

Lecture 7: STM Atomic Imaging of Metal and Semiconductor Surface

- Surface structure vs. surface science;
- Atomic imaging of surface with STM;
- Nanoscale surface probing with STM;
- Exploration of surface catalysis.

In history of Nobel Prize in Chemistry:

14% of the Years, 19% of the winners went to catalysis

Surface Science



**The Nobel Prize in Chemistry
2007**

"for his studies of chemical processes on
solid surfaces"



Gerhard Ertl

Germany

Fritz-Haber-Institut der Max-Planck-
Gesellschaft

Berlin, Germany

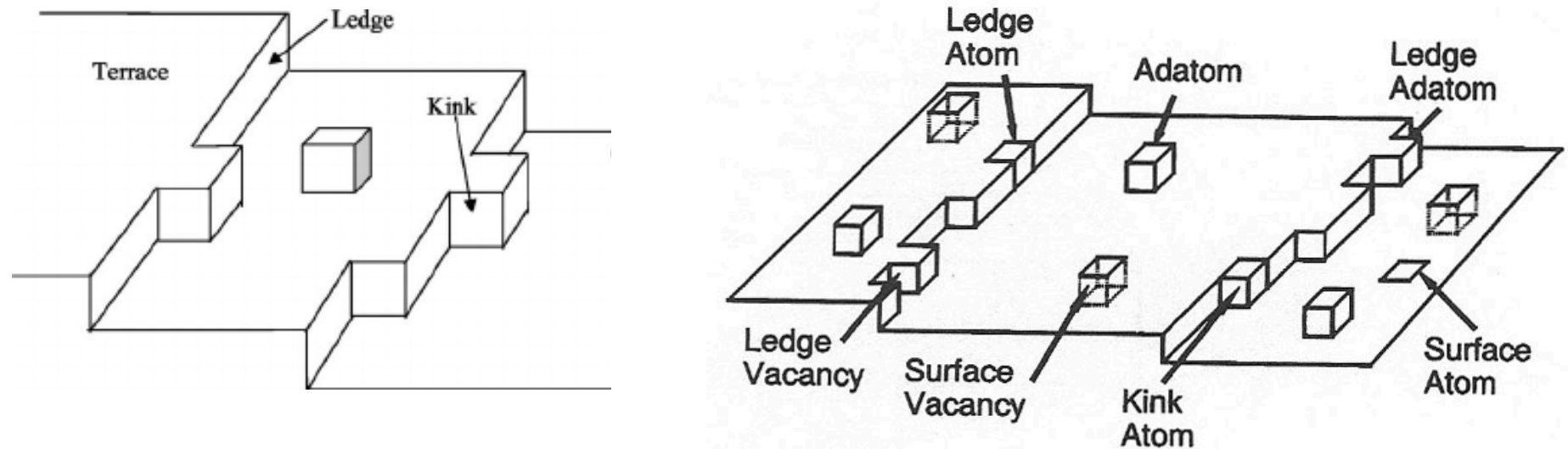
b. 1936

Description of crystalline surface: Terrace Step Kink (TSK) model

TSK model, also referred to as **Terrace Ledge Kink (TLK)** model, describes the thermodynamics of crystal surface formation and transformation, as well as the energetics of surface defect formation. The TSK model can be applied successfully to surface science topics such as crystal growth (including epitaxial growth), surface diffusion, roughening, and vaporization, because it considers the two major points about the surface:

1. The **energy of an atom's position** on a crystal surface is determined by its bonding to neighboring atoms;
2. Phase **growth or transition** simply involves the counting of broken and formed bonds.

The TSK model was originally proposed by **Kossel and Stranski**.

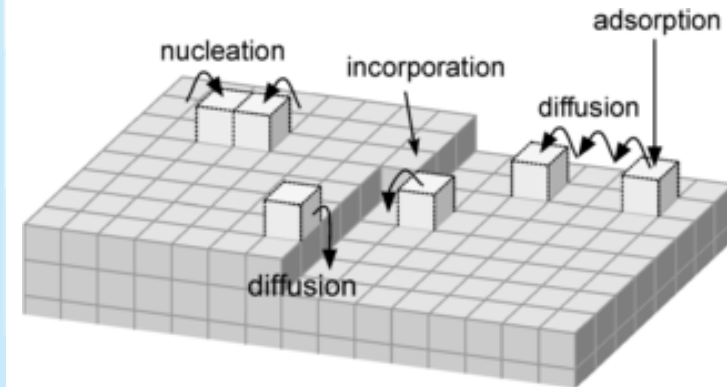
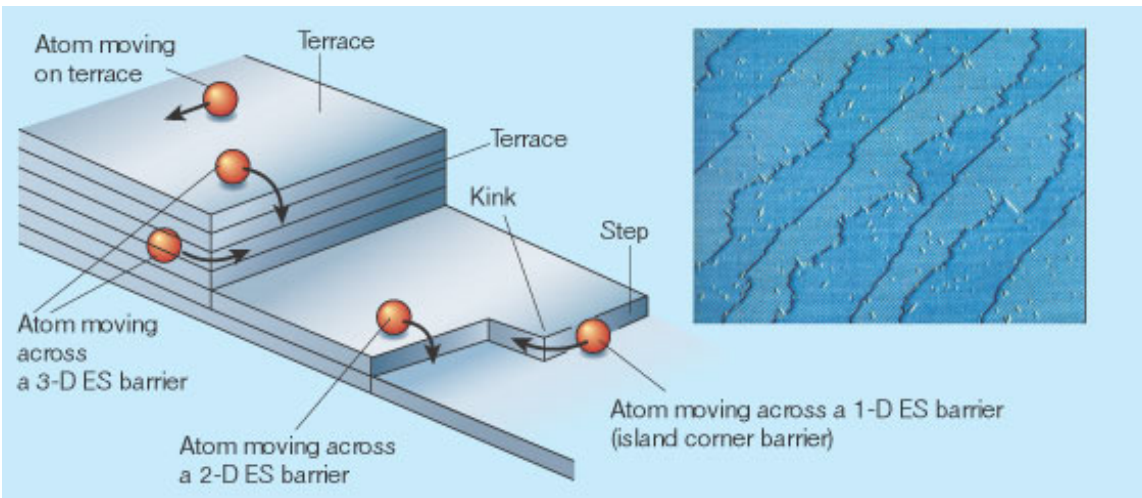


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note:

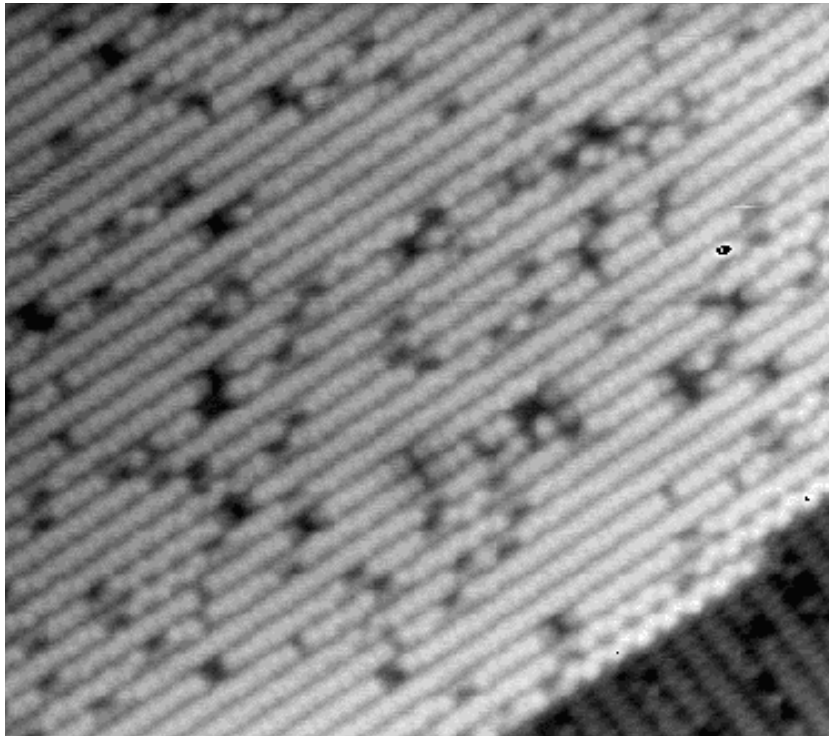
ES barrier refers to Ehrlich-Schwoebel (ES) step-edge barrier.

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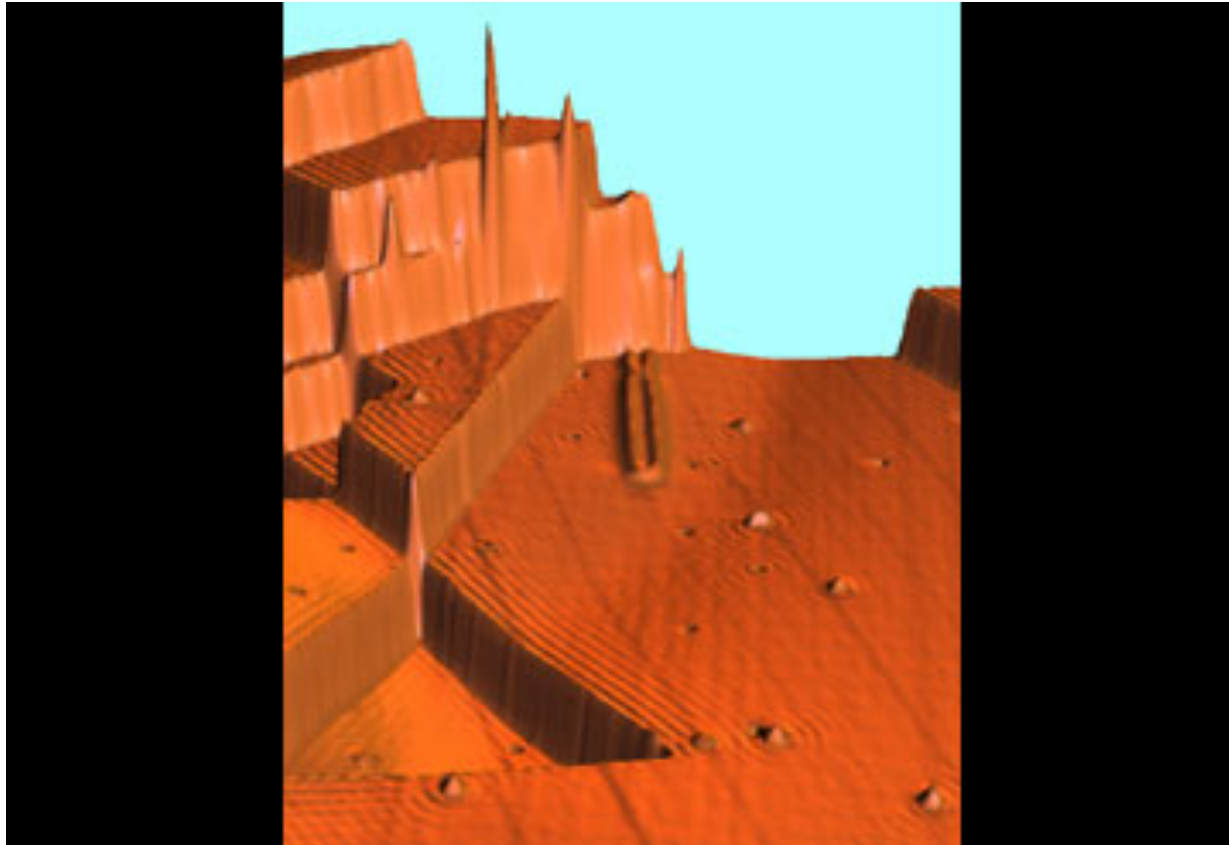
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An **STM** image of the Si(001) surface. There is a **step** in the bottom right corner.

Beautiful view under STM: Terrace



A Copper Surface

This is what a copper surface looks like through the STM

What is Surface?

- Surface --- the boundary layer between a solid and a vacuum, gas, or liquid. Occasionally surface also refers to the boundary between liquid and gas phase.
- Surface differs substantially from the interior of the solid both in chemical composition and physical properties (what differences?): *unsaturated atoms for binding or adsorption, more exposure to air or liquid, more?*
- As the dimension of a solid becomes smaller (in nanometer range), the ratio of surface atoms increases dramatically (draw scheme on board: 4 atoms cube). *For a 3 nm CdSe nanoparticle, ~ 50% atoms are on surface, while for a large bulk material, the surface layer is generally only a tiny fraction of the total solid.*

Surface Science

- **Surface science** is the study of **physical** and **chemical** phenomena that occur at the surfaces.
- **Surface science** includes the fields of surface chemistry and surface physics, though some related practical applications are classed as **surface engineering**.
- **Surface science** covers the concepts such as
 1. heterogeneous catalysis, see slides
 2. semiconductor devices (p-n junctions, interfacial CT), see slides
 3. fuel cells, see slides
 4. self-assembled monolayers, see slides
 5. corrosion and adhesion,
 6. metal/alloy surface,
 7. behavior and function of biological membranes.

