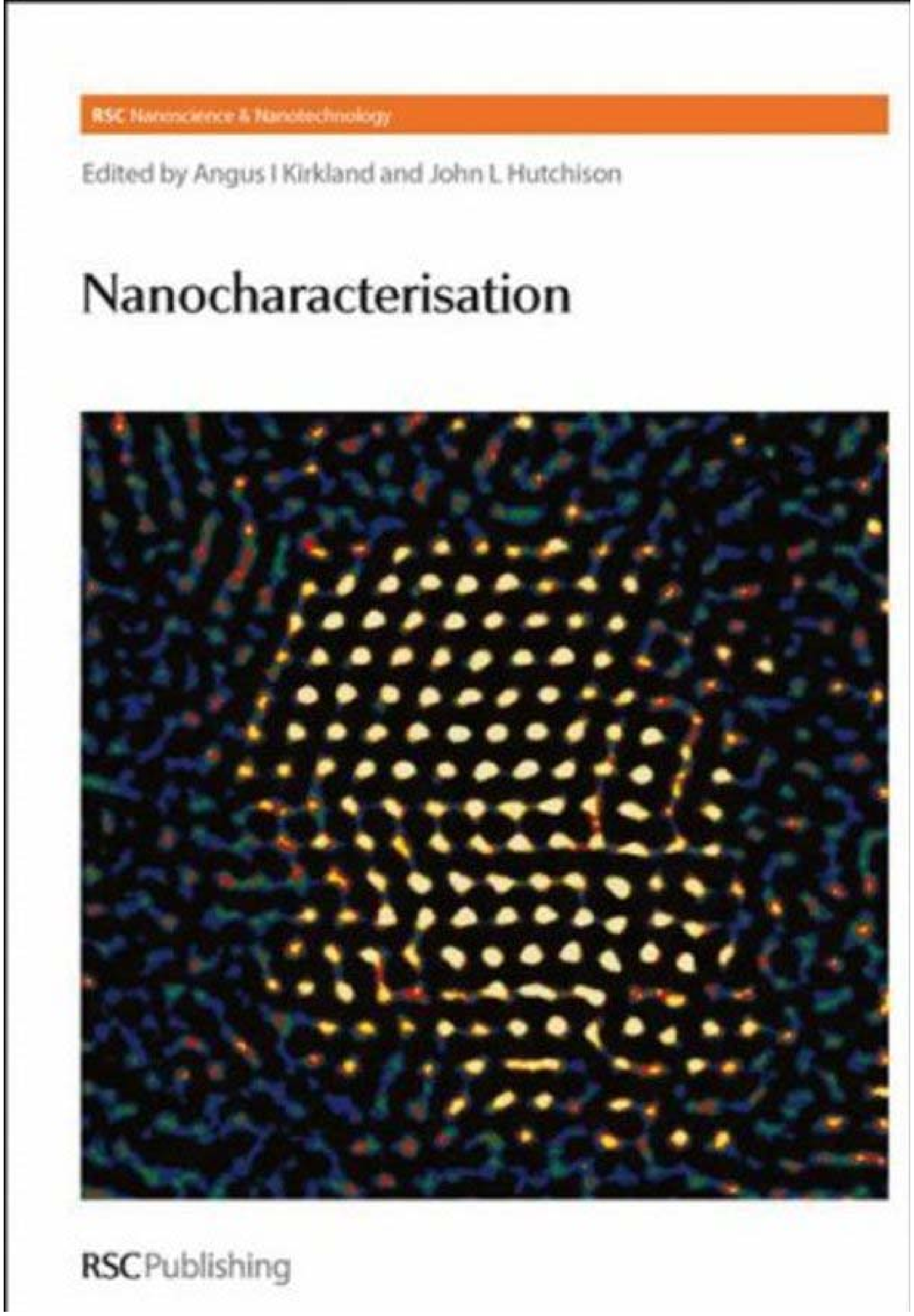
Scanning Probe Microscopy

Scanning Tunneling Microscopy, STM

Atomic Force Microscopy, AFM

Nanocharacterization tools



Examples of application of STM for imaging of of atomic structures

Basic Principle of the Scanning Tunneling Microscopy

Scanning with a sharp metal tip over a surface whilst maintaining a gap of a few Å (10^{-10} m) between the sample surface and the tip. A voltage is applied between the tip and the sample, which gives rise to a tunneling current, so called because it relies on the quantum mechanical phenomenon of electron tunneling. This tunneling current is of the order of a nano A (10^{-9} Ampere) and can reveal the positions of individual atomic locations on the sample surface.

To image the top atomic layer of a sample it needs to be free of contamination and this can only be achieved in a vacuum environment (UHV).

History of the STM

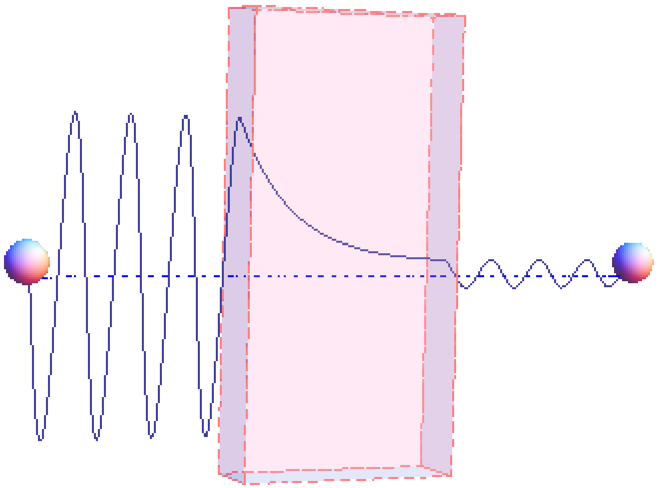
The Scanning Tunneling Microscope (STM) was invented in 1981 by a team including Gerd Binnig and Heinrich Rohrer at the IBM Zurich Research Laboratories.
The first publications showing atomic resolution appeared in 1982, and the pair of researchers were awarded the Nobel Prize for their invention in 1986.

STM became a popular technique so rapidly after its invention:

1. the only technique to provide atomic resolution images of large flat surfaces,
2. due to the development of an adequate vibration damping systems made the technique easy to implement.

Based on the achievements in STM the invention of the atomic force microscope by Binnig was possible.
STM probes the density of states of a material using the tunneling current.

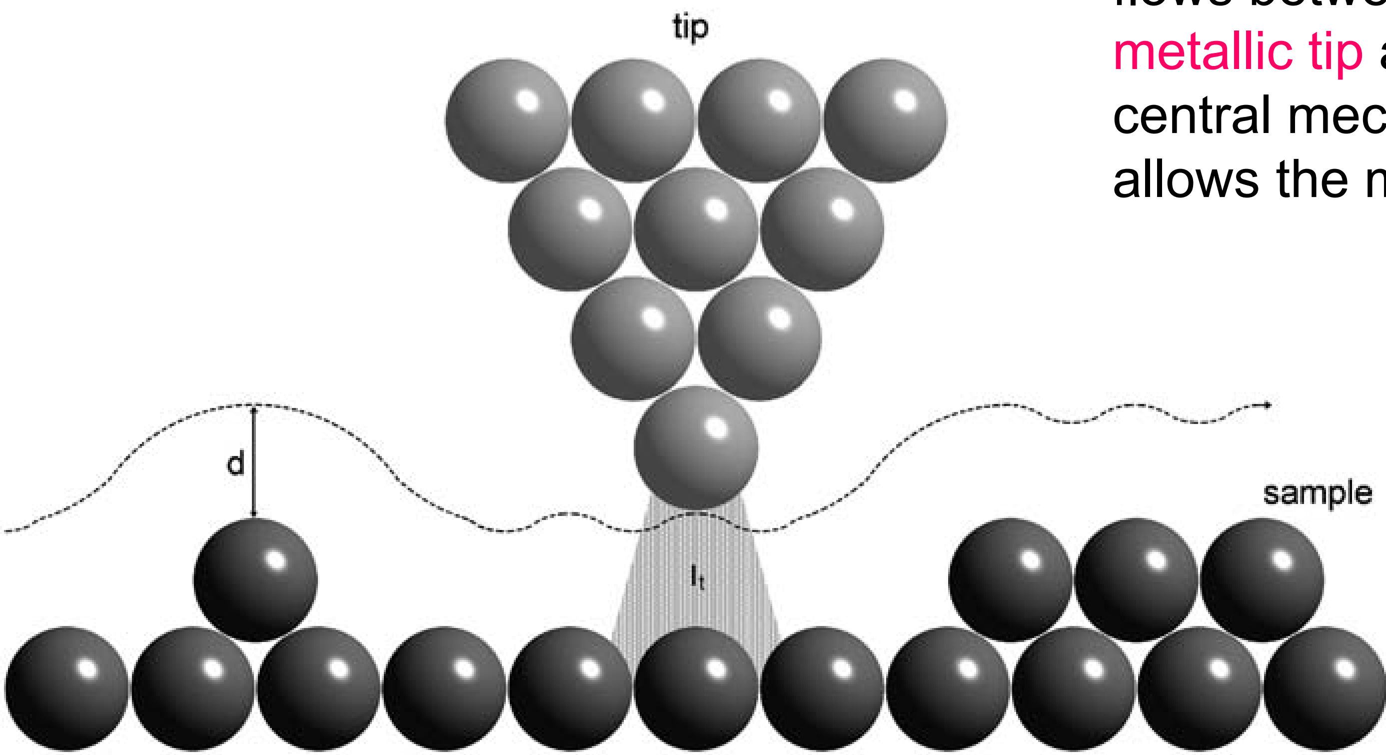
Quantum tunneling interaction



Classically, not allowed, electrons don't have sufficient kinetic energy to overcome the vacuum barrier.
The movement of electrons across the barrier is therefore known as tunneling, because the electrons "tunnel" through the vacuum barrier.

When two conductors are separated by a macroscopic vacuum gap, then electrons will not travel from one to the other unless a voltage above the field-emission threshold is applied.
If, however, the conductors are brought into the proximity of less than a few Å , then their quantum-mechanical wavefunctions overlap to an extent that allows electrons to be shared between them.

Interactions between tip and the surface atoms



The tunneling current that flows between the sharp metallic tip and the sample is the central mechanism that allows the microscope to work

The atom at the apex of the tip is the one from which the majority of the electrons tunnel. In turn, electrons will only tunnel into the closest sample atoms, and this is the reason why STM images show only the structure of the top atomic layer of a sample.

Tunneling current

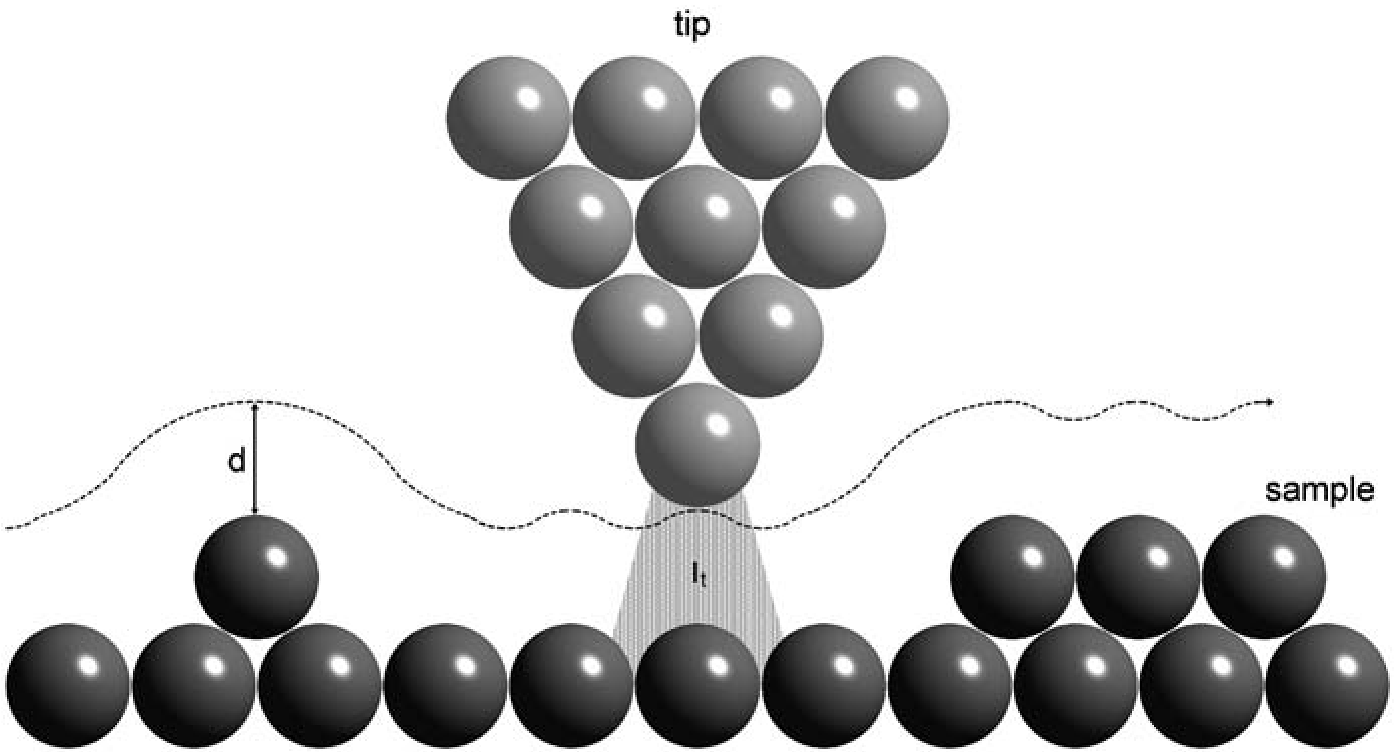
$$I_t \sim V\,\Phi^2\,\rho_s\,\rho^t\,e^{-kd}$$

inverse exponential relationship between distance and tunneling current

I_t is the tunneling current, V is the voltage applied between the sample and the tip, Φ is the average barrier height, ρ_s is the density of sample states, ρ^t is the density of tip states, k is a constant related to the decay length for the wavefunctions in a vacuum and d is the tip–sample separation

An increase in tip–sample separation from 5 Å to 6 Å will cause the tunneling current to drop by almost an order of magnitude. It is this extreme sensitivity of the tunneling current to tip–sample separation that gives the STM its extremely high vertical resolution.

