Experimental methods in physics

Surface analysis techniques

1. Introduction

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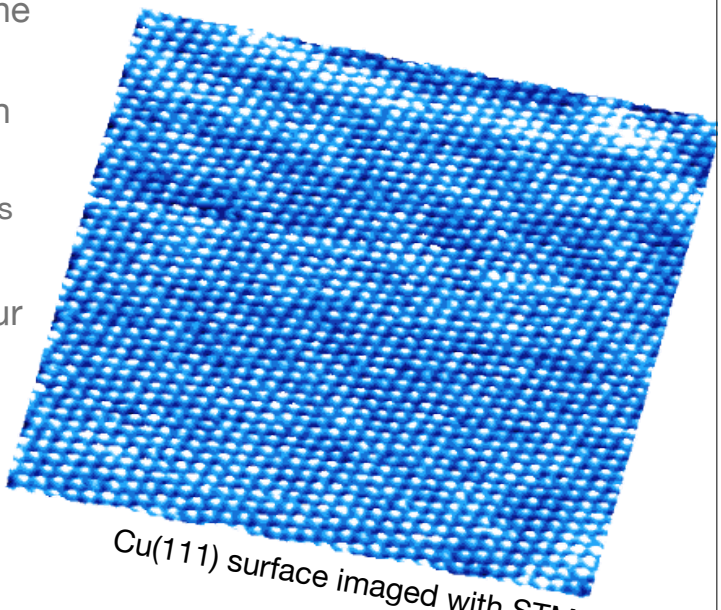
Academic year 10-11

Surface physics

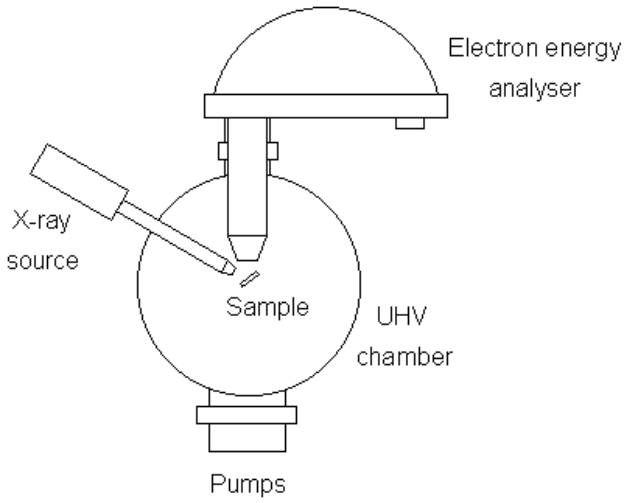
- Interface between a solid and the outside world
- Many phenomena take place on a surface
  - Chemical reactions and exchanges
  - Diffusion, coalescence, growth
- Physical and chemical behaviour different from bulk solid
  - Crystal and electronic structure
- Industrial applications
  - Catalysis
  - Substrate for deposition…



