Surface Science September 20, 2010

Diffraction methods: LEED; RHEED; Scanning probe

References and sources:

Woodruff and Delchar (2nd ed.), pp 105-212
http://venables.asu.edu/grad/lectures.html
http://www.cem.msu.edu/~cem924sg/
http://www.cem.msu.edu/~cem924sg/Topic06.pdf
http://www.chem.qmul.ac.uk/surfaces/scc/
http://philiphofmann.net/surflec3/surflec014.html
http://www.material.tohoku.ac.jp/~kaimenb/B_RHEED.html
Wikipedia (!)

Electrons in the ~ 20 – 200 eV range have wavelengths comparable to lattice dimensions

λ= h/p (de Broglie relation)

$E_{kinetic} = p^2/2m$

so $p = \text{sqrt}(2m\, E_{kinetic})$

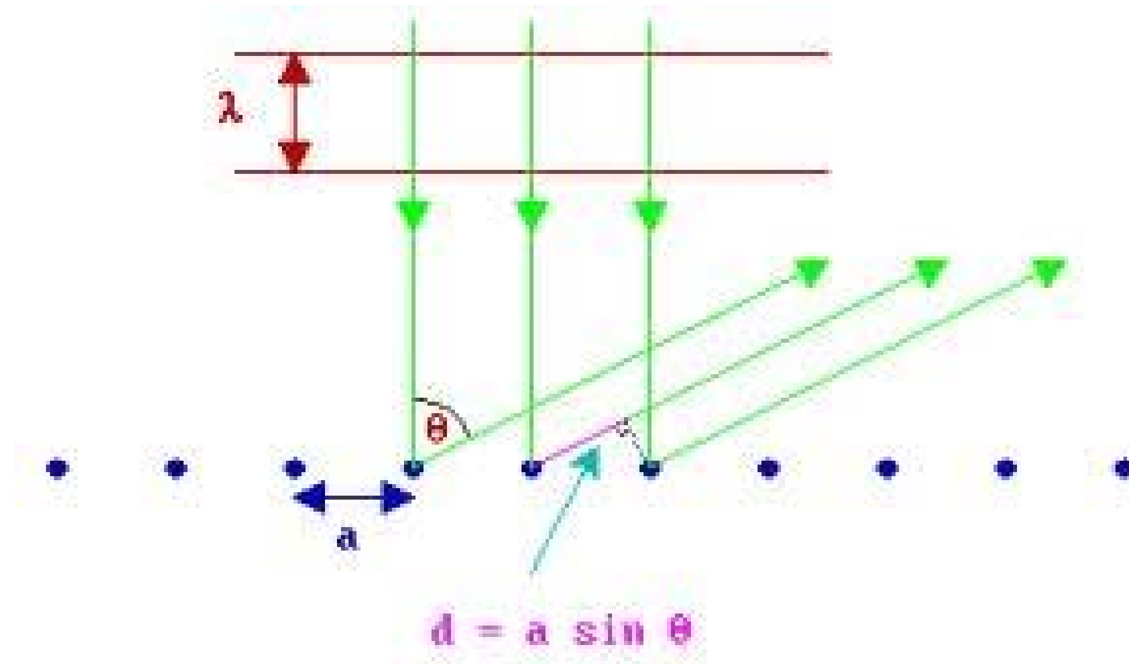
and $\lambda = h/ \text{sqrt}(2m\, E_{kinetic})$

Now, put in numbers!
$h = 6.62 \times 10^{-34}$ Js
$m = 9.11 \times 10^{-31}$ kg
If we express E in eV (1 eV =1.60×10^{-19} J)
and λ in Å (1 Å = 1×10^{-10} m)

We get: λ (in Å) = 12.4/ sqrt($E_{kinetic}$ (in eV))

Therefore $E_{kinetic}$ = 36 eV (easy to do!) gives λ = 2.1 Å!!
Just about right!!!

Basic idea of LEED: Scattering off a two dimensional array of atoms.



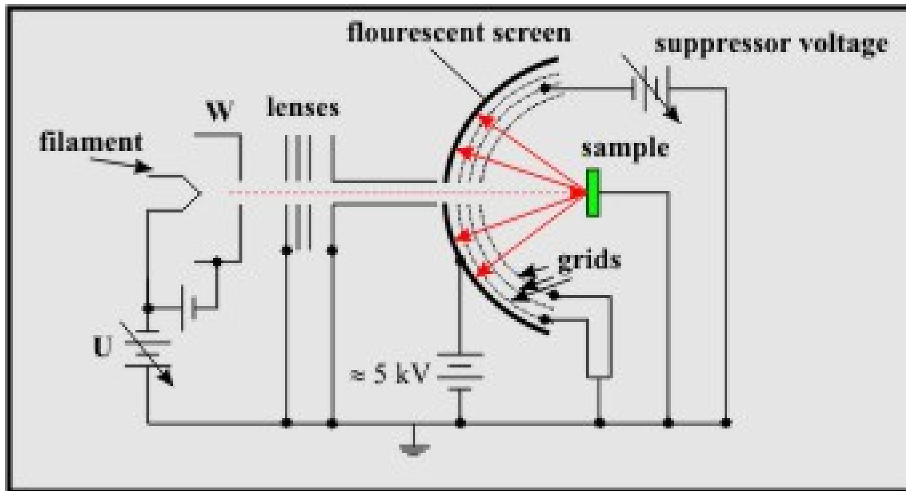
If d = nλ, we get constructive interference!
What happens to Θ when λ is changed?
Why two dimensional, not 3D??

Low Energy Electron Diffraction (LEED)

LEED is an important diffraction technique for the determination of surface structures. It may be used in one of two ways.

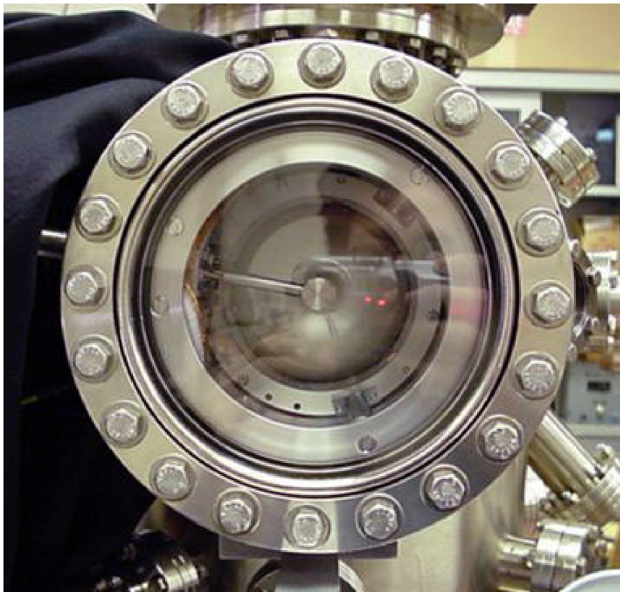
<u>Qualitatively</u> : The diffraction pattern is recorded. An analysis of the spot positions yields information on the size, symmetry and rotational alignment of the surface unit cell.

<u>Quantitatively</u> : The intensities of the various diffracted beams are recorded as a function of the incident electron energy to generate **I-V curves** which, by comparison with calculated curves, gives accurate information on atomic positions.