Topography of a line of atoms



The tip-to-sample separation is d, and the tunneling current is I_t. In the constant current mode, shown here, the tip is scanned over the atomic line at constant I_t resulting in an atomic topography indicated by the dashed line.

Formation of STM image

Scanning the surface with the tip creates a surface topography map

Scanning procedure

Once a tip and sample form a tunnel junction, the tip can can be scanned in 3D to create an image. Scanning the tip is achieved by attaching it to piezoelectric crystals that change the length when a voltage is applied to them. The simplest form of scanning is using 3 separate piezoelectric crystals responsible for movement in x-,y- and z-directions. The advantage of piezoelectric scanners is that their expansion and contraction, and hence the movement of the tip, can be controlled very precisely.

Scanning modes

1. **Constant–height mode**, scanning in plane over the surface and record the tunneling current as a function of x and y, brightest regions where the current is greatest (for rapid scanning over very flat surfaces)

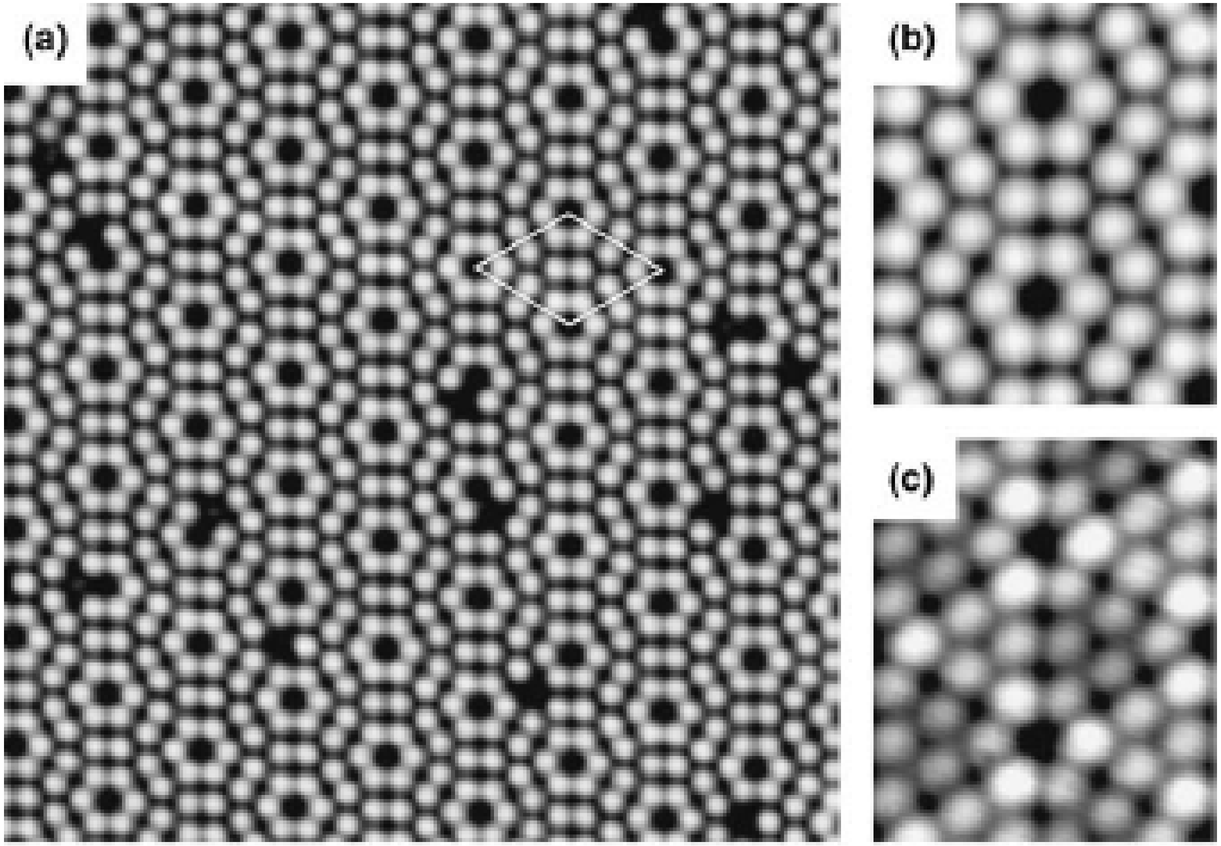
2. **Constant–current mode**, the tunneling current is determined by the user, the tip height is adjusted by computer to keep constant tunneling current. During the scanning the height is recorded. The higher the tip the brighter that region in the image. Can operate over much greater z- distances.

Resolution of STM

1. Nature of the electronic structure of the atom at the tip apex.
2. Vibrations
3. Noise in the control electronics,
4. Noise in the tunneling current
5. Electronic structure of the sample surface.

Generally, the x and y resolution is around 1Ǻ, and the vertical z better than 0.1Ǻ

Atomic Resolution Imaging of Surface

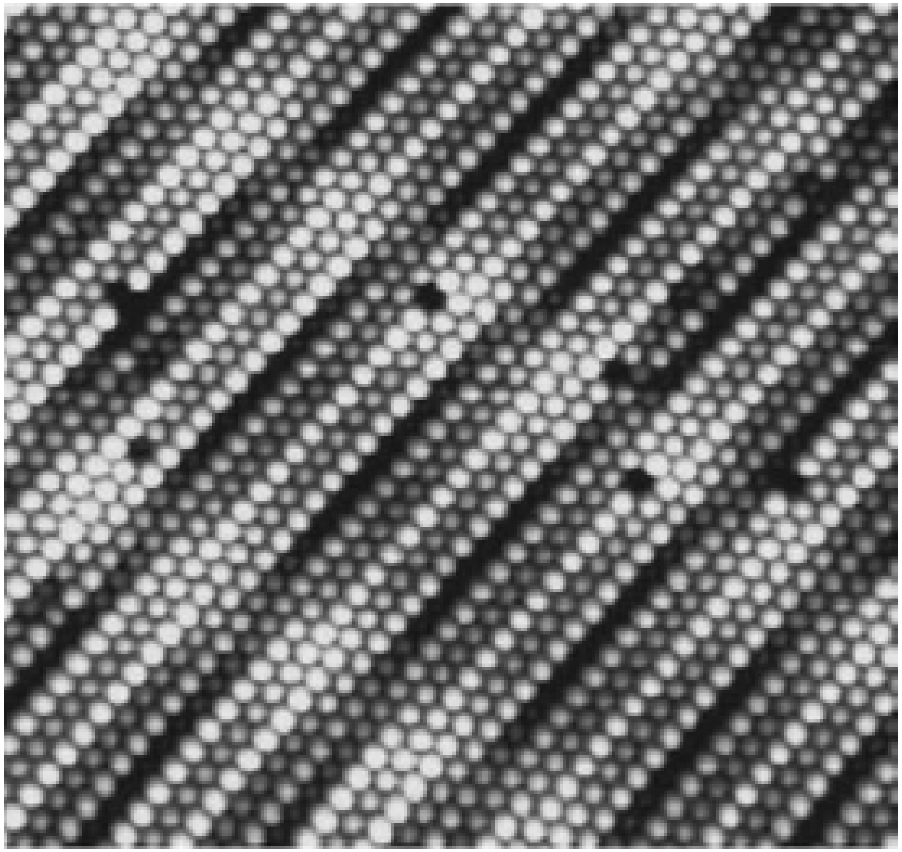


+2 V, equal brightness

-2 V, unequal brightness, difference in DOS

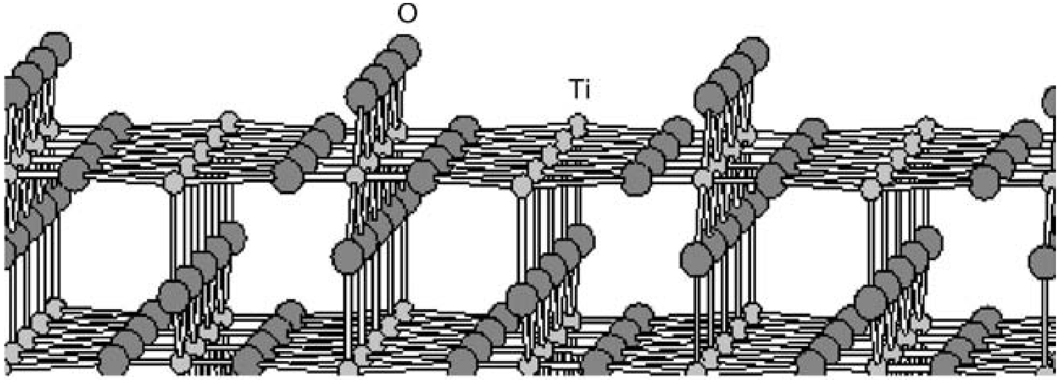
A (111) Si crystal surface, surface periodicity (unit cell), bright spots are related to the atoms in closest proximity to the tip atom (outer atomic layer), deeper layers don't contribute, several single-atom defects (dark spots),

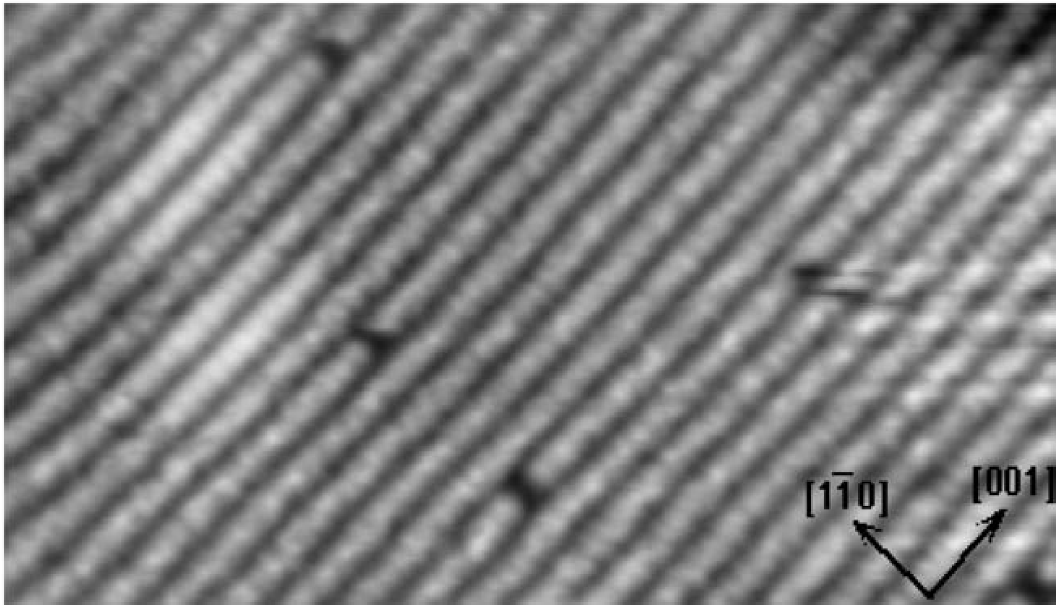
Atomic image of a metal surface



A Pt (001) surface, the diagonal corrugation, individual atomic vacancies

STM image of TiO_2





Bright rows in the STM image are due to the under-coordinated Ti ions on the surface showing higher density of states and more electrons can tunnel

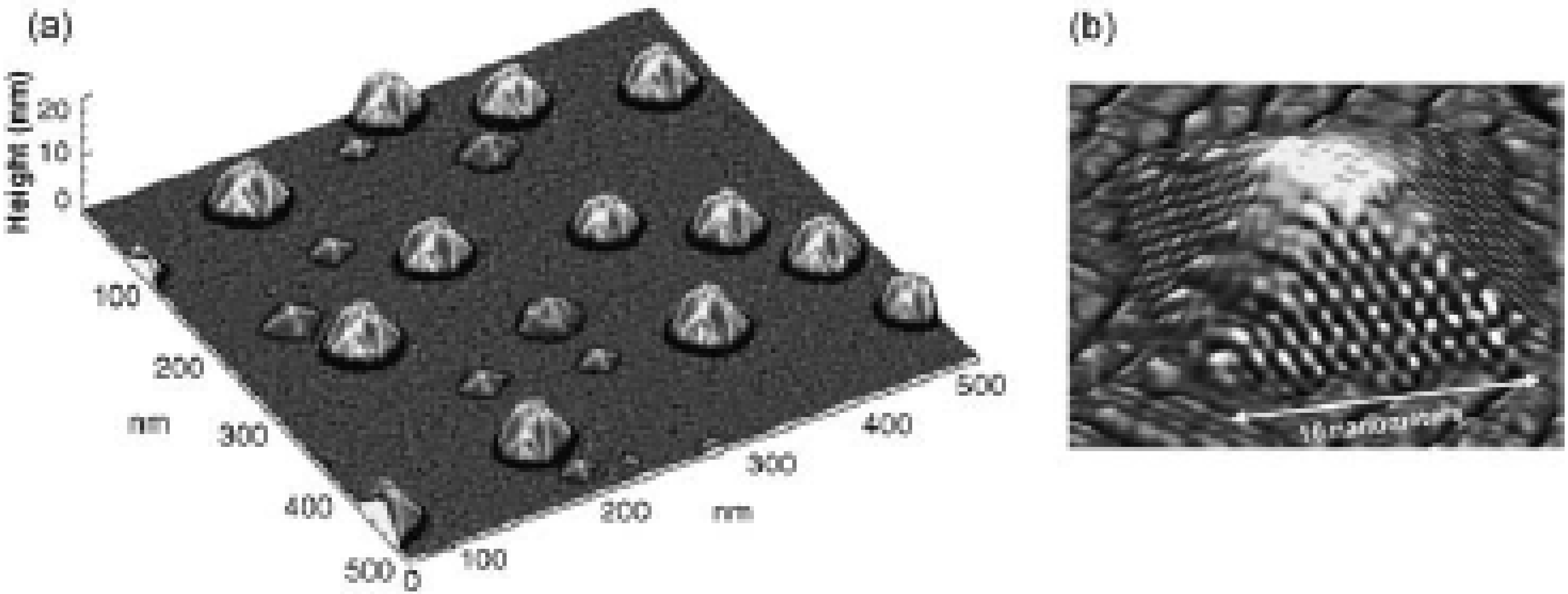
Imaging of surface nanostructures

Any material of nanometer dimensions.
Top-down: electron beam or UV lithography followed by chemical etching and evaporation onto a patterned substrate to produce small structures
Bottom-up: the building blocks are atoms, atom clusters and molecules.

