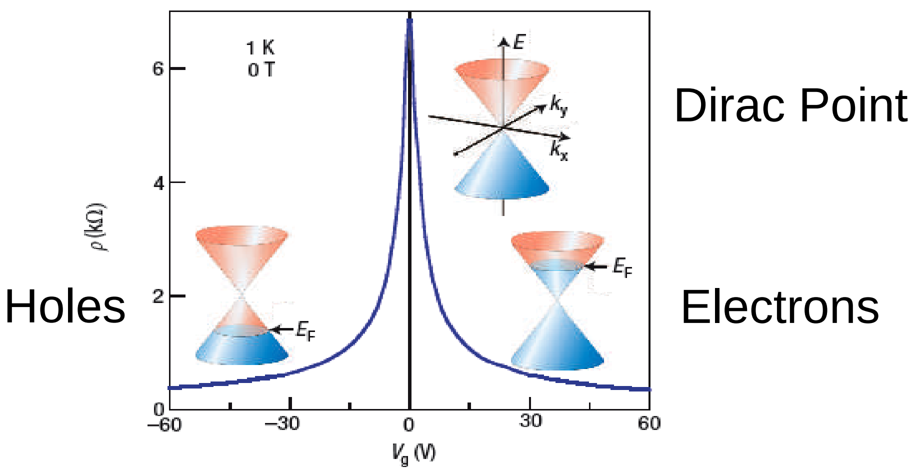
F. Sanchez et al., *J. Cryst. Growth*, 310 (14) (2008).
F. Sanchez et al., *Phys. Rev.* B, 73 (7) (2006).
A. Gura et al., *Phys. Rev. B,* Submitted.

- Graphene/Ferroelectric hybrid devices

Graphene



Graphene Field Effect Transistor (FET)