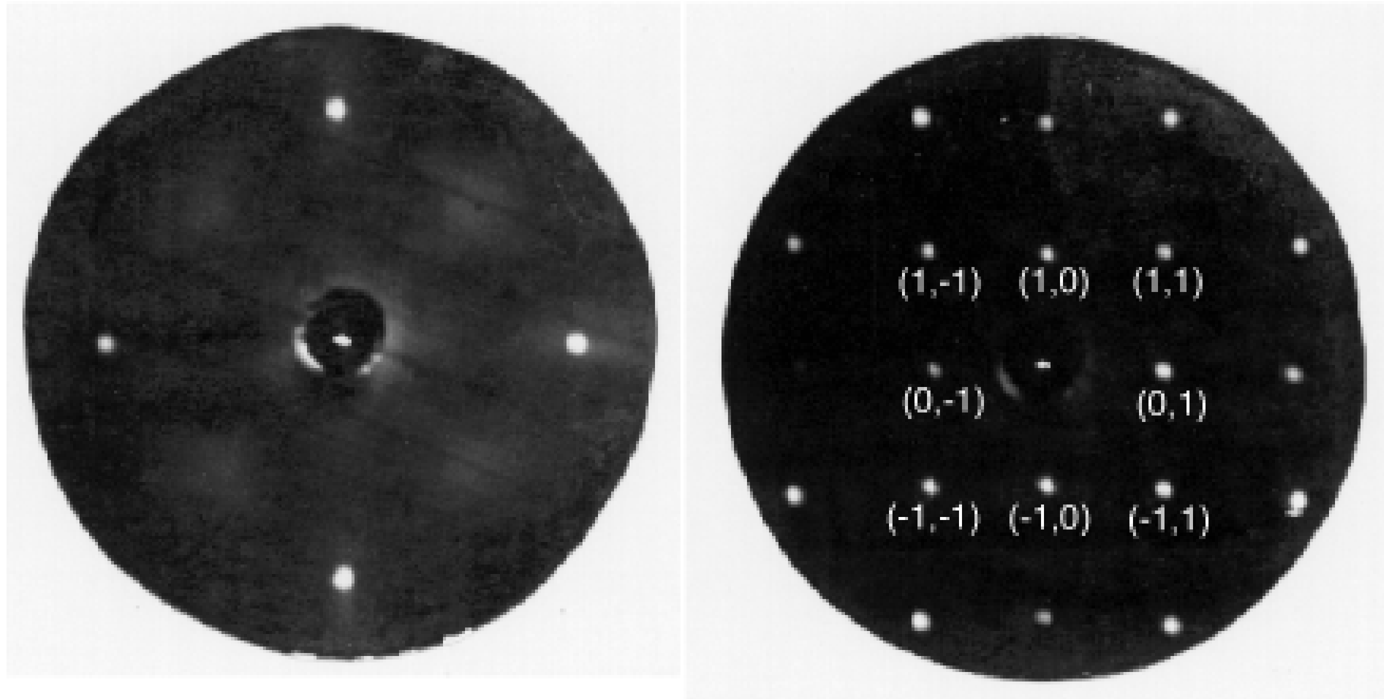


chematic picture of a LEED apparatus

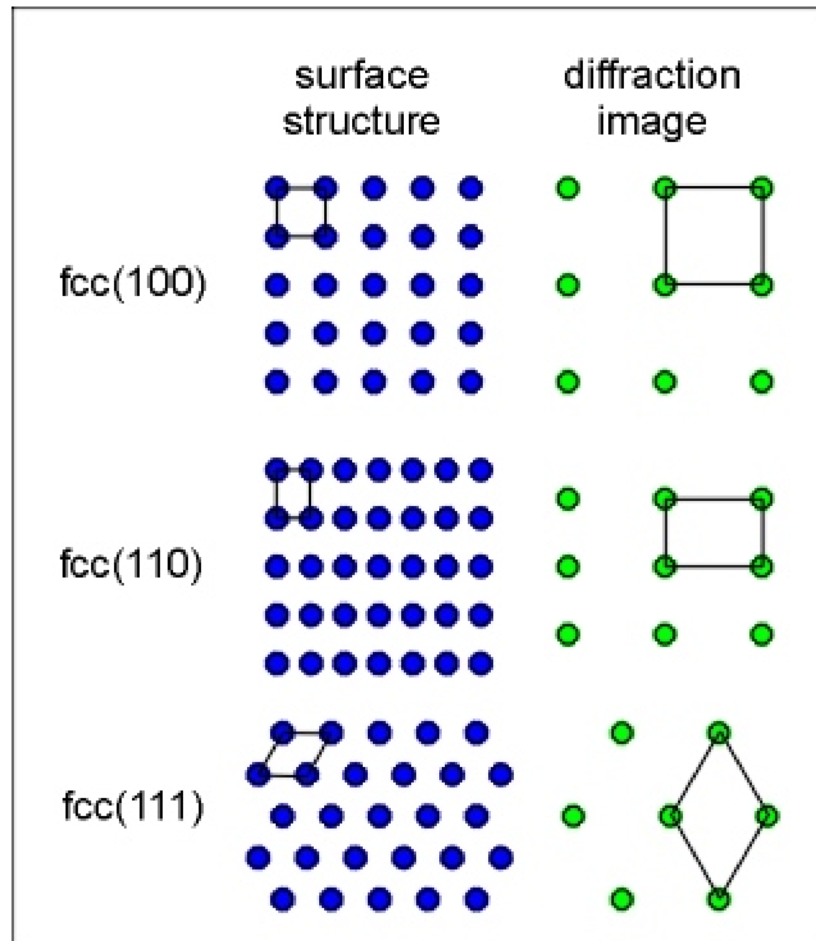
Commercial LEED apparatus



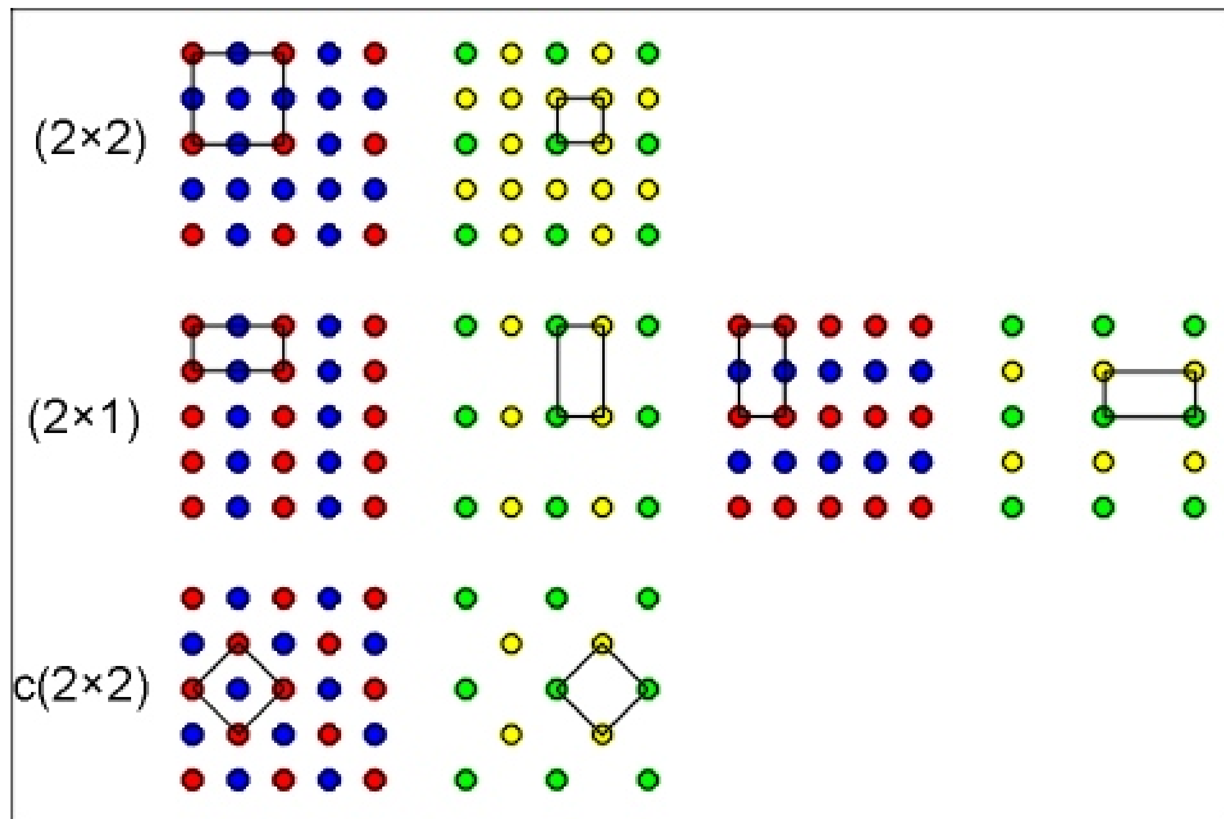
LEED apparatus mounted in UHV chamber



LEED diffraction patterns from W(100) at two different energies

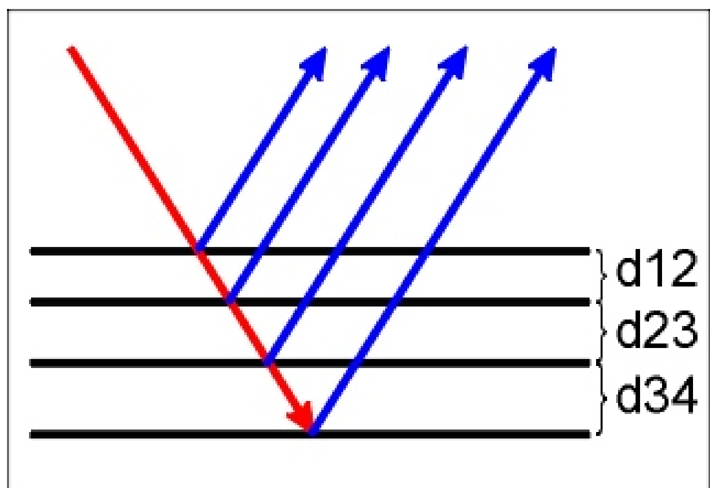


Real and reciprocal space pictures of unit cells

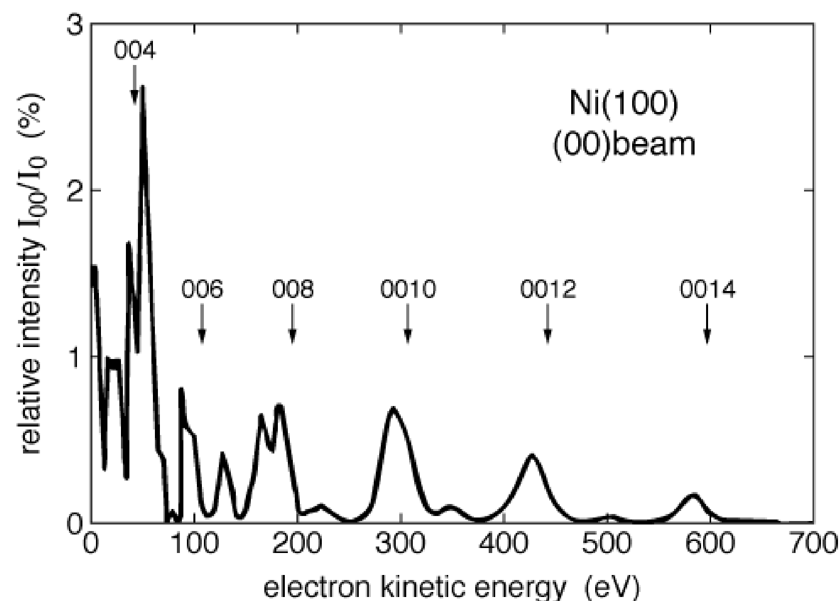


Superstructures

First complication: Scattering from different layers parallel to the surface can interfere constructively or destructively



Interference between different layers (single scattering)



I-V curve (intensity profile) for Ni(100)

Second complication: Multiple scattering

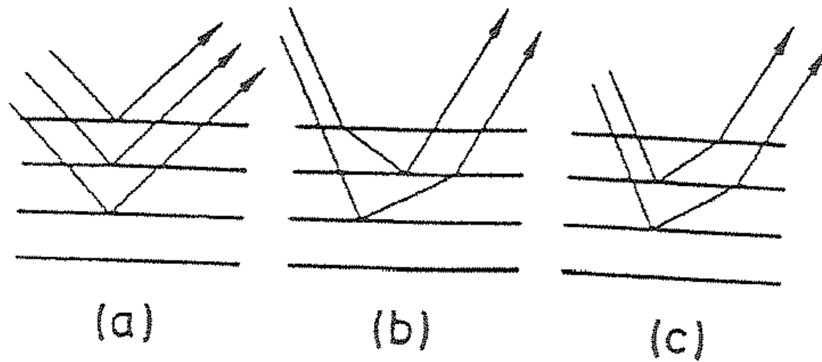


Fig.4.10a-c. Schematic representation of single and multiple scattering processes in LEED. (a) single-scattering events at the "lattice planes" cause a regular Bragg reflec-tion. (b) Double-scattering events with forward- and subsequent back-scattering con-tribute to the (00) Bragg spot. (c) Double-scattering event with back-scattering and subsequent forward-scattering

