

# Surface Studies by Scanning Tunneling Microscopy

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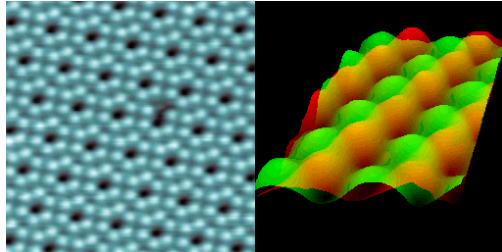
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# Significance of Surface Science

- Characterization of surface structures is essential for the development of new materials
- Surface characteristics are typically different from bulk characteristics
- A few applications:

**Semiconductors:** As electronic components get smaller, it becomes more important to understand nanoscale characteristics

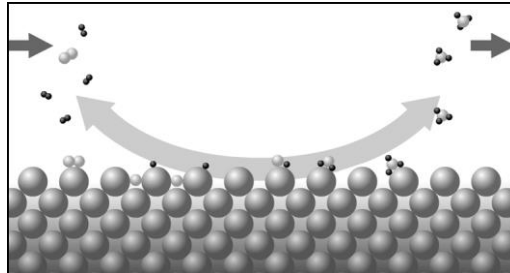


Scanning tunneling microscope (STM) image of Si(111)5x5 reconstructed surface

<http://www.andrew.cmu.edu/user/feenstra/stm/>

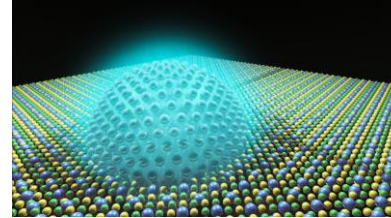
STM image of the GaAs(110) surface.

**Catalysis:** Determining how and why catalytic reactions occur and designing surfaces for specific outcomes



<http://www.spaceflight.esa.int/impress/text/education/Catalysis/Commercial.html>

**Quantum dots:** Applications in solar energy, transistors, LEDs, medical imaging



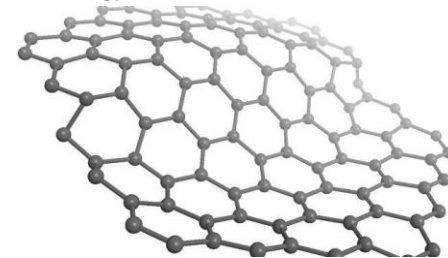
<http://jqi.umd.edu/news/quantum-bit/2014/01/20/quantum-dots-nanocrystals-packed-potential>

**Solar Panels:** Surface properties are paramount to optimizing efficiency



<https://www.sciencedaily.com/releases/2016/09/160928151119.htm>

**Graphene:** Strong, light, flexible, transparent, and conductive; possible applications in electronics, energy, and medicine



<https://phys.org/news/2016-10-scientists-graphene-high-resistance-ozonation.html>

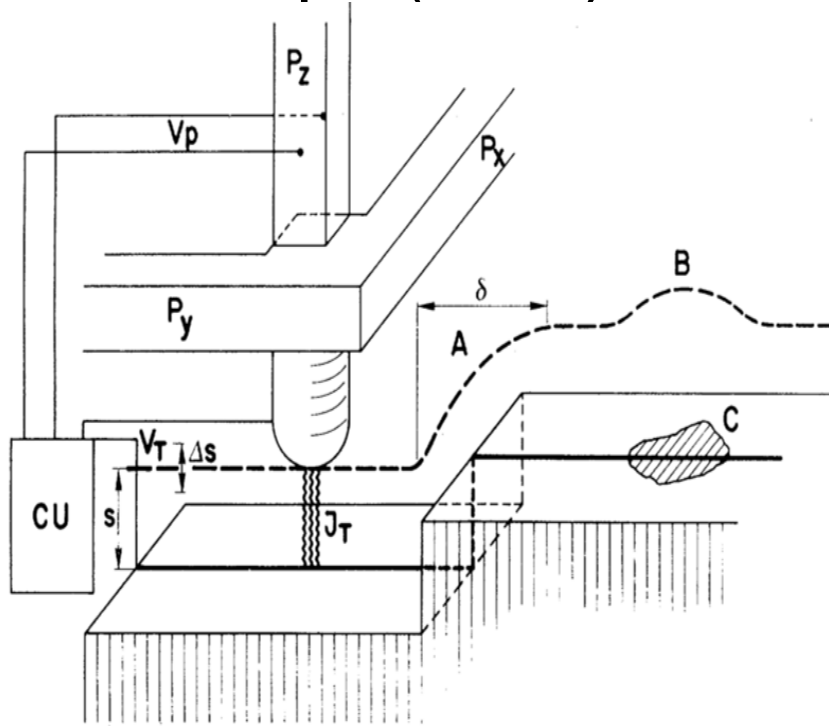
# Surface Characterization Techniques, 1920s-1970s

