Surface analysis techniques

1. Introduction

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

- 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

Surface analysis

- Structural analysis
  - Direct space: microscopy
  - Reciprocal space: diffraction
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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: $\sim 10^{15}$ atoms cm$^{-2}$
  - Bulk: $\sim 10^{23}$ 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 $d$
  - $P(d) \propto \exp(-d/\lambda)$
  - $\lambda$ (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…
- Efficient excitation/detection
  - $\lambda >$ distance between sample and source/detector
- Mean free path $\lambda$ of a particle in a gas
  - Collisions between particle and gas molecules
  - Maxwell-Boltzmann velocity distribution
  - $\lambda = \frac{1}{\sqrt{2} \rho \sigma}$
  - Pressure $\rho$, cross-section $\sigma$ ($\sim 10^{-19}$ m$^2$)
- $\rho = 1013$ mbar: $\lambda \approx 10^{-7}$ m
- $\rho = 10^{-4}$ mbar: $\lambda \approx 1$ 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 $F$
  - $F = \frac{nv}{4} = \frac{p}{\sqrt{2\pi m kT}}$ [mol m$^{-2}$ s$^{-1}$]
  - Density $n$, mean velocity $v$
  - Adsorption probability $S$
  - Time needed to form a monolayer $t \approx 10^{19}/(FS)$
- Reliable measurement
  - Measurement time $< \text{time needed to form a monolayer}$
  - $p = 1013$ mbar: $t \approx 10$ ns
  - $p = 10^{-10}$ mbar: $t \approx 1$ 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

<table>
<thead>
<tr>
<th></th>
<th>Rough vacuum</th>
<th>Medium vacuum</th>
<th>High vacuum</th>
<th>Ultrahigh vacuum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>p [mbar]</td>
<td>$10^6$ - $10^7$</td>
<td>$10^3$ - $10^4$</td>
<td>$10^2$ - $10^3$</td>
</tr>
<tr>
<td>Particle number density</td>
<td>n [cm$^{-3}$]</td>
<td>$10^4$ - $10^5$</td>
<td>$10^3$ - $10^4$</td>
<td>$10^2$ - $10^3$</td>
</tr>
<tr>
<td>Mean free path</td>
<td>$\lambda$ [cm]</td>
<td>$&lt; 10^{-4}$</td>
<td>$10^{-4}$ - $10^{-3}$</td>
<td>$10^{-3}$ - $10^{-2}$</td>
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<tr>
<td>Impingement rate</td>
<td>$Z_i$ [cm$^{-2}$ s$^{-1}$]</td>
<td>$10^5$ - $10^6$</td>
<td>$10^4$ - $10^5$</td>
<td>$10^3$ - $10^4$</td>
</tr>
<tr>
<td>Volume-related collision rate</td>
<td>$Z_v$ [cm$^{-3}$ s$^{-1}$]</td>
<td>$10^4$ - $10^5$</td>
<td>$10^3$ - $10^4$</td>
<td>$10^2$ - $10^3$</td>
</tr>
<tr>
<td>Mean decay time</td>
<td>$\tau$ [s]</td>
<td>$&lt; 10^{-4}$</td>
<td>$10^{-4}$ - $10^{-3}$</td>
<td>$10^{-3}$ - $10^{-2}$</td>
</tr>
<tr>
<td>Type of gas flow</td>
<td></td>
<td>Viscous flow</td>
<td>Knudsen flow</td>
<td>Molecular flow</td>
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<tr>
<td>Other special features</td>
<td></td>
<td>Convective dependent on pressure</td>
<td>Significant change in thermal conductivity of a gas</td>
<td>Significant reduction in volume-related collision rate</td>
</tr>
</tbody>
</table>

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...

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<table>
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<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stainless steel</td>
<td>K  \text{ and Au}</td>
<td>Ni</td>
<td>Fe</td>
</tr>
<tr>
<td></td>
<td>$4 \times 10^{-10}$</td>
<td>$2 \times 10^{-10}$</td>
<td>$6 \times 10^{-10}$</td>
<td>$5.6 \times 10^{-10}$</td>
</tr>
<tr>
<td></td>
<td>$9 \times 10^{-10}$</td>
<td>$5.2 \times 10^{-10}$</td>
<td>$2.6 \times 10^{-10}$</td>
<td>$2.8 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

Table X: Outgassing rates (standard values) as a function of time

1. All values given in langmuir per square centimeter.
1. Introduction

1.3. Annexes

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
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

(c(2 x 2) or (√2 x √2)R45)

c: centred
R: rotation

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

<table>
<thead>
<tr>
<th>Detection</th>
<th>Excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrons, $e^-$</td>
<td>Ions, neutrals, $A^+$, $A^-$, $A^0$</td>
</tr>
<tr>
<td>$e^-$</td>
<td>AES, LEED, RHEED</td>
</tr>
<tr>
<td>$A^+$, $A^-$, $A^0$</td>
<td>ESD</td>
</tr>
<tr>
<td>$h\nu$</td>
<td>EDX, IPES</td>
</tr>
</tbody>
</table>

## Surface analysis techniques II

<table>
<thead>
<tr>
<th>Detection</th>
<th>Excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat, $kT$</td>
<td>Electric field, $F$</td>
</tr>
<tr>
<td>$A^+$</td>
<td>TDS</td>
</tr>
<tr>
<td>$A^-$</td>
<td>TDS</td>
</tr>
<tr>
<td>$h\nu$</td>
<td>STM, STS</td>
</tr>
<tr>
<td>Displacement</td>
<td>AFM</td>
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</tbody>
</table>
### Acronyms

**Electronic excitation**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-Ray Spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>EFTEM</td>
<td>Energy Filtered Transmission Electron Microscopy</td>
</tr>
<tr>
<td>ESD</td>
<td>Electron Stimulated Desorption</td>
</tr>
<tr>
<td>IPES</td>
<td>Inverse Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflection High Energy Electron Diffraction</td>
</tr>
<tr>
<td>SAM</td>
<td>Scanning Auger Microscopy</td>
</tr>
</tbody>
</table>

### Acronyms -

**Excitation by ionised and neutral atoms**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAES</td>
<td>Ion excited Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>LEIS</td>
<td>Low Energy Ion Scattering</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford Backscattering Spectroscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectroscopy</td>
</tr>
<tr>
<td>SNMS</td>
<td>Secondary Neutral Mass Spectroscopy</td>
</tr>
</tbody>
</table>
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
Bibliography (a few among many)

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  • A. Zangwill, “Physics at surfaces” (Cambridge University Press, 1988)
  • C. Wöll, Landolt-Börnstein New Series III/42A2 chapitre 2

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