How to get quantitative results from LEED

The inspection of the LEED pattern gives a qualitative picture of the surface periodicity i.e. the size of the surface unit cell and to a certain degree of surface symmetries. It will give no information about the atomic arrangement within a surface unit cell or the sites of adsorbed atoms.

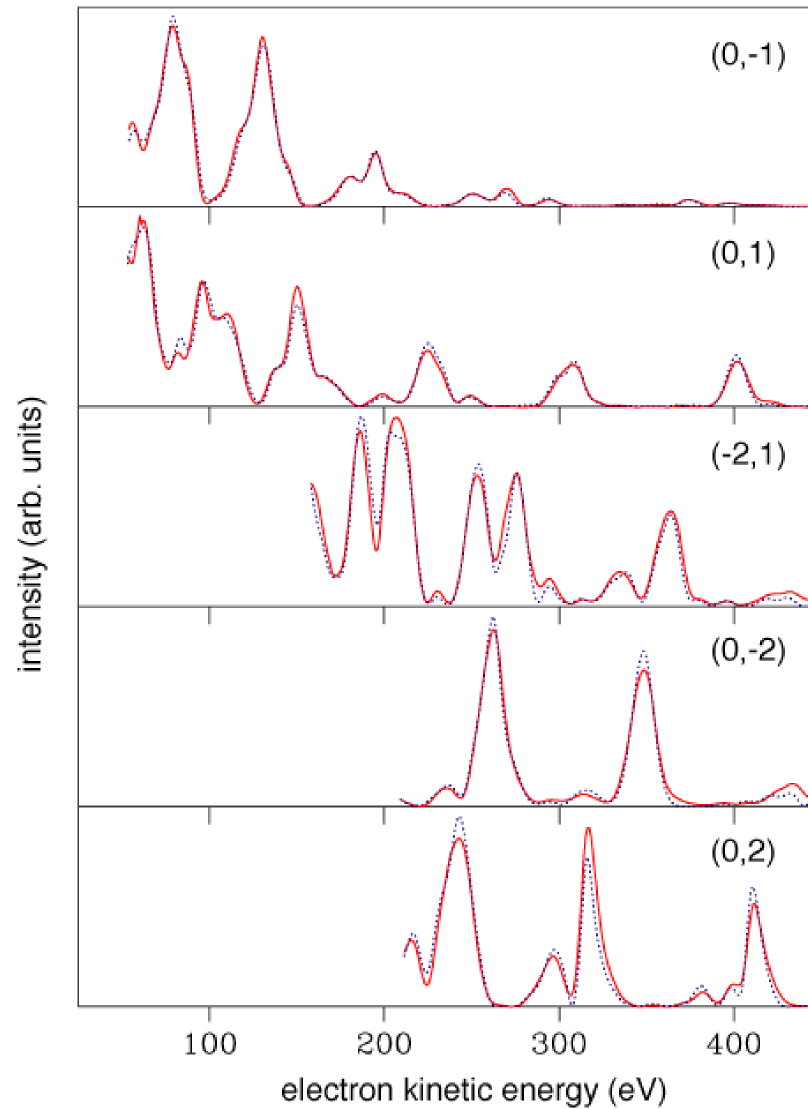
A more quantitative analysis of LEED experimental data can be achieved by analysis of I-V curves (measurements of the intensity versus incident electron energy). These curves are then compared to computer calculations based on the assumption of a particular model. The model is changed in an iterative process until a satisfactory agreement between experimental and theoretical curves is achieved. A quantitative measure for this agreement is the so called *reliability*- or R-factor, for example:

$$R = \sum_g \int (Y_{\mathrm{gth}} - Y_{\mathrm{gexpt}})^2 dE / \sum_g \int (Y_{\mathrm{gth}}^2 + Y_{\mathrm{gexpt}}^2) dE,$$

