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The basics of Scanning Probe Microscopy

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Scanning Tunneling Microscopy: Fundamentals and Applications
Contents

• Introduction on ‘nano-tools’
• Scanning Tunneling Microscopy (STM)
• Manipulation by STM
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Nano–tools

By increasing by a factor of 10 the resolving power of the Human eye, Galileo was able to discover Jupiter’s satellites

”The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom”

“The problems of chemistry and biology can be greatly helped if our ability to see what we are doing, and to do things on an atomic level, is ultimately developed – a development which I think cannot be avoided”

From: R. Feynman: There's Plenty of Room at the Bottom (1959)
Length scales – Nano-tools

Human hair

Cells

Lithography
Integrated circuits

Biological
Macromolecules

Atoms and molecules

Optical Microscopy

Electron Microscopy

Scanning Probe Microscopy

Science in ACTION for a World in EVOLUTION
Scanning Probe Microscopy

Principle of a scanning probe microscope.

Surface is scanned line by line with a probe using a fine positioning system (scanner).

With a coarse positioning device, the distance between the sample and the probe is reduced until the interaction regime is reached.

Vibration isolation shields the microscope from external vibrations.
The STM principle

G. Binnig and H. Rohrer,
(Nobel Prize in Physics, 1986)

A sharp metal tip (W, Pt–Ir) is brought into close proximity of a conducting sample, and a bias is applied: electrons tunnel from tip to sample (or vice versa)
The STM principle

Principle of a scanning tunnelling microscope. Once the gap between tip and sample is about as small as the diameter of an atom, a tunnelling current flows.
Operation of an STM$^{1,2}$

Scanning Tunneling Microscopy

Once the tip is in "tunneling contact", it is scanned above the surface using three separate piezoelectric transducers for precise movements in x, y, z.

Pt(110)–(1x2) with atomic resolution
gentle touch of a nano-finger:

If the interaction between tip and sample decays sufficiently rapidly on the atomic scale, only the two atoms that are closest to each other are able to "feel" each other.

Tunnelling Current

\[ I_t \propto V_t \exp(-A\sqrt{\Theta} \ z) \]

\( \Theta \)..... Workfunction, typically 3-5 eV

\( z \)..... Tip-sample separation, typically 4-10 Å

\( \Delta z = 1 \ \text{Å} \quad \Rightarrow \quad \Delta I \ \text{one order of magnitude!} \)

Explains atomic resolution
Imaging Si(111) 7x7

Si(111) clean surface (reconstructed 7x7) imaged with atomic resolution

First STM work:
Binnig et al.,
Si(111) 7x7 in real space
The Herringbone Reconstruction on the Au(111) Surface

[Image of atomic structure with annotations: [112], [110], pinched, bulged, x-type, y-type, FCC, HCP, (23x√3) unit cell, 1211 x 1227 Å², 87 x 90 Å²]
Au(110)-(1x2)

Missing row reconstruction

8.16 Å

[110]

[100]
Cu(110) with atomic resolution

Cu(110) 1x1

[1 -1 0]
[0 0 1]

100x100 Å²
Six STM snapshots from ‘STM film’ of Cu(110) recorded after progressively higher oxygen exposure. Cu atoms are removed from step edges during oxygen exposure: added -Cu–O- rows nucleate and grow on the terrace along the [001] direction.
Oxygen nanopattern on Cu(110)

Cu(110)  O₂ chemisorption: Cu–O rows (2x1)

Cu–O rows (2x1)  4–6 Langmuir O₂ at 625 K

Bare Cu  partial 2x1 reconstruction (“patches”)

added row structure

65x65 Å²

• : Cu atoms
  ● : O atom
Close up on Cu–O

$O_2$ chemisorption on Cu(110): partial 2x1 reconstruction ("patches")

35x35 Å$^2$    20x20 Å$^2$
• Scanning Probe Microscopy was developed following the need to obtain **local** information on morphology, structure, etc.

• Other advantages over “similar” techniques (e.g. SEM): SPM is less damaging, and can be used to “manipulate” objects on the atomic scale
Unknown/Challenges:

1. Chemical nature of STM tip
   (problem for spectroscopy, corrugation)
2. Relaxation of tip/surface atoms
   (tip sample separation not equal to piezo scale)
3. Effect of tip potential on electronic surface structure
   (quenching of surface states)
4. Influence of magnetic properties on tunnelling current/surface corrugation
   (is spin-STM possible?)
5. Relative importance of the effects
Thermal drift

Touching the microscope (e.g. sample, cantilever) will change its temperature T. Shining light on it too! Cantilever has a mass of ~ 1 ng, and thus a VERY small heat capacity.