Technique	Year	Features
Auger Electron Spectroscopy	1922	Composition
Low-Energy Electron Diffraction (LEED)	1927	Surface lattice structure and its level of regularity/perfection
Transmission Electron Microscopy	1931	Requires an ultrathin section of the material
Field Emission Microscopy	1936	Requires a needle-shaped sample
X-Ray Photoemission Spectroscopy	1954	Composition
Scanning Probe Microscopy (Topografiner)	1972	Surface features with vertical resolution of $\sim 30\text{\AA}$ and horizontal resolution of $\sim 4000\text{\AA}$

Invented in 1982, [Scanning Tunneling Microscopy](#) offered scanned images of atoms on the surface of a sample at unprecedented levels of resolution ( $\sim 2\text{\AA}$  horizontal and  $\sim 0.1\text{\AA}$  vertical) with an instrument much less susceptible to vibrational noise than its predecessor, the Topografiner.

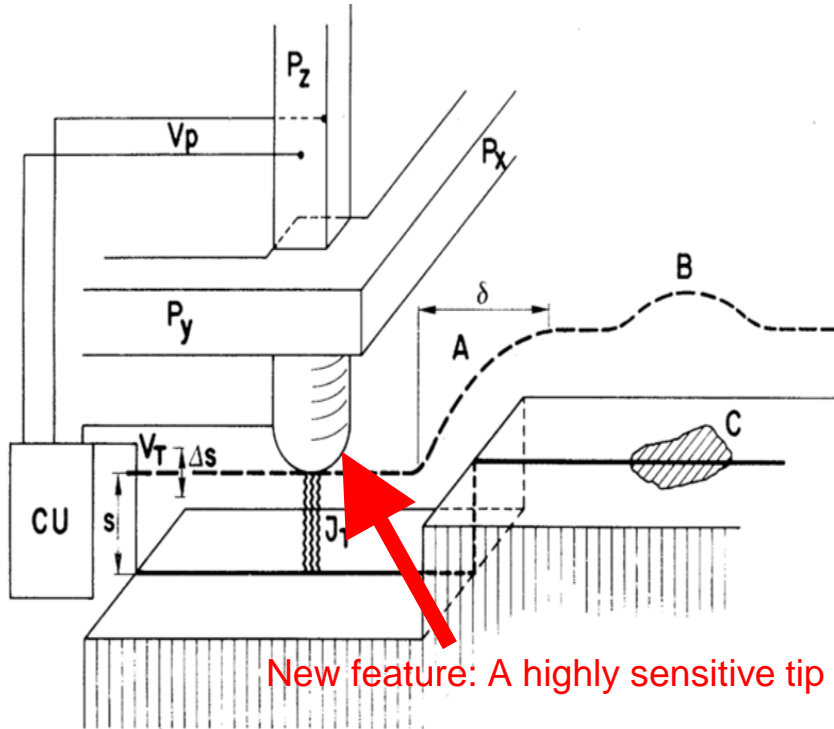
Binnig and Rohrer won the Nobel Prize for STM in 1986.

# Principle of Operation of a Scanning Tunneling Microscope (STM)



- Metal tip scanning the surface at a constant tunnel current  $J_T \propto \exp(-A\phi^{1/2}s)$   
 $A = (4\pi/h)(2m)^{1/2} = 1.025 \text{ \AA}^{-1} \text{ eV}^{-1/2}$   
 $\phi$ : average barrier height (work function)  
 $s$ : width of barrier (z-distance)
- Voltages applied to piezo elements  $P_x, P_y$  and  $P_z$  map the surface topography directly

# Principle of Operation of a Scanning Tunneling Microscope



- Theoretically, lateral resolution  $< 100\text{\AA}$  require tip radius  $\sim 100\text{\AA}$
- Solid metal rods of 1mm diameter and ground  $90^\circ$  tips. Overall tip radii  $\sim 1000\text{\AA}$ - $1\mu\text{m}$
- Minitips and 'mini-spot-welding' increase lateral resolution to up to  $10\text{\AA}$
- Separation of true structures and work function mimicked structures, although can be done in principle, was not studied in detail

# Resolution Capability of STM: $\text{CaIrSn}_4$ (110) Surfaces

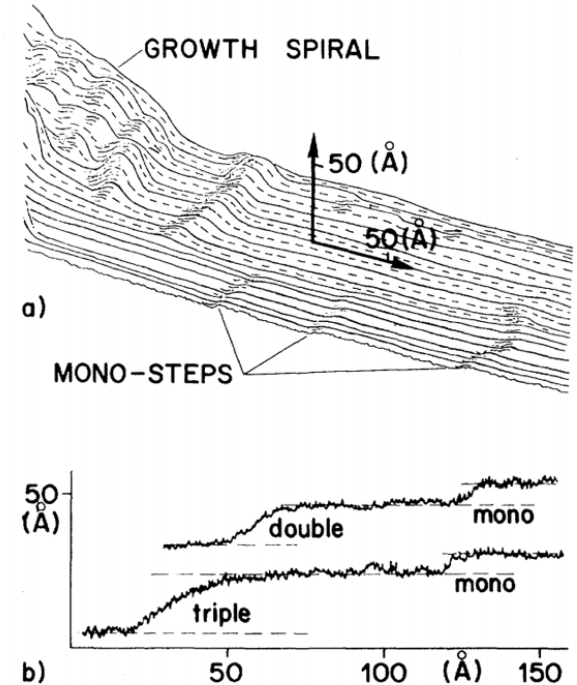
The Ir layers are very inert after solvent etching: good for the STM at moderate vacuum