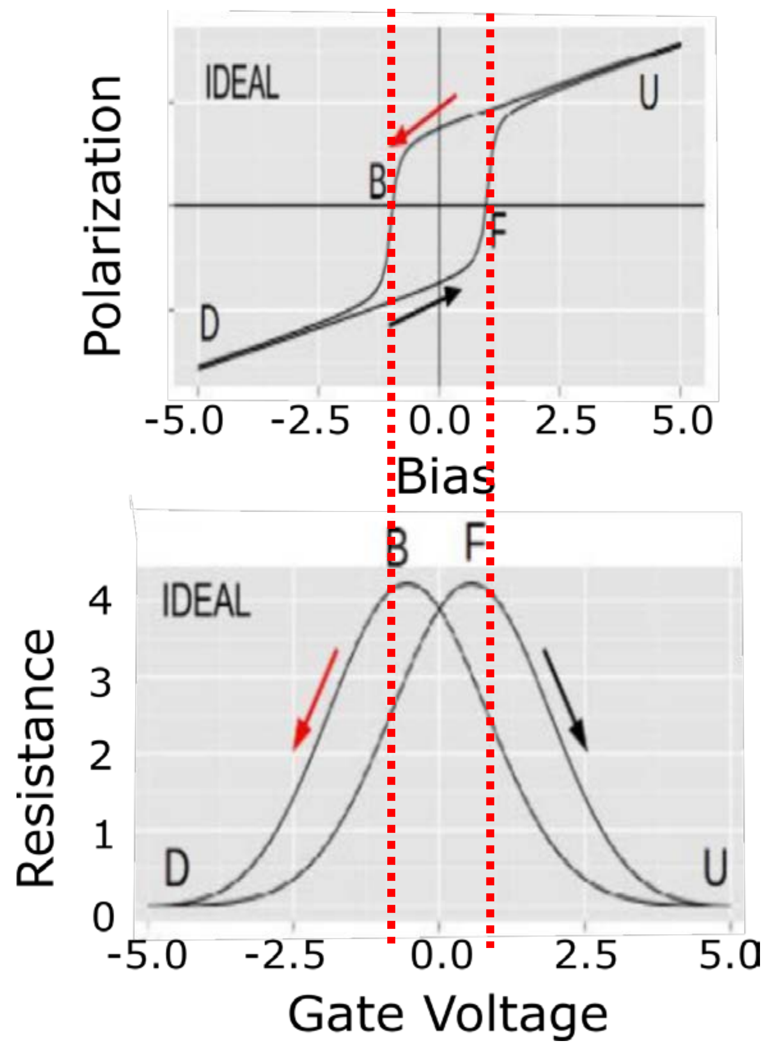


Graphene Gating Curve

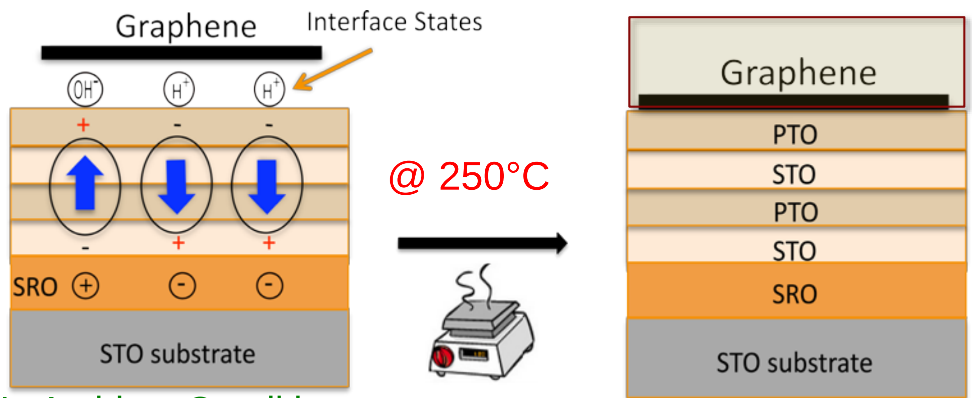
(A. Geim et al., Nat. Mater., **6**, 183, (2007))

Motivation

Hysteresis



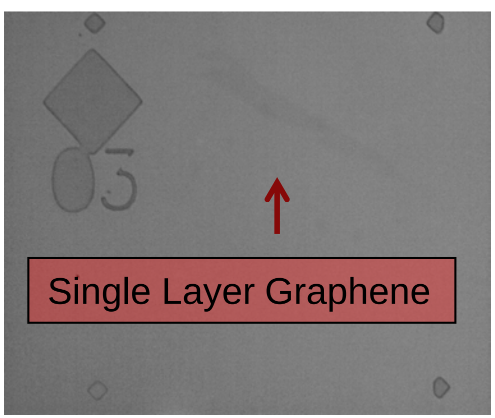
Graphene Deposition and Interface Dependence