So what!?! 

$$\frac{\Delta L}{L} = \text{const} \Delta T; \text{const} \sim 10^{-5}$$
Pushing and pulling single atoms

Using the tip of a Scanning Tunnelling Microscope

Quantum Corral (Fe on Cu): Visualization of electron wavelets
D. Eigler, IBM Almaden

Xe on Ni(111) at 4 K
D. Eigler, IBM Almaden
Manipulation – Atom by atom

Japanese Kanji character for Atom, written with atoms

D. Eigler, IBM Almaden
Lateral Manipulation of individual atoms and molecules by STM

The tunneling resistance $R = V / I$ measures the separation of the tip from the surface:

$I \sim V \exp(-2kz)$

By reducing $V / I$, the tip approaches the substrate, thus leading to a stronger tip–surface interaction.
Important features for STM manipulation

- "freezing" the motion of single adsorbates: low (variable) temperature STM

- long operating time and working at low coverages (0.001–0.01 ML); requirements:
  - high cleanliness: scanner completely surrounded by 4 K radiation shield
  - controlled deposition of small amounts of adsorbates: small hole in the radiation shield, with small solid angle (1:3000)

- flexible and precise tip positioning; requirements:
  - high x,y,z stability
  - $I(V)$: electronic / vibrational spectroscopy
  - $I(z)$: tip – adsorbate interaction
  - Tip height / current positioning during manipulation
Idealized sketch of picking up / putting down of CO molecules on Cu(111). CO stands upright on the surface and has to switch its orientation when transferred to the tip.

Vertical Manipulation of CO on Cu(111)

Transfer of single CO molecules from the right to the left terrace by vertical manipulation

Cu(111) terrace intersected by a lower terrace

CO molecules are imaged as depressions with a metal tip and as protrusions with a CO tip

Pulling

“Pulling” Mode

Tip

Sample

Current

Tip Position
Pushing

"Pushing" Mode

Tip

Sample

Current

Tip Position
Single–molecule synthesis by STM

Synthesis of biphenyl (C\(_{12}\)H\(_{10}\)) from iodobenzene (C\(_6\)H\(_5\)I)

STM tip-induced synthesis steps of a biphenyl molecule. (a), (b) Electron–induced abstraction of iodine from iodobenzene. (c) Removal of iodine by lateral manipulation. (d) Bringing together two phenyls by lateral manipulation. (e) Electron–induced chemical association of the phenyl couple to biphenyl. (f) Pulling the synthesized molecule with the STM tip to confirm the association.

Surface diffusion:
in general, it is a 2 D random walk

\[ \nu = \nu_0 \exp(-E_D/kT) \]

Hopping rate: counting the proportion of molecules that have not moved between two consecutive images:

\[ P_0 = M / N = F(ht) \]
Surface diffusion

hopping rate: \( h = h_0 \exp(-E_D/kT) \)

random walk: \( \langle (\Delta x)^2 \rangle = \lambda^2 ht \)
\( \lambda \) - RMS jump length

tracer diffusion coefficient:

\[ D = \frac{\langle (\Delta x)^2 \rangle}{2t} \]

\[ D = D_0 \exp(-E_D/kT) \]

with \( D_0 = h_0 \lambda^2/2 \)
STM movie: Diffusion of Pt adatoms

Pt(110):
1x2 reconstruction (missing row)
Deposition of Pt
Observation of diffusion at several temperatures:
- Arrhenius behavior
- Activation energy for diffusion
- Prefactor

STM – Movies: www.ifa.au.dk/camp
STM movie: Dynamics of Pt dimers

Slightly higher Pt coverage

Diffusion of vacancies along the rows

Formation and diffusion of Pt dimers


STM – Movies: www.ifa.au.dk/camp

80×73 Å²
Metal-on-metal growth

Island Formation

Binary Alloy

Chemical change of overlayer due to substrate
STM of Au alloyed into the Surface of Ni(110)

Au-Ni Surface Alloy
Au–Ni(111)

STM – Movies:
www.kfa-juelich.de/video/voigtlaender/

B. Voigtlander

observation of step-flow growth

Homoepitaxy of Si on Si(001):
Layer by Layer growth
Growth Movies - 2

Homoepitaxy of Si on Si(111):
Layer by Layer growth

2 D island nucleation and coalescence
Growth Movies - 3

heteroepitaxy of Ge on Si(001):
Stranski – Krastanow growth
(layer by layer, then 3 D island nucleation)
Growth Movies - 4

heteroepitaxy of Ge on Si(111): Stranski – Krastanow growth
Tip shadow
STM on insulators

Atomic resolution at $V_t = 5.9$ V: Close to field emission regime. Tunneling occurs into the conduction band of the sample.