Cu(111) surface imaged with STM

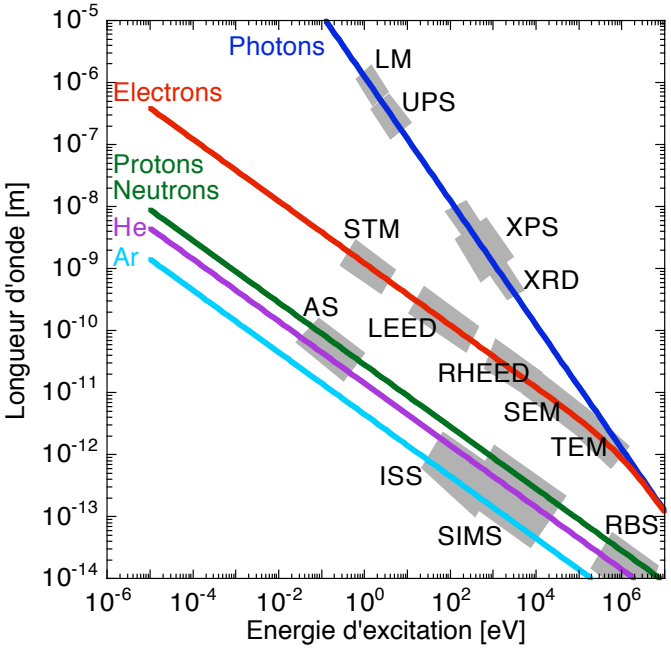
1. Introduction

1.1. Analysis techniques



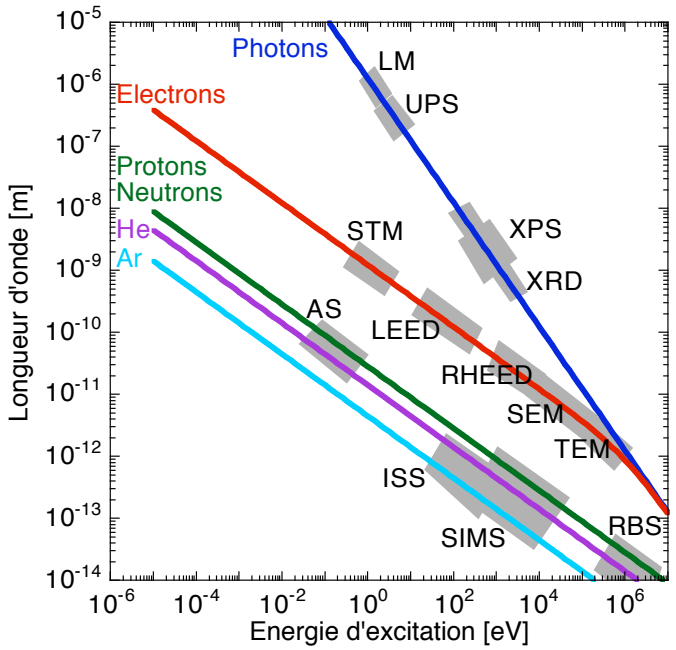
Surface analysis

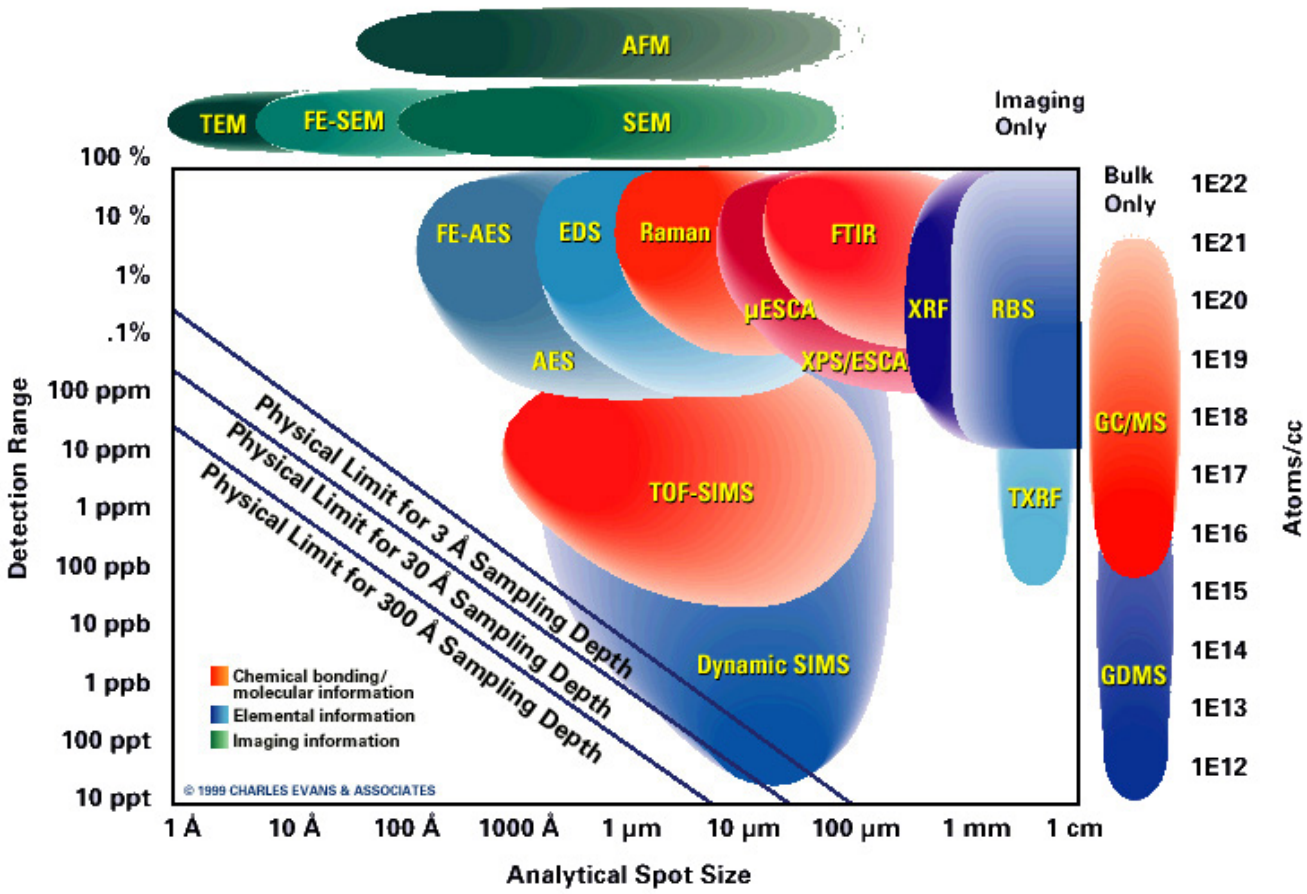
- Structural analysis
  - Direct space: microscopy
  - Reciprocal space: diffraction
- Chemical analysis
  - Core electrons transitions
  - Ion desorption
  - Optical methods (chemical bonds)
- Electronic analysis
  - Fine structure of core or valence electron transitions
  - Band structure around the Fermi level