In Ambient Conditions

$$P \; \alpha \; (T_c - T)^{0.5}$$

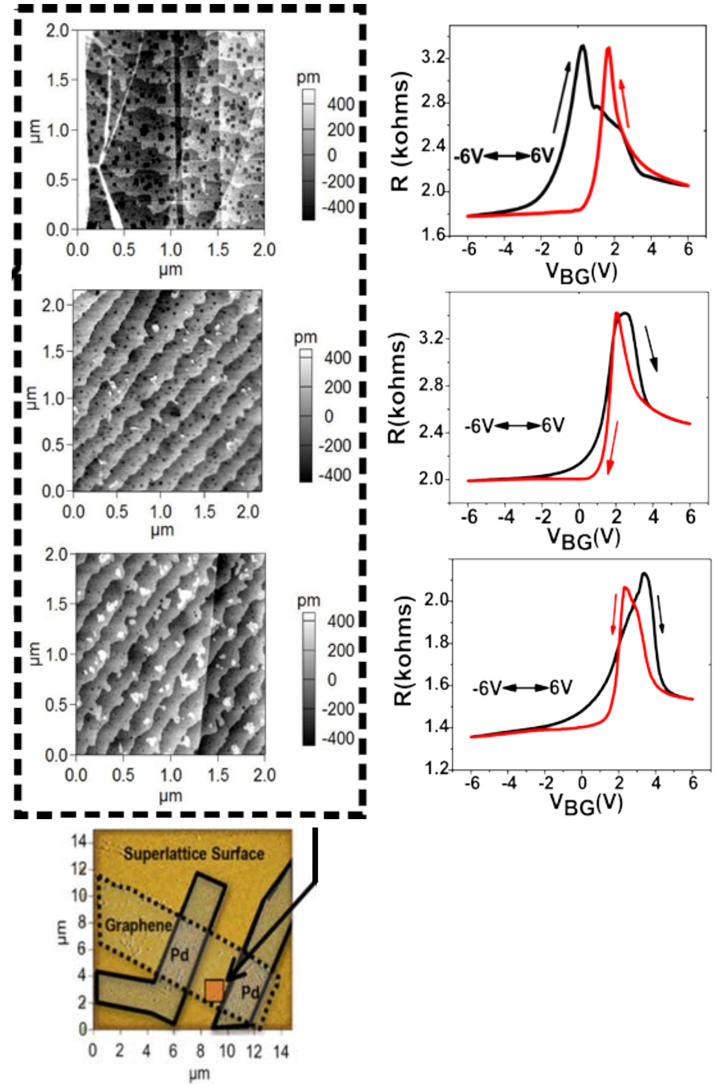
Polarization Reduction as much as 70%



Locating Graphene

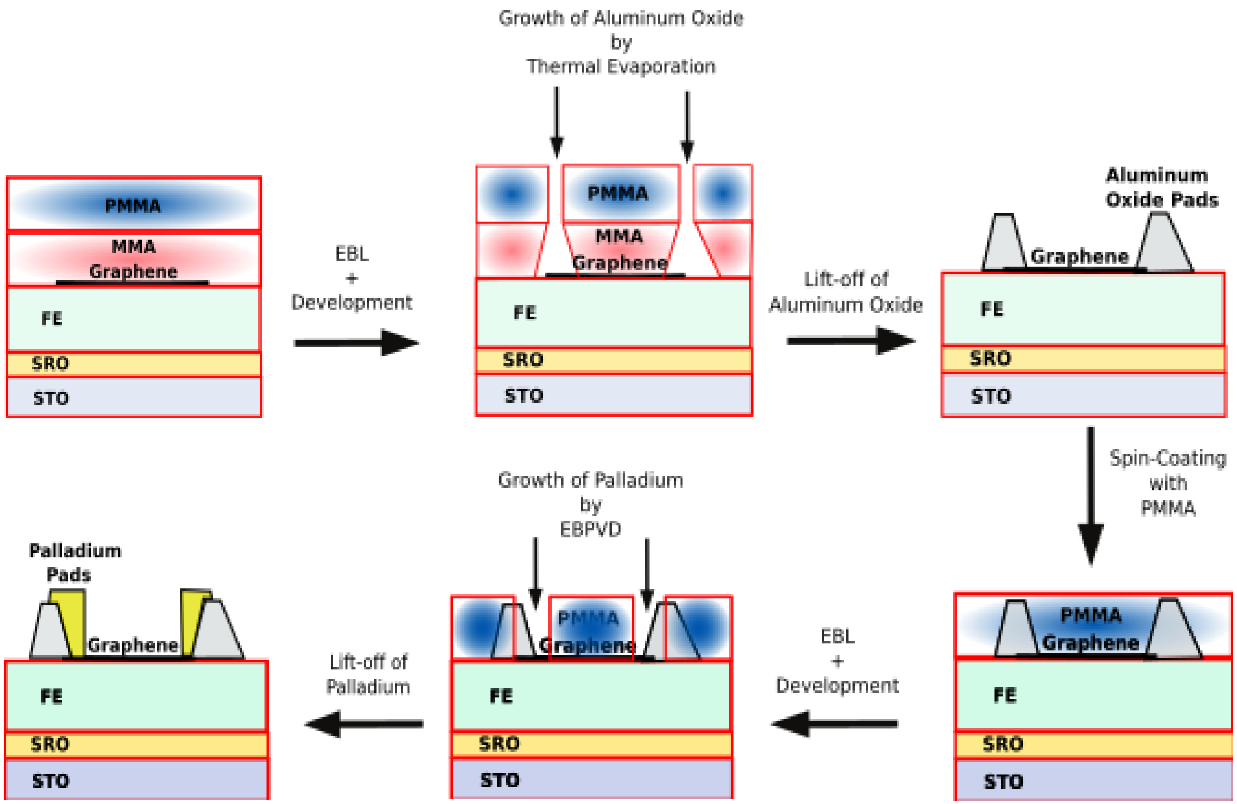
AFM Maps

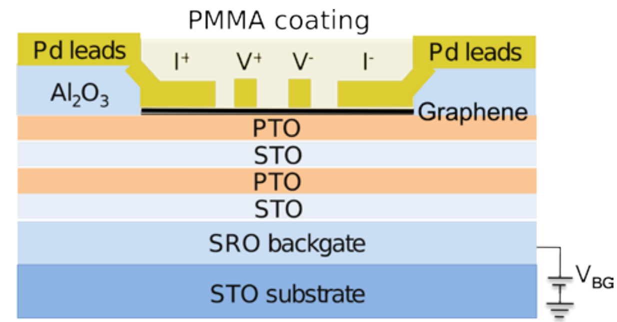
Channel Behavior



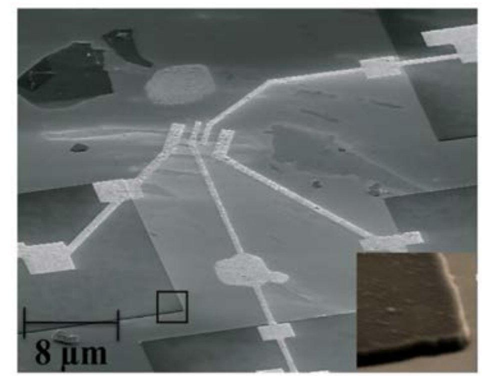
(M. H. Yusuf et al., Nano Letters, **14**, 5437, (2014))