STM has the ability to move around individual atoms to build nanostructures atom by atom.

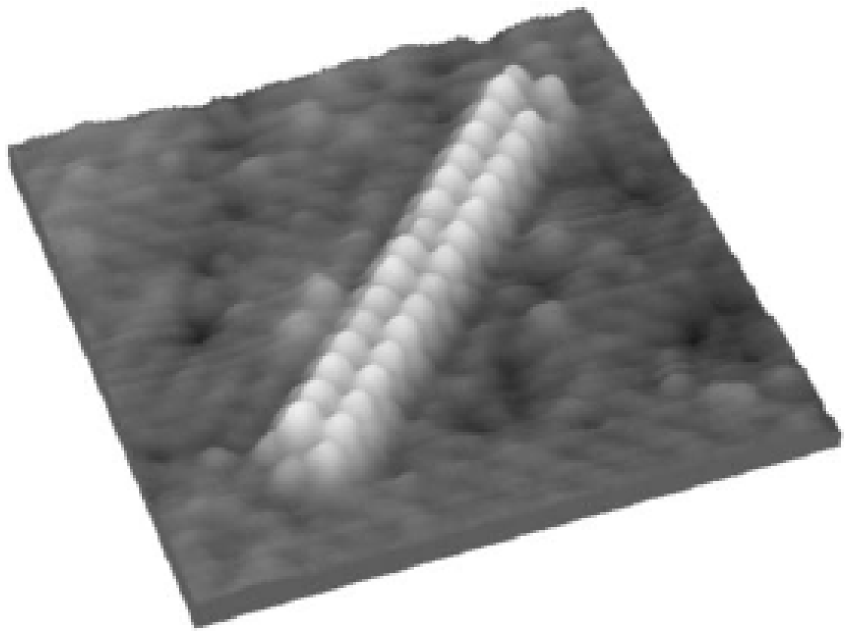
Technology uses molecular and atomic interaction between the building blocks to create nanostructures, e.g. evaporated atoms form regular structures bonded to the substrate.

Imaging of surface topography of nanostructures



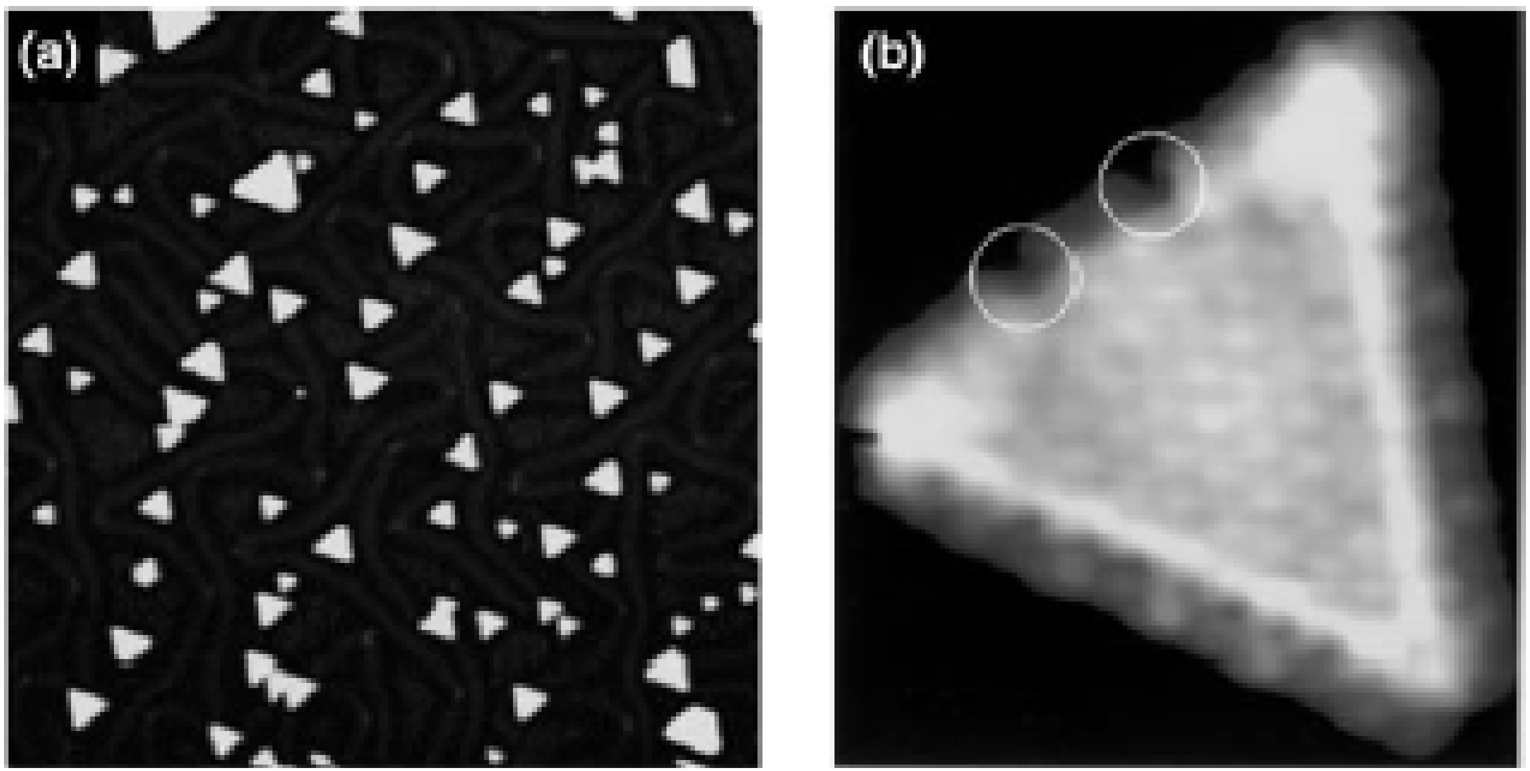
Formation of Ge islands on Si (001) by interatomic potential, a few monolayers cover the surface, the strain is removed by formation of islands, the shape changes as they grow in size

Formation of nanostructures by interatomic potential



A 3D 12 nm long nanoline of paired atoms on the surface of $SrTiO_3$ demonstrating atomic resolution capability of STM

Study of catalytic activity of MoS_2 clusters

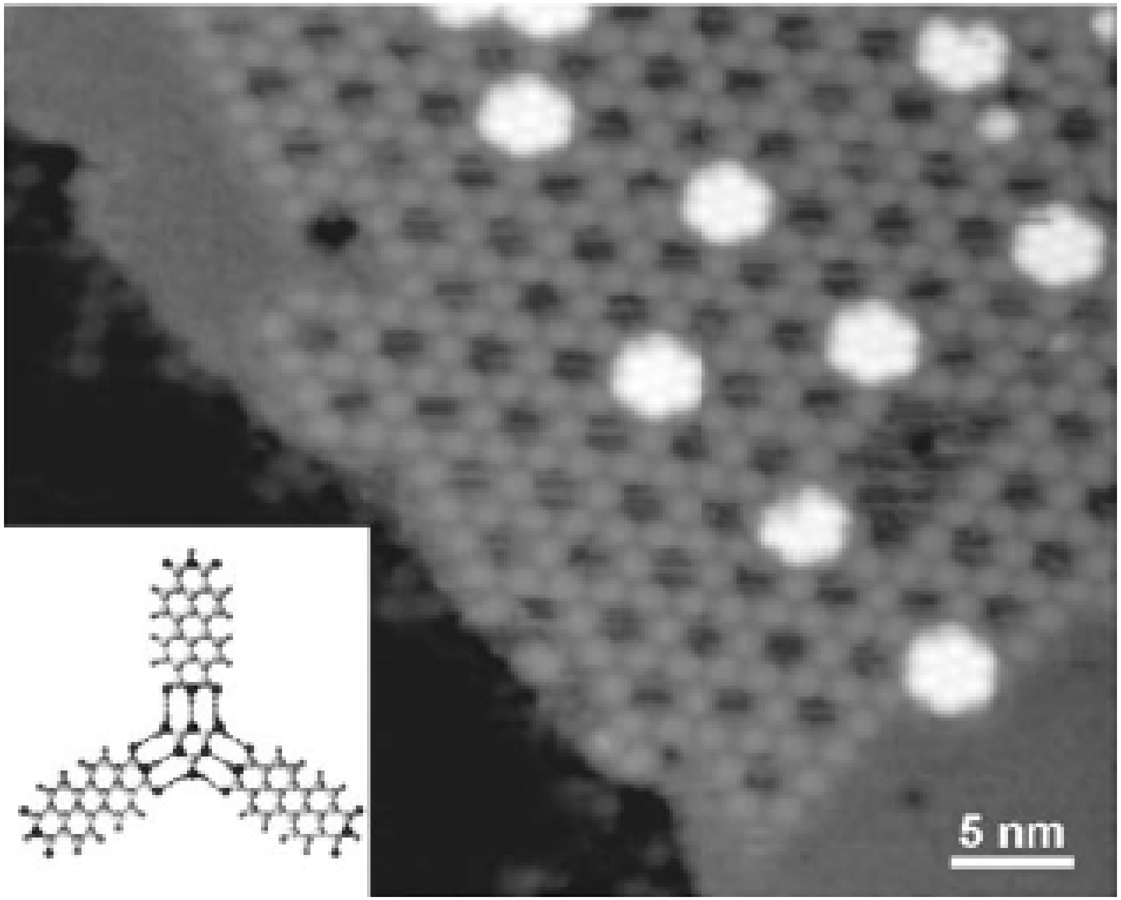


MoS_2 triangular shaped clusters on Au(111), the irregular edges have catalytic activity

Formation of nanostructures via noncovalent interactions

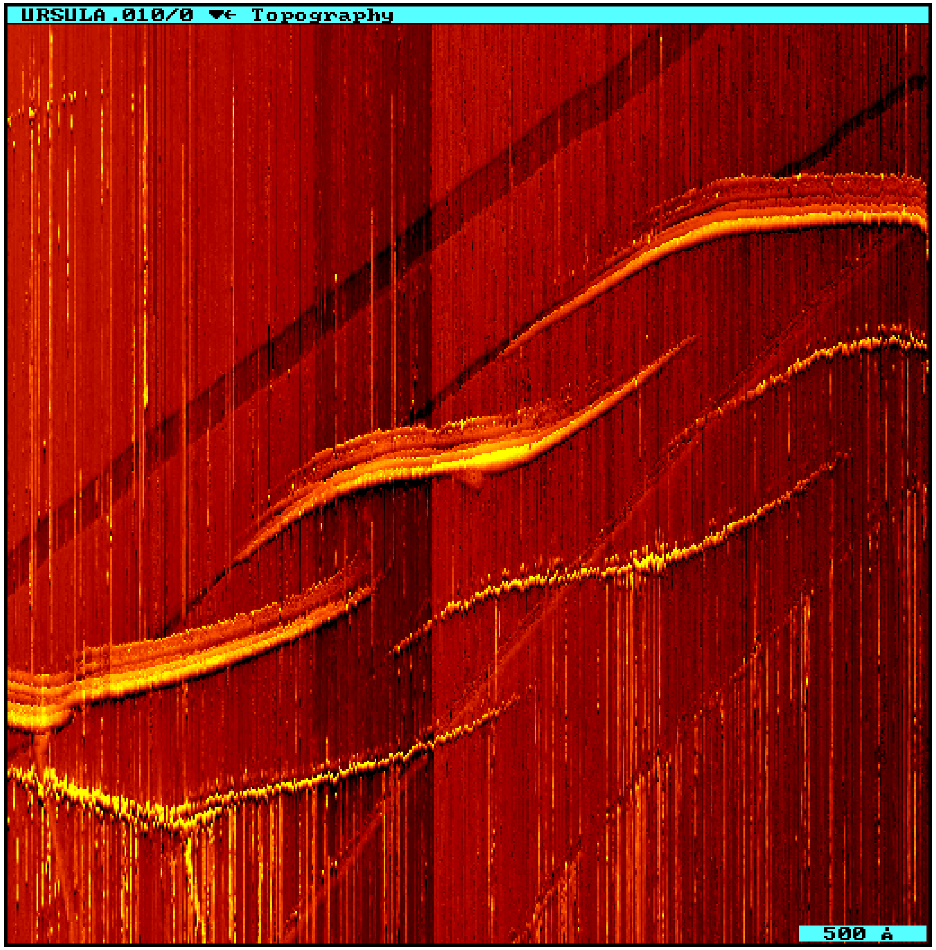
An alternative is to use molecules as the building blocks (via H-bondings). Self assembled pattern of different types of molecules can create supramolecular nanostructured architectures.