where $L(E) = I'/I.$

$$Y(E) = L^{-1}/(L^{-2} + V_{oi}^2)$$

and V_{oi} is the imaginary part of the electron self-energy



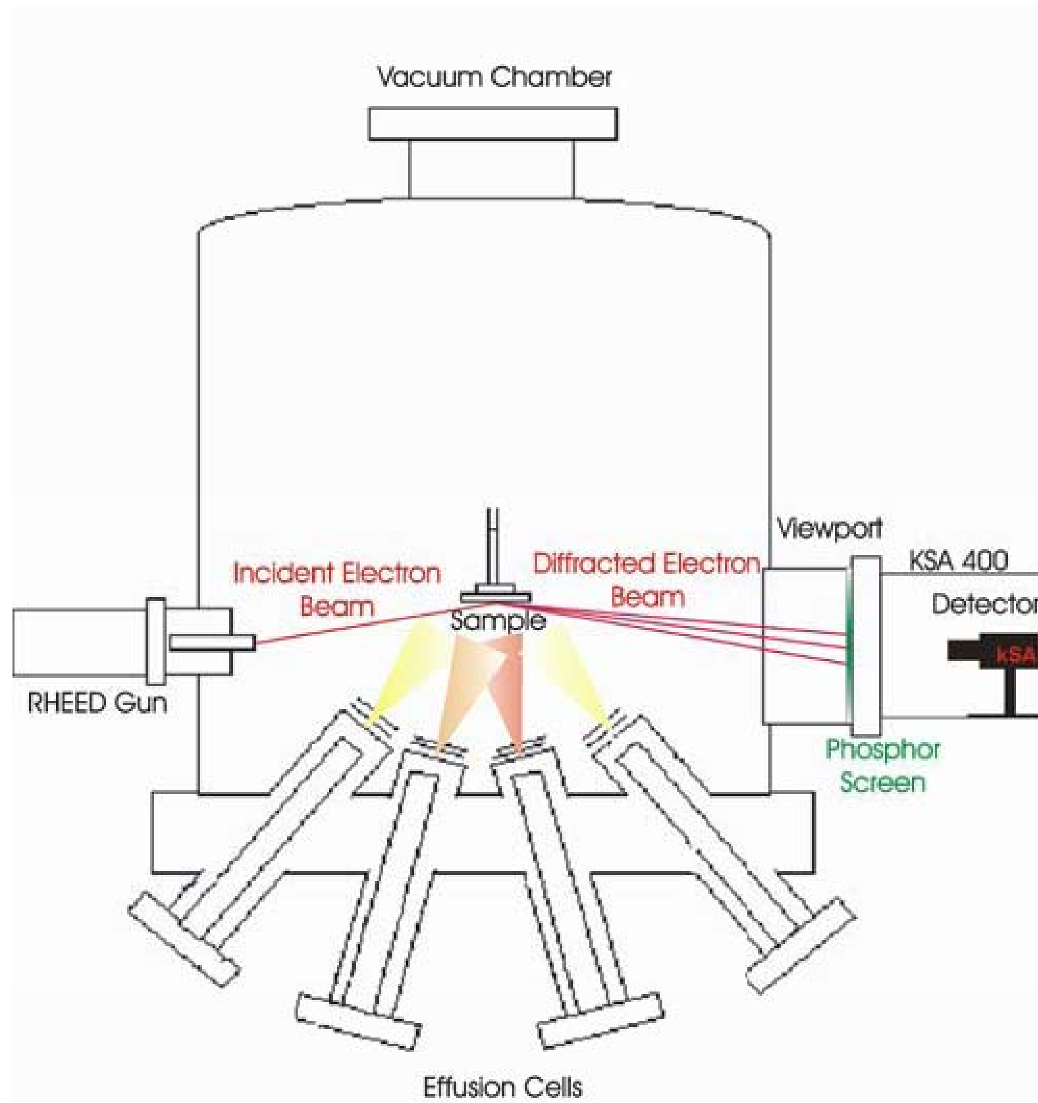
Theory vs. experiment (red) for I-V profiles for Al(111)

Summary

Range of elements	All elements, but not element specific
Destructive	No, except in special cases of electron-beam damage
Depth probed	4–20 Å
Detection limits	0.1 monolayer; any ordered phase can be detected; atomic positions to 0.1 Å; step heights to 0.1 Å; surface disorder down to ~10% of surface sites
Resolving power	Maximum resolvable distance for detecting disorder: typically 200 Å; best systems, 5 μm
Lateral resolution	Typical beam sizes, 0.1 mm; best systems, ~10 μm
Imaging capability	Typically, no; with specialized instruments (e.g., low-energy electron microscopy), 150 Å
Sample requirements	Single crystals of conductors and semiconductors; insulators and polycrystalline samples under special circumstances; 0.25 cm^2 or larger, smaller with special effort
Main uses	Analysis of surface crystallography and microstructure; surface cleanliness

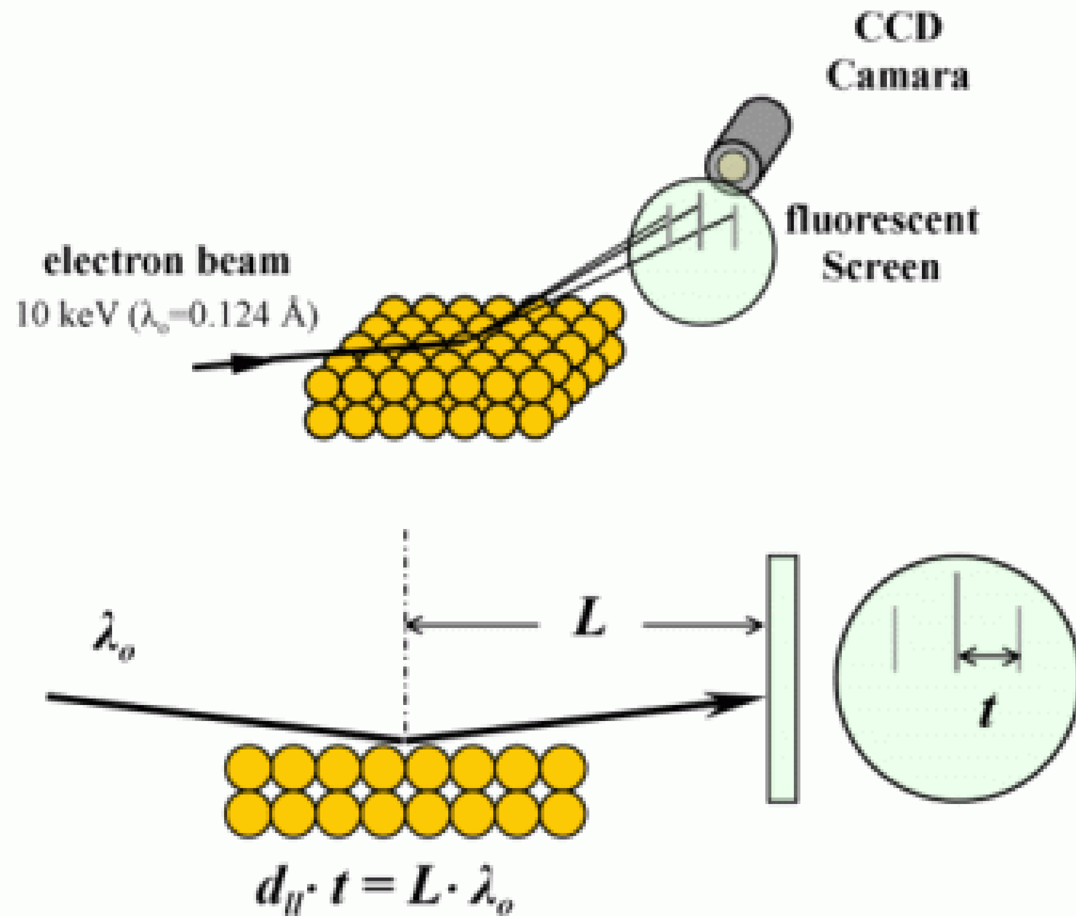
Reflection High Energy Electron Diffraction (RHEED)

- High energy electrons (10 – 30 keV)
- Grazing incidence geometry
- Widely used to monitor epitaxial growth
- Not as well understood quantitatively as LEED
- No energy filtering