Surface Chemistry: *about structure or composition change*

- **Surface chemistry** can be roughly defined as the study of chemical reactions at interfaces, aiming at modifying the chemical composition of a surface by incorporation of selected elements or functional groups that produce various desired effects or improvements in the properties of the surface or interface. Surface chemistry is of particular importance to the field of heterogeneous catalysis.
- Particularly, the adhesion of gas or liquid molecules to the surface is known as adsorption. Although this can be due to either chemisorption or by physisorption, these two are included in surface chemistry.
- The field of **surface chemistry** started with heterogeneous catalysis pioneered by Paul Sabatier on hydrogenation and Fritz Haber on the Haber process. Irving Langmuir was also one of the founders of this field, and the Langmuir adsorption equation is used to model monolayer adsorption where all surface adsorption sites have the same affinity for the adsorbing species.
- Most recent developments in surface sciences include the 2007 Nobel Prize of Chemistry winner Gerhard Ertl's advancements in surface chemistry, specifically his investigation of the interaction between carbon monoxide molecules and platinum and other catalysts surfaces, as well as their catalytic conversion into carbon dioxides.

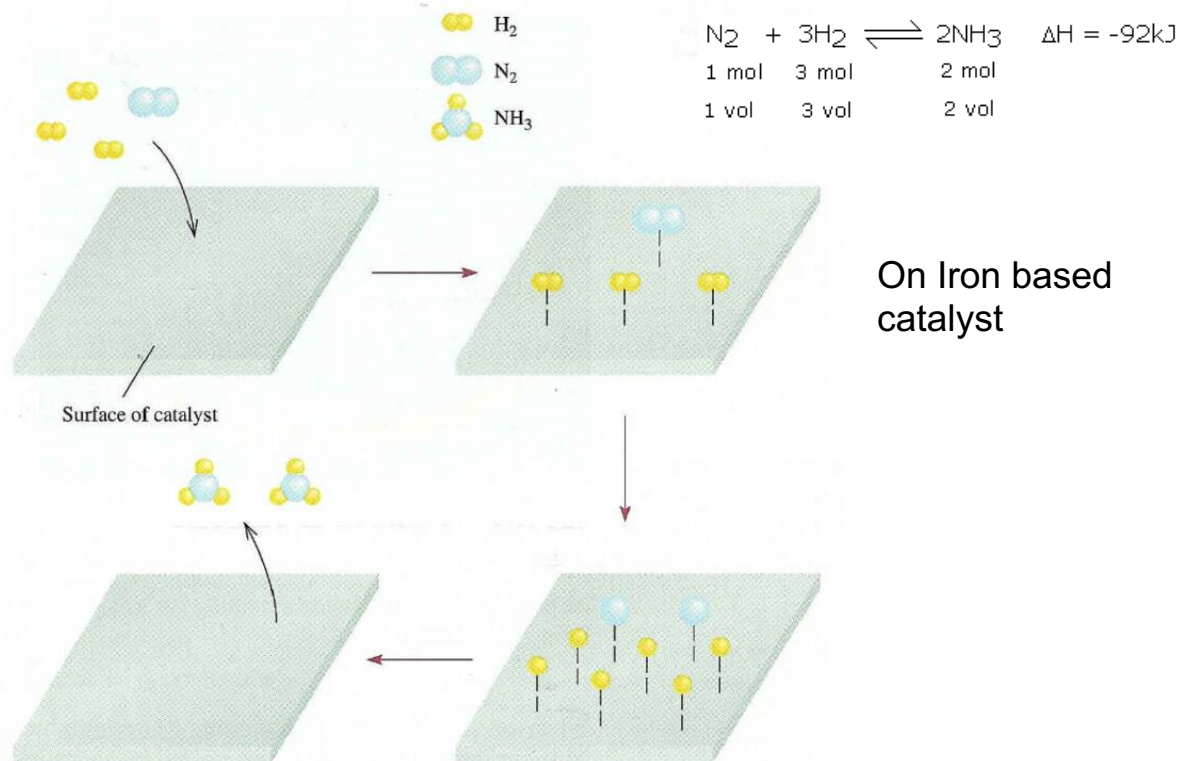
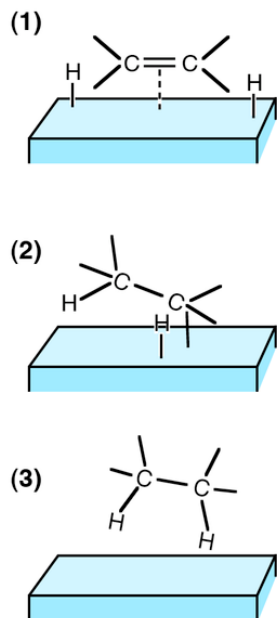
Surface Physics: more general and broader

- **Surface physics** can be roughly defined as the study of physical changes that occur at interfaces. Some of the things investigated by surface physics include surface states, surface diffusion, surface reconstruction, surface phonons and plasmons, epitaxy and surface enhanced Raman scattering, the emission and tunneling of electrons, spintronics, and the self-assembly of nanostructures on surface. Very often, **Surface physics** overlaps with **surface chemistry**, particularly at the very ultimate atomic or molecular scale, where physics and chemistry are no longer distinct by the traditional definition.
- As traditionally defined, a physical change in a substance doesn't change what the substance is. In a chemical change where there is a chemical reaction, a new substance is formed and energy is either given off or absorbed. For example, if a piece of paper is cut up into small pieces it still is paper. This would be a physical change in the shape and size of the paper. If the same piece of paper is burned, it is broken up into different substances that are not paper. *Then, what about putting two atoms or molecules together under STM? --- an atomic process, with no distinction between chemistry and physics.*
- Also, as traditionally defined, physical changes can be reversed, chemical changes cannot be reversed with the substance changed back without extraordinary means, if at all. For example, a cup of water can be frozen when cooled and then can be returned to a liquid form when heated. *However, this definition does not stand at the atomic scale. For example, under UHV a molecule like carbon mono-oxide can be reversibly adsorbed and desorbed from a metal (e.g., platinum) surface? is such a adsorption or desorption physical or chemical?*

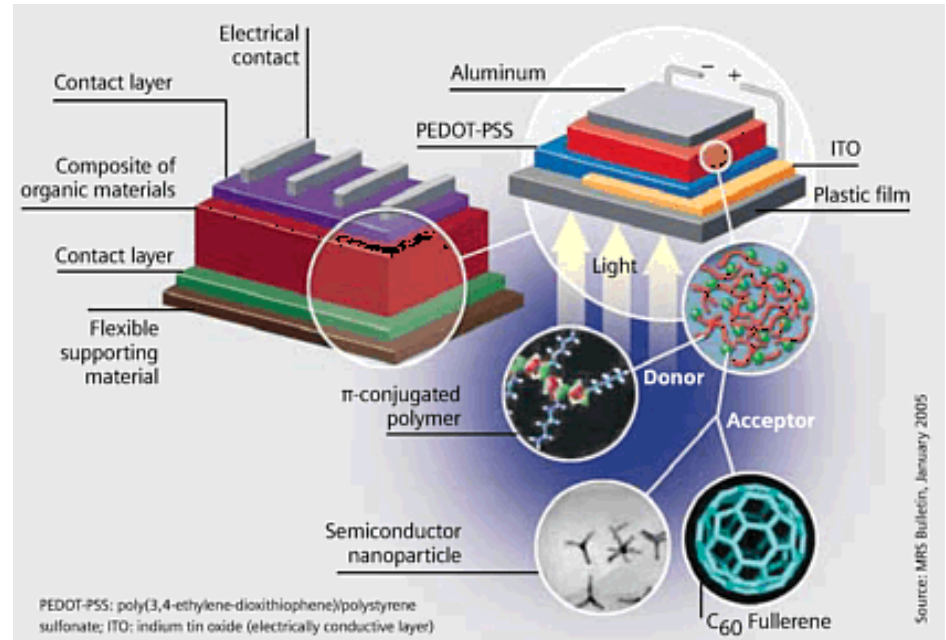
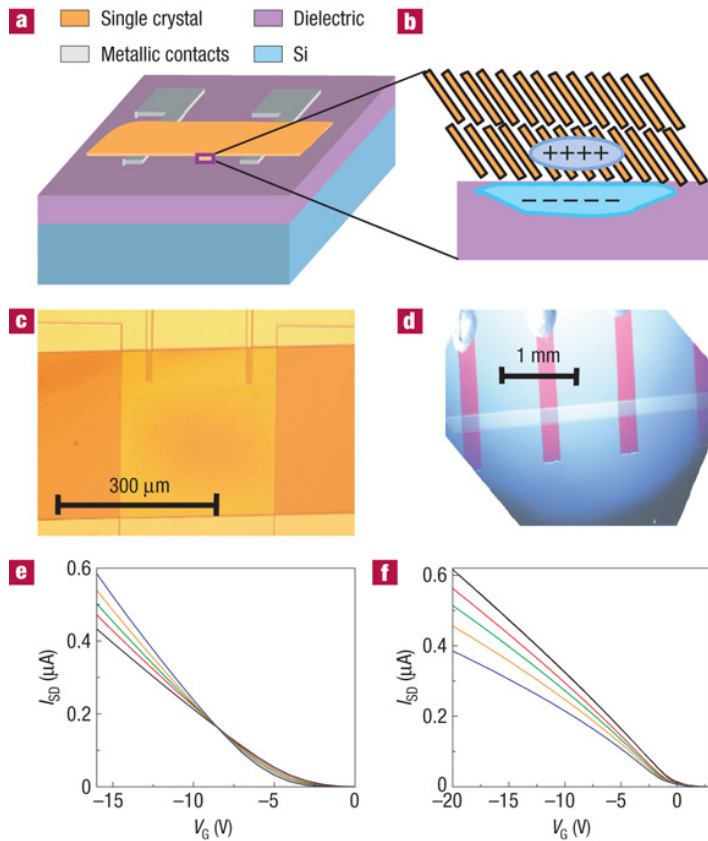
Heterogeneous catalysis

- In chemistry, **heterogeneous catalysis** refers to the form of catalysis where the phase of the catalyst differs from that of the reactants. Phase here refers not only to solid, liquid, vs gas, but also immiscible liquids, e.g. oil and water. The great majority of practical heterogeneous catalysts are solids and the great majority of reactants are gases or liquids.
- Heterogeneous catalysis** is of paramount importance in many areas of the chemical and energy industries.
- Heterogeneous catalysis** has attracted **3 times Nobel prizes** for **Fritz Haber and Carl Bosch in 1918, Irving Langmuir in 1932, and Gerhard Ertl in 2007**.
- Two typical cases of **Heterogeneous catalysis**: hydrogenation pioneered by Paul Sabatier (who got Nobel prize in 1912 for discovering Grignard reagent, but not hydrogenation catalysis), and Haber process for nitrogen fixation by Fritz Haber.

Surface catalyzed Hydrogenation on Nickel



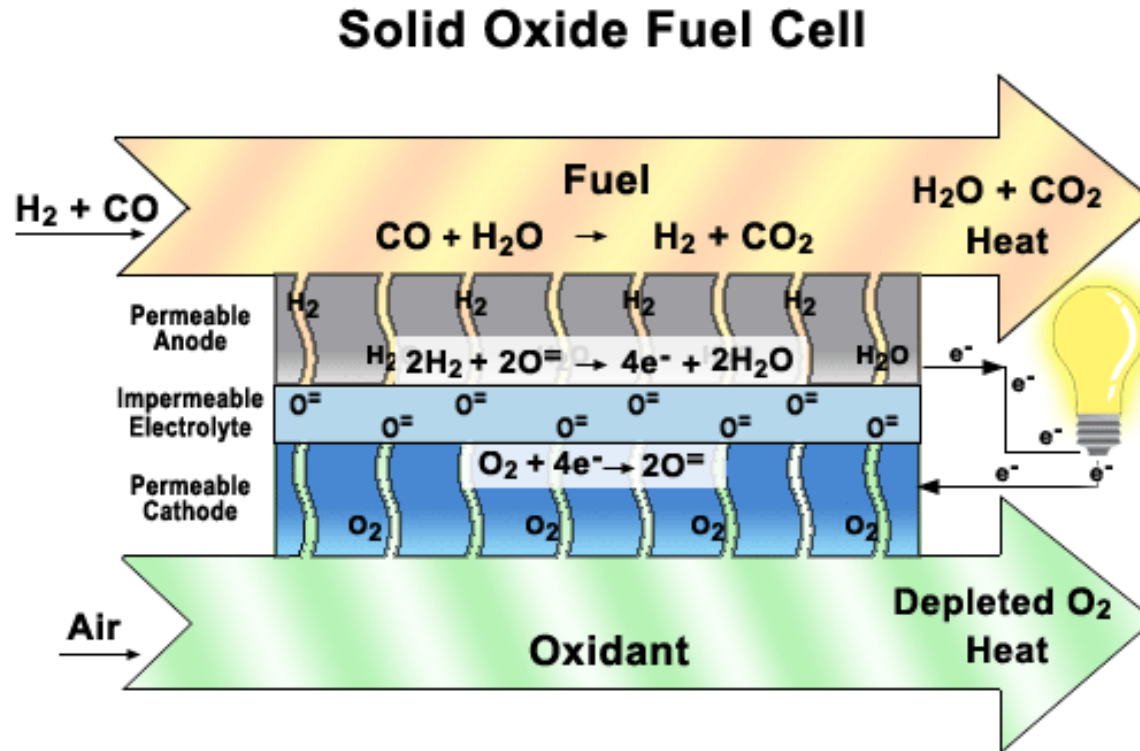
Interface is critical for semiconductor devices: *where molecules interact*



Plastic, paint-on solar cells

High-quality organic single-crystal transistors
Nature Materials 5, 982 - 986 (2006)

Fuel cells: *controlled by interfacial molecular processes and reactions*



A **fuel cell** is an [electrochemical cell](#) that converts a source fuel into an electric current. It generates electricity inside a cell through reactions between a fuel and an oxidant, triggered in the presence of an electrolyte. The reactants flow into the cell, and the reaction products flow out of it, while the electrolyte remains within it. Fuel cells can operate continuously as long as the necessary reactant and oxidant flows are maintained.

