Introduction to Nanotechnology

- Textbook：

  Nanophysics and Nanotechnology

  by:

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Classroom: A209
Time: Thursday; 13:40-16:30 PM
Office hour: Thur., 10:00-11:30 AM or by appointment

Physical-based Experimental Approaches to Nanofabrication and Nanotechnology

Subjects: Today class

1. AFM-BASED NANOFABRICATION
2. Smooth Surface
3. Scanning Tunneling Microscopy

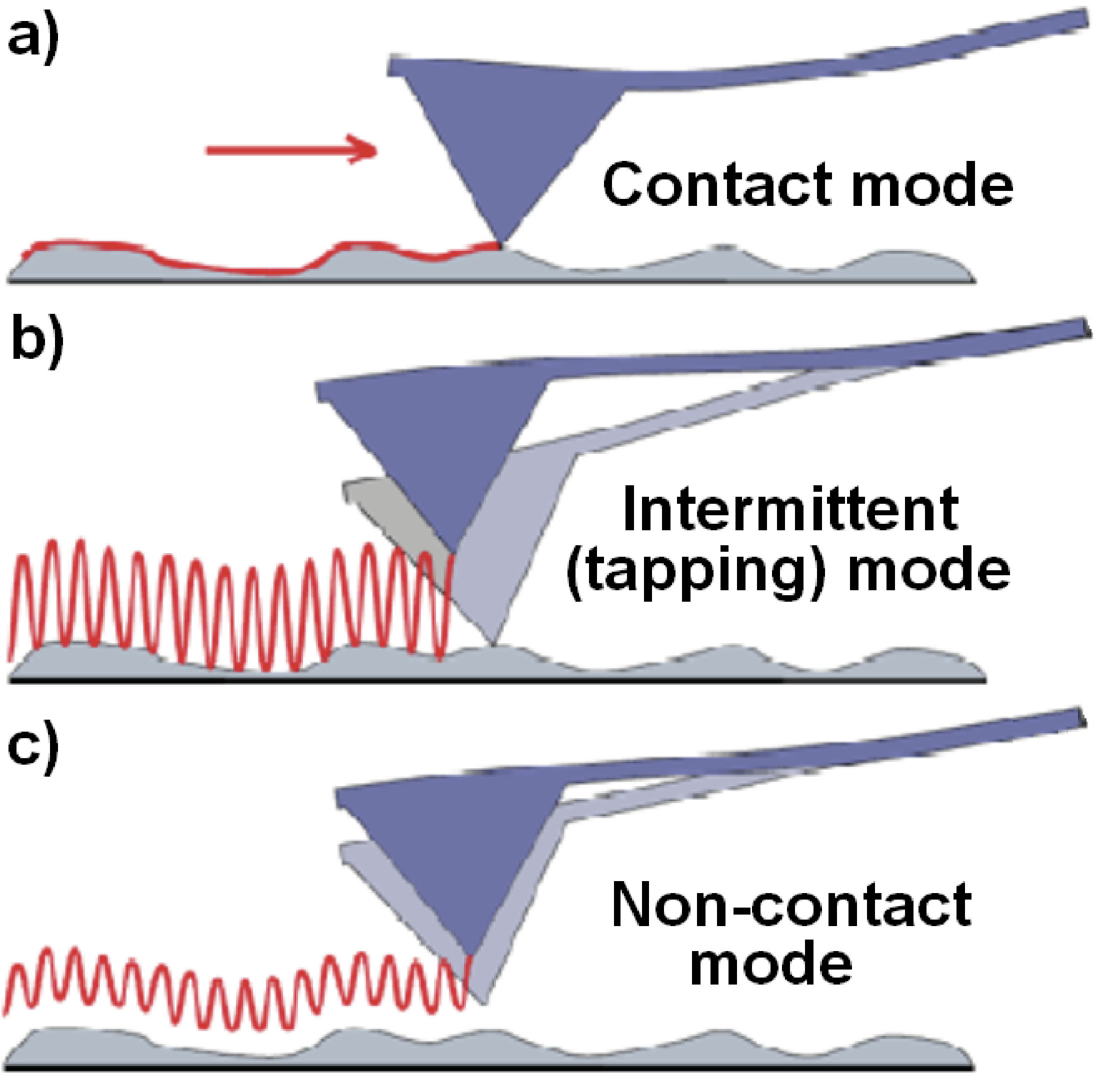
WHAT IS AFM-BASED NANOFABRICATION

- **Atomic Force Microscopy (AFM) -based nanofabrication is using a functionalized cantilevered-tip for performing nanofabrication.**
- **Nanofabrication aims at building nanoscale structures (0.1 – 100 nm), which can act as components, devices, or systems with desired properties, performance, reliability, reproducibility, in large quantities at low cost.**
  - **Methodology or Processing Technology**
  - **Toolbox** (**Equipment:** hardware, software, system)
  - **Nanostructured Materials or Raw Materials**
  - **Physical Product** (Components, device, system….)

AFM-Based Nanofabrication: Milestones

- **1982: Scanning Tunneling Microcopy (STM) invented by Binnig, Rohrer, and Gerber** (1986 Nobel Physics Prize).
- **1984: Scanning Near-Field Optical Microscopy (SNOM) introduced by Pohl, Denk, Lanz, & Lewis, Isaacson, Harootunian, Muray.**
- **1986: Atomic Force Microcopy invented by Binnig** (US Patent 4,724,318)**.**
- **1990s: Lithography Using Scanning Tunnelling Micoscopy (STM) and AFM.**
- **2000s: Lithography Using (SNOM) and Deep Pen Nanofabrication (DPN).**
- **2008: APMC** (led by Zyvex Labs) **Awarded US$9.7 Millions by DARPA & Texas ETF for Commercialization of Tip Based Nannofabrication (TBN) (focusing on AFM).**
- **2009/10 DOE Solicitation Upcoming.**
- **2009/10 NSF Solicitation Upcoming.**
- **• 2009-2013: $100 million in 5 years in USA.**

Three Modes of Operation



- **Contact mode**: also known as static mode, an AFM tip makes soft "physical contact" with the sample. The tip is attached to the end of a cantilever with a low spring constant. The contact force causes the cantilever to bend to accommodate changes in topography.

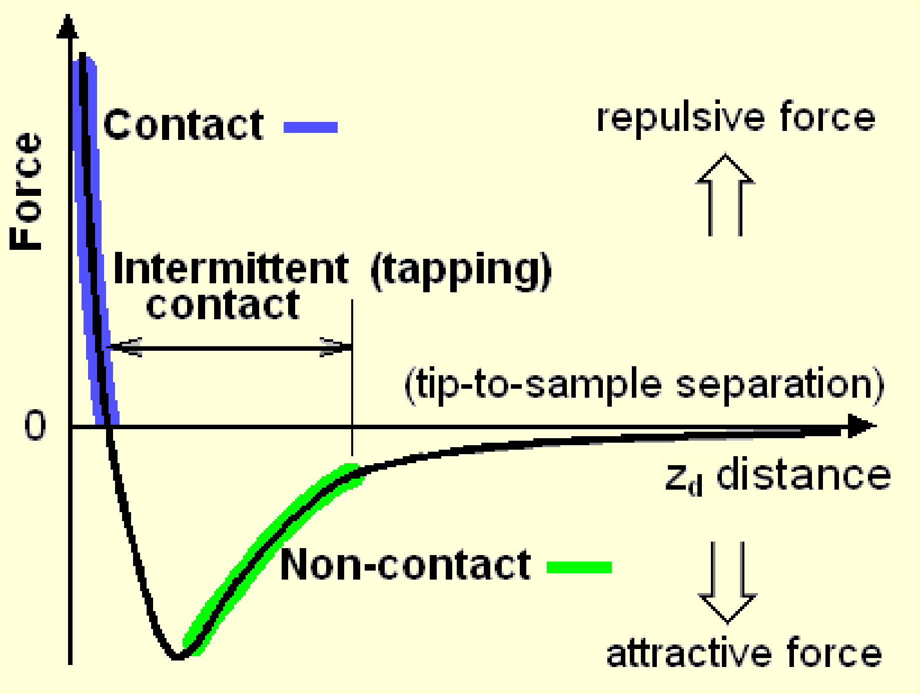
  Measurement: displacement (δ)

  Feedback signal: force (F) = kδ

- **Intermittent contact mode**: also known as tapping mode, the cantilever is driven to oscillate up and down at near its resonance frequency by a small piezoelectric element mounted in the AFM tip holder. The amplitude of this oscillation is greater than 10 nm, typically 100 to 200 nm. A tapping AFM image is therefore produced by detecting the force of the oscillating contacts of the tip with the sample surface

Operation Modes and Van der Waals Curve

AFM can be operated in three different modes. Each mode is operated in a different level of Van der Waals force



Interatomic force versus distance

Operated at Frequency Modulation or Amplitude Modulation

Measurement:

displacement, $\delta = \delta(t)$

Feedback signal:

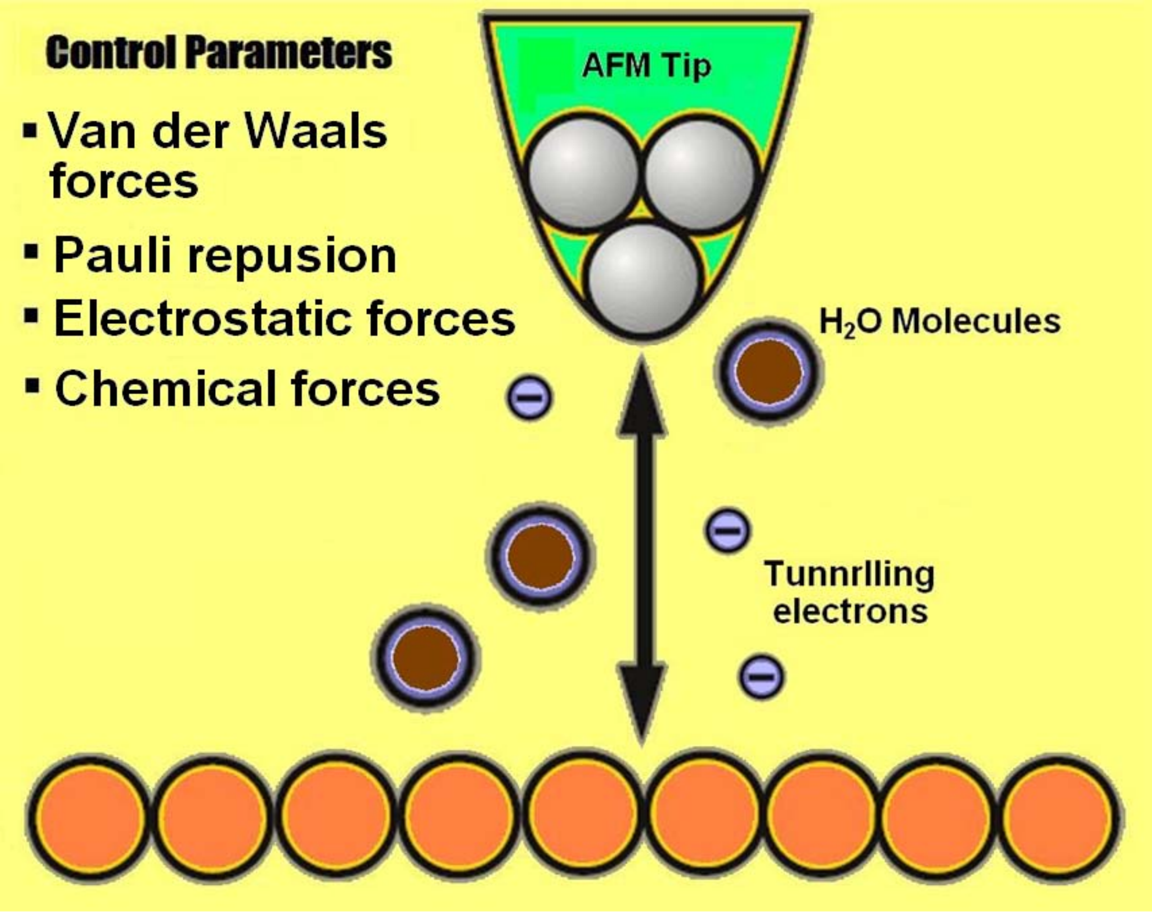
dynamic force, $F_d = F(k, \delta, t)$

- Non-contact (NC) mode: also known as dynamic mode, the cantilever is vibrated near but not contact to the sample surface at a frequency slightly above its resonance frequency (typically, 100 - 400 kHz)) where its amplitude is typically a few nm. Due to interaction of forces acting on the cantilever when the tip comes close or taps to the surface (within 10 nm), Van der Waals force or other forces ($\sim 10^{12}$ N) act to decrease the resonance frequency of the cantilever. This decrease in resonance frequency combined with the feedback loop system maintains a constant oscillation amplitude or frequency by adjusting the average tip-to-sample distance. Measuring the tip-to-sample distance at each data point allows the scanning software to construct a topographic image of the sample surface. The absence of repulsive forces in NC mode permits its use in the imaging “soft” samples.

INTERACTION BETWEEN TIP AND SAMPLE

Presently AFM is loaded with forces and electric voltages in ambient environment

In additional to develop better instrumentation, the quantitative information on these controlling parameters is needed in almost all AFM pattering or lithography processes, including nanoscale manipulation, scratching, anodic oxidation, deep pen, near field and many other emerging techniques



Control Parameters

- Van der Waals forces
- Pauli repusion
- Electrostatic forces
- Chemical forces

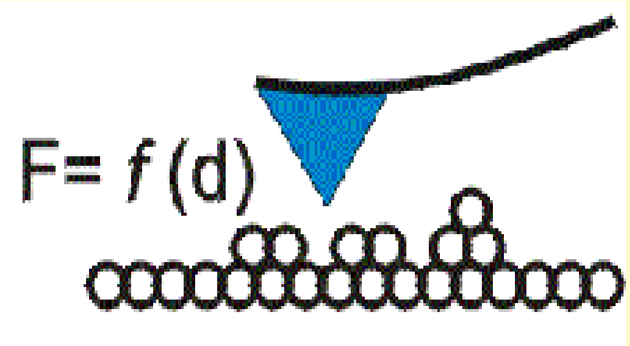
● **To better perform AFM tasks**

● **To develop new AFM capabilities**

TYPICAL ATOMIC FORCE MICROSCOPE

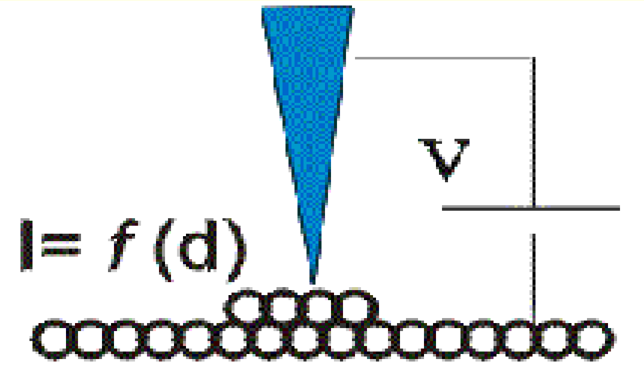
Digital Instruments Nanoscope IIIA

AFM: d = tip gap

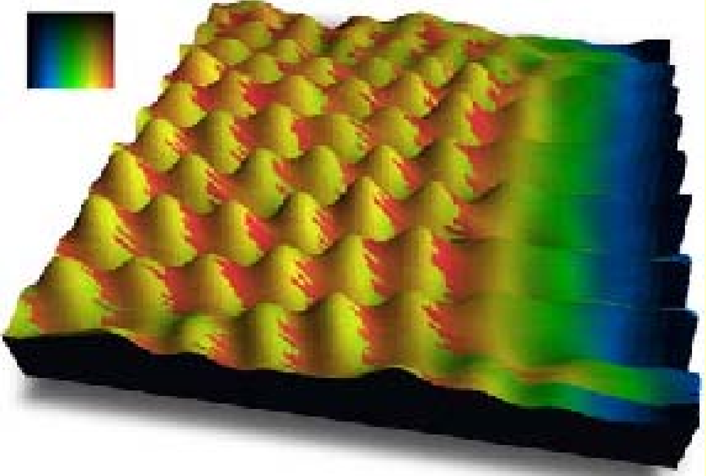


- Feedback signal is
  Force (F)
- Room environment
  Low cost
- Cantilever provides
  Dynamic mode

STM: d = tip gap

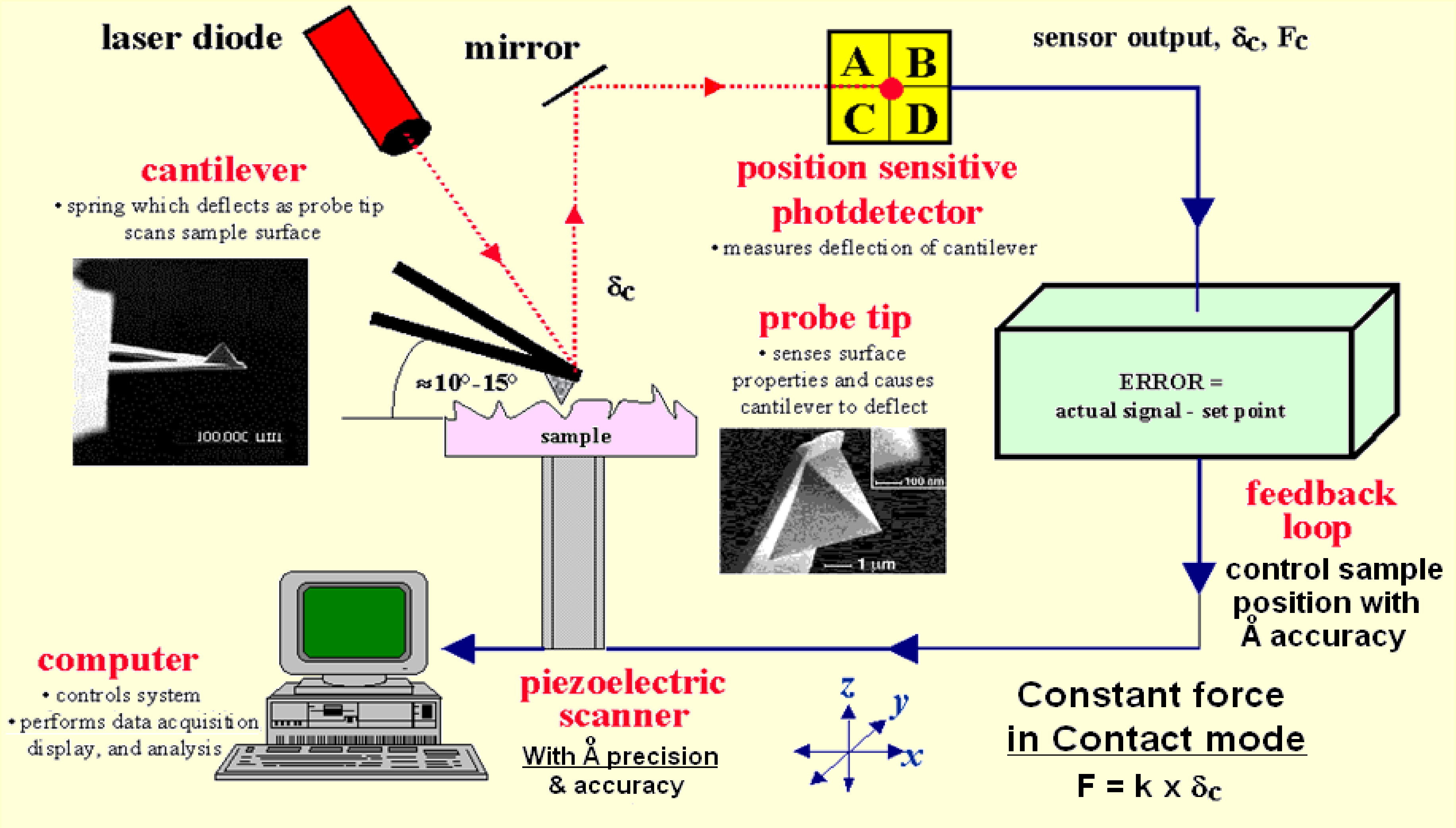


Feedback signal is
current (I)
Vacuum environment
High cost



2.5 x 2.5 nm simultaneous topographic and friction image of highly oriented pyrolytic graphic (HOPG). The bumps represent the topographic atomic corrugation, while the coloring reflects the lateral forces on the tip. The scan direction was right to left

Atomic Force Microscope (AFM)



cantilever
- spring which deflects as probe tip scans sample surface

position sensitive photodetector
- measures deflection of cantilever

probe tip
- senses surface properties and causes cantilever to deflect

ERROR = actual signal - set point

feedback loop
control sample position with Å accuracy

computer
- controls system
- performs data acquisition display, and analysis

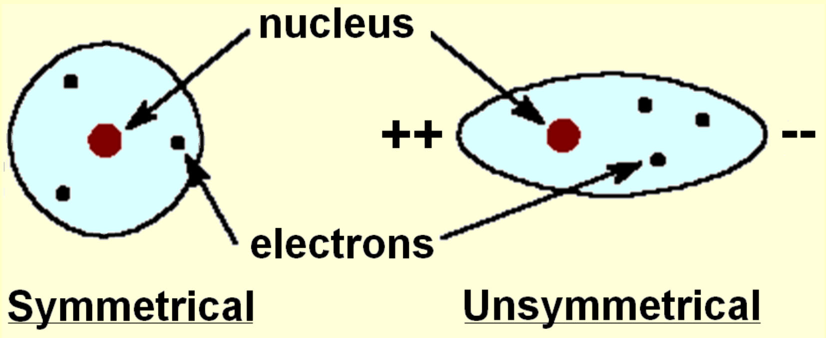
piezoelectric scanner
With Å precision & accuracy

Constant force in Contact mode

$F = k \times \delta_c$

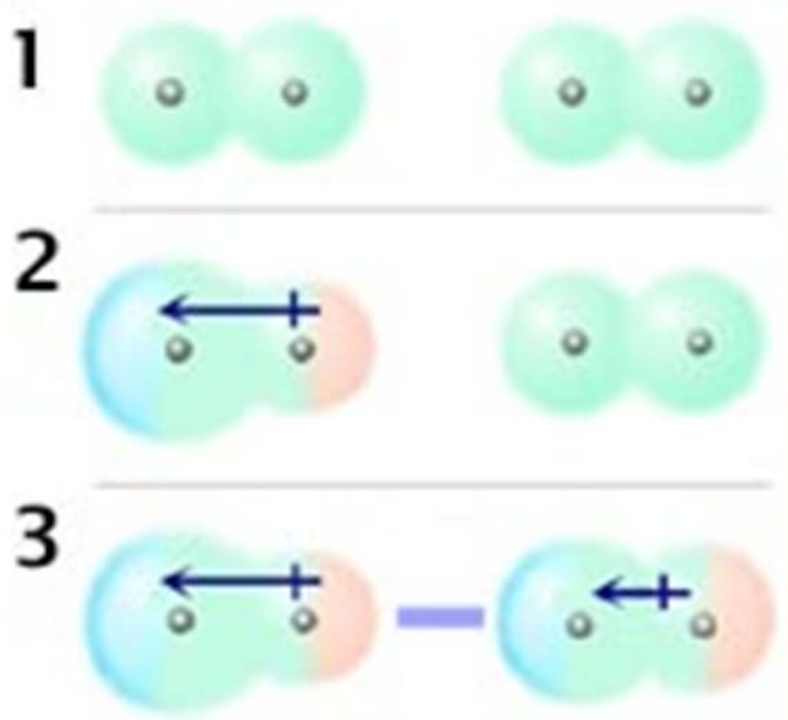
- **The AFM combines the technology developed for the surface profiler with the scanning tunnelling microscope.**
- **AFM works on insulating materials and is the most widely used scanning probe microscope**

Interaction Between Atoms or Molecules



London forces (ven der Waals) arise from the temporary variations in electron density around atoms and non-polar molecules (1) depicts the average electron clouds of two nonpolar molecules. However at any *instant* the electron distribution around an atom or molecule will likely produce a dipole moment (2) which will average out to zero over a period of time. But even a temporary or transient dipole moment can induce a (temporary) dipole moment in any nearby molecules (3) causing them to be attracted to the first molecule.

