Surfaces

Chapter 1 – Concepts

- Diffraction methods (LEED, RHEED, GIXD, LEEM)
- Electron spectroscopy (XPS, AES, PEEM)
- Scanning probe methods (STM, AFM, MFM)

Adsorption - the process whereby a molecule forms a bond to the surface.
(Absorption - the process whereby molecules enter into the bulk of the substrate.)

Associative adsorption occurs when a molecule adsorbs to the surface from the gas phase without fragmentation – otherwise it's called dissociative. Two broad classifications of adsorbate bonding:
- *Physiorption* – The bonding interaction is long range but weak and associated with van der Waals-type interactions. Bonding is characterized by a redistribution of electron density within the adsorbate and the adsorbent separately. Because it is weak, it also tends to be reversible – the adsorbate always in equilibrium with the gas molecules.
- *Chemisorption* – Characterized by an exchange of electrons between the adsorbate and the adsorbent and spectroscopic methods can confirm the nature of the surface bonding.

The chemical and physical properties of the surface will depend ultimately upon its electronic structure. This in turn will depend on the nature of the atoms on the surface and their spatial distribution.

To ensure that experiments are performed on *well-defined* structures (one type of atoms and controlled amount surface defects/coverage with distinguishable adsorbates), single crystals are used as substrates. Therefore crystal planes will contain a limited number of well-defined sites.

The primitive surface unit cell is the smallest possible repetitive unit cell of a bcc, and it's a rhombus.

Cleaning
Two problems:
- How to clean it?
- How to keep it clean?

It's important to reduce the ambient pressure as much as possible to maintain a clean surface. *UHV* (ultra-high vacuum) means that the pressure is reduced to below 10^{-9} Torr and is an essential condition in order to study reactive solid-gas interfaces. How to clean a surface depend on the substrate - some can be simply cleaved in UHV, grown atomically clean, cleaned by chemical reactions or other methods. However the most common method is *sputtering*- argon ion bombardment in which physical removal is used (energy transfer from ions causes bonds to break). This damages the surfaces though, and can often be fixed with annealing (this is a repeated cycle).

Surface sensitivity
Two factors against the study of gas-solid surfaces:
- The absolute number of atom in a surface in small (sensitivity problem)
- The ratio of surface atoms to bulk atoms is also very small (selectivity problem)

This means you need analytical methods that probe the top few atomic layers of a material and are compatible with UHV environment -> spectroscopies based on the interaction of electrons with matter! The decay of intensity as a function of kinetic energy for an electron is dependent upon the

inelastic mean free path. The larger the angle of emission/incidence, the larger the effective path length and the more likely is the process of energy loss. A big angle will increase the surface sensitivity in electron-based spectroscopies.

Naming overlayer structures

Wood's notation relates the overlayer mesh to the substrate mesh. Define the unit cell in the overlayer with vectors a_o and b_o, and express it in terms of the bulk layer unit cell with vectors a_s and b_s .

$$M(hkl)\left(\frac{a_o}{a_s} x \frac{b_o}{b_s}\right) R\theta - A$$

M is the substrates chemical name, *(hkl)* the Miller index of surface plane, θ the angle between substrate and overlayer meshes (rotation) and *A* the chemical symbol of the surface species. It's possible to choose between several unit cells as long as you name them right relating to the bulk mesh (1x1).

c(2x2) or (√2x√2)R45°
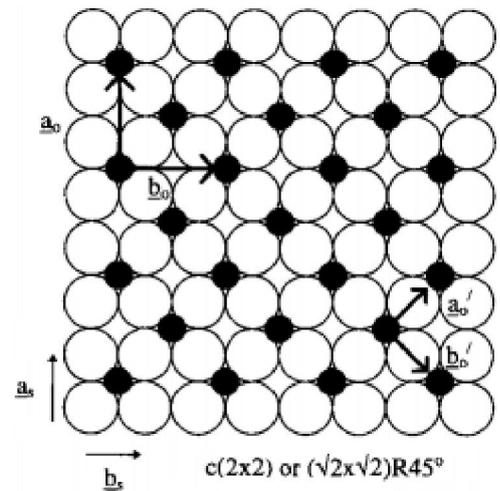
Chapter 2 – Spectroscopic techniques for probing solid surfaces

The classical thermodynamic methods in chapter 1 tend to yield average properties of the system, not atomic/molecular specificity. To get this data, you need to probe surface properties at the molecular level. Surface-sensitive spectroscopies provided information about geometric structure, chemical composition and electronic properties of a solid surface. Proving a surface requires a stimulus leading to a response (heat, electric field, photons, neutrals, electrons, ions)., and any combination may form the basis of a spectroscopy. We want to answer:
- What types of atoms are present and what is their surface concentration?
- Where are they located on a surface, what bond lengths/angles do the molecules exhibit?
- How strong is the bonding of adsorbate atoms to a surface and how does the nature of the surface influence surface reactivity?