Typical methods for surface analysis

Surface analysis is crucial for explaining many surface phenomena and improving the properties of many solid materials and devices.

Two major instrumentation techniques for surface analysis:

1. Surface spectroscopy:

- a) identifying the surface chemical species and determining the concentrations;*
- b) providing both qualitative and quantitative (less used) information about the composition of surface layer (a few to a few tens of Å depth).*

Two major spectroscopy techniques:

X-ray photoelectron spectroscopy (XPS); Auger electron spectroscopy (AES) --- depth profile of composition via sputtering

2. Surface microscopy:

- a) imaging the surface and determining the morphology, atomic crystalline structure, and other physical properties and features at different size scale (nanometers to micrometers);*
- b) 3-dimensional surface structure with high resolution.*

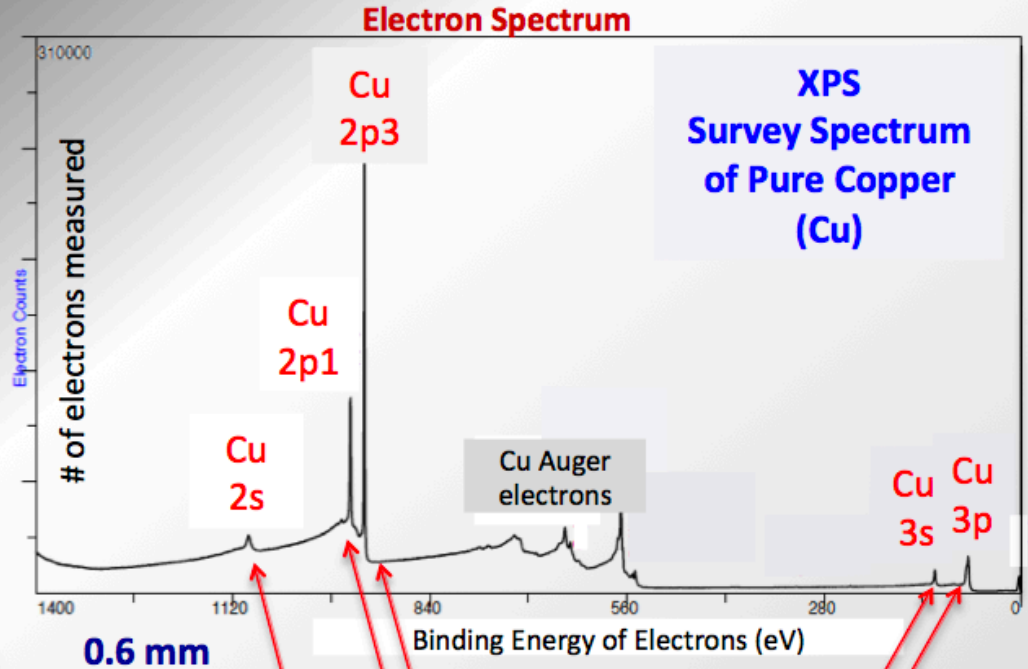
X-ray Gun

XPS = X-ray Photo-electron Spectroscopy*

*aka ESCA

Aluminum X-rays (Photons)
Energy=1486 eV

X-rays IN
Electrons OUT
Inside Vacuum



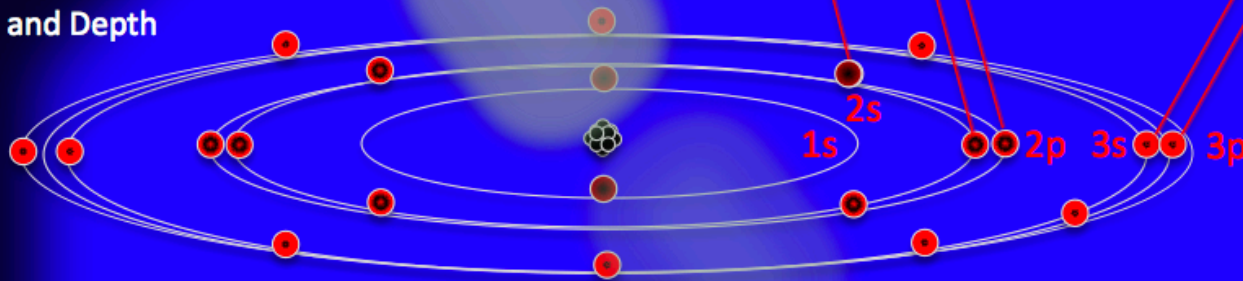
0.6 mm

0.4 mm

Usual Analysis Area and Depth

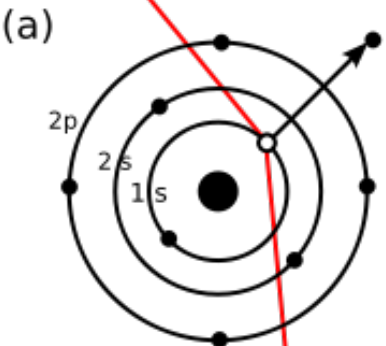
10 nm
(0.01 micron)

X-rays excite atoms.
Electrons jump out.

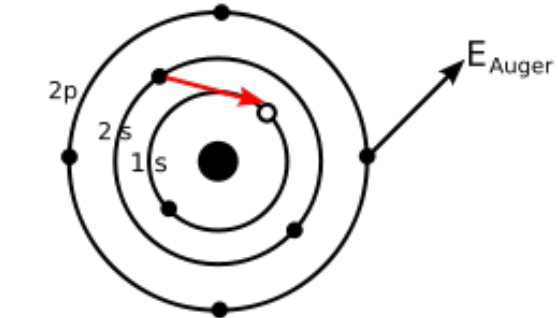
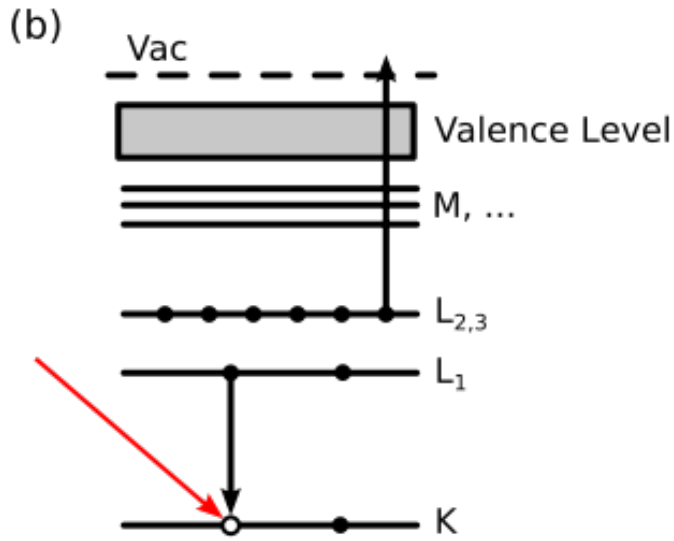


Top 20 atomic layers

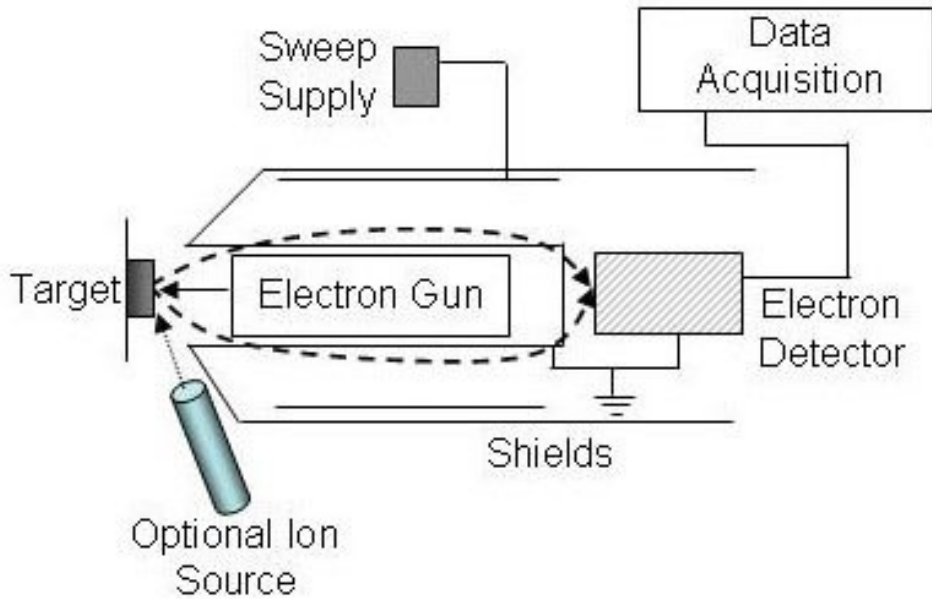
Auger electron spectroscopy



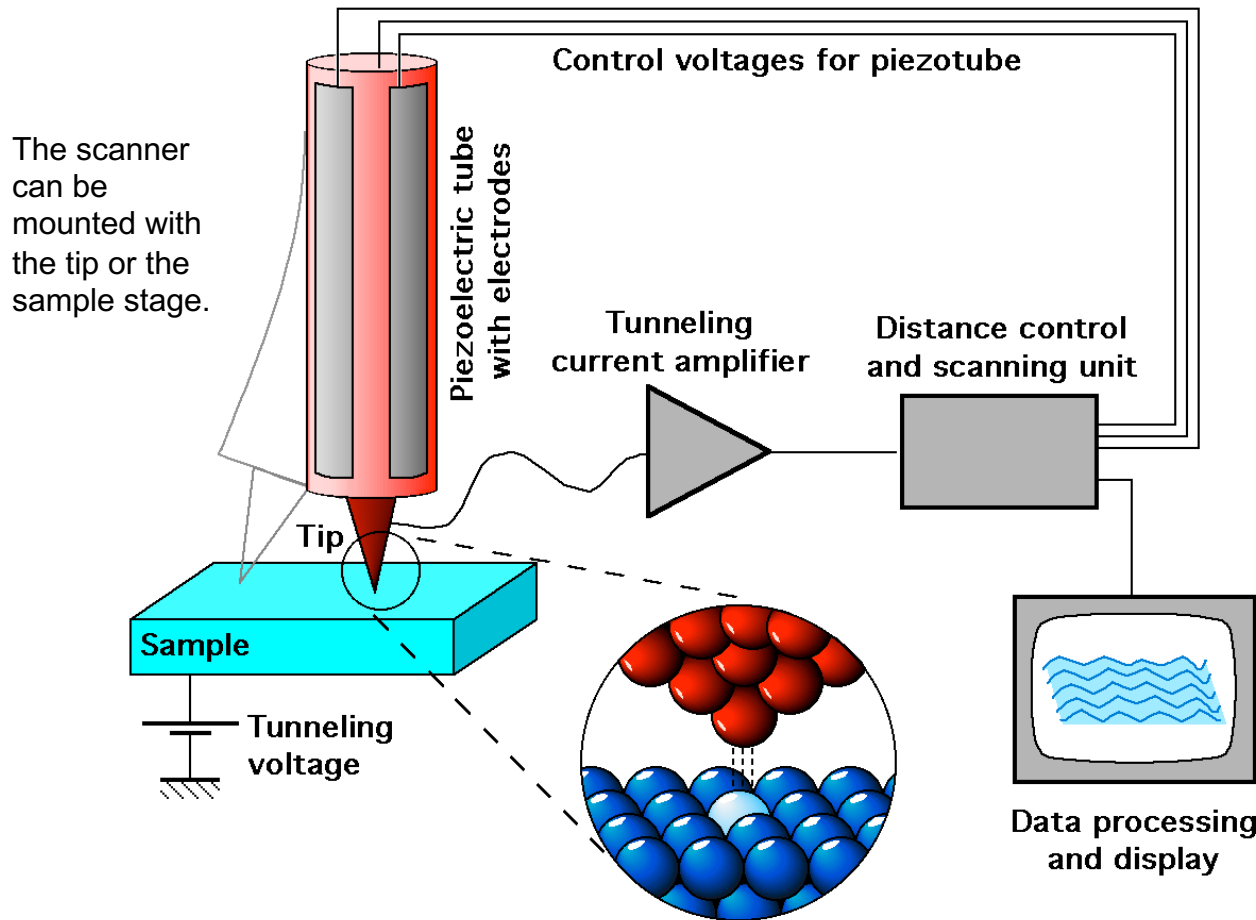
Electron collision



Auger electron emission



Basic components of STM:



Five basic components:

1. Metal tip,
2. Piezoelectric scanner,
3. Current amplifier (nA),
4. Bipotentiostat (bias),
5. Feedback loop (current).

- Tunneling current from tip to sample or vice-versa depending on bias;
- Current is exponentially dependent on distance;
- Raster scanning gives 2D image;
- Feedback is normally based on constant current, thus measuring the height on surface.