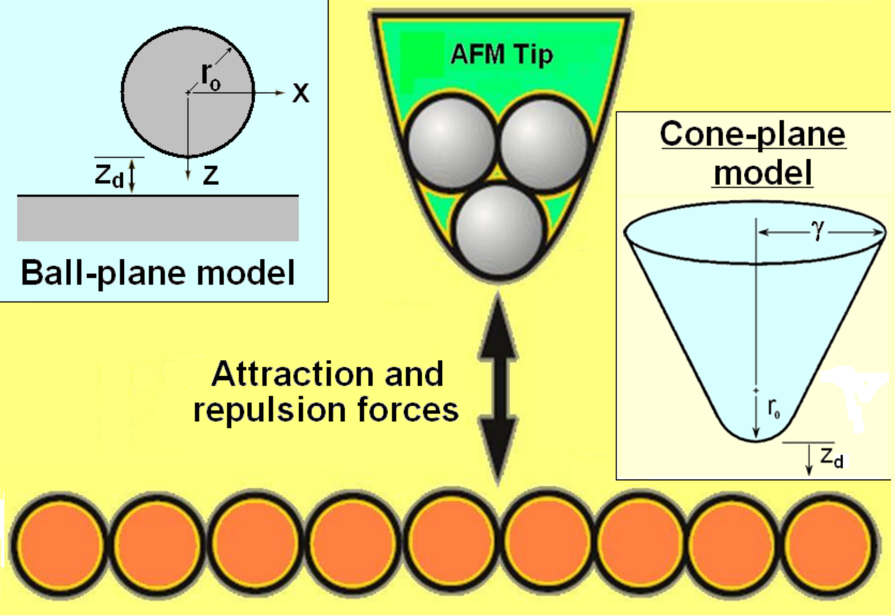
Atoms & Molecules



After discovered by Lord van der Waals, the vdW force was quantified by London (1930). The potential of the vdW interaction (p_v) can be approximated as

$$p_v(z) = -A_1 / z^6 \qquad (1)$$

where A_1 is the interaction constant defined by London (1930) and dependent on the polarization and ionization potential associated and z is the distance between the centers of the paired atoms. In general, the above equation is effective only up to several tens nm. When the interactions are too far apart the dispersion potential, p_v, decays faster than $1/z^6$; this is called the retarded regime (Israelachvilli, 1991).



Hamaker (1937) performed the integration of the interaction potential of Eq. (1) to calculate the total interaction of the sphere-plane geometry. By assuming that the total interaction can be obtained by the pairwise summation of the individual contributions and the summation can be replaced by an integration over the volumes of the interacting elements with a uniform density of the plane, $\rho_1$and and the sphere, ρ_2, the total potential for a sphere interacting with a smooth plane, P_v, should be

$$P_v(z) = -\rho_2\rho_1\int (A_1/z^6)dV_1dV_2$$

where V_1 and V_2 are the volume of the plane and sphere, respectively. If the distance between one element (dV_2) in the sphere and one element (dV_1) in the plane is $(x^2+z^2)^{1/2}$ where dV_1 is located in a ring volume of $2\pi xdxdz$, the above equation, the above equation becomes

$$P_v(z) = -2\pi\rho_2\rho_1A_1\int\int_0^\infty\int_0^\infty x/(x^2+z^2)^3\,dxdzdV_2 = -\frac{2\pi\rho_1\rho_2}{12}\int z^{-3}dV_2$$

By considering a circular section of area ($\pi x^2dz'$), where z' varies from 0 to r_0, the integration of the whole sphere interaction with the plane can be found. Since $x^2 = r_0^2 - z'^2$ and $z = z' + z_d$ the above equation becomes

$$P_v(z',z_d) = -\frac{\pi\rho_1\rho_2A_1}{6}\int_{-r_0}^{r_0}\pi[(r_0^2-z'^2)/(z'+z_d)^3]dz' = -\frac{A_hr_o}{6z_d}\left[1+\frac{z_d}{2r_o+z_d}+........\right]$$

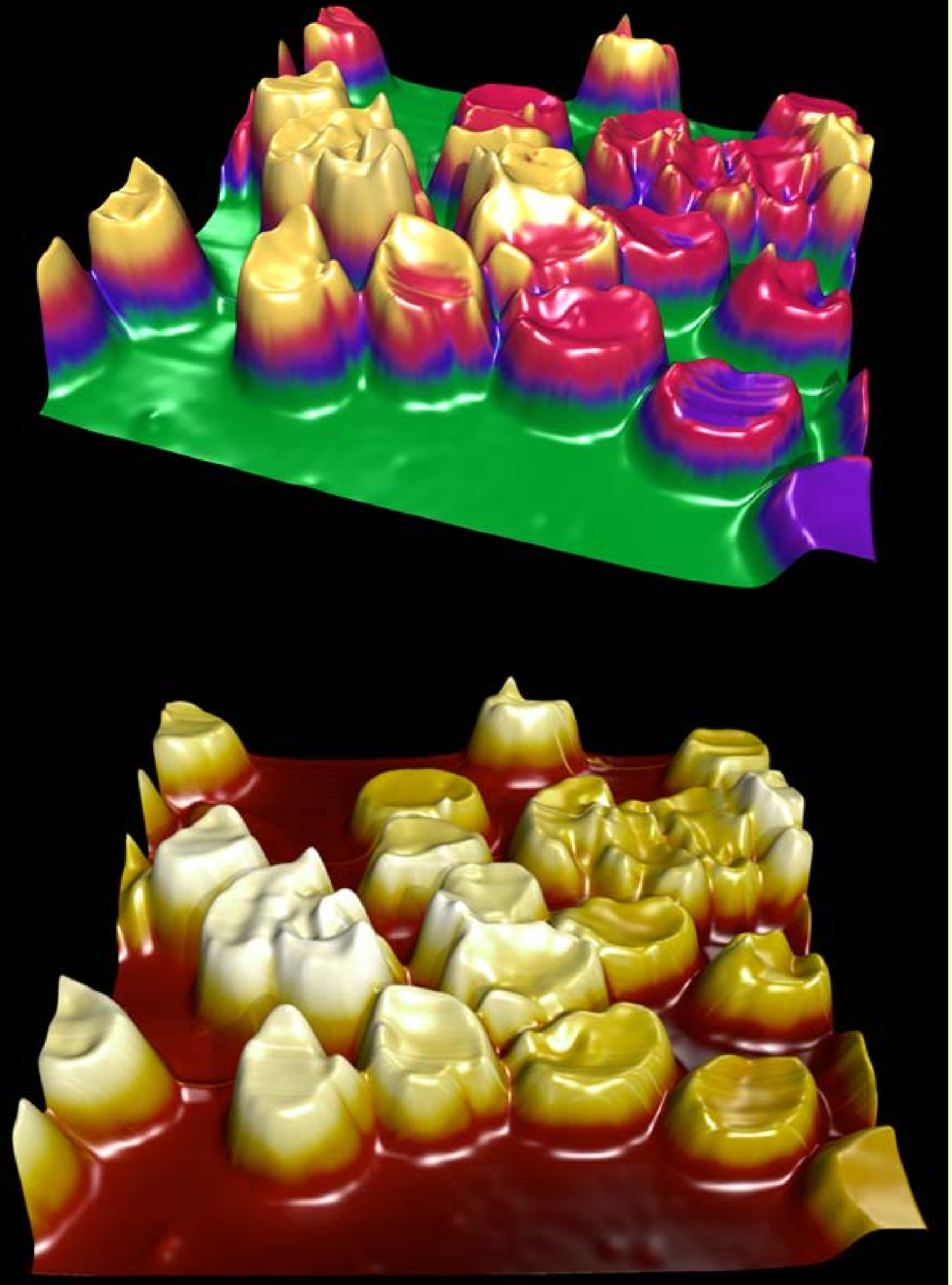
Since the associated wdW force (F_v) can be found to be the gradient of that potential, i.e $F_v = -\nabla P_v(z_d)$

$$F_v(z_d) = -\frac{A_hr_o^3}{3z_d^2(z_d+2r_o)^2}$$

If $z_d \ll r_o$, the above equation can be reduced to

$$F_v(z_d) = -A_hr_o/(6z_d^2)$$

where A_h is the well-known Hamaker constant equal to $A_1\pi^2\rho_1\rho_2$.



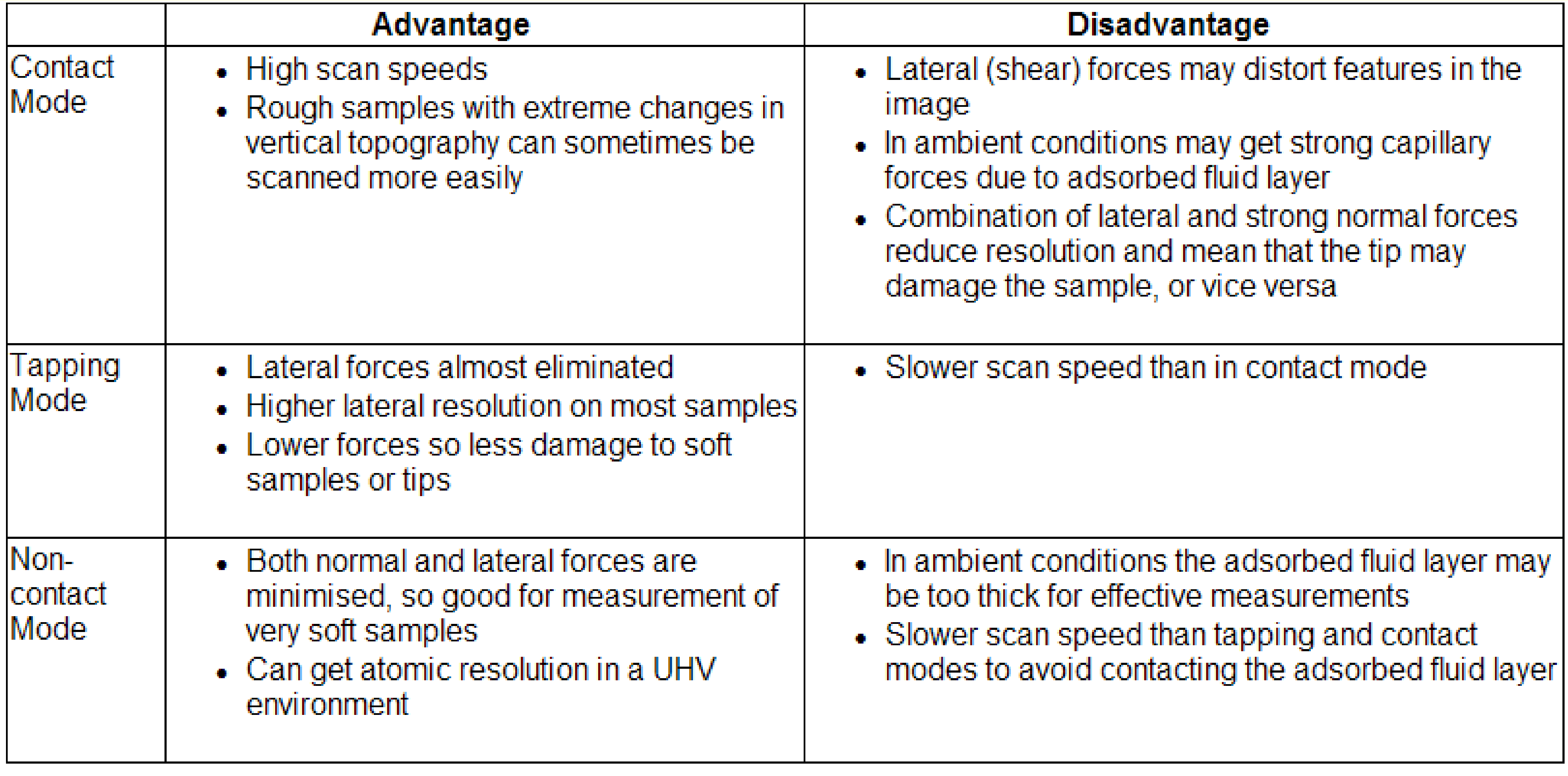
AFM HEIGHT IMAGES

Using Non-contact mode for soft materials

Topographical 3D Rendering of Red Blood Cells. Raw atomic force microscope data is visualized as 3D surface

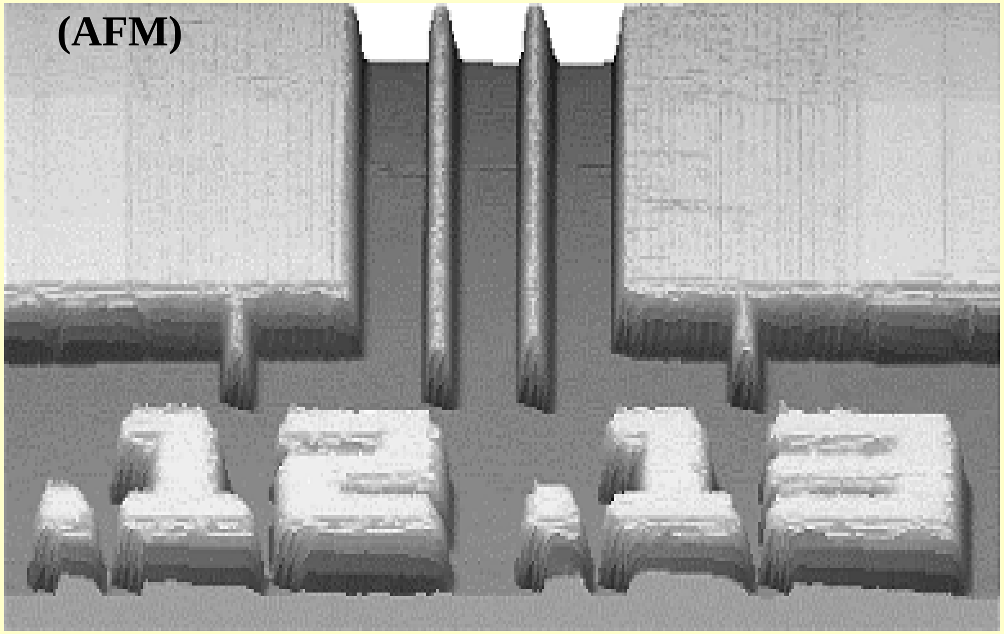
Data by Janelle Gunther, 3D Rendering by Ben Grosser (in www.itg.uiuc.edu/exhibits/gallery)

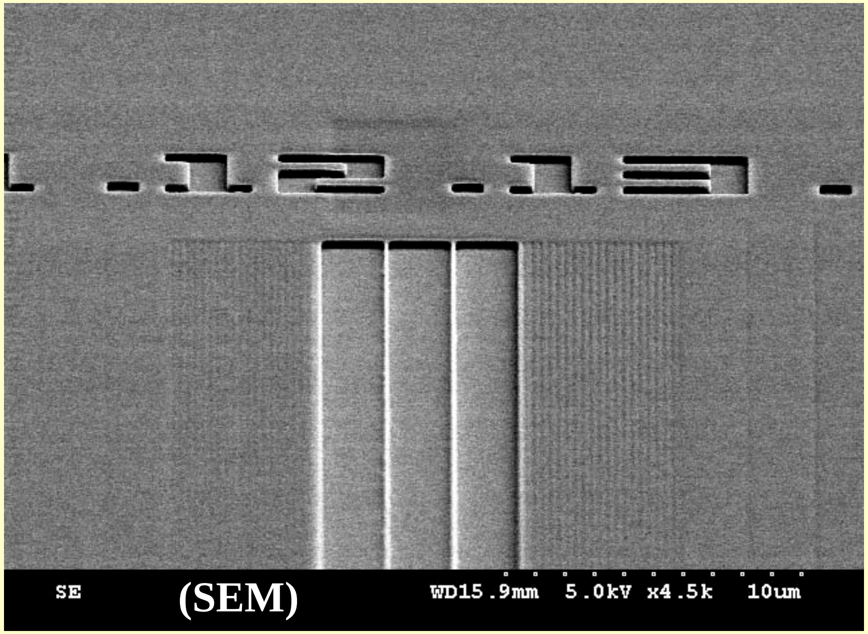
Comparison of Three Modes of Operations



	Advantage	Disadvantage
Contact Mode	• High scan speeds • Rough samples with extreme changes in vertical topography can sometimes be scanned more easily	• Lateral (shear) forces may distort features in the image • In ambient conditions may get strong capillary forces due to adsorbed fluid layer • Combination of lateral and strong normal forces reduce resolution and mean that the tip may damage the sample, or vice versa
Tapping Mode	• Lateral forces almost eliminated • Higher lateral resolution on most samples • Lower forces so less damage to soft samples or tips	• Slower scan speed than in contact mode
Non-contact Mode	• Both normal and lateral forces are minimised, so good for measurement of very soft samples • Can get atomic resolution in a UHV environment	• In ambient conditions the adsorbed fluid layer may be too thick for effective measurements • Slower scan speed than tapping and contact modes to avoid contacting the adsorbed fluid layer

IMAGING COMPARISON OF AFM AND SEM

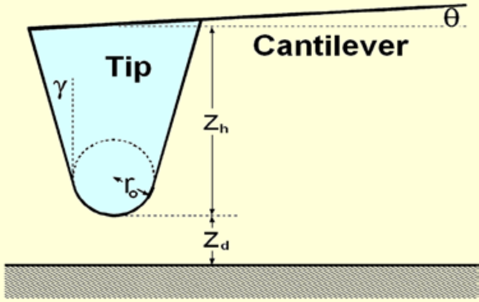




Atomic Force Microscopy
- Contrast on flat samples
- 3D magnification
- Works in ambient air

Scanning Electron Microscopy
- Good depth of field
- Fast scanning
- 2⅓D magnification

Electrostatic Potential and Forces



- The Lennard-Jones potential is important for the interaction between neutral atoms or molecules. The electrostatic interaction force becomes important, if the particles are electrically charged and conductive.

- Frequently, in calculating the interaction forces, the molecules with permanent dipoles can be treated as point charges.

- An appropriate understanding of electrostatic forces is of a wide interest for better controlling the electromagnetic induced reactions and the related charging mechanisms in performing many AFM-based nanopatterning processes, such as local anodic oxidation and electrostatic nanolithography as well as Kelvin probe microscopy.

- The electrostatic potential (p_e), also known as Coulomb potential, is an effective pair potential that describes the interaction between two point charges. It acts along the line connecting the two charges (q_1, q_2):

$$p_e = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

where r is the distance between two charges and ε_0 is the electric constant (permittivity of free space).