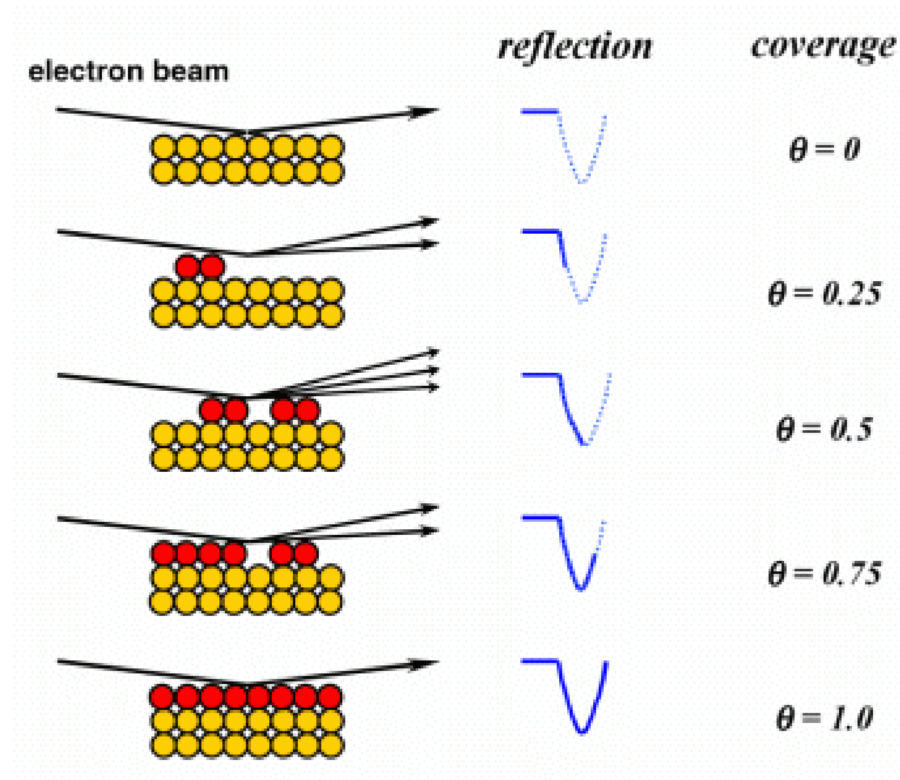


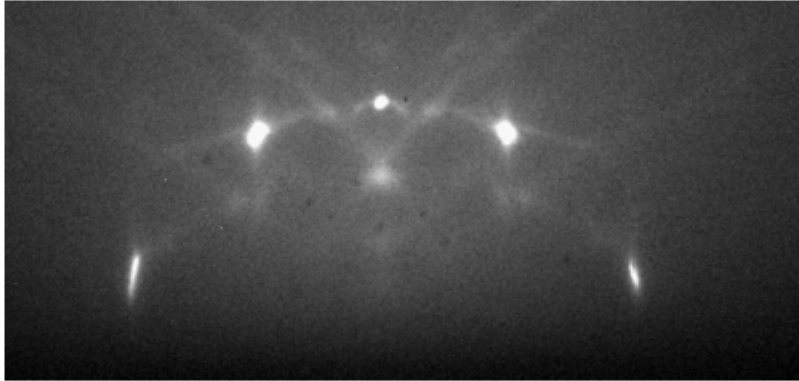
MBE apparatus with RHEED

RHEED experimental geometry

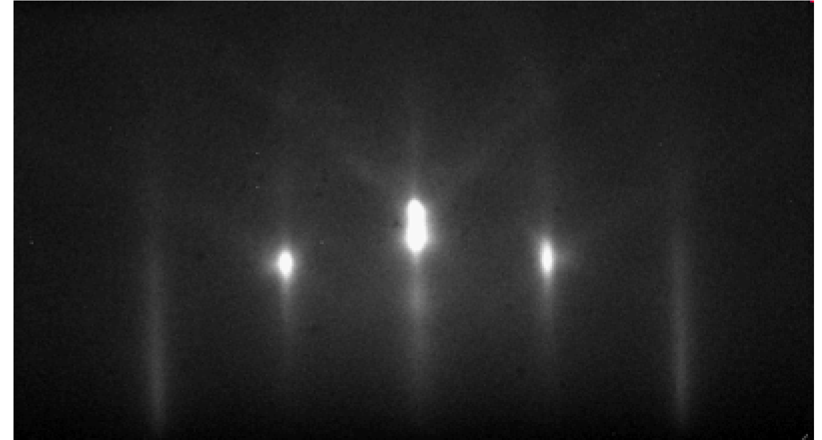


(Schematic) origin of RHEED oscillations





A RHEED pattern from a TiO_2 (110)

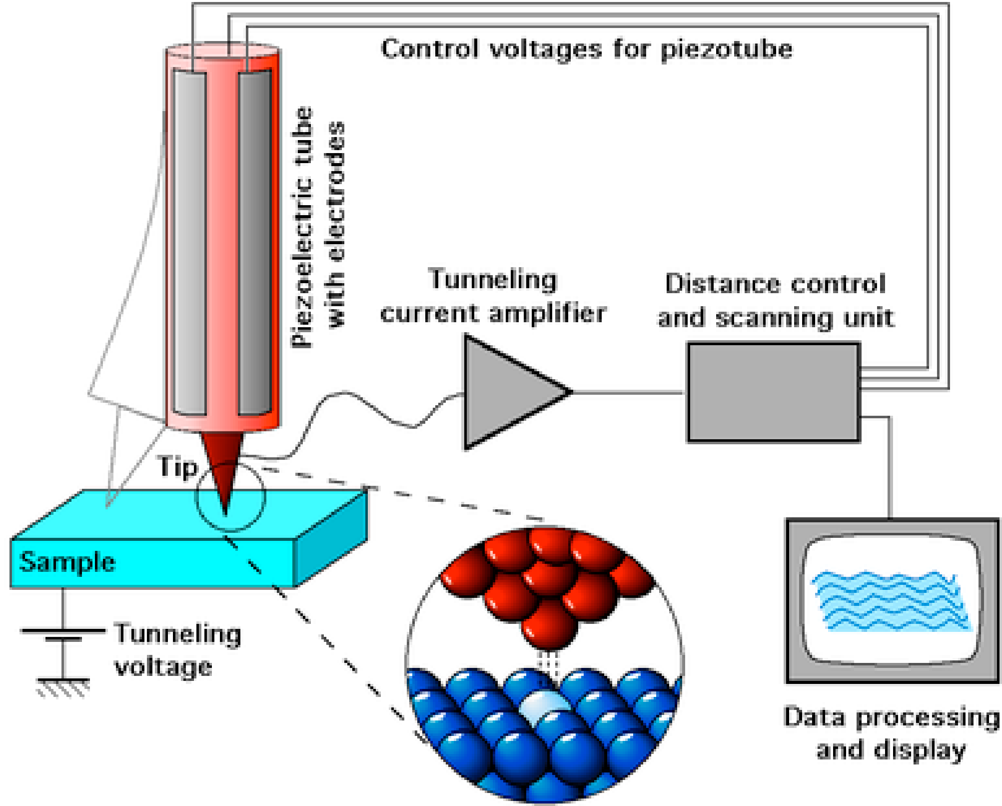


Streaked RHEED pattern from the TiO_2(110) surface. The sample had a terraced surface, which caused noticeable streaking compared to the RHEED pattern from the flat TiO_2(110) surface shown to the left.