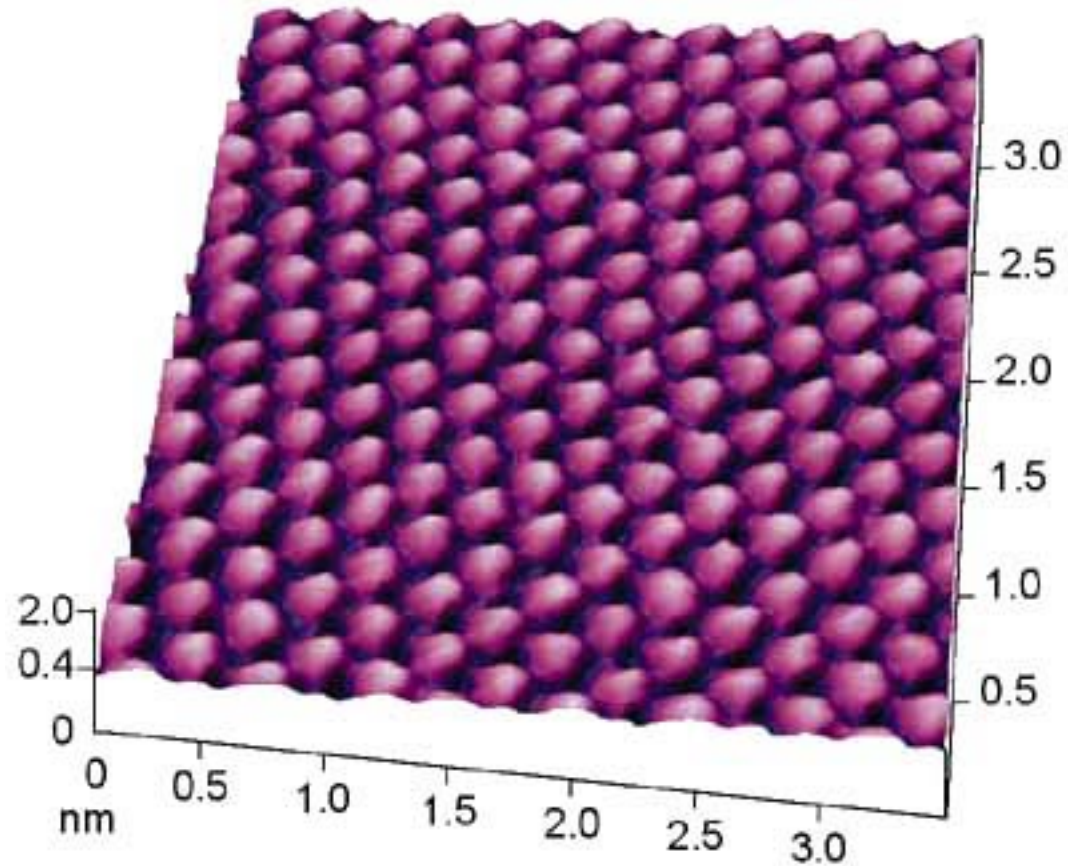
Advantages of STM for surface analysis

- *High resolution (angstrom to nanometers) **scanning**, and atomic or even sub-atomic level **imaging**. Atomic scale represent the ultimate resolution in terms of chemical composition and reactions.*
 - *Why able to probe atomic scale? --- single-atom scanning due to the tunneling mechanism, which is sensitive to the tip-sample distance. Only the outermost atom on tip is involved in measurement.*
 - *Feasible for both UHV and ambient conditions (only for some special samples which is not sensitive to surface contamination).*
 - *Direct imaging of atomic structure.*
 - *In situ characterization of surface reaction at atomic scale.*
-

Graphite surface: standard for STM

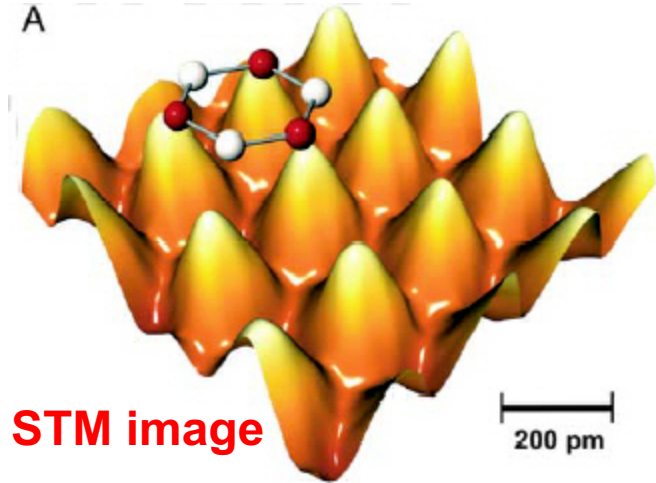
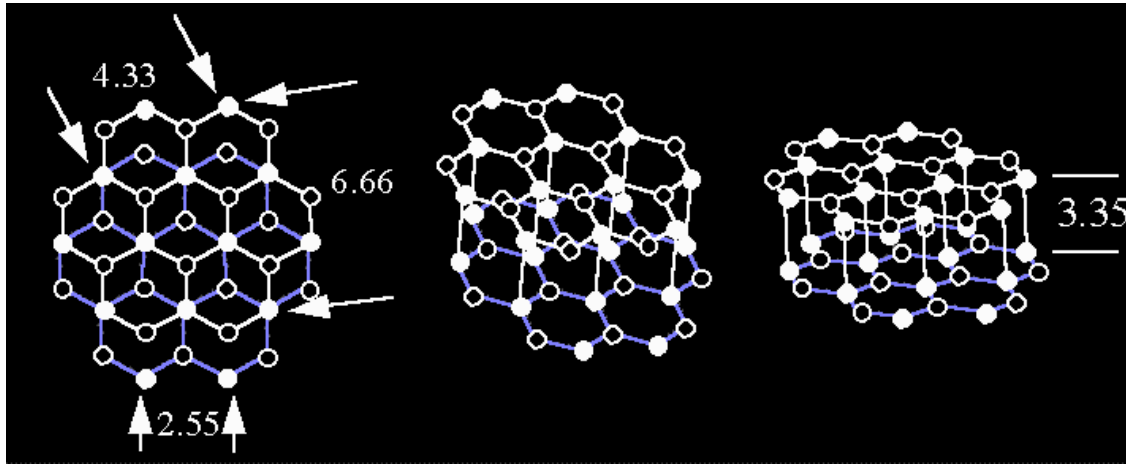
- One of the factors affecting resolution is *corrugation*, i.e. how much the electron density of surface atoms varies in height above the surface.
- *Graphite has a large corrugation, and is very planar, and thus is one of the easiest materials to image with atomic resolution.*
- *HOPG is used the most: highly ordered pyrolytic graphite.*

Graphite surface: standard for STM



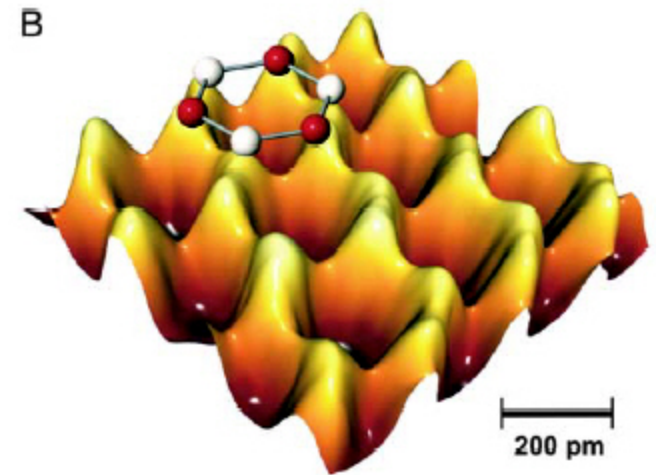
STM atomic resolution on Highly Oriented Pyrolytic Graphite

STM does NOT probe the nuclear position directly, but rather it is a probe of the **electron density**, so STM images do not always show the position of the atoms.



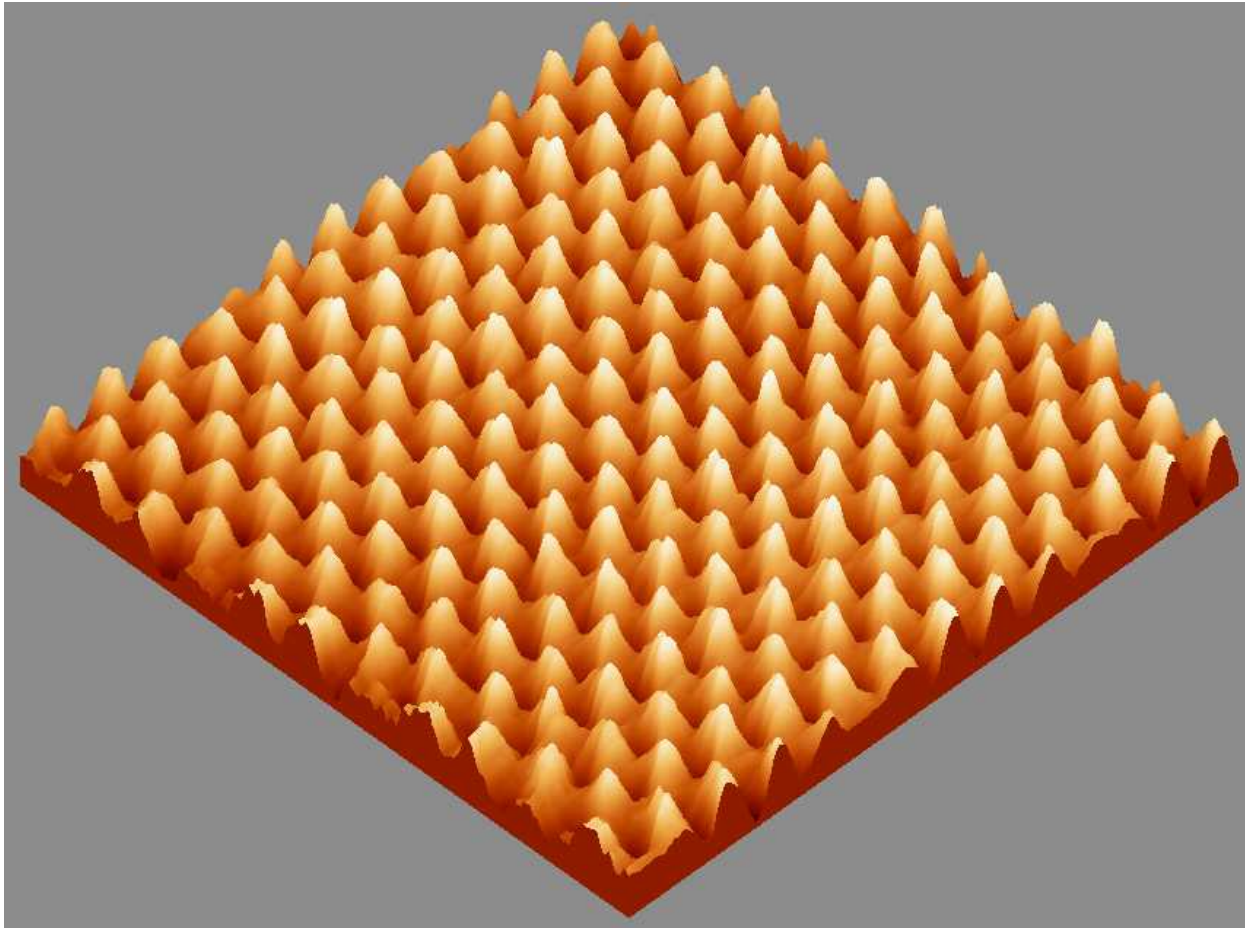
Graphite layer comprises of totally conjugated carbons as demonstrated above. Among the 6 carbons in a ring, only the 3 β atoms (marked as open circle) can be imaged under constant current mode, since these 3 carbons give much higher tunneling current, which in turn is due to their much higher local density of states, resulting in so called “giant corrugations” (enormous apparent heights of atoms). So, STM image of a graphite layer shows a triangular lattice as shown on the right (Figure A).

However, AFM images individual atoms through the inter-atomic interaction feedback. The hexagonal carbon rings are visible for AFM imaging as shown on the right (Figure B), and the complete surface lattice is imaged.



