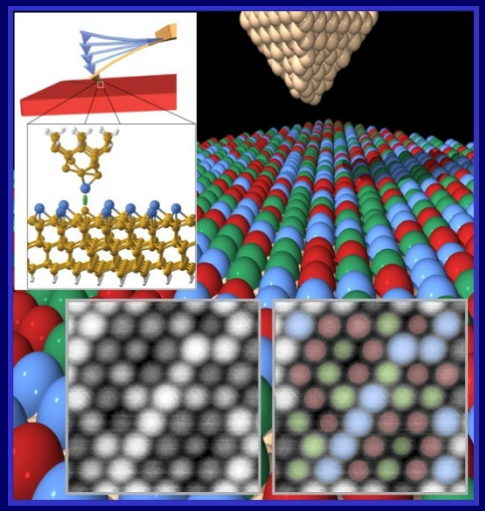
Imaging, Manipulation and Chemical Identification of Individual Atoms with dynamic Force Microscopy: A theoretical perspective.

Rubén Pérez
Nanomechanics & SPM Theory Group
Departamento de Física Teórica de la Materia Condensada
http://www.uam.es/ruben.perez



UAM
UNIVERSIDAD AUTONOMA
DE MADRID

NanoSpain, Zaragoza March 9-12th 2009

Outline

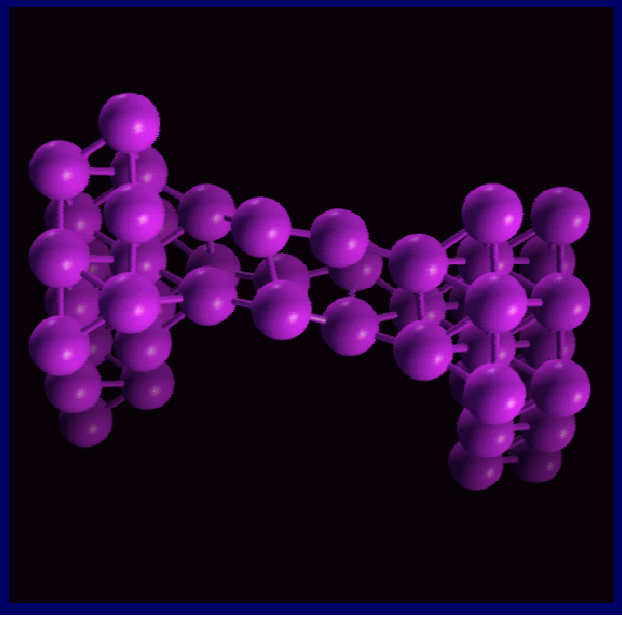
1. Nanomechanics & SPM Theory Group: Forces & Transport in Nanostructures with ab initio methods

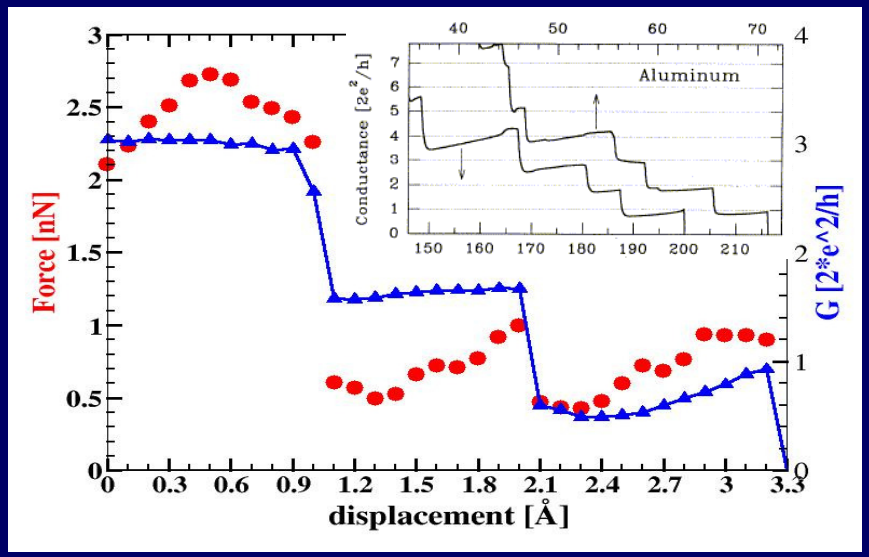
2. "Tip-Induced Reduction of the Resonant Tunneling Current on Semiconductor Surfaces"
Phys. Rev. Lett. 101, 176101 (2008)

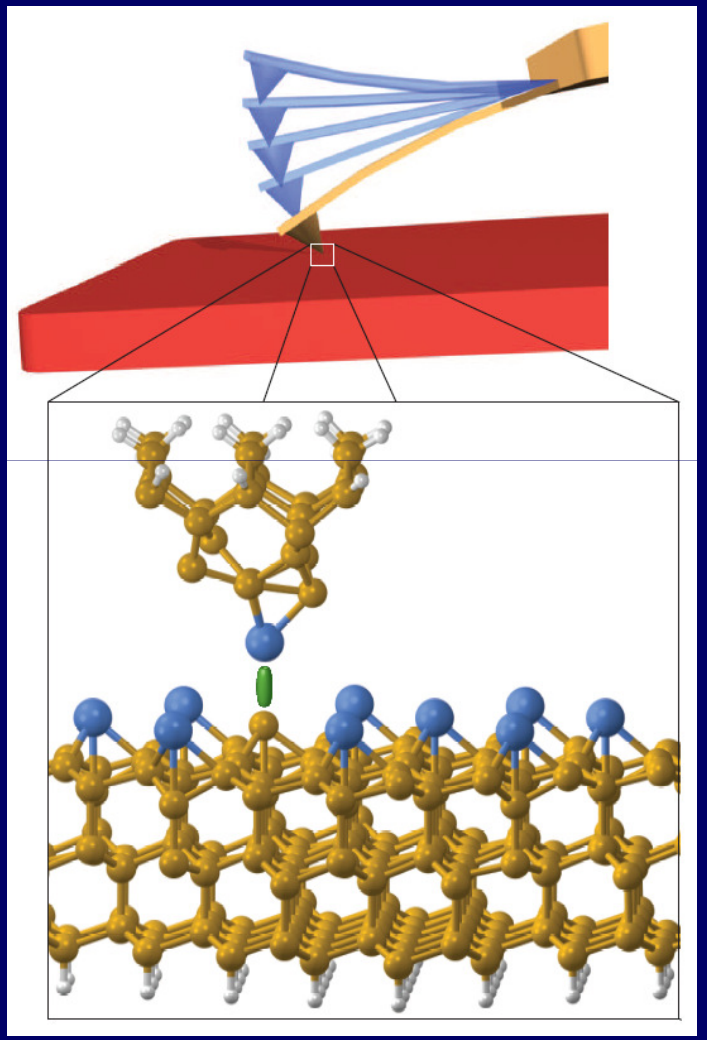
3. "Fullerenes from Aromatic Precursors by Surface Catalysed Cyclo-dehydrogenation"
Nature 454, 865 (2008)

4. "Complex Patterning by Vertical Interchange Atom Manipulation Using Atomic Force Microscopy"
Science 322, 413 (2008)

Forces & Transport in Nanostructures: First-principles calculations







Methodology

"The computer is a tool for clear thinking" Freeman J. Dyson

Ab-initio total energy methods

(based in Density Functional Theory)

Non-equilibrium Green's Functions

both plane wave & local orbital basis: accuracy/efficiency balance

Linked with the local orbital description

Structure + electronic properties

FIREBALL, OPENMX
CASTEP, VASP

Electronic transport

“Tip-Induced Reduction of the Resonant Tunneling Current on Semiconductor Surfaces”

Phys. Rev. Lett. 101, 176101 (2008)

Ab initio Simulations:

UAM: P. Pou, R. Perez

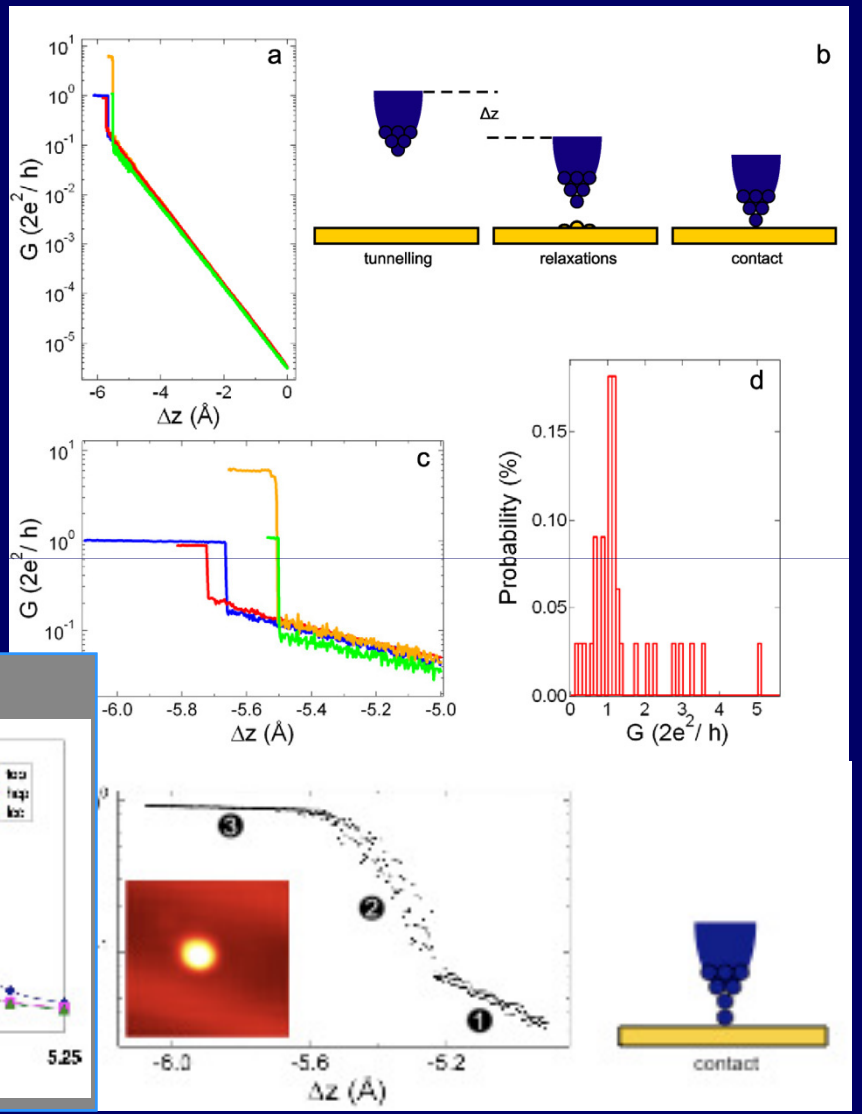
FZU(Prague): P. Jelinek

STM Experiments:

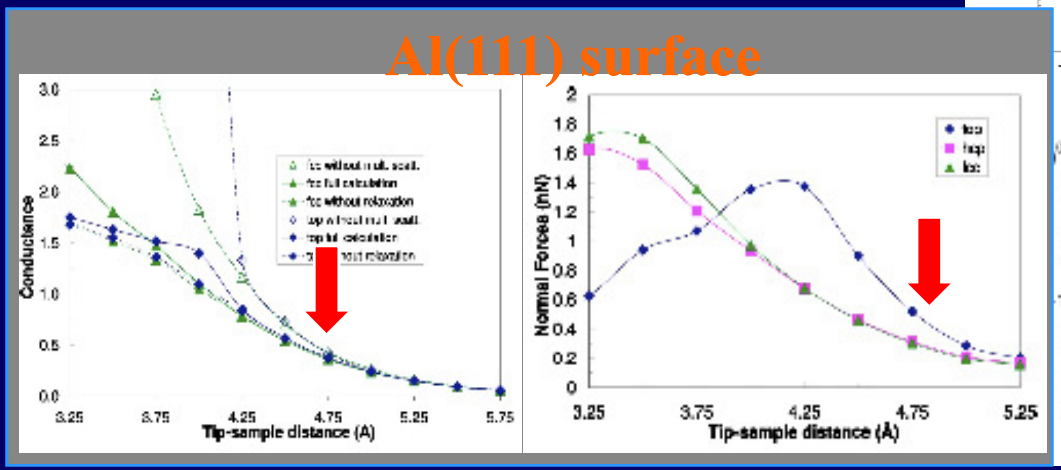
FZU (Prague): M. Švec, V. Chab

Atomic contact: metals

- **metal surfaces** - **monotonic increase** of the **conductance** observed while approaching the tip to the sample
- transition to the contact related relaxation of the atoms
- **correlation** between **multiple scattering** effects and **SR forces:** **no** longer **exponetial behavior**