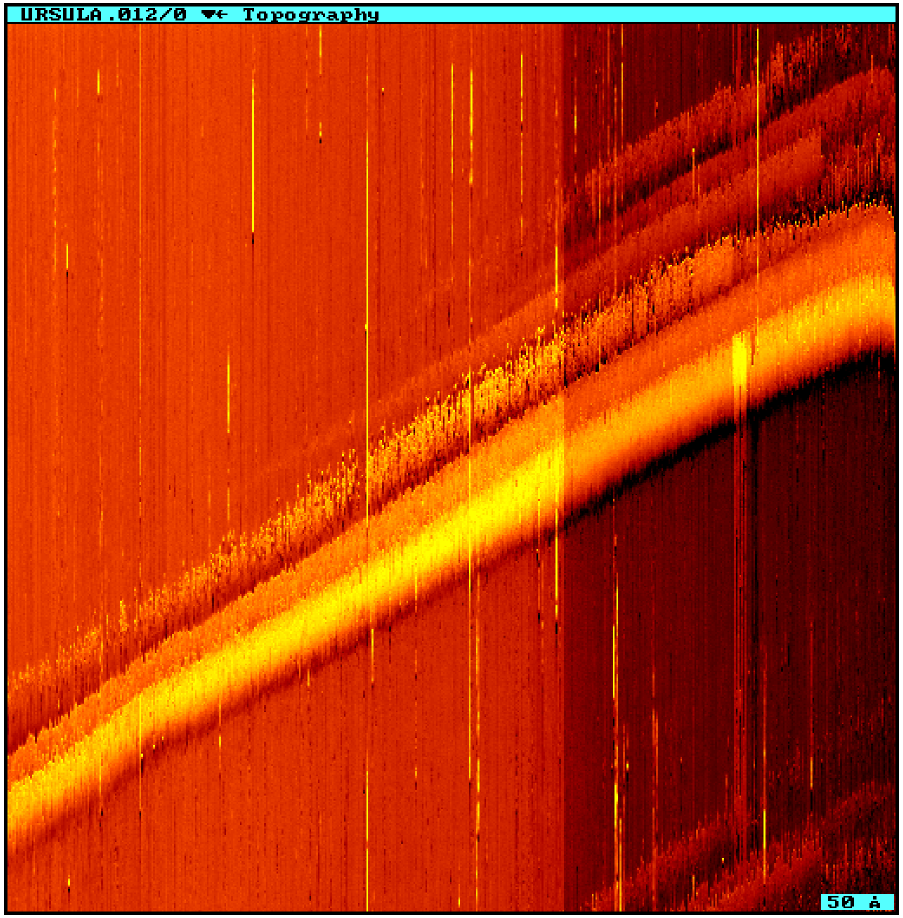
Formation of nanostructures via noncovalent interactions



Co-adsorption of 2 molecules on the substrate leads to a formation of a honeycomb network with large pores, which can be used to capture other molecules such as C60 (bright spots are 7 C60), nanoscale vessels promote local chemical intractions

Topography of CNT





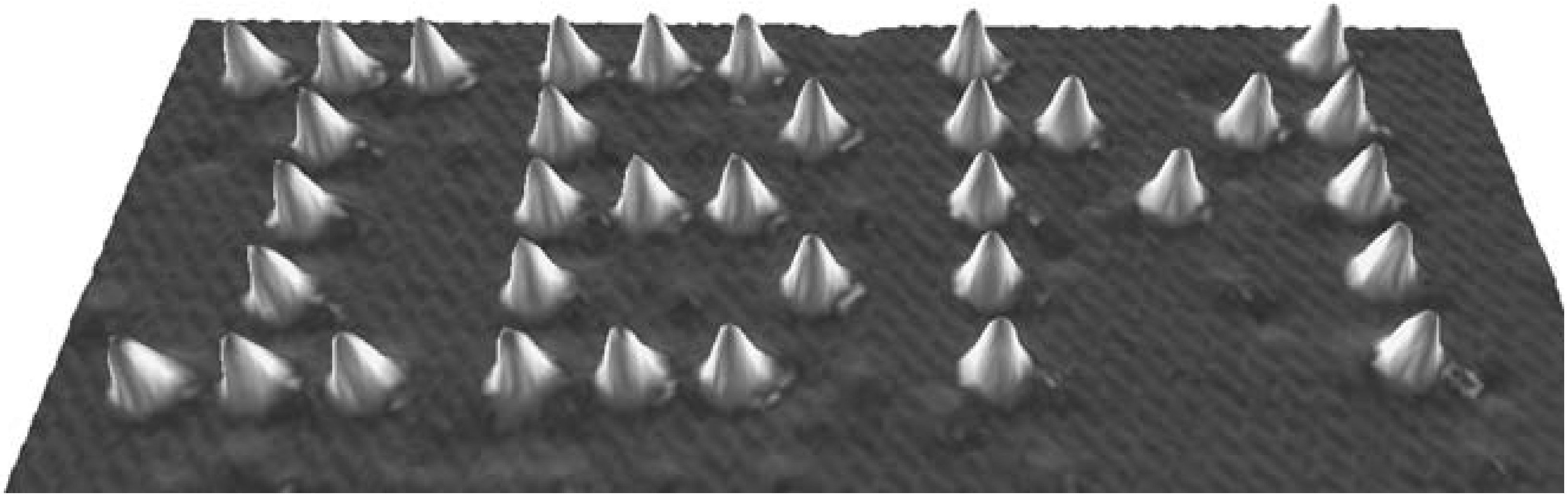
Manipulation of adsorbed atoms and molecules

1. Self-assembling requires sufficient thermal energy for surface diffusion of molecules, RT.

2. At low temperature the molecules are fixed in place.

3. STM tip can be used to drag or push the adsorbed molecules to defined positions.

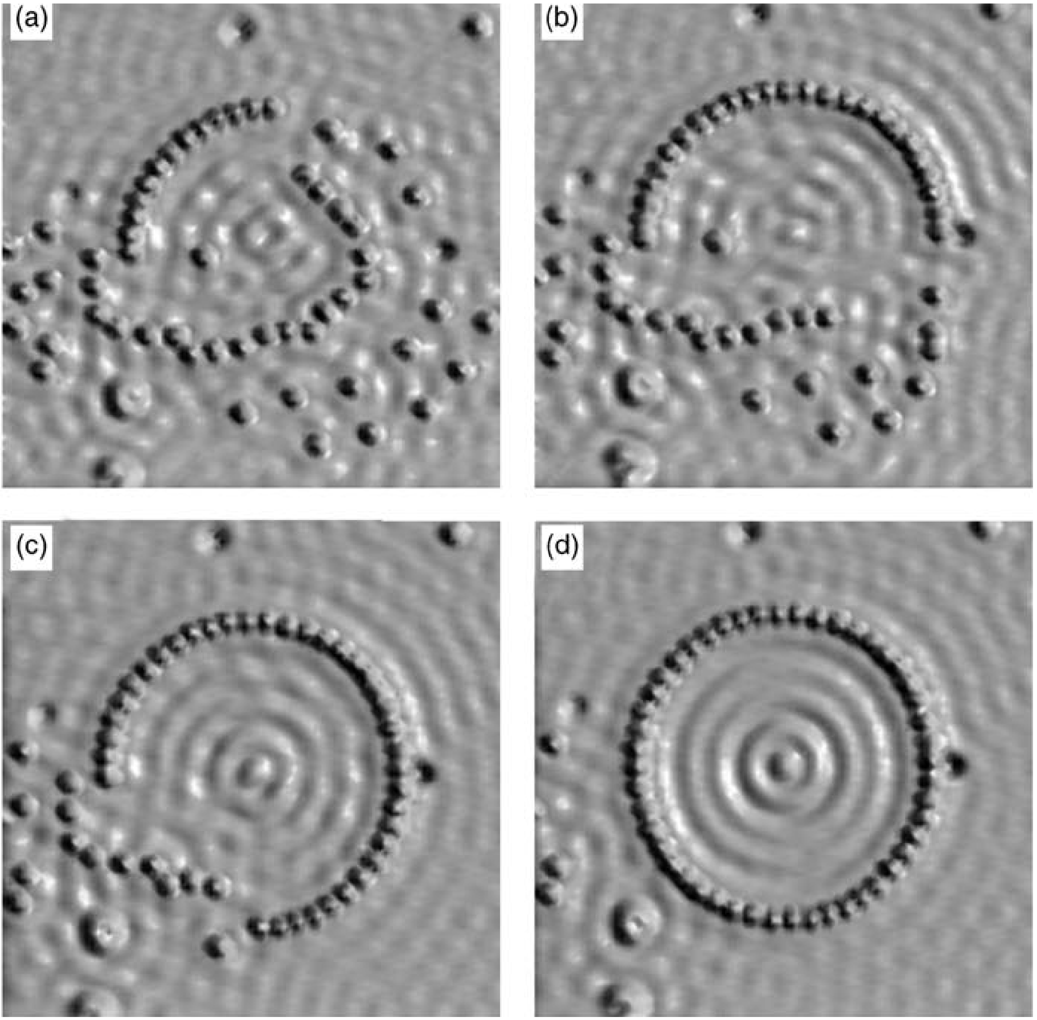
Individual Xe atoms are moved with the STM tip across the surface



Eigler'group exeriments at
the IBM Almaden Research Center

Atomic manipulation showing the IBM logo was carried out at 4 K by a cryogenic STM. The adsorbed Xe atoms appear as bumps on the surface of Ni(110). Increase in current, reduces the distance, increase the Van der Waals interactions between tip and atoms. Versatility of STM, bottom-up tool for material processing, significant breakthrough

Quantum confinement of electrons in a surface state



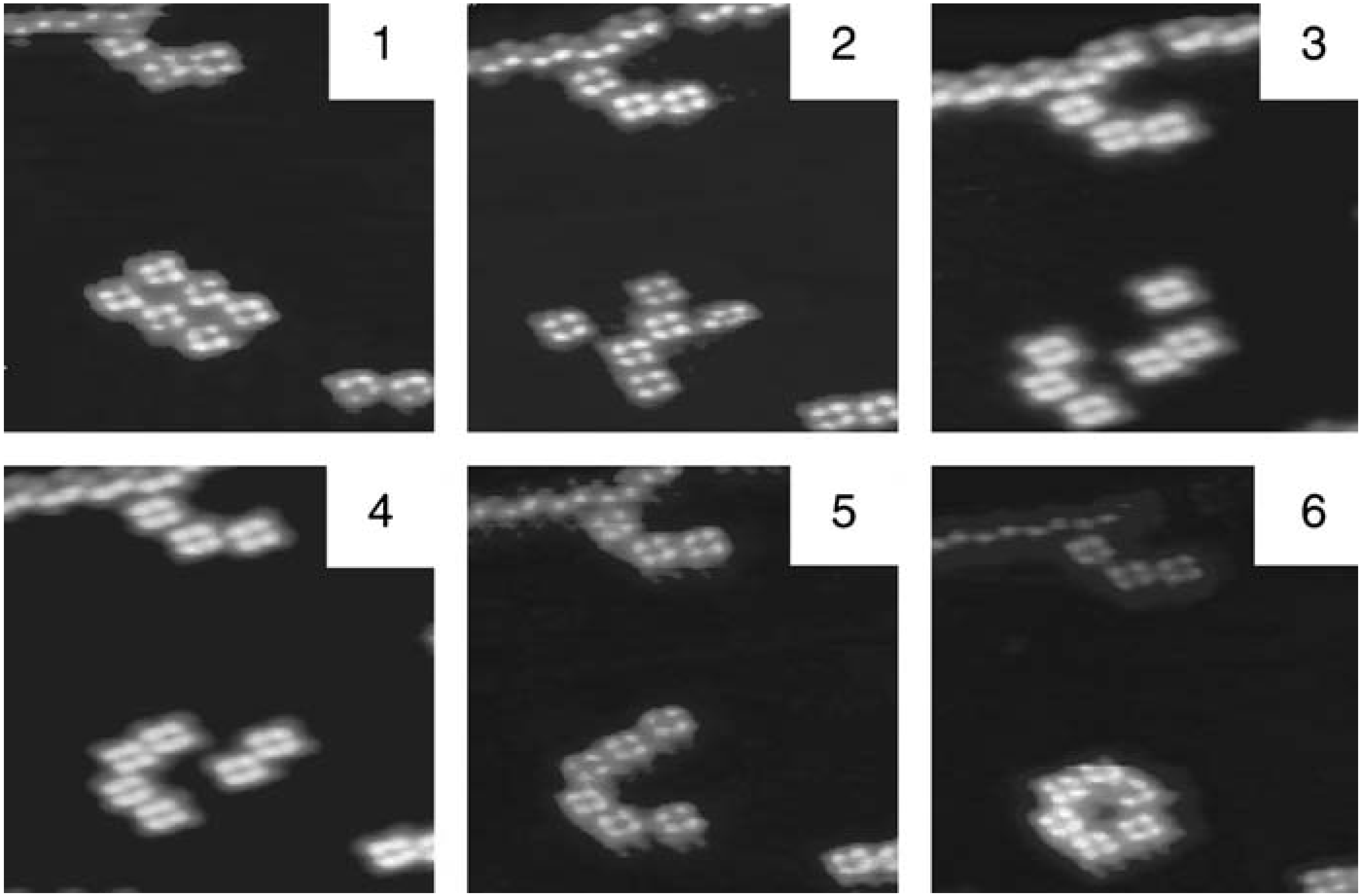
Surface-state electrons scatter from adsorbed atom. In a circle of atoms the electrons are trapped and create a standing wave pattern, which results in a high electron density at the maxima and low at the minima.

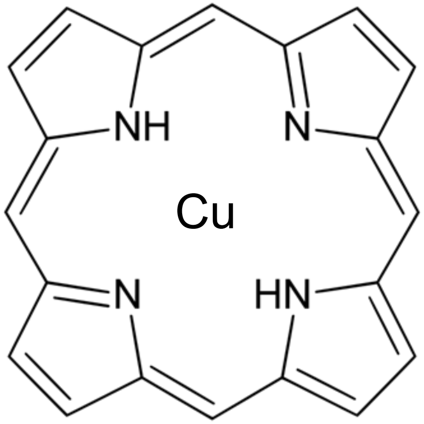
Circle of 48 Fe atoms created by STM on a Cu(111) surface

Eigler'group exeriments at the IBM Almaden Research Center

STM image shows the variation of the electron density within the limited surface, quantum particles confined in a potential well

Manipulation of adsorbed macrocyclic molecules





Cu-porphyrin appeared as 4 bright spots clustered together. The STM tip gets closer to the molecules and push them across the surface and arrange into a hexagonal ring

Manipulation of adsorbed atoms and molecules

1. astonishing breakthroughs, but not realistic manufacturing technology,

2. self-assembly of nanostructures is viewed as potential method for the easily scale up from the lab to the factory.