AFM image

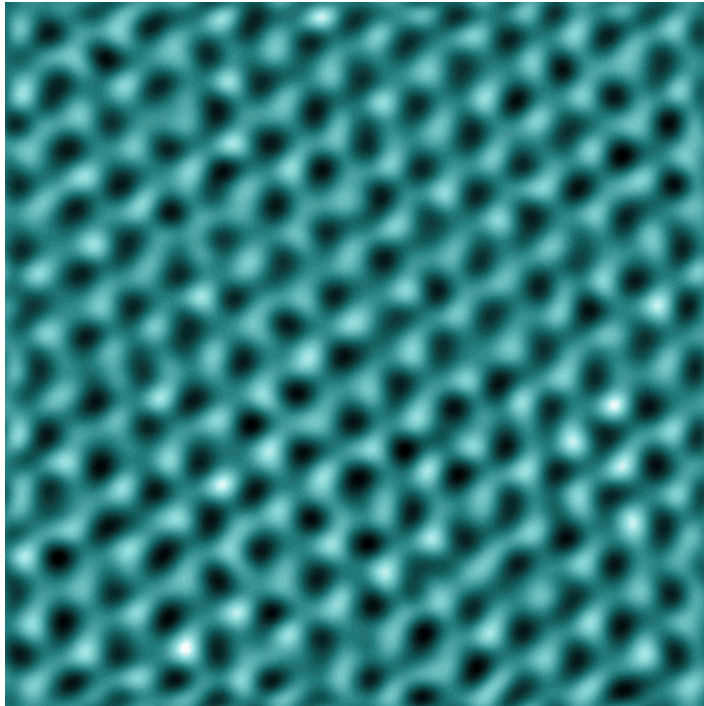
Graphite surface: standard for STM



STM atomic resolution on Highly Oriented Pyrolytic Graphite

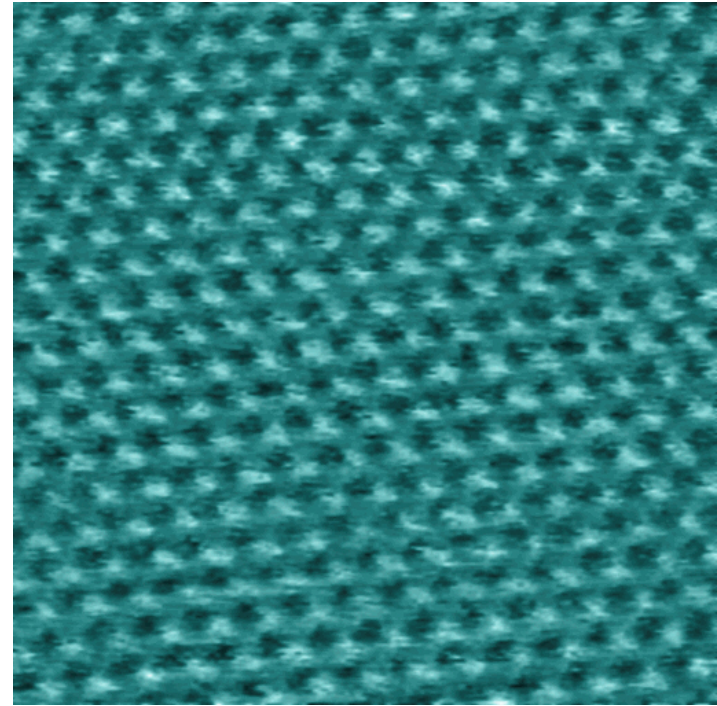
Imaged under constant current mode

Graphite surface: temperature dependence (thermal agitation of electrons)



77 K

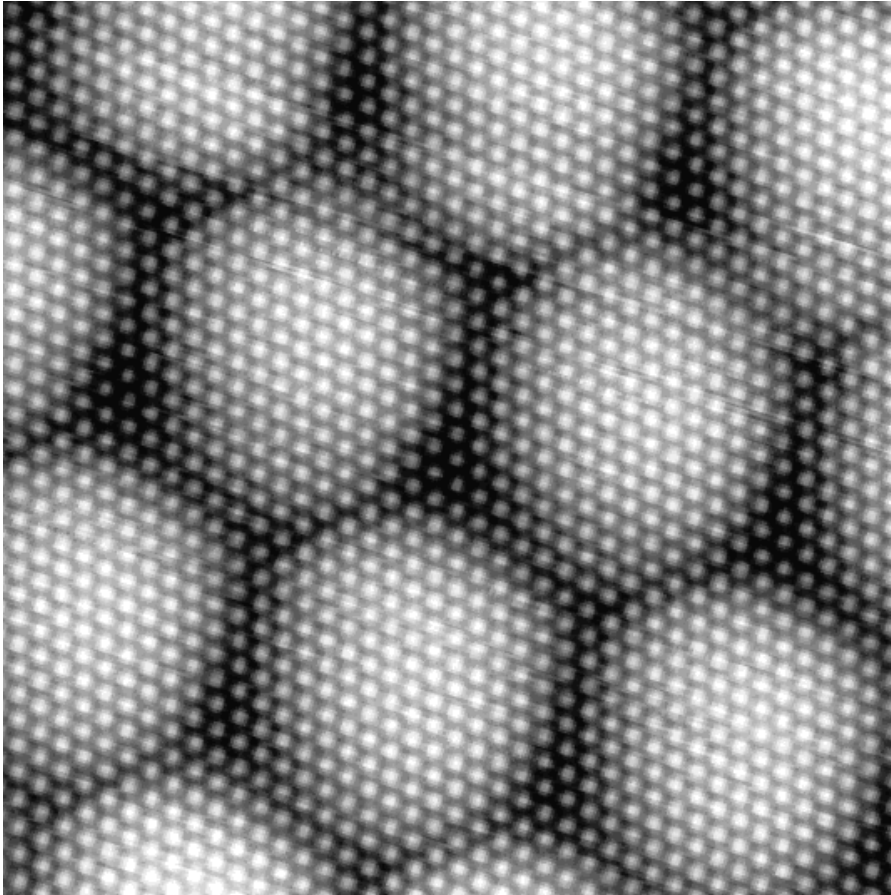
29 Å x 29 Å



295 K

37 Å x 37 Å

Xe atoms get organized on graphite lattice: epitaxial



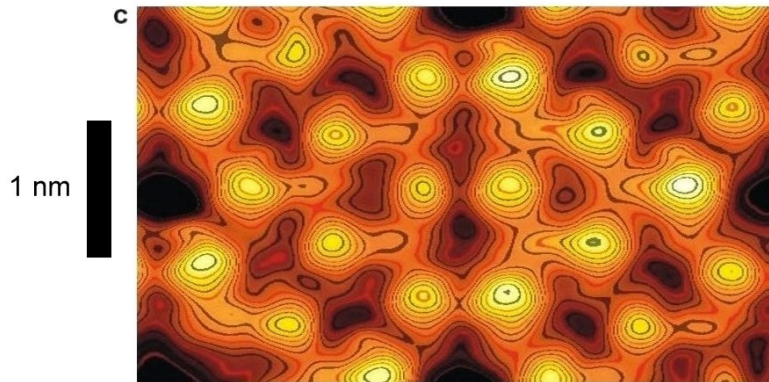
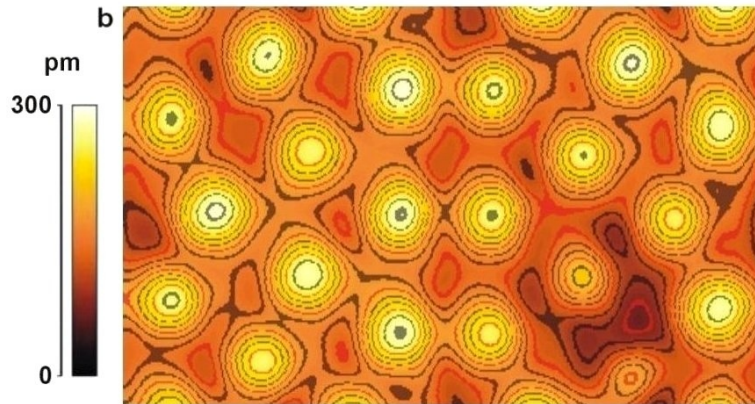
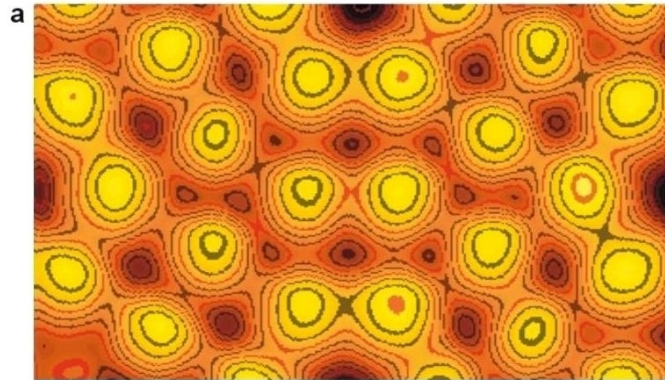
STM image of **Xe** on graphite

atomically resolved hexagonal Xe domains arranged in a **hexagonal honeycomb**-like structure.

image size 16 nm x 16 nm.

- Xe atoms form **hexagonal patches** about 15 atomic rows wide, separated by **domain walls** which appear in the STM signal as a smooth contrast several atomic rows in width.
- Xe atoms forming domain walls are slightly darker in the image than the surrounding Xe atoms in the domains, leading to an apparent height difference in the STM image of up to 0.03 nm (**0.3 angstrom!**).

Imaging Angular Momentum



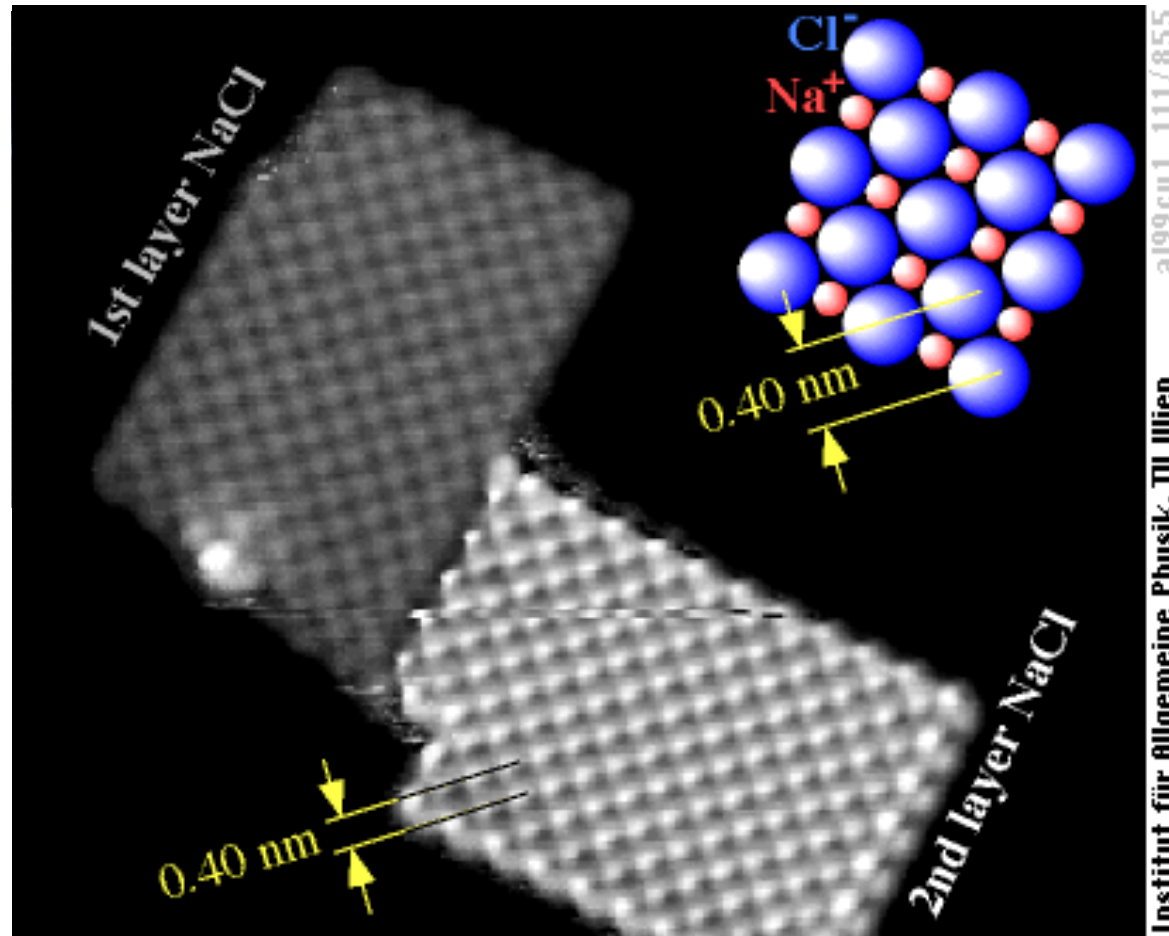
Experimental images of a Si surface imaged in the dynamic (constant height) STM mode.

The different radii of the atomic images in a)-c) are explained by different higher angular momentum tunneling states.