B.M. Law, F. Rieutord, Phys. Rev. B 66 (2002) 035402; S. Watanabe, K. Hane, T. Ohye, M. Ito, T. Goto, J. Vac. Sci. Technol. B 11 (1993) 1774.; C. Bo¨hm, C. Roths, U. Mu¨ ller, A. Beyer, E. Kubalek, Mater. Sci. Eng. B 24 (1994).

The corresponding Coulomb force (F_e) between two charges can be found as:

$$F_e = \frac{-q_1 q_2}{4\pi\varepsilon_0 r^2}$$

The total interaction force can be found by integrating all charged particles involved. Analytical integration solutions do existing for very limited simple cases. The formula developed by Law and Rieutord (2002) for a conical tip with a spherical apex of r_0 and a rectangular include angle, θ is selected:

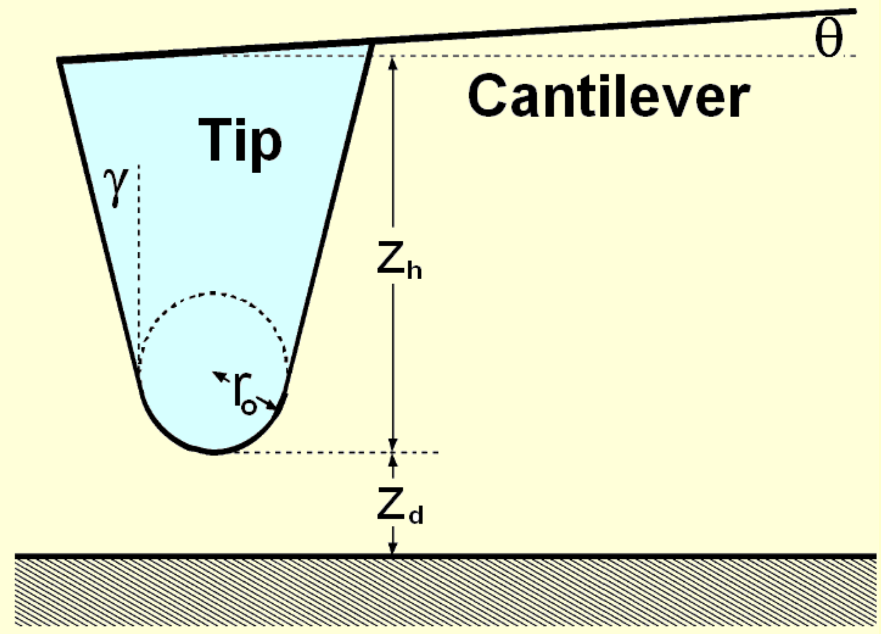
$$F_e = \pi\varepsilon_0 V^2 z(z_d)$$

where V is the applied voltage and $z(z_d)$ is a geometrical function including the contributions from the spherical apex and conical part of the tip and the cantilever (as shown in the attached figure). By assuming θ = 0, an approximation for $z(z_d)$ adopted by Butt et al. (2005) can be applied here. Then, the electrostatic force becomes:

$$F_e = \pi\varepsilon_0 \frac{r_0^2 V^2}{z_d (z_d + r_0)}$$

If θ>>0, a more complicated solutions are needed. Numerical solutions for non-simplified geometries reported by Watanabe, et al. (1993) and Bohm et al. (1994) can also be used for the present electrostatic force calculation.

Electrostatic Potential and Forces

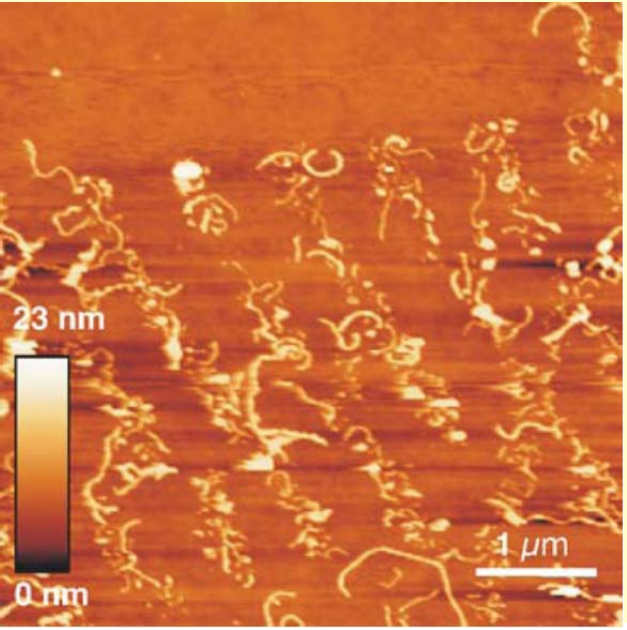


For good conductors, the electric potential is identical to the applied potential. In a calculation that implies that the field lines are oriented perpendicular to the surfaces. The induced capacitance, C, can also be use to estimate the electrostatic forces involved. A calculation of the electrostatic force is given by

$$F_e(z) = -\frac{dC}{2dz}V^2$$

where C is the capacitance of tip and sample and V is the applied voltage. To precisely evaluate the capacitance variation, numerical techniques are normally used.

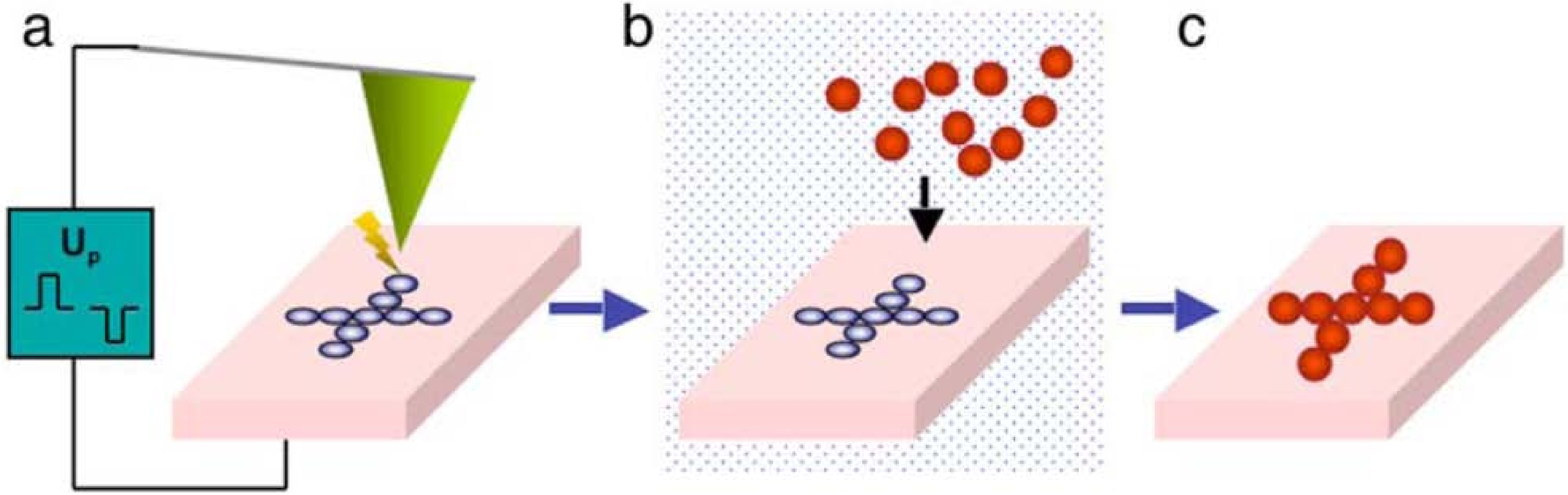
Electrostatic Patterning: Nano-Xerography



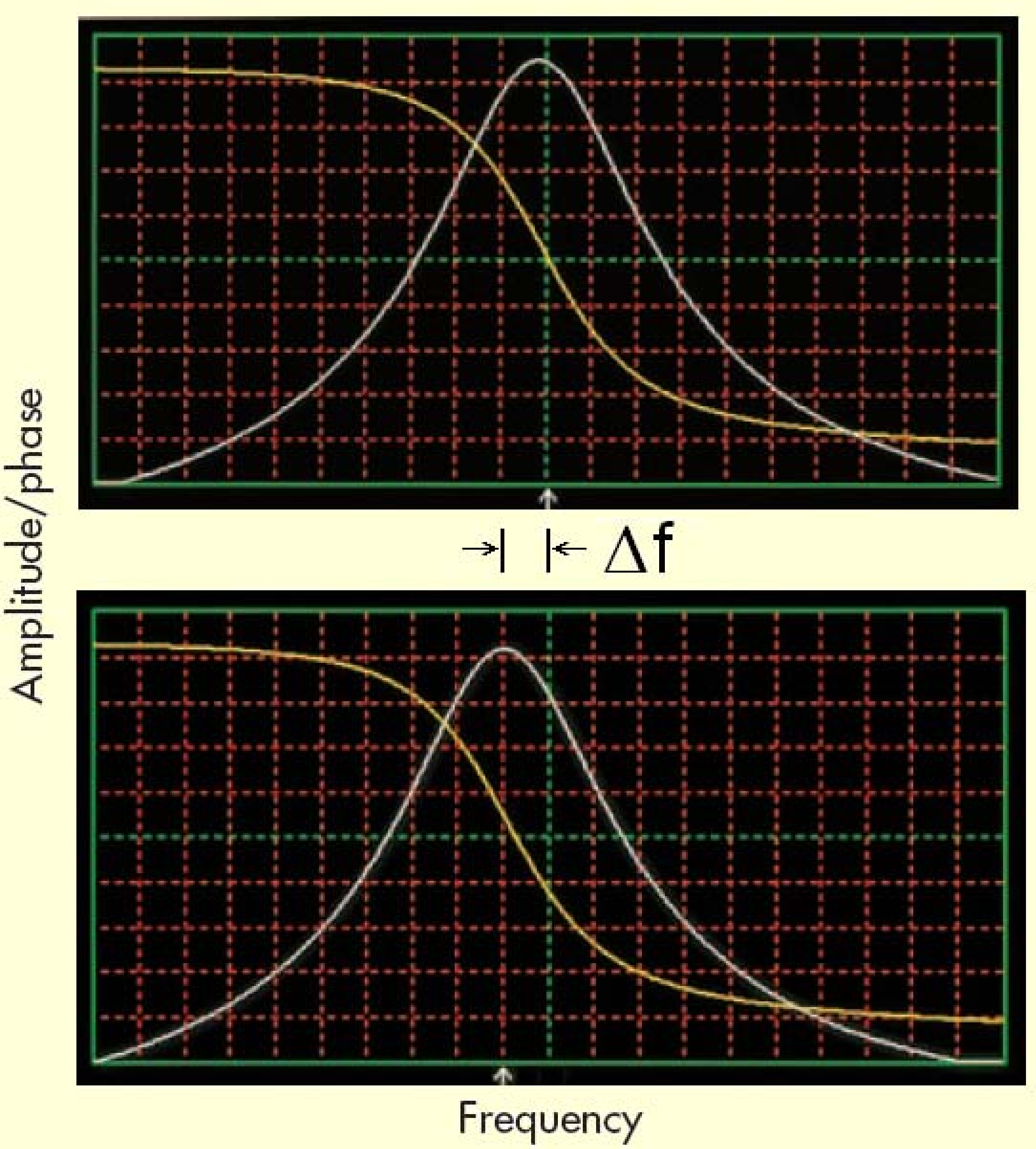
Nano-xerography of carboxyl functionalized multiwalled carbon nanotubes.

A Stemmer, D Ziegler, L Seemann, J Rychen N Naujoks,
J. Physics: Conference Series
142 (2008) 012048

Nano-xerography: (a) Charge patterns are written into an electret layer on a solid substrate by applying voltage pulses to a conductive AFM tip. (b) The sample is developed in a suspension of nano-objects. (c) After rinsing and drying, the nano-objects remain selectively attached to the predefined pattern.

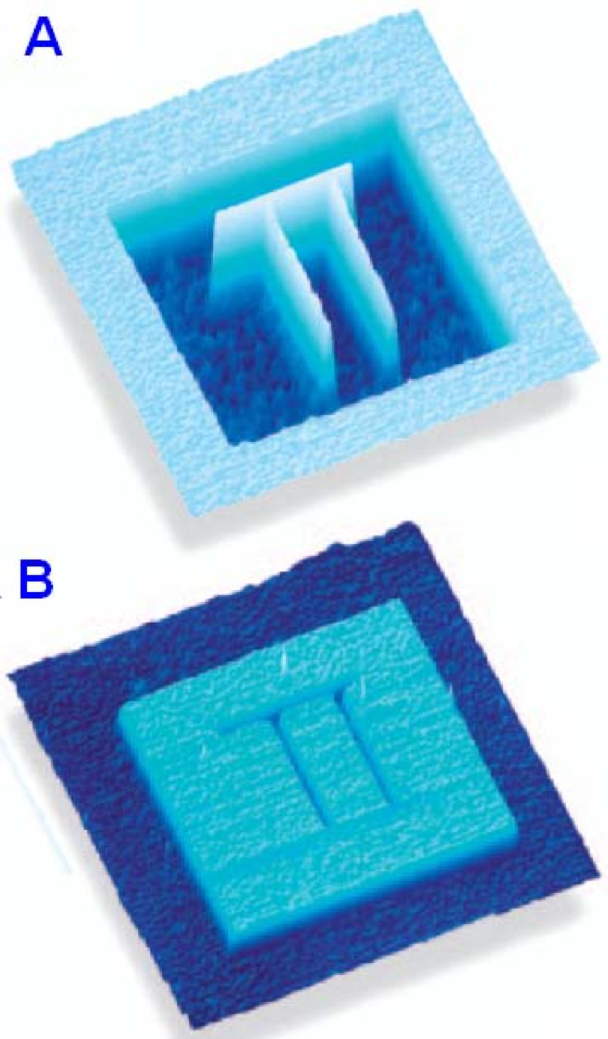


Resonance Shift by Electrostatic (Coulomb) Force

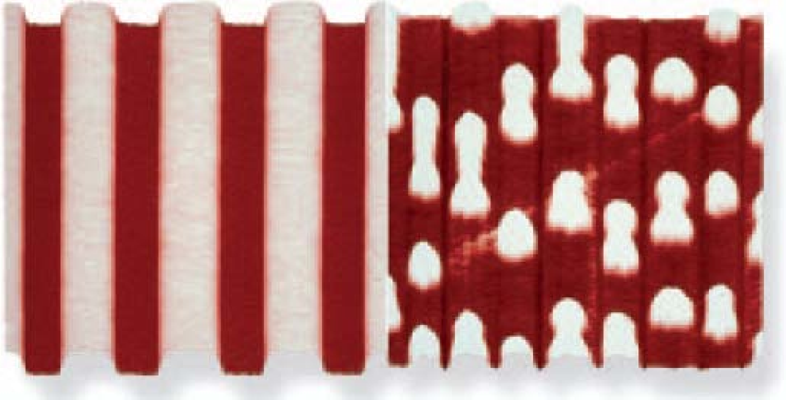


A conductive AFM tip can interact with the sample through long-range Coulomb forces: Amplitude (white) and phase (yellow) resonance response of a metal-coated AFM cantilever/tip above a sample of aluminum, held at 0V (top) and 10V (bottom) relative to the grounded tip. The tip is never in contact with the sample. In the presence of the electric field (bottom plot), the tip experiences an attractive force toward the sample. Effectively, the stiffness (spring constant) and thus the resonance frequency of the cantilever is reduced; the entire resonance curve shifts down along the frequency axis (horizontal). Changes in the cantilever's amplitude and phase are used to characterize electrical properties on, or just beneath, the surface of the sample.

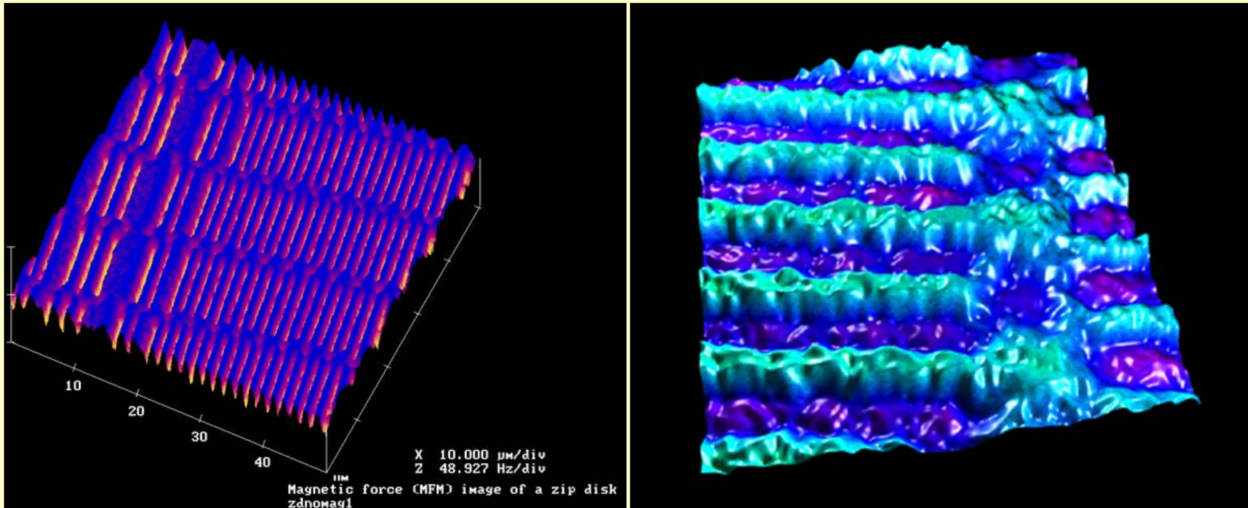
Electric & Magnetic Forces Map by AFM



15µm scan Electric Force images showing reversed tip bias from A to B of polarized ferroelectric domains in an epitaxial, single crystalline Pb($Zr_{0.2}Ti_{0.8}$)O_3 thin film. The polarization pattern was created using the same metal-coated AFM tip that moments later captured these images (corresponding topography is featureless (not shown), with 0.2nm RMS roughness). Courtesy of T. Tybell, C.H. Ahn, and J.M. Triscone,

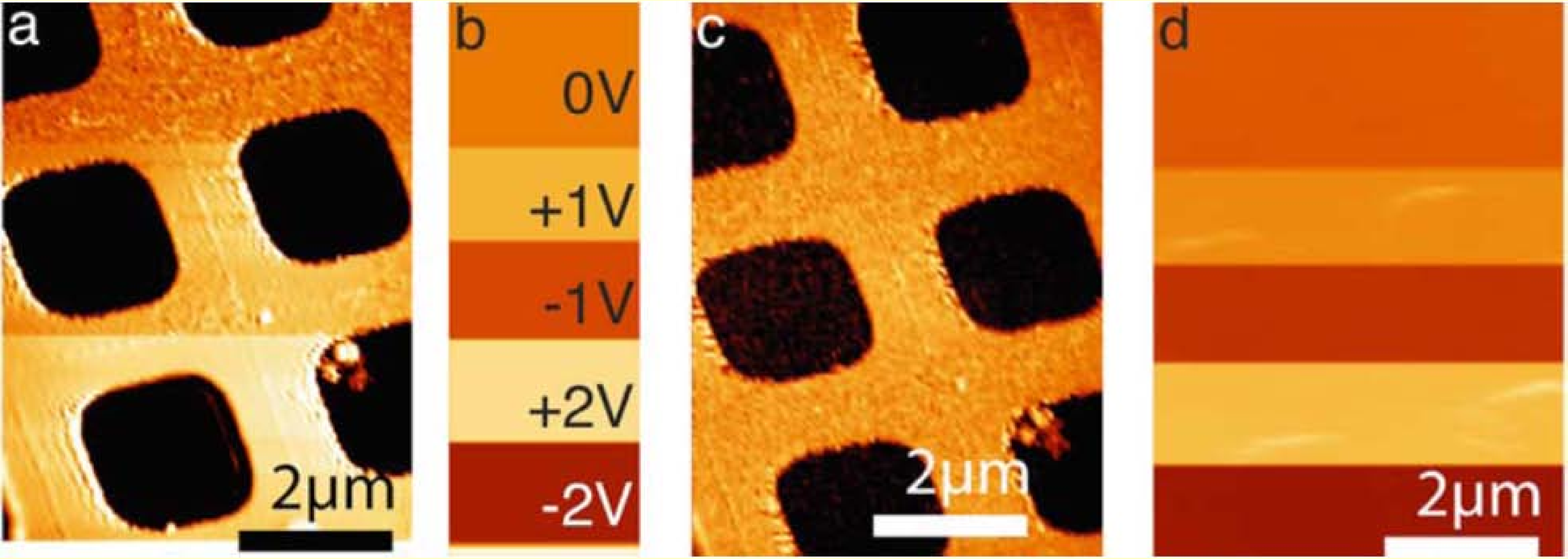


Topography (left) & Surface Potential (right) images of a CD-RW. SP image locates the position of the bits. **Courtesy of Yasudo Ichikawa,**