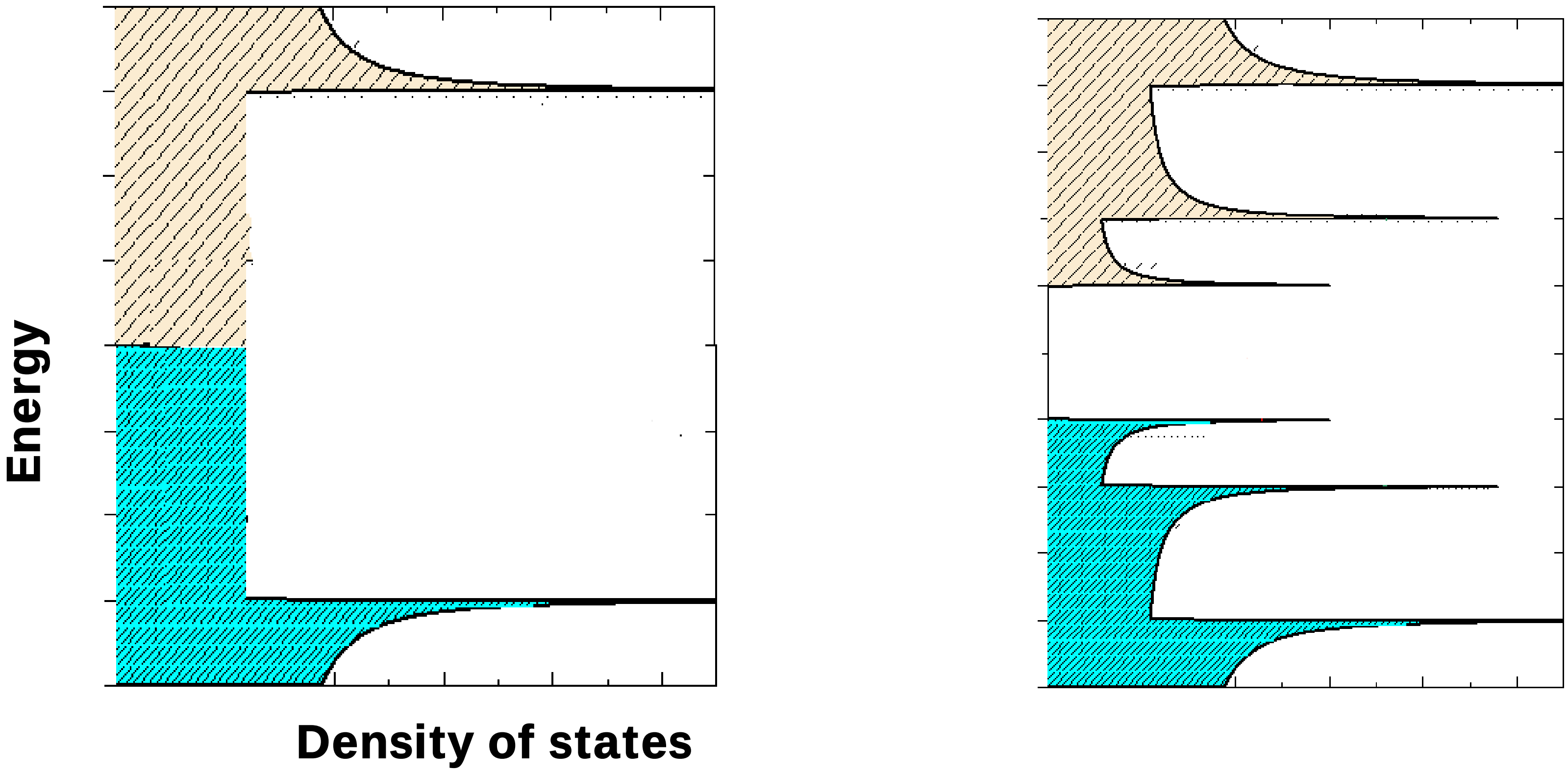
Questions

Tunneling spectroscopy

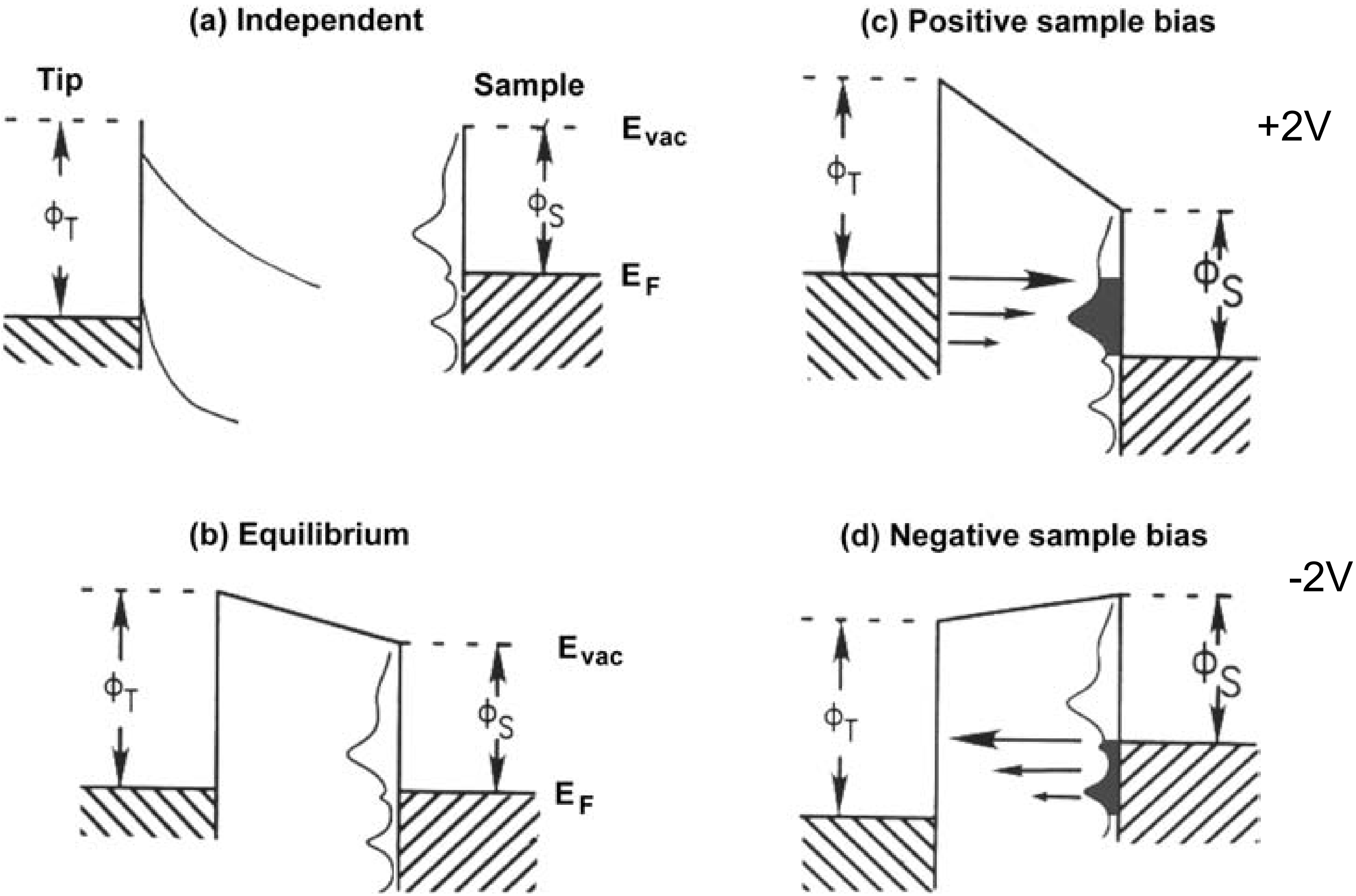
It is possible to use the STM to visualize local electron density of filled and empty sample states.

Density of states DOS

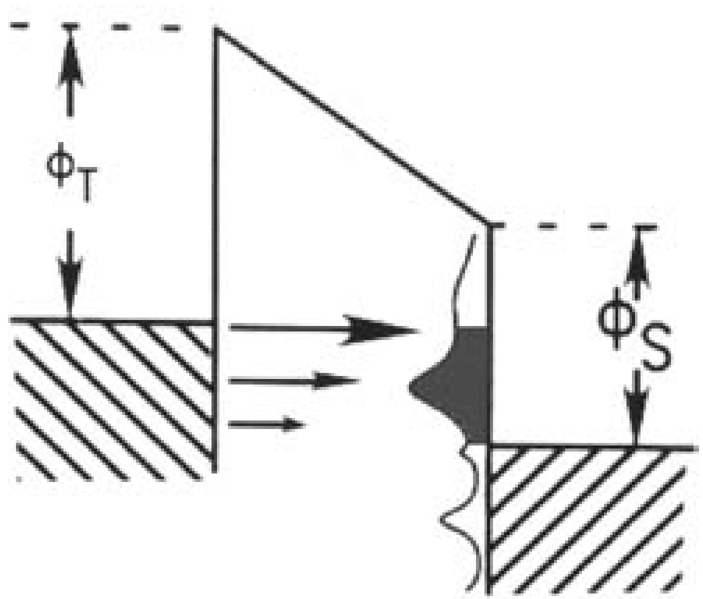
Energetic levels available for the electrons to occupy



Energy levels between tip and sample



Energy levels between tip and sample

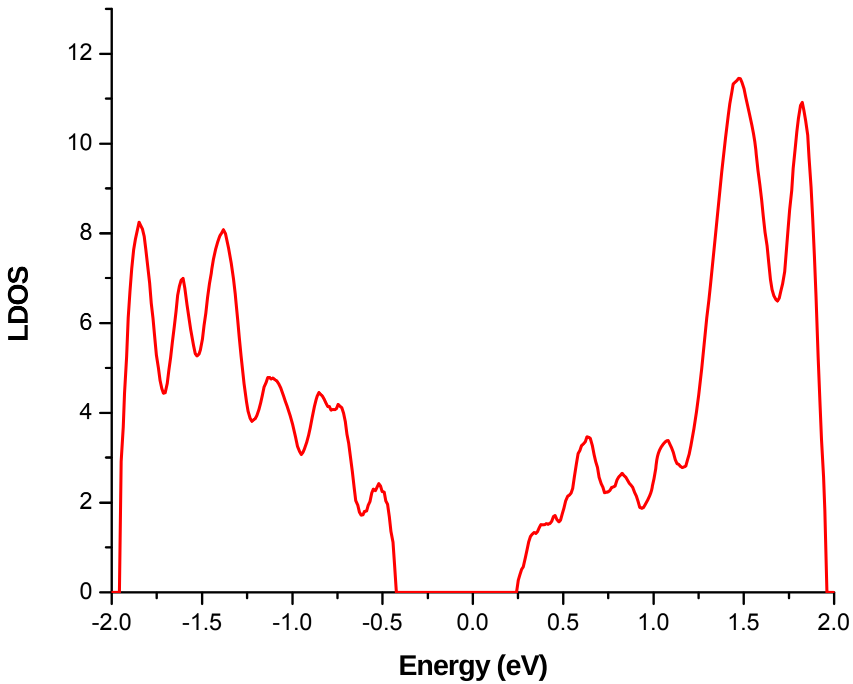


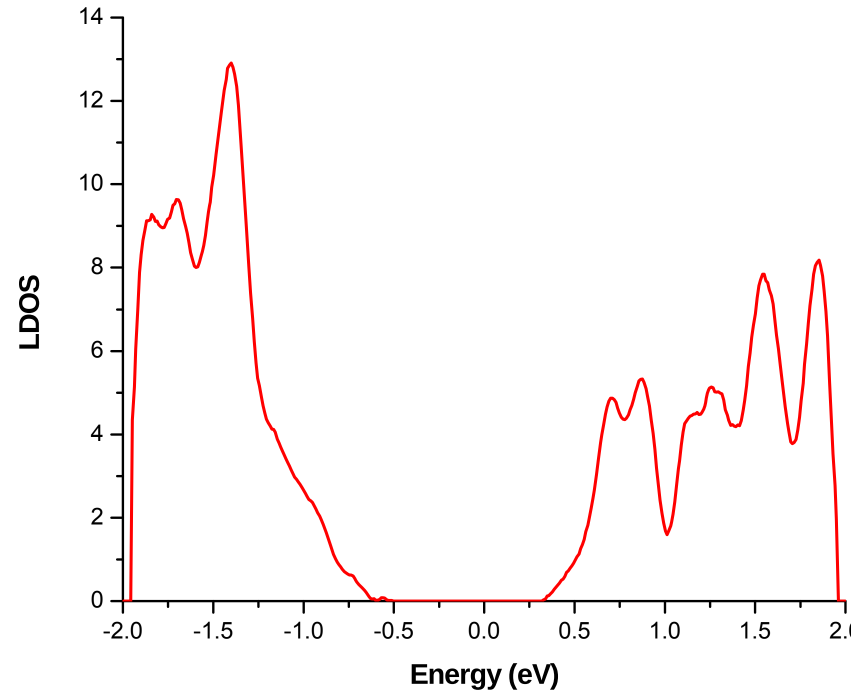
Positive sample bias

+2V

Keeping the tip to sample distance constant and varying the sample bias it is possible to measure the local density of empty sample states