Al(111) surface

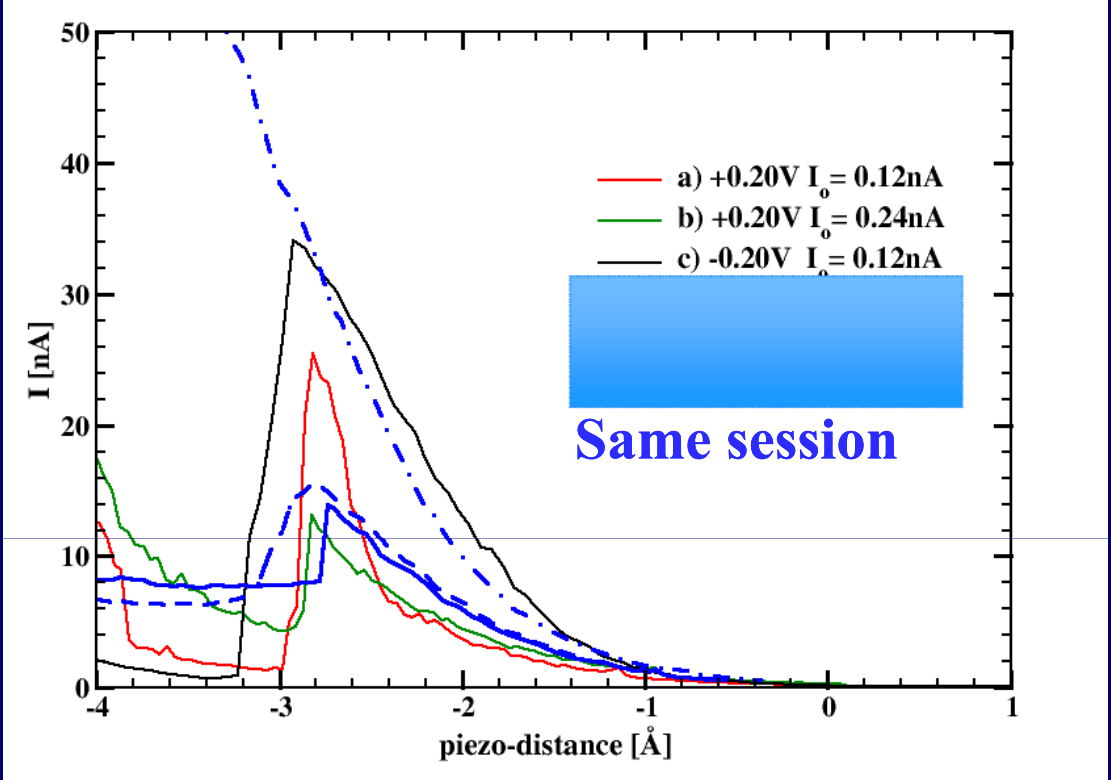


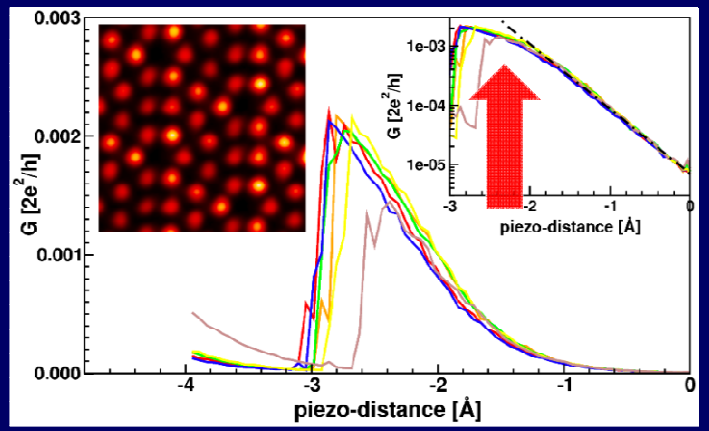
*J.M. Blanco et. al. PRB **70** **085405** (2004)*

*J.Krőger et. al. New Journal of Physics **9** **153** (2007)*

semiconductor surfaces – almost **no information**

Conductance drop: summary

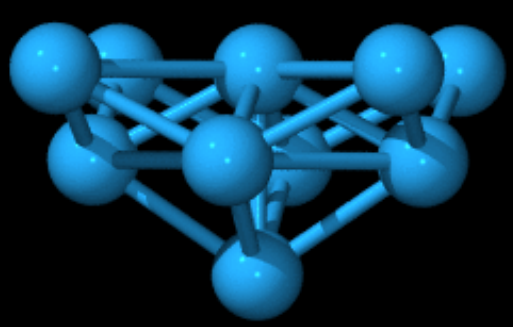




- well reproducible during different sessions
- observable only **at small bias voltage**
- tip structure slightly modify the shape but not the feature
- observed at **both polarities** and **both scan z-directions** of tip
- before jump almost exponential behavior

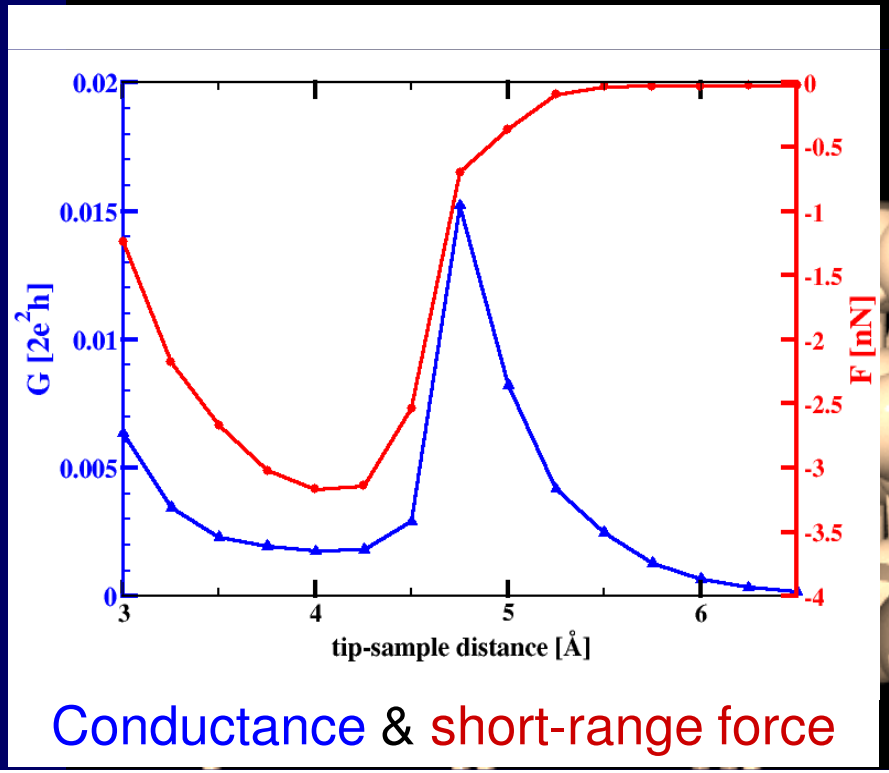
P. Jelinek et. al. PRL 101, 176101 (2008)

DFT simulation: CoA Si7x7 + tip W

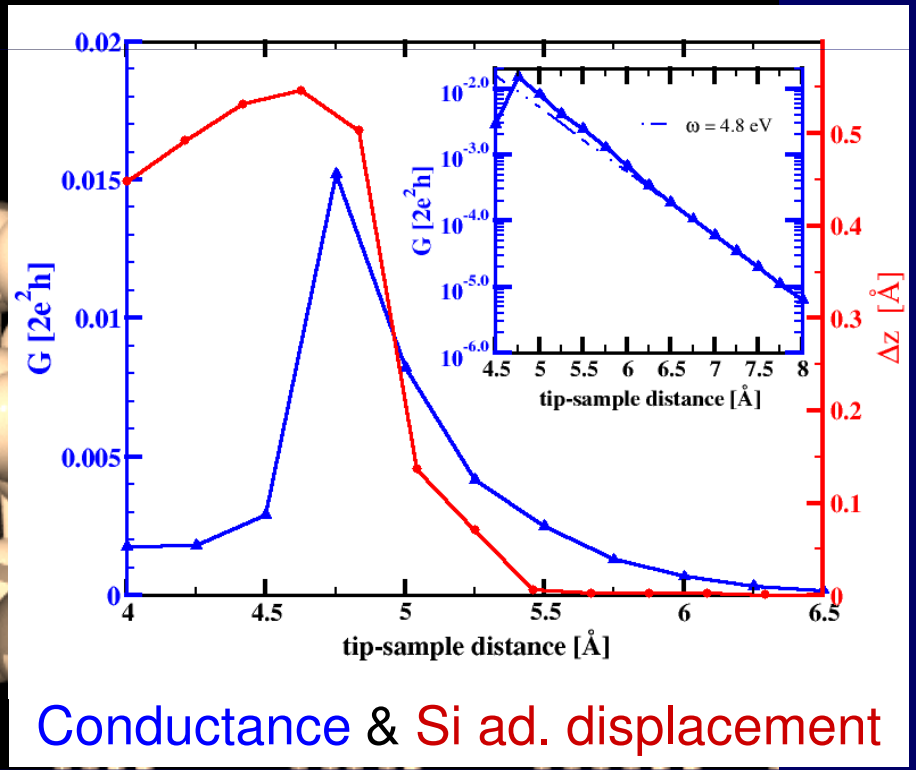


- distortion of the local structure of the tip and sample at short distances
- reversible process
- attractive short-range force onset corresponds to the drop in the conductance

Conductance and force: Si corner adatom

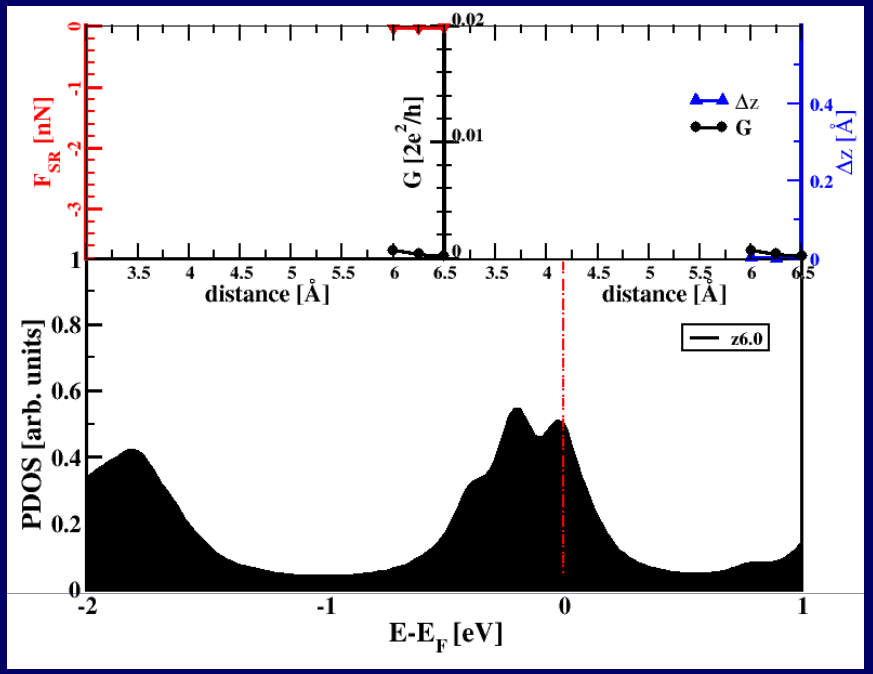


Conductance & short-range force



Conductance & Si ad. displacement

Electron density along the path

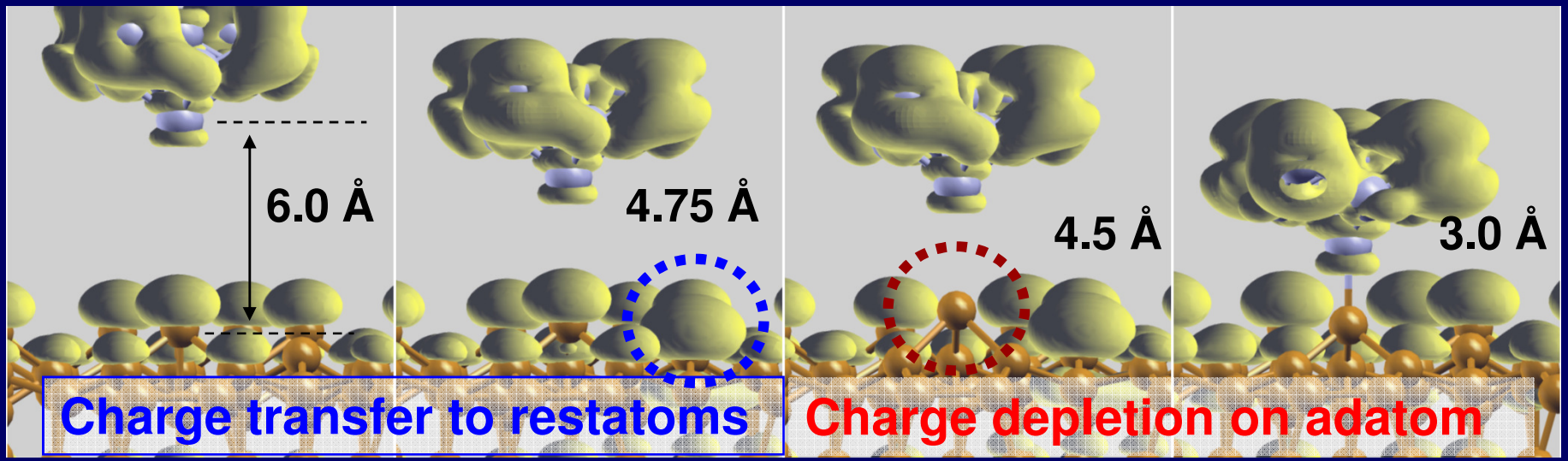


- chemical interaction between the tip and sample changes the position of Si dangling bonds near the Fermi level