Chemical analysis of the surface

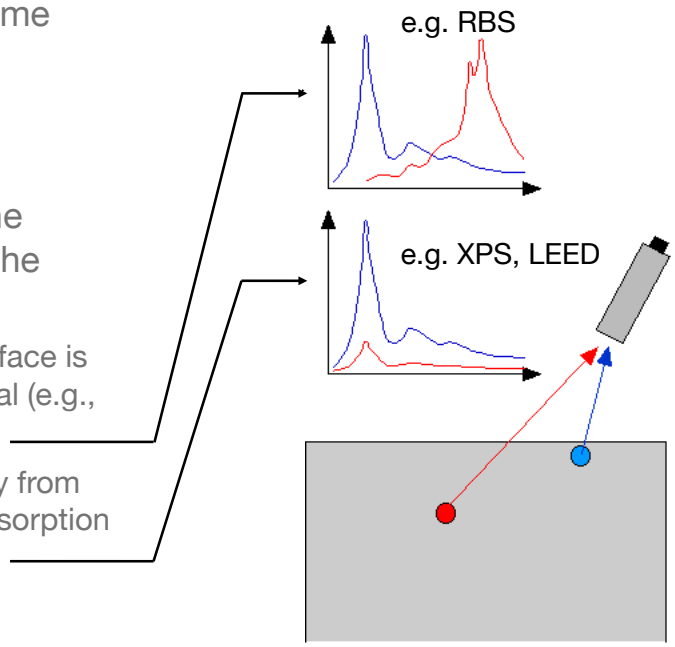
- Which method should one choose?
  - What can be measured?
    - Presence of an element, qualitative or quantitative analysis, binding state, isotopes…
  - Sensitivity
    - Detection limit
  - Lateral and depth resolution
    - Spatial distribution, layer thickness
  - Cost/means
  - Sample preparation
  - Time needed for a measurement





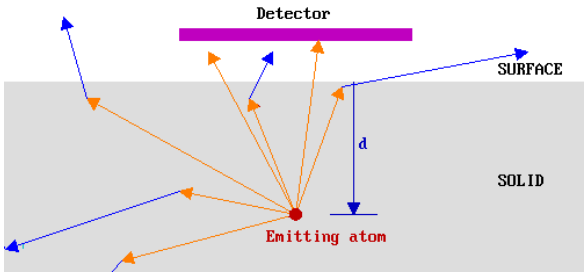
How can we measure the surface (and only the surface)?

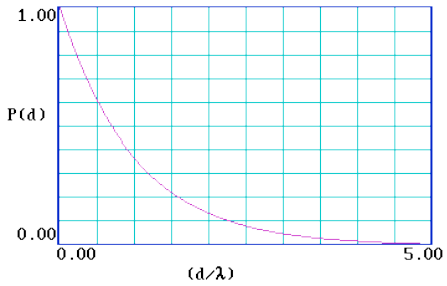
- Where does the signal come from?
  - Surface: ~10^{15} atoms cm^{-2}
  - Bulk: ~10^{23} atoms cm^{-3}
- We have to ensure that the technique is sensitive to the surface
  - Signal coming from the surface is different from the bulk signal (e.g., different energies)
  - Detected signal comes only from the surface (e.g., strong absorption in the bulk)

