Multiple Modulation and Higher Harmonic SPM Probing Complex Properties

Dawn A. Bonnell,

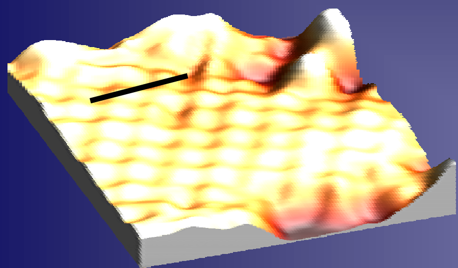
M. Nikiforov, S-H. Kim, R. Shao, D. Strachen, C. Staii, A. T. Johnson

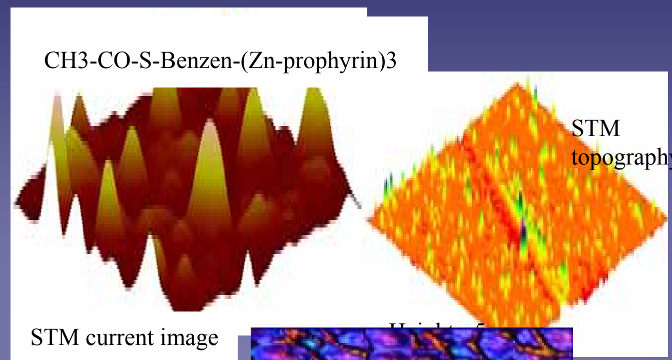
The University of Pennsylvania

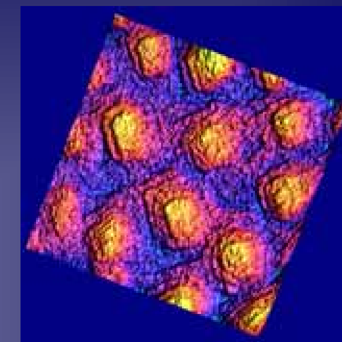
NSF: NIRT, NSEC, MRSEC

Not Only Structure ….. Also Properties

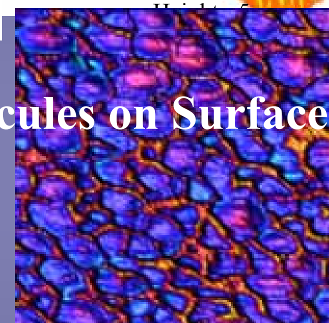
Functional Oxide Structure





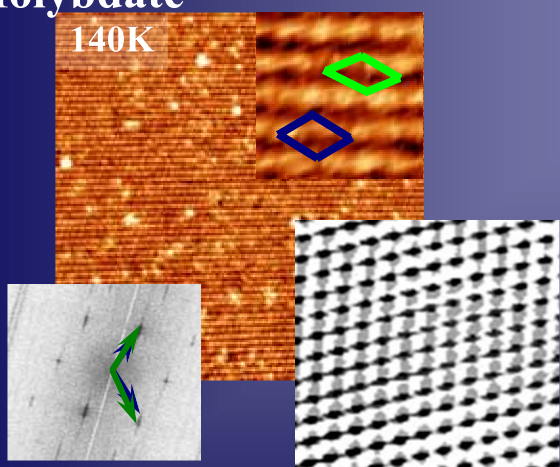


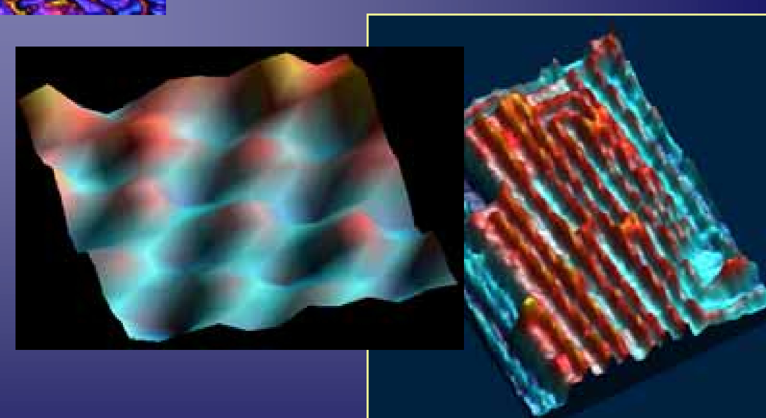
Biomolecules on Surfaces



Spin and Charge: La Manganates

Separating Atomic Lattice and Charge Lattice: Potassium Molybdate





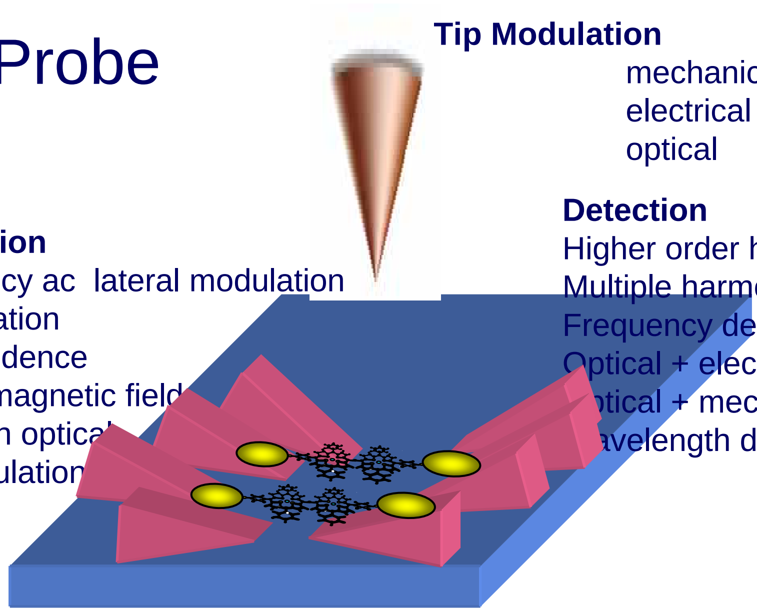
Atomic Structure and Ferroelectric Polarization; BaTiO3

The Ideal Probe

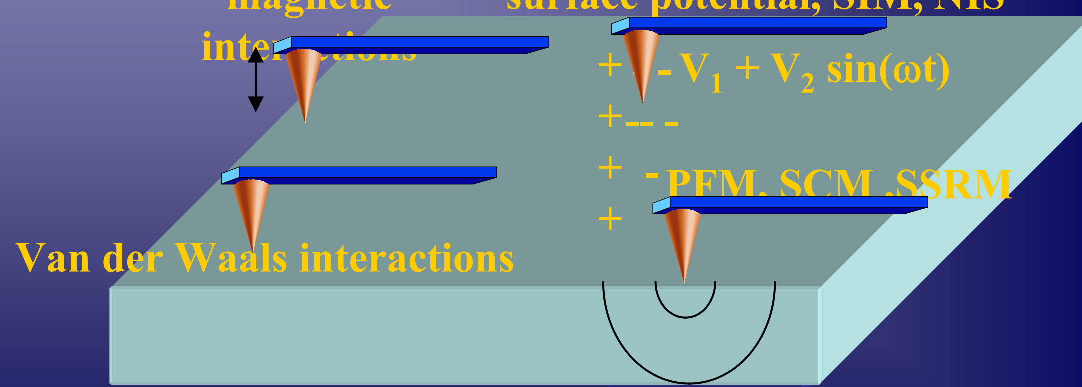
Tip Modulation
- mechanical
- electrical
- optical

Detection
- Higher order harmonics
- Multiple harmonics
- Frequency dependence
- Optical + electrical
- Optical + mechanical
- Wavelength dependence

Sample stimulation
- dc + high frequency ac lateral modulation
- Back gate modulation
- Frequency dependence
- Dc + modulated magnetic field
- Single wavelength optical
- Wavelength modulation



Temperature
Chemical environment



Mechanically driven **electrostatically driven**

Multiple Modulation/Higher Harmonics Yield Properties

Technique	Mode	Property
AFM	nc/ic, mech, phase/amp	VdW interaction, topography
EFM	nc, mech, phase/amp	electrostatic force,
MFM	nc, mech, phase/amp	magnetic force, current flow
MM-MFM	nc, elec, phase/amp	potential, potential corrected magnetic force, current
SSPM, KPM	nc, elec, 1st harmonic	potential, work function, adsorbate enthalpy/entropy
SCM	c, F, cap sensor	capacitance, relative dopant density
SCFM	c, elec, 3rd harmonic	dC/dV, dopant profile
SSRM	c, F, dc current	resistivity, relative dopant density
SIM	nc, elec, phase/amp	interface potential, capacitance, time constant, local band energy, potential, current flow
NIS	c,F, freq spectrum	interface potential, capacitance, time constant, quantitative dopant profiling
PFM	c, elec, phase/amp	piezo electric coefficient, d33
NPFM	c, elec, 2nd harmonic	switching dynamics (relaxation time and domain nucleation)
SNDM	c, F, 1st or 3rd harmonic	dC/dV, dielectric constant
SMM	c, F, phase	microwave losses, dielectric constant

Shao and Bonnell, Critical Opinions In Solid State 2004

Scanning Impedance Microscopy

- exploiting sample perturbation and frequency dependence
- electrons trapped at an interface
- band energies in a nanotube

Higher Harmonics

- dielectric constant of a thin film
- dielectric constant of nanowires
- density of states of nanotubes

Higher Harmonics in Tip Scattered Optical Signal

- dielectric function of porphyrin

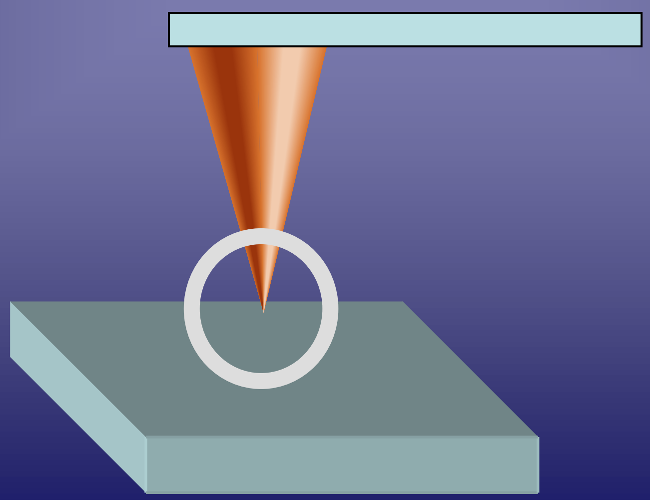
An Oscillating Electrical Signal

$$F(z) = \frac{1}{2}\frac{\partial C(z)}{\partial z}\left[\left(V_{dc} - V_{surf}\right)^2 + \frac{1}{2}V_{ac}^2\left[1 - \sin(2\omega t)\right] + 2\left(V_{dc} - V_{surf}\right)V_{ac}\cos(\omega t)\right]$$

$$F_{dc}(z) = \frac{1}{2}\frac{\partial C(z)}{\partial z}\left[\left(V_{dc} - V_{surf}\right)^2 + \frac{1}{2}V_{ac}^2\right]$$

$$F_{1\omega}(z) = \frac{\partial C(z)}{\partial z}\left(V_{dc} - V_{surf}\right)V_{ac}$$

$$F_{2\omega}(z) = \frac{1}{4}\frac{\partial C(z)}{\partial z}\mathrm{V}_{\mathrm{ac}}^2$$



An Oscillating Electrical Signal

$$F_{1\omega}(z) = \frac{\partial C(z)}{\partial z}\left(V_{dc} - V_{surf}\right)V_{ac}$$

$$F_{2\omega}(z) = \frac{1}{4}\frac{\partial C(z)}{\partial z}\mathrm{V}_{\mathrm{ac}}^{2}$$

Scanning Surface Potential Microscopy/Kelvin Force Microscopy
Scanning Impedance Microscopy
Gated Scanning Impedance

An Oscillating Electrical Signal

$$F_{1\omega}(z) = \frac{\partial C(z)}{\partial z}\left(V_{dc} - V_{surf}\right)V_{ac}$$

$$F_{2\omega}(z) = \frac{1}{4}\frac{\partial C(z)}{\partial z}\mathrm{V}_{\mathrm{ac}}^{2}$$

New Variants of SSPM/KFM and EFM

Dielectric function
Quantum capacitance
Density of states

An Oscillating Electrical Signal

$$F(z) = \frac{1}{2}\frac{\partial C(z)}{\partial z}\left[\left(V_{dc} - V_{surf}\right)^2 + \frac{1}{2}V_{ac}^2\left[1 - \sin(2\omega t)\right] + 2\left(V_{dc} - V_{surf}\right)V_{ac}\cos(\omega t)\right]$$

$$F_{dc}(z) = \frac{1}{2}\frac{\partial C(z)}{\partial z}\left[\left(V_{dc} - V_{surf}\right)^2 + \frac{1}{2}V_{ac}^2\right]$$

$$F_{1\omega}(z) = \frac{\partial C(z)}{\partial z}\left(V_{dc} - V_{surf}\right)V_{ac}$$

$$F_{2\omega}(z) = \frac{1}{4}\frac{\partial C(z)}{\partial z}\mathrm{V}_{\mathrm{ac}}^2$$

