Scanning Tunneling Microscopy

Wei-Bin Su, Institute of Physics, Academia Sinica
Transmission Electron Microscopy

Field Ion Microscopy

Topografiner
1970, Young et al.

A precursor of STM

- Included most of the elements of an STM
- Resolution: 500 nm

Problems were overcome by Gerd Binnig and Heinrich Rohrer at the IBM in 1980

80-400 Kev electron beam
The Nobel Prize in Physics 1986
Tunneling effect

Field emission

1000 – 10000 V

metal

metal Vacuum

metal

metal-vacuum-metal tunneling

< 10 Å
Scanning Tunneling Microscopy (STM)

- Sample (conductor)
- Bias
- Metal tip
- Tunneling current
- Preamp
- Scanner
- Feedback

$Si(111)7\times7$

$Pt(100)\text{-}R0.7^\circ$

$I_t = \text{const}$
\[ I \sim \exp(-2\kappa s); \ \kappa = \left(\frac{2m\phi}{\hbar^2}\right)^{1/2}; \phi = \frac{\phi_t + \phi_s}{2} \]

\[ \kappa \sim 1 \text{ Å}^{-1} \rightarrow \text{the current decays about } e \approx 7.4 \text{ times} \]

when \( s \) increases by 1 Å
Tunneling current

\[ I \propto \int_{0}^{eV} \rho_s(E_F-eV+\varepsilon) \rho_T(E_F+\varepsilon)d\varepsilon \exp(-2ks) \]

\[ \rho_T \text{ is constant} \]
\[ \Rightarrow \frac{dI}{dV} \propto \rho_s(E_F-eV) \]
1. **Constant Current Mode**
   By using a feedback loop the tip is vertically adjusted in such a way that the current always stays constant.

\[ I \propto \int_0^{eV} \rho_s(E_F-eV+\varepsilon) \rho_T(E_F+\varepsilon) d\varepsilon \exp(-2\kappa s) \]

\[ \rho_s \uparrow \quad s \uparrow \]
2. **Constant Height Mode**

In this mode the vertical position of the tip is not changed, equivalent to a slow or disabled feedback. The current as a function of lateral position represents the surface image. This mode is only appropriate for atomically flat surfaces as otherwise a tip crash would be inevitable. One of its advantages is that it can be used at high scanning frequencies (up to 10 kHz). In comparison, the scanning frequency in the constant current mode is about 1 image per second or even per several minutes.

\[ I \propto \int_{0}^{eV} \rho_s(E_F-eV+\varepsilon) \rho_T(E_F+\varepsilon)d\varepsilon \exp(-2\kappa s) \]

- Not suitable to observe surface morphology
- Suitable to observe dynamics phenomenon such as diffusion of surface atom.
Structure of STM

RT UHV STM
Homemade Low Temperature STM

cryostat

thermal shielding

transfer line
Home made LT UHV STM

Homemade STM

UHV-compatible LHe Cryostat

Lowest temperature ~ 5 K
LHe consumption rate ~12 liter/37 hours
Thermal drift ~ 6 Å/ hour
Merits of LT STM

Phase transition

\[(3 \times 3)\text{Pb/Si}(111) \rightarrow (\sqrt{3} \times \sqrt{3})\text{Pb/Si}(111)\]

Interference wave of surface state

Superconducting gap

Tip

The tip is the trickiest part in the STM experiment. It needs a small curvature to resolve coarse structures. For atomic resolution a minitip with a one atomic end is necessary. Tips typically are made out of tungsten or Pt-Ir wire.

A sharp tip can be produced by:
- Cutting and grinding (Pt-Ir)
- Electrochemical etching (W)

Most often the tip is covered with an oxide layer and contaminations from the etchant and is also not sharp enough. Thus other treatments to the tip, like annealing or field evaporation are necessary.
Tube Scanner

Piezoelectric ceramic PZT \([\text{Pb}(\text{Zr},\text{Ti})\text{O}_3]\) (piezo)

can be deformed by applying voltage

The contrast in STM image is the variation of voltage on \(z\) electrode.
1,3: Piezo-clamp
2: Piezo-tube
Pan-style Stepper invented by S. H. Pan