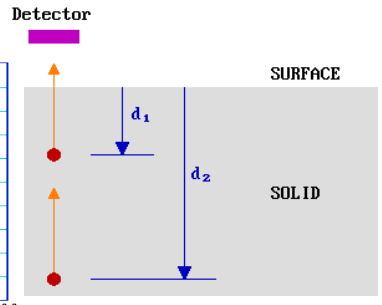


Measuring a surface with electrons I

- Atom emits electrons
  - Energy E_0
- Probability of reaching the surface without collisions depends on d
  - $P(d) \propto \exp(-d/\lambda)$
  - λ (mean free path) depends
    - E_0 (a lot)
    - Material (somewhat)

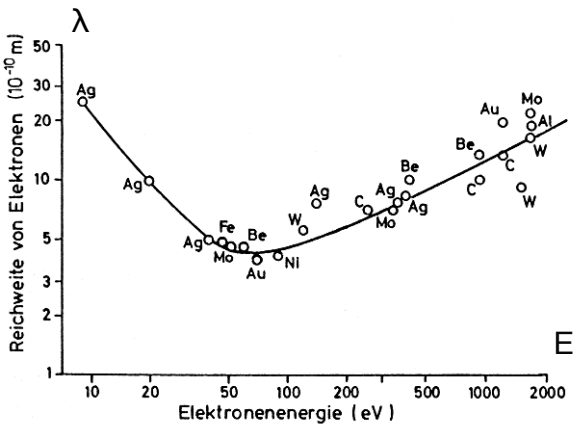




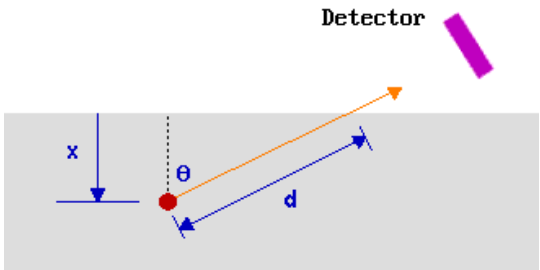


Measuring a surface with electrons II

- Two possibilities
- Detecting low energy electrons (10…500 eV)
  - Photoelectron spectroscopy
  - Auger spectroscopy
  - Low energy electron diffraction

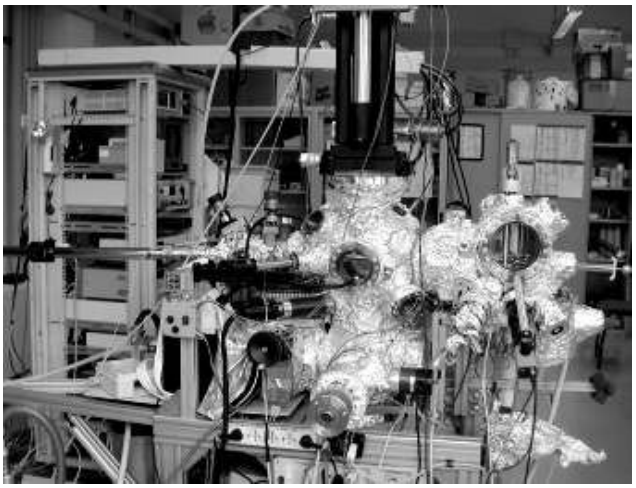


- Detecting electrons with grazing incidence
  - High energy electron diffraction
  - Angle-resolved photoelectron spectroscopy



1. Introduction

1.2. Vacuum



A surface is best studied…

- A surface is probed with
  - Charged particles (electrons, ions)
  - Neutral particles (neutrons, He)
  - Photons (X-rays, visible)
- Interaction products
  - Particles…
  - Light…

- Mean free path λ of a particle in a gas
  - Collisions between particle and gas molecules
  - Maxwell-Boltzmann velocity distribution

$$\lambda = \frac{kT}{\sqrt{2}} \frac{1}{p\sigma}$$

  - Pressure p, cross-section σ (~10^{-19} m^2)

- Efficient excitation/detection
  - λ > distance between sample and source/detector

- p = 1013 mbar: λ ≈ 10^{-7} m
- p = 10^{-4} mbar: λ ≈ 1 m

A surface is best studied…

- The surface has to remain in the same state during the measurement
  - Temperature
  - Stability of the structure
  - Contamination
    - Gas molecules adsorb on the surface
    - Formation of a monolayer: all adsorption sites are occupied (typ. 10^{19} m^{-2})

- Incident flow of gas on the surface F

$$F = \frac{nv}{4} = \frac{p}{\sqrt{2\pi mkT}} \left[mol \quad m^{-2} s^{-1} \right]$$

- Density n, mean velocity v
- Adsorption probability S
- Time needed to form a monolayer $t \approx 10^{19}/(FS)$

- Reliable measurement
  - Measurement time < time needed to form a monolayer

- p = 1013 mbar: t ≈ 10 ns
- p = 10^{-10} mbar: t ≈ 1 h

…under vacuum!