No single spectroscopy can answer these, you need a multi-technique approach.

XPS – X-ray photoelectron spectroscopy

The basis lies in the photoelectric effect. An X-ray beam is incident upon a solid surface, causing *photoemission* (light in, electrons out) from both core and valence levels of surface atoms into the vacuum. The core electrons are largely insensitive to their surroundings in solid phase and retain binding energies signatures of the atoms type.

$$E_k = h\nu - E_B + \emptyset$$

This is the energy it takes to excite an electron from the innermost shell to vacuum. E_k is the electron's kinetic energy, $E_B + \emptyset$ the binding energy of electron in solid and $h\nu$ the photon energy, where $\emptyset$ is the energy consumed in overcoming the potential barrier. E_B of a core level is measured to the Fermi level Electrons with higher energies and lower energies get filtered out by and electrostatic energy analyzer. The background intensity in the spectra at high binding energies increases owing to inelastically
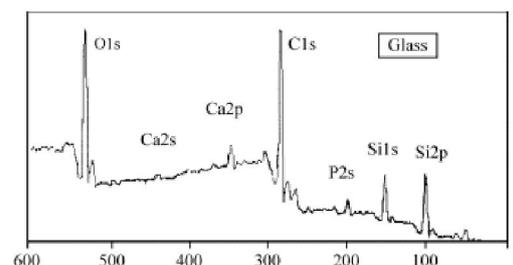
scattered electrons originating from parent XPS peaks.

While, in principle, a separate XPS peak should be observed for every chemically distinct atom it's often different in practice as the energy spread of the incident radiation often is much larger than the chemical shift. Peaks separated by small chemical shifts remain unsolved. The relative intensity depends on concentration of atoms of an element, probability of photoemission for a particular core level and efficiency of the spectrometer. If two elements A and B are distributed homogenously throughout the sampling depth, the relative concentrations may be obtained:

$$\frac{C_A}{C_B} = \frac{I_A}{I_B} \cdot \frac{\sigma_B}{\sigma_A}$$

AES – Auger electron spectroscopy

An incident photon/electron causes photoemission of a core electron. The hole created can be neutralized by an electron transition from a higher electron state. The energy difference can be removed as a photon (X-ray fluorescence) or transferred to a third electron which can escape into the vacuum – the Auger electron. This electron's kinetic energy is independent of the incident radiation energy and is characteristic to the binding energies of electrons within the atom. Auger processes dominate for elements of low atomic number. Signal damping with increasing coverage. AES electrons with energy under 500 eV are inherently surface sensitive due to their small mean free path.

XPS and AES rely on the short mean free path of low energy electrons in solids for achieving surface sensitivity.

PEEM – Photoemission electron microscopy

Diffraction methods

LEED – Low energy electron diffraction

Low-energy electron diffraction (LEED) is a technique for the determination of the surface structure of crystalline materials by bombardment with a collimated beam of low energy electrons (20-200eV). Incident electrons back scatter elastically from a surface and are analyzed in the energy range (20-1000 eV which means they only travel a short way into the sample). These electrons possess de Broglie wavelengths of the same order of magnitude as the atomic spacing at the surface and may undergo diffraction if the surface atoms are arranged periodically. Apparatus filter out electrons with other energy than the incident beam energy. You can get information about periodicity, variations in unit cell size, surface geometry, bond lengths.

At particular angles discrete diffracted beams will be seen. The diffraction pattern (*DP*) consists of equally spaced lines perpendicular to the lattice in which the atom spacing is inversely related to the periodic spacing (see further details in the TEM book about diffraction patterns). It's quite often sound that adsorption on to single crystals produces overlayers that are ordered and have a periodicity larger than that of the substrate unit cell, thus having smaller spacing between spots in the diffraction pattern.