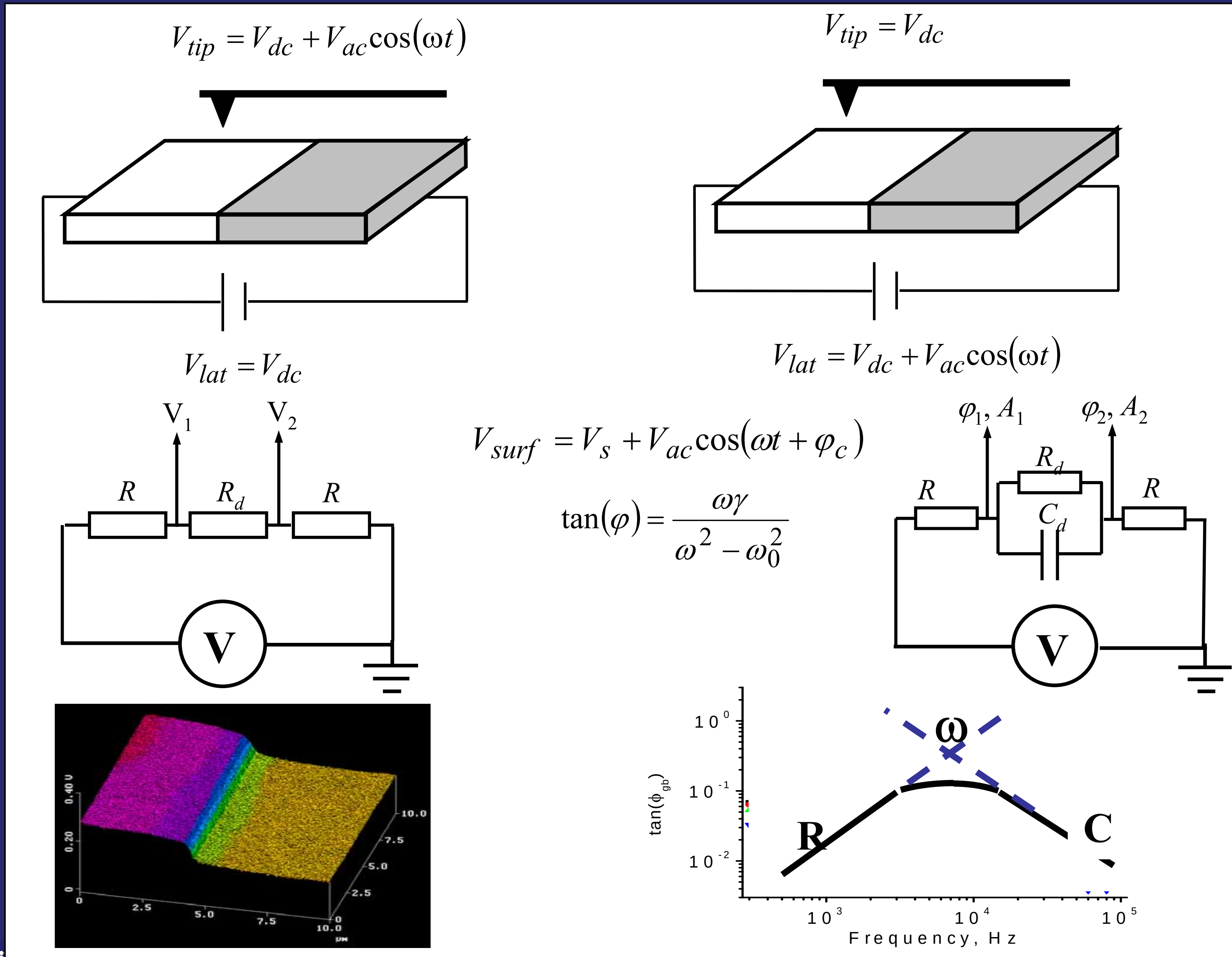
An Oscillating Electrical Signal

$$F_{1\omega}(z) = \frac{\partial C(z)}{\partial z}\left(V_{dc} - V_{surf}\right)V_{ac}$$

$$F_{2\omega}(z) = \frac{1}{4}\frac{\partial C(z)}{\partial z}\mathrm{V}_{\mathrm{ac}}^{2}$$

Scanning Surface Potential Microscopy/Kelvin Force Microscopy
Scanning Impedance Microscopy
Gated Scanning Impedance