- Excitation/detection with particles
  - Vacuum of 10^{-4} mbar or better
- Surface analysis
  - 10^{-10} mbar or better if the presence of contaminants influences the measured properties

- Exceptions
  - Excitation by and detection of photons (optical microscopy, …)
  - Force measurement (atomic force microscopy)
  - Measurement in a liquid

		Rough vacuum	Medium vacuum	High vacuum	Ultrahigh vacuum
Pressure	p [mbar]	1013 – 1	1 – 10^{-3}	10^{-3} – 10^{-7}	< 10^{-7}
Particle number density	n [cm^{-3}]	10^{19} – 10^{16}	10^{16} – 10^{13}	10^{13} – 10^{9}	< 10^{9}
Mean free path	λ [cm]	< 10^{-2}	10^{-2} – 10	10 – 10^{5}	> 10^{5}
Impingement rate	Z_A [$cm^{-2} \cdot s^{-1}$]	10^{23} – 10^{20}	10^{20} – 10^{17}	10^{17} – 10^{13}	< 10^{13}
Vol.-related collision rate	Z_V [$cm^{-3} \cdot s^{-1}$]	10^{23} – 10^{23}	10^{23} – 10^{17}	10^{17} – 10^{9}	< 10^{9}
Monolayer time	τ [s]	< 10^{-5}	10^{-5} – 10^{-2}	10^{-2} – 100	> 100
Type of gas flow		Viscous flow	Knudsen flow	Molecular flow	Molecular flow
Other special features		Convection dependent on pressure	Significant change in thermal conductivity of a gas	Significant reduction in volume-related collision rate	Particles on the surfaces dominate to a great extend in relation to particles in gaseous space

Table IX: Pressure ranges used in vacuum technology and their characteristics (numbers rounded off to whole power of ten)

What is limiting the pressure?

- Common problems
  - Outgassing of chamber/sample
  - Leaks of seals/weldings…
  - Hydrocarbons
- Solutions
  - Heating at 150 °C
  - Clean pumps, cold traps

- UHV systems
  - Materials (no plastics, Cu seals, ceramic isolators, …)
  - Cleanliness
  - Patience and a lot of time…

At room temperature									
Standard values[1] (mbar · ℓ · $s^{-1} \cdot cm^{-2}$)			Metals 10^{-9} … · 10^{-7}				Nonmetals 10^{-7} … · 10^{-5}		
Outgassing rates (standard values) as a function of time									
Examples:	½ hr.	1 hr.	3 hr.	5 hr.	Examples:	½ hr.	1 hr.	3 hr.	5 hr.
Ag	$1.5 \cdot 10^{-8}$	$1.1 \cdot 10^{-8}$	$2 \cdot 10^{-9}$		Silicone	$1.5 \cdot 10^{-5}$	$8 \cdot 10^{-6}$	$3.5 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$
Al	$2 \cdot 10^{-8}$	$6 \cdot 10^{-9}$			NBR	$4 \cdot 10^{-6}$	$3 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$	$1 \cdot 10^{-6}$
Cu	$4 \cdot 10^{-8}$	$2 \cdot 10^{-8}$	$6 \cdot 10^{-9}$	$3.5 \cdot 10^{-9}$	Acrylic glass	$1.5 \cdot 10^{-6}$	$1.2 \cdot 10^{-6}$	$8 \cdot 10^{-7}$	$5 \cdot 10^{-7}$
Stainless steel		$9 \cdot 10^{-8}$	$3.5 \cdot 10^{-8}$	$2.5 \cdot 10^{-8}$	FPM, FKM	$7 \cdot 10^{-7}$	$4 \cdot 10^{-7}$	$2 \cdot 10^{-7}$	$1.5 \cdot 10^{-7}$

[1] All values depend largely on pretreatment!