Images taken with tips made from different elements: a) silicon tip b) cobalt tip c) samarium tip

[\[Phys. Rev. B 68, \(2003\)\].](#)

Imaging single crystal lattice: NaCl



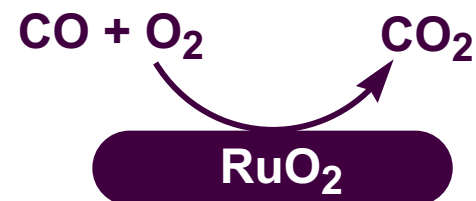
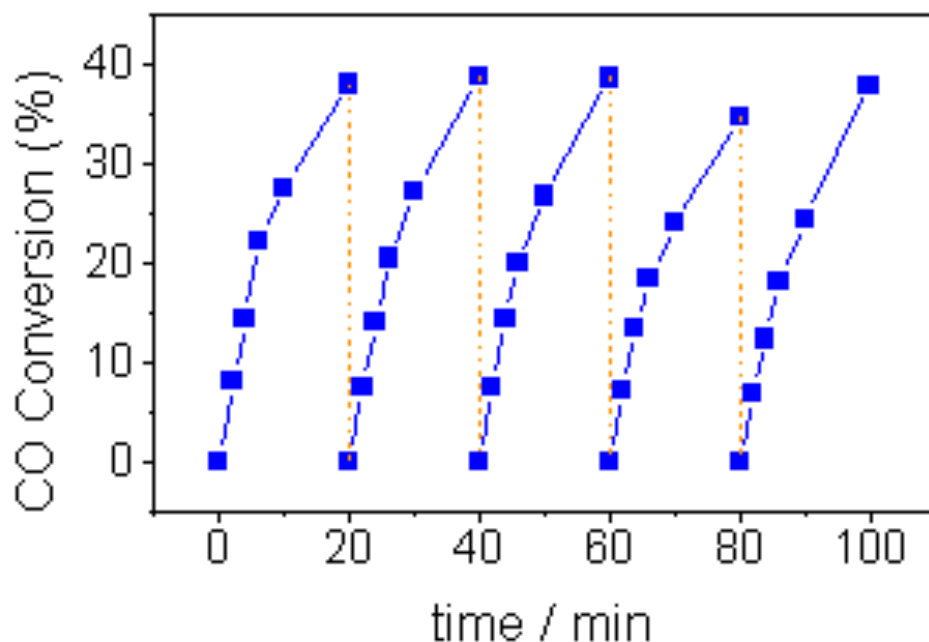
The aluminum supporting is shown black.

A case study of atomic imaging

Conversion of carbon mono-oxide (CO) to carbon dioxide (CO₂)

- Numerous applications in mining safety, vehicle exhaust treatment, carbon dioxide lasers, etc.
- Must be operated at room temperature.
- Cost effective: current catalysts are mostly based on precious metals like platinum.
- Development of new catalysts demands exploration of surface reaction mechanism, especially at atomic scale.

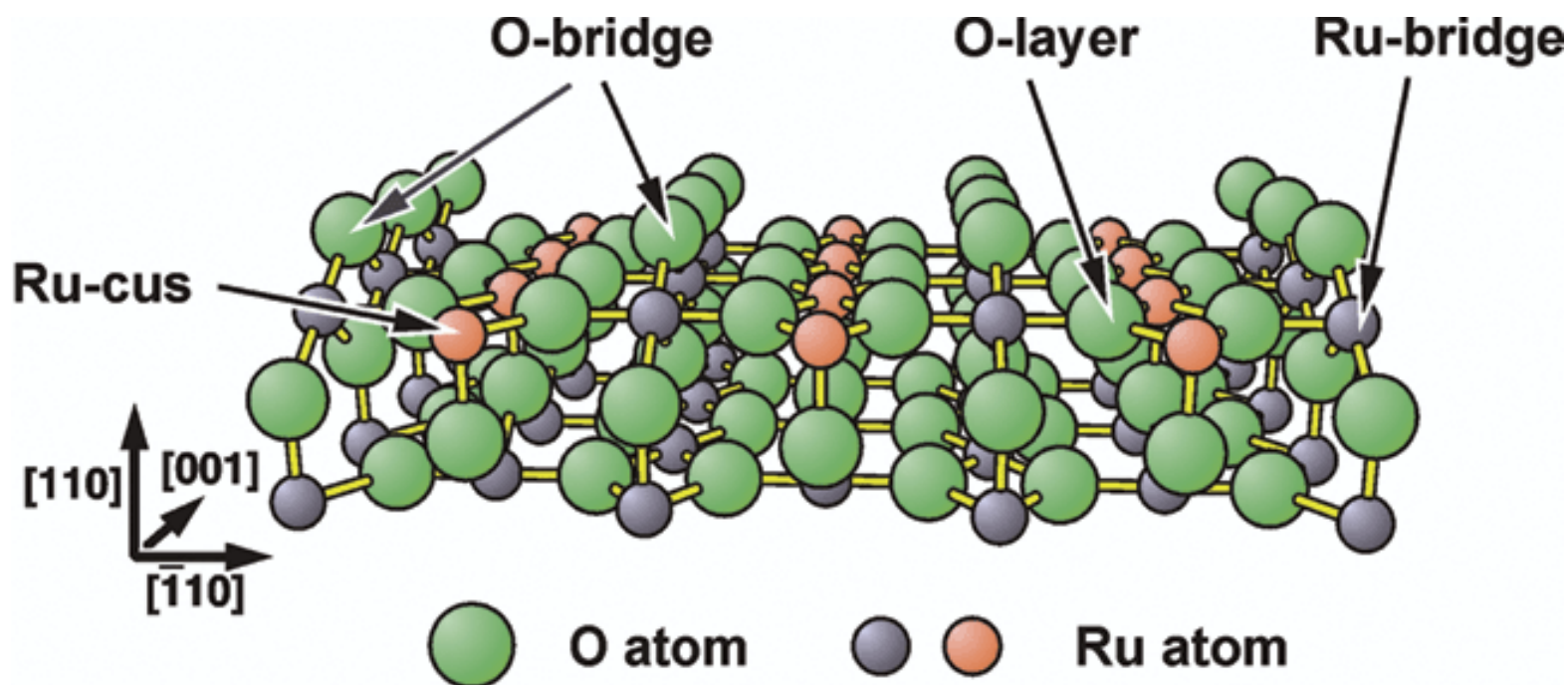
Room Temperature Oxidation of CO over Amorphous Nanocrystalline RuO₂



No significant loss of activity after 5 cycles

Five successive cycles for CO oxidation over a new oxidic catalyst

Ball-and-Stick Model of the RuO₂(110) Surface



Ru-cus: coordinatively unsaturated sites



2007

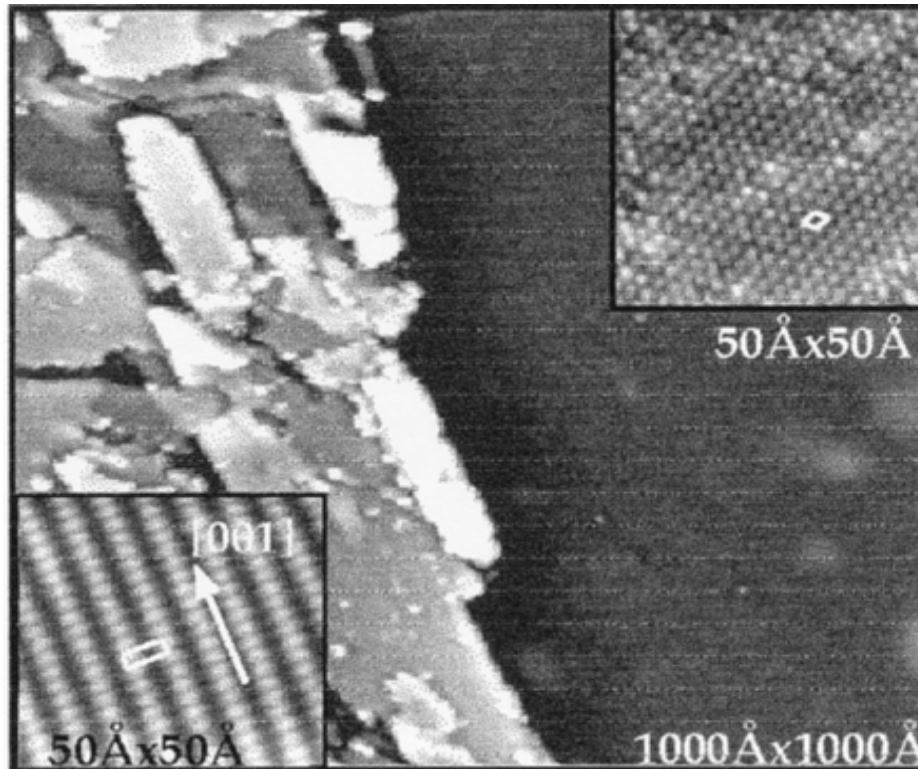


K. Jacobi, H. Over & **G. Ertl** et al. *Science* **2000**, 287, 1474.
J. Am. Chem. Soc. **2001**, 123, 11807.
J. Phys. Chem. B, **2002**, 106, 3422.

STM probing of RuO₂ single-crystal surface

On the left side, RuO₂(110) domains are visible.

The magnified inset shows the internal structure of this phase (parallel rows along the [001] direction) and its rectangular unit cell.



The right side represents a domain of the Ru(0001)-(1 × 1)-O surface;

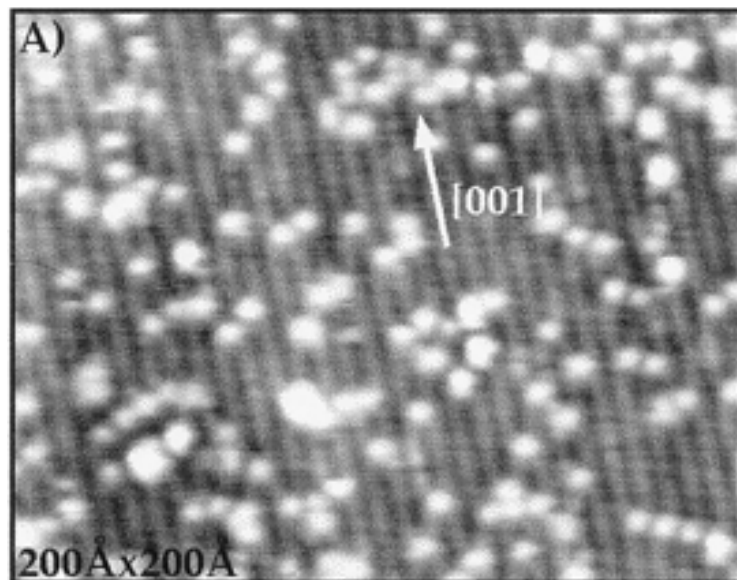
The magnified inset reveals a hexagonal arrangement of dots corresponding to the Ru(0001) lattice.

The dark spots mark the locations of the chemisorbed O atoms in the (1 × 1) overlayer.

The bright spots represent Ru atoms coordinated to three O atoms.

Large-scale STM image (1000 Å by 1000 Å) together with enlargements (50 Å by 50 Å) as insets. Tunneling parameters are $U = 1.21$ V and 0.46 nA

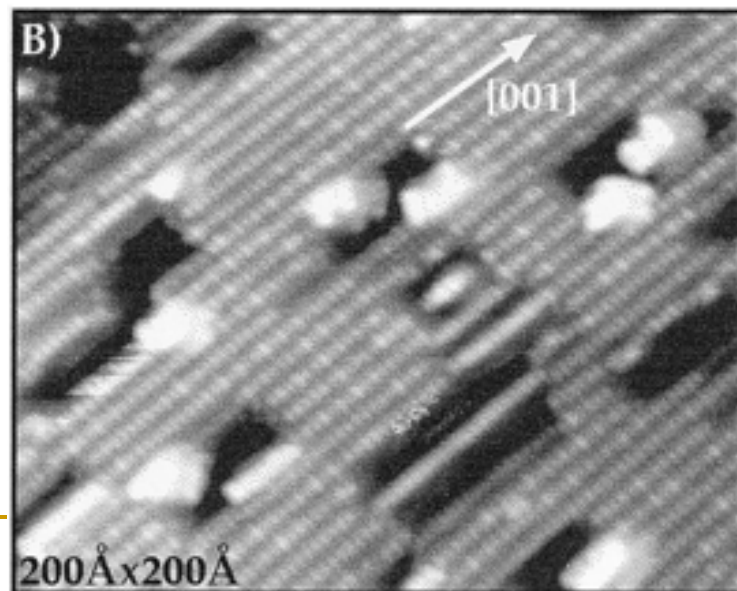
STM probing of RuO₂ single-crystal surface deposited with CO



STM image (200 Å by 200 Å, $U = 1.08$ V, $I = 0.46$ nA, constant current mode) of the RuO₂(110) surface after exposure of **10-layer of CO**.

The **CO molecules are imaged as bright protrusions** with an apparent height of 0.5 Å.