Simple inspection of the DP gives information on relative sizes but no discrimination between adsorption sites or details. However, quantitative structural information (bond length/angles) is contained within the variation of the diffracted beam intensities with energy. Strong intensity maxima occur when Bragg conditions are satisfied because of scattering from outermost surface layers.
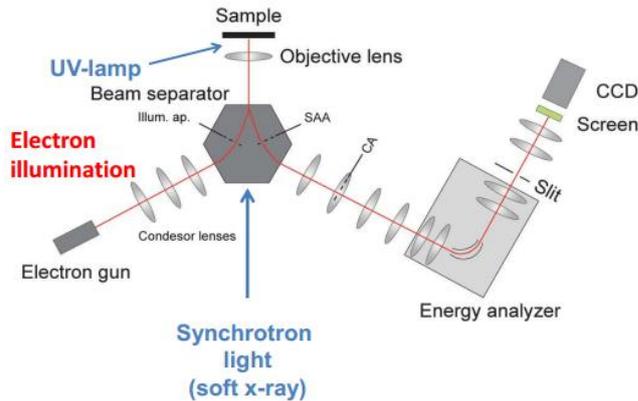
If the LEED pattern is exactly the same, you scan still tell that the structures are different when changing the voltage as the intensity in the spots will differ.
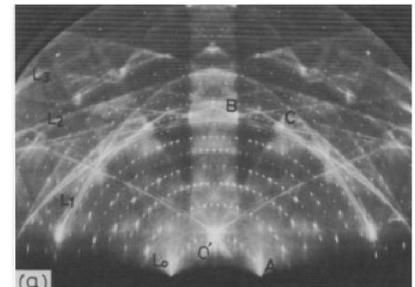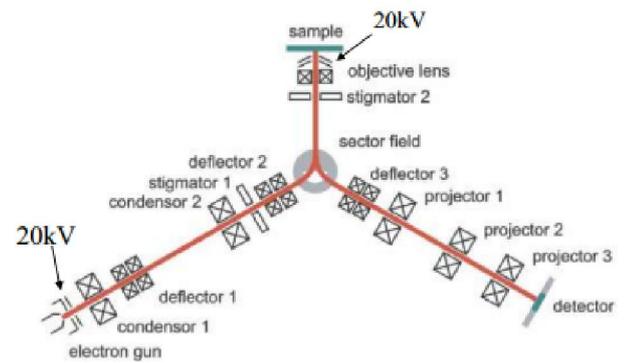
Other methods

LEEM – Low energy electron microscopy
Optics as in SEM, but decelerate electrons at sample to LEED pattern.

SPELEEM (spectroscopic photoemission and low energy electron microscope) – chemical/structural contrast.


RHEED – Reflectance high energy electron diffraction
Uses an electron gun. Primary beam hits the surface and the diffracted beam emerge at very gazing incidence. This combined with high forward scattering probability and notwithstanding the high primary energy ensures a high surface sensitivity.

GIXD - Grazing incidence X-ray diffraction
Uses X-rays/neutron beam. Quite similar to RHEED. Detector can probe larger part of reciprocal space, more precisely. The probe can be in any environment, but only one point is probed at a time. It often needs intense synchrotron X-ray beam which is expensive. Bulk, not surface sensitive.
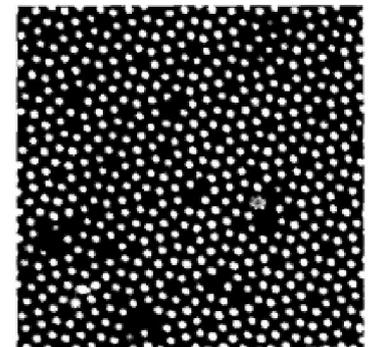
|	LEED	RHEED
Surface sensivity	Mean free path	Grazing incidence
+	Easy to interpret, very surface sensitive and sensitive to interlayer distances	Easy access with many sources
-	High vacuum needed, difficult to combine with evaporators	High vacuum needed, interpretation difficult

Scanning probe methods

STM – Scanning tunneling microscopies

An atomically sharp tip is brought very close to the conducting surface and a small potential difference is applied between tip and sample. Electrons tunnel through the small space of vacuum. The direction depends on the potential difference.

Depending on if you want to study the empty or the filled states in the conductive/valence band you change the bias. Tip biased positively → current from tip to sample → electrons from sample to tip (to lower their potential energy → most intensity in parts with high DOS as most electrons come from here.

The magnitude of the small current is exponentially dependent on the tip-surface separation. Larger distance → smaller current. Atomic resolution can be achieved. The STM current depends on the lateral variation of electron density of the sample, which is dependent on the surface geometry.