High rigidity

Rev. Sci. Instrum., 70, 1459
The tip-sample distance must be kept constant within 0.01Å to get good atomic resolution. Therefore it is absolutely necessary to reduce inner vibrations and to isolate the system from external vibrations. Environmental vibrations are caused by:

- Vibration of the building 15 - 20 Hz
- Running people 2 - 4 Hz
- Vacuum pumps
- Sound

Vibration damping can be done by
- Suspension with springs (including additional eddy current dampers)
- Pneumatic systems

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1. Auto approach

STM electronics

Scanner extension in z axis (tip moves toward sample)

Tunneling current?
- No
- Yes

Scanner contraction & stepper moves one step

Data acquisition

Extension in z axis > one step of stepper
2. Data acquisition

The tunneling current (0.01nA-50nA) is converted into a voltage by a current amplifier. To get a linear response with respect to the tunneling gap (the current is exponentially dependant on the tip-sample distance) the signal is processed by a logarithmic amplifier. The output of the logarithmic amplifier is compared with a predetermined voltage which is used as a reference current. The error signal is passed to feedback electronics, which applies a voltage to the z piezo to keep the difference between the current set point and the tunneling current small. Care has to be taken to keep the noise signal ratio on a low level. Also the response time of the feedback has to be minimized without loosing accuracy.
Applications of scanning tunneling microscopy

Surface reconstruction

Atoms at surface experience different bonding environment than bulk - causes relaxation and reconstruction.

FCC(111)

FCC(100)

Relaxation

Reconstruction

Selvedge
22\times3 \text{ Reconstruction of Au}(111) \text{ surface}
Reconstruction on Pt(100)

FCC(100)

Pt(100)-R0.7°

Close packed lattice (0.965 A) / square lattice (A)
A=lattice constant
STM image of Si(111)7×7 (empty state)

Reconstruction on Si(111)

Filled state

Atomic Model of Si(111)-(7×7)

Top view

Side view

0.8 Å

1st
2nd
3rd
4th
5th
Bulk

Si adatom
Si rest atom with a dangling bond

dangling bond

faulted half
unfaulted half

2nd layer rest atom
Surface Diffusion

Einstein Equation: $D = \frac{\langle x^2 \rangle}{2\alpha\gamma}$

$D$: diffusion coefficient,
$\langle x^2 \rangle$: mean square displacement of atom
$\alpha = 1$ for one dimensional diffusion
$\alpha = 2$ for two dimensional diffusion ($\langle x^2 \rangle + \langle y^2 \rangle$)
$\gamma$: time interval

$\langle x^2 \rangle$ can be related to the number of jumps $N$

According to random walk theory $\langle x^2 \rangle = Nd^2$

$L$: mean jump distance

$\Gamma$ is defined as the number of atom jumps per time interval $= N/\gamma$

$\ln \left( \frac{\langle x^2 \rangle}{2\alpha\gamma} \right) = \ln(D_0) - \frac{E_d}{kT}$

$D = \frac{d^2\Gamma}{2}$

$\Gamma = \nu_0 \exp(-E_d/kT)$

$\nu_0$ is vibration frequency,
$E_d$ is activation energy

$D = D_0 \exp(-E_d/kT) = \frac{\langle x^2 \rangle}{2\alpha\gamma}$

$D_0$ is the diffusivity $= \nu_0 d^2/2$
Site Hopping of Single Chemisorbed O$_2$ Molecule on Si(111)7×7

with the lapse of time

350°C


<table>
<thead>
<tr>
<th>Hopping</th>
<th>Activation energy</th>
<th>Frequency factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>FE to FE</td>
<td>2.04 ± 0.04 eV</td>
<td>10$^{15.0}$ s$^{-1}$</td>
</tr>
<tr>
<td>FE to FO</td>
<td>2.29 ± 0.06 eV</td>
<td>10$^{15.2}$ s$^{-1}$</td>
</tr>
<tr>
<td>FO to FE</td>
<td>2.13 ± 0.11 eV</td>
<td>10$^{15.6}$ s$^{-1}$</td>
</tr>
<tr>
<td>UE to UE</td>
<td>2.16 ± 0.04 eV</td>
<td>10$^{15.9}$ s$^{-1}$</td>
</tr>
<tr>
<td>UE to UO</td>
<td>2.01 ± 0.10 eV</td>
<td>10$^{14.6}$ s$^{-1}$</td>
</tr>
<tr>
<td>UO to UE</td>
<td>1.96 ± 0.13 eV</td>
<td>10$^{14.1}$ s$^{-1}$</td>
</tr>
</tbody>
</table>
$300^\circ$C

**FIG. 5.** The model for the site hopping.
Atom Manipulation and Nanolithography By STM

The Concept

The Realization

Overview of manipulation processes.