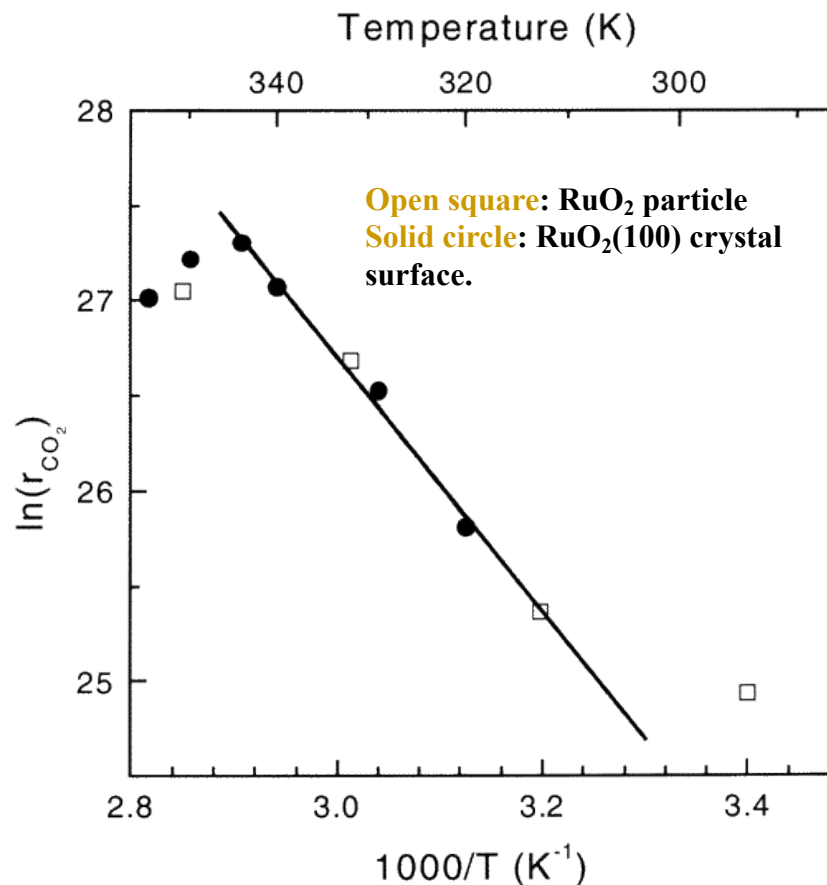
The CO molecules are sitting **between the bright rows (Ru)**.



STM image (200 Å by 200 Å, $U = 0.82$ V, $I = 3.34$ nA) of the CO-covered RuO₂(110) surface of after annealing to 600 K.

The removal of CO molecules is accompanied by the creation of **1.5 Å to 3.0 Å deep holes --- vacancies**, due to the partial removal of O atoms from the substrate lattice by reaction with CO.

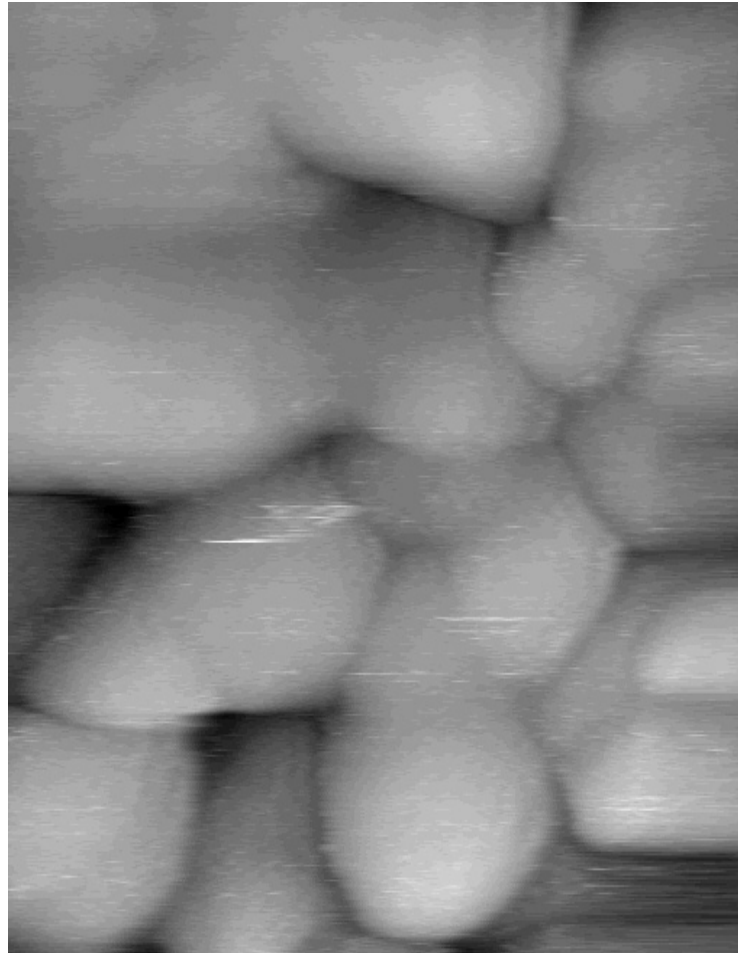
Excellent Agreement between **Ambient** and **UHV**: *Arrhenius plot*



The absolute pressure of CO & O₂ differed by about 10 orders of magnitude!

Note: Only the slope (activation energy) holds for the interest of agreement, as the absolute Y scale should be related to the active surface area. Y-axis is given in arbitrary units on which both sets of data were arbitrarily displaced vertically until best agreement was reached.

Real surface of Gold



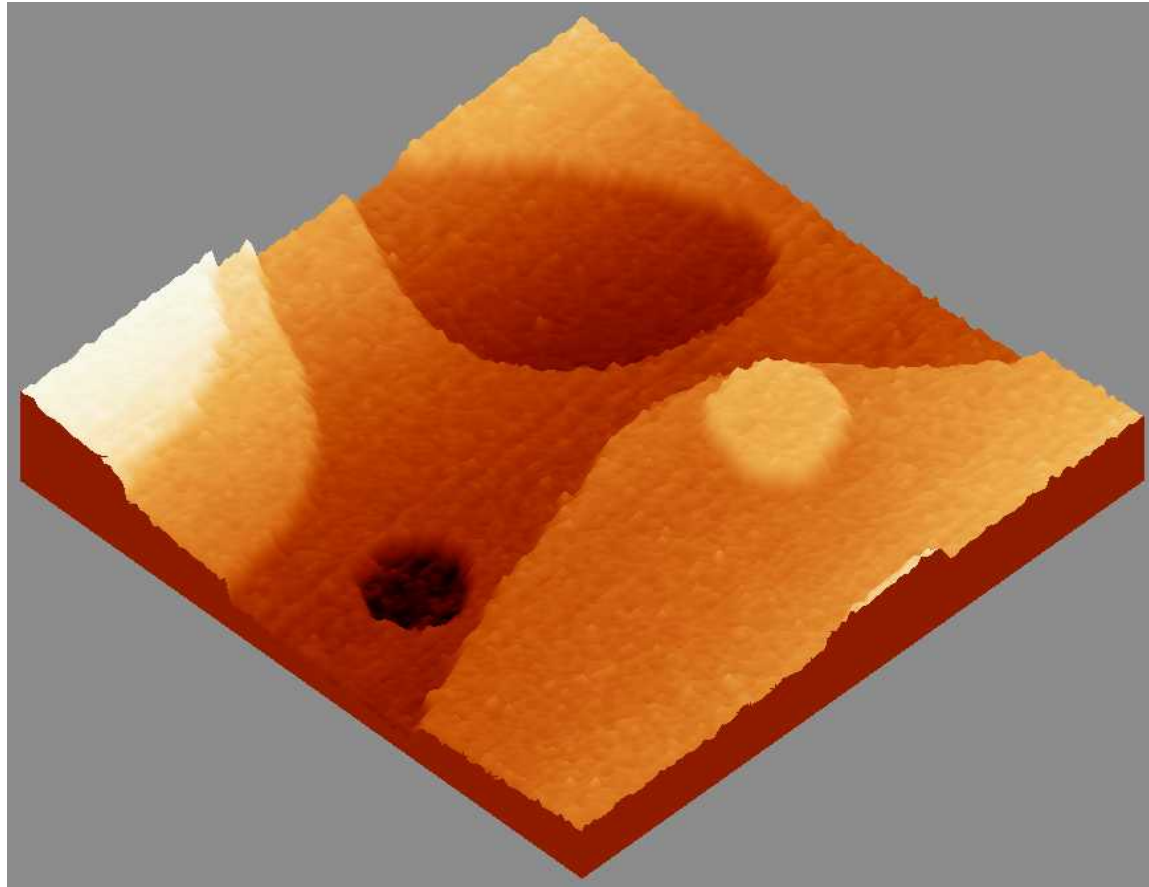
Gold surface,

120X120 nm, 4K,

no atomic structure

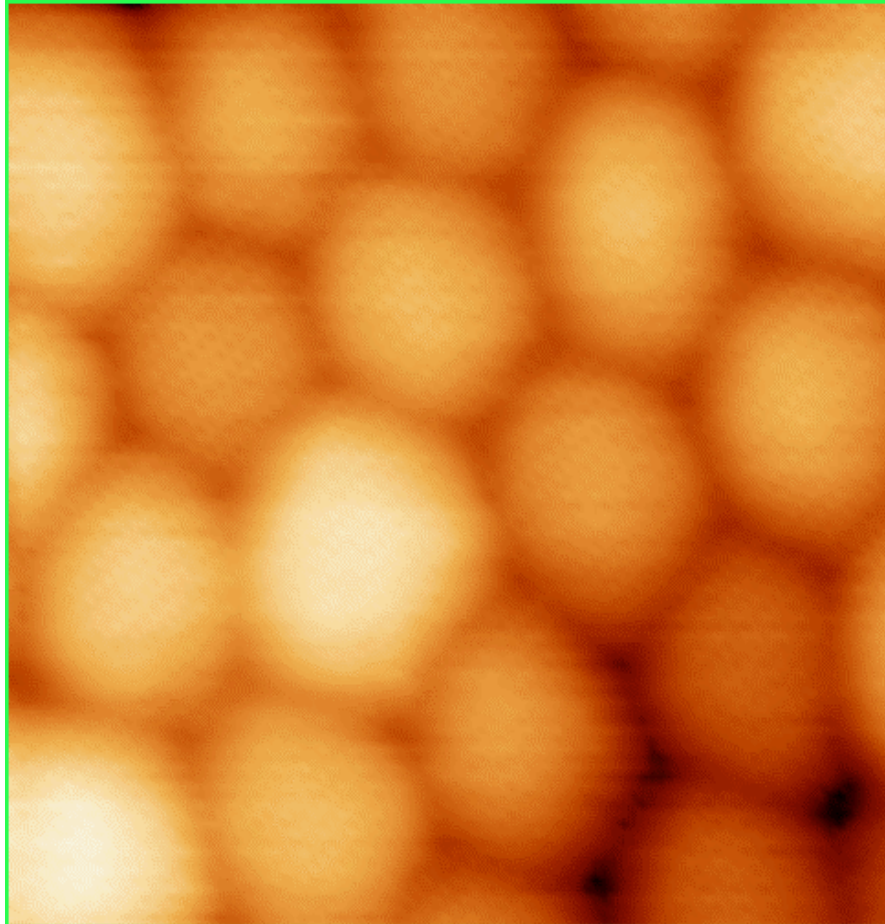
Be careful --- When you try to say you got a flat surface.

Real atomic flat!