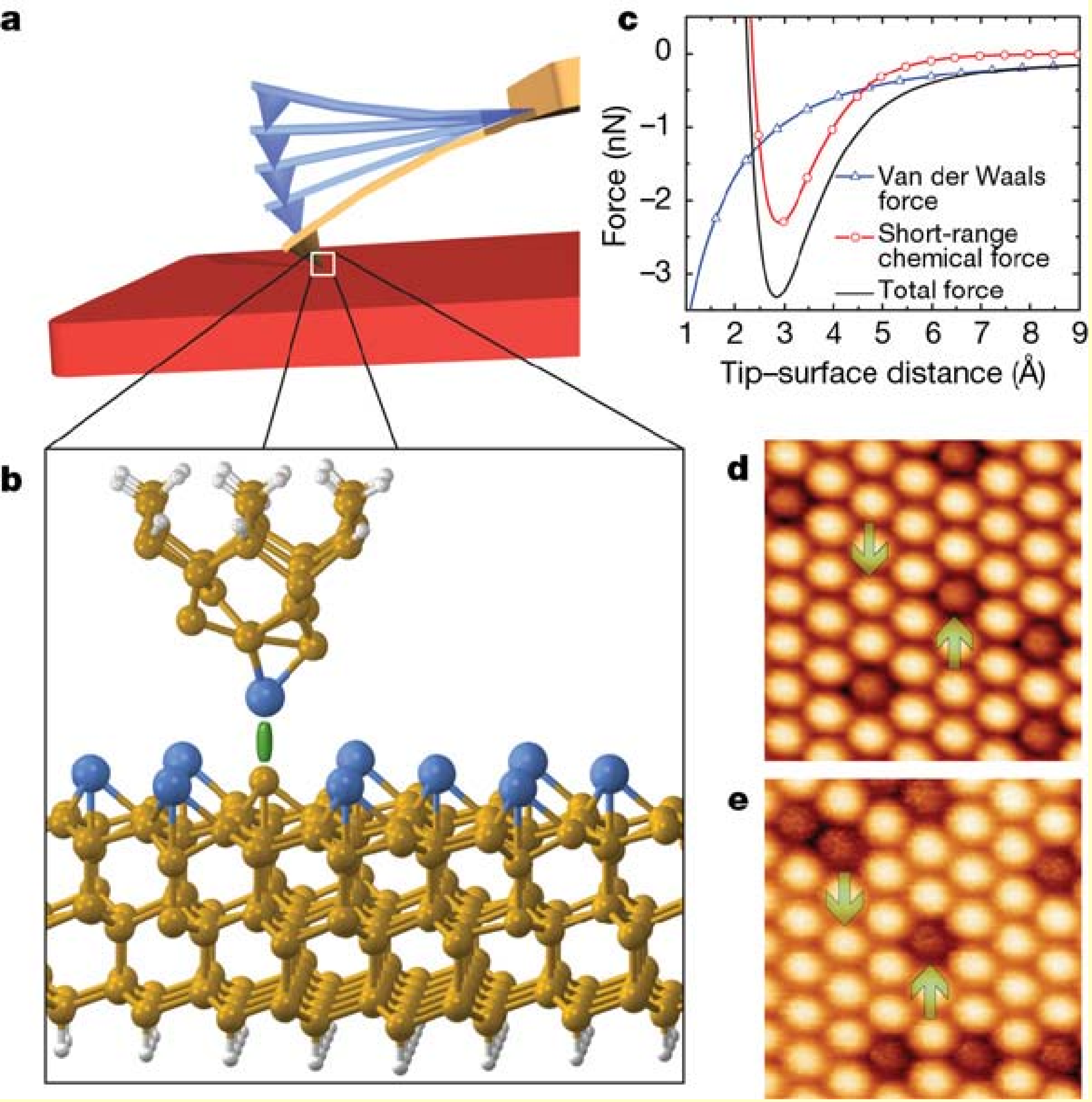


Magnetic Force Map of Surface of Zip Disk

Effect of Electrostatic Forces in Topography Measurements



Compensation of electrostatic forces leads to true topography measurements in tapping mode atomic force microscopy. Topography (a) of a gold-coated silicon grating showing height offsets when forces due to an externally applied bias voltage (b) are not compensated. True topography (c) when electrostatic forces are compensated locally by applying a voltage corresponding to the measured surface potential (d).

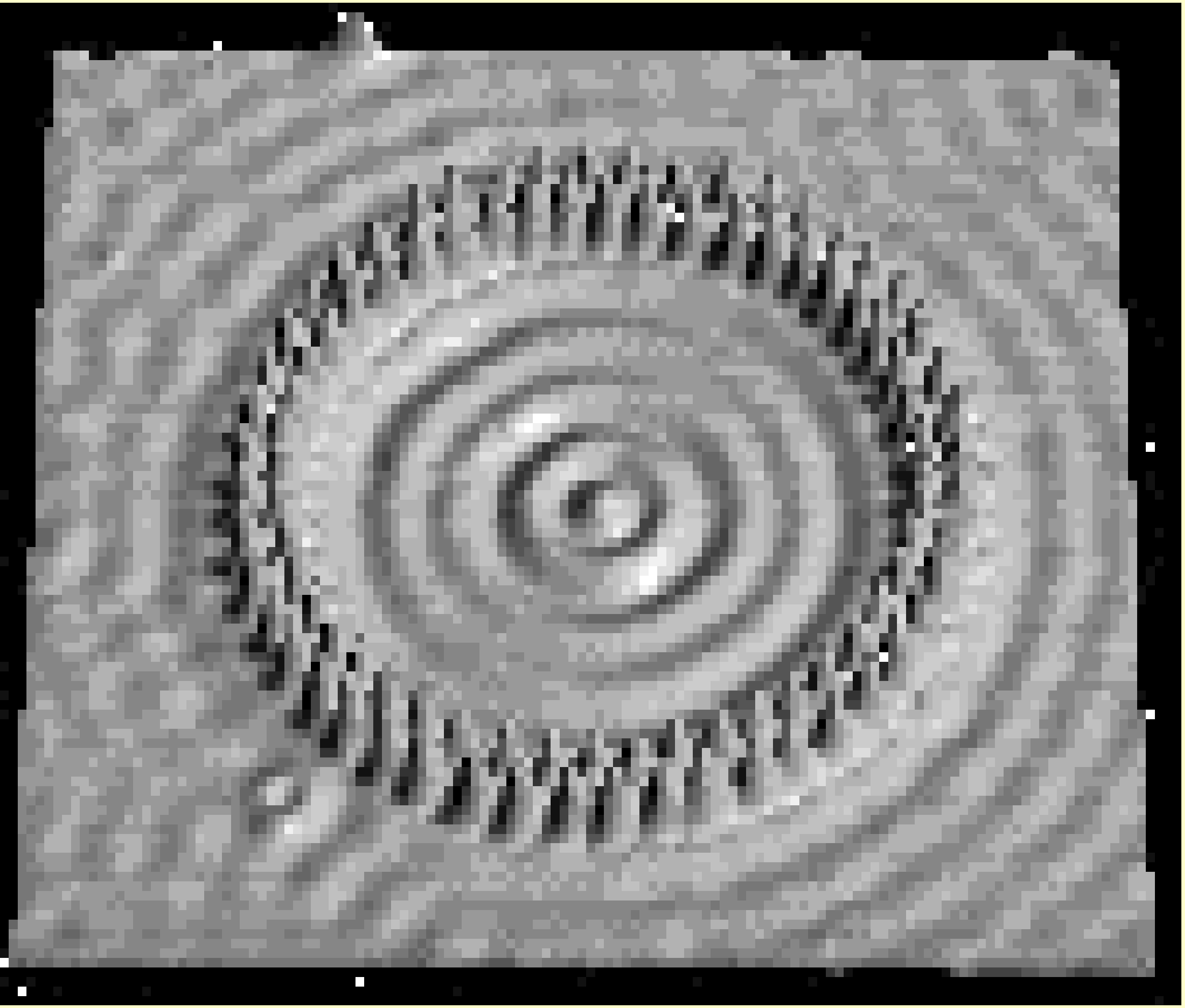


AFM Operation In Dynamic Mode

(a), and of the onset of the chemical bonding between the outermost tip atom and a surface atom (highlighted by the green stick) that gives rise to the atomic contrast (b). However, the tip experiences not only the short-range force associated with this chemical interaction, but also long-range force contributions that arise from van der Waals and electrostatic interactions between tip and surface (though the effect of the latter is usually minimized through appropriate choice of the experimental set-up). c) Curves obtained with analytical expressions for the van der Waals force, the short-range chemical interaction force, and the total force to illustrate their dependence on the absolute tip–surface distance.

d–e), Dynamic force microscopy topographic images of a single-atomic layer of Sn (d) and Pb (e) grown, respectively, over a Si(111) substrate. At these surfaces, a small concentration of substitutional Si defects, characterized by a diminished topographic contrast, is usually found. The green arrows indicate atomic positions where force spectroscopic measurements were performed. Image dimensions are (4.3 4.3) nm^2; for the acquisition parameters (Sugimoto et al., Nature 2007).

From Atomic Imager To Nanoscale Manipulator



Electron waves on a metal surface and quantum corrals: Iron on Copper (111)

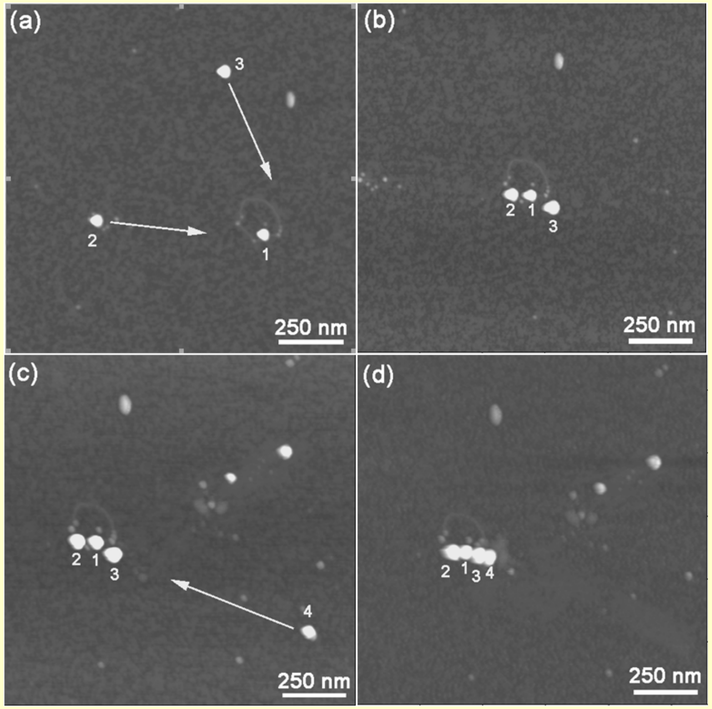
Crommie, et al. (1995)

Milestones in Atomic Characterization and Manipulation

- **1986: Atomic Force Microcopy invented by Binnig** (US Patent 4,724,318)
- **1987: AFM with vibrated cantilever** (Martin, Willams, Wickramasinghe, J. Appl Phys)
- **1991: Single Xe atoms positioned on Ni (110) surface*** (Eigler, Schweizer, Nature)
- **1993: Quantum confined structures built*** (Crommie, Lutz, Eigler, Science)
- **1999: Magnetic nanostructures built*** (Chen, Jamneala, Madhavan, Crommie, Phys. Rev)
- **1999: Single bonds characterization*** (Lee, Ho, Science)
- **2000: Artificial molecules built*** (Hla, Bartels, Meyer, Rieder, Phys. Rev. Lett)
- **2000: Atomic chemical reaction*** (Hla, et al., Phys. Rev. Lett)
- **2002: Atomic wire built*** (Nilius, Wallis, Ho, Science)
- **2002: Molecular computation: molecular cascades*** (Heinrich, Lutz, Gupta, Eigler, Science)
- **2003: Single molecule device*** (Nilius, Qiu, Ho, Science)
- **2004: Single molecule doping*** (Yamachika, et al., Science)
- **2005: Moving atom at room temperature by AFM** (Sugimoto, et al., Nature Mater)
- **2007: Chemical identification of single atoms by AFM** (Sugimoto, et al., Nature)
- **2008: Force measurements in moving atoms by AFM** (Ternes, et al., Science)
- **2009: Quantum confinement of electrons in 3D*** (Moon et al., Nature Nanotech)

***by STM**

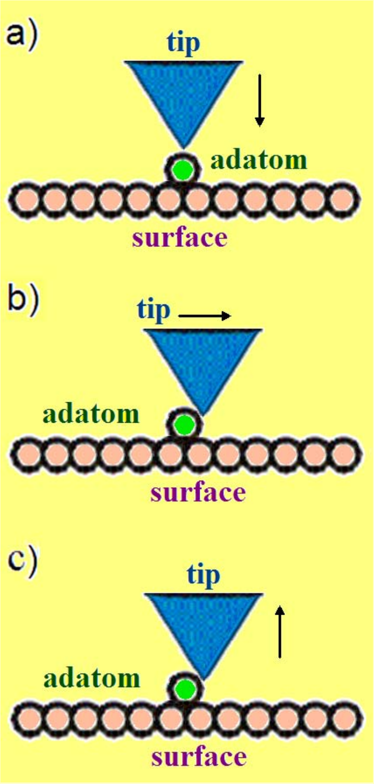
Nanomanipulation



AFM images of lateral manipulation of 24-nm Au nanoparticles to create chain-like nanostructure by FM-AFM: a) pushing nanoparticles labeled with 2 and 3 along direction shown by arrows, b) nanoparticles 2 and 3 are pushed close to nanoparticle 1, c) moving nanoparticle 4 towards nanoparticle 1, d) final chain-like nanostructure

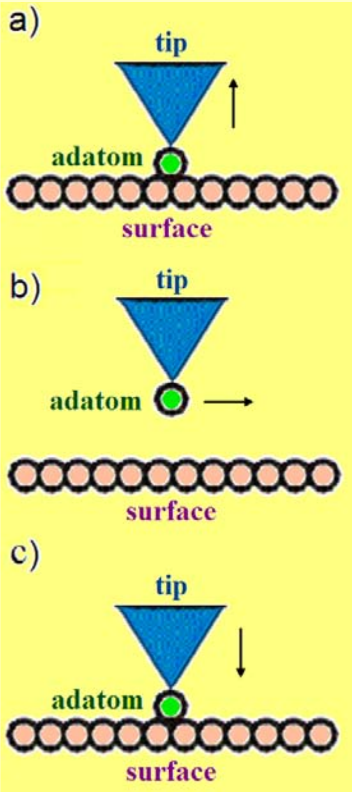
(A. A. Tseng and Z. Li, J. Nanosci. Nanotech., 2007)

Lateral Manipulation

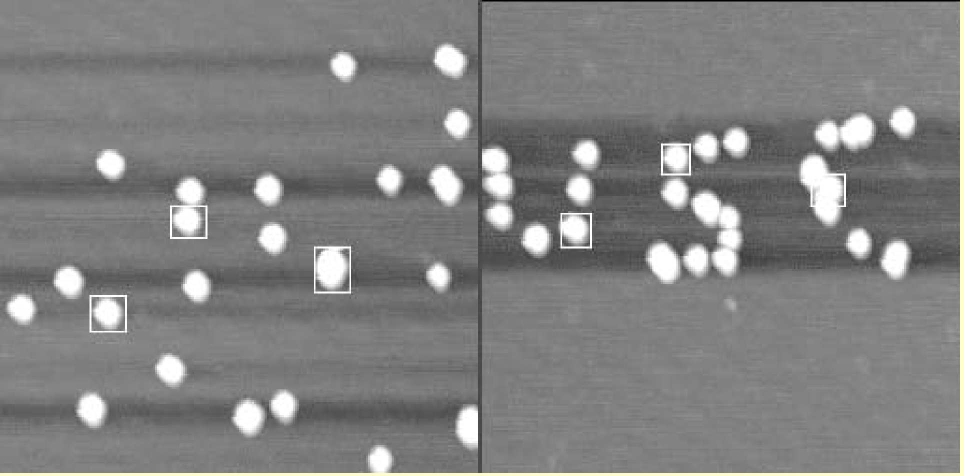


Adatom remains bound to surface and pushed or dragged by tip: a) pulling where adatom discontinuously follows tip from one adsorption site to another due to attractive forces, b) sliding where adatom is trapped under tip and follows its motion instantaneously and continuously, c) tip is retracted at desired place.

Vertical manipulation



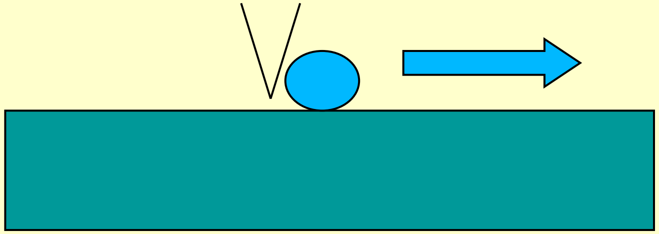
Adatom is transferred from surface to STM tip and back to surface: a) tip picking adatom from adsorption site and adatom dissociation occurring, b) tip lifting adatom from surface and moving to desired place due to attractive forces, c) tip with adatom is loaded at desired site.



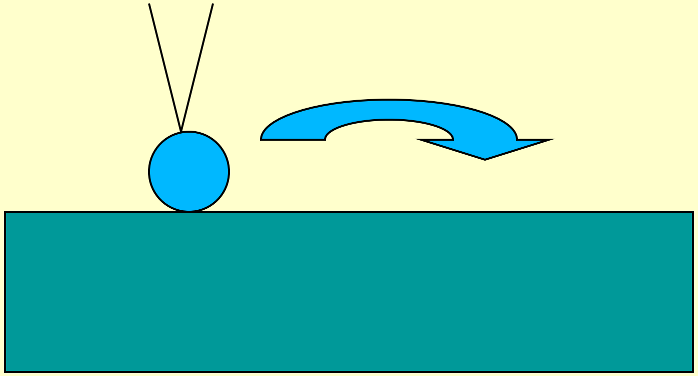
Nanoscale Manipulation

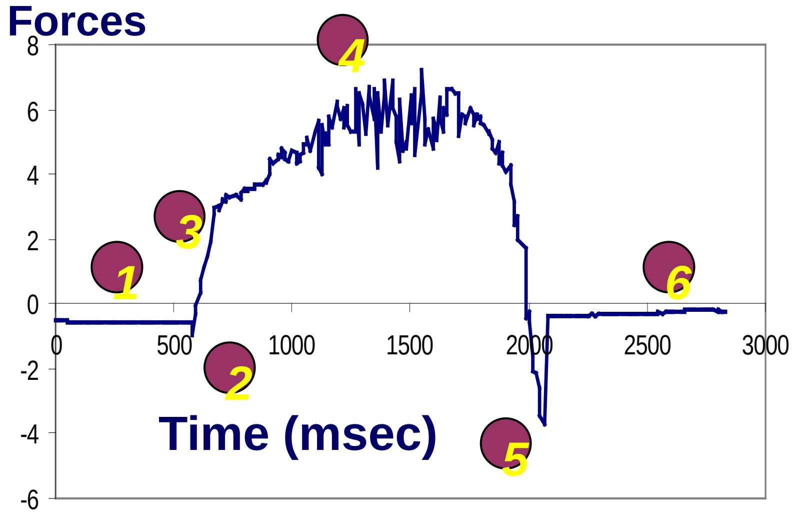
(Bottom-up)

