Chemical Resolution in NC-AFM Imaging with Silicon Tips: Theoretical Predictions

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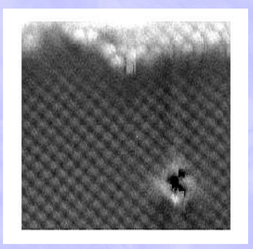
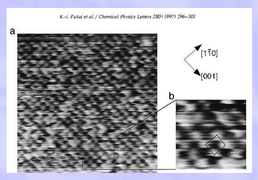
Atomic Resolution

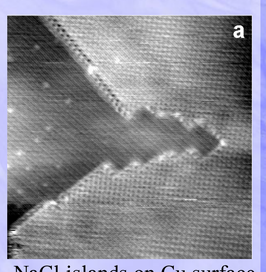
- Atomic resolution is the ultimate goal, although most studies do not achieve/need this - UHV.



NiO (001) 6x6
W. Allers
University of Hamburg

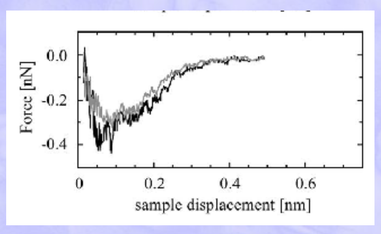


Formate on the (110) TiO_2 Surface 13.3x13.3 nm



NaCl islands on Cu surface. 18x18 nm
R. Bennewitz *et al*, Phys. Rev. B **62** (2000) 2074

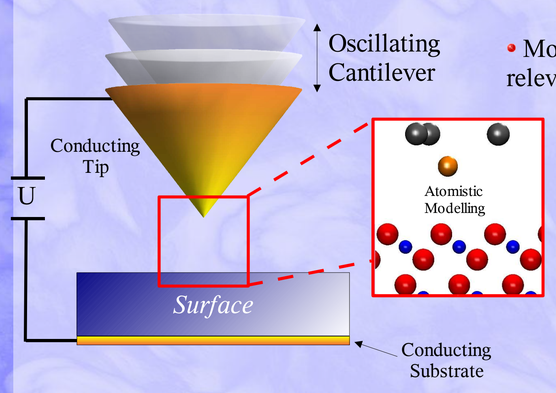
- Interpretation of images is difficult:
  - Identity of imaged features unknown.
  - Contrast not always due to physical surface structure.
  - Microscopic tip structure unknown and can change during scanning.



- Experimental atomic site specific force curves on KBr.
R. Hoffmann et al., *Appl. Surf. Sci.* **188** (2002) 238

- Advances in experimental sensitivity due to low temperature measurements mean that it is now possible to extract the force curves over specific atomic sites – but without knowledge of the tip apex their usefulness is questionable.

NC-AFM modelling



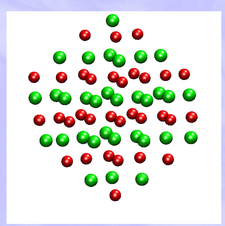
- Model includes all forces relevant to NC-AFM:
  - Chemical Forces
  - Van der Waals Force: micro + macro

- Tip and surface atoms allowed to relax fully with respect to chemical, electrostatic and image forces.

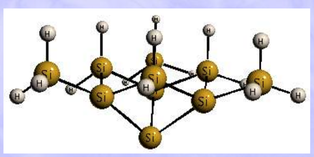
Modelling the tip – microscopic

- Tip originally silicon, but exposure to air and contact with the surface means it can be contaminated – different models?

Oxide model



Silicon model



- Ionic – positive or negative potential from apex
- Atomistic simulation – fast, but no electronic structure
- Covalent – dangling bond from apex (contaminants)
- *Ab initio* – slow, but charge density effects included

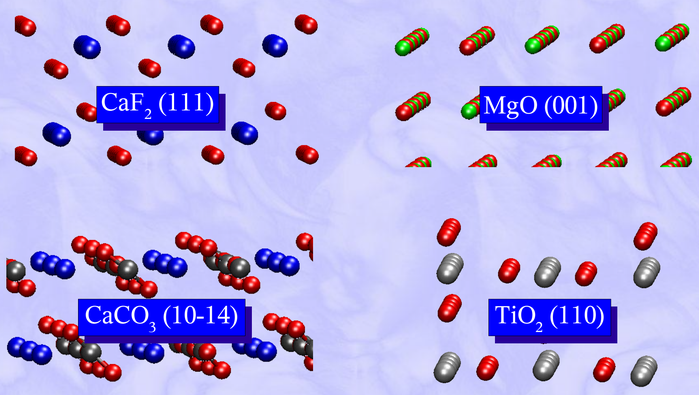
Both have demonstrated good agreement with experiment.

Modelling philosophy

- Initial goal was to develop a model which would obviate the need for full simulations.
- Currently we seem to need not only to perform full simulations for every experiment, but we need to do the simulations with 4 or 5 different tips.
- Even in that case interpretation is not always possible – perhaps we can try just one tip on 4 or 5 different surfaces?