Scanning Impedance Microscopy: a local probe



NANO / BIO INTERFACE CENTER

Kalinin and Bonnell, Appl. Phys. Lett., 2001, US patent

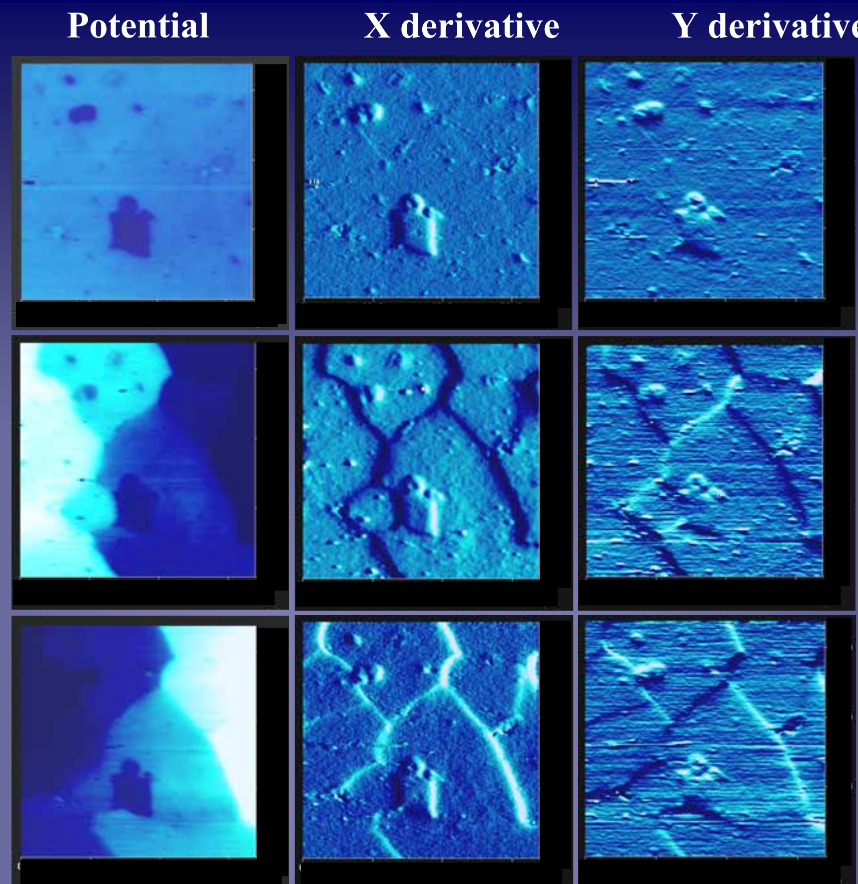
Shao, Kalinin, Bonnell, APL 2003

ZnO Varistor Device in Operation

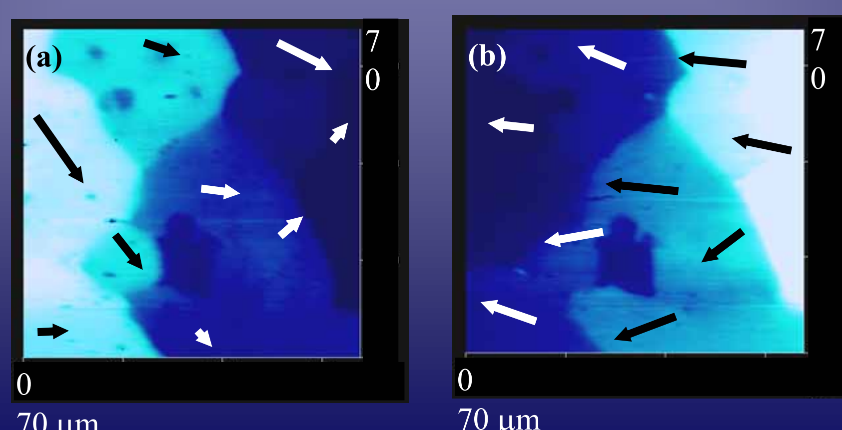
No applied bias

Positive lateral bias

Negative lateral bias

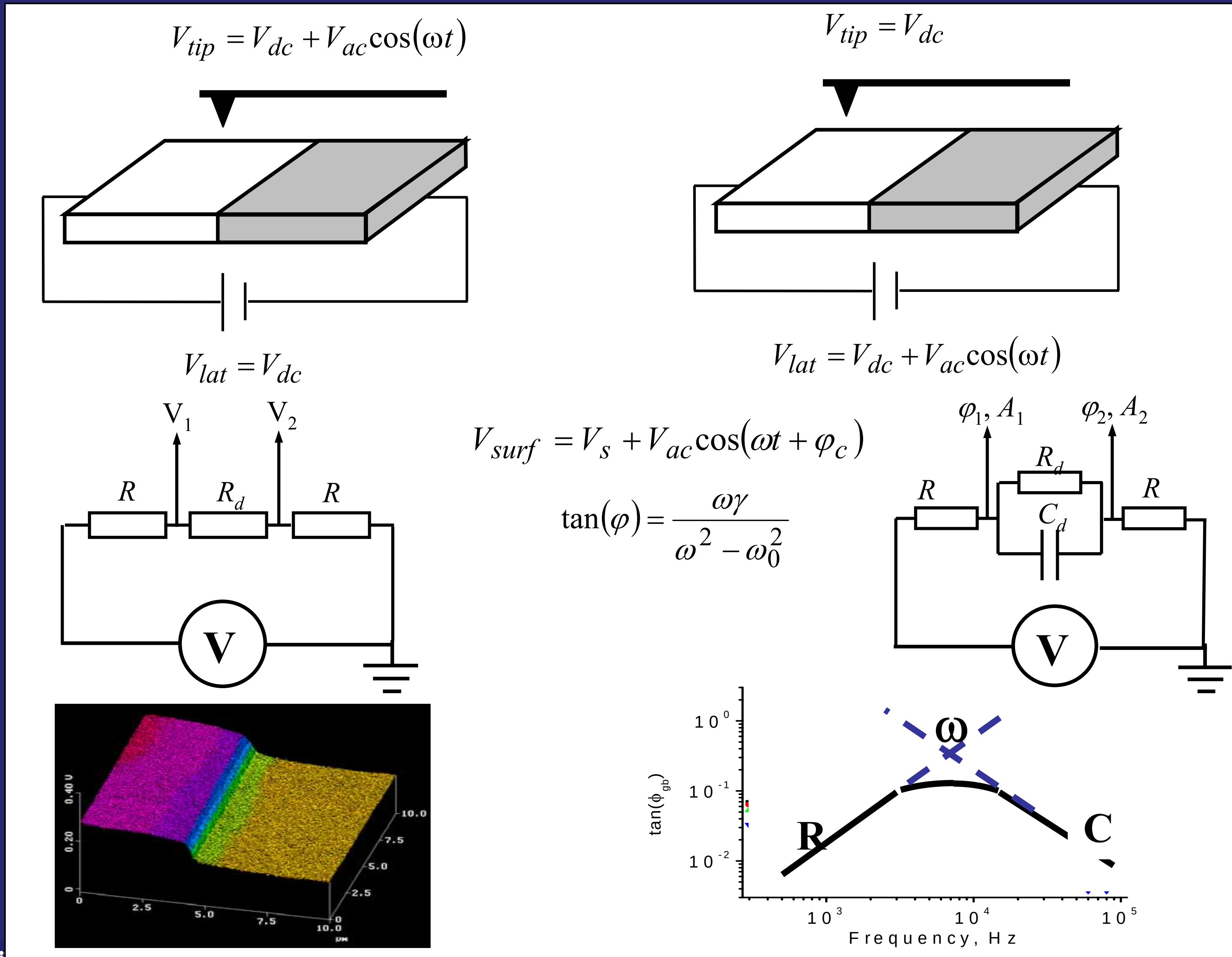


Current Flow Maps



D. A. Bonnell,S. Kalinin
Proc. of Int, PolySe (2000)

Scanning Impedance Microscopy: a local probe

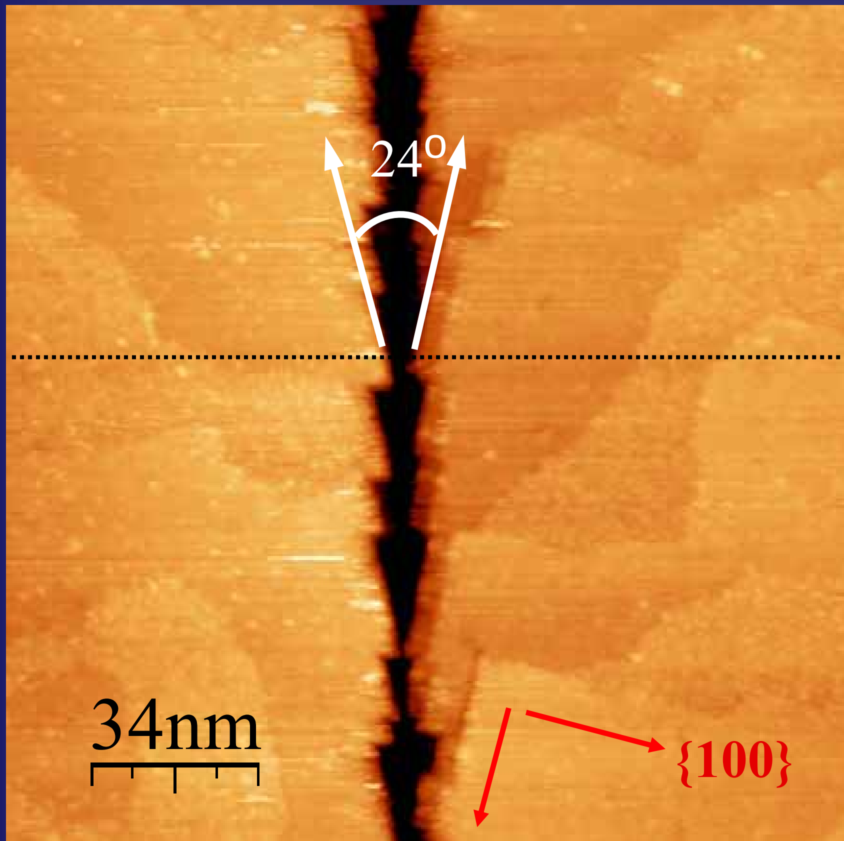


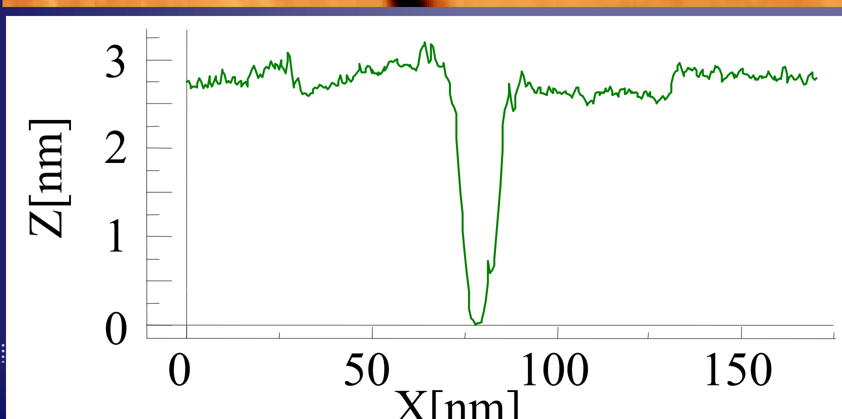
NANO / BIO INTERFACE CENTER

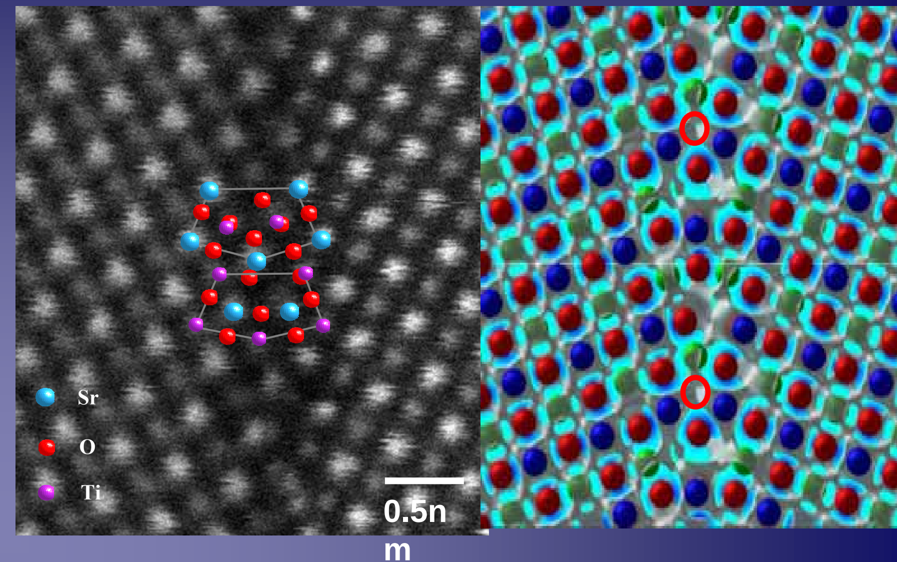
Kalinin and Bonnell, Appl. Phys. Lett., 2001, US patent

Shao, Kalinin, Bonnell, APL 2003

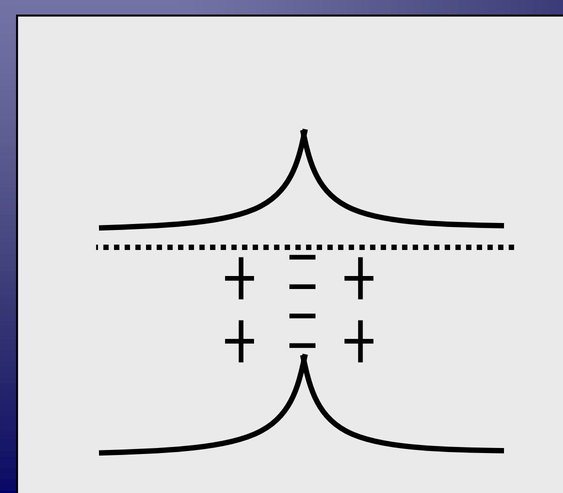
Grain Boundary Structure



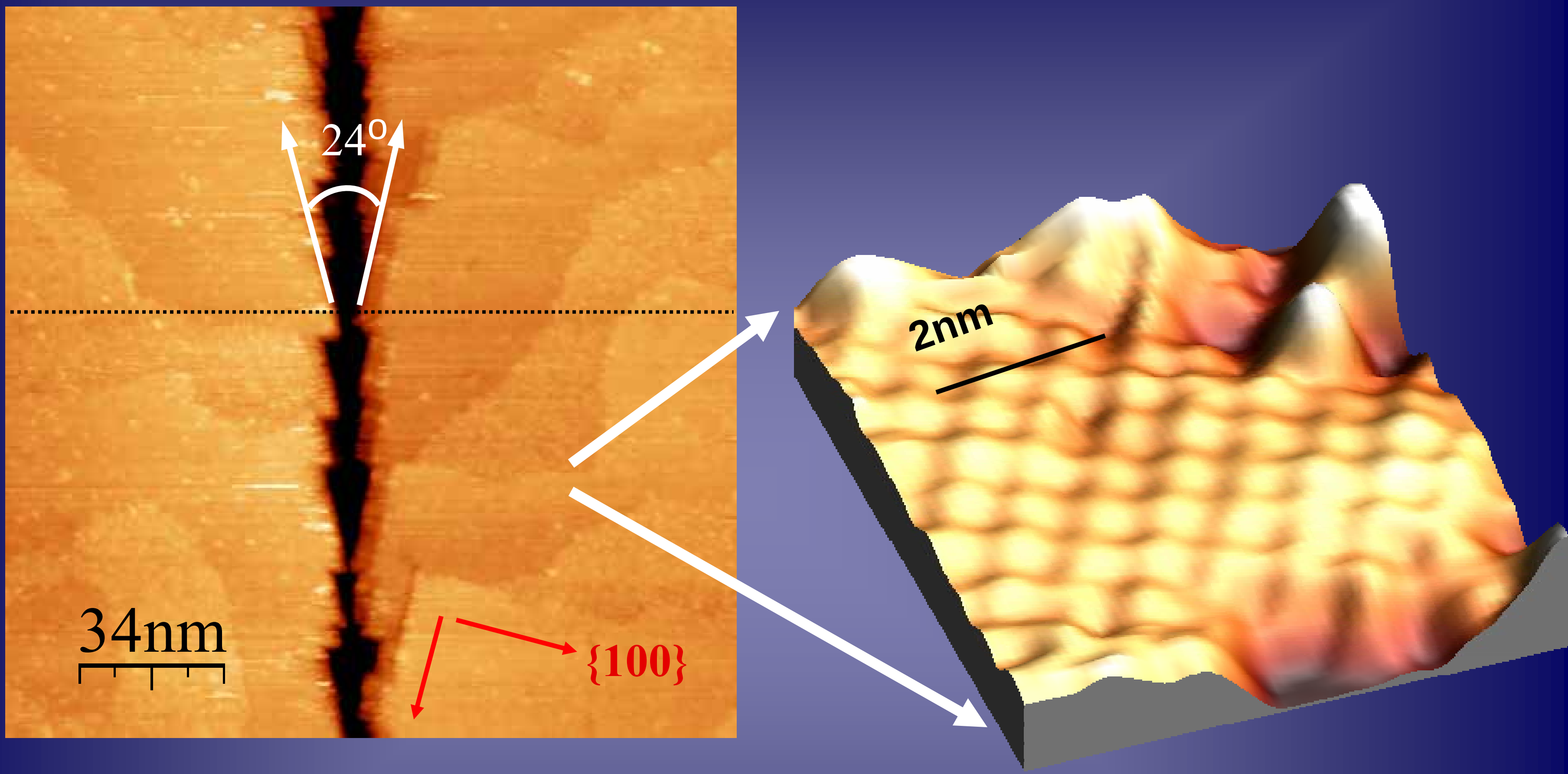




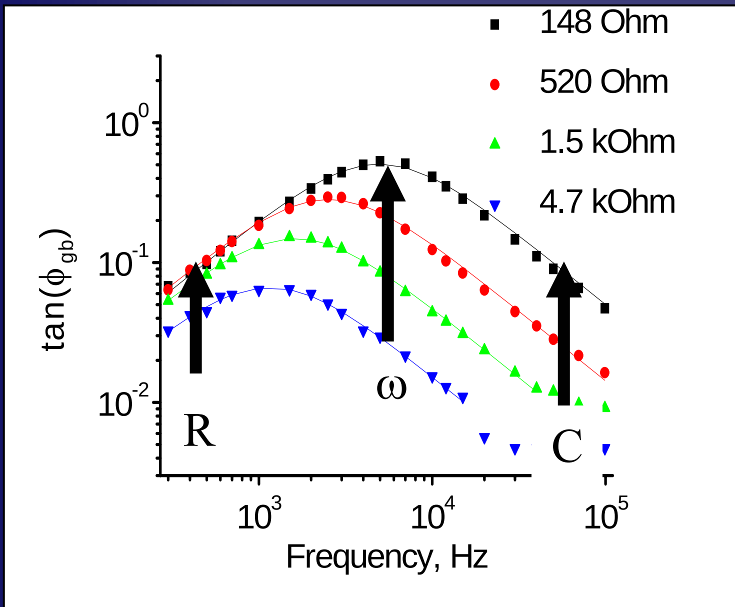
Aberration corrected STEM image of a $SrTiO_3$ bicrystal and calculated charge density

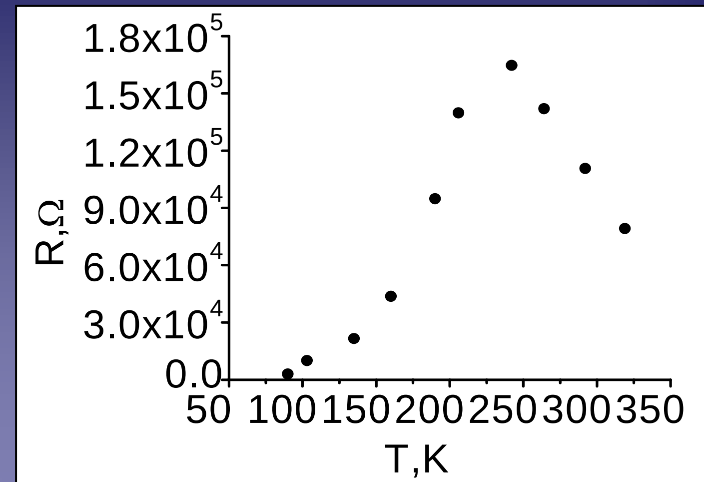


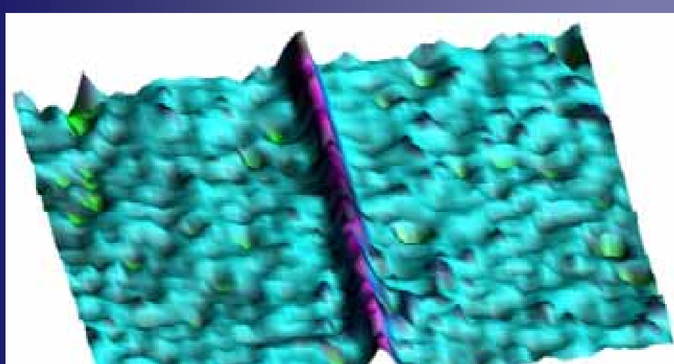
Fine Structure at the Grain Boundary



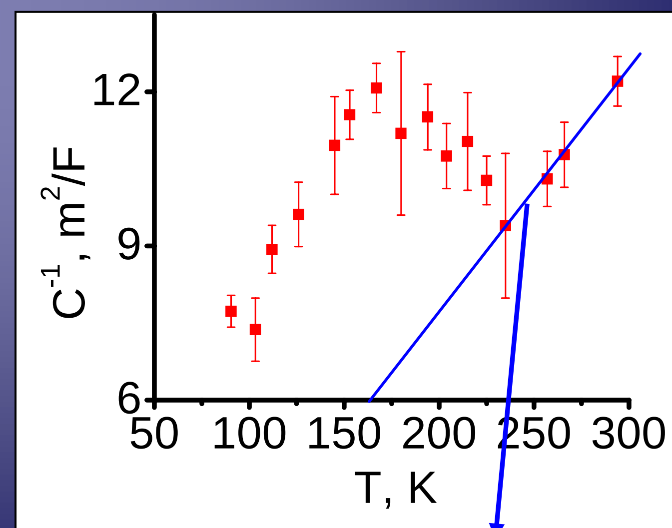
Temperature Dependent SIM Identifies an Interface Induced Ferroelectric Phase Transition in $SrTiO_3$