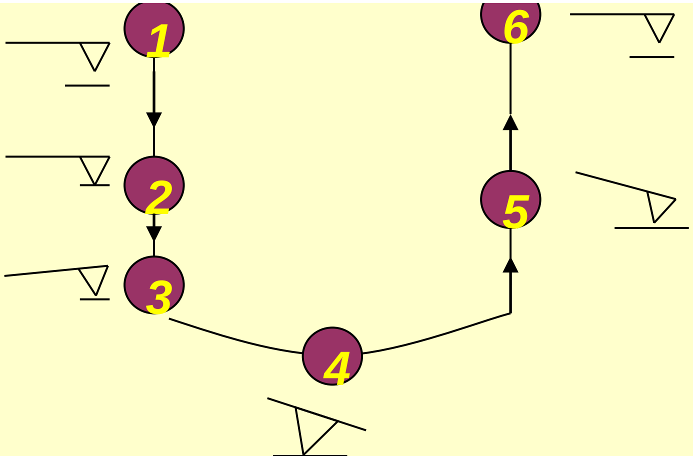
Push Objects



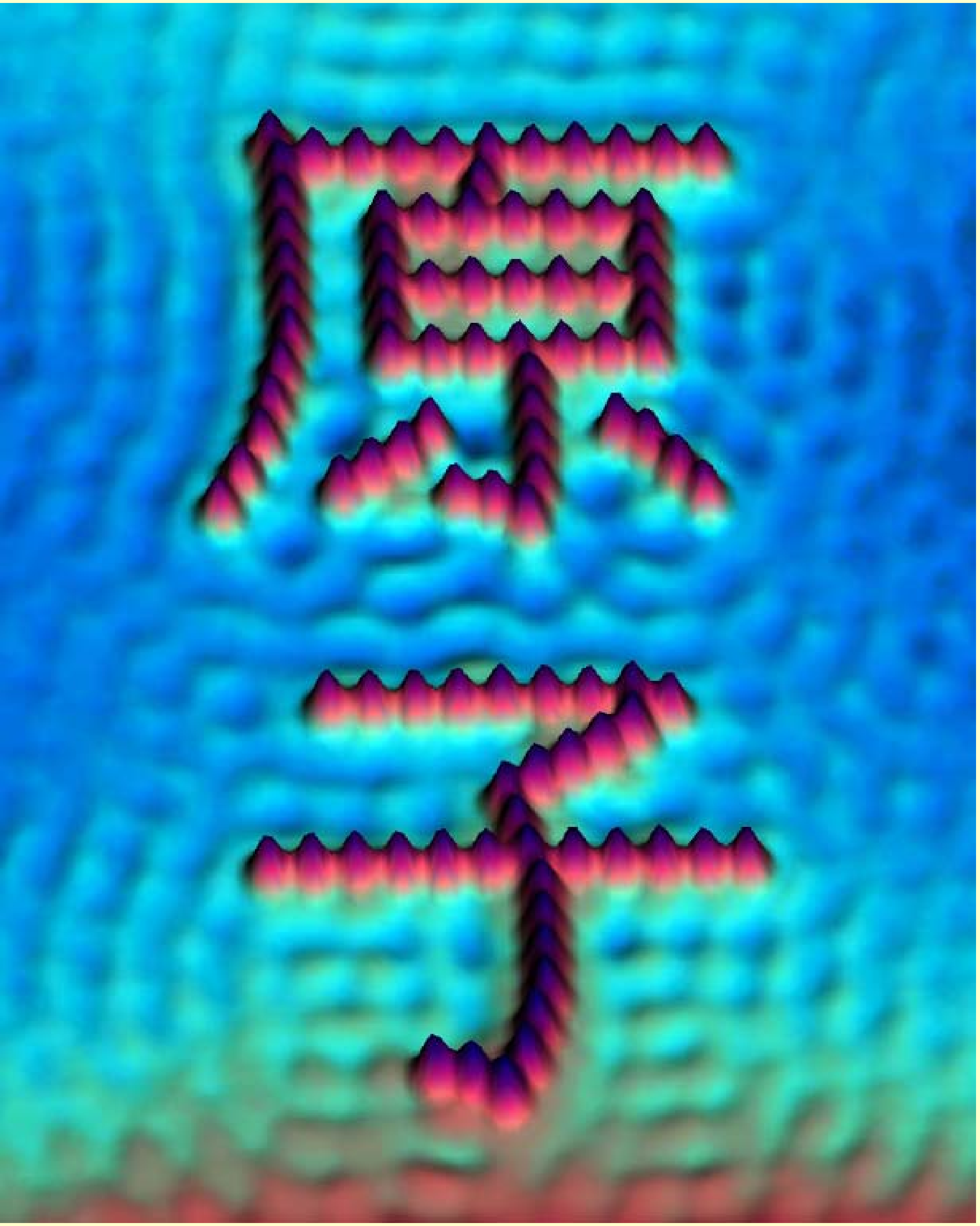
Lift-Drop



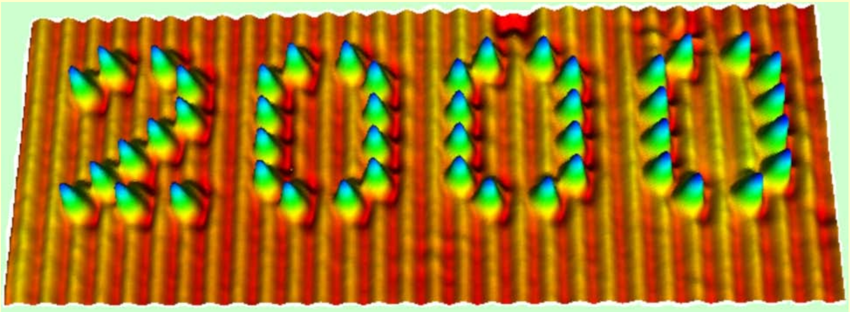




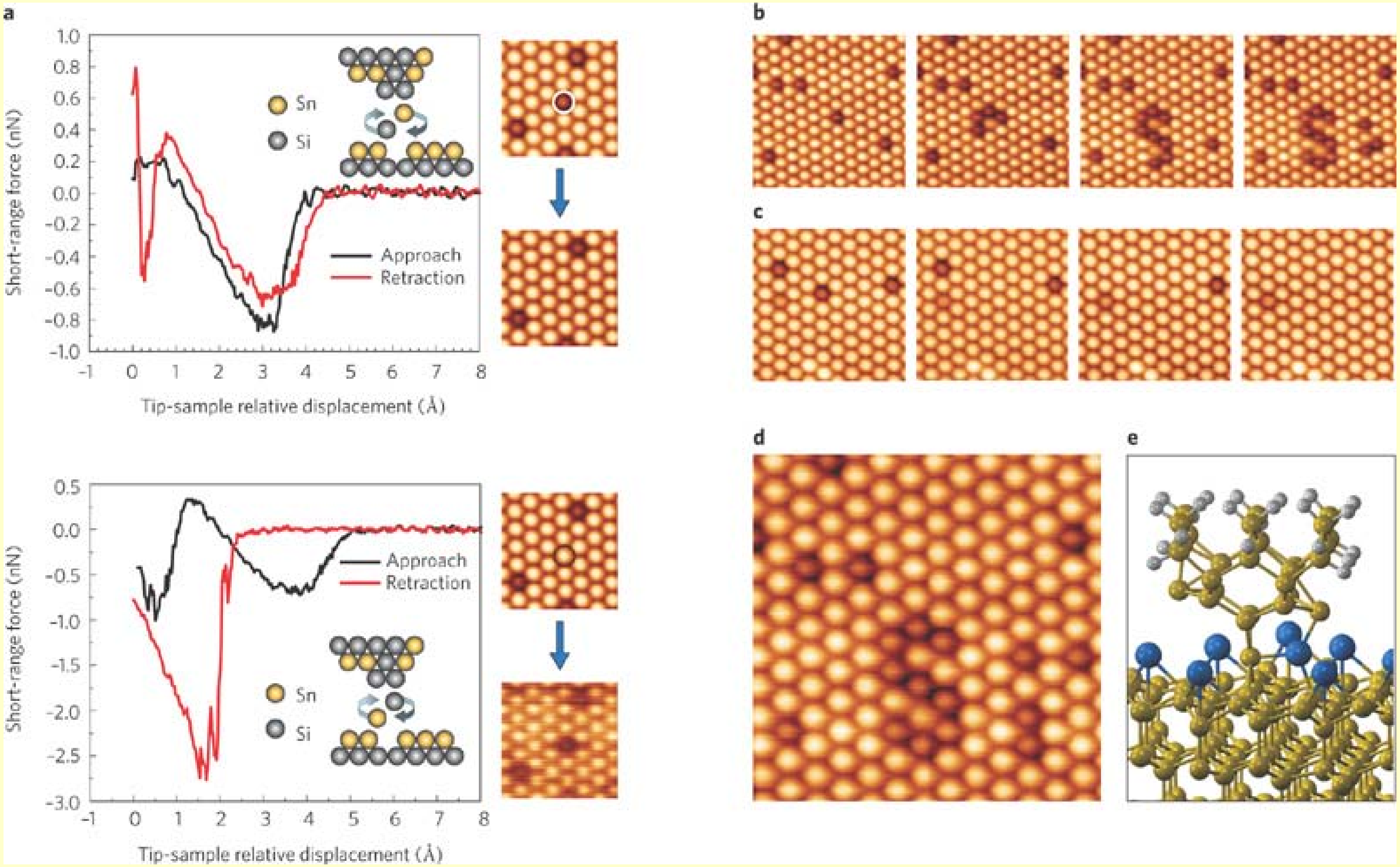
ATOMIC AND MOLECULAR MANIPULATION



STM image of atomic manipulation of iron atoms on copper(111) surface in writing Chinese characters for "atom" by C. P. Lutz and D. M. Eigler, to which the literal translation is something like "original child" (courtesy of IBM Research, Almaden Research Center)



STM image of nanoscale millennial numbers "2000" are constructed with 47 CO-molecules regulated on a Cu(211) surface using lateral manipulation at 15 K (courtesy of Dr. Gerhard Meyer of IBM Zurich Research Laboratory, Rüschlikon, Switzerland).

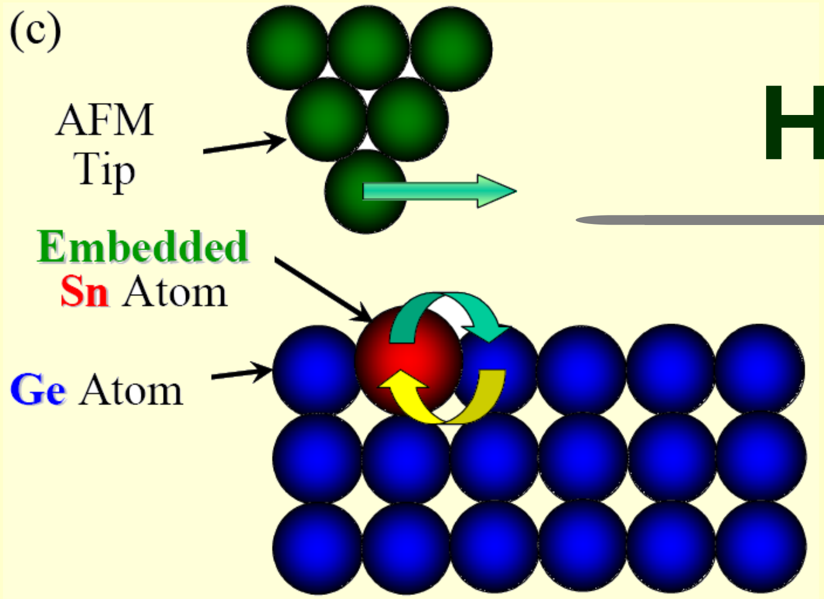


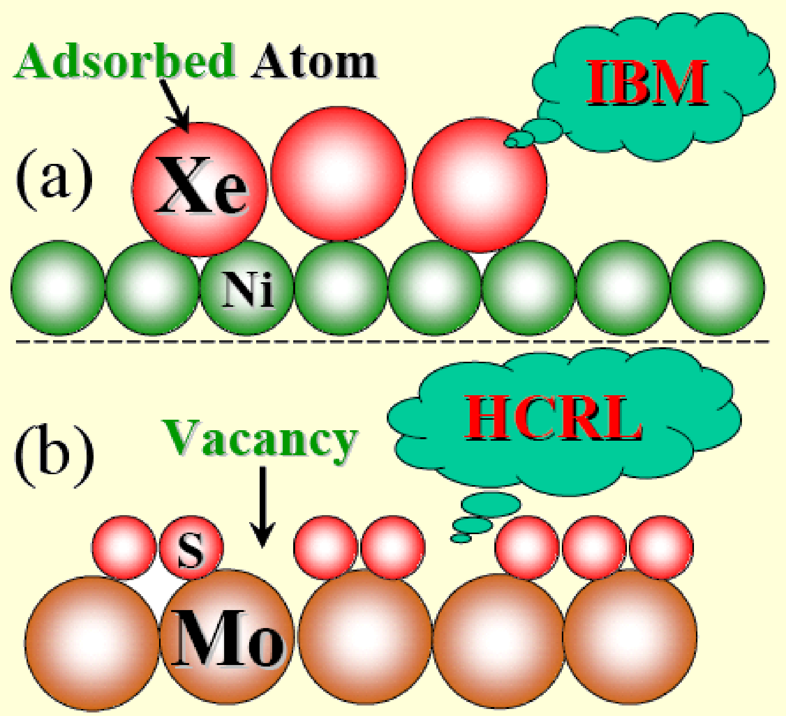
In e), silicon, tin and hydrogen atoms are represented by yellow, blue and white spheres, respectively, and the tip apex and surface models correspond to the atomic arrangements in the upper and lower halves respectively.

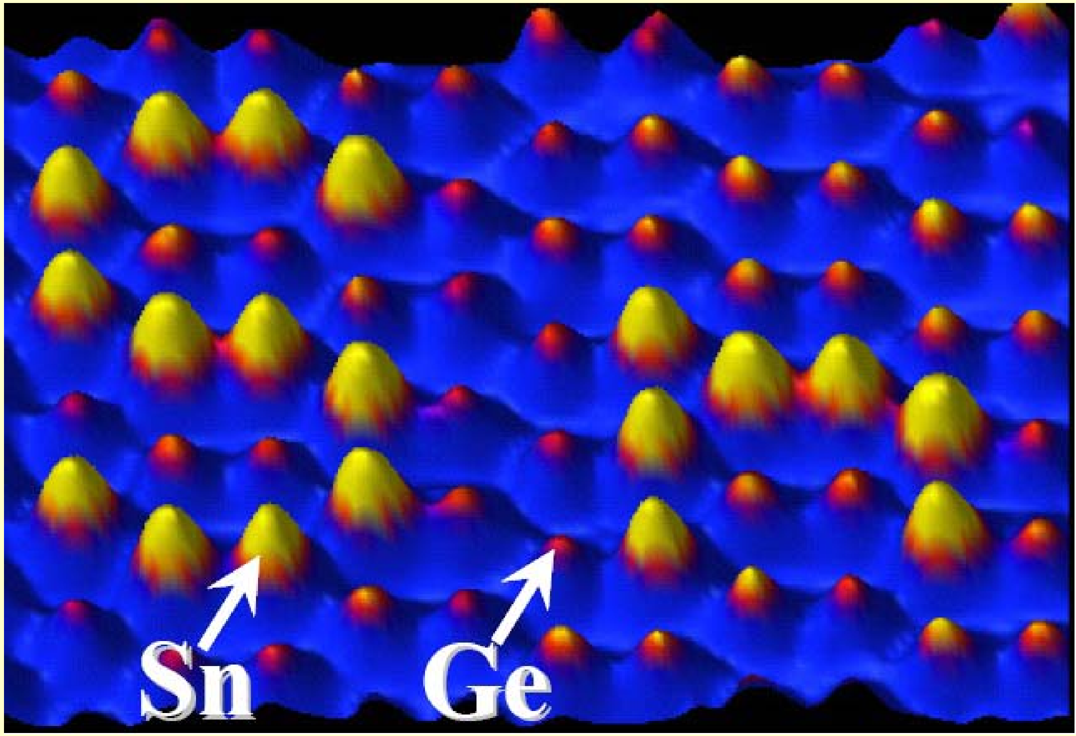
a) By gently exploring the repulsive forces of the bonding interaction between the foremost atom of the AFM tip and atoms probed at a surface, it is possible to induce the vertical interchange of the interacting atoms. Here, a Si defect of the Sn/Si(111)-(3x3)R30° surface (white circle) was replaced by a Sn atom coming from the AFM tip. In a subsequent process, the newly deposited Sn atom (dark circle) was substituted by a Si atom coming from the tip. Applying this manipulation method in heterogeneous semiconductor surfaces enables one to 'write' (b) and 'erase' (c) atomic markers by respectively depositing and removing the atoms in lower concentration (Si in the case of b and c). Reproducibility of this manipulation method provides another way to create atomic designs on surfaces with an AFM at room temperature (d). These vertical-interchange manipulations involve complex multi-atom contacts between tip and surface.

(**Custance et al., Nature Nanotechnology 2009**).

How to Move an Atom



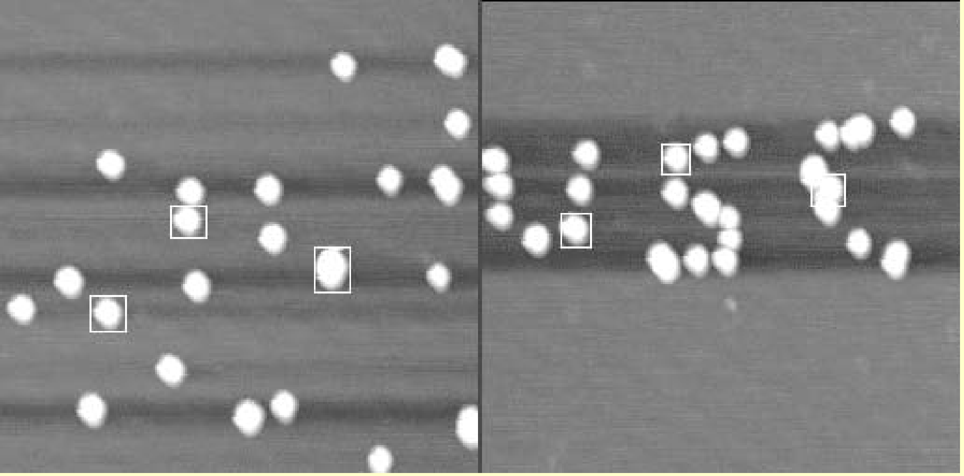




“Atom Inlay”, that is, atom letters ”Sn” consisted of 19 Sn atoms embedded in Ge(111)-c(2 × 8) substrate

Sugimoto et al. Nature Mater. 4, 156-159, 2005

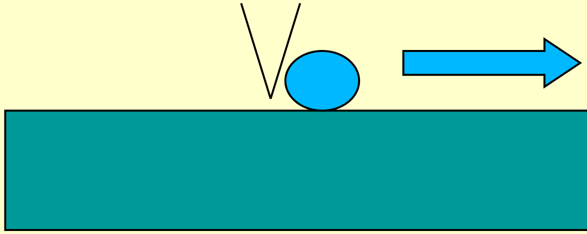
Schematic models of lateral atom manipulation (a) IBM group (STM low temperature), (b) Hitachi group (AFM low temperature), and (c) Osaka group (AFM room temperature).



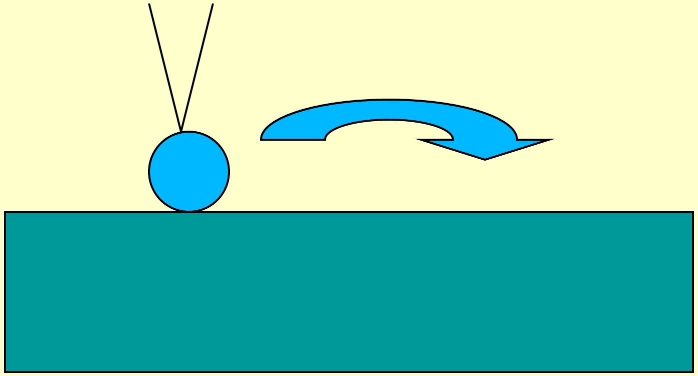
ATOMIC AND MOLECULAR MANIPULATION

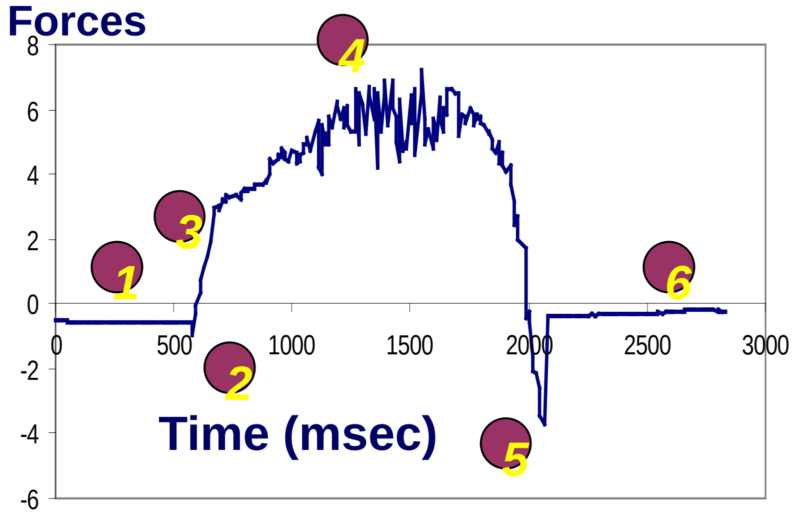
(Bottom-up)