→ direct impact on the tunnelling current along the tip-sample distance

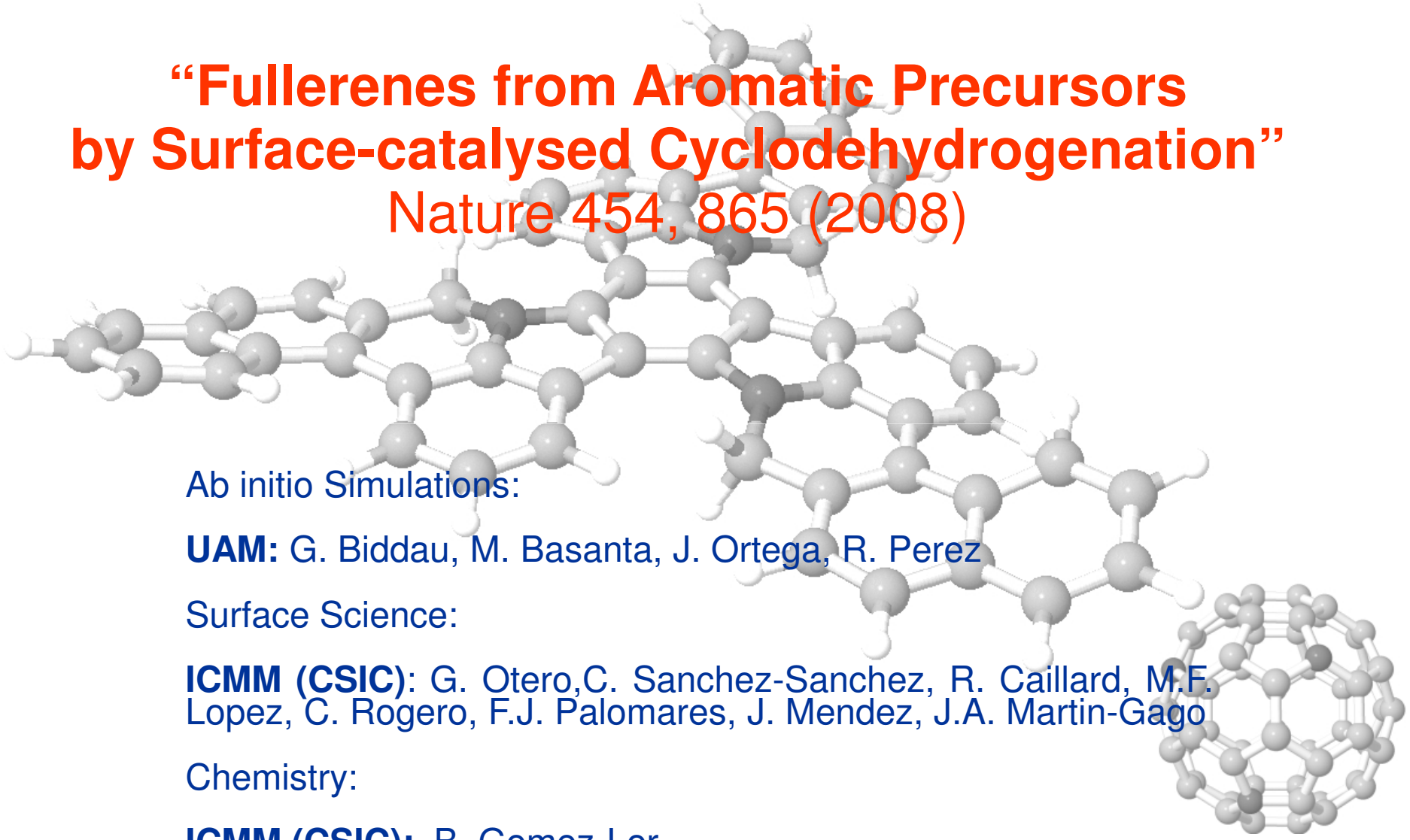
P. Jelinek et. al. PRL 101, 176101 (2008)

Isosurfaces of 0.05 e/Å^3
in the energy range E_F, E_F-0.4 eV



“Fullerenes from Aromatic Precursors by Surface-catalysed Cyclodehydrogenation”

Nature 454, 865 (2008)



Ab initio Simulations:

UAM: G. Biddau, M. Basanta, J. Ortega, R. Perez

Surface Science:

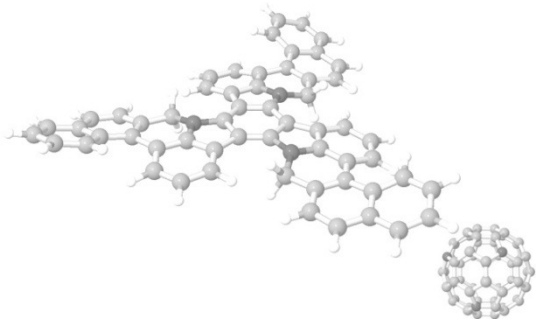
ICMM (CSIC): G. Otero,C. Sanchez-Sanchez, R. Caillard, M.F. Lopez, C. Rogero, F.J. Palomares, J. Mendez, J.A. Martin-Gago

Chemistry:

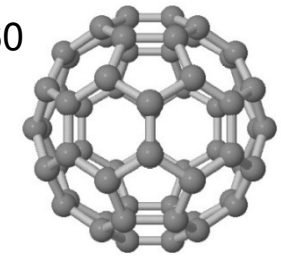
ICMM (CSIC): B. Gomez-Lor

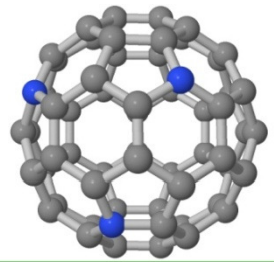
ICIQ: N. Cabello, A.M. Echevarren

Objective and motivations



OBJECTIVE:
Study and efficient synthesis fullerenes and triazafullerenes

C_{60} 

$C_{57}N_3$ 

MOTIVATIONS:
microelectronics, superconductivity, corrosion resistence, non linear optics, organic ferromagnetism...

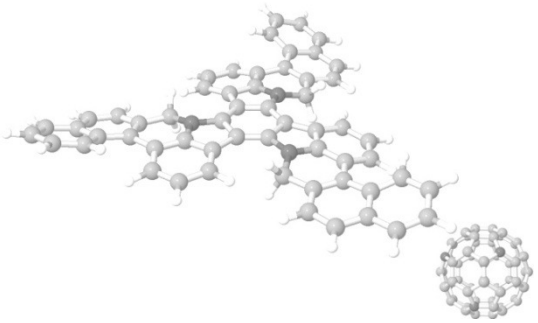
Available synthesis methods:

Fullerenes:
- Graphite Vaporization ***(uncontrolled)***
- Through dehydrogenation[1] ***(low efficiency)***

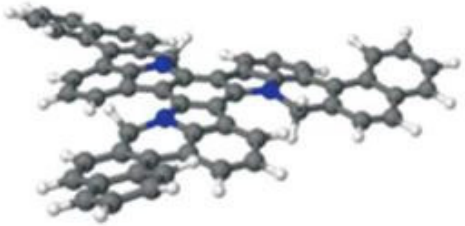
Triazafulleres:
none

1] Scotts et al., Science 295, 1500-1503 (2002)

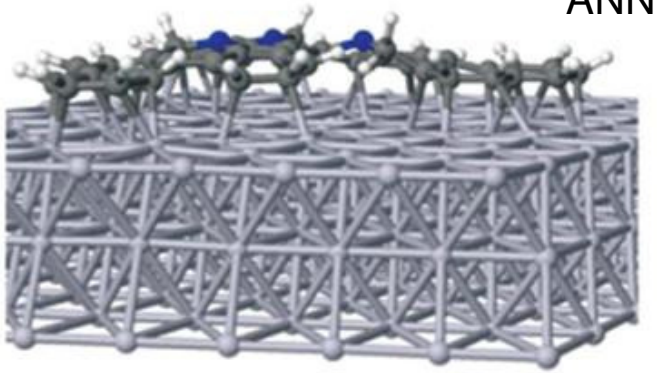
The Process



VACUUM THERMAL EVAPORATION

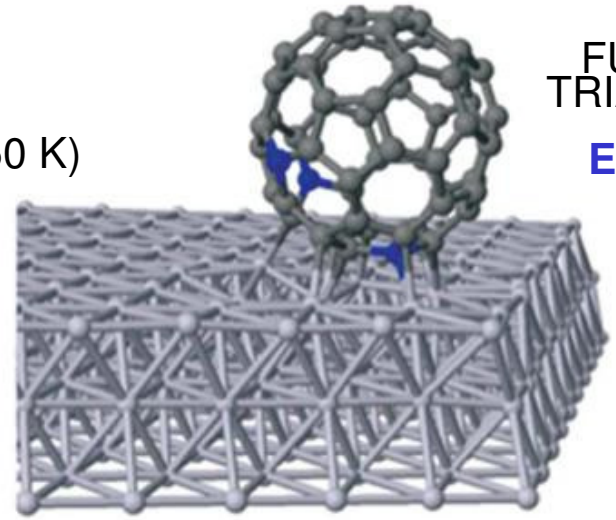


Adsorption process



ANNEALING (750 K)

Cyclodehydrogenation



FULLERENE AND TRIAZAFULLERENES

Efficiency ~100%

G.Otero et al., Nature 454, 865 (2008)

“Complex Patterning by Vertical Interchange Atom Manipulation Using Atomic Force Microscopy”

Science 322, 413 (2008)

Ab initio Simulations:

UAM: P. Pou, R. Perez

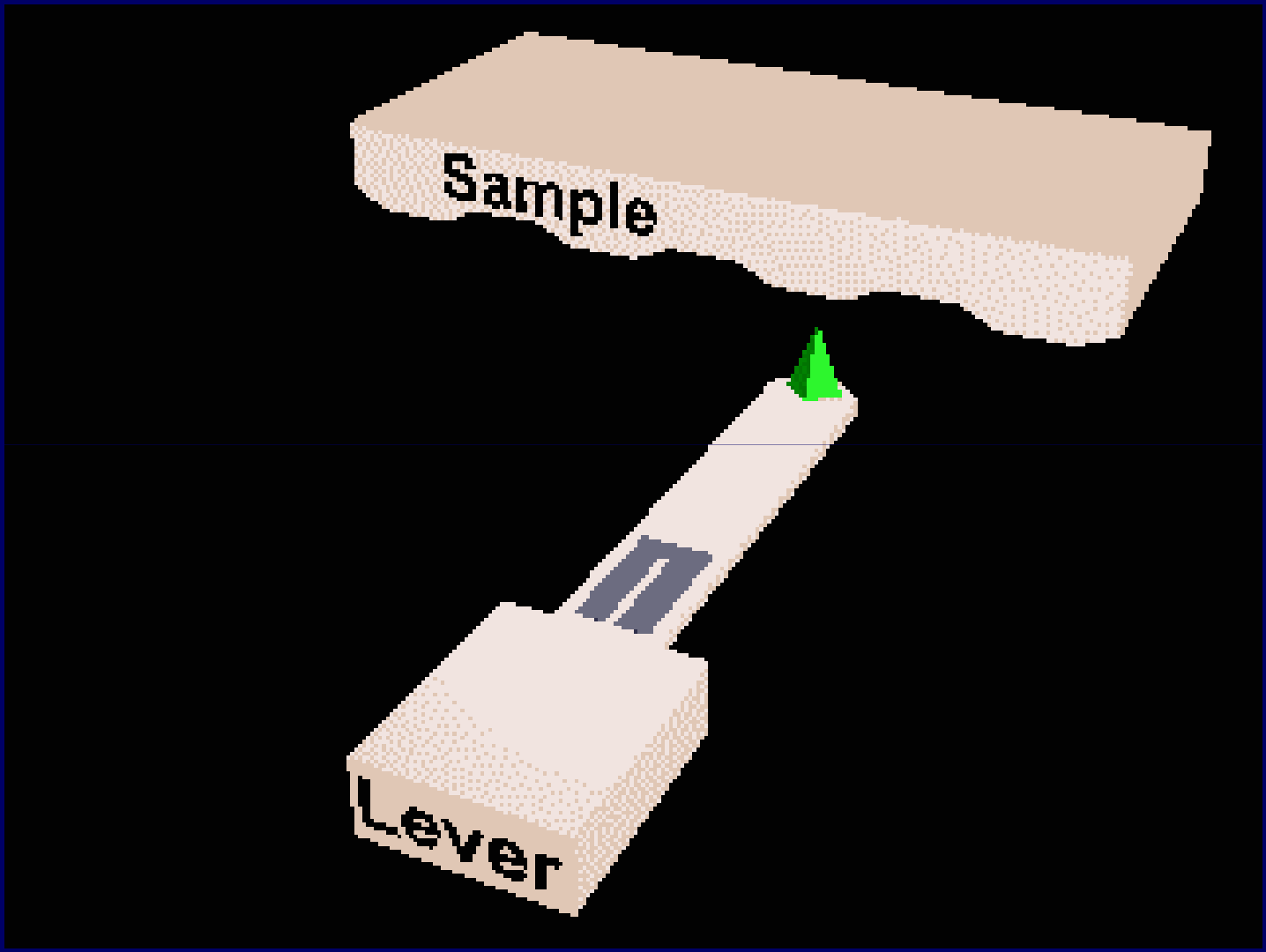
FZU(Prague): P. Jelinek

AFM Experiments:

Osaka University:Y. Sugimoto, M. Abe, S. Morita

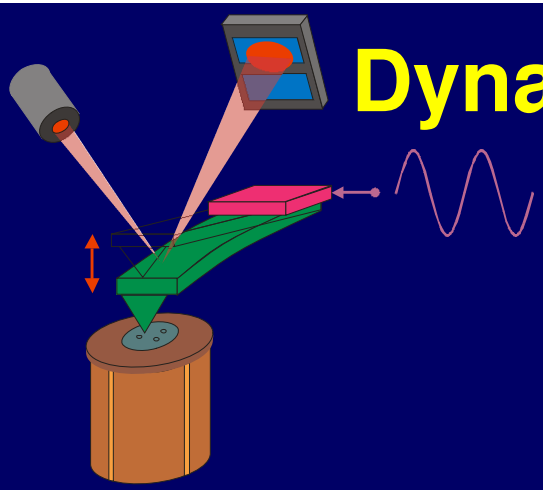
NIMS (Tsukuba, Japan): O. Custance

Dynamic AFM

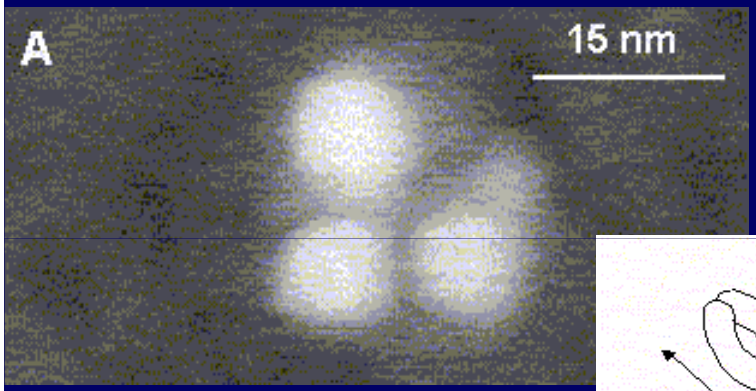


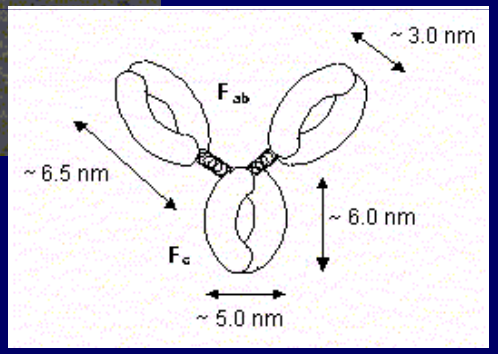
http://monet.physik.unibas.ch/famars/afm_prin.htm