Nanofabrication and Device Architecture





Device Schematics

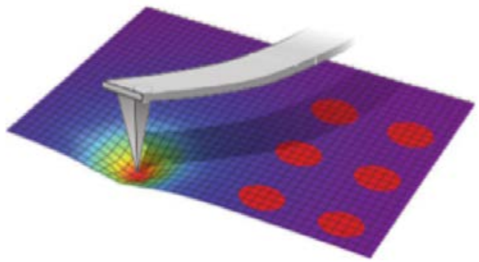


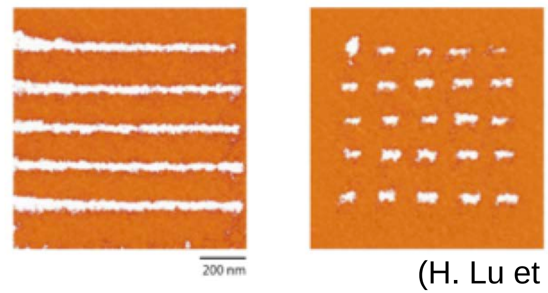
SEM Micrograph of a Device
Inset: 150 nm Al_2O_3 Electrical Insulation

(M. H. Yusuf et al., Nano Letters, **14**, 5437, (2014))

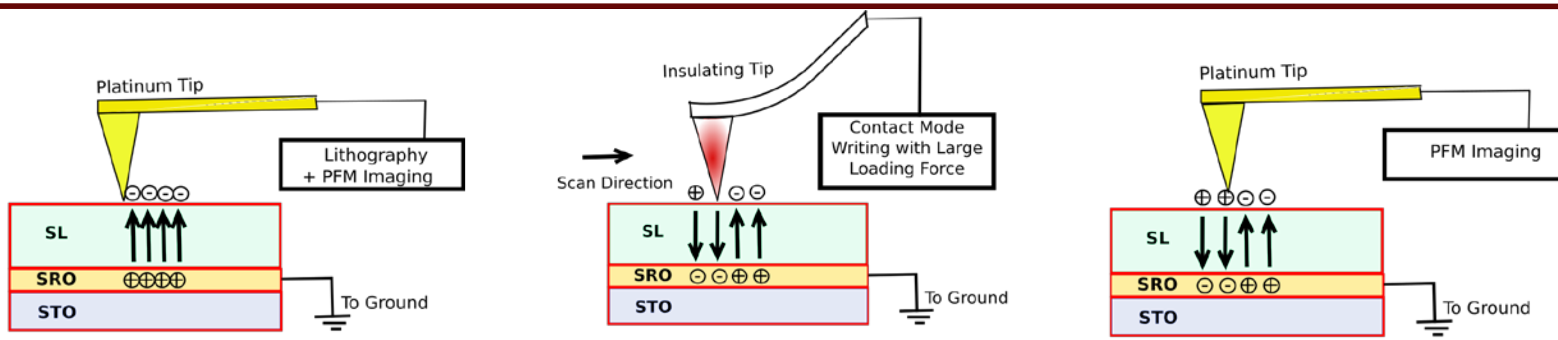
Flexoelectric Switching on 15 PTO/ 3 STO Superlattices