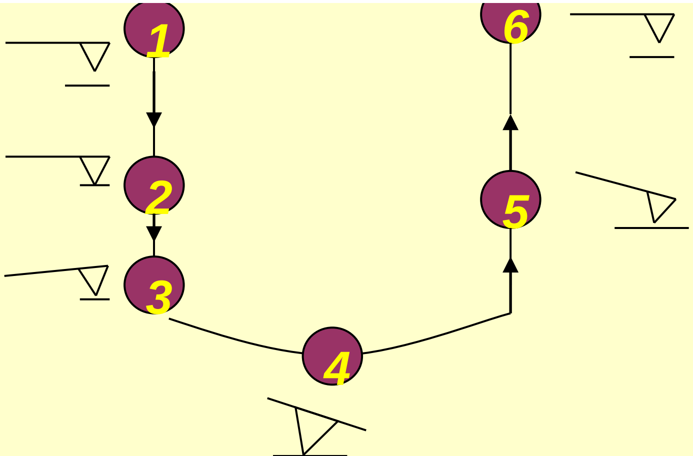
Push Objects



Lift-Drop

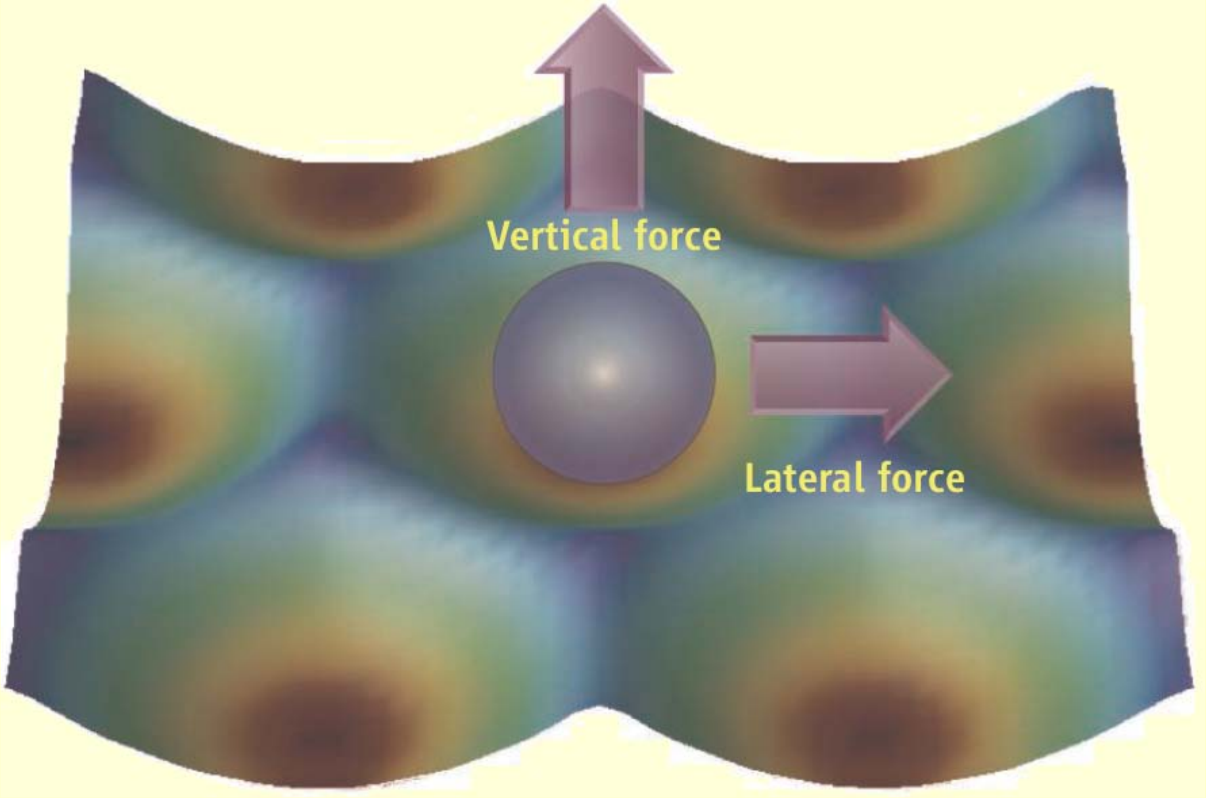






ATOMIC & MOLECULAR MANIPULATION

(Bottom-up)

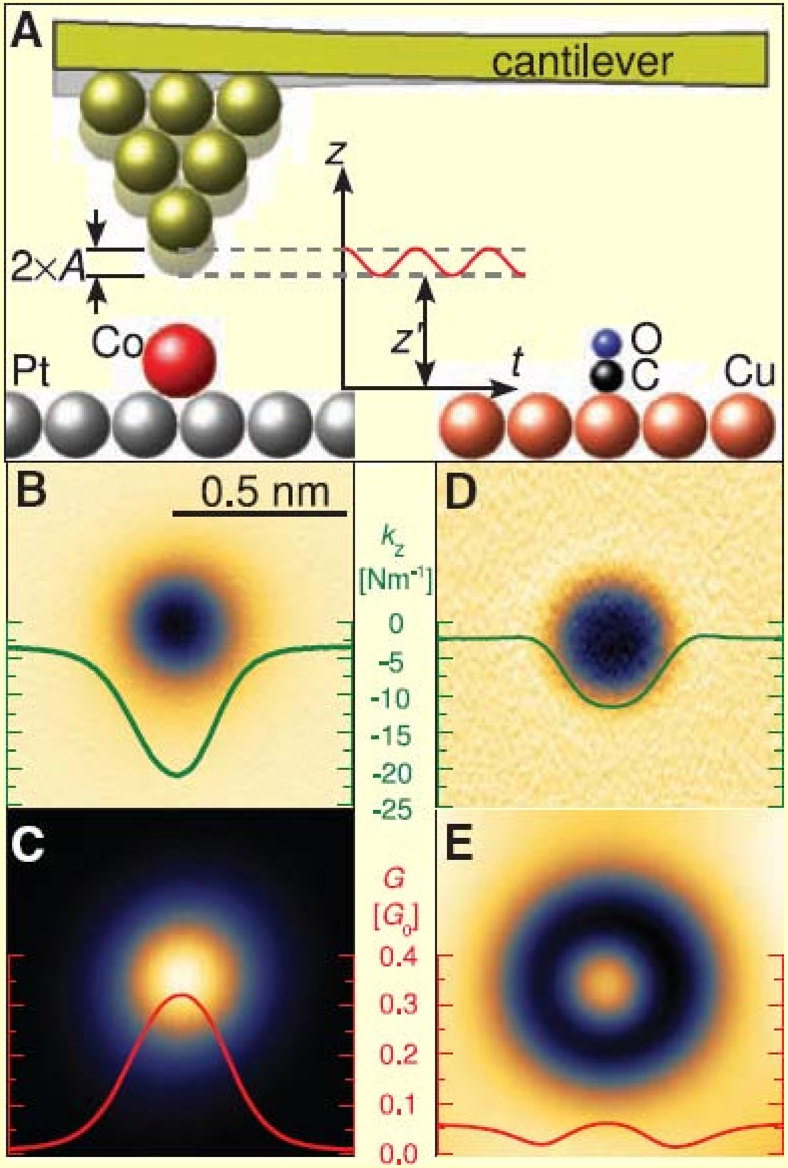


Atomic manipulation. Using a sophisticated scanning probe implementation, Ternes *et al.* (2008) determine how much lateral and vertical force is required to pull an atom on a metallic surface and how these forces are related to each other.

M. Ternes et al., Science 319, 1066 (2008)

Atomic Manipulation Force Measurements

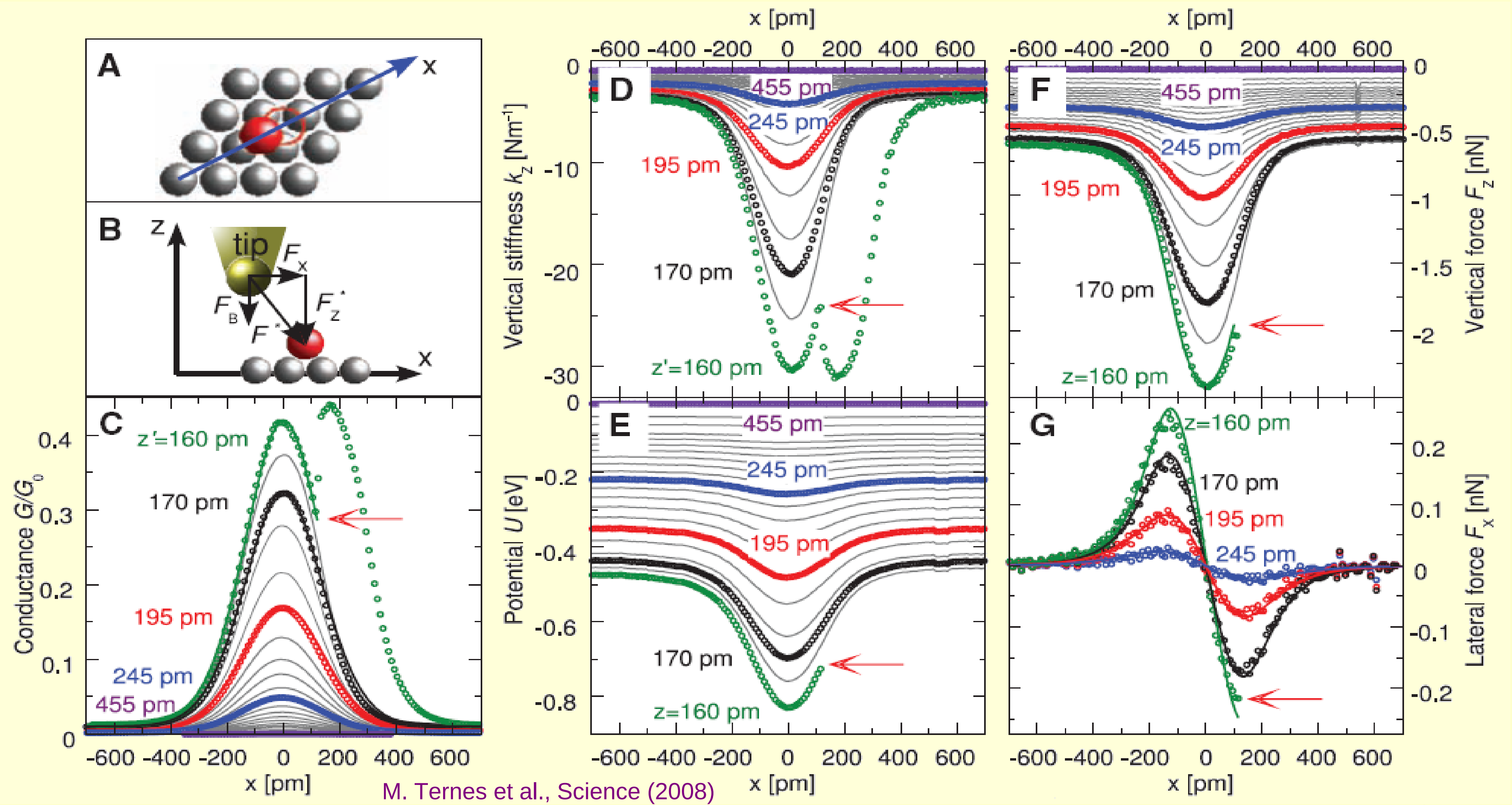
210 pN to moving Co on Pt (111) laterally & 17 pN to moving Co on Cu (111) laterally



Simultaneous AFM and STM measurements of individual adsorbates: A) An atomically sharp metal tip is oscillating in z with an amplitude **A = 30 pm** over a flat metal surface on which an individual Co atom or CO molecule is adsorbed. The measured frequency shift of the cantilever from its natural resonance frequency is proportional to the vertical stiffness **k_z** of the tip-sample interaction. A small bias voltage of **1 mV** was applied between tip and sample to measure the tunneling current, which is proportional to the conductance **G,** given in units of the single-channel, spin-degenerate quantum of conductance **$G_0 = 2e^2/h = (12{,}906 \text{ ohm})^{-1}$**, where e is the elementary charge and h is Planck's constant. The inset graph shows the tip motion z(t) between its closest distance (z') and farthest distance (z' + 2A) from the sample. The ball models of the surfaces are scaled to match the dimensions of the images in the following panels. (B to E) Images measured at a constant height z' close to the threshold for adsorbate motion. (B) The tip-sample stiffness of a single **Co atom on Pt(111).** (C) Tip-sample conductance measured simultaneously for the same system as in (B). (D and E) Same as (B) and (C) for a single **CO molecule on Cu(111).** The colored curves in the panels are horizontal cross sections through the centers of the images.

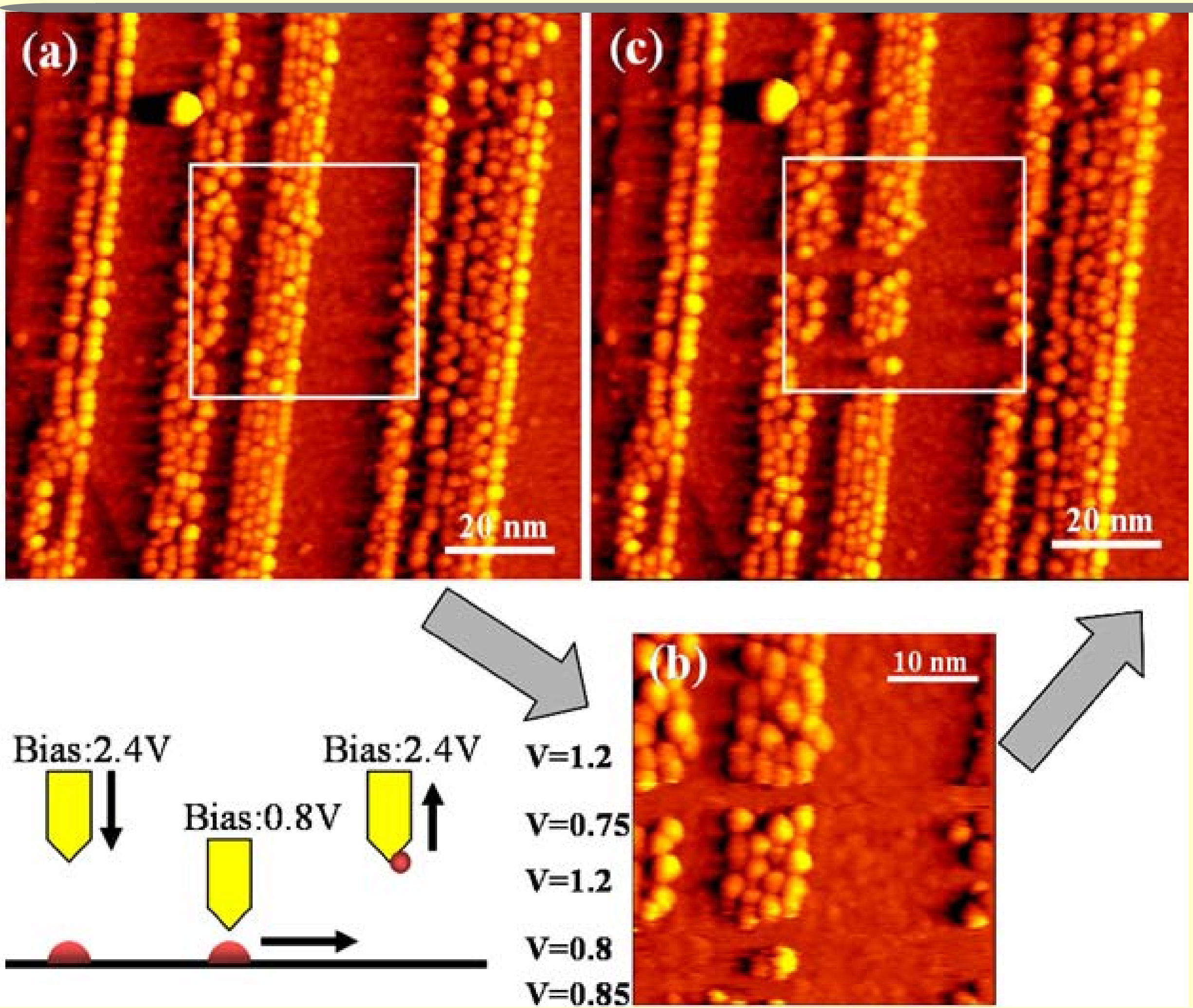
M. Ternes et al., Science 319, 1066 (2008).

Measuring the force to move Co on Pt(111). (A) Schematic top view of the Pt(111) surface atoms (gray) and the adsorbed Co atom (red). In the following panels, constant-height line scans in the direction of easiest adsorbate motion (x direction) were taken at successively reduced tipsample separations until the Co atom hopped to the adjacent adsorption site [red circle in (A)]. The scan speed was ~0.5 nm/s. (B) The force F* between tip apex and the Co atom can be divided into the lateral force F_x and the vertical force F_z*. The total vertical force F_z is the sum of F_z* and the **background force F_B** (C and D). Simultaneously measured conductance G and stiffness k_z (circles and gray lines). Note that these values are time-averaged over the cantilever oscillation between z = z' and z = z' + 2A. We label selected line scans with the closest approach z' during the oscillation . (E to G) Tip-sample interaction energy U, vertical force F_z, and lateral force F_x extracted from the stiffness k_z data in (D). Selected line scans are labeled with the tip height z; here, the oscillation amplitude has been deconvolved from the curves. The red arrows in (C) to (G) indicate the hop of the Co atom to the neighboring binding site. Colored lines in (C), (F), and (G) are fits with the s-wave model.



M. Ternes et al., Science (2008)

MANIPULATION OF NANOCLUSTERS BY STM



STM images showing removal of the Co clusters by reducing the bias during scanning. (a) STM image of Co clusters grown on ordered Al2O3/NiAl(100) surface (bias = 2.4 V and tunneling current = 0.8 nA). (b) Zoom in the area shown by the square in (a). The bias was lowered to different values as indicated in the figure (I = 0.8 nA) during scanning.

(c) STM image of the same surface region as in (a) after zoom out (b) scanned with same imaging parameters (2.4 V, 0.8 nA). The inset cartoon illustrates the procedure.

A. A. Tseng, S.D. Sartale, M.F. Luo, C.C. Kuo in Nanofabrication: Fundamentals and Applications, ed. by A. A. Tseng (2008),

Nanomanipulation: Milestones & Applications

- **1991: Single Xe atoms positioned on Ni (110) surface** (Eigler, Schweizer, Nature)
- **1993: Quantum confined structures built*** (Crommie, Lutz, Eigler, Science)
- **1999: Magnetic nanostructures built*** (Chen, Jamneala, Madhavan, Crommie, Phys. Rev)
- **1999: Single bonds characterization** (Lee, Ho, Science)
- **2000: Artificial molecules built*** (Hla, Bartels, Meyer, Rieder, Phys. Rev. Lett)
- **2000: Atomic chemical reaction *** (Hla, et al., Phys. Rev. Lett)
- **2002: Atomic wire built*** (Nilius, Wallis, Ho, Science)
- **2002: Molecular computation: molecular cascades** (Heinrich, Lutz, Gupta, Eigler, Science)
- **2003: Single molecule device** (Nilius, Qiu, Ho, Science)
- **2004: Single molecule doping** (Yamachika, et al., Science)
- **2005: Moving atom at room temperature** (Sugimoto, et al., Nature Mater)
- **2007: Chemical identification of single atoms** (Sugimoto, et al., Nature)
- **2008: Force measurements in moving atoms** (Ternes, et al., Science)
- **2009: Quantum confinement of electrons in 3D** (Moon et al., Nature Nanotech)

*** One atom at a time**

Equipment to Have Precision of ~1 nm

- **Develop closed-loop control strategy to reduce the geometric errors induced by equipment including hysteresis creep by piezo scanner, AFM tip, mechanical drift, thermal drift…,**

  - To reduce the hysteresis creep, feedback signal uses direct-measuring, non-contact capacitive position sensors (high motion linearity, long-term stability, phase fidelity)

  - To reduce mechanical drift, positioning and scanning use frictionless flexure guidance (within 0.01 nm/s)

  - To reduce thermal drift, invar or low thermal expansion materials is used for the stage (within 0.01 nm/s)

  - The total inaccuracy should be less than 1 nm/mm and 0.01 nm/s.

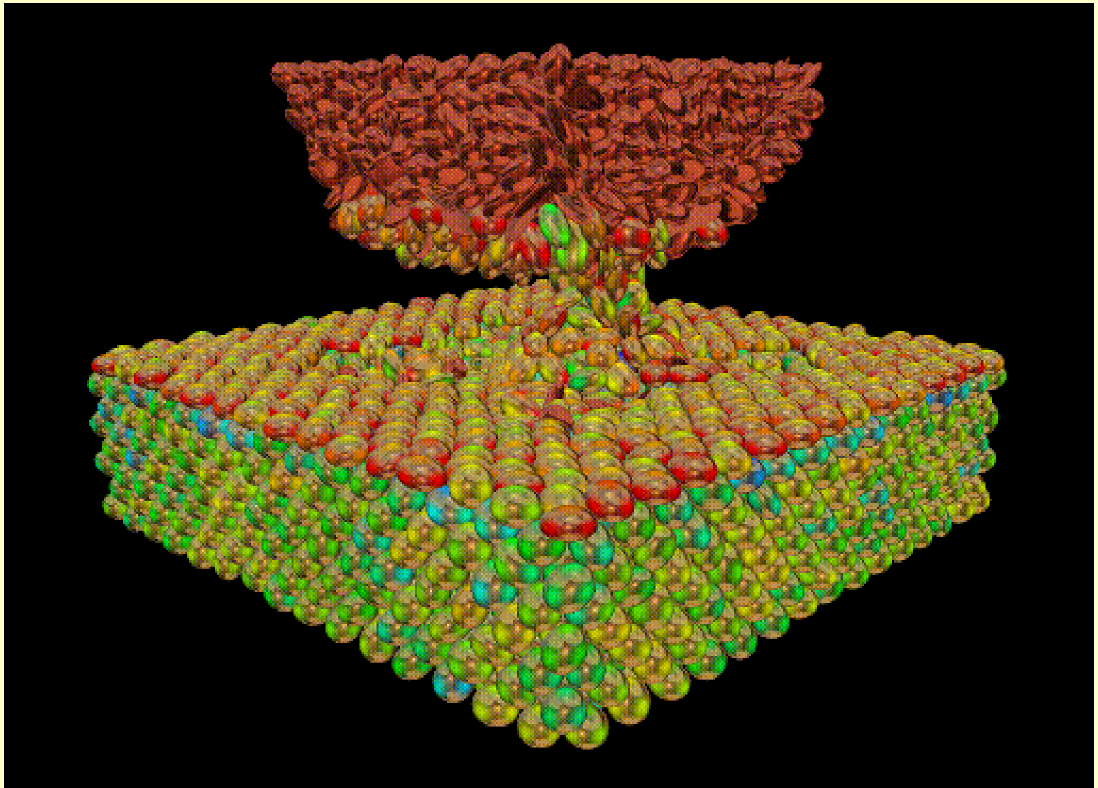
DESIGN SOFTWARE FOR PRECISION PARTERNING

- **Dimension and accuracy of patterns are highly affected by operating parameters: contact mode, tip material, scanning speed, humidity, applied voltage….**
- **Accuracy of patterning scheme requires further refining, and better processing procedures need to be developed.**
- **Height and width modulation by adjusting the phase and the duration time of pulsed voltage (short pulse voltage restricting lateral diffusion while high voltage pulse producing fast growing in height).**
- **Develop CAD software for the design and control of AFM (including DPN, STM, SNOM) oxidation and scratching patterning.**

MOLECULAR DYNAMICS SIMULATION

In general, atomistic molecular mechanics methods have the following properties:

- ▲ Each atom is simulated as a single particle
- ▲ Each particle is assigned a radius (typically the van der Waals radius), polarizability, and a constant net charge (generally derived from quantum calculations and/or experiment)
- ▲ Bonded interactions are treated as "springs" with an equilibrium distance equal to the experimental or calculated bond length

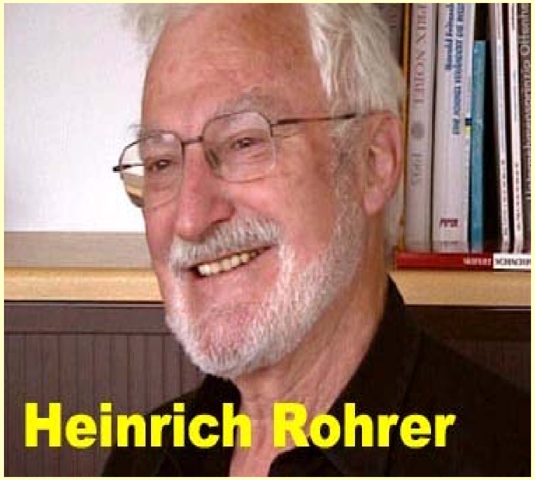


A scene from a molecular dynamics simulation of an atomic force microscope. Here a hard nickel tip comes down to a soft gold substrate. Before the tip can touch, the surface gold atoms jump up and coat the tip, leaving a neck of gold joining the surface with the tip. Elongation of the atomic spheres and spot coloring are used to indicate elongation/compressive and shear forces.