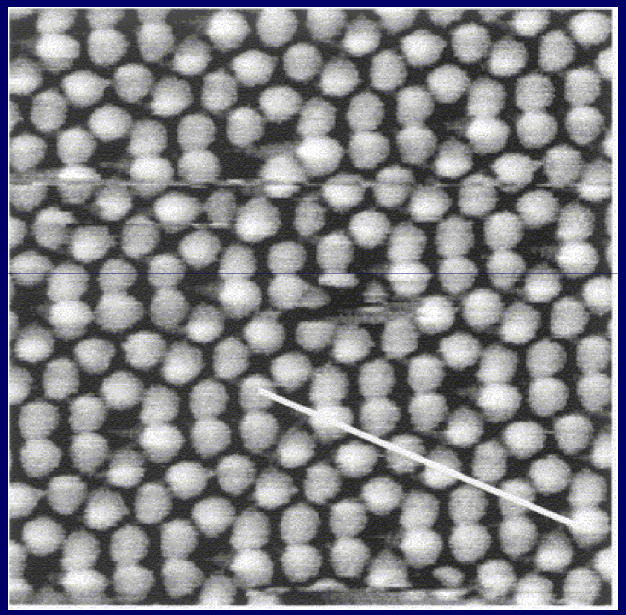
Dynamic AFM: Our Goal



Why changes observed in the dynamic properties of a vibrating cantilever with a tip that interacts with a surface make possible to:







AM-dAFM

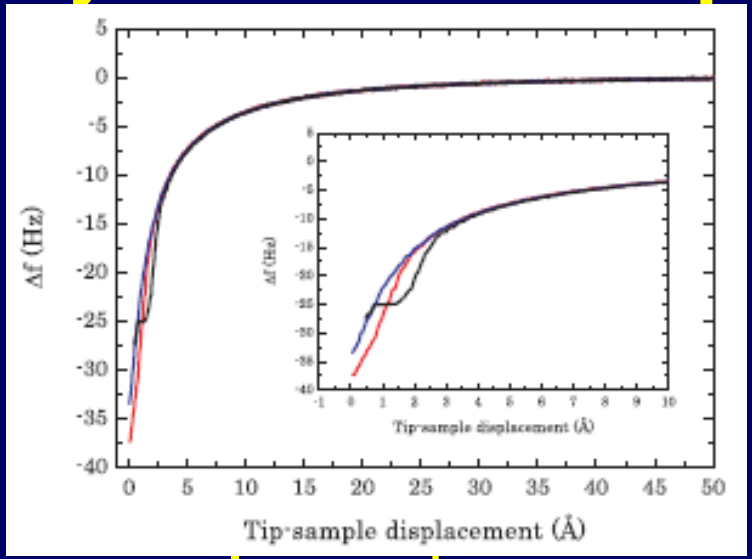
• Obtain molecular resolution images of biological samples in ambient conditions.

•Resolve atomic-scale defects in UHV.

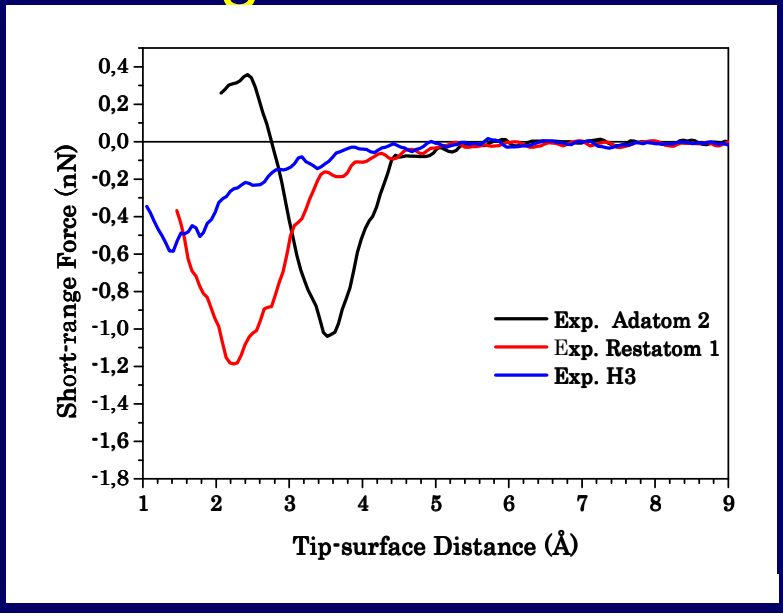
FM-dAFM

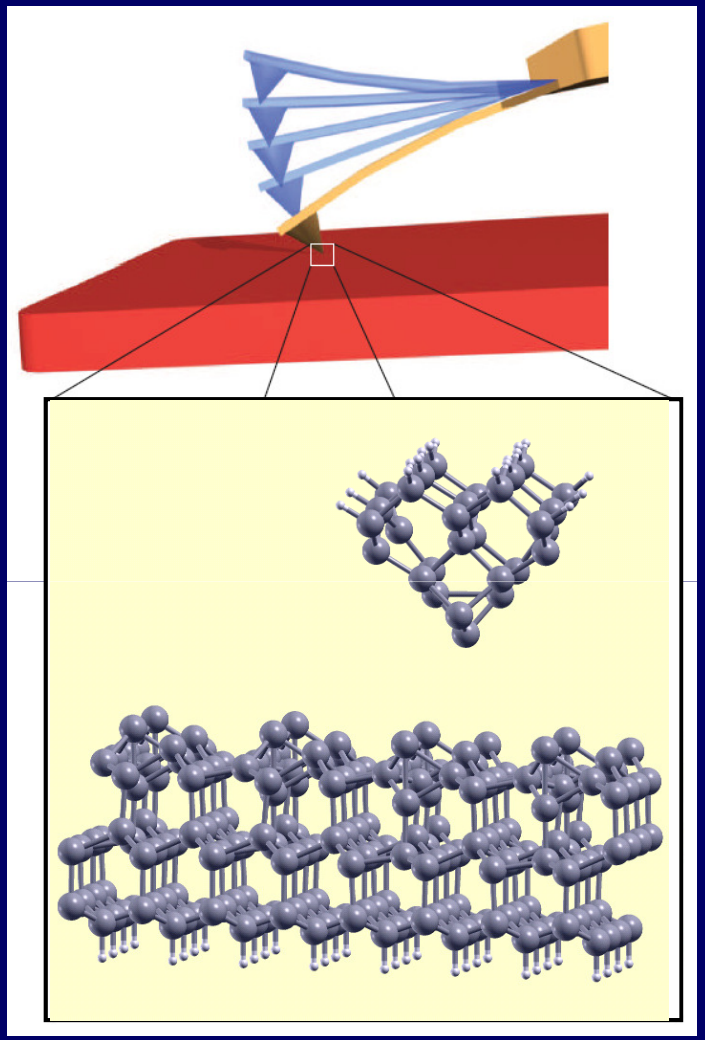
R. García and R. Pérez, Surf. Sci. Rep. 47, 197 (2002)

Dynamic Force Spectroscopy: Access to F_{ts}



Inversion algorithms



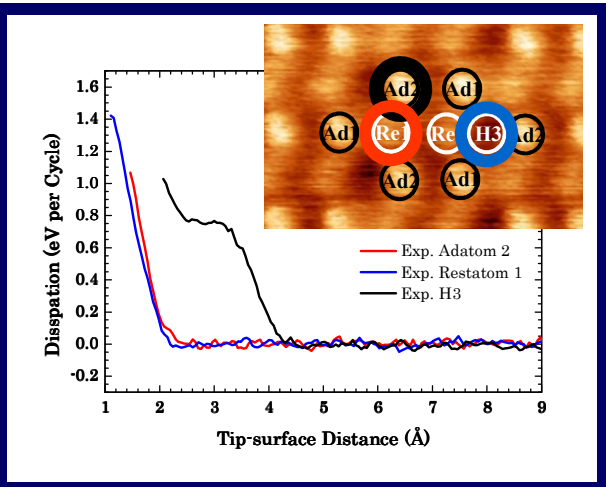


SR forces amenable to ab initio calculations

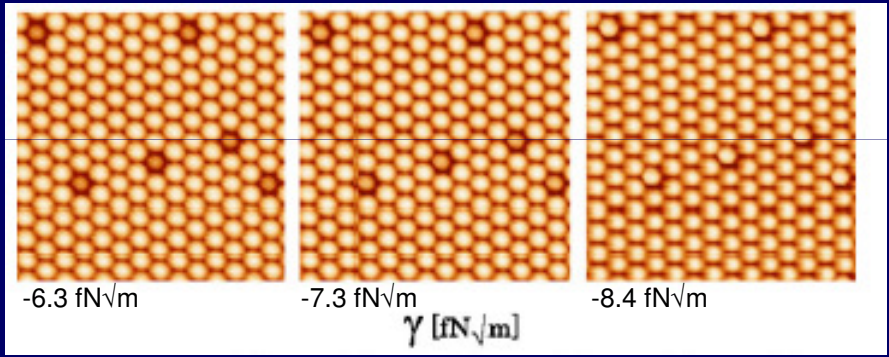
Recent developments in FM-AFM

1. DISSIPATION: Characterizing the tip structure and identifying a dissipation channel due to single atomic contact adhesion.

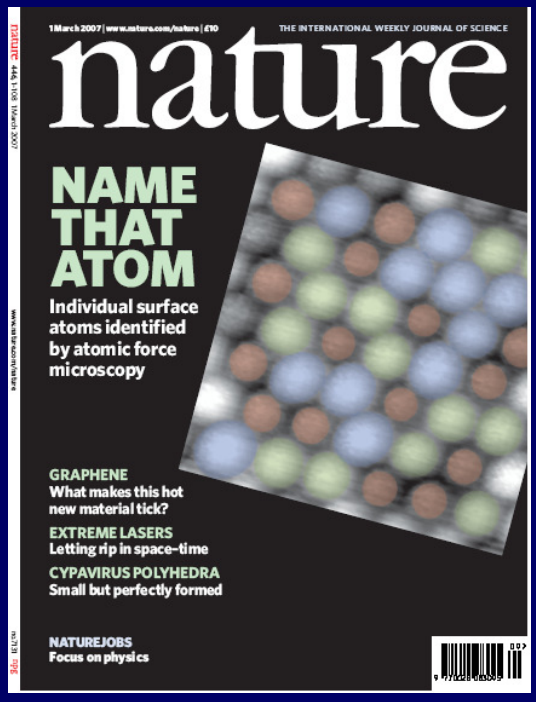
N. Oyabu et al. Phys. Rev. Lett. 96, 106101 (2006).



2. IMAGING: changes in topography: access to the real surface structure?



Y. Sugimoto et al
Phys. Rev. B 73, 205329 (2006).



3. CHEMICAL IDENTIFICATION:

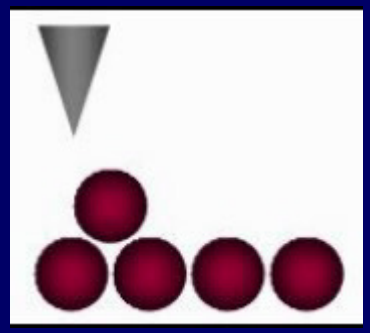
based on the relative interaction ratio of the maximum attractive force measured by dynamic force spectroscopy

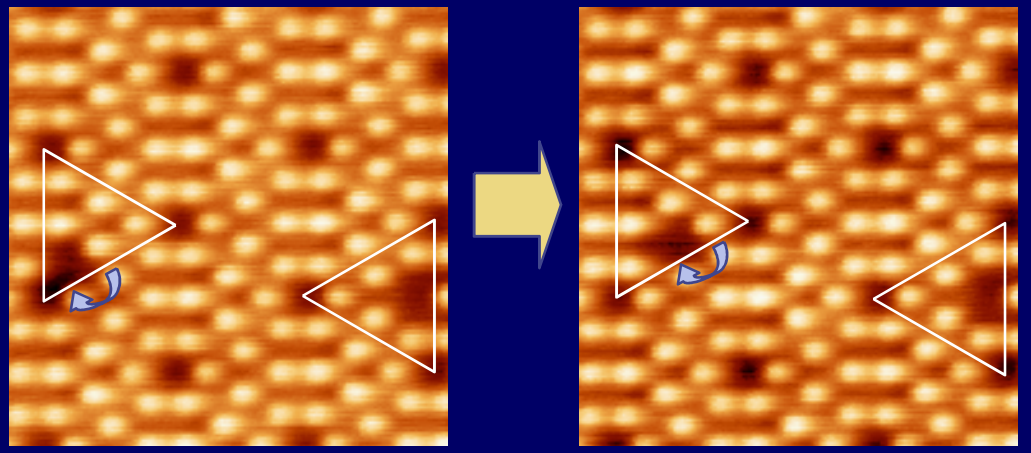
Y. Sugimoto et al Nature 446, 64 (2007).