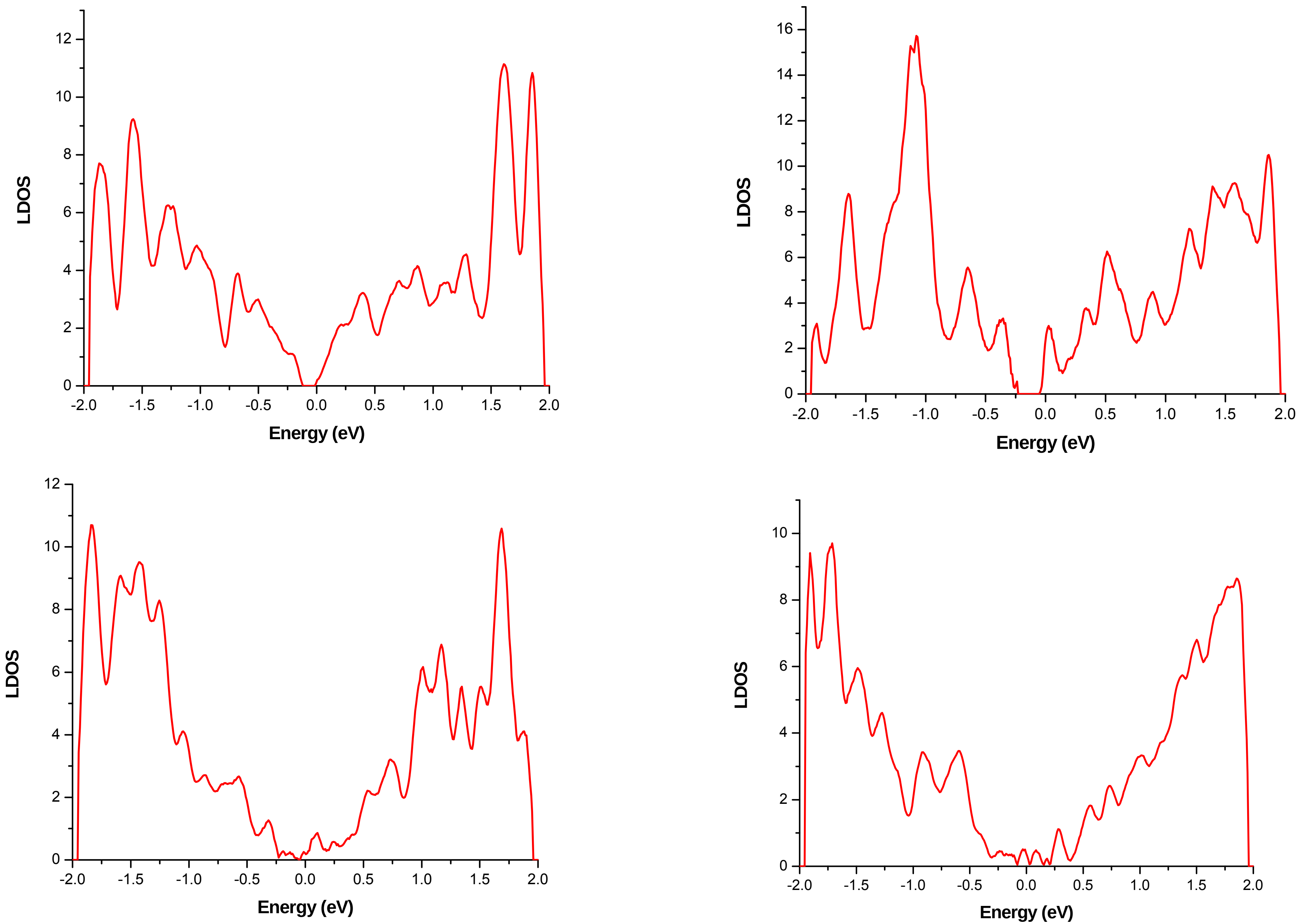
Tunneling spectroscopy of CNT



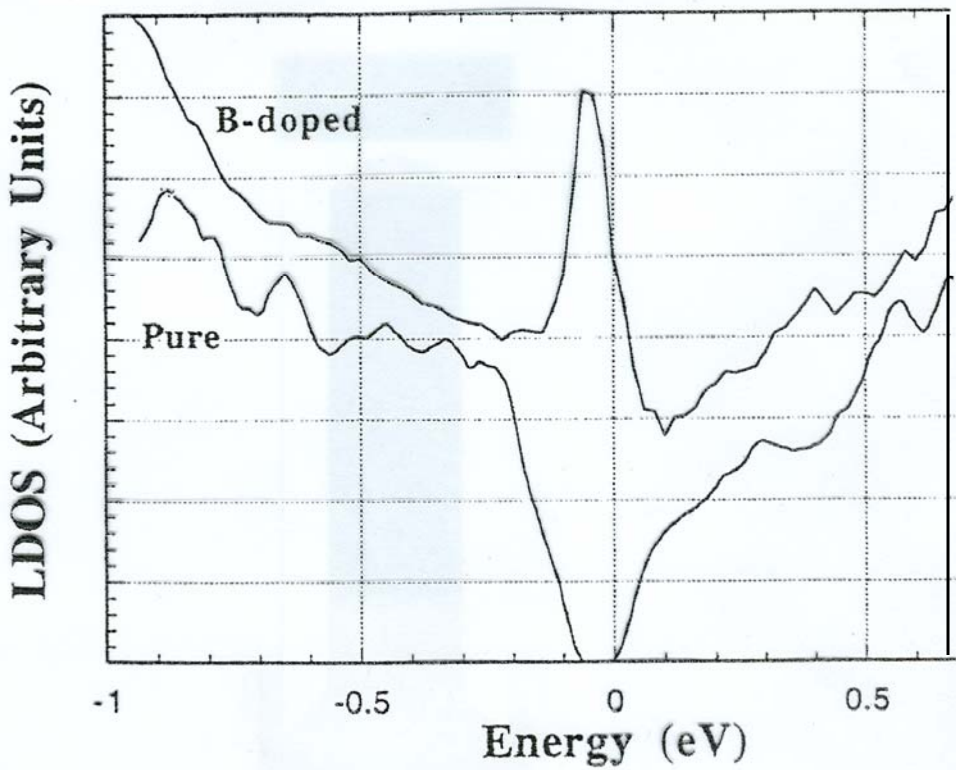


Local density of states measured by STM for semiconducting tubes

Tunneling spectroscopy of chemically doped CNT

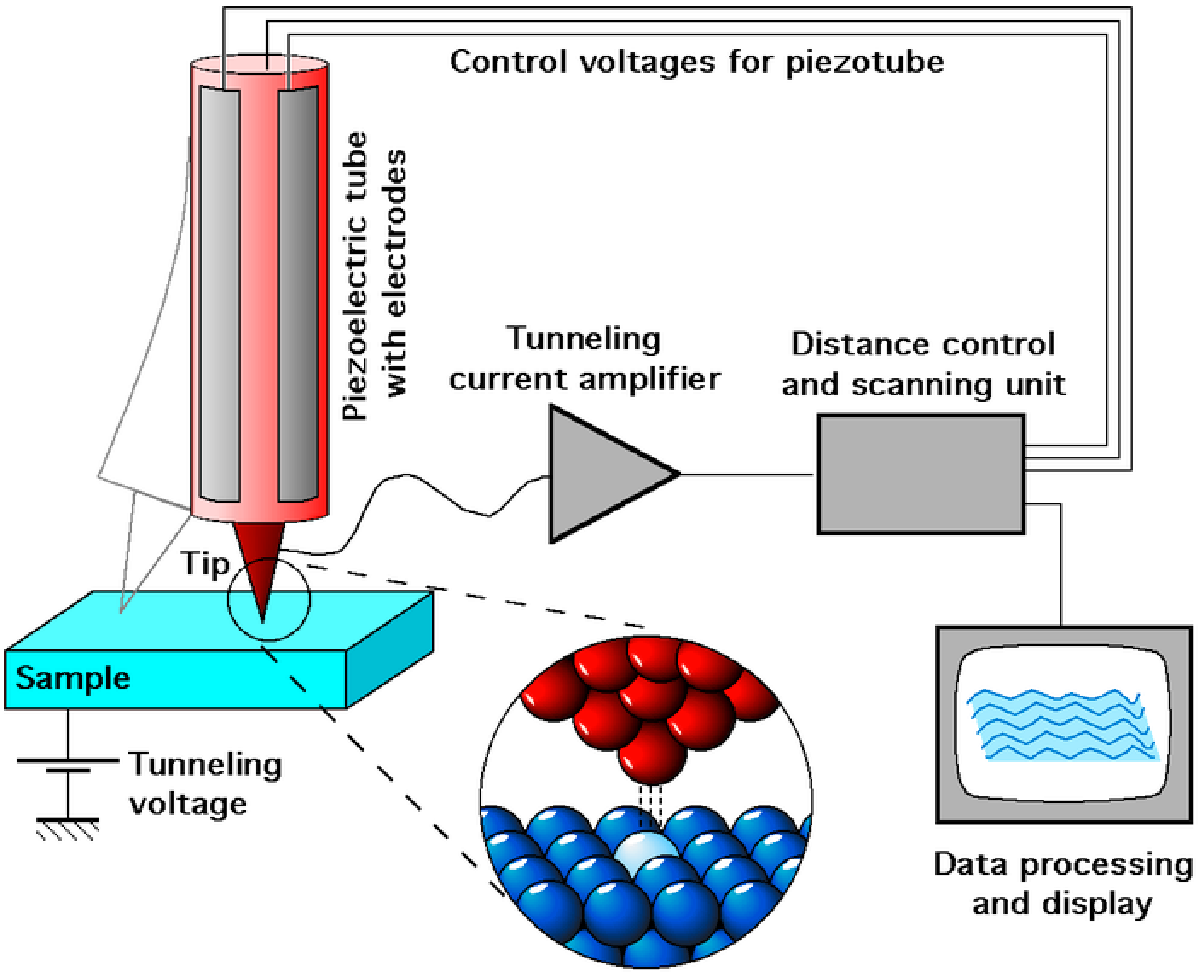


Tunneling spectroscopy of the “in situ” doped CNT, dopant boron



Comparison of density of states of pure carbon nanotub
boron-doped nanotube (peak at Fermi level).

Instrumentation

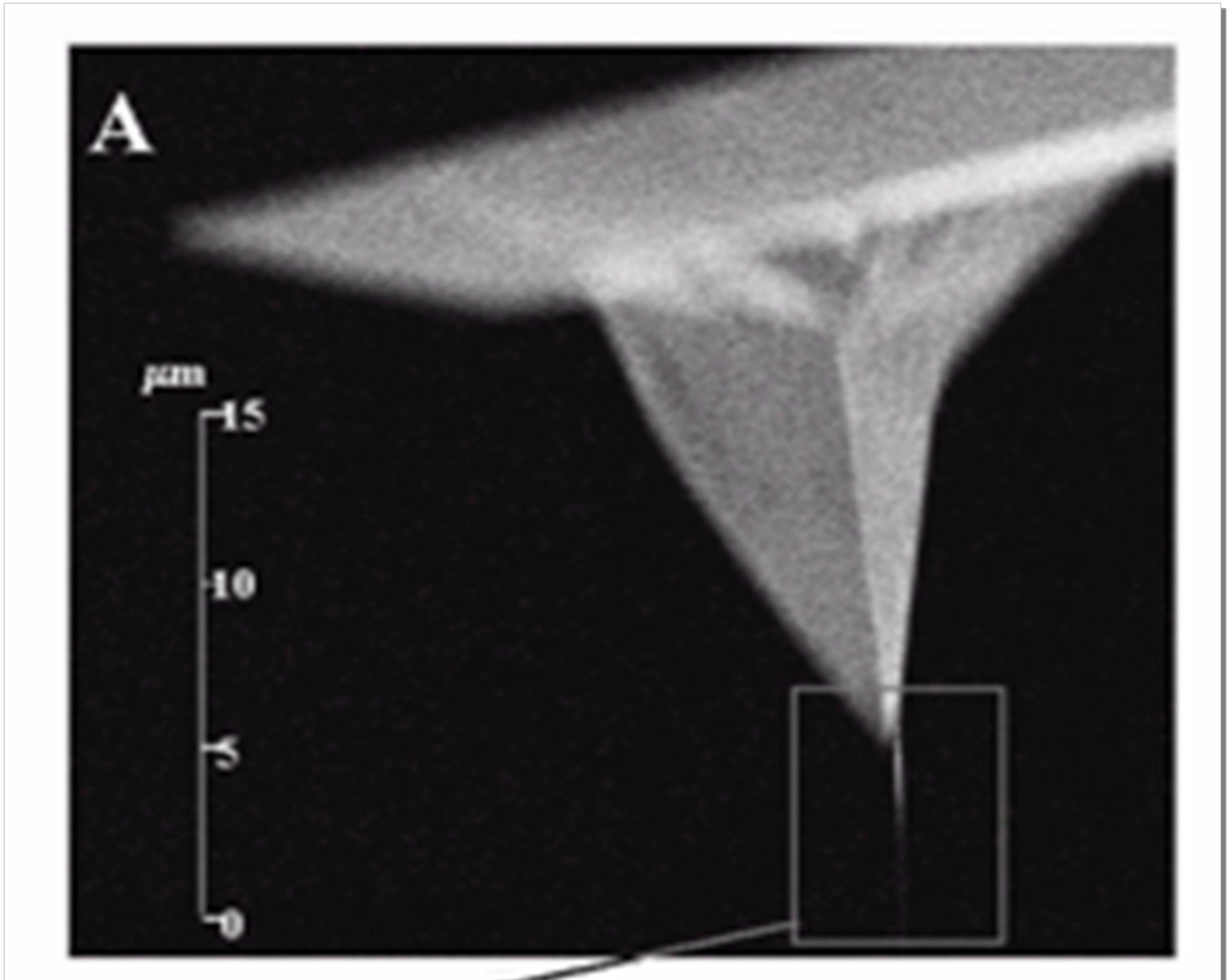


Components:

1. Ached sharp W tip
2. Piezoelectric height controller
3. Tunneling current amplifier
4. Scanner
5. Vibration isolation system
6. Computer for data processing

Schematic view of a STM

Tip for STM: CNT grown on Si tip



The resolution of an image is limited by the tip radius of curvature

Atomic Force Microscopy, AFM

The AFM is invented 1986. It is a type of scanning probe microscope that forms images of surfaces using a physical probe.

An image of the surface is obtained by mechanically moving the probe in a raster scan, line by line, and recording the probe surface interaction as a function of position.

The information about the scanned surface is gathered by "feeling" the surface with a mechanical probe.

In a raster scanning, an image is divided into a sequence of (usually horizontal) strips known as "scan lines". Each scan line can be divided into discrete pixel for processing in a computer system.

Atomic Force Microscopy, AFM

It is one of the foremost tools for imaging, measuring and manipulating of nanomaterials adsorbed on the surface.