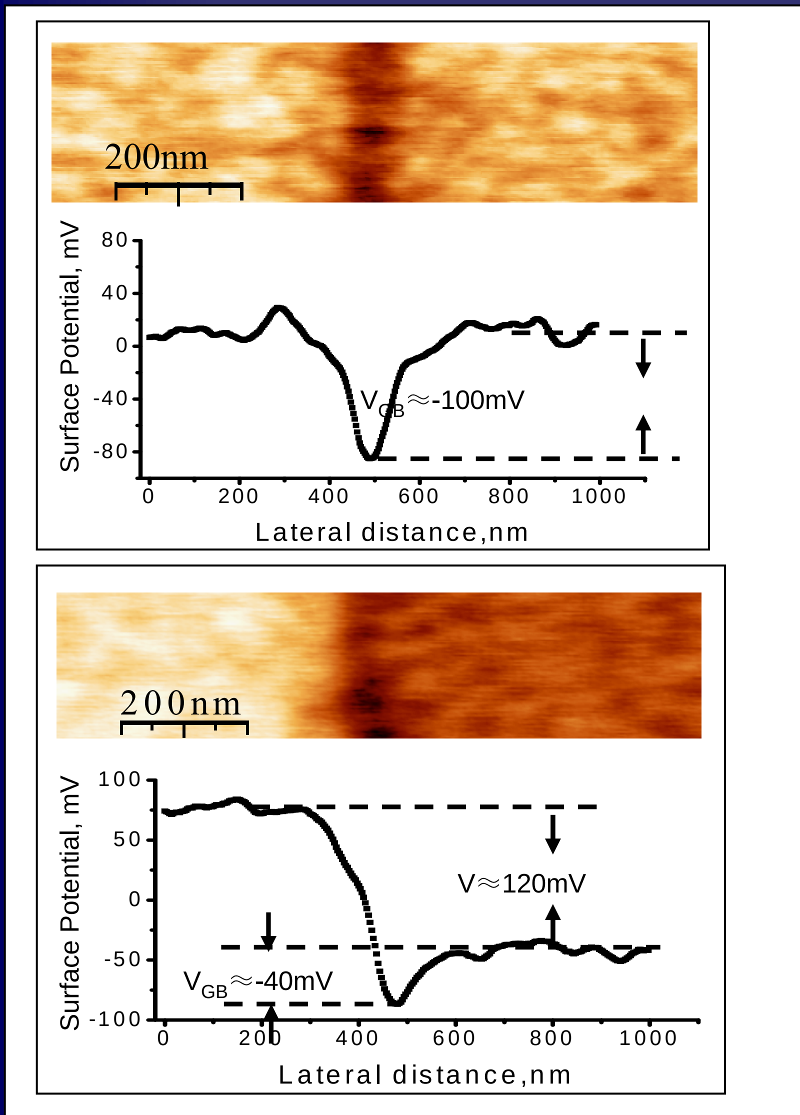
Scanning surface potentiometry

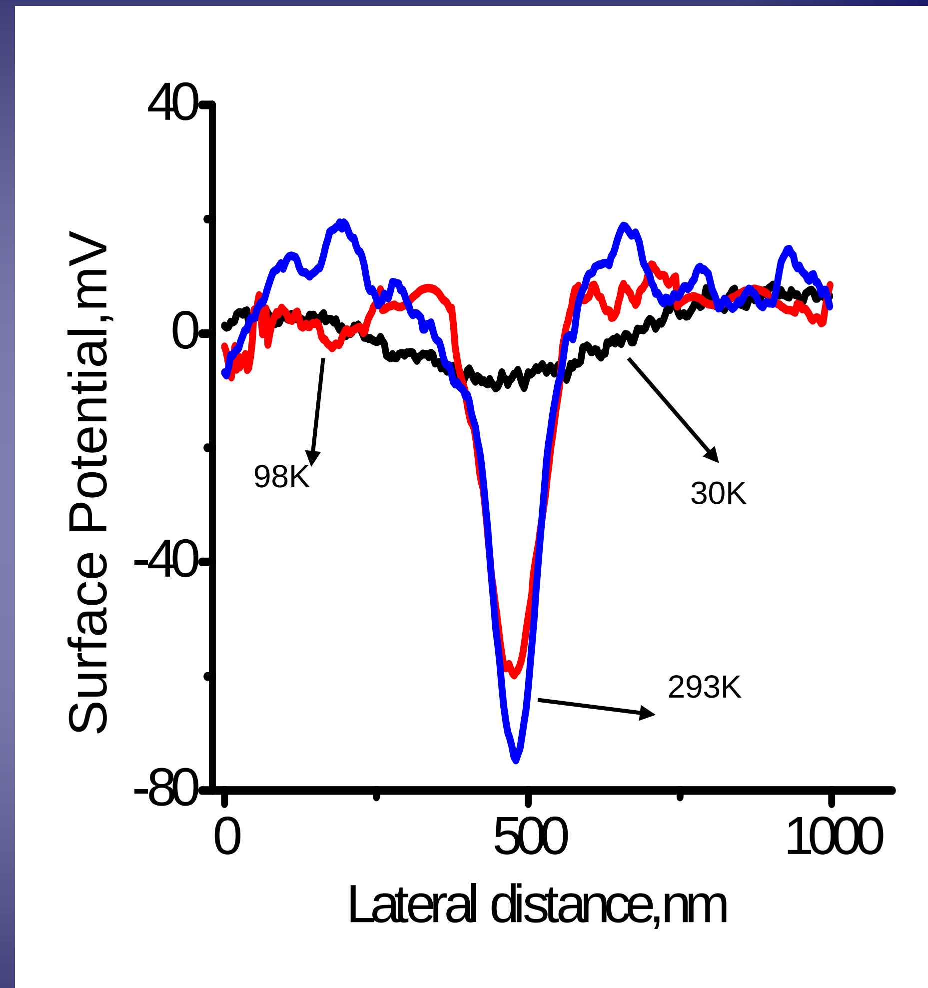


Curie-Weiss Law: $C_{gb}^{-1} \propto T - T_C$ **and** T_C=40K

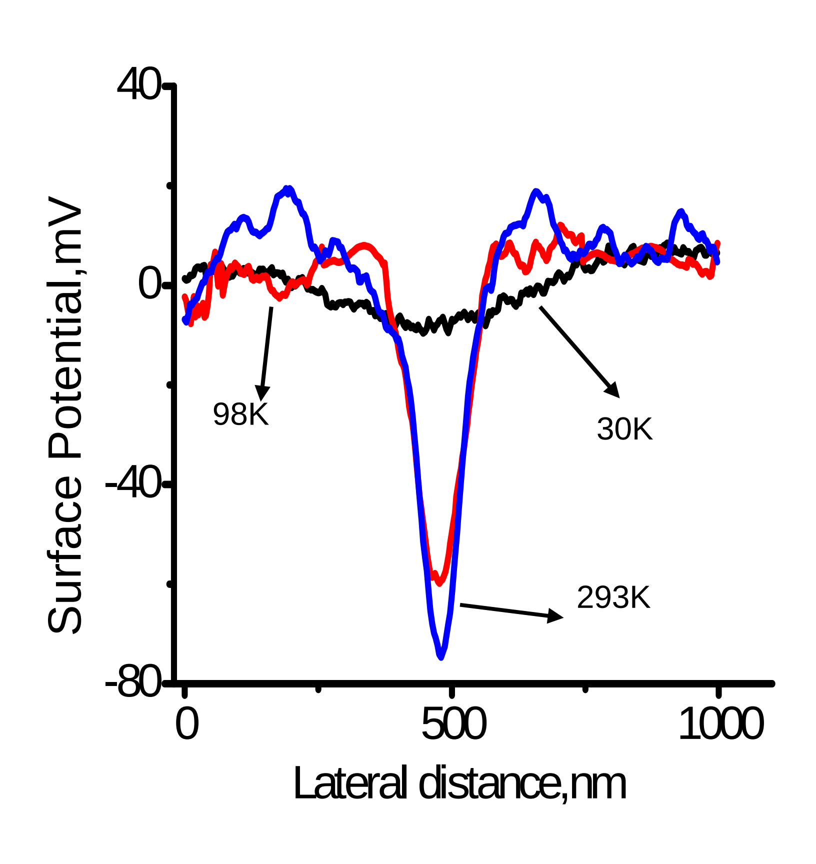
Shao, Duscher, Chisholm, Bonnell, PRL (2005)

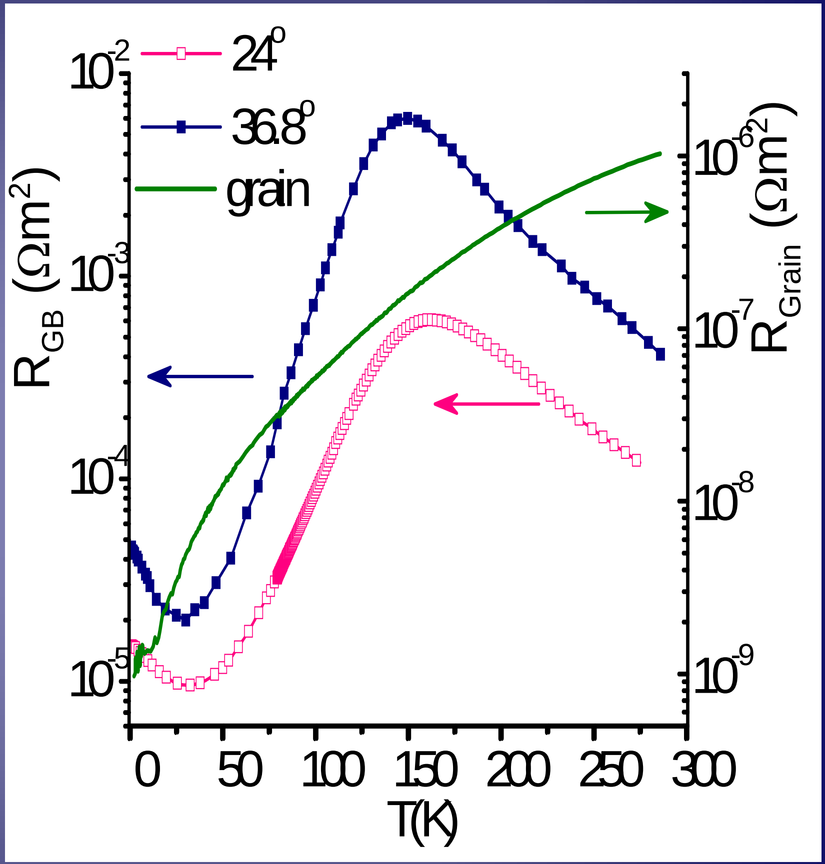
Direct Imaging of the Boundary Potential





Temperature Dependent Transport Reveals Collapse of the Interface Potential Barrier in $SrTiO_3$

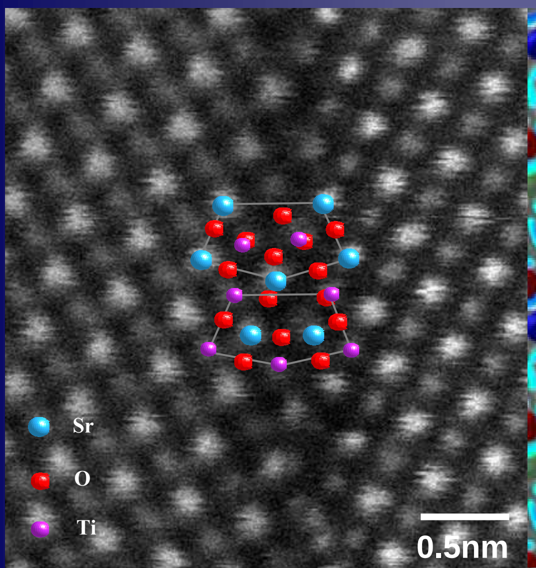




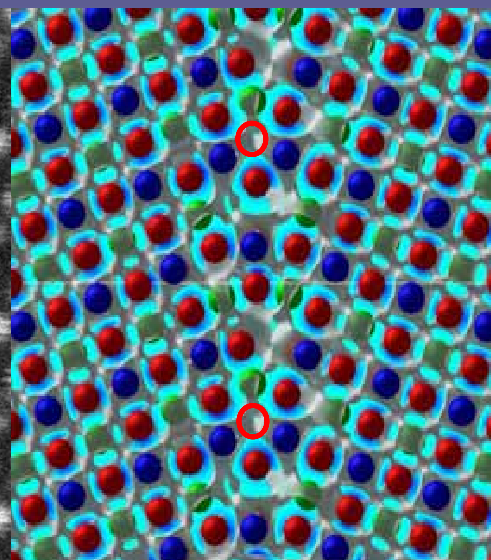
NANO / BIO
INTERFACE
CENTER

Shao, Duscher, Chisholm, Bonnell, PRL (2005)