Recent developments in FM-AFM

Understanding RT DFM-based single-atom manipulation

4. LATERAL MANIPULATION: Si vacancy on Si(111)-7x7 (tip assisted thermal hopping)

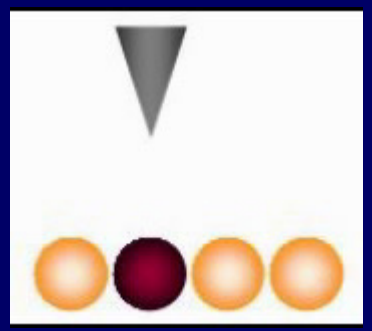




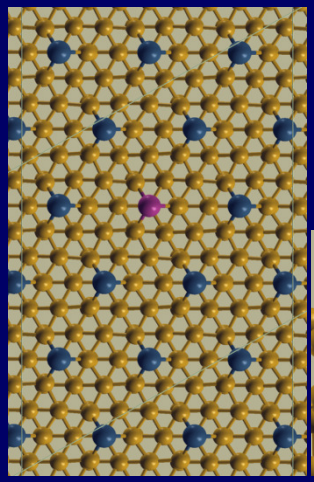
Y. Sugimoto et al. Phys. Rev. Lett. 98, 106104 (2007).

5. VERTICAL MANIPULATION:

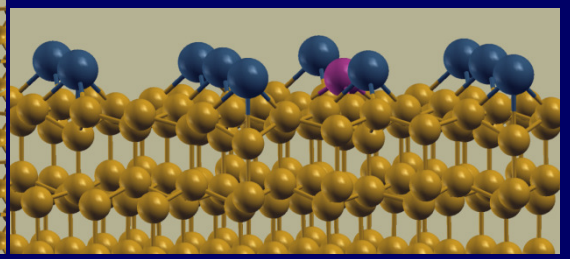
Tip/sample exchange of atoms on Sn/Si(111)

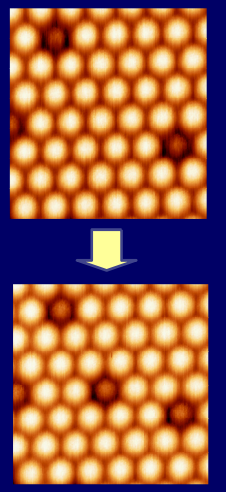


Y. Sugimoto et al., Science 322, 413 (2008).



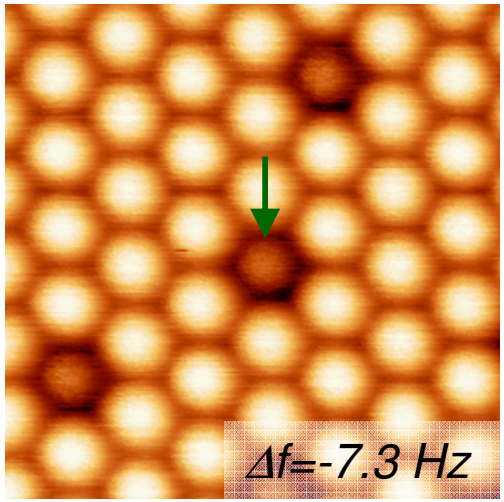
α-Sn/Si(111)-(√3x√3)

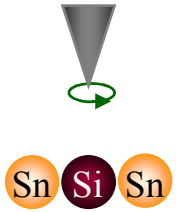




Interchange vertical manipulation: Si→Sn

Tip positioning over a selected Si atom





Atom tracking technique

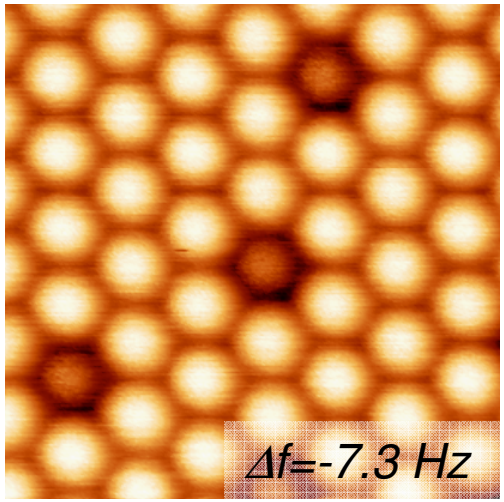
Lateral precision: ±0.1 Å

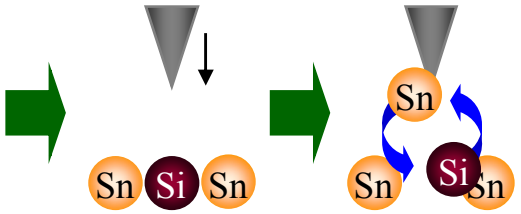
M. Abe, Y. Sugimoto, O. Custance, and S. Morita, Appl. Phys. Lett. 87 (2005) 173503.

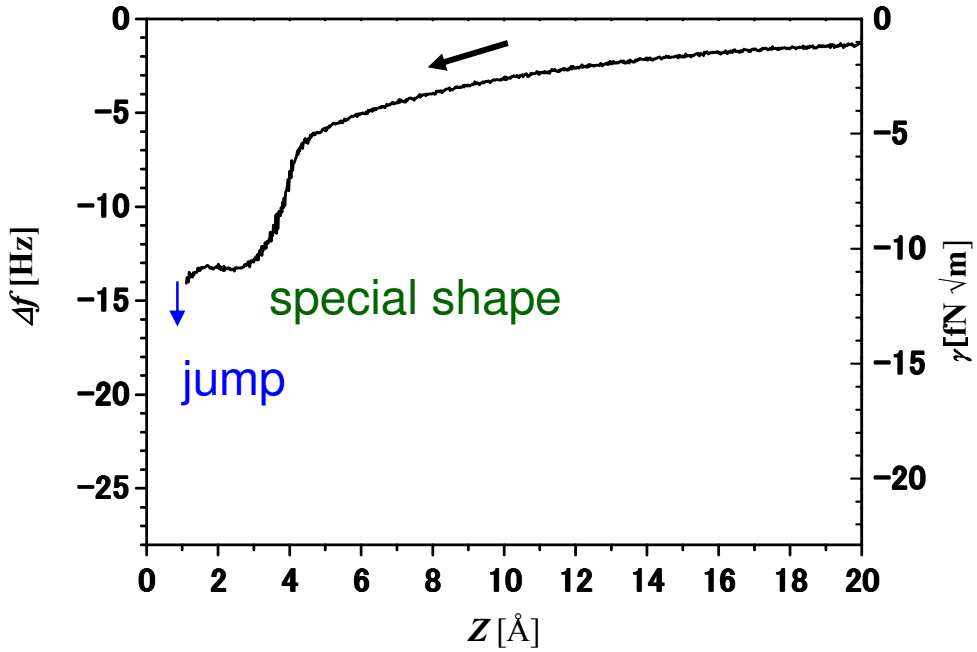
M. Abe, Y. Sugimoto, O. Custance, and S. Morita, Nanotechnology 16 (2005) 3029.

Interchange vertical manipulation: Si→Sn

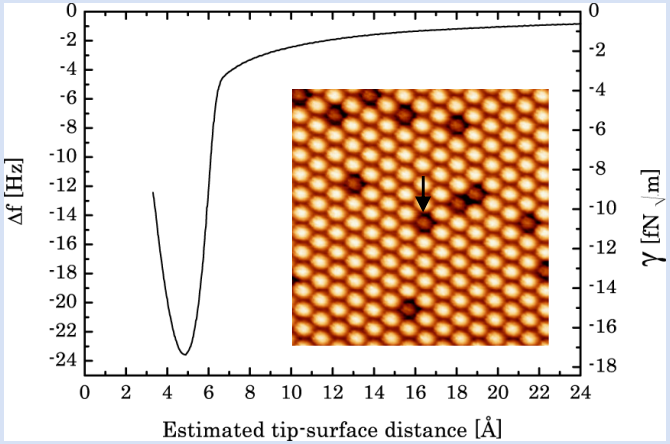
Tip approach toward the Si atom





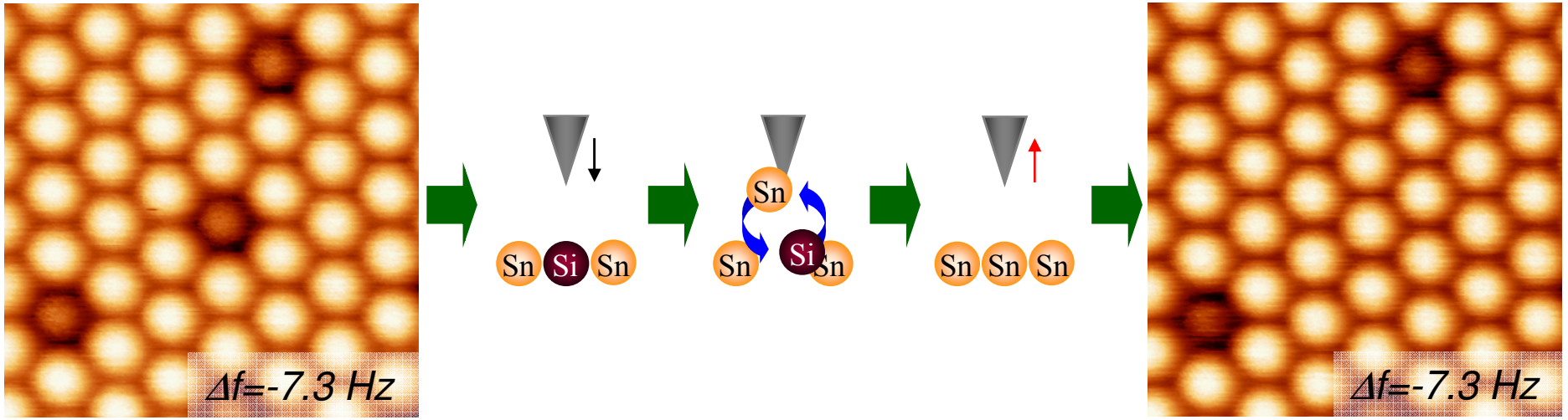


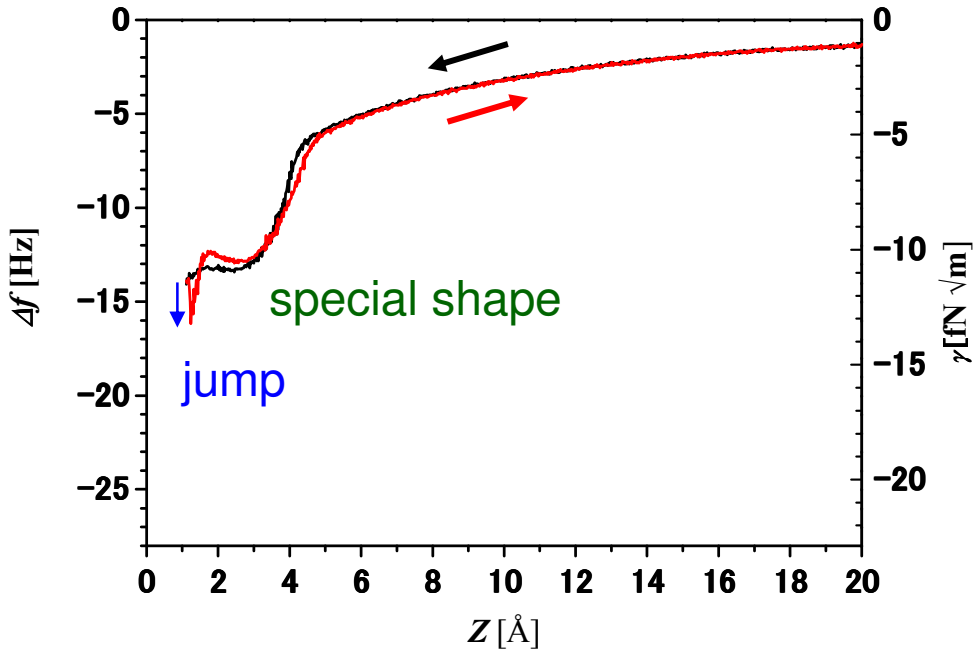
Ref. Typical *Δf-Z* curve



Interchange vertical manipulation: Si→Sn

Tip retraction from the surface

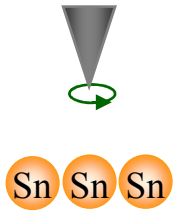


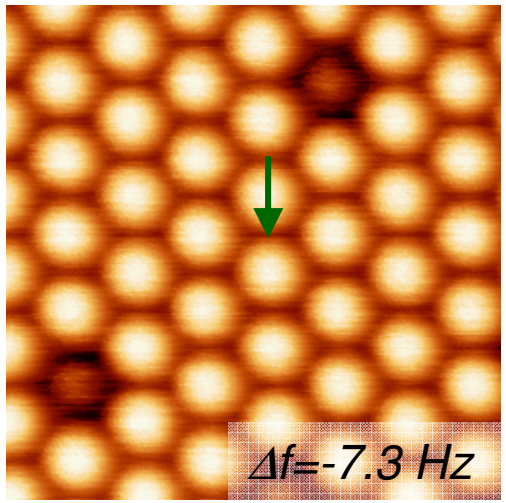


- The Si atom on the surface was interchanged with a Sn atom at the tip apex.
- The contrast of the images before and after manipulation are almost same.