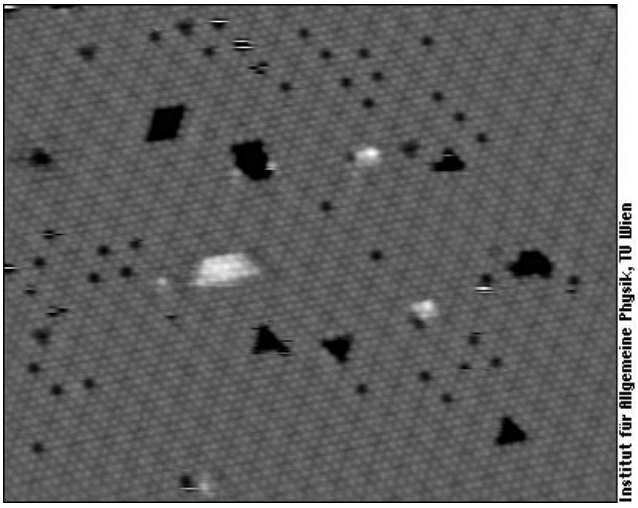
Table X: Outgassing of materials in mbar · ℓ · s^{-1} cm^{-2}

1. Introduction

1.3. Annexes

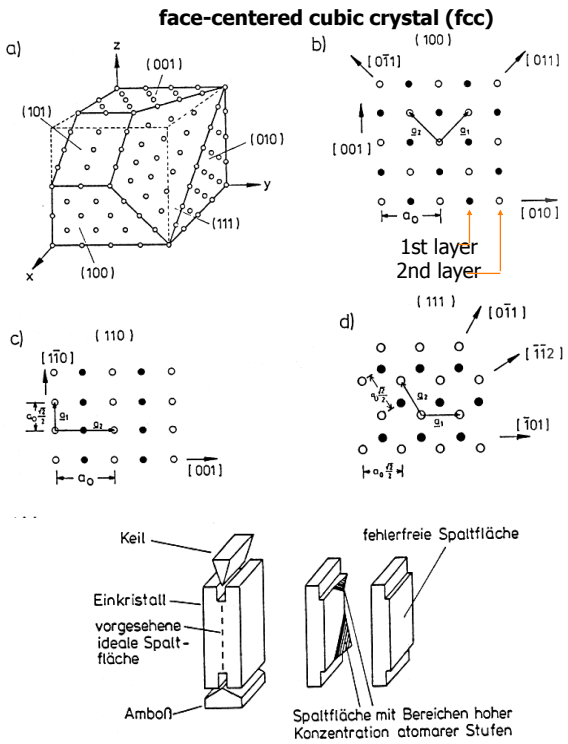
1. Introduction

1.3.1. Surface structure



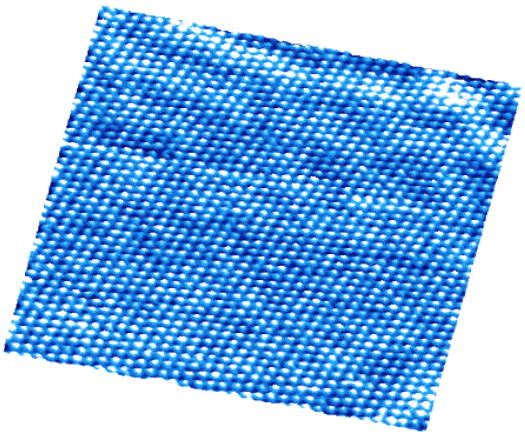
Preparing a surface

- Metal/semiconductor: well-defined crystalline structure
  - In theory, one should be able to form a surface of arbitrary orientation
  - In practice: only a few orientations are energetically favourable
- Preparation
  - Cleavage
  - Machining
  - Chemical etching
  - Ion bombardment
  - Vacuum annealing…



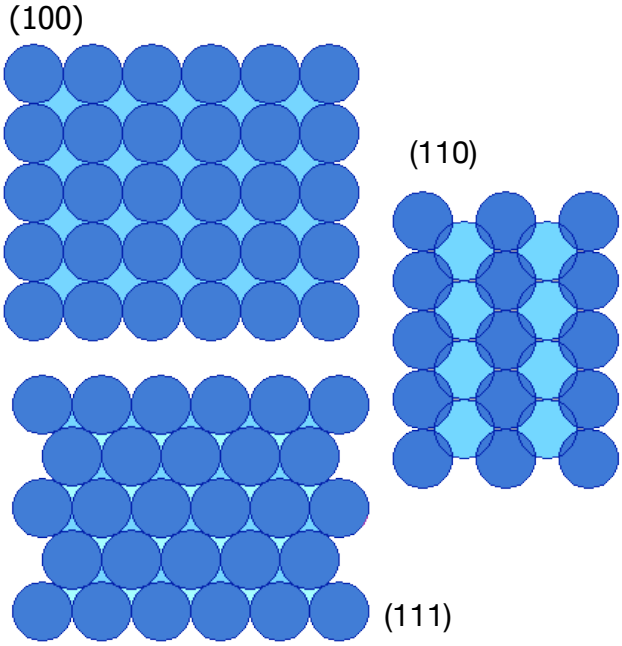
High symmetry surfaces

- Most common surfaces
  - High density of atoms
  - High number of neighbouring atoms
- Notation: Miller indices