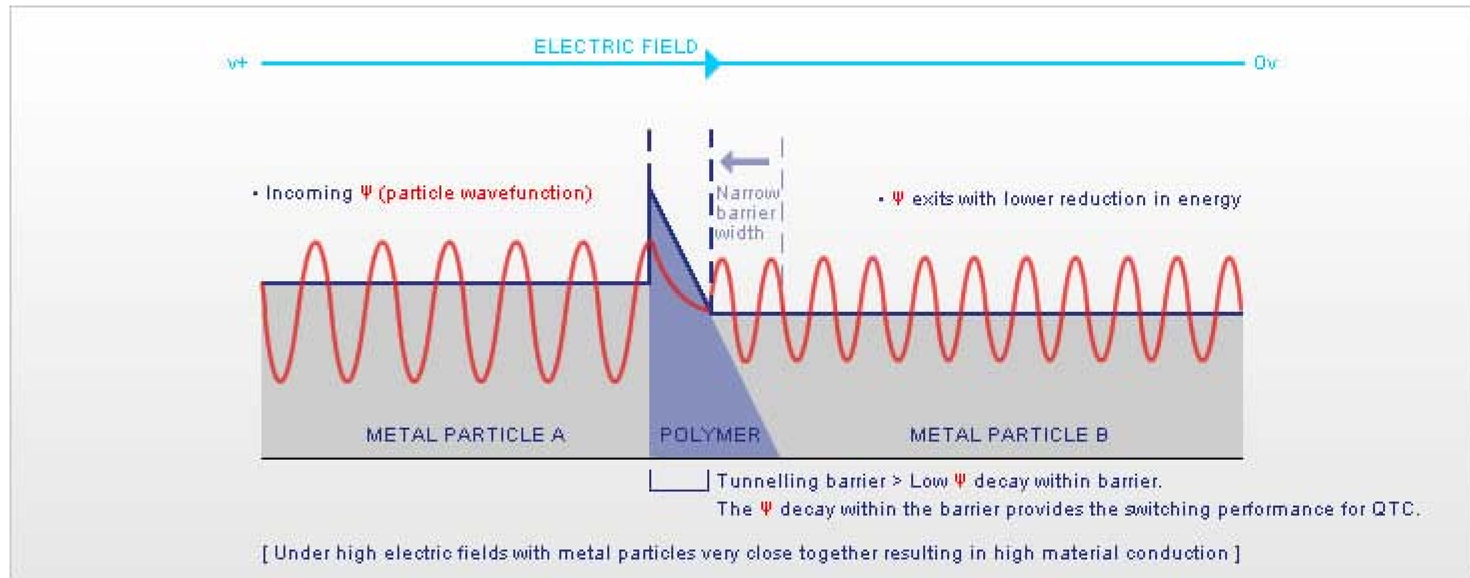
RHEED summary

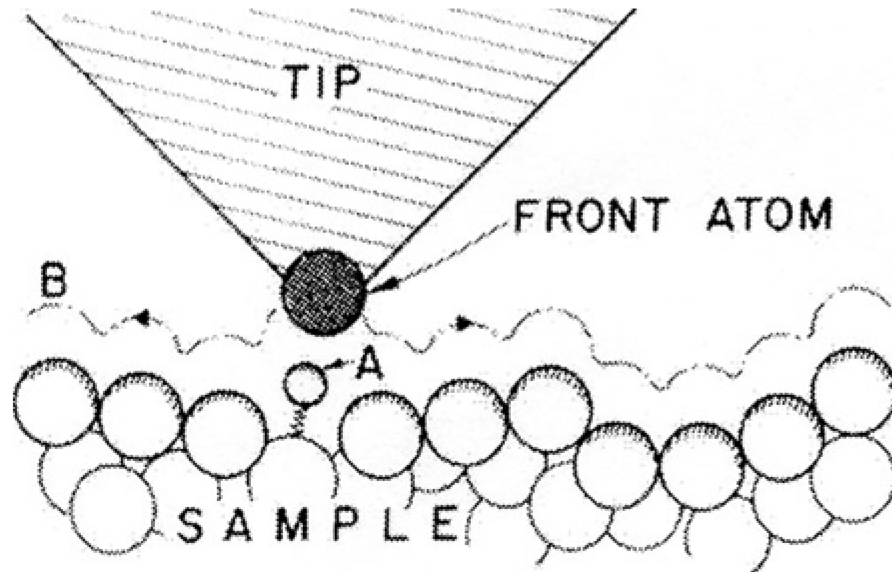
Range of elements	All, but not chemical specific
Destructive	No, Except for electron-sensitive materials
Depth probed	2–100 Å
Depth profiling	No
Lateral resolution	200 μm × 4 mm, in special cases 0.3 nm × 6 nm
Structural information	Measures surface crystal structure parameters, sensitive to structural defects
Sample requirements	Usually single crystal conductor or semiconductor surfaces
Main use	Monitoring surface structures, especially during thin-film epitaxial growth; can distinguish two- and three-dimensional defects

Scanning tunneling microscopy (STM)



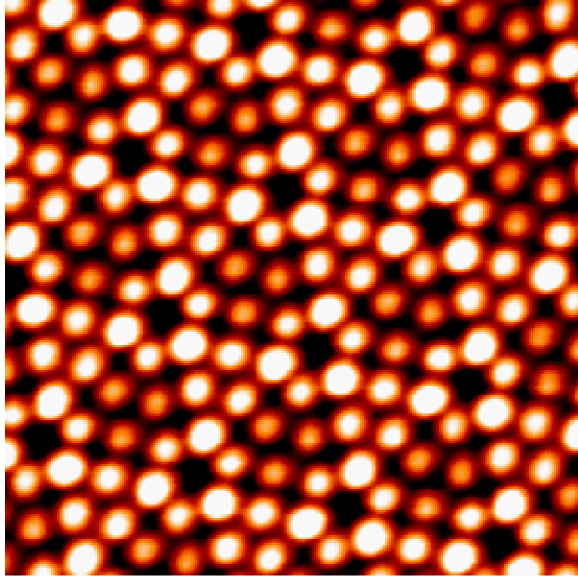
Quantum tunneling

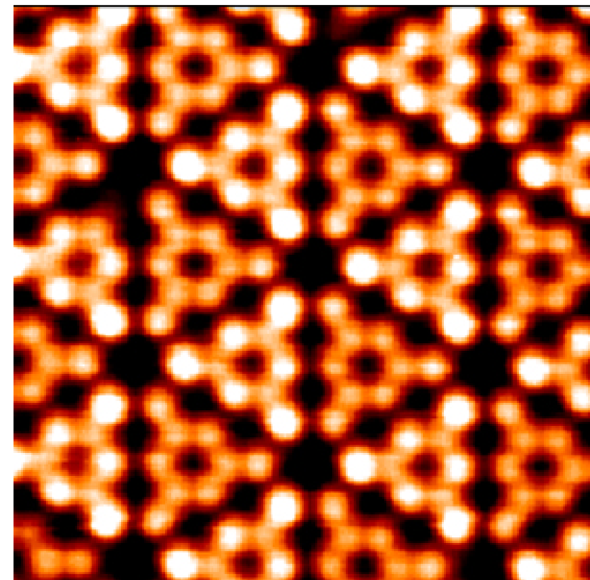




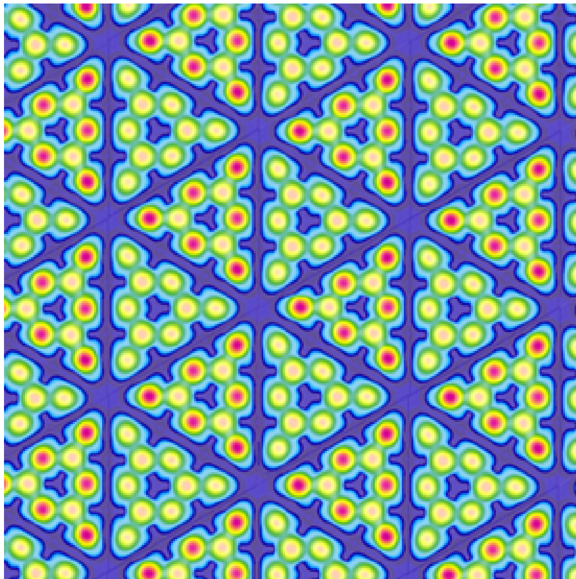
Description of the principle operation of an STM as well as that of an AFM.
The tip follows contour B, in one case to keep the tunneling current constant (STM) and in the other to maintain constant force between tip and sample (AFM, sample, and tip either insulating or conducting). The STM itself may probe forces when a periodic force on the adatom A varies its position in the gap and modulates the tunneling current in the STM. The force can come from an ac voltage on the tip, or from an externally applied magnetic field for adatoms with a magnetic moment.

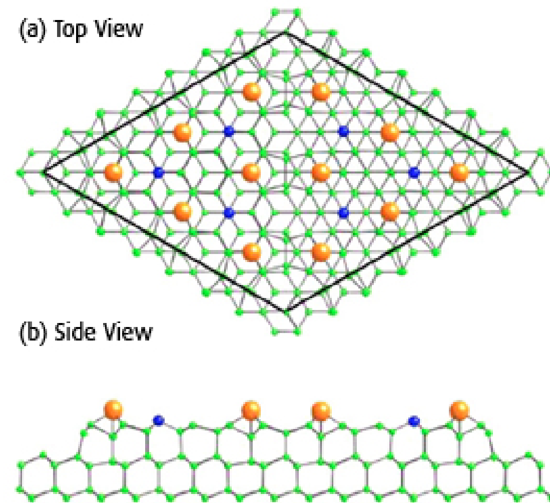
The STM measures charge density, not directly atomic positions