Interchange vertical manipulation: Sn→Si

Tip positioning over the previously deposited Sn atom





Atom tracking technique

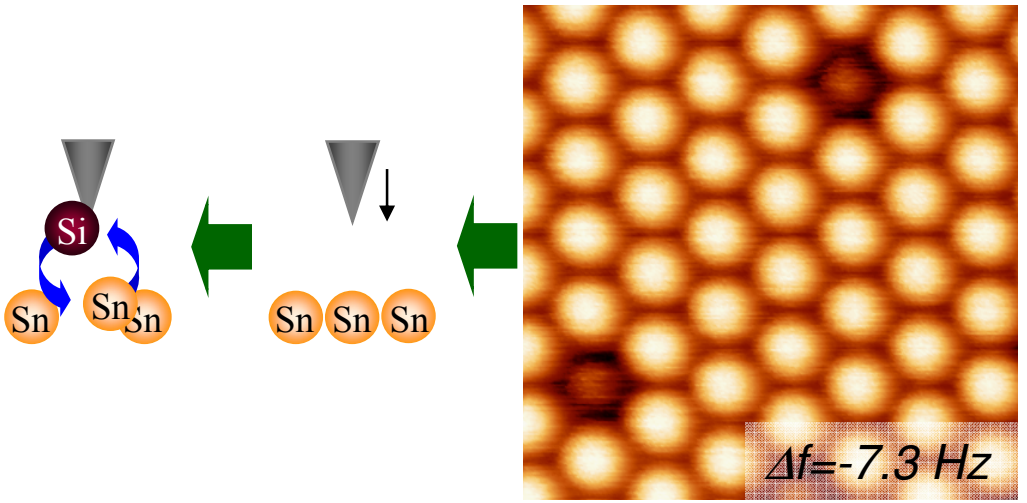
Lateral precision: ±0.1 Å

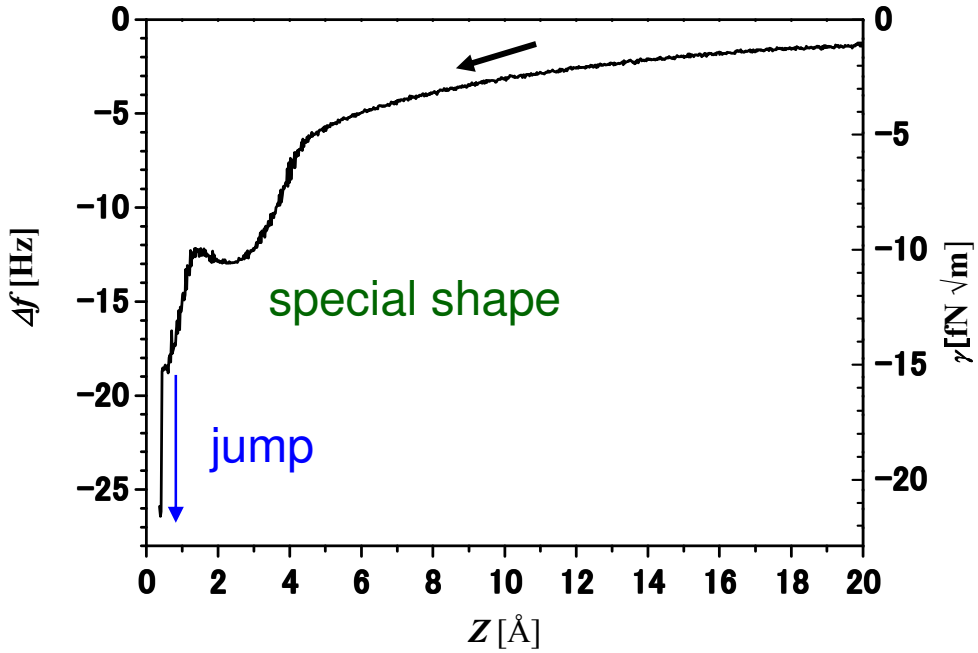
M. Abe, Y. Sugimoto, O. Custance, and S. Morita, Applied Physics Letters 87 (2005) 173503.

M. Abe, Y. Sugimoto, O. Custance, and S. Morita, Nanotechnology 16 (2005) 3029.

Interchange vertical manipulation: Sn→Si

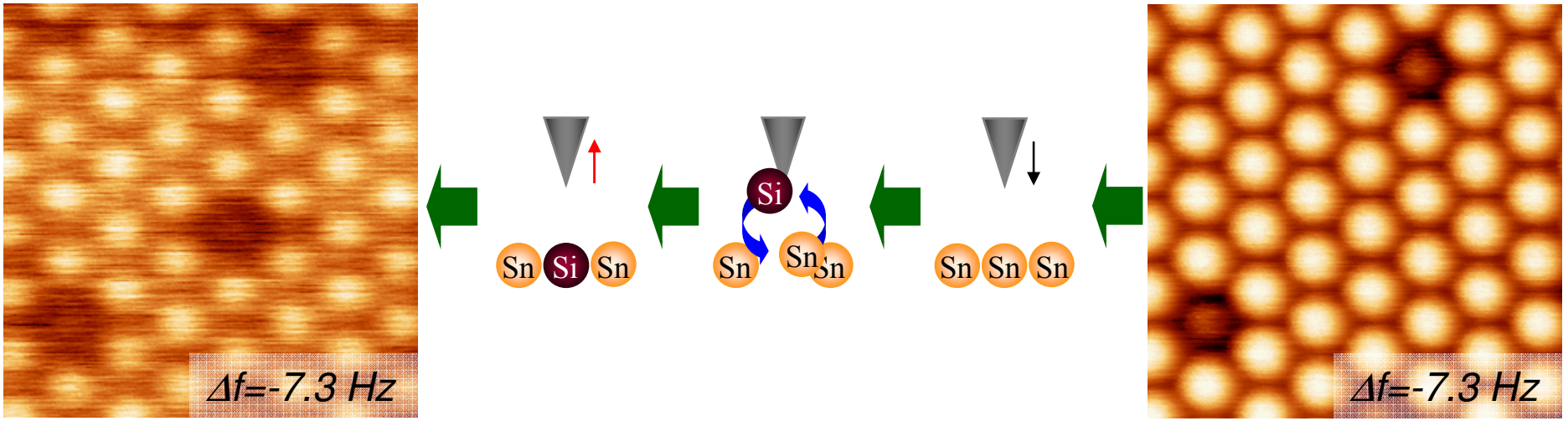
Tip approach toward the deposited Sn atom



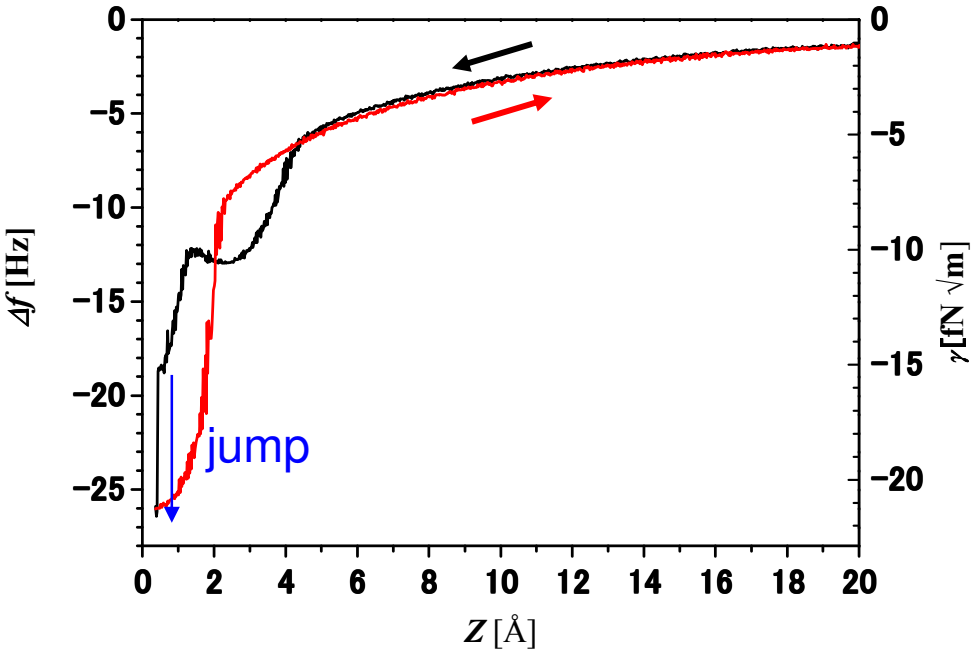


Interchange vertical manipulation: Sn→Si

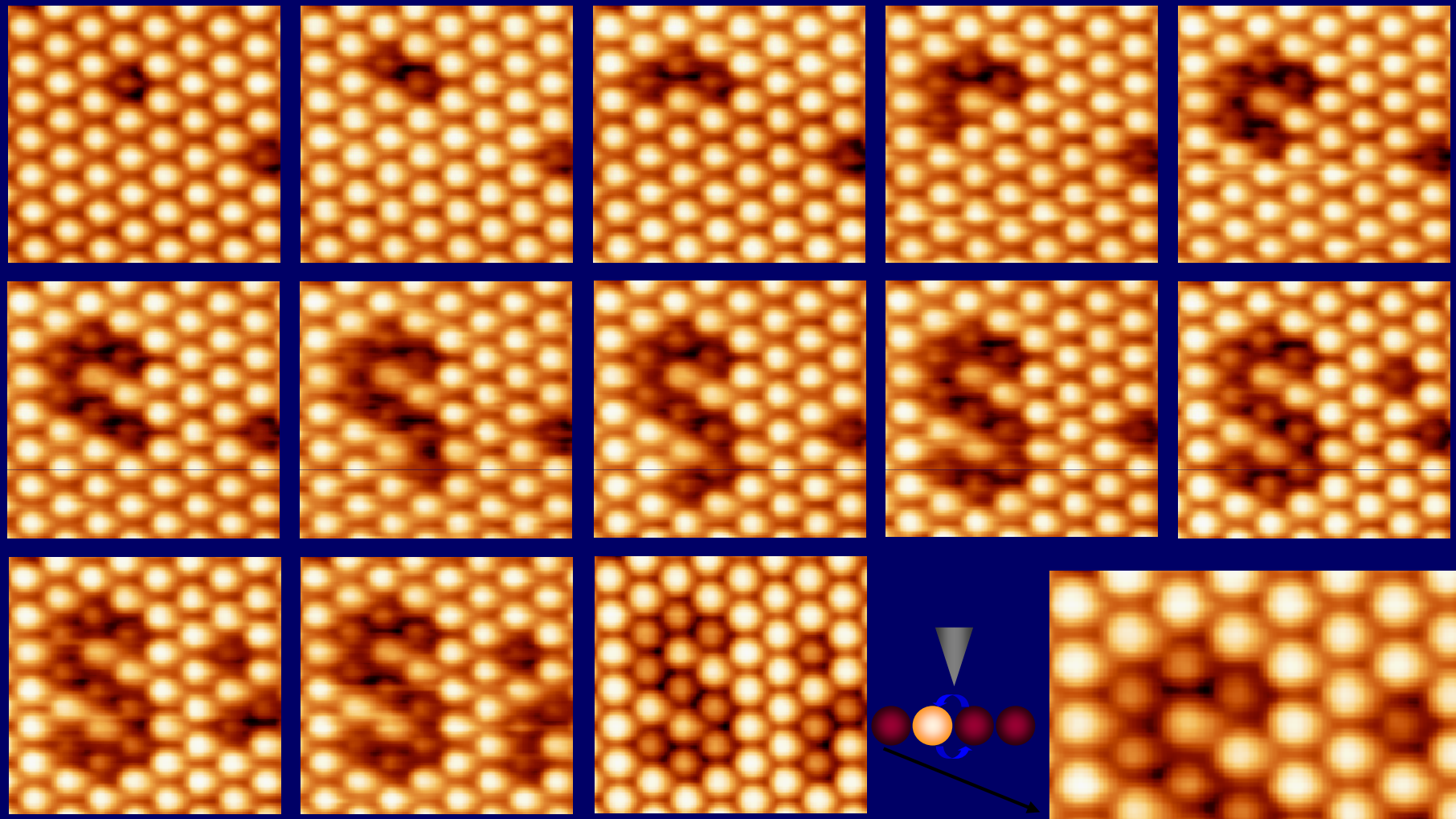
Tip retraction from the surface



- The Sn atom on the surface was interchanged with a Si atom at the tip apex.
- The image contrast dramatically changed after atom interchange.

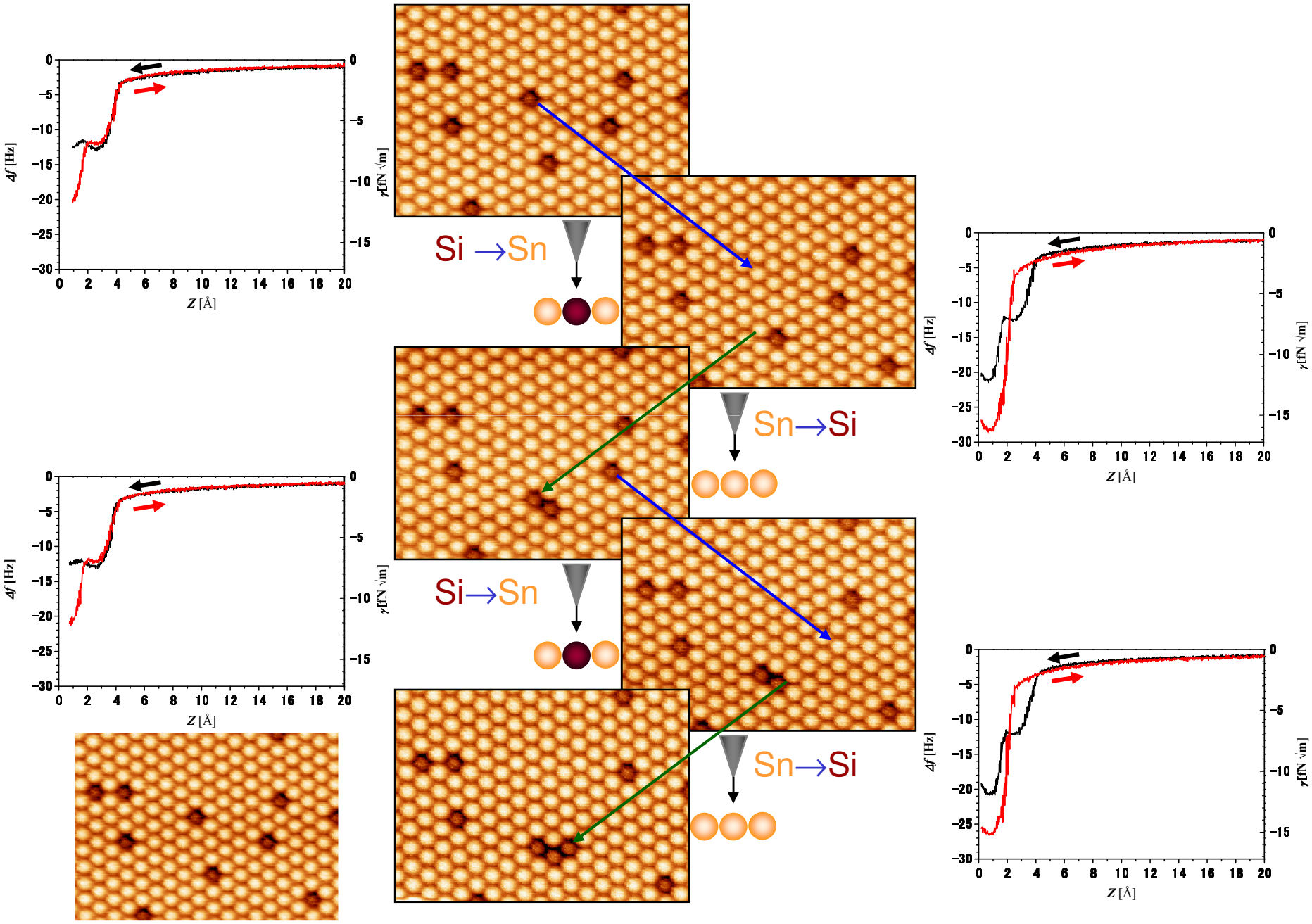


Atomic “dip-pen” nanolithography



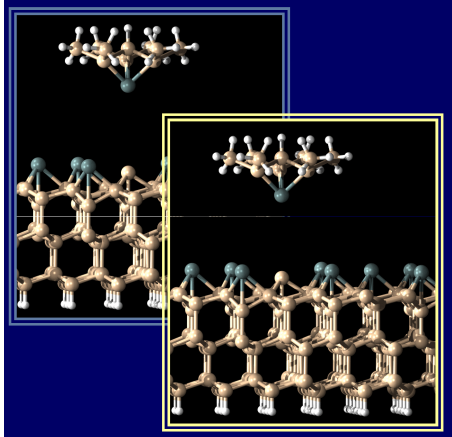
- 11 Interchange vertical manipulations
  + 1 Interchange lateral manipulation
- The construction time was reduced to 1.5 hours.