Data of its crystal structure were available in literature

Weak and homogeneous contamination

Height of steps: a few atoms

Average spacing  $6.7\text{\AA}$ : consistent with crystallography  
(Mater. Res. Bull. 15, 799)



# Resolution Capability of STM: Au (110) Surfaces

Reconstruction of Au (110) surfaces was of interest

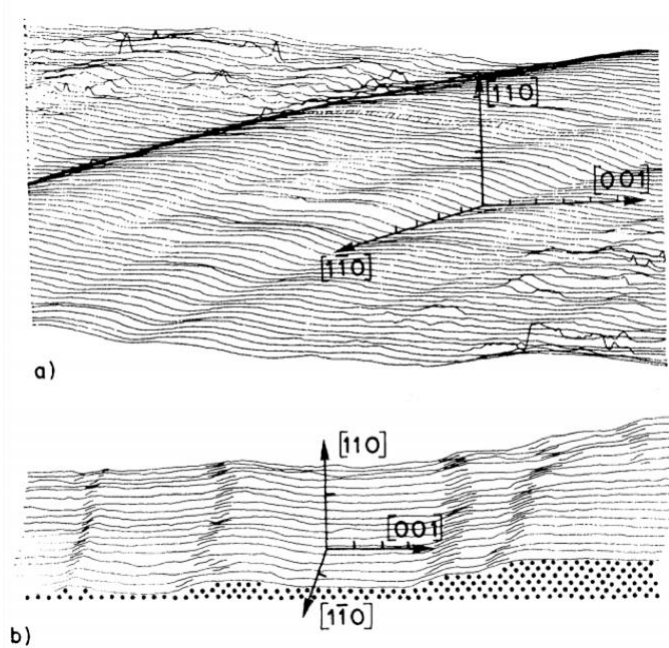
Scanned at room temperature and 300°C, both after annealing at 600°C

- a) Room temperature: smooth corrugation
- b) 300°C: more abundant steps

Reconstruction of Au (110) was controversial

- 2×1 reconstruction: favored by LEED (Surf. Sci. 77, 265, 283), but NOT observed by STM
- Distorted hexagonal topmost layer model? (Verh. Dtsch. Phys. Ges. 1, 278)

Future study: combination of LEED and STM



# Early Implications of Scanning Tunneling Microscopy

- The STM technique developed in this paper has orders of magnitude better resolution than previous scanning techniques (e.g., scanning electron microscopy).
- The method is non-destructive.
- The method has potential use in any field that uses microscopy.
- STM technique can, in principle, separate true structural features from “work function-mimicked” features. Work function profiles, however, weren’t studied in detail, and rather were used to get an overall picture of the surface condition.



# Critiques: Scientific Validity

- Developed better-suited tip to suppress vibrations
- Recognized possibility of work-function-mimicked structures and took measures to attenuate them
- Used smooth-surfaced materials for tests where results confirmed previous measurements (Ir(110) plane spacing and SEM-located growth spirals) and also demonstrated the ability to rule out theories of surface reconstruction in Au
- Did not really explain the details of modulating signals to rule out the variation in work function

# Critiques: Importance

- This was the first paper with surface topography using STM.
- The authors verified that tunnel current depends strongly on barrier width.
  - It was possible to see monoatomic step resolution.
  - Precise measurement of corrugation resulted in better understanding of surface reconstructions.
- Broad impacts: the technique enables
  - Detailed understanding of the microscopy of adsorbed molecules,
  - Study of crystal growth,
  - Confirmation of the fundamental aspects of tunneling, and
  - Space-resolved tunneling spectroscopy.

# 3189 Citations



# Critiques: Accessibility

- Although it was probably necessary, the paper heavily referenced other literature, which at times made it a difficult read.
- The paper did not explicitly include some technical details, but it was in general easy even for non-experts to read to get a big picture of STM.
- Some terms were used without a clear definition or reference: “work-function-mimicked”, “work function profile”, etc.
- The reasons why Au was used were not explained in detail by the paper.

# Summary

- The paper reports the first experimental results on surface topography in high resolution using STM, a technique that revolutionized the field of surface science, particularly with respect to the study of surface reconstruction.
- The introduction of a new type of scanning tip
  - improved the resolution by several orders of magnitude,
  - reduced vibrational impacts, and
  - presented a non-destructive method of surface determination.
- The STM technique can, in principle, be used to separate true surface structures from those introduced by changes in work function.
- Topographies of  $\text{CaIrSn}_4$  (110) surfaces and Au (110) surfaces were shown to demonstrate the capabilities of STM.