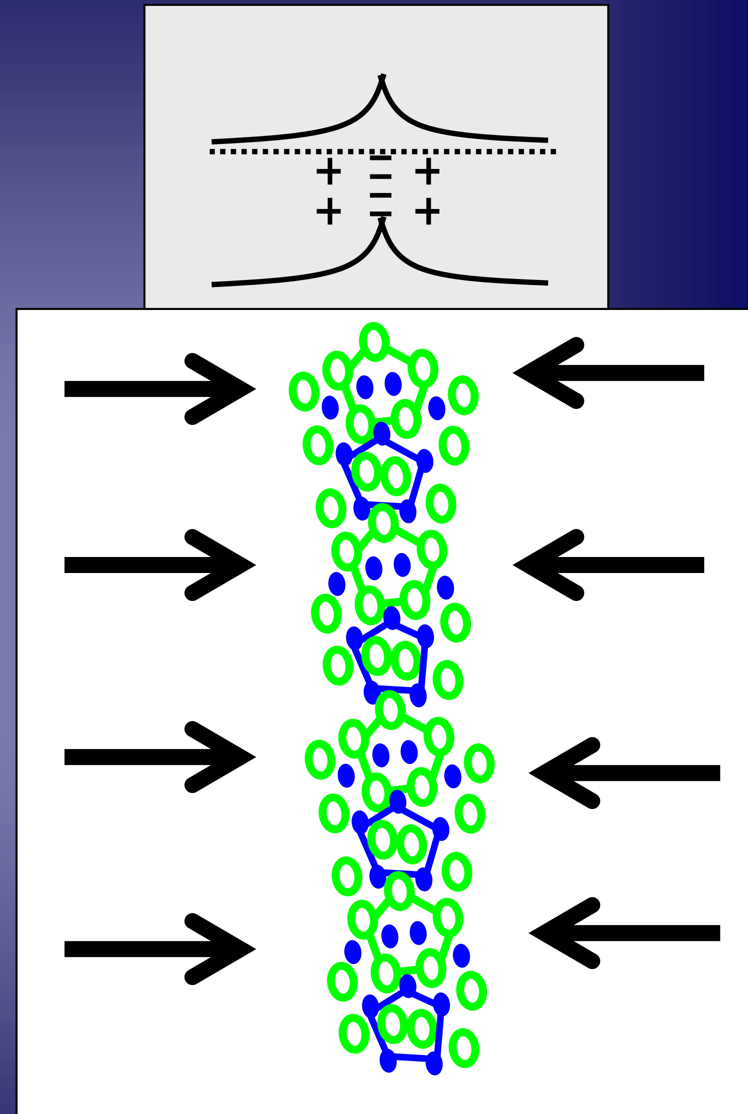
Interface charge determined from first principles calculations and transport measurements are in good agreement



Aberration corrected Z contrast TEM



DFT calculations



Field Induced Dipole Alignment

Boundary charge=0.06C/m2

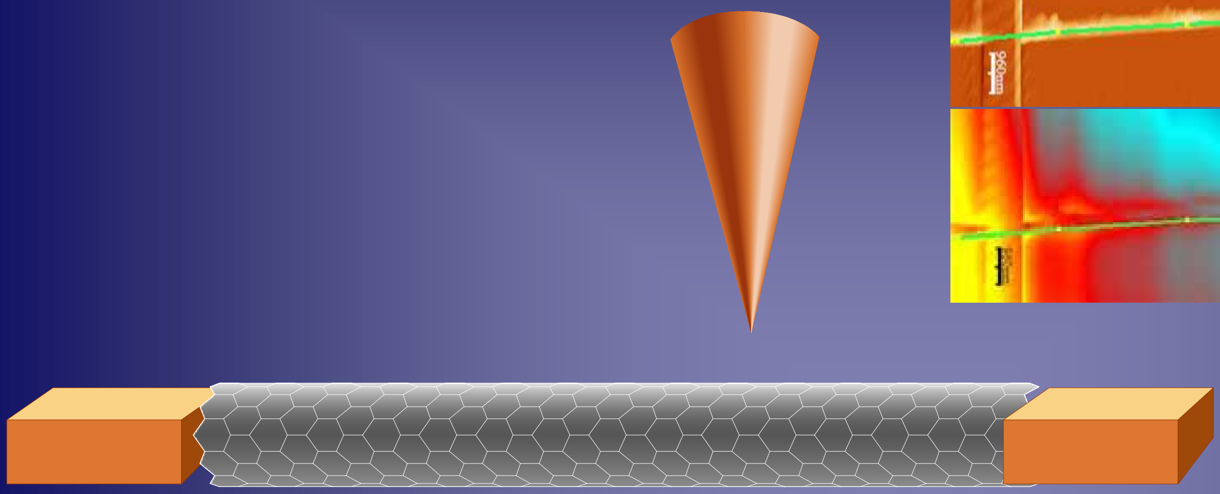
That is 0.3 electron/unit cell

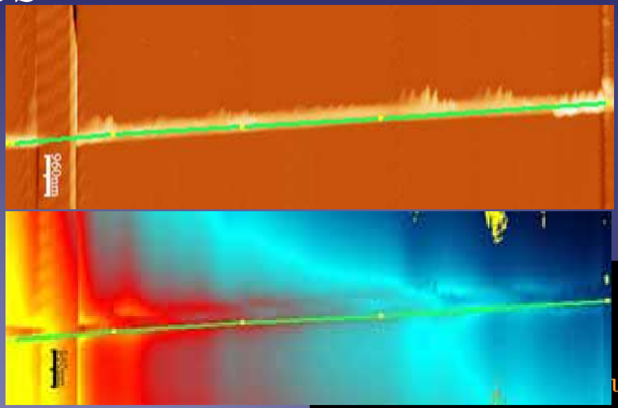
That is 0.8 electrons/Ti unit

NANO / BIO INTERFACE CENTER

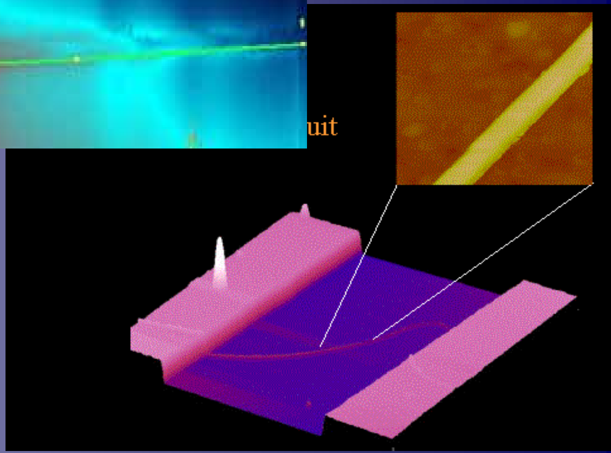
Shao, Duscher, Chisholm, Bonnell, PRL (2005)

Scanning Impedance on Reduced Dimension Structures





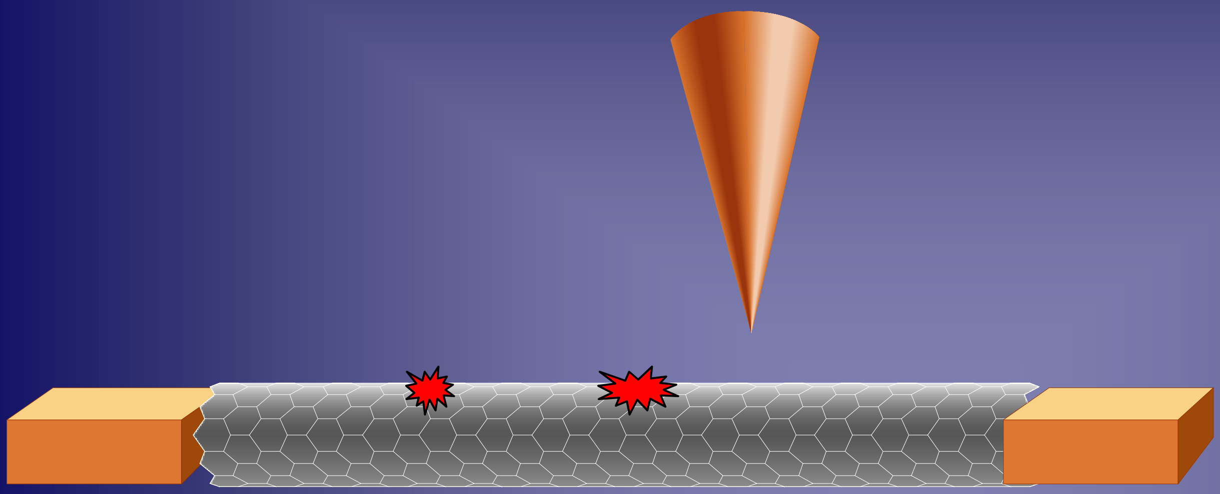
Samples from Craighead & MacDiarmid Groups

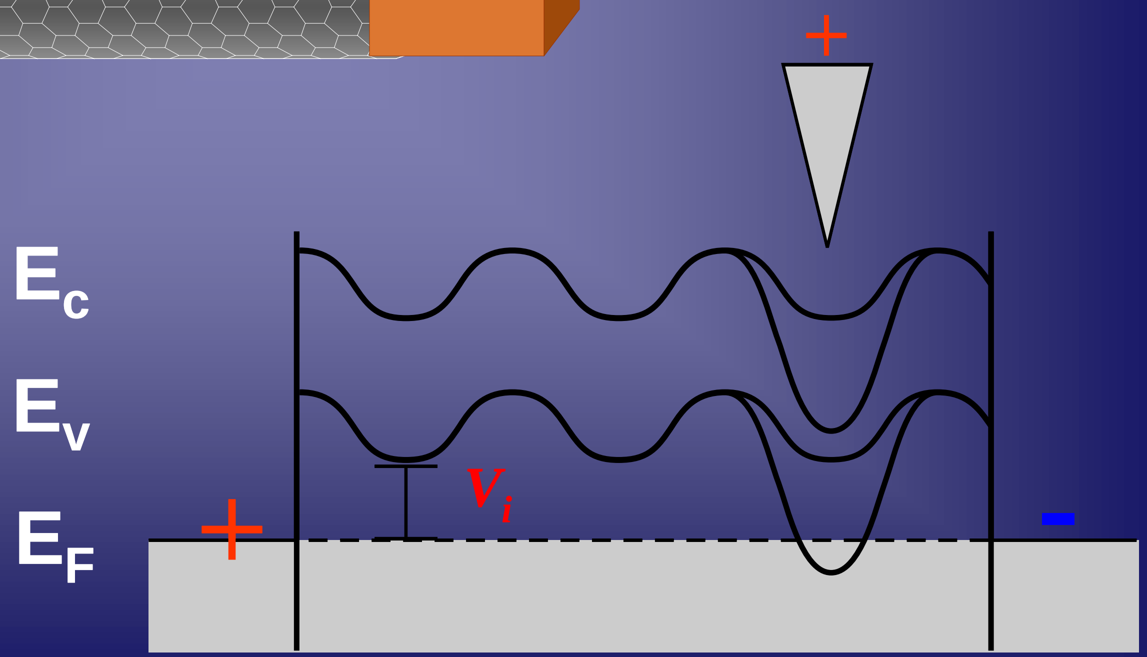


Nikiforov, Liu, Bellan, Craighead, Bonnell
Nano Letters 2005

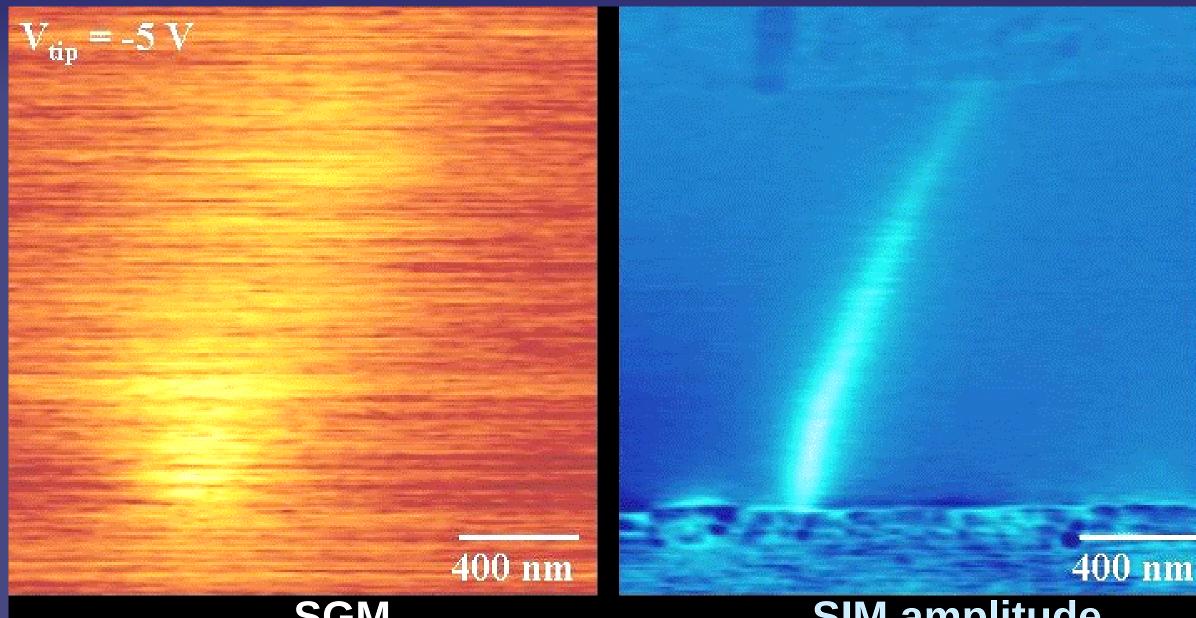
NANO / BIO INTERFACE CENTER

Scanning Impedance on Reduced Dimension Structures





SIM Determines the Electronic Structure of Individual Defects in Molecular Wires and Nanotubes