Reproducibility

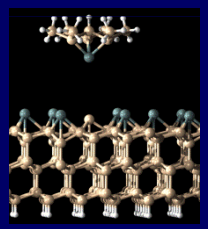


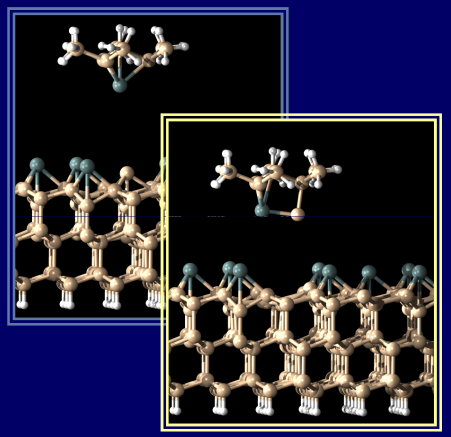
A complex phase space...

- Manipulation in the strong tip-surface interaction regime.
- Tip and sample modification, several solutions (complex phase space): plastic deformations.
- Jumps between solutions also upon retraction. **Different "final" configurations!!** (depending on the indentation depth, the position or the atomic structure of the tip).

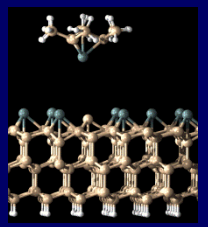


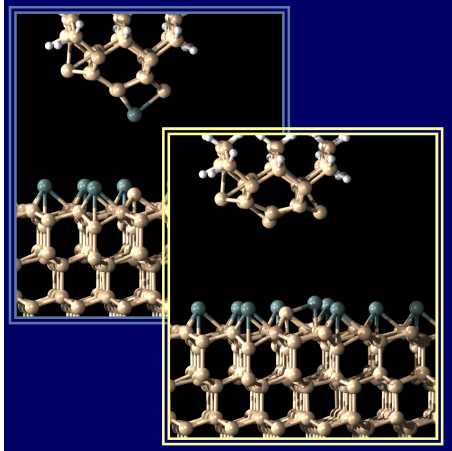
Final configuration
||
Initial configuration



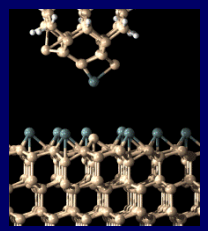


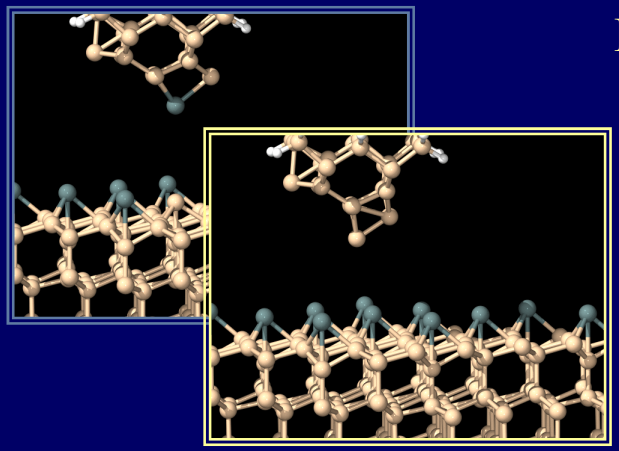
Final configuration:
Surface atom transferred to tip.
Creation of an atomic vacancy
(N. Oyabu et al, PRL 2003)



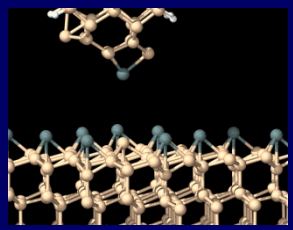


Final configuration:
Deposition of a tip atom in the surface
(N. Oyabu et al, PRL 2003)





Final configuration:
Atom interchange
(Sugimoto et al,
Science 322, 413, 2008)



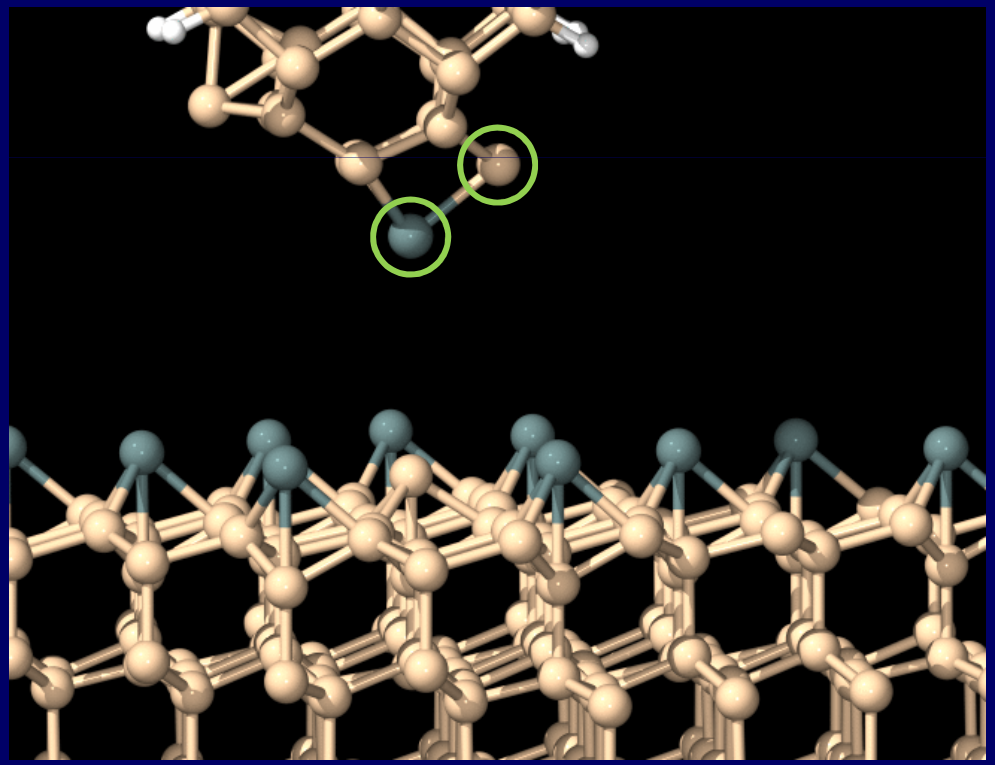
Mechanism: Tip model

- Small tip surface distances: multi-atom contact
- Complex phase space
- Experimental tip: stable at the strong tip-surface interaction regime
- Apex model: all the atoms fixed but the two outermost ones.

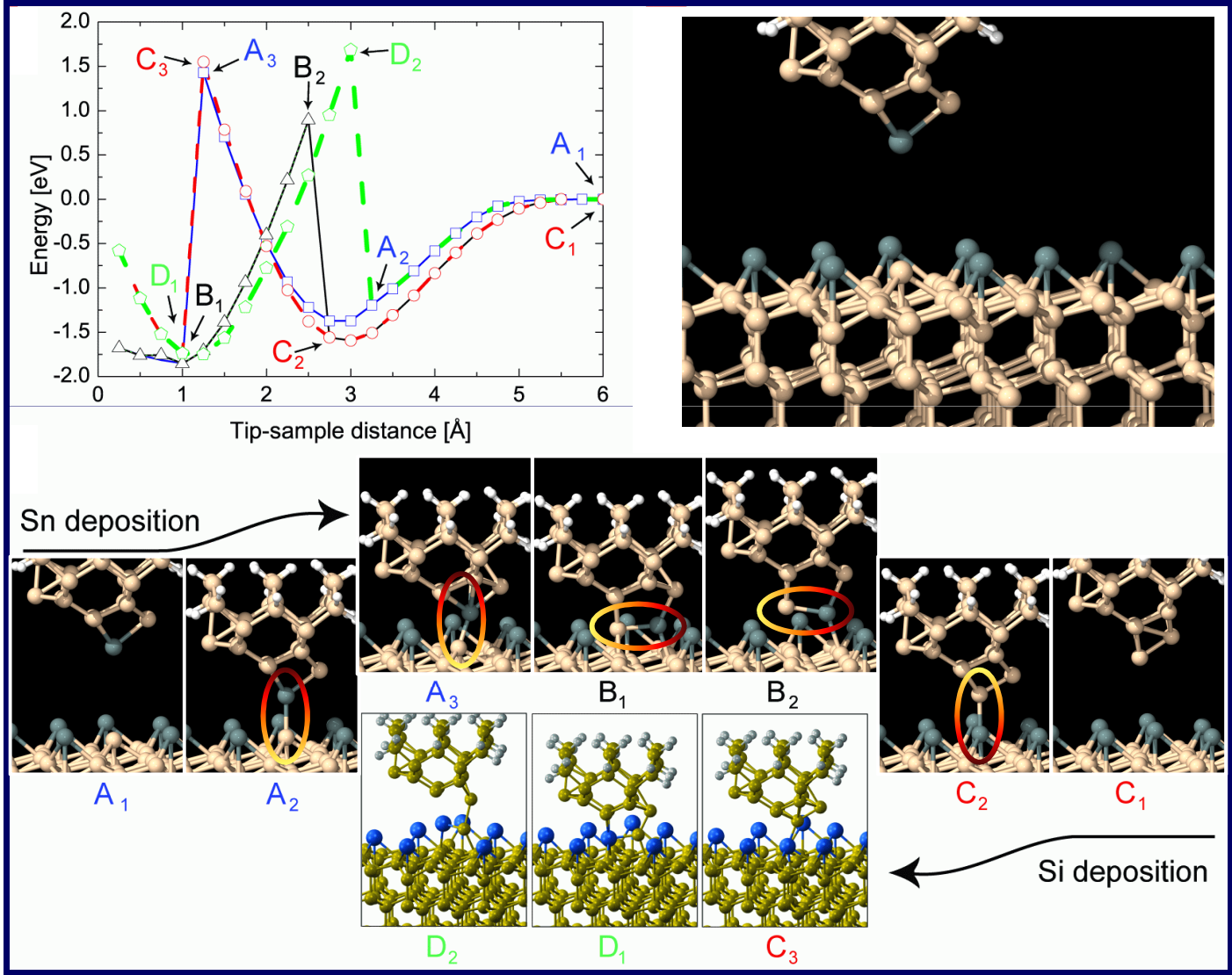
Advantages:

I. Stability

II. Simplification of the phase space



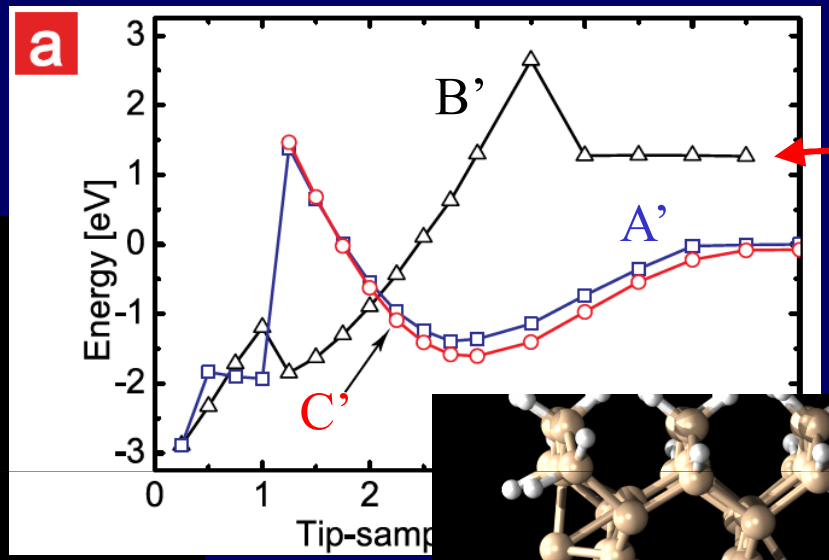
Mechanism: Vertical scan

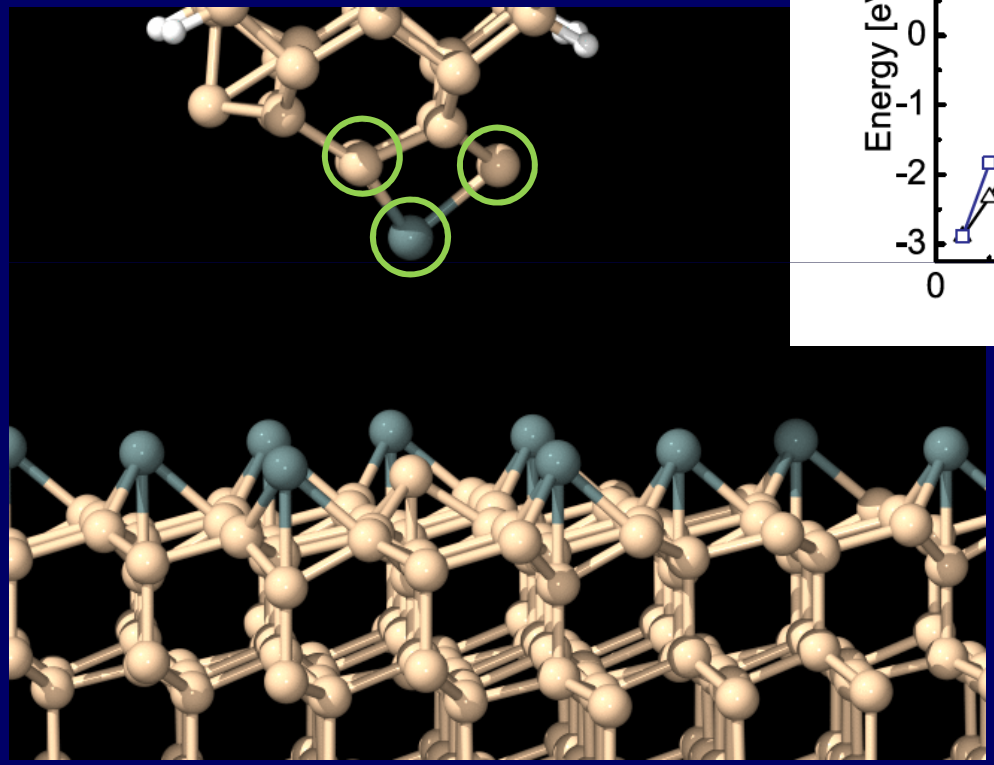


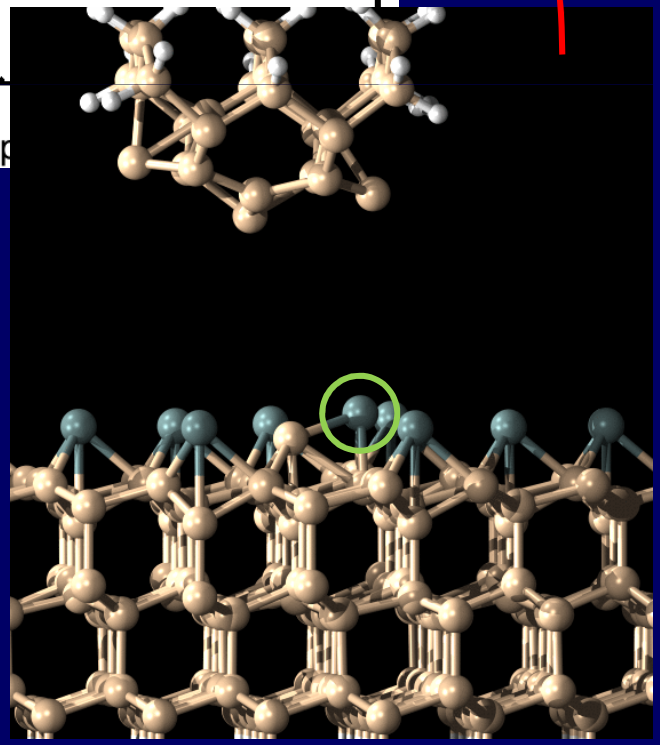
- Vertical manipulation as combination of mechanical and thermal process.
- Formation of characteristic dimer structure along deformation path (energetically stable).
- Atomic rearrangement reflects by energy & forces discontinuities.
- Local character of the tip-sample deformation.
- Temperature effect not included in the simulation.

Mechanism: Energy Barriers

- Tip model: 4 atoms free
- Complicated configuration space; only limited phase space explored

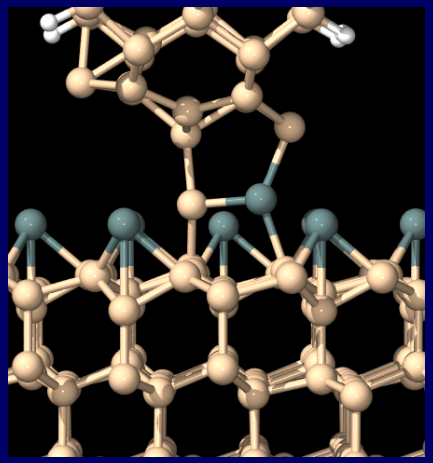


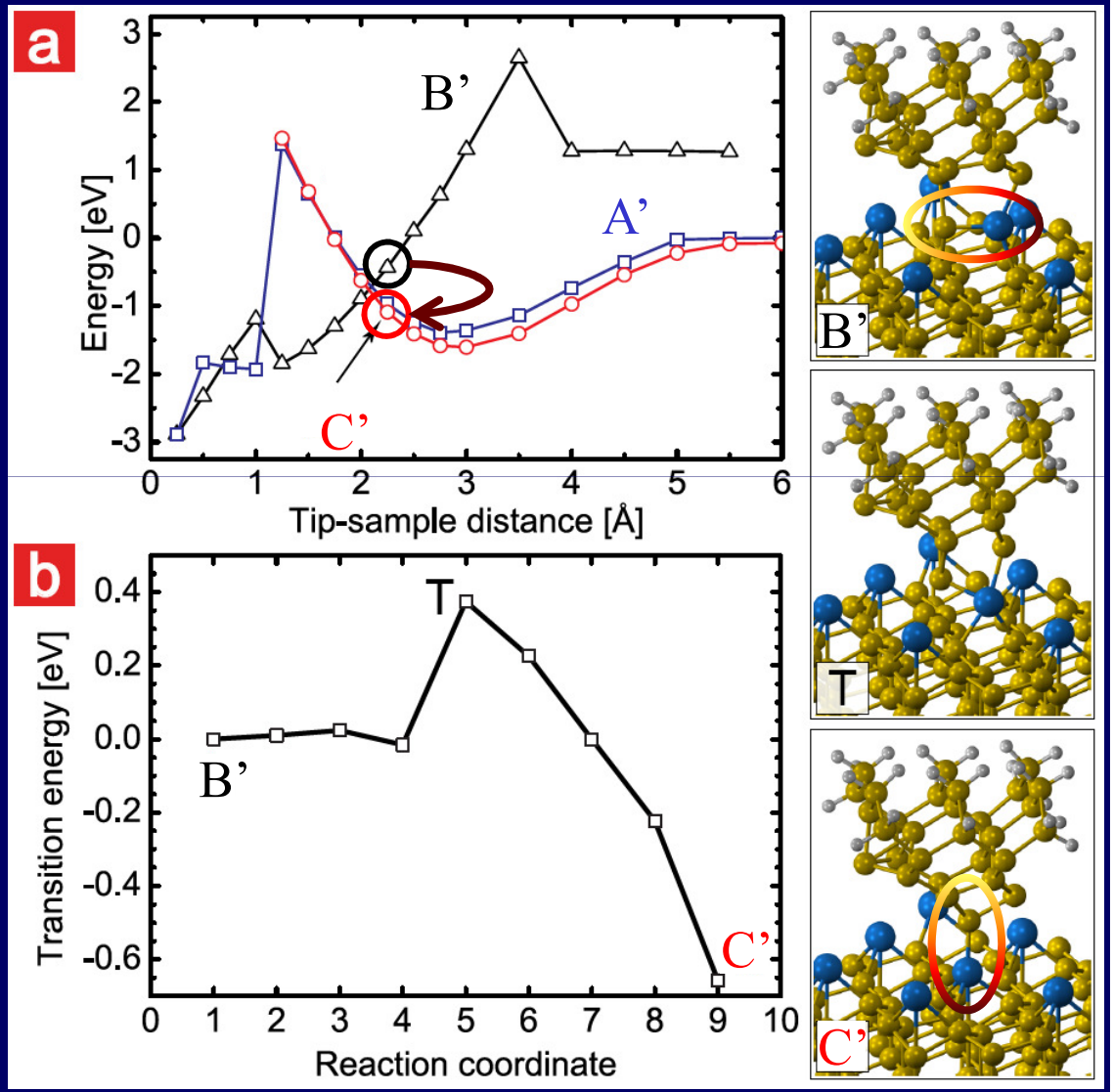




Mechanism: Energy Barriers

- Explore possible dimer rearrangement due to thermal & mechanical movement
- Complicated configuration space; only limited phase space explored
- Estimated energy barriers ~ 0.4 eV (Nudged elastic band calculation).
- Dependence on the tip-sample distance, tip elasticity & structure, temperature...

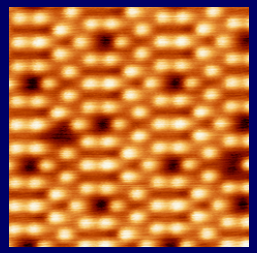


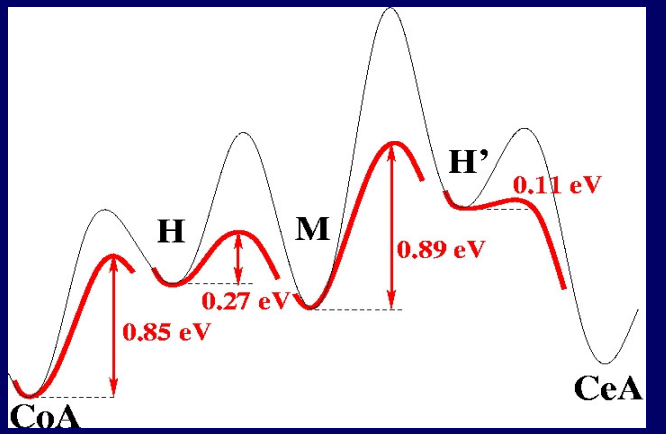


Conclusions

Single-atom manipulations: atomistic insight into these processes.

Lateral Si-vacancy manipulation

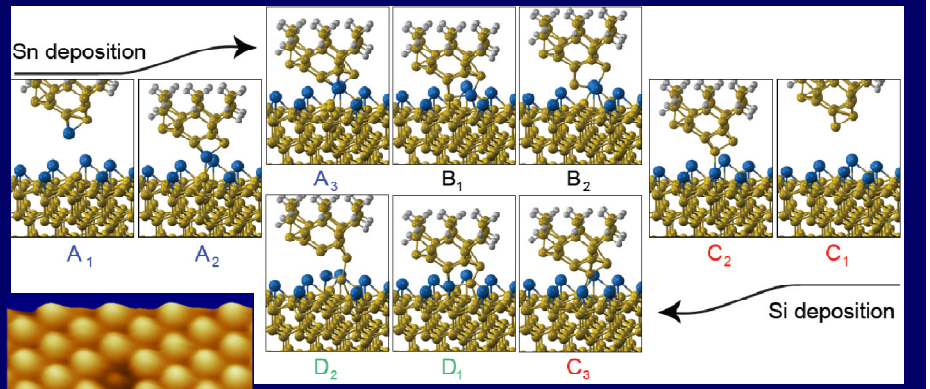


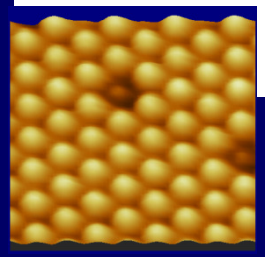


- Significant reduction of activation energy due to the tip proximity
- Operating at the attractive force regime

Y. Sugimoto et al, Phys. Rev. Lett. 98, 106104 (2007)

Vertical Si/Sn-exchange manipulation





- New manipulation method: 'Interchange vertical manipulation'
- Characteristic mechanical deformation: the "hybrid tip-surface" dimer structure
- Operating at the repulsive force regime
- Combination of mechanical and thermal processes

Y. Sugimoto et al, Science 322, 413 (2008).

Summary

1. Nanomechanics & SPM Theory Group: Forces & Transport in Nanostructures with ab initio methods

2. "Tip-Induced Reduction of the Resonant Tunneling Current on Semiconductor Surfaces"
Phys. Rev. Lett. 101, 176101 (2008)

3. "Fullerenes from Aromatic Precursors by Surface Catalysed Cyclo-dehydrogenation"
Nature 454, 865 (2008)

4. "Complex Patterning by Vertical Interchange Atom Manipulation Using Atomic Force Microscopy"
Science 322, 413 (2008)

Acknowledgements & Funding

THEORY: UAM, Spain:

Pablo Pou, Wojciech Kaminski, Pavel Jelinek (FZU,Prague)

Giulio Biddau, Krzysztof Kosmider

EXPERIMENTS:

FM-AFM: Osaka University & NIMS (Tsukuba), Japan:

N. Oyabu, Y. Sugimoto, M. Abe, S. Morita & O. Custance

FULLERENES: ICMM (CSIC): G. Otero,C. Sanchez-Sanchez, R. Caillard, M.F. Lopez, C. Rogero, F.J. Palomares, J. Mendez, J.A. Martin-Gago

Chemistry ICMM: B. Gomez-Lor ICIQ: N. Cabello, A.M. Echevarren

STM: FZU (Prague): M. Švec, V. Chab

MEC (Spain): Projects MAT2005-01298, NAN2004-09183-C10-07

EU FP-6: STREP project FORCETOOL (NMP4-CT-2004-013684)

RES (Computing): Magerit (CesViMa) & Mare Nostrum (BSC)