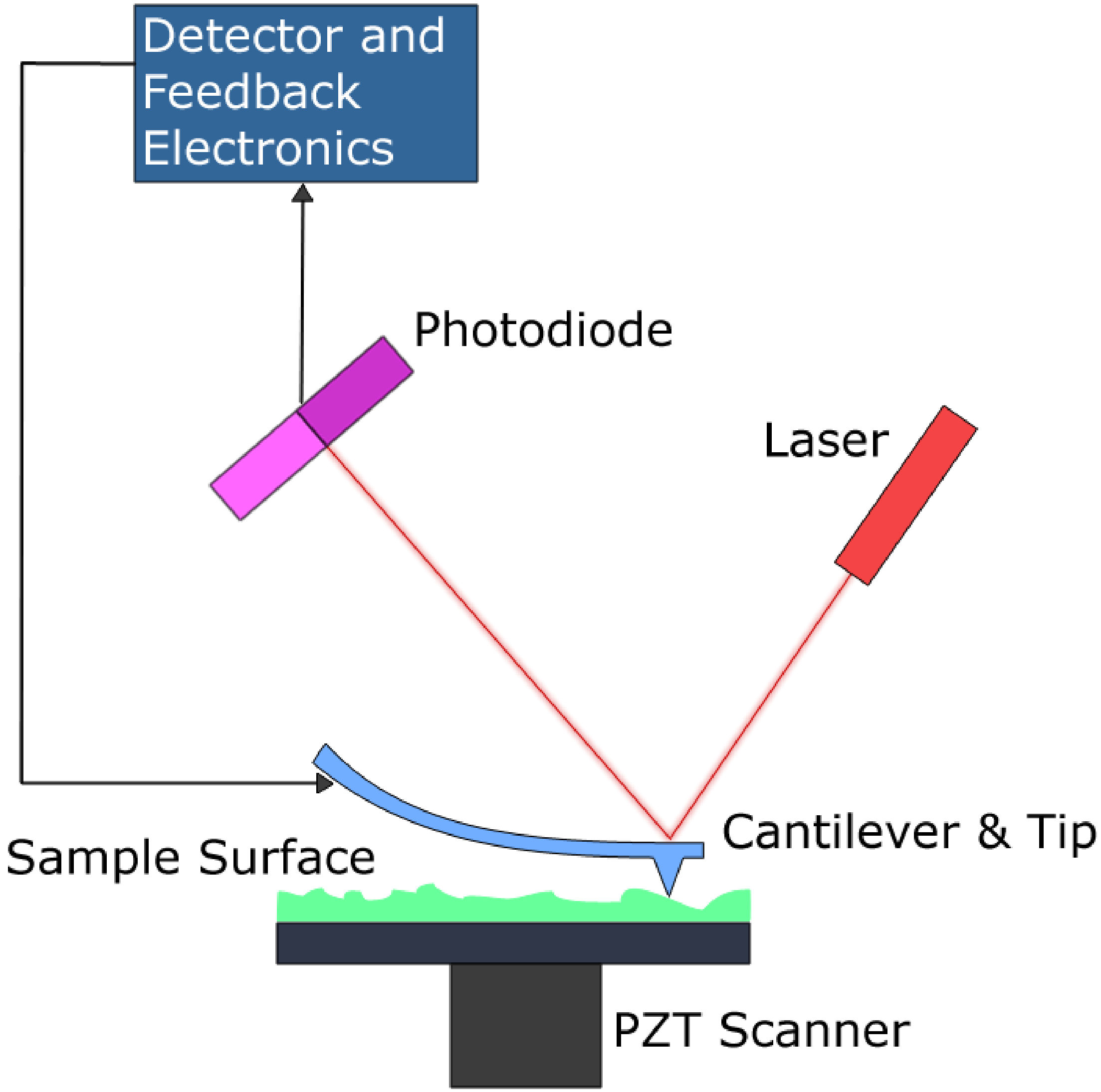
How does it work?

The technique is based on piezoelectric actuators which execute motions with a precision and accuracy at the atomic level.

Measuring the tip-to-sample distance at each (x,y) data point allows the scanning software to construct a topographic image of the sample surface.

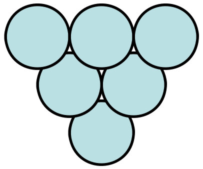
The data are typically obtained as a two-dimensional picture of data points, visualized in as a computer image.

Detection of the laser beam deflection



When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever.
The deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes.

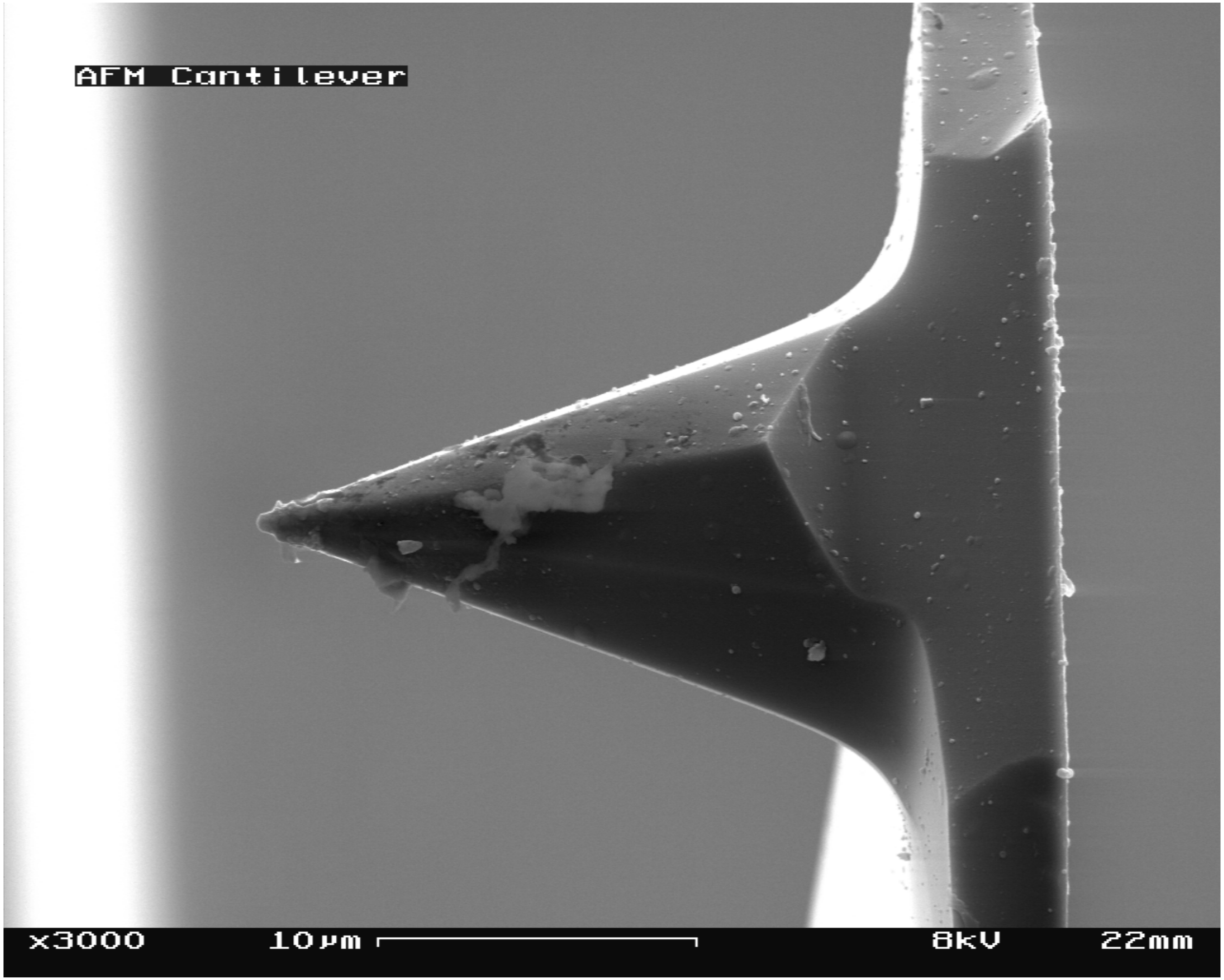
Probe tips



Probe tips are typically made of silicon or silicon nitride with the curvature of nanometer size

A sharp probe tip of one atom in diameter can be obtained by acid etching along crystallographic faces.

Microscale cantilever with a scanning tip



Scanning process

If the tip was scanned at a constant height, a risk would exist that the tip collides with the surface, causing damage.
Hence, a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample.

The resulting map of the area $s = f(x,y)$ represents the topography of the sample.

Imaging modes

1. Static – contact mode
2. Dynamic mode

Contact mode

In contact mode, the force between the tip and the surface is kept constant.

The static tip deflection is used as a feedback signal.

Tips with low stiffness are used to boost the deflection.

Dynamic - tapping mode

The cantilever is externally oscillated with its resonance frequency. Both the oscillation amplitude, and resonance frequency are modified by tip-sample interaction forces.

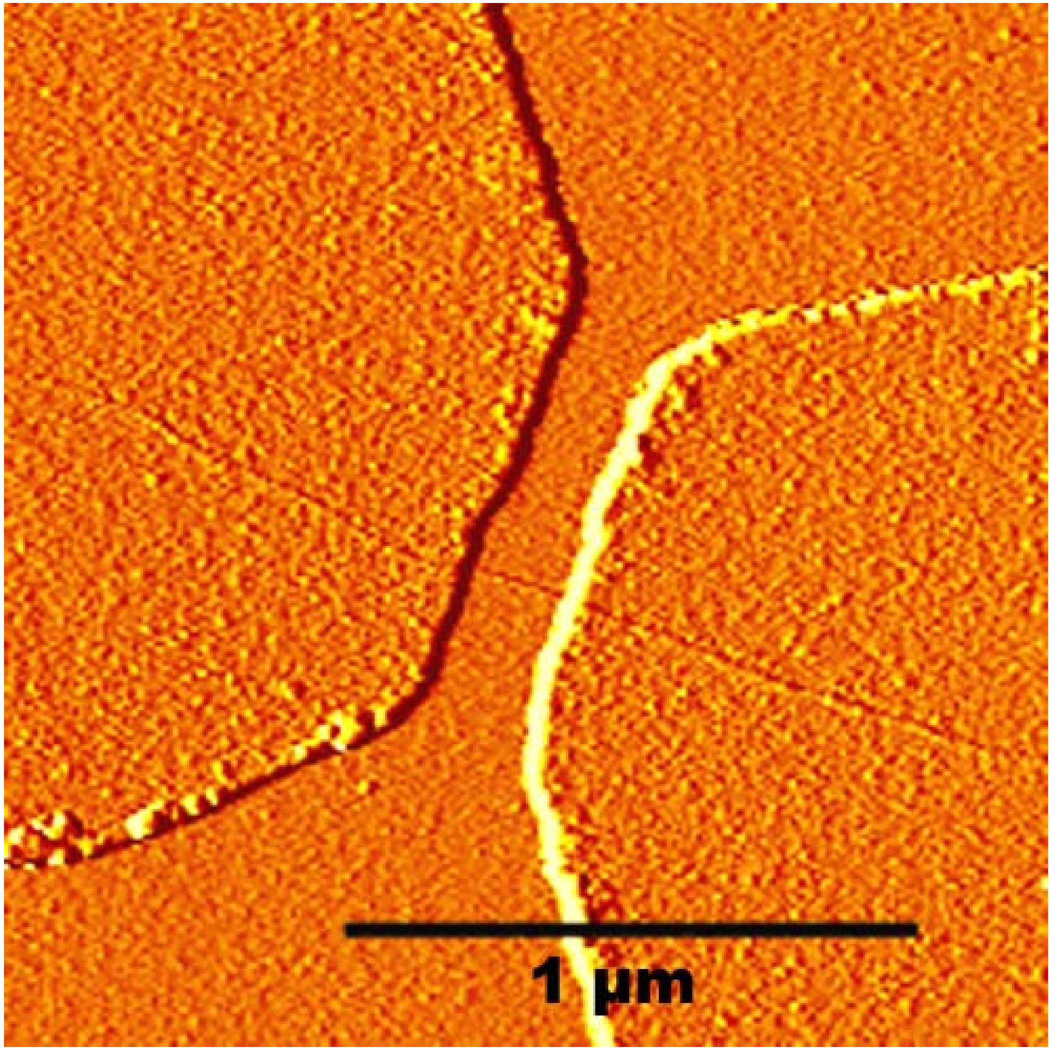
Frequency can be measured with very high sensitivity and thus the frequency modulation provide precise information about tip-sample interactions.

In amplitude modulation, changes in the oscillation amplitude or phase provide the feedback signal for imaging.

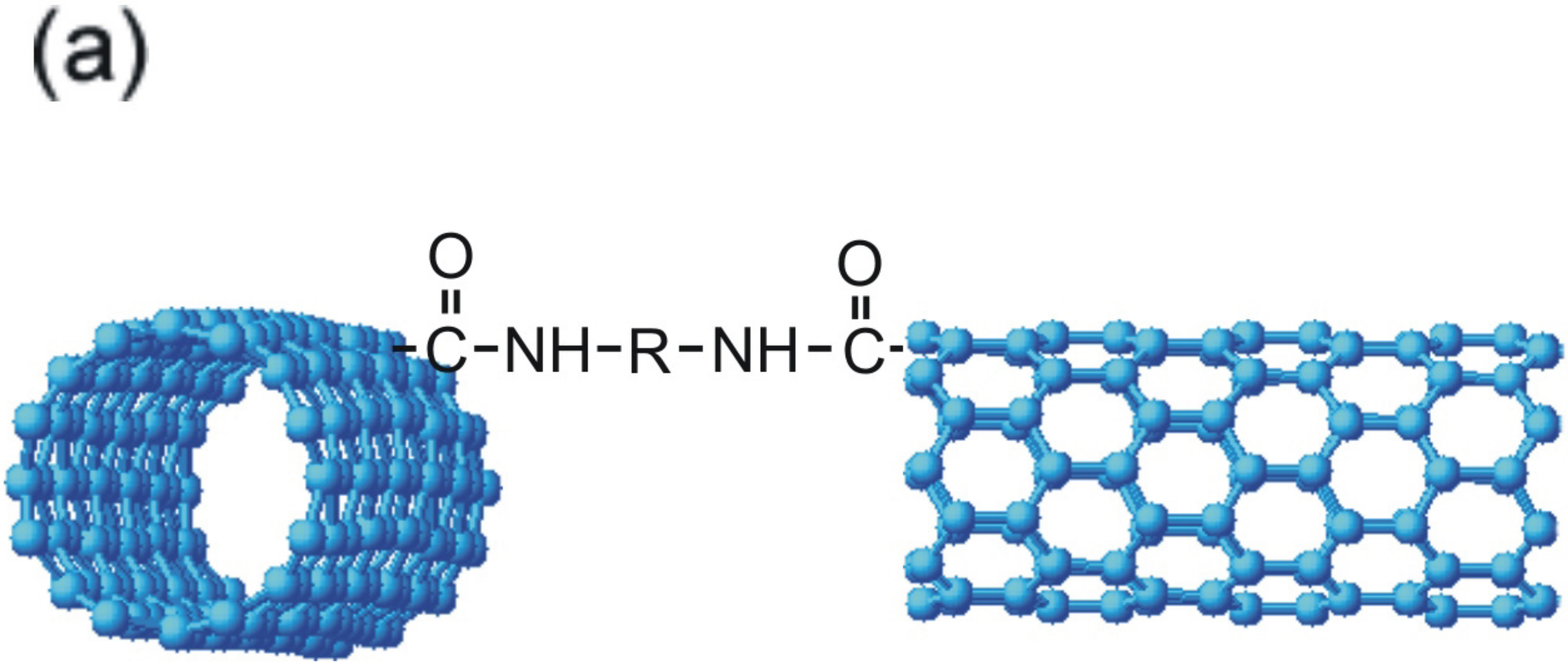
Tapping mode

Due to the interaction of forces acting on the cantilever when the tip comes close to the surface, the amplitude of this oscillation decreases.
An electronic servo uses the piezoelectric actuator to control the height of the cantilever above the sample.