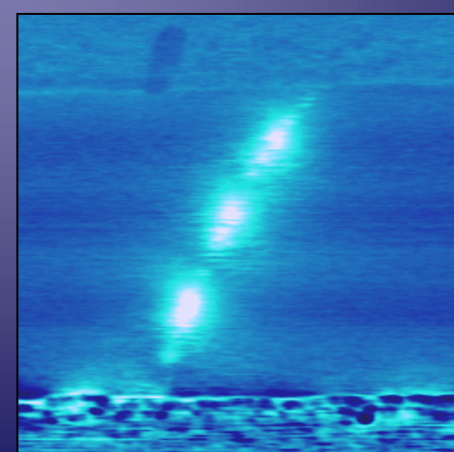
SGM (current through the nanotube) **SIM amplitude** (local potential amplitude)

Spot diameter : $D_i = \frac{V_{tip}}{V_i^*} \frac{\alpha R}{\kappa + 1}$

where: $\kappa_{SiO_2} = 3.9$

$\alpha = \frac{C_{tip-surface}}{C_{free\_sphere}} \sim 1.33$

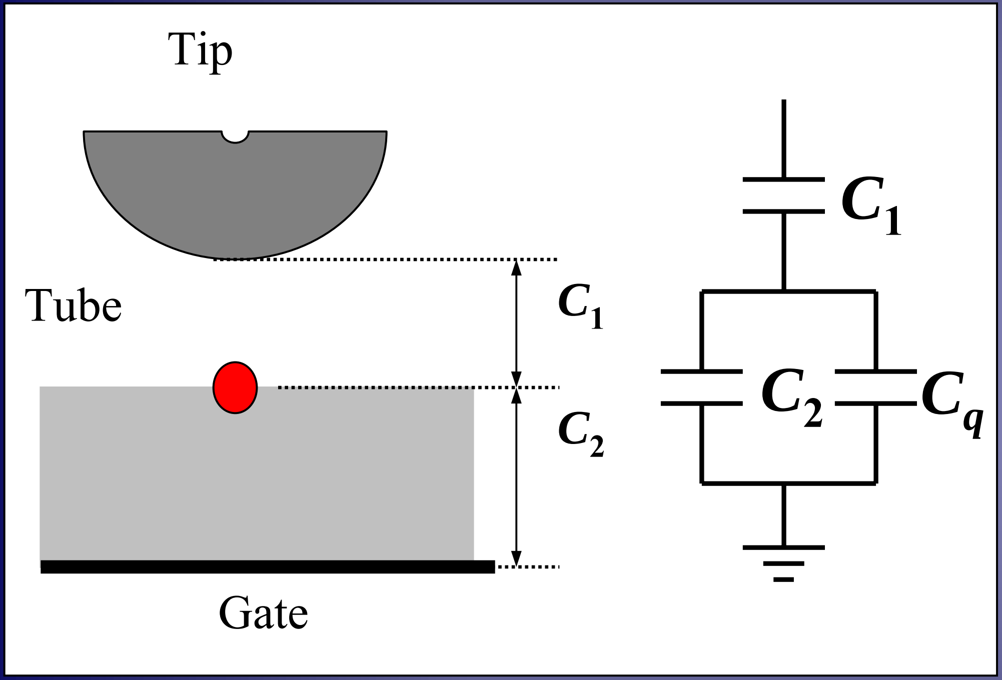
$R = \text{Tip radius} \sim 20\,nm$



NANO / BIO INTERFACE CENTER

Freitag, Johnson, Kalinin, Bonnell, Phys Rev Lett (2002)

Electronic Structure of Individual Defects



Quantum electrostatics

$$\Phi_{tube} = \frac{C_1}{C_1 + C_2 + C_q} V_{surf}$$

C_q - quantum capacitance

C_1, C_2 – geometric capacitances

Onset of depletion

$$\Delta\Phi_{tube} = V_i$$

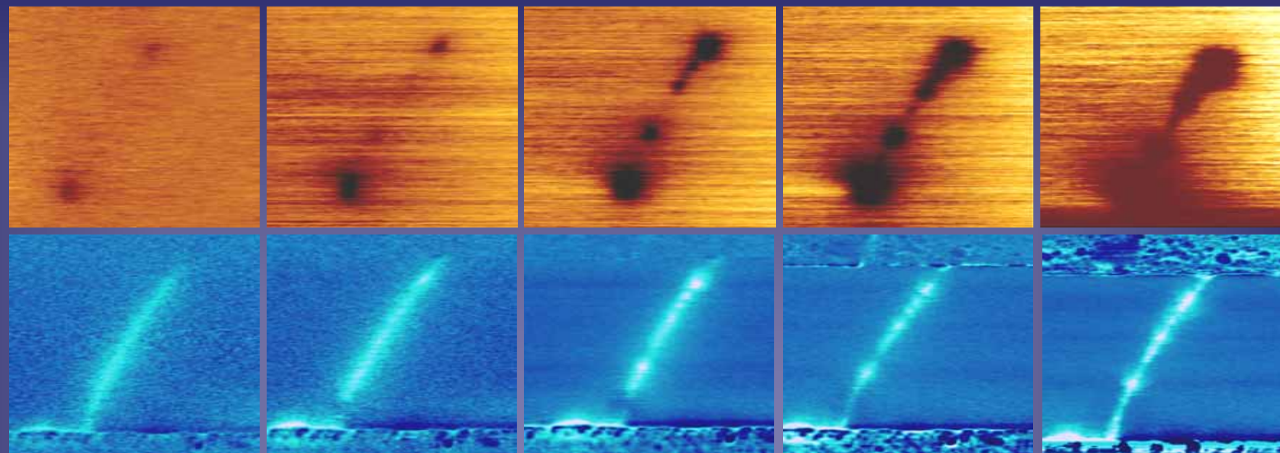
NANO / BIO INTERFACE CENTER

S. Lyrui, Appl. Phys. Lett. 52, 501 (1988),
M. Freitag, S.V. Kalinin, A.T. Johnson, D.A. Bonnell, PRL (2002)

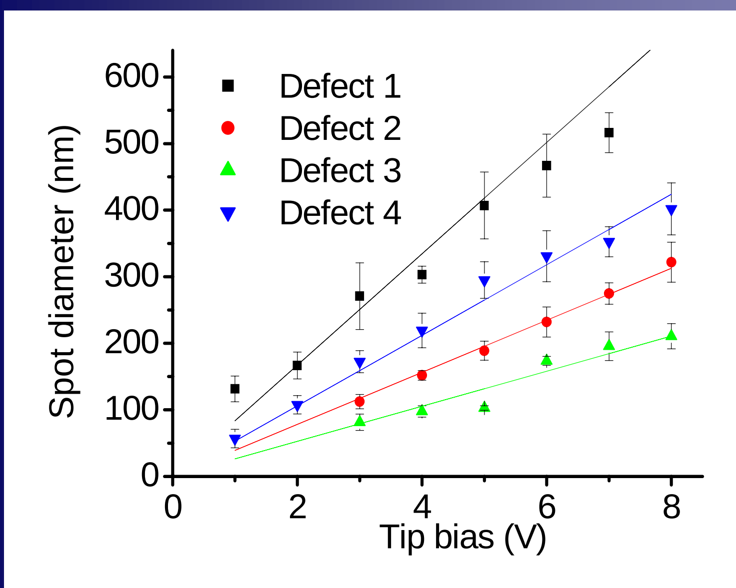
Defect contrast is related to the local electronic structure

SGM

SIM



Increasing tip bias



Defect	Slope [nm/V]	V_i [mV]	V_i^* [meV]
1	83.6 ± 3.6	65	**20**
2	39.1 ± 0.4	139	**40**
3	26.4 ± 1.1	206	**55**
4	53.0 ± 1.2	102	**30**

NANO / BIO INTERFACE CENTER

M. Freitag, S.V. Kalinin, A.T. Johnson, D.A. Bonnell, PRL (2002)

An Oscillating Electrical Signal

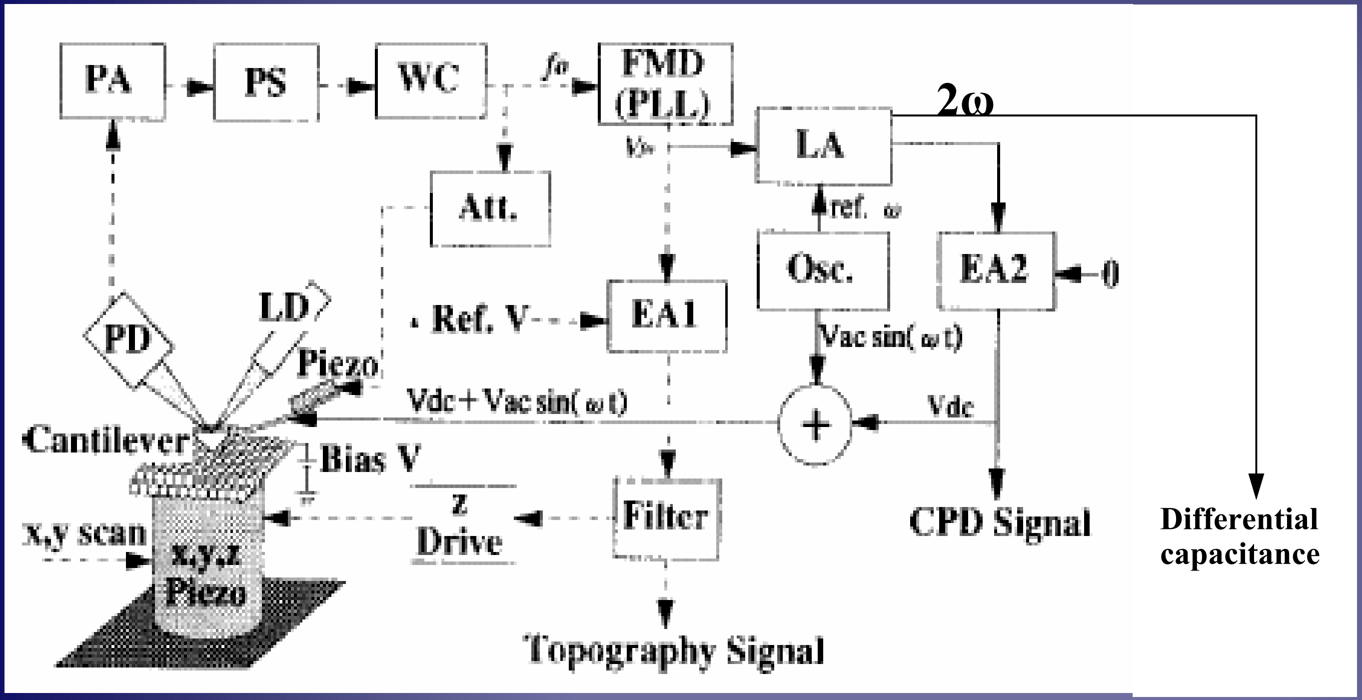
$$F_{1\omega}(z) = \frac{\partial C(z)}{\partial z}\left(V_{dc} - V_{surf}\right)V_{ac}$$

$$F_{2\omega}(z) = \frac{1}{4}\frac{\partial C(z)}{\partial z}\mathrm{V}_{\mathrm{ac}}^{2}$$

New Variants of SSPM/KFM and EFM

Dielectric function
Quantum capacitance
Density of states

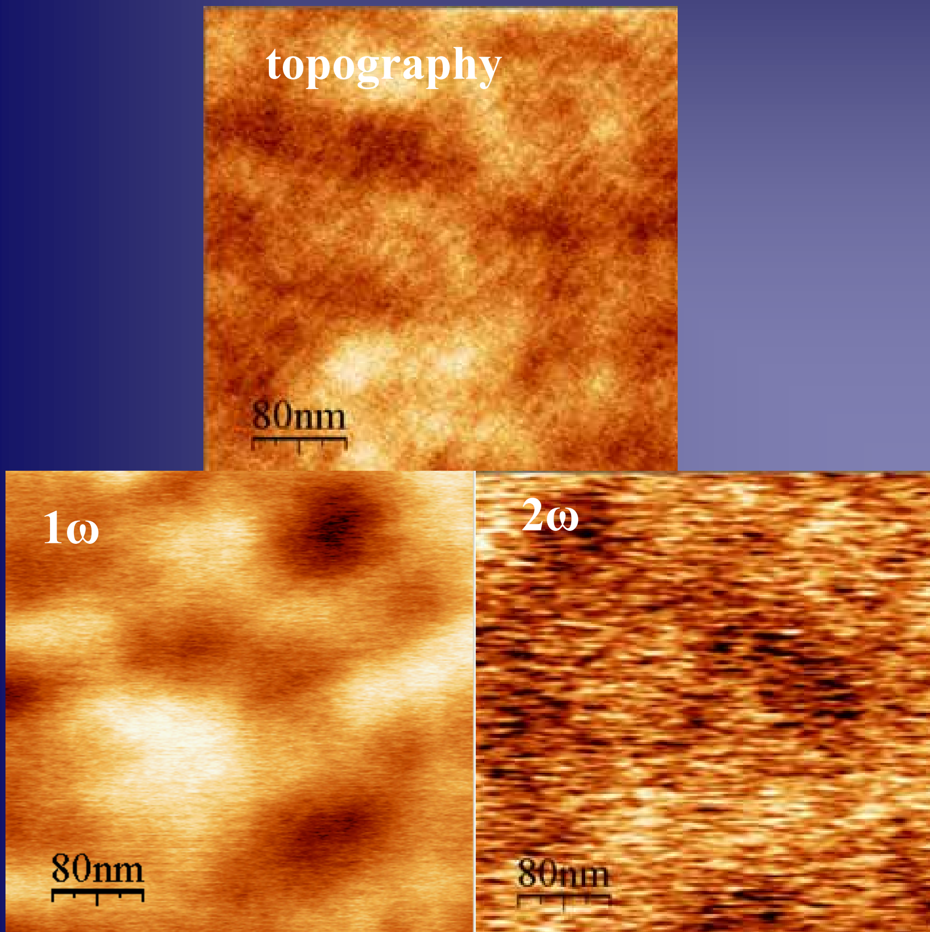
Simultaneous topographic signal, 1st harmonic and 2nd harmonic detection
Implemented on custom designed Omicron VT AFM/STM