Scanning Tunneling Microscopy

Introduction

- Invented by Binnig and Rohrer at IBM in 1981 (Nobel Prize in Physics in 1986).

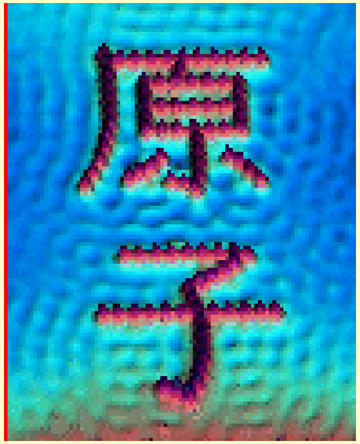


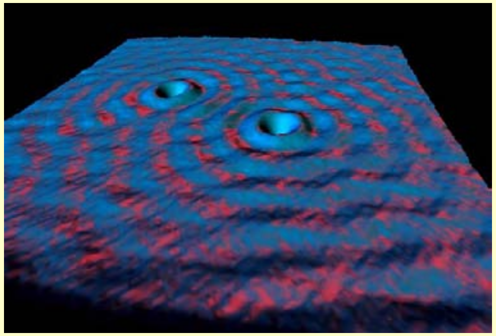
Binnig also invented the Atomic Force Microscope(AFM) at Stanford University in 1986.

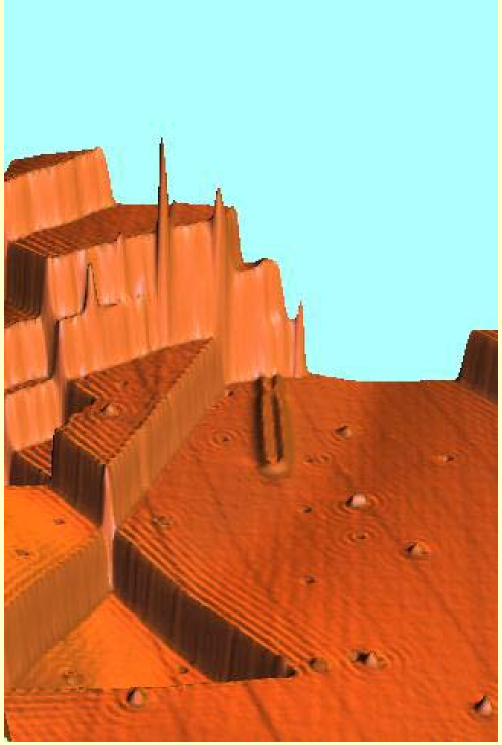
Introduction

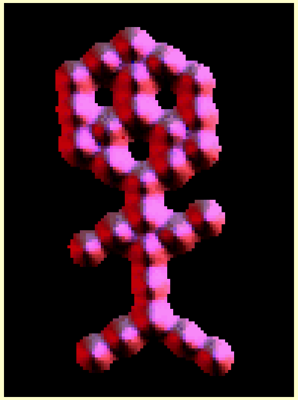
Topographic (real space) images

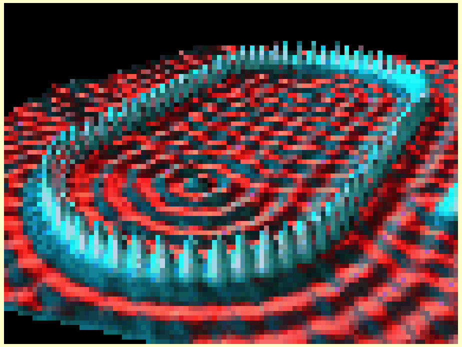
Spectroscopic (electronic structure, density of states) images











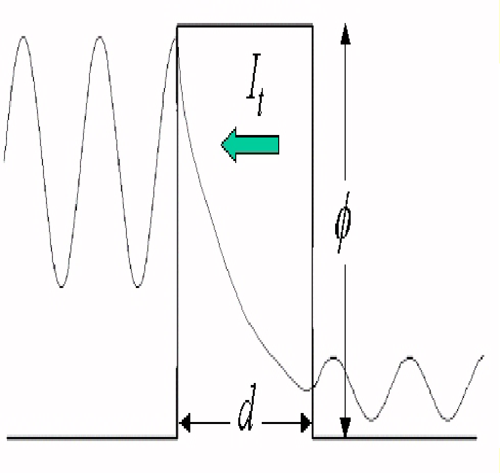
Introduction

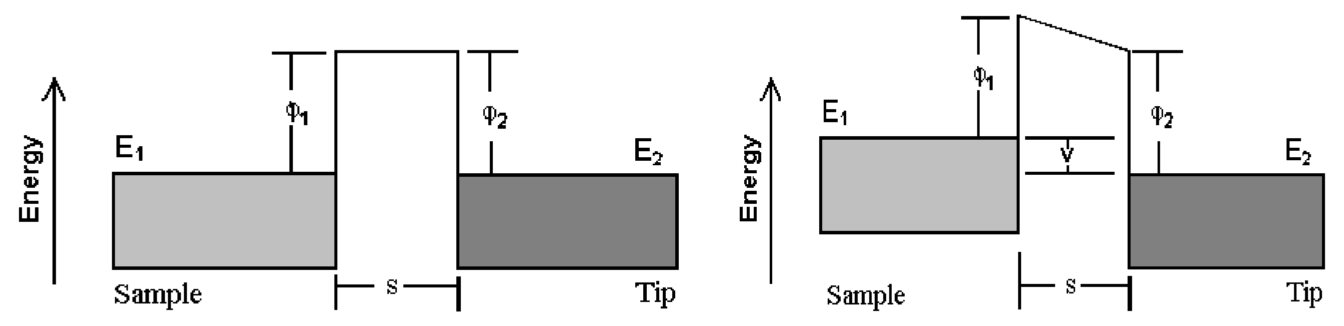
- Atomic resolution, several orders of magnitude better than the best electron microscope
- Quantum mechanical tunnel-effect of electron
- In-situ: capable of localized, non-destructive measurements or modifications
- material science, physics, semiconductor science, metallurgy, electrochemistry, and molecular biology
- Scanning Probe Microscopes (SPM): designed based on the scanning technology of STM

Theory and Principle

Tunneling Current

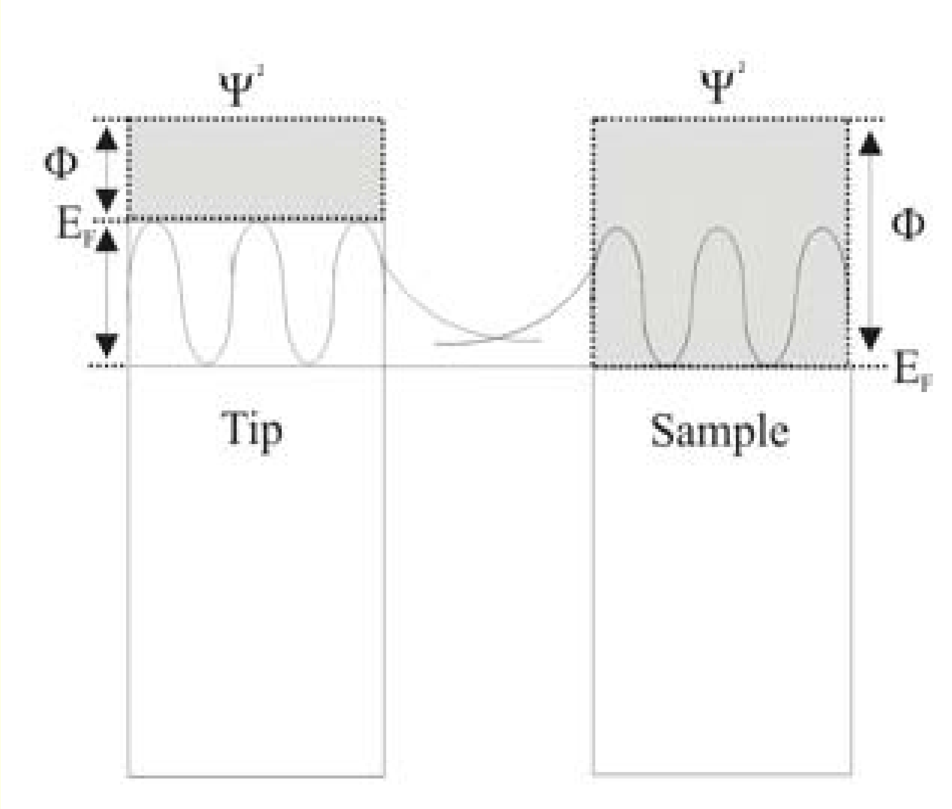
- A sharp conductive tip is brought to within a few Angstroms of the surface of a conductor (sample).
- The surface is applied a bias voltage, Fermi levels shift
- The wave functions of the electrons in the tip overlap those of the sample surface
- Electrons tunnel from one surface to the other of lower potential.





Theory and Principle

- The tunneling system can be described as the model of quantum mechanical electron tunneling between two infinite, parallel, plane metal surfaces



E_F is the Fermi level

ψ is the wave function of the electron

Φ is the work function of the metal.

Electrons tunnel through a rectangular barrier.

Theory and Principle

- The tunneling current can be calculated from Schrödinger equation (under some further simplifications of the model).

$$i\frac{\partial}{\partial t}\Psi(\vec{z},t) = \mathrm{H}\Psi(\vec{z},t) \quad \longrightarrow \ldots\ldots \longrightarrow \quad I_t \propto V \exp[-(\phi_{av})^{1/2}\, d]$$

I_t is the tunneling current; V is the sample bias
Φ_{av} is the average work function (barrier height), about 4 eV above the Fermi energy for a clean metal surface
d is the separation distance

Tunneling current exhibits an exponentially decay with an increase of the separation distance!

Exponential dependence leads to fantastic resolutions. Order of 10^{-12} m in the perpendicular direction and ~10^{-10} m in the parallel directions

Theory and Principle

How tunneling works → Simple answer

- In classical physics e flows are not possible without a direct connection by a wire between two surfaces
- On an atomic scale a quantum mechanical particle behaves in its wave function.
- There is a finite probability that an electron will “jump” from one surface to the other of lower potential.

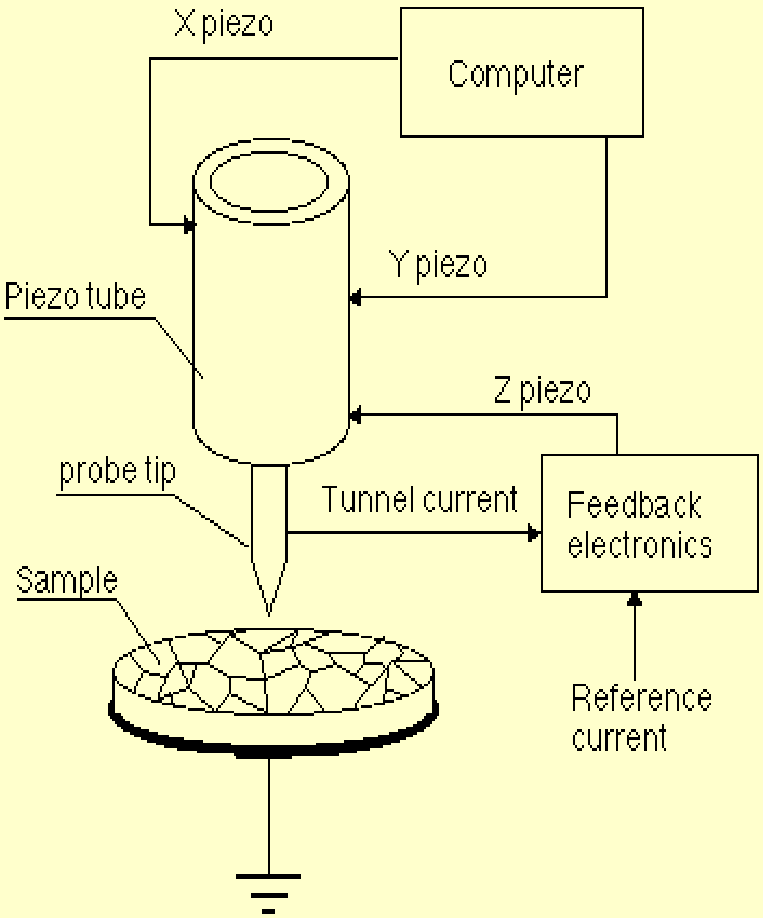
"... I think I can safely say that nobody understands Quantum Mechanics"

Richard P. Feynman

Experimental methods

Basic Set-up

- the *sample* you want to study
- a sharp *tip* mounted on a piezoelectric crystal tube to be placed in very close proximity to the sample
- a mechanism to control the location of the tip in the x-y plane parallel to the sample surface
- a *feedback* loop to control the height of the tip above the sample (the z-axis)

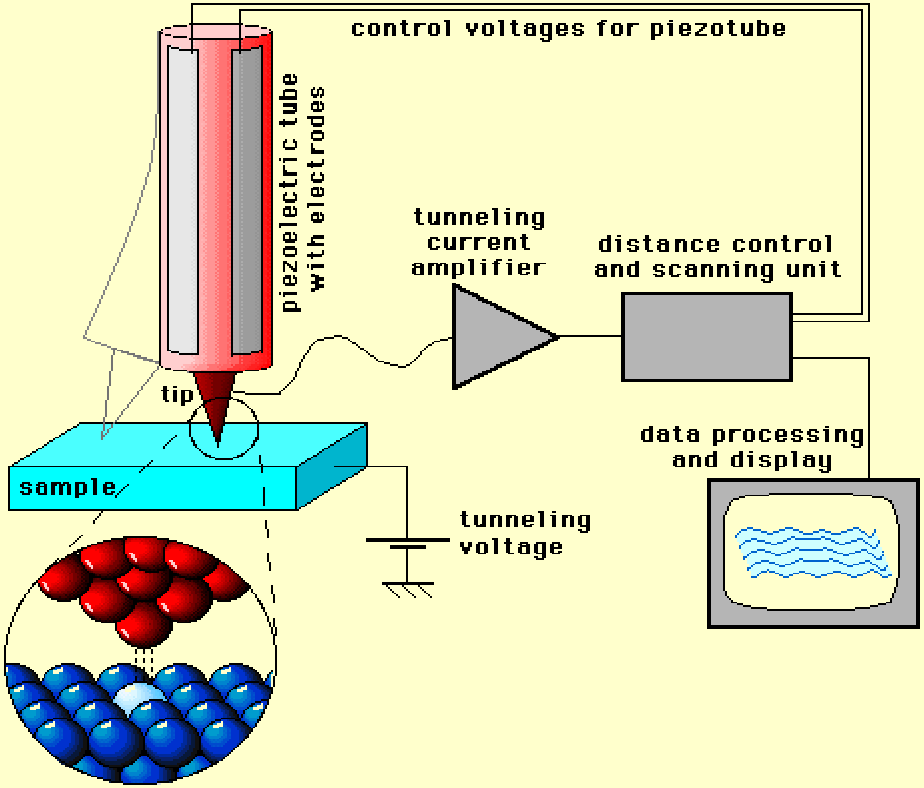


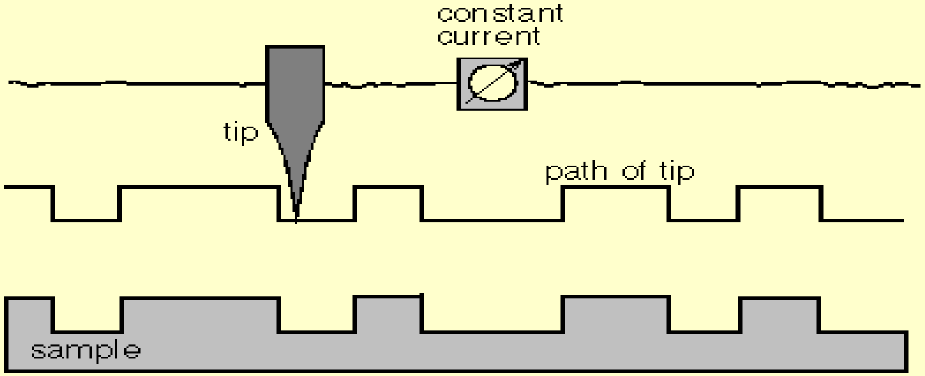
How to operate?

Raster the tip across the surface, and using the current as a feedback signal.

The tip-surface separation is controlled to be constant by keeping the tunneling current at a constant value.

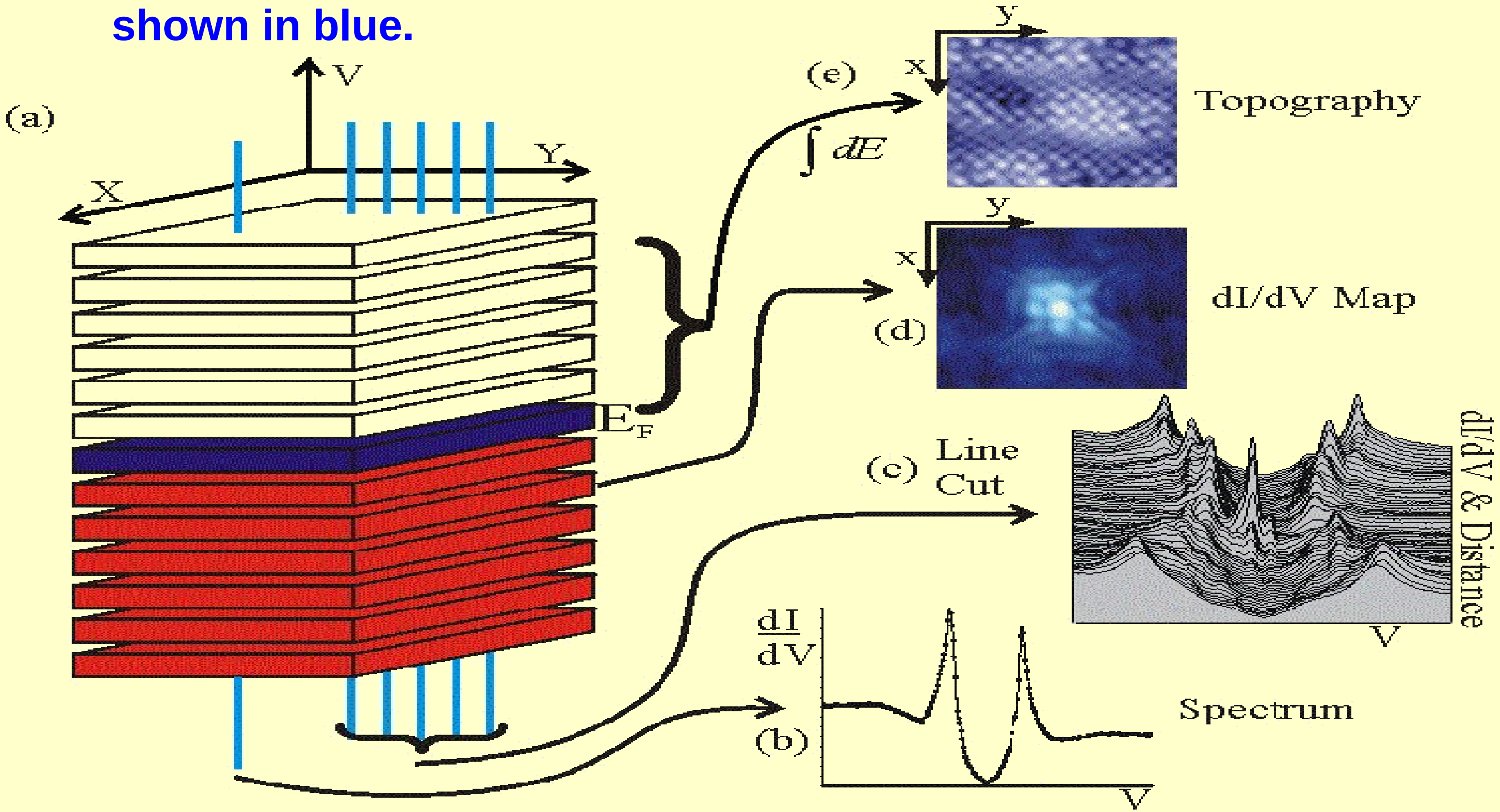
The voltage necessary to keep the tip at a constant separation is used to produce a computer image of the surface.