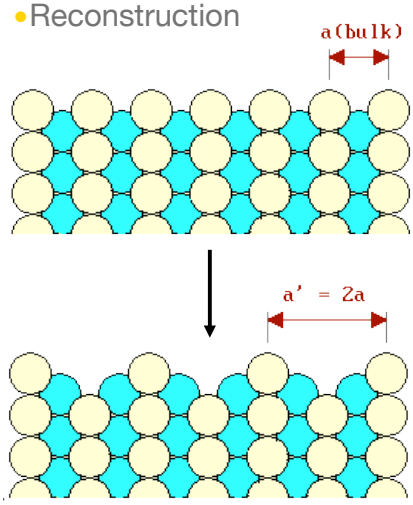
STM image of a Cu(111) surface

fcc structures (Cu, Pt, Si…)

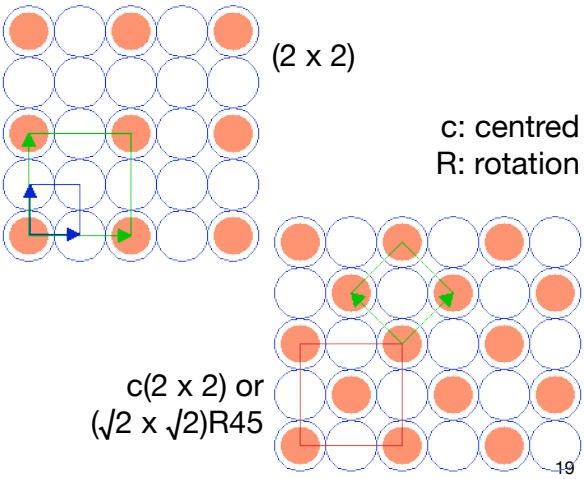


Surface reconstruction

- Lowering of the free surface energy
  - Relaxation
  - Reconstruction

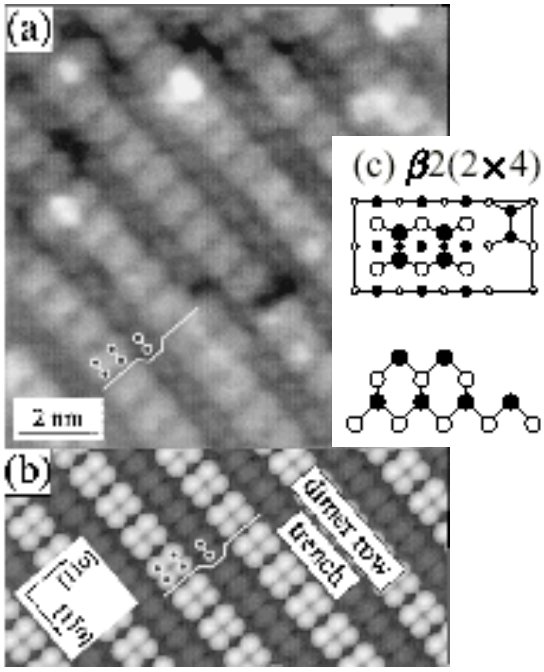


- Notation (Wood):
  Size and orientation of unit cell of the reconstruction with respect to the 2D unit cell

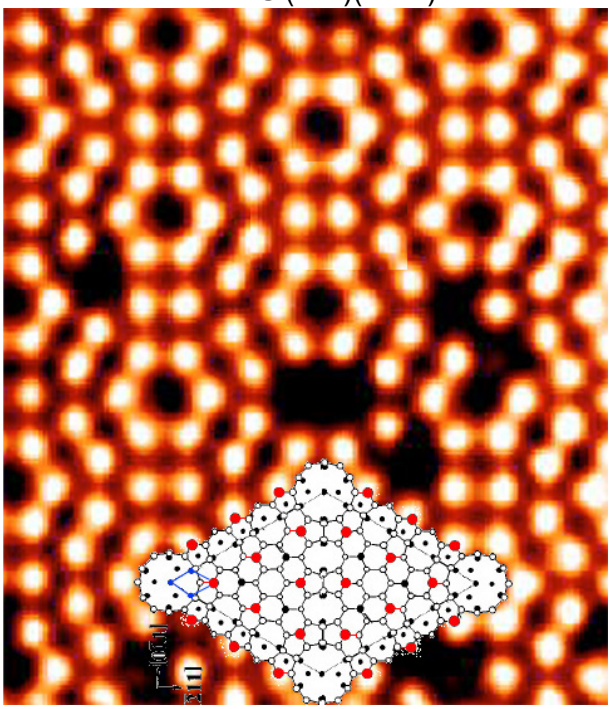


Surface reconstruction

GaAs c(2 x 4)