Mechanical Switching of Polarization

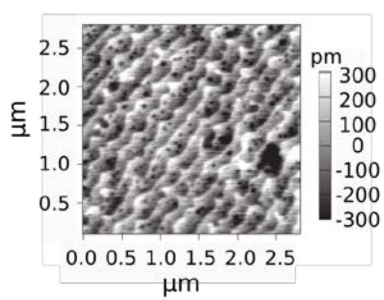




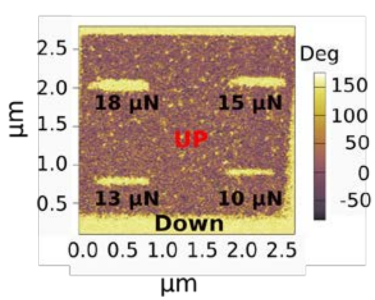
(H. Lu et al., Science, **336**, 59, (2012))



PFM Imaging After Flexoelectric Switching

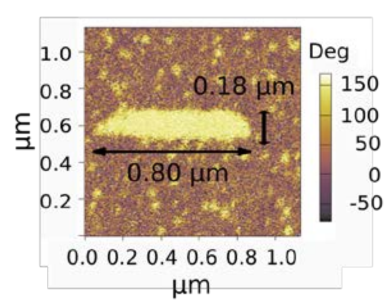


Height Map

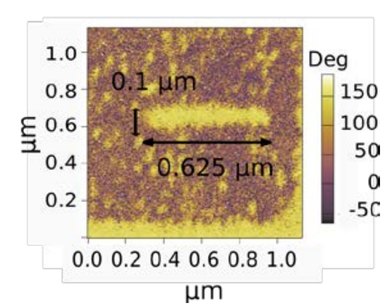


PFM Phase Map

Resolution of the Features with Varying Force



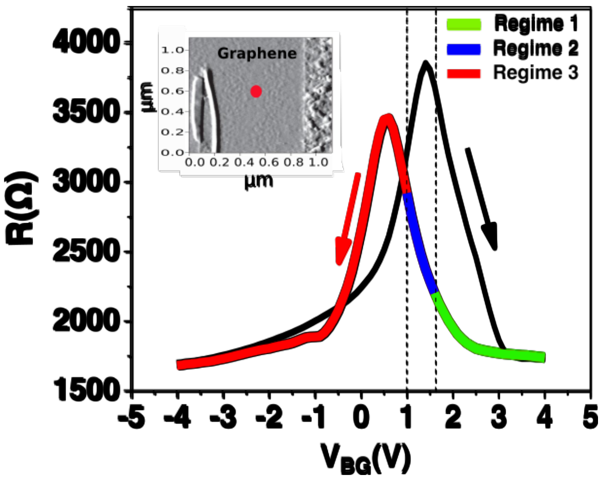
18 µN (Zoomed)



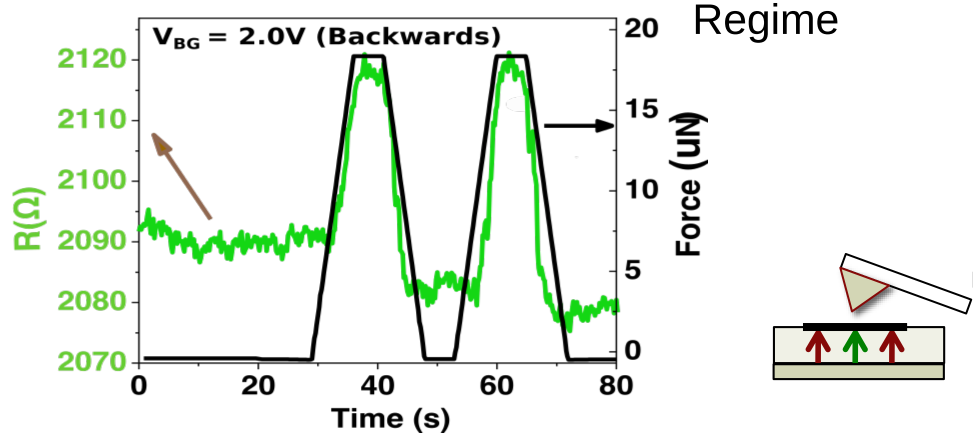
10 µN (Zoomed)

(M. H. Yusuf et al., 2D Materials, (2017))