AFM: for SWNT imaging

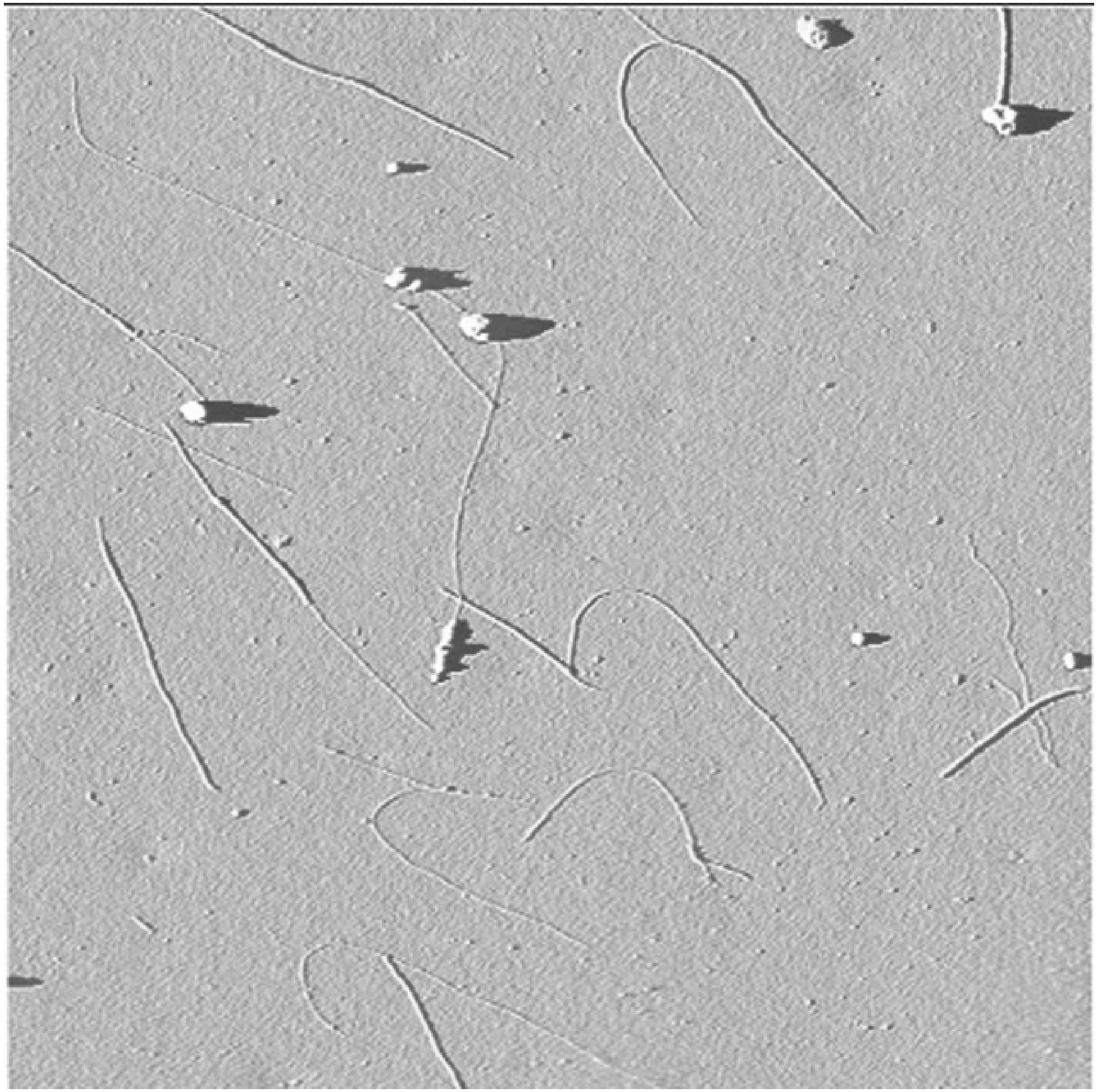


Single SWNT transisitor on gold electrodes



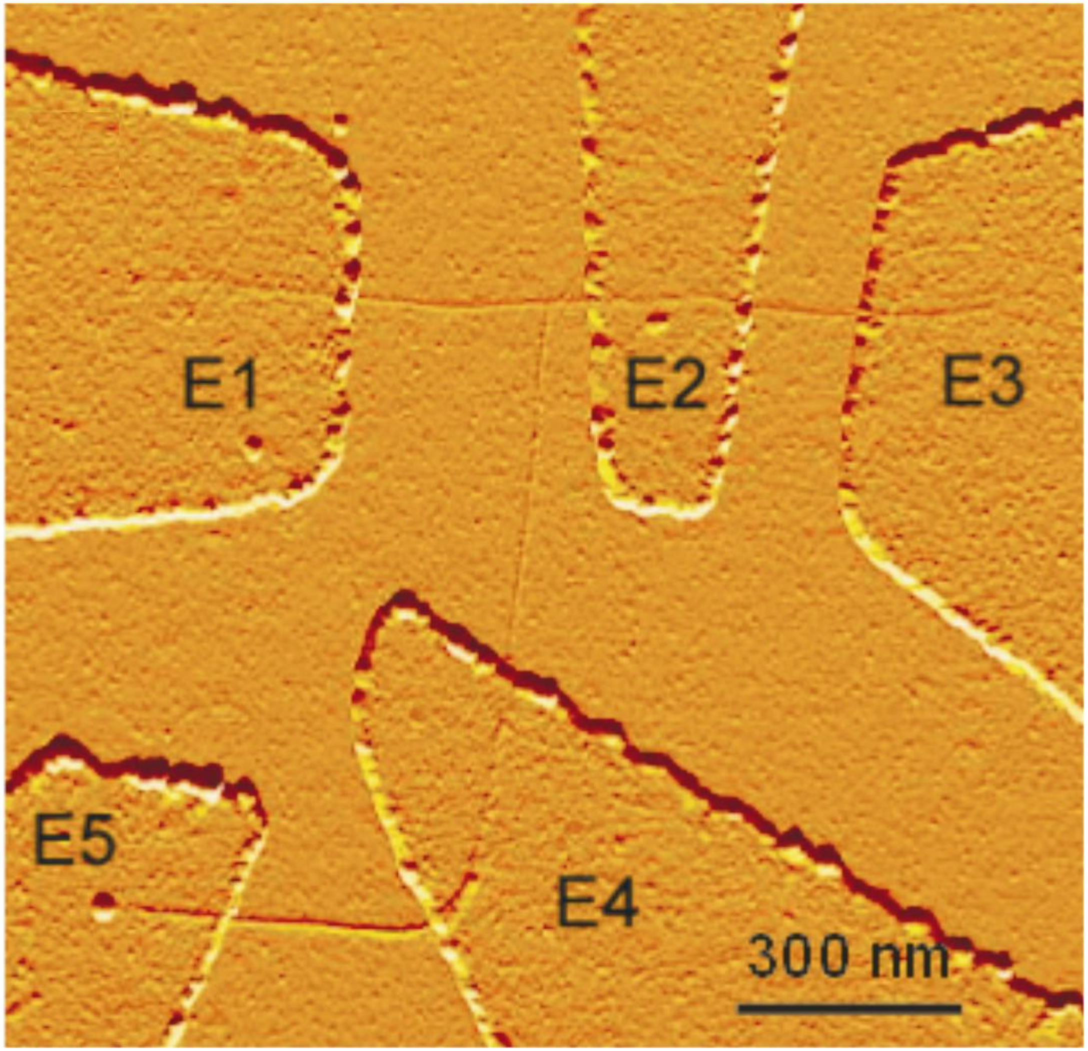
Wet-chemical synthesis of nanotube junctions

AFM: SWNT junctions



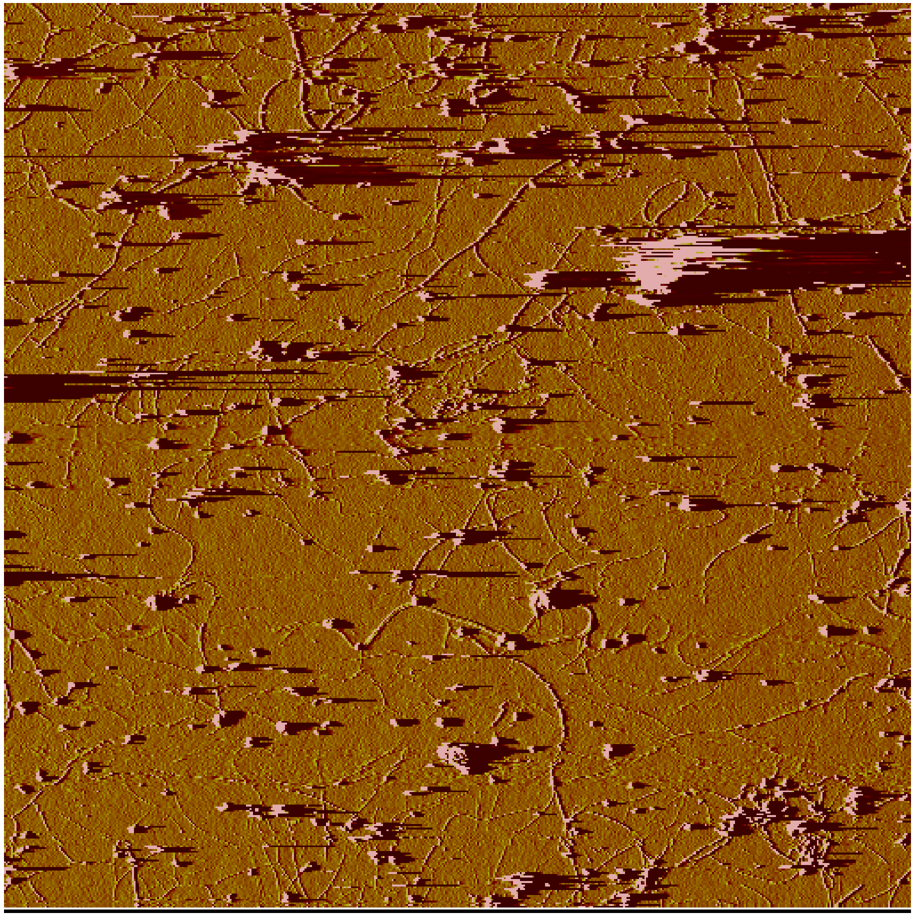
SWNT junction image

AFM: SWNT junctions

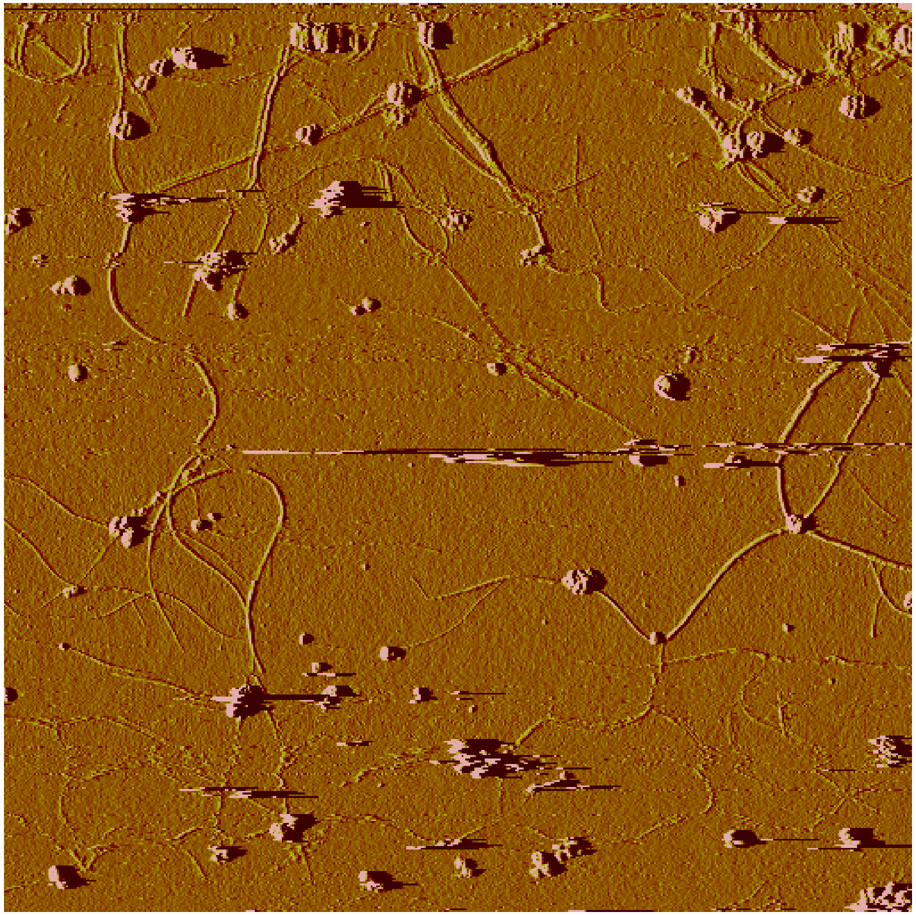


All carbon transistor

AFM: $LiMnPO_4$ with CNT



14.5 µm



5.68 µm

Advantages and disadvantages of AFM over SEM

AFM	SEM
true 3-dimensional surface profile Higher resolution	2-dimensional projection, image
No pretreatment, C or metal coating	C or metal coating
ambient air	Vaccum environment
Micrometer size image Slow rate of scanning,Min Cannot measure steep walls	Milimeter size image Fast scanning

Conclusions

The invention of STM led to the development of the AFM.

Both techniques contributes to the fundamental understanding of atomic and electronic surface structure.

STM and AFM very important instruments in research of nanosructures and can be regarded as one of the drivers of the nanotechnology and nanoresearch.

Questions