What an STM measures?------*local density of states*

Each plane represents a different value of the tip-sample bias V, and the lateral position on the plane gives the x,y position of the tip. Filled states are given in red. The plane at the Fermi energy (V=0) is shown in blue.



Experimental Optimization

- Control of environment vibration:
  - building the instrument with sufficient mechanical rigidity;
  - hung on a double bungee cord sling to manage vibration;
  - vibration isolation systems have also been made with springs and frames;
  - ***operate at night with everything silent***.
- Ultrahigh vacuum (UHV): to avoid contamination of the samples from the surrounding medium. (The STM itself does not need vacuum to operate; it works in air as well as under liquids.)
- Using an atomically sharp tip.

Instrumentation details

- STM tip: atomically sharp needle and terminates in a single atom

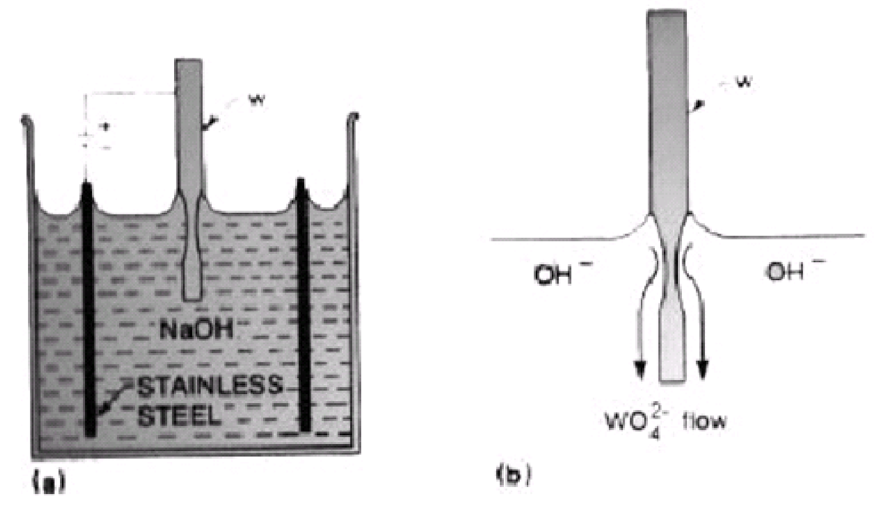
Pure metals (W, Au)

Alloys (Pt-Rh, Pt-Ir)

Chemically modified conductor (W/S, Pt-Rh/S, W/C…)

Preparation of tips: cut by a wire cutter and used as is

cut followed by electrochemical etching



Electrochemical etching of tungsten tips. A tungsten wire, typically 0.25 mm in diameter, is vertically inserted in a solution of 2M NaOH. A counter electrode, usually a piece of platinum or stainless steel, is kept at a negative potential relative to the tungsten wire.

The etching takes a few minutes. When the neck of the wire near the interface becomes thin enough, the weight of the wire in electrolyte fractures the

Typical Applications of STM

Electrochemical STM (ECSTM)

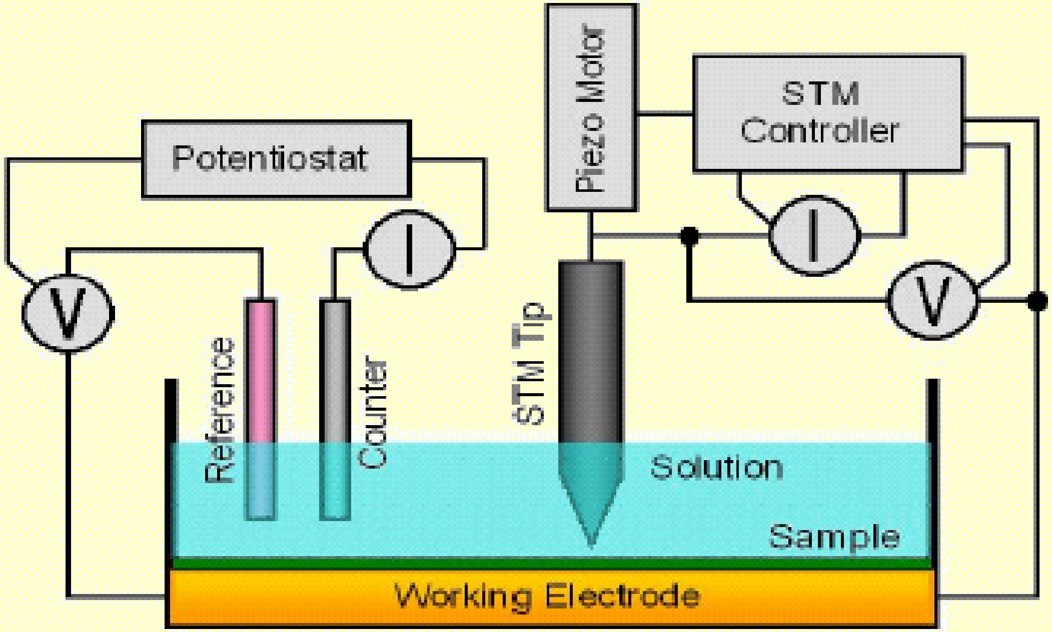
- Powerful imaging tool, directly visualize electrochemical processes in-situ and in real space at molecular or atomic levels.

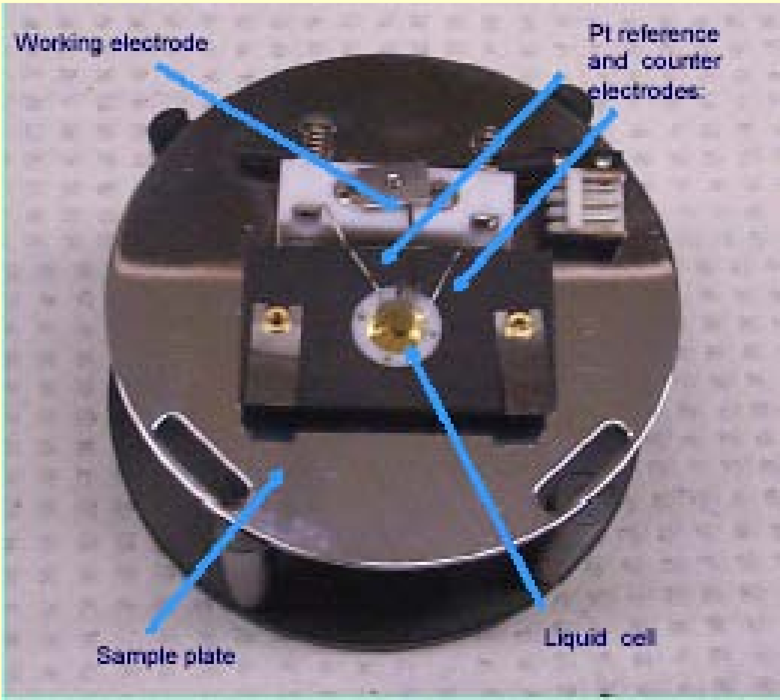
- Such interfacial electrochemical studies have been dramatically expanded over the past decade, covering areas in electrode surfaces, metal deposition, charge transfer, potential-dependent surface morphology, corrosion, batteries, semiconductors, and nanofabrication.

- Events in the EC data correlate with changes in the topography of the sample surface.

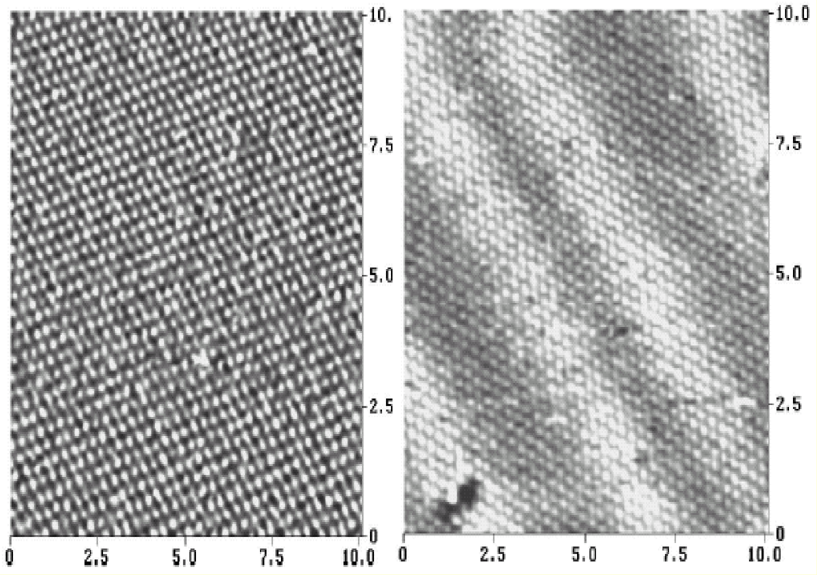
Electrochemical STM

- Three-electrode system+ STM: the STM tip may also become working electrode as well as a tunneling tip.
- Need to insulate all but the very end of the STM tip with Apiezon wax to minimize faradic currents, which can be several orders of magnitude larger than the tunneling current and make atomic resolution unfeasible or even trigger other unwanted electrochemical reactions.





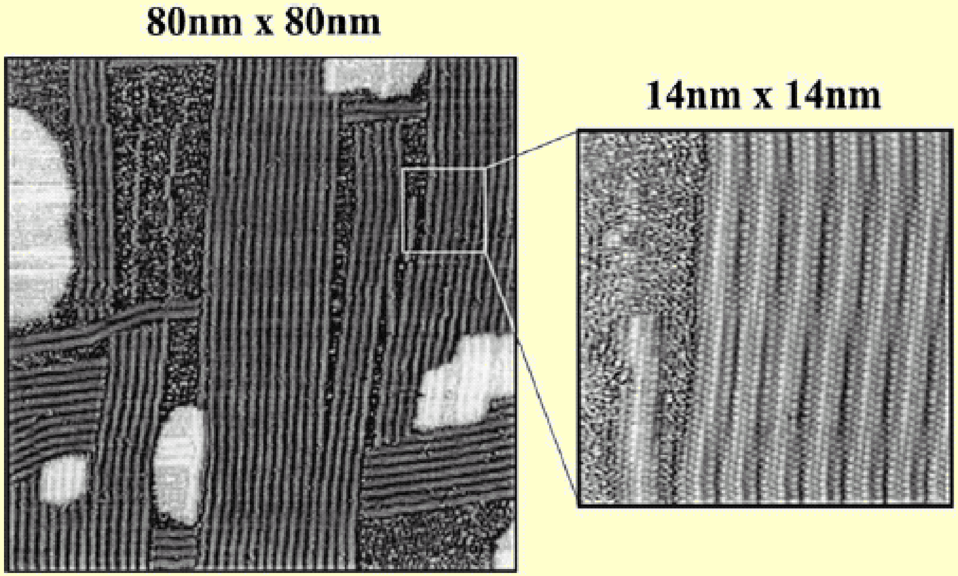
Imaging the structure of electrode surface



STM images of the Au(111) electrode surface

(Right) the reconstructed surface at negative charge densities

(Left) unreconstructed surface at positive charge densities


80nm x 80nm

14nm x 14nm

STM images of the Au (100) electrode surface

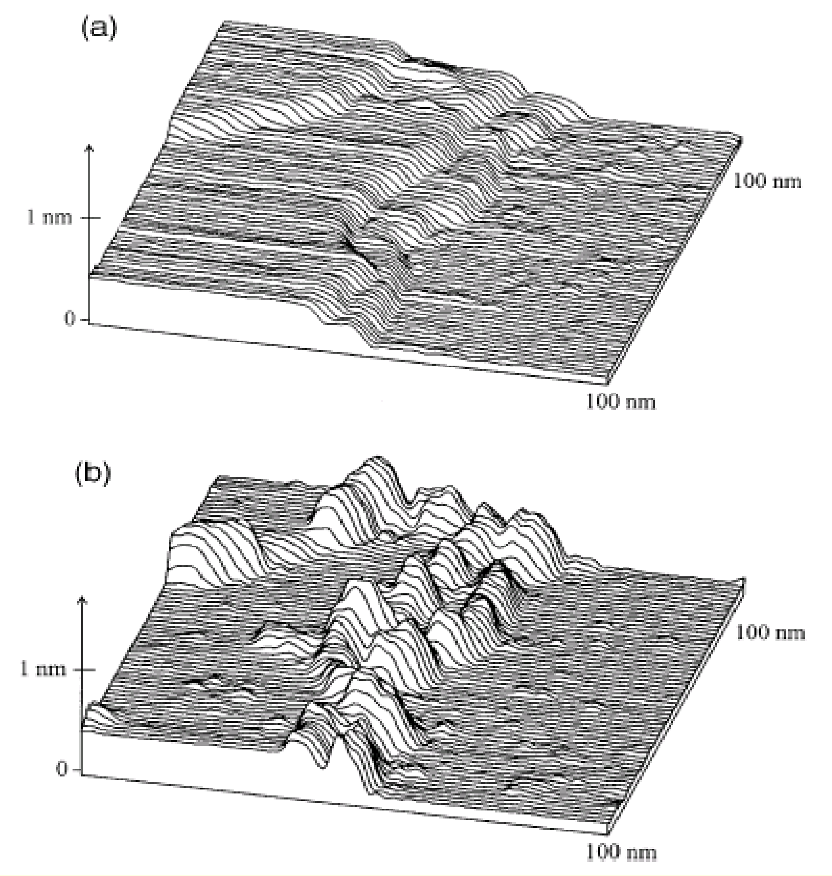
(Left) Au (100) electrode in 0.1 M H2SO4 at -0.25 V vs. SCE, where potential-induced reconstruction proceeds. The initially unreconstructed surface is being gradually transformed into the reconstructed form.

(Right) The zoom shows a section of the surface, 3/4 of which has already been reconstructed; one single

Metal deposition

When applying an potential negative of the equilibrium potential Er to cathode, bulk deposition of metal takes place.

As a nucleation-and-growth process, deposition of metal preferentially occurs at the surface defects, such as steps or screw dislocations.



STM images of Au(111) surface in 5 mM H_2SO_4 + 0.05 mM $CuSO_4$ before (panel a) and during (panel b) copper deposition.

The bare gold surface has atomically flat terraces separated by three monoatomic high steps.

After a potential step to negative values, deposition of bulk Cu occurs almost preferentially at the monoatomic high steps, namely, the growing Cu clusters

STM-based electrochemical nanotechnology

STM tip: a tool for manipulating individual atoms or molecules on substrate surface and directing them continuously to predetermined positions

ECSTM tip-generated entities are clearly larger than single atoms due to their low stability to survive electrochemical environment at room temperature.

Tip crash method: (surface damaged) use the tip to create surface defects, which then acted as nucleation centers for the metal deposition at pre-selected positions.

Jump-to-contact method: (surface undamaged) metal is first deposited onto the tip from electrolyte, then the metal-loaded tip approaches the surface to form a connective neck between tip and substrate.
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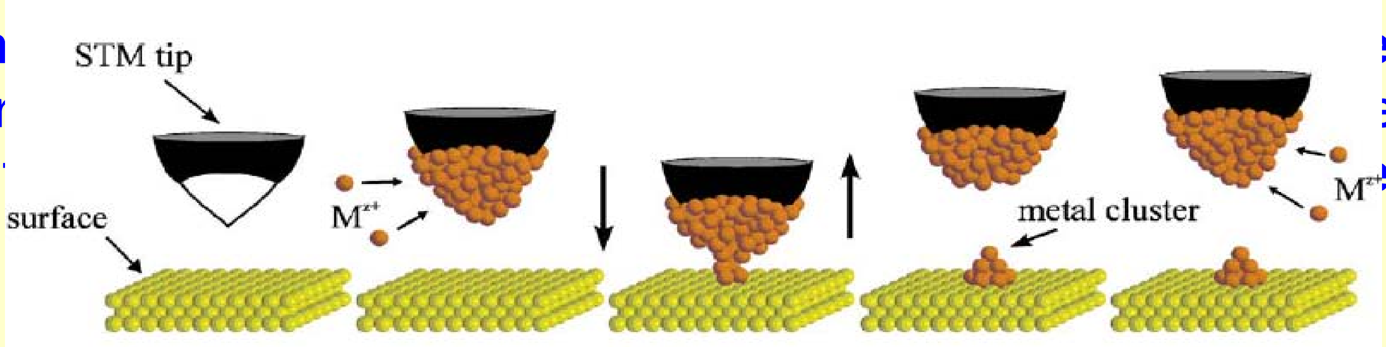
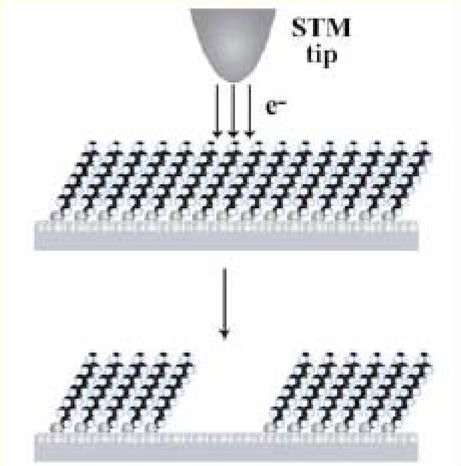


Application of STM in SAMs

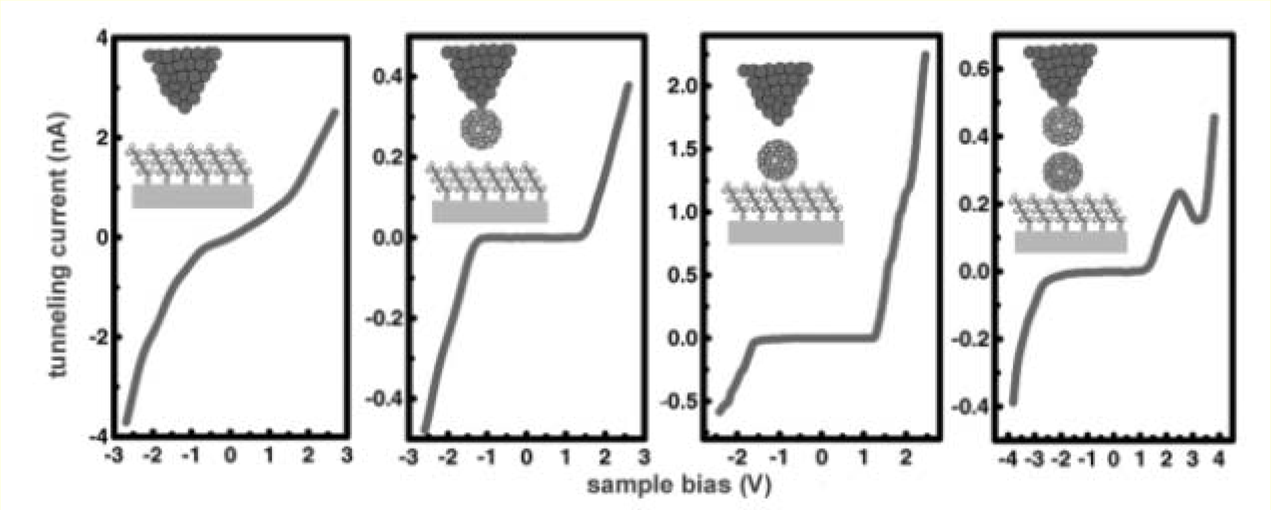
- Electrochemistry can be used to manipulate the adsorbates themselves by electrolytically cleaving the Au–SR bond at the interface, resulting in a free thiolate and Au.
- Electrochemical desorption:

$$\text{RS-Au} + e^{-} \longrightarrow \text{RS}^{-} + \text{Au}$$

Different thiols have different reductive potentials, varying from -0.75 V to -1.12 V



The I-V curves obtained from 4 kinds of tunneling structures (from left to right): bare Pt-Ir tip over thiols, C60 tip over thiols, bare Pt-Ir tip over C60, C60 tip over C60.



Concluding remarks

STM is one the most powerful imaging tools with an unprecedented precision.

Disadvantage of STM:

1. **Making atomically sharp tips remains something of a dark art!**
2. **External and internal vibrations from fans, pumps, machinery, building movements, etc. are big problems.**
3. **UHV-STM is not easy to built and handle.**
4. **The STM can only scan conductive surfaces or thin nonconductive films and small objects deposited on conductive substrates. It does not work with nonconductive materials, such as glass, rock, etc.**
5. **The spatial resolution of STM is fantastic, but the temporal resolution is typically on the order of seconds, which prevents STM from imaging fast kinetics of electrochemical process.**

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