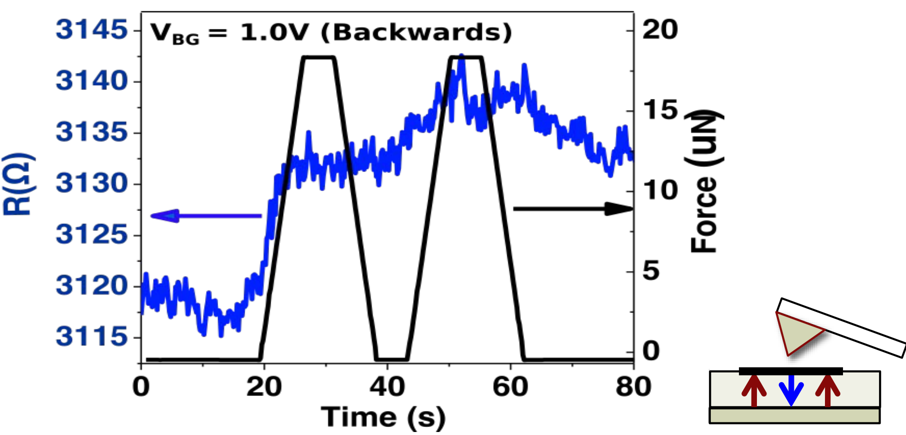
Switching Regimes on Graphene



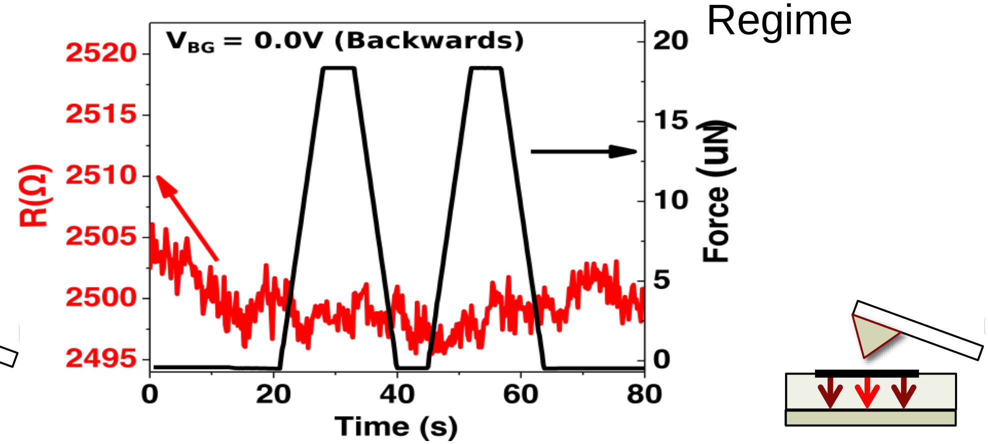
"Up-Dominant" Regime



"Writing Window"

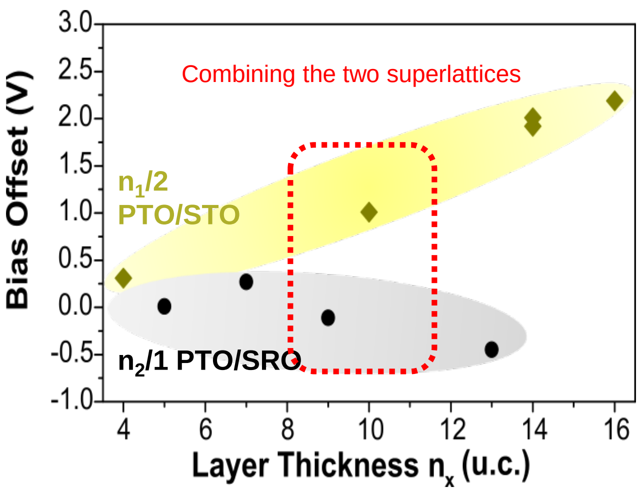


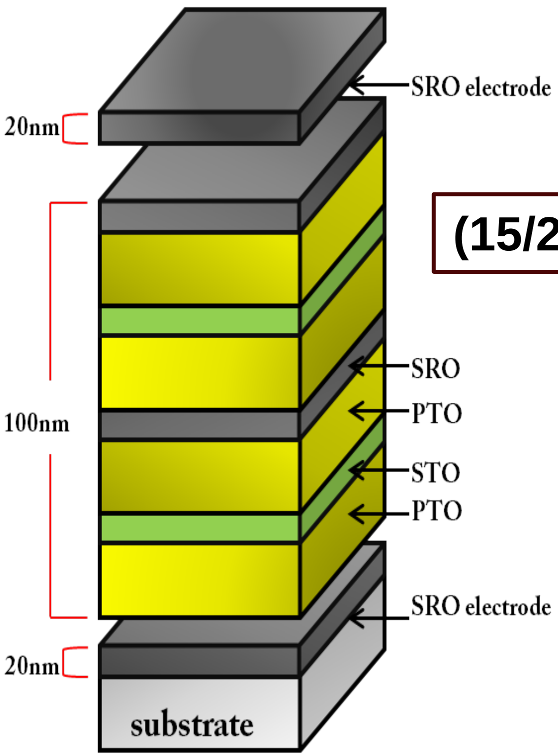
"Down-Dominant" Regime



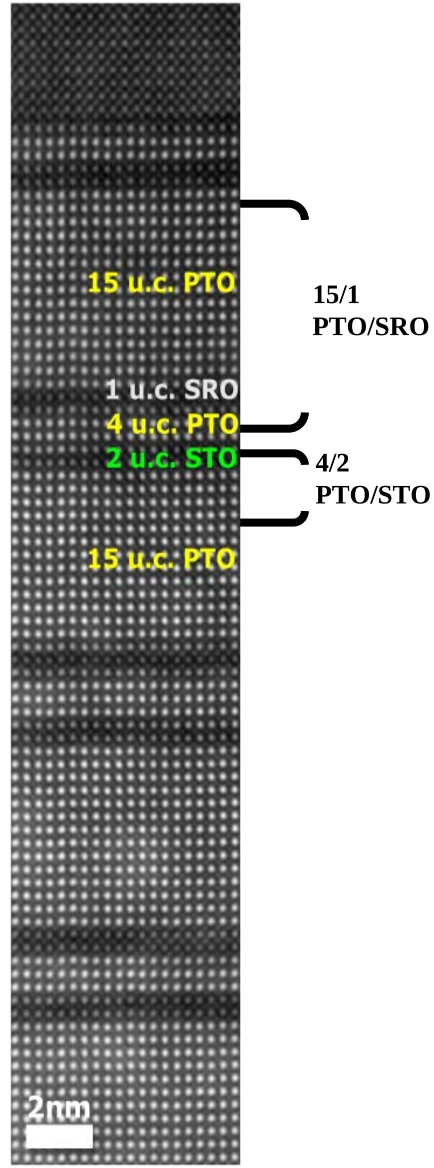
(M. H. Yusuf et al., 2D Materials, (2017))

Hybrid Superlattice to Eliminate Internal Bias



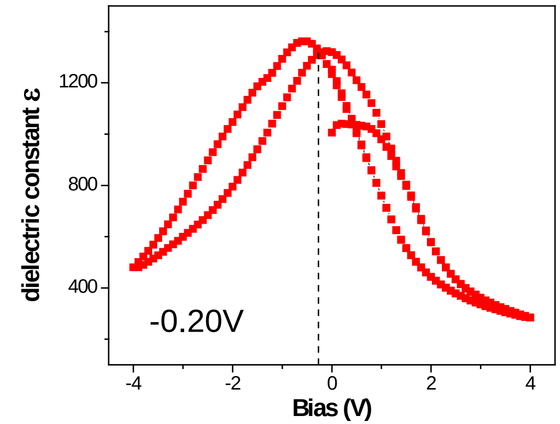


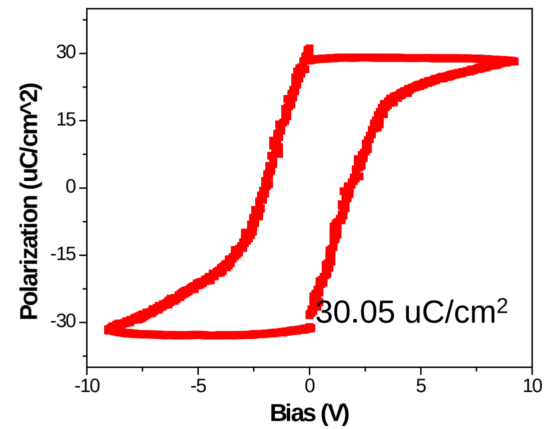
(15/2/4/1)

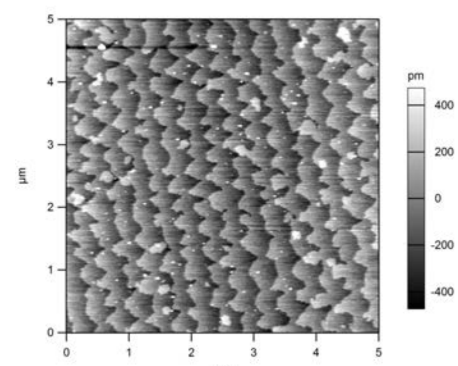


TEM image

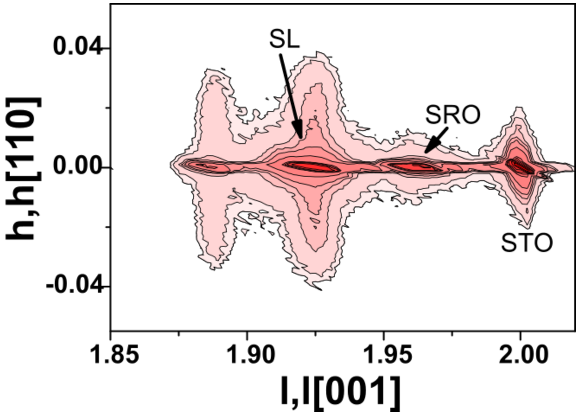
(Greg Hsing)



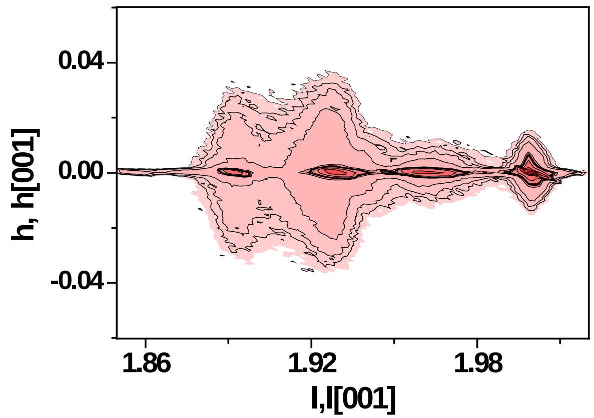




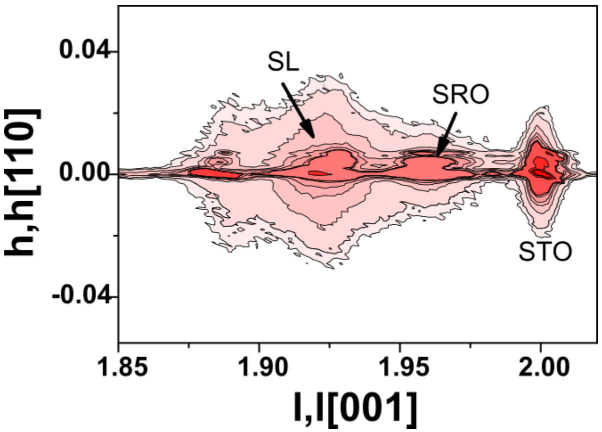
Top Electrode Effect on Internal Bias



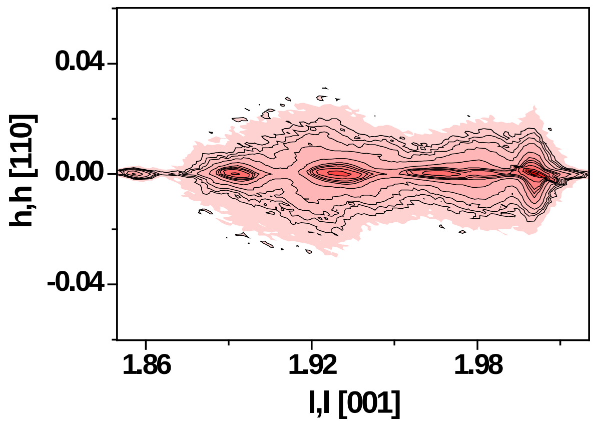
Sample grown *without* top SRO electrode



Sample grown *without* top SRO electrode ***pre-anneal***



Sample grown *with* top SRO electrode



Sample grown *without* top SRO electrode ***post-anneal***

Thank you for your attention!

Humed Yusuf (Intel)

Greg Hsing

Matt Dawber

Ben Bein

Me, again

Rui, again

Ferroelectric Oxides Group at Stony Brook University