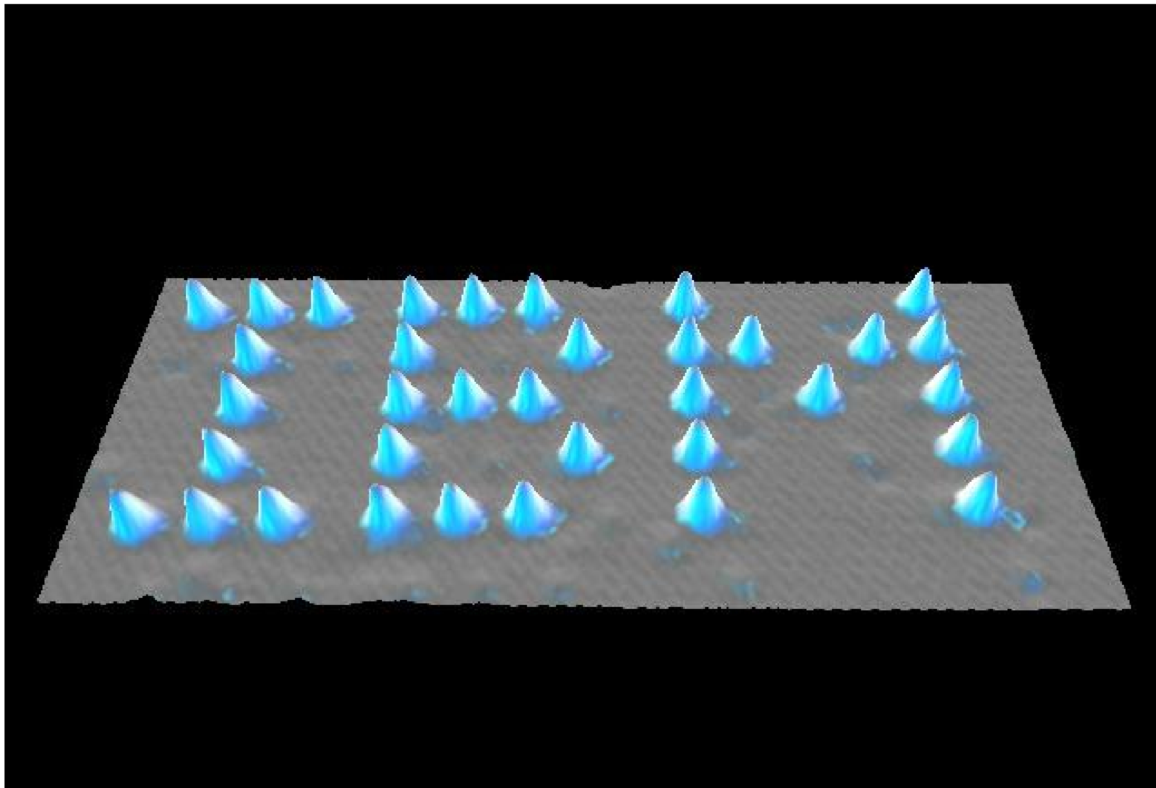


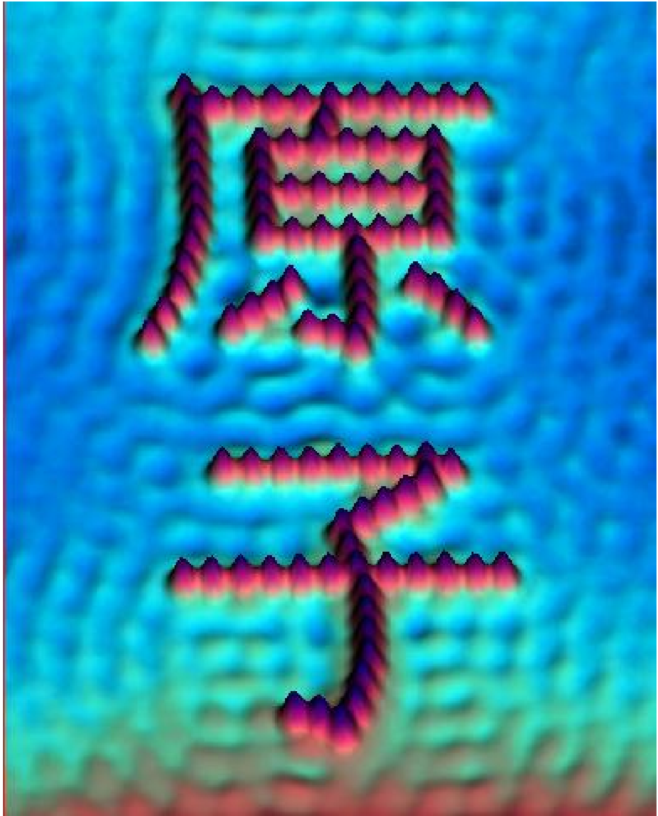
STM of Si(111) (7x7) at good (top left) and optimal (right) resolution

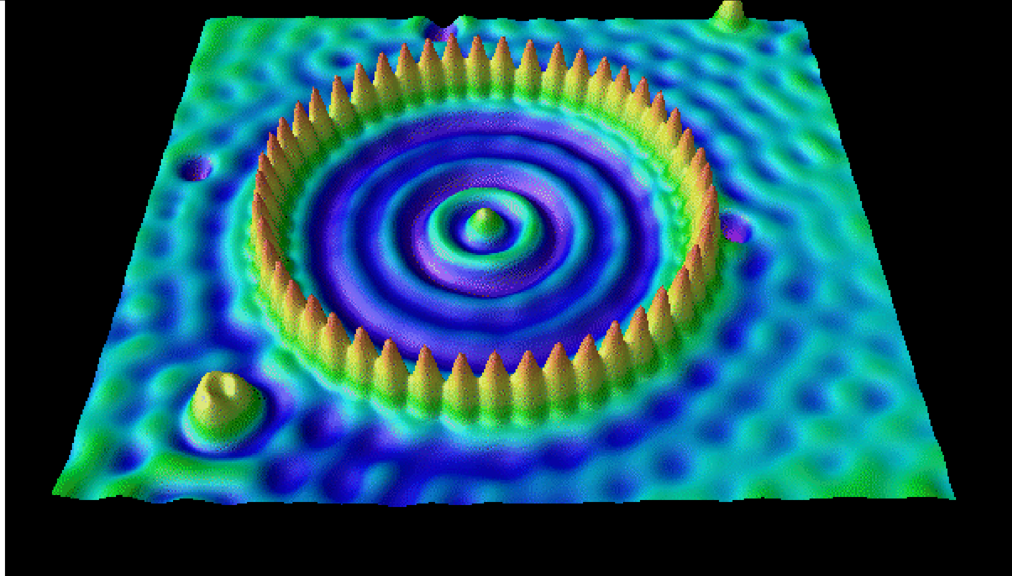




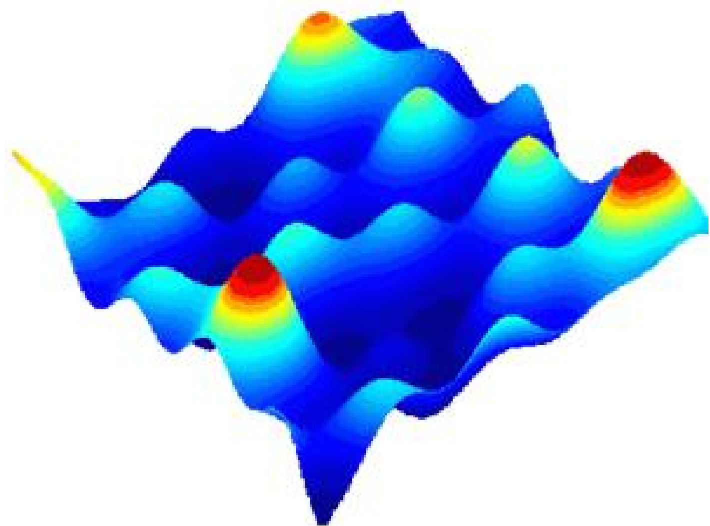
Calculated (left) STM pictures for the surface structure at right

