

17.7.3 Characterisation of surface structures

Low energy electron diffraction (LEED) See 17.3.

A LEED spot pattern defines the two-dimensional lattice, and (importantly) shows that long range order exists on the surface (but neglects short-range structural disorder). LEED is widely used for these purposes.

Reflection high energy electron diffraction (RHEED) See 17.3.

LEED derives its surface sensitivity from the high scattering cross-section for low energy electrons which impinge perpendicular to the surface. RHEED represents an alternative approach: surface specificity is obtained by using higher energy electrons (typically 20 keV) incident at near to grazing incidence. Since the diffracted beams are recorded at grazing exit