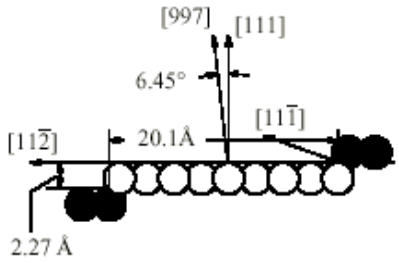


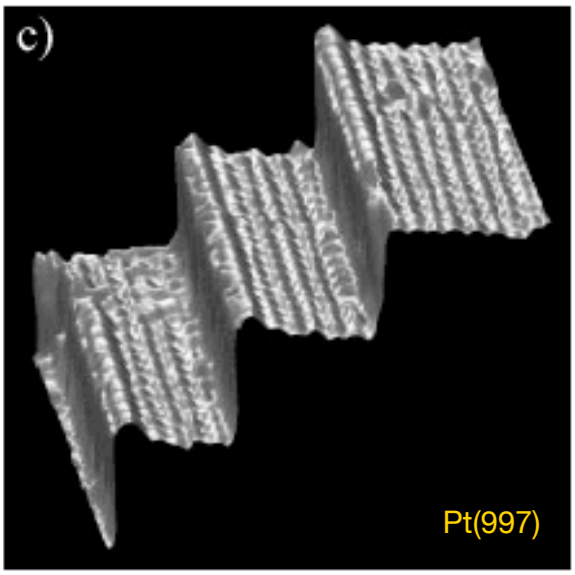
Si(111)(7 x 7)



Vicinal surface

- Surface with an orientation that is very close to a high symmetry surface
  - Low indices surface with periodic terraces
  - Diffusion/segregation studies…





1. Introduction

1.3.2. Acronyms

Surface analysis techniques I

Detection	Excitation					
	Electrons, e^-		Ions, neutrals, A^+, A^-, A^0		Photons, $h\nu$	
e^-	AES LEED RHEED	SAM EELS EFTEM	IAES		XPS UPS	
A^+, A^-, A^0	ESD		SIMS SNMS	RBS LEIS		
$h\nu$	EDX	IPES			TXRF XRD RAIRS FT-IR	Raman SERS ELL SNOM

Surface analysis techniques II

Detection	Excitation		
	Heat, kT	Electric field, F	Mechanical force
A^+	TDS	APFIM	
A^-	TDS		
$h\nu$		STM, STS	
Displacement			AFM

Acronyms
Electronic excitation

AES	Auger Electron Spectroscopy
EDX	Energy Dispersive X-Ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
EFTEM	Energy Filtered Transmission Electron Microscopy
ESD	Electron Stimulated Desorption
IPES	Inverse Photoelectron Spectroscopy
LEED	Low Energy Electron Diffraction
RHEED	Reflection High Energy Electron Diffraction
SAM	Scanning Auger Microscopy

Acronyms -
Excitation by ionised and neutral atoms

IAES	Ion excited Auger Electron Spectroscopy
LEIS	Low Energy Ion Scattering
RBS	Rutherford Backscattering Spectroscopy
SIMS	Secondary Ion Mass Spectroscopy
SNMS	Secondary Neutral Mass Spectroscopy

Acronyms
Photonic excitation

ELL	Ellipsometry
FT-IR	Fourier-Transform Infrared Spectroscopy
RAIRS	Reflection-Absorption Infrared Spectroscopy
Raman	Raman spectroscopy
SERS	Surface-Enhanced Raman Spectroscopy
SNOM	Scanning Near Field Optical Microscopy
TXRF	Total Reflection X-Ray fluorescence analysis
UPS	Ultraviolet Photoelectron Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Acronyms
Other excitations

AFM	Atomic Force Microscopy
APFIM	Atom-Probe Field Ion Microscopy
STM	Scanning Tunnelling Microscopy
STS	Scanning Tunnelling Spectroscopy
TDS	Thermal Desorption Spectroscopy

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