Lateral Manipulation

Dissociation

Atomic/Molecular Manipulation

Vertical Transfer

Synthesis

Desorption

Change of Conformation
Lateral Manipulation

1. 

2. Closer tip-sample Distance

3. Pulling atom with tip

4. 

5. 

6. 

By Eigler et al. Nature 344, 524 (1990)

Science 262, 218 (1993)
Vertical Manipulation

High voltage pulse

Ge(111)


Nanolithography

Nano Au cluster created by Au STM tip/Au (in air)


High negative voltage pulse

Melt-then-contact Mechanism
Nucleation and Epitaxial Growth

$N \sim \eta(\Theta)(r/\nu)^X \exp[\chi(E_d + E_i / i)/k_B T]$

$E_d$: activation energy
$E_i$: binding energy of critical size $i$

$\bullet \rightarrow$ number of atoms to form stable nucleation

FIG. 1. STM images, 100 x 100 nm$^2$, of single-layer Fe islands (white) on the Fe(001) surface (black). Sample temperatures during growth are (a) 20°C, (b) 108°C, (c) 163°C, (d) 256°C, (e) 301°C, and (f) 356°C. Fe was deposited for a fixed time for all measurements with a flux of 1.4 ± 0.3 x 10$^{13}$ atoms cm$^{-2}$ s$^{-1}$, yielding a coverage of 0.07 ± 0.016 ML (1 ML = 1.214 x 10$^{15}$ atoms cm$^{-2}$).

Critical size \(i\)

- \(i=0\): monomer
- \(i=1\): dimer
- \(i=2\): trimer
- \(i=3\): tetramer

**Scaling theory**

\[
N_s = \theta S^2 f_i (s/S)
\]

- \(N_s\): island density at size \(s\)
- \(\theta\): coverage
- \(S\): average island size

\[
N_s \frac{S^2}{\theta} = f_i (s/S)
\]

\(f_i (s/S)\) is an universal
Scaling function at critical size \(i\)

J. G. Amar and F. Family
Epitaxial Growth Mode

\[ \gamma_s < \gamma_a + \gamma^* \]

\[ \gamma_s > \gamma_a + \gamma^* \]

(a)  \hspace{10em}  (b)  \hspace{10em}  (c)

Volmer-Weber (VW) \hspace{10em} Frank-van-der-Merwe (FM) \hspace{10em} Stranski-Krastonov (SK)

\[ \gamma_s : \text{surface free energy of substrate} \]

\[ \gamma_a : \text{surface free energy of adsorbate} \]

\[ \gamma^* : \text{interfacial free energy} \]
Pb/Si(111) at RT

Stranski-Krastanov growth mode
3D islands Growth

Layer + Island (SK) Growth
The Growth of 2D Pb islands on Si(111)7×7 surfaces at Low Temperature

$T=208\,\text{K}$, $\theta = 3.2$ ML Pb

Topography

3D image of topography

2 ML wetting layer

100 nm

Quantum Size Effect-Driven Epitaxial Growth

\[ \lambda = \text{de Broglie wavelength of electron} \]

\[ L \gg \lambda \quad L \cong \lambda \]

$N \sim \exp\left[\frac{(iE_d+E_i)}{(i+2)k_B T}\right]$

$E_d$ : the activation for diffusion
$E_i$ : the binding energy for the critical size $i$

The nucleation and the quantum size effect are two independent factors in the formation of an island, the former results in the creation of an island and the latter determines the thickness of the created island.
2.72 ML

3.52 ML

4.32 ML

(500×500 nm²)

Average island area (nm²)

Coverage (ML)

Ratio

Island thickness (layer)

2D growth behavior
2.3 ML, 170 K

- Growth transition induced by the quantum size effect
- Independent transition pathway: N-layer thickness island is transformed from N-layer height cluster
- Identical cluster can be of different electronic structure (quantum size effect).