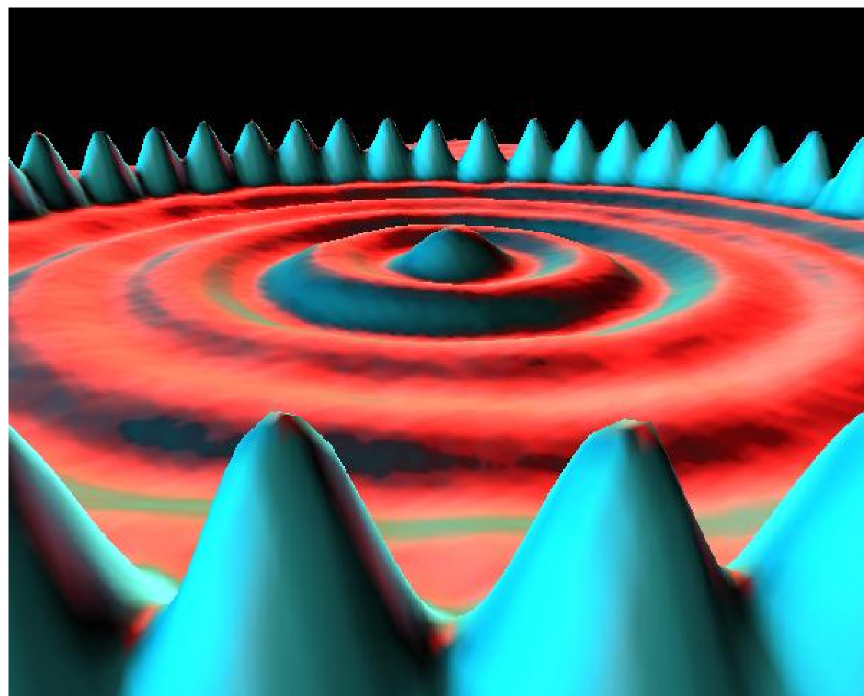


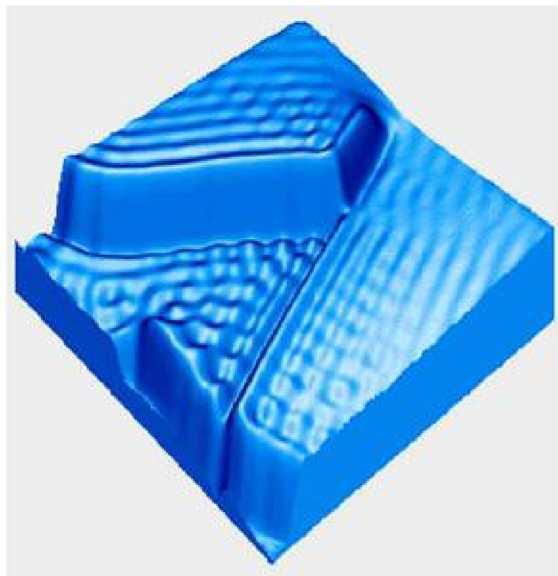


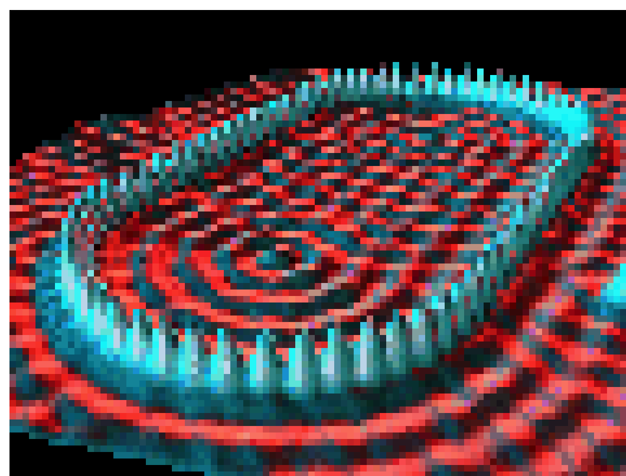


Atomic manipulation
using the STM tip

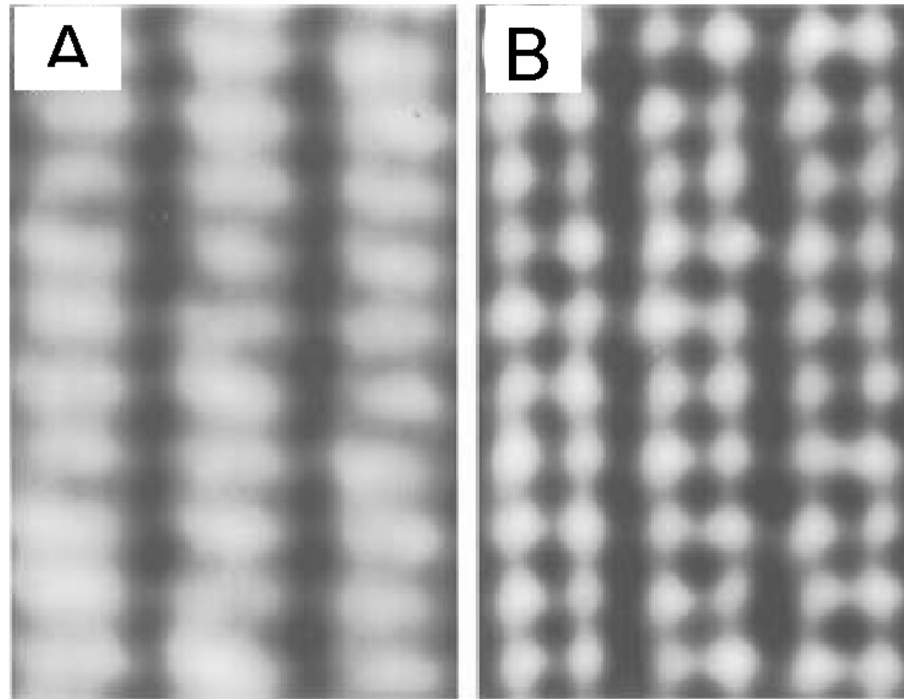


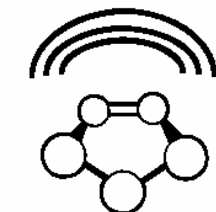


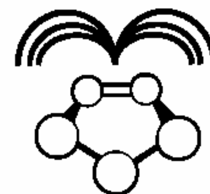




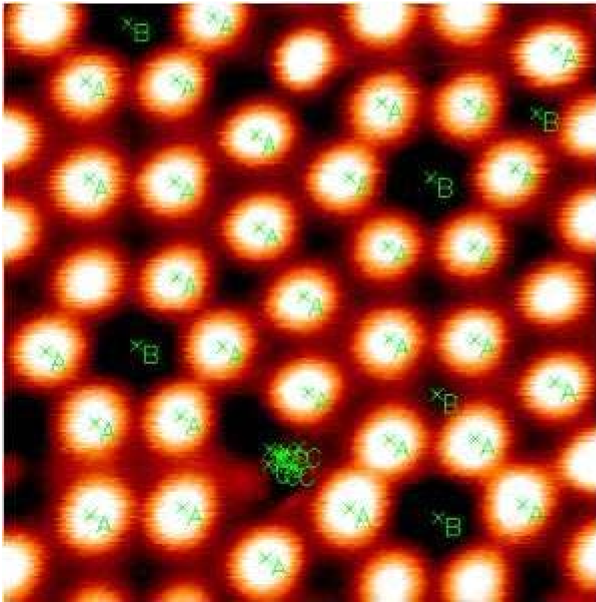
The influence of bias: Si(100) (1x2)

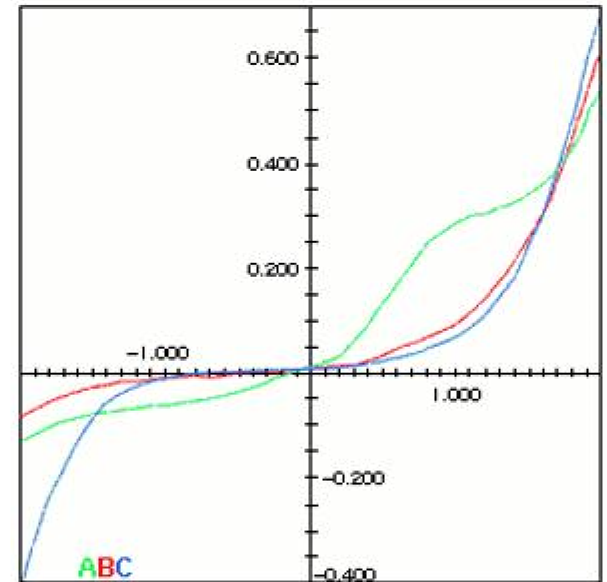






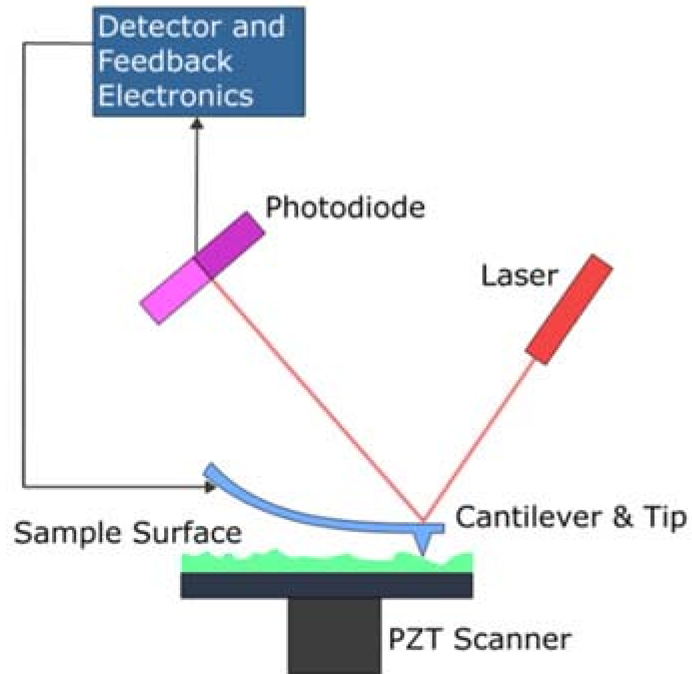
Spectroscopy: Si(111)

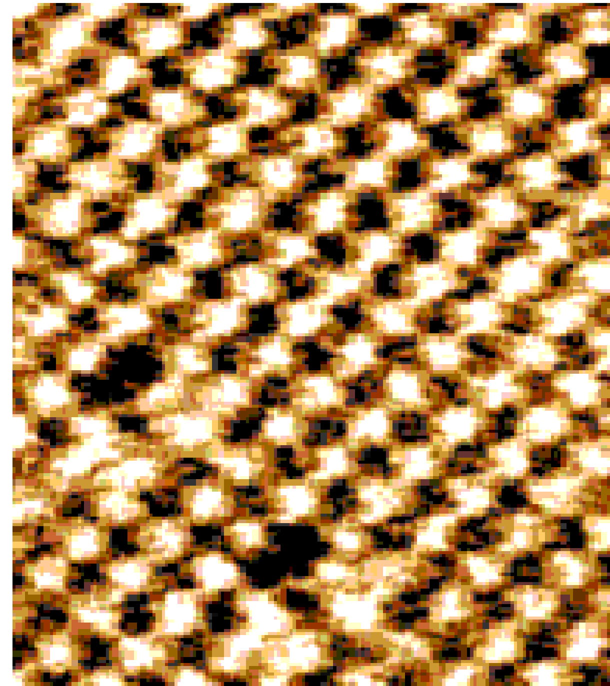




adatom sites A,
corner holes B
vacancy sites C

Atomic force microscopy (AFM)





AFM image of NaCl