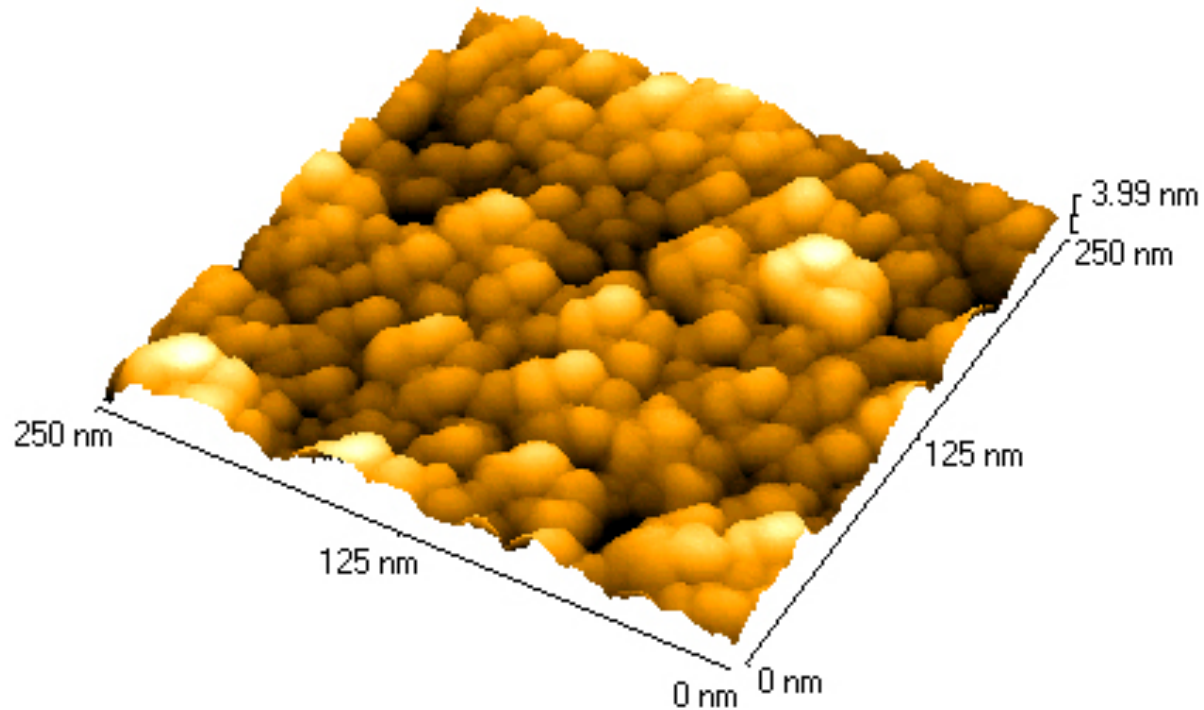
Atomically flat Au film

STM does good job for imaging metal cluster



2-D network of 4 nm Au cluster array on GaAs

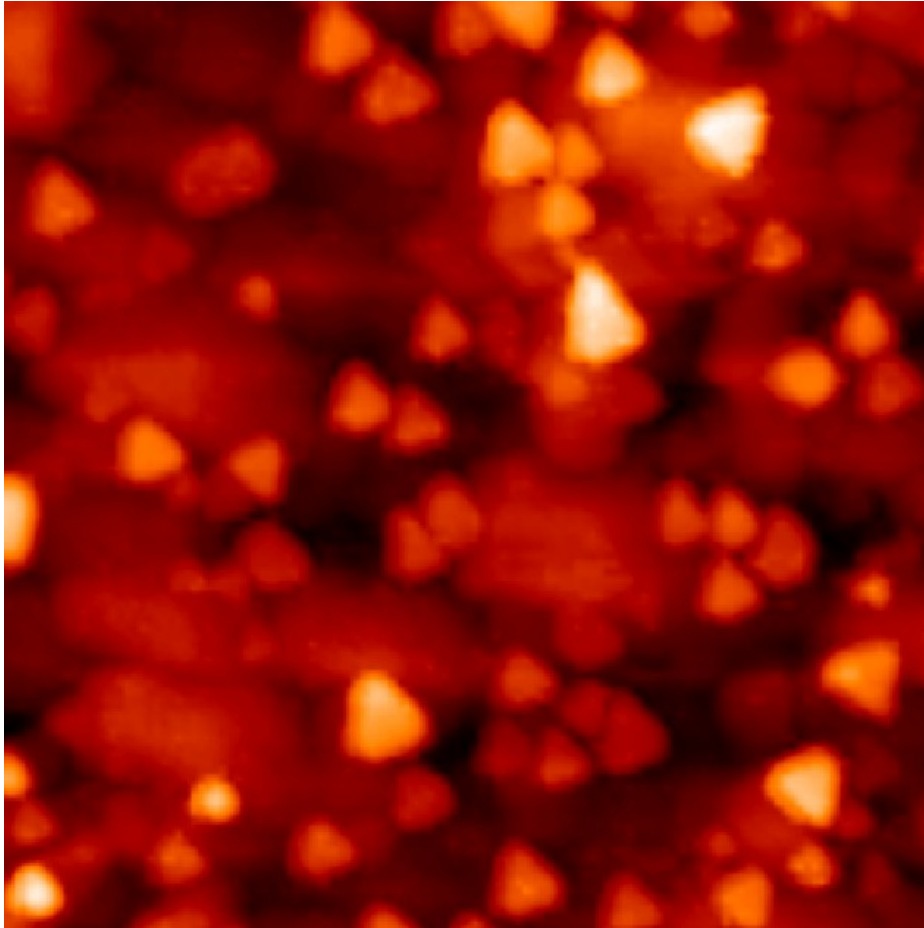
STM does good job for imaging metal cluster



STM under control: gold cluster packing @copyright NESMI lab ZANG 2004

3-D piling of **2** nm Au clusters

Shape control of transition metal nanoparticles



Why control the shape?

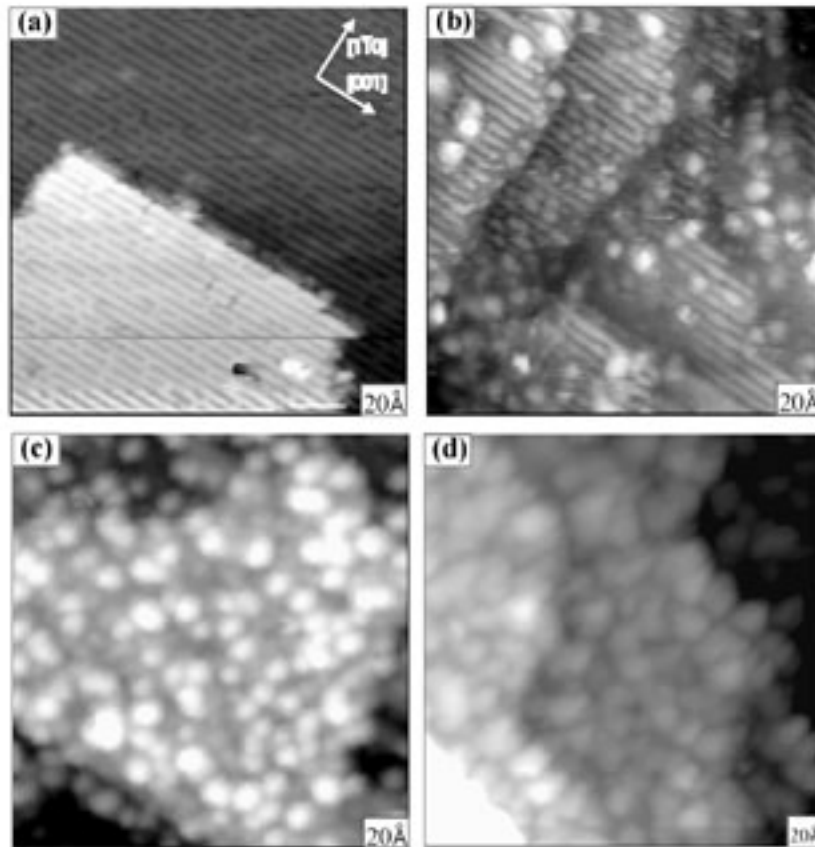
Non-linear optical properties;

Surface enhanced Raman;

Catalysis.

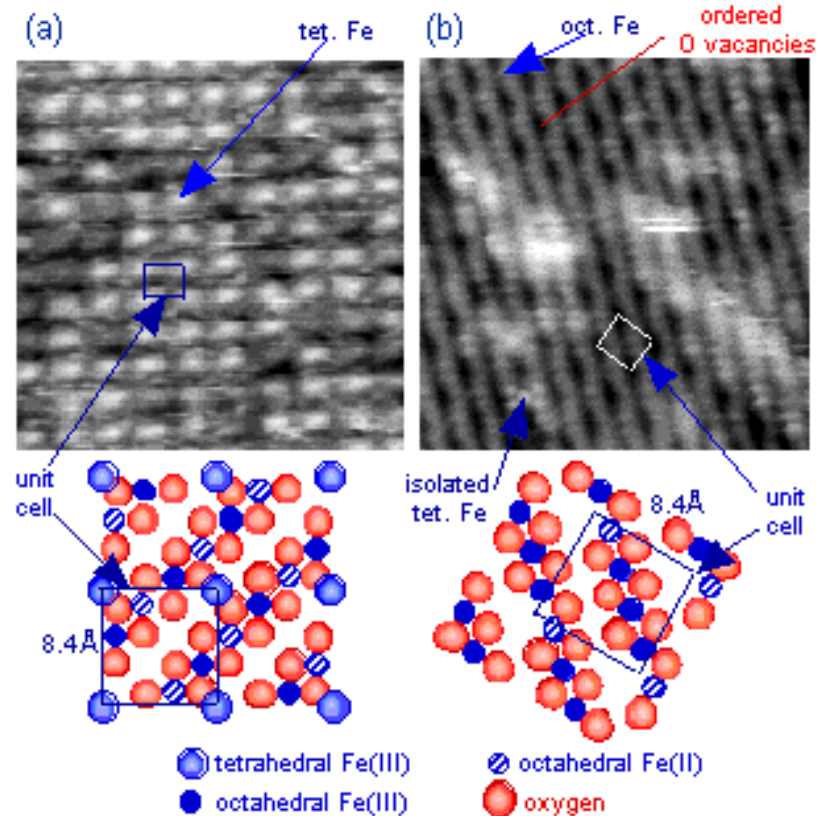
(George Schatz work at NW)

Single crystalline Titanium oxide: doping of vanadium



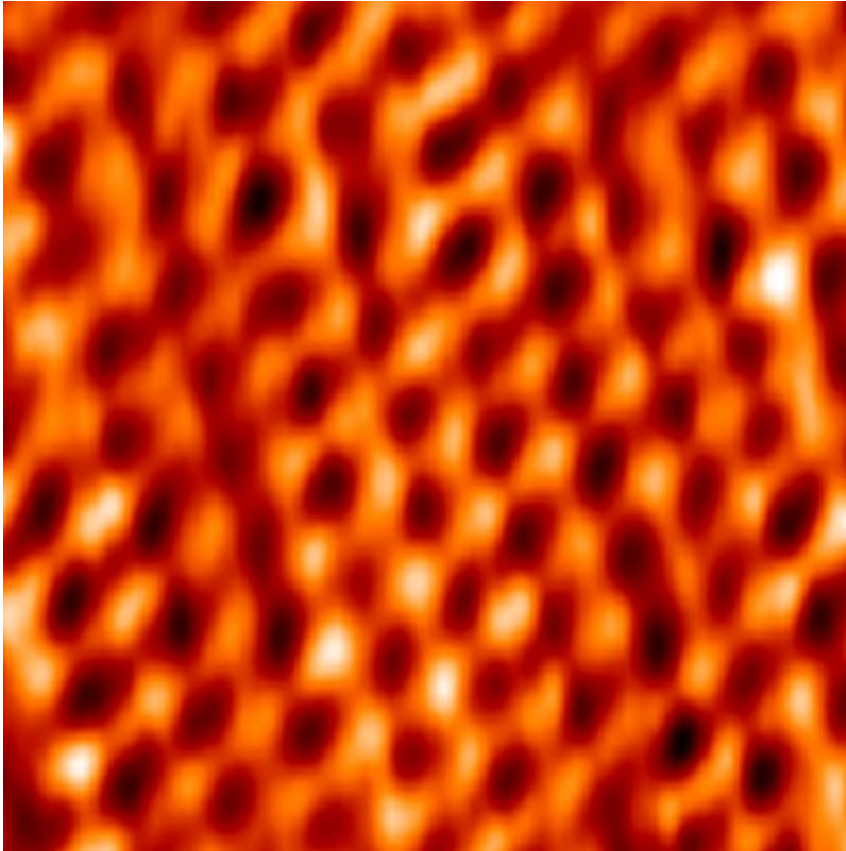
STM images obtained for (a) clean TiO₂(110), and deposition of vanadium metal thereon; (b) 0.03 ML(monolayer), (c) 0.25 ML , (d) 2.0 ML.

Iron oxides: important materials for recording



Atomically resolved STM images of tetrahedral-Fe terminated (a) and octahedral-Fe terminated (b) $\text{Fe}_3\text{O}_4(001)$.

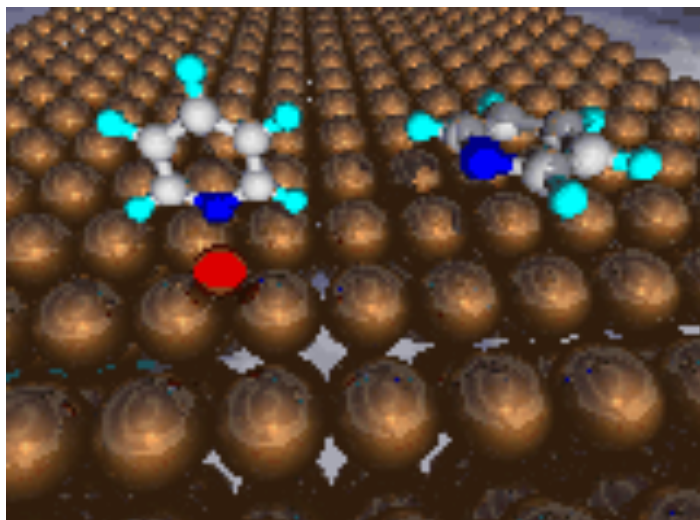
STM exploration of physical properties



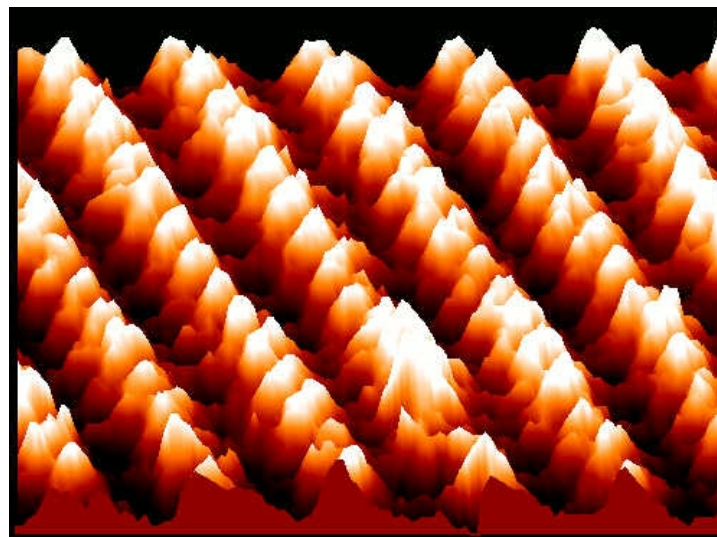
Atoms of n-type MoS2
--- a common **dry lubricant**.

The bright spots indicate **S atoms**, which account for its excellent lubrication properties.

Imaging organic reaction on surface



Physisorbed **pyridine** and **pyridine-oxide** at a Cu(110) surface



3D representation of an STM image of **Pyridine oxide** at a Cu(110) surface