Scanning Tunneling Spectroscopy (STS)

\[ I \propto \int_{0}^{eV} \rho_s(E_F-eV+\varepsilon) \rho_T(E_F+\varepsilon) d\varepsilon \]

\( \rho_T \) is constant

\[ \Rightarrow \frac{dI}{dV} \propto \rho_s(E_F-eV) \]

Numerical differentiation

Lock-in technique
Lock-in technique

\[ V_{\text{bias}} + V_{\text{mod}} \sin(\omega t) \quad \omega: 500-5000 \text{ Hz} \]

\[ I(V_{\text{bias}} + V_{\text{mod}} \sin(\omega t)) \sim I(V_{\text{bias}}) + \frac{dI(V_{\text{bias}})}{dV} \cdot V_{\text{mod}} \sin(\omega t) \]

detected by lock in amplifier

modulation of current

Bias voltage and tunneling current modulated during the I-V curve
Quantum Confinement Effect

Square potential

Triangular potential

quantum-well states

metal film

free electron property

substrate

STM gap

tip

sample

standing-wave state
Visualization of quantum confinement effect by STS
Application of standing-wave state in STM gap on work function measurement of thin metallic film

Both techniques are consistent. Precision can be better than 20 meV.

Phase contribution of image potential on empty quantum well States

Pb island/Cu(111)

\[ 2k(N+1)d = 2n\pi \]

\[ \Delta E = \frac{\hbar^2(2n+1)\pi^2}{2m^*}(N+1)^2d^2 \]

Phys. Rev. Lett. 102, 196102 (2009)
Phase contribution of image potential on empty quantum well States

For simple square well:

\[
2k(N+1)d = 2n\pi
\]

Including phase \( \phi_B \) contributed from image potential

\[
2k(N+1)d + \phi_B = 2n\pi
\]

\[
\phi_B / \pi = [3.4 \text{ eV} / (E_V - E)]^{1/2} - 1
\]

E: energy of quantum well state

\( E_V \): vacuum level

Pb band structure along $\Gamma$-L direction: probed with quantum-well states

$$2k(N+1)d + \phi_B = 2n\pi$$

$$\frac{\phi_B}{\pi} = [3.4 \text{ eV}/(E_V - E)]^{1/2} - 1$$


angle-resolved photoemission spectroscopy, $k_F=1.598$ Å$^{-1}$ (bulk)
Field effect

Field-induced energy shift of surface state

Surface state on Cu(111)

Electric field in STM junction $\sim 0.3$ V/Å

Field-induced energy shift of empty quantum well states in Pb islands on Cu(111)


2-layer

\( \Delta E = 110 \) meV

9-layer

\( \Delta E = 60 \) meV

First mode

Second mode

Mode distribution with thickness dependence

- First mode
- Second mode
The first mode is the only choice. The second mode cannot be explained (negative energy shift).
When electric field is applied,

\[ 2(k + \Delta k)(N + 1)d + \phi_B + (\alpha - \beta) = 2n\pi \]

\[ \alpha > 0 \]

\[ \alpha - \beta < 0 \] positive energy shift (\( \Delta k > 0 \))

\[ \alpha - \beta > 0 \] negative energy shift (\( \Delta k < 0 \))
Local expansion deformation due to electrostatic force in STM gap

(i) $\Delta t$ increases with increasing $F$
(ii) $\Delta t$ is proportional to thickness

Solid state physics

$\Delta t = N \Delta d$

$\Delta d$: expansion of interlayer spacing
Scanning Probe Microscopy

Scanning Tunneling Microscopy (STM)

Gerd Binnig, Heinrich Rohrer
1986 Nobel Prize in Physics

Detecting the interaction between probe and sample:

- Atomic force (AFM)
- Magnetic force (MFM)
- Electrostatic force (EFM)
- Near field optics (NSOM)

bias
<10Å
metal tip
tunneling current
scanner
feedback
preamp
sample