Silicon as a standard tip

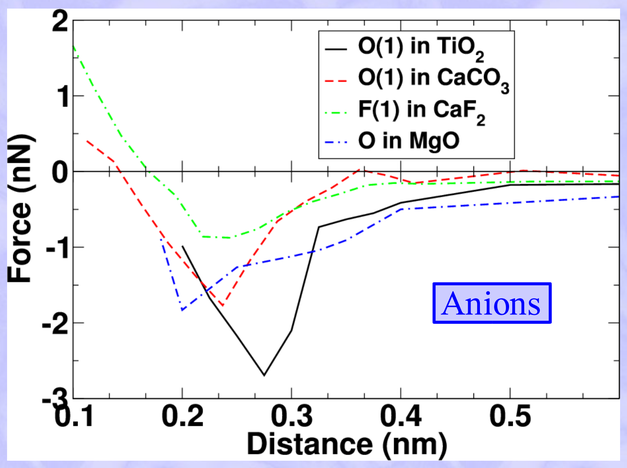
- Cantilever is originally silicon and, if sputtered, a clean silicon surface can be exposed – in UHV only contact with the surface will then change the tip.



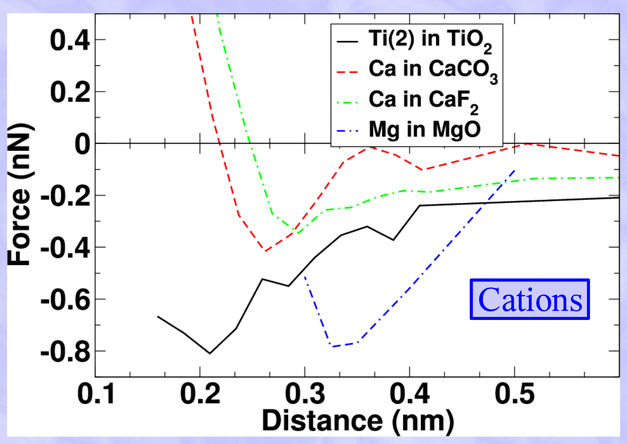
- Take pure silicon tip and simulate NC-AFM on a range of characteristic surfaces.

Silicon tip forces

- Overall magnitude of forces increases with reduction of the ionicity of the surface - largest forces over TiO_2.

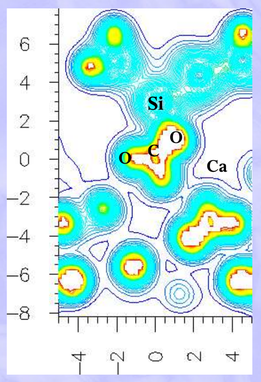


- Force is consistently larger over the anions in the surface - largest for 'highest' anion in more complex surfaces.



Mechanism of contrast

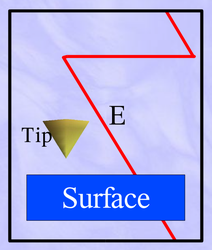
- Force is dominated by formation of covalent bonds between the tip and atoms in the surface.



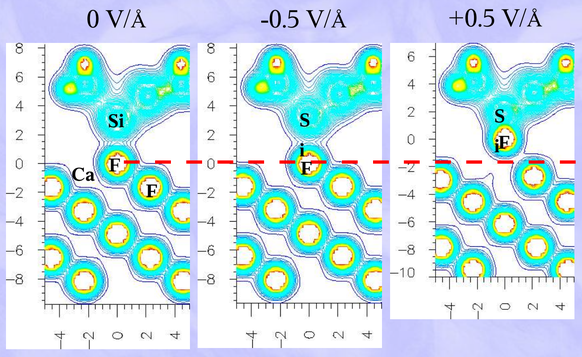
- Anions, by definition, have higher electronegativity and more electrons 'available' to form a bond.
- On more ionic surfaces, the highly localized charge density is reluctant to form bonds with the tip and the force is smaller – polarization of tip density.
- For this small sample, the forces seem to scale well with the band gap, but structural factors are important – Mg interaction, CO_3 molecule.

Voltage effects

- The sensitivity of the interaction to the surface electronic structure implies that it may strongly affected by applied voltage.



- Electric field (E) applied across whole cell with tip at 3.2 Å.

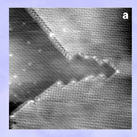


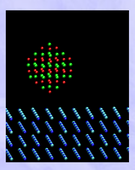
Force (eV/Å)	-0.25	-0.01	-0.42
Charge to Tip (e)	+0.10	-0.30	+0.50
F disp. (Å)	0.00	-0.09	+1.31

- Applying 0.5 V/Å over Ca produces very little change in force for either bias direction – force change only relevant for anions chemical marker.

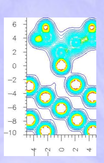
Summary

- Interpretation of atomically resolved images is possible – symmetry, defects, atomic force curves.





- Interpretation of atomically resolved images is painful – tip, full simulation, tip, low temperature, UHV, tip. Same story in STM.
- Developing methods for controlling the tip chemical structure would make interpretation much easier. Silicon is a possible candidate as the preparation techniques already exist and the theory is ready – insulators and semiconductors.



- Applying equal and opposite voltage during measurements of atomic force curves should also allow chemical resolution after removal of background force – differential curves.

Acknowledgements
C. Barth, M. Reichling and R. Hoffmann