The tip influences the sample – it pulls the atom a bit up from the surface. It can damage/influence the specimen, especially those with loosely bound atoms.
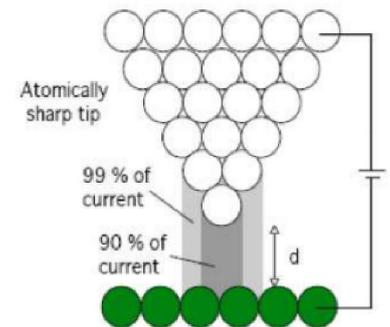
AFM – Atomic force microscope

Works generally in the same way as a STM, but does not need conductive samples. The tip is mounted on a cantilever of force constant that is steered by piezo crystals. When in contact with surface, the tip experiences a small force as a result of interaction with the surface atoms. Here It scans very close to the surface, leading to that the tip is repelled or attracted as it scans. The repulsive force originates both nuclear and tip atoms forced to interpenetrate. The attractive force arises as a result of the decrease in potential energy of the system caused by chemical bonding through electron overlapping.
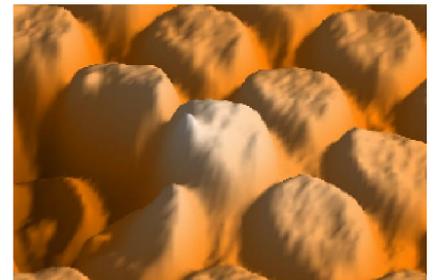
The deflection of the cantilever is magnified with instruments and a laser beam onto a photodetector. The tip is fixed, the sample moved while scanning.
The tip can have artifacts such as a blunt edge or a double tip, these can give a false image where structures can have disappeared and nonexistent structures can occur.
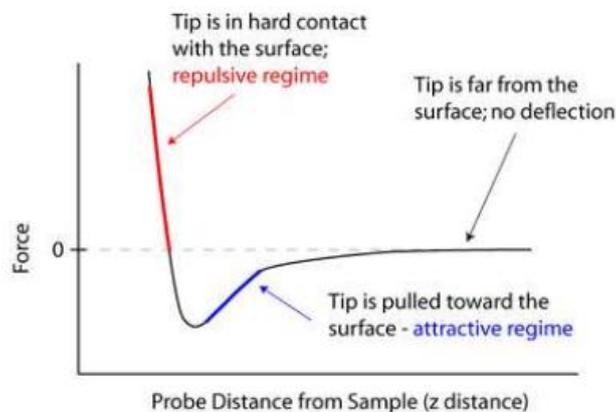
Contact AFM – The tip makes soft physical contact with the surface. The tip is attached to the cantilever with a low spring constant. During scanning, contact forces causes the cantilever to bend to accommodate changes in topography.

Non-contact AFM – Vibrating stiff cantilever close to sample surface. The signal to measure is very small. The cantilever vibrates near its resonance frequency, and the variations in frequency/amplitude are detected.

Spectroscopy	XPS	AES	LEED (also RHEED, GIXD)	STM	AFM
Sort of analysis	Electron spectroscopy	Electron spectroscopy	Diffraction methods	Scanning probe method	Scanning probe method
Studies	Surfaces chemically (composition)	Surfaces chemically (composition)	Surfaces physically (periodic structures, atom positions, morphology)	Atomic structure (periodic structures, atom positions, morphology)	Atomic structure (periodic structures, atom positions, morphology)
Technique basis	X-ray beam excites core electrons.	Electrons/photons gives Auger response.	Electron beam gives electrons bouncing back with different wavelength..	Probe with applied voltage arise tunneling of electrons from sample to tip.	Small tip on a cantilever scanning surface and is repelled/attracted.
Measures	Outgoing electrons kinetic energies.	Auger electrons kinetic energy.	Wavelengths from elastically backscattered electrons.	Constant height-> difference in current. Constant current -> electric voltage vs. lateral position.	Deflection of the cantilever onto an image.
Spectra – 1 Diffraction pattern – 2 Image – 3	1 – Displayed on binding energy scale.	1 – Shown In derivative mode to resolve from large SE background.	2 – spots reflect the symmetry and crystalline order.	3 – Tunneling current variations as a function of position in the surface plane.	3 – Changes in topography is detected by laser and formed into an image.
Special		Processes dominate for elements with low-Z.	Varying the acceleration voltages gives detail surface info Electron energy 20-500 eV	Utilized both in vacuum and air and in liquid environments. Fast method. Sample need to be conductive.	Sample do not need to be conductive. Can be done in air/liquid.
Methods within	Quantitative	*SAM *Ion bombardment (depth profiling)		*Constant height *Constant current	*Contact mode *Non-contact mode (tapping mode)