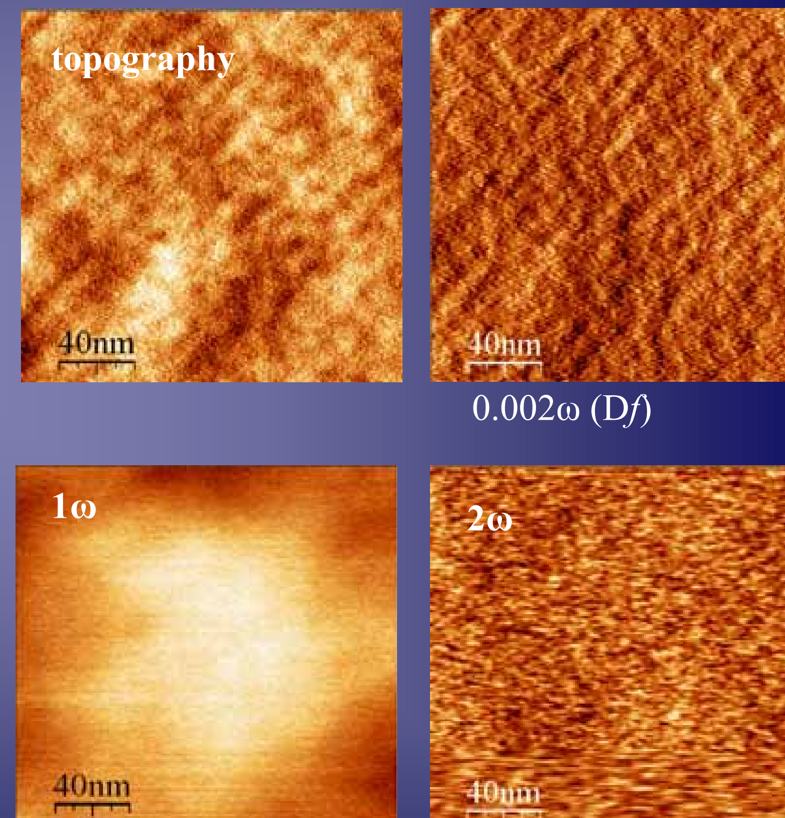


Effectively 2 lock-in signals

Additional filters on the frequency demodulator signal

Simultaneous imaging of topography, surface potential (1ω), and differential capacitance (2ω) of high-k oxide film (2nm HfO_2 on Si).





Omicron UHV VT-AFM/STM

In situ surface potential (first harmonic in electrostatic modulation)

Sample modulation over a wide frequency range (SIM,NIS)

- **electrons at interfaces in devices**
- **band energies at defects in nanotubes**

Simultaneous first and second harmonic

- **potential (work function) and dielectric constant**
- **quantum capacitance, DoS in confined systems**

Two frequency electrical modulation

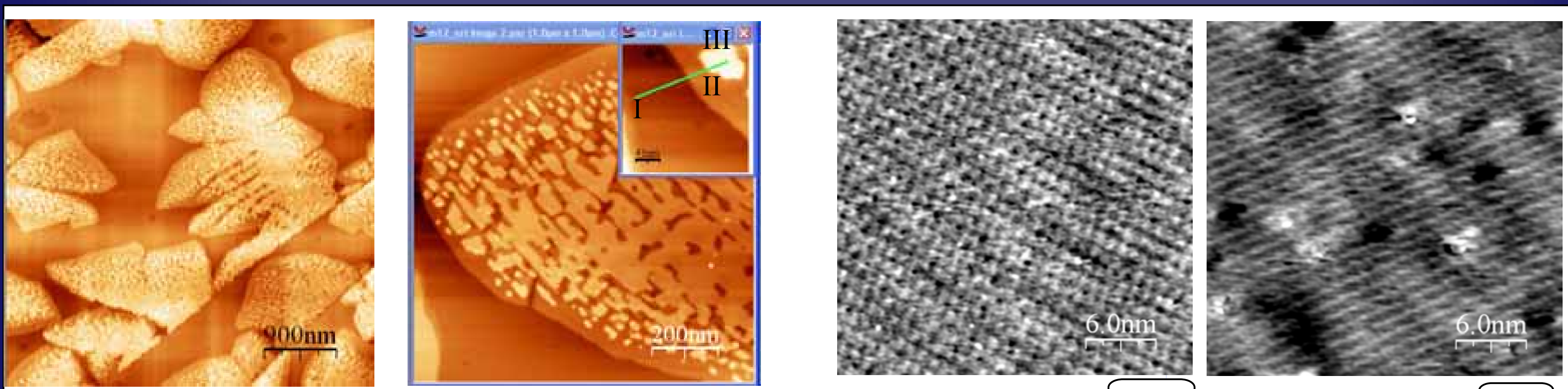
- **dielectric constant**

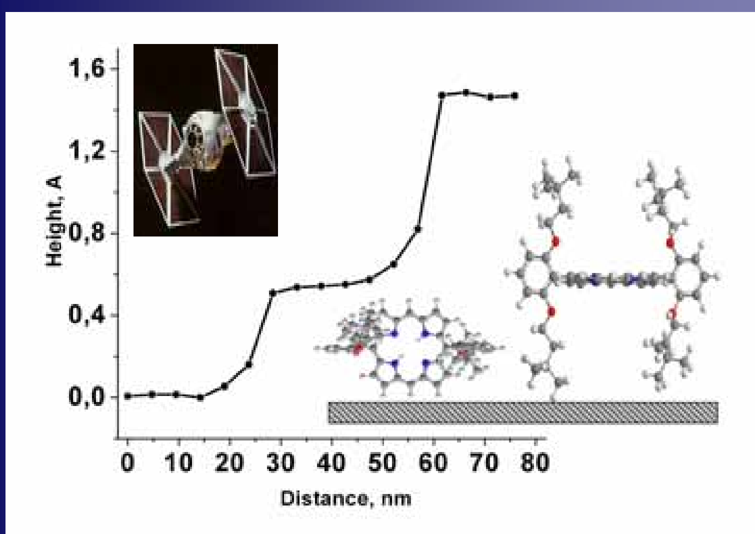
↓

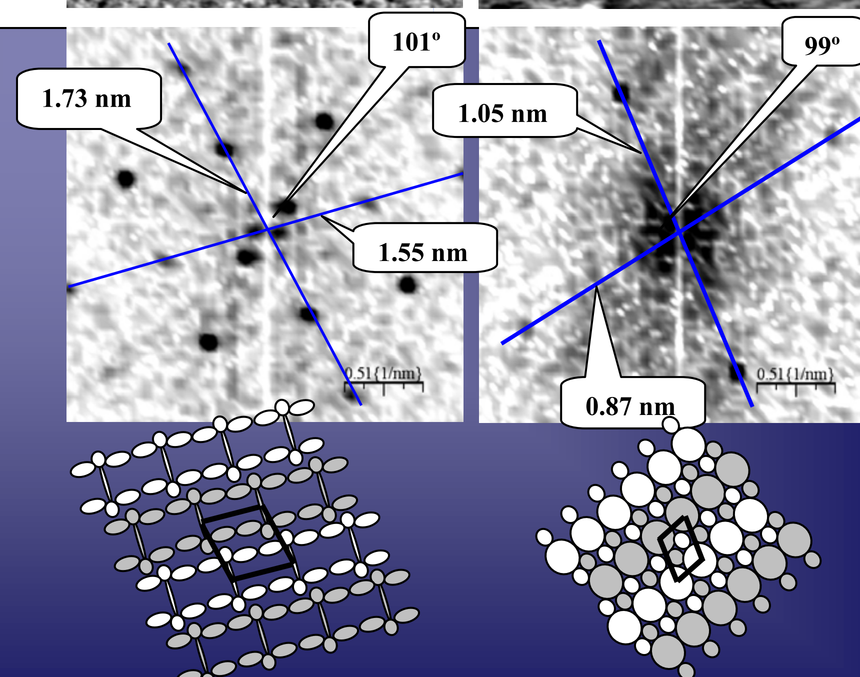
Adding optical techniques

- **work function and dielectric function**

Porphyrin on Graphite
Orientation of the molecule within the islands



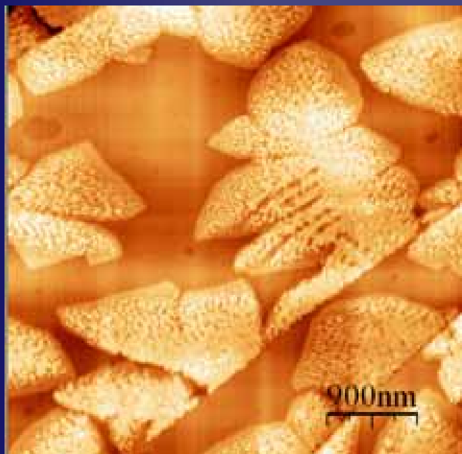


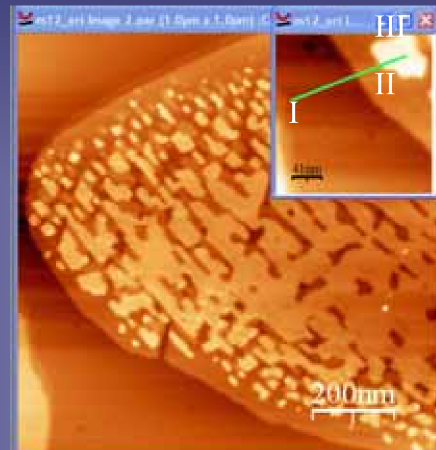


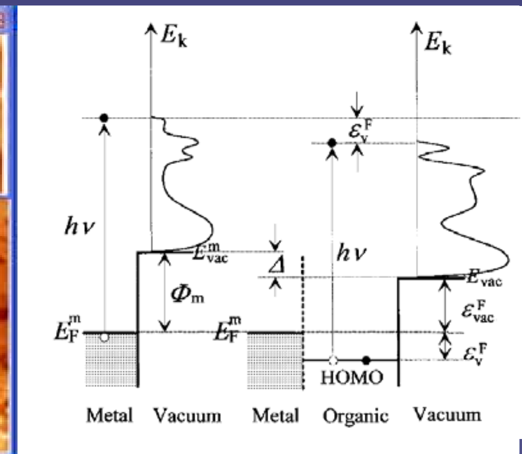
NANO / BIO
INTERFACE
CENTER

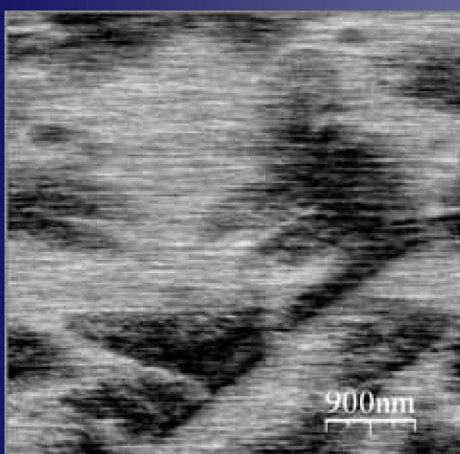
Nikiforov, Shnaider, Zerwek, Eng, Bonnell

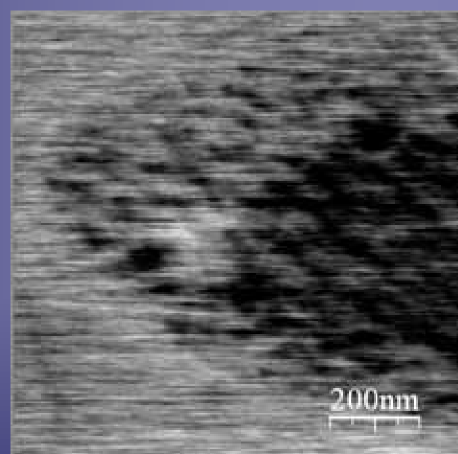
Dependence of the surface potential on orientation











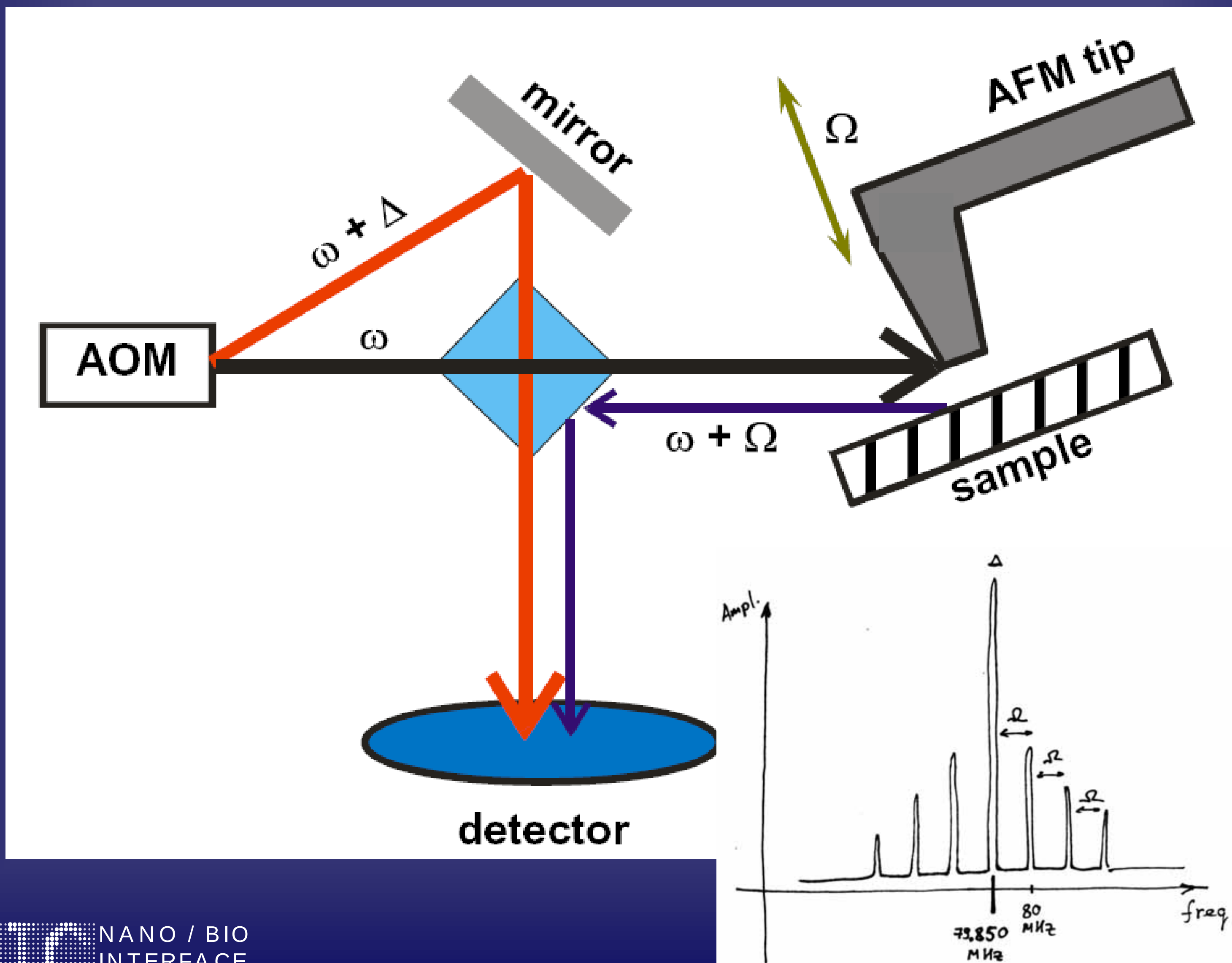
$\Delta \sim 50$ mV **indicates the formation of dipole at the interface**

Coupling between pi orbitals in the substrate plane and molecule depends on orientation

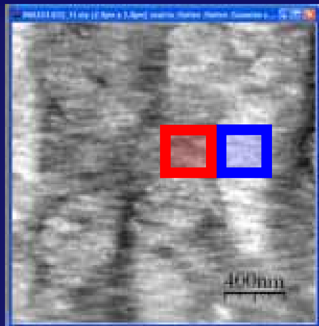
NANO / BIO INTERFACE CENTER

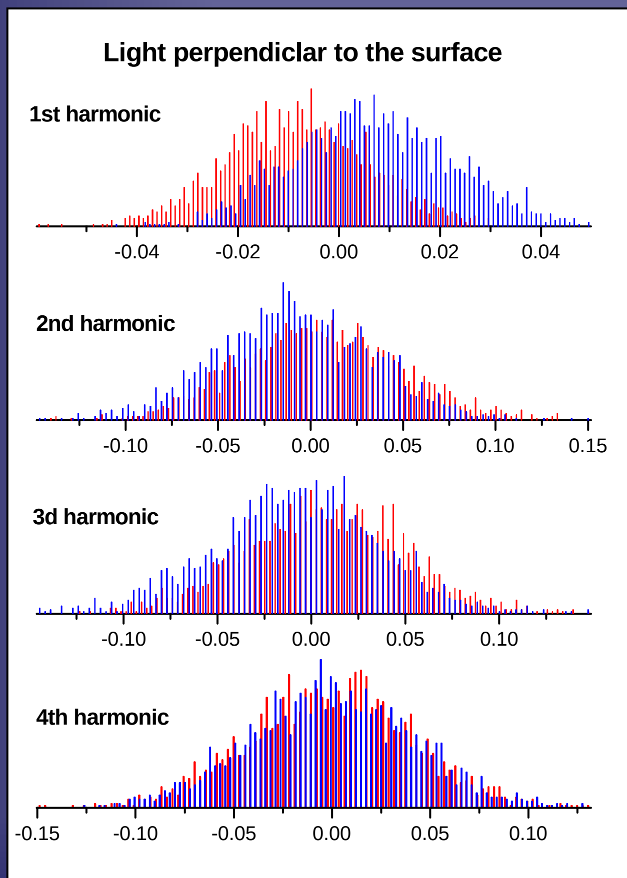
Nikiforov, Shnaider, Zerwek, Eng, Bonnell

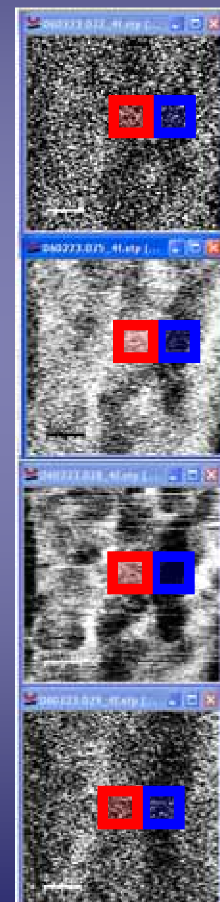
Scattering near field optical microscopy overview

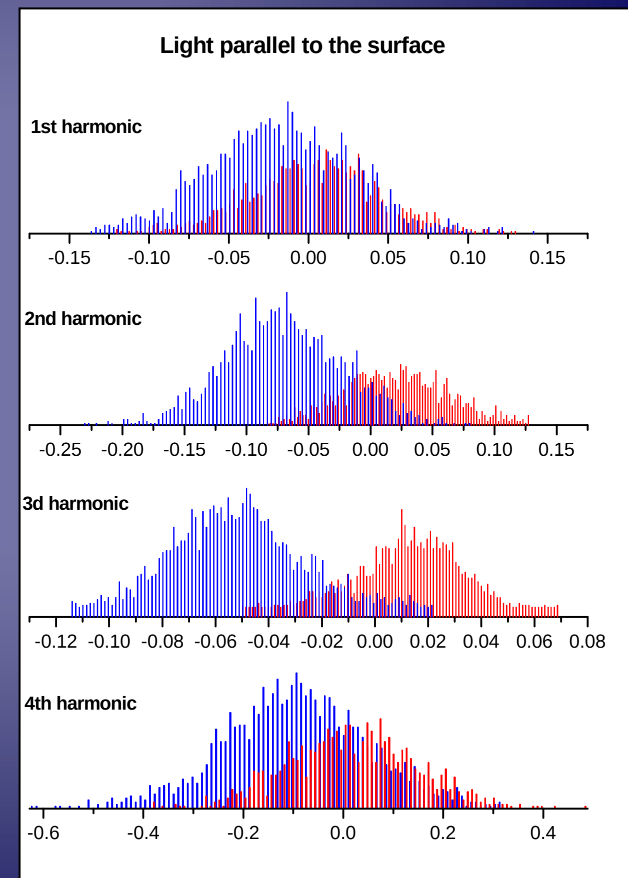


S-SNOM of porphyrin island on HOPG









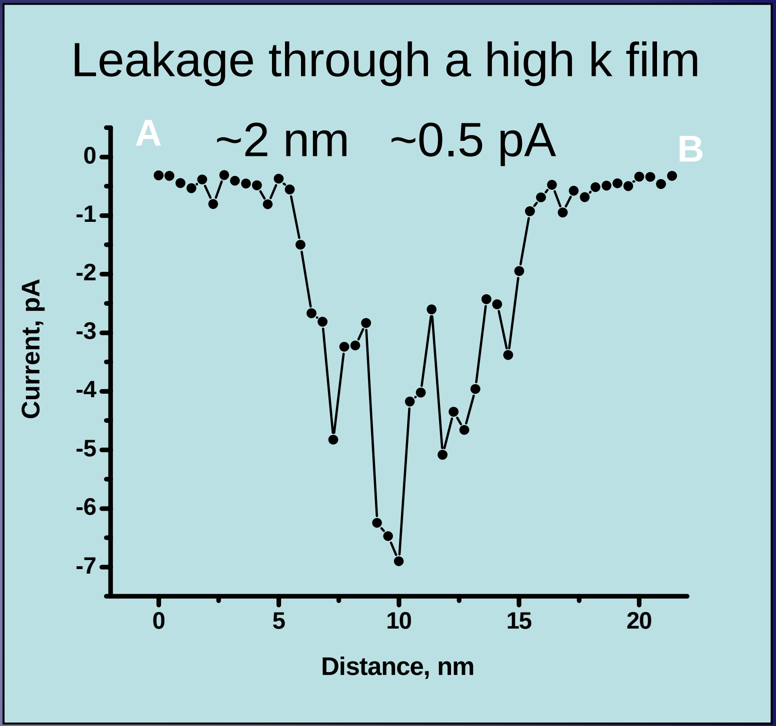
NANO / BIO INTERFACE CENTER

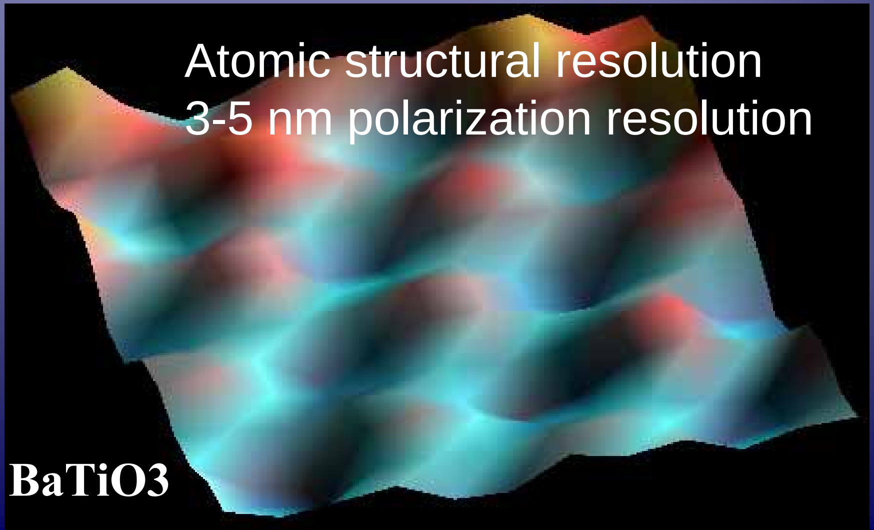
Nikiforov, Shnaider, Zerwek, Eng, Bonnell

Challenges in applying SPM to metrology of complex properties

Sensitivity limit
Spatial resolution
Frequency range limit

Cross talk
Extracting absolute properties
Theory





There is much information in the 'long range' interactions; it is not simple to extract it!!

Combining multiple modulations of tip signals and sample perturbations yields new information

- **Scanning Impedance Microscopy**
- **Nano Impedance Spectroscopy**
  - **trap state time constants**
  - **dielectric anomalies**

Accessing higher harmonics with multiple signals yields complex properties

- **Surface Potential vs Dielectric Constant**
  - **polarizability !!!**

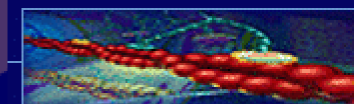
Exploiting boundary conditions related to sample configuration can yield fundamental information.

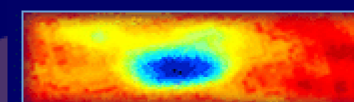
- **Quantum Capacitance** — **Defect electronic structure**
- **Density of States** — **Quantization at Interfaces**

NANO / BIO INTERFACE CENTER

n

Some of the most challenging issues in the 'Nanotechnology Era' will be associated with interfacing physical and biological systems. These interfaces have relevance in many dimensions: from the sociology of the human/machine interface to molecular interactions at physical interfaces. The Nano-Bio Interface Center addresses fundamental principles of molecular function at interfaces.





l

P
a
r

The International Nano/Bio Probe Network

provide a platform that facilitates advances in the field by:

articulating a global vision for the scientific community
informing science funding agencies
defining the future directions of the field

providing a mechanism for junior scientists to rapidly exchange information
enabling routine communications between international collaborators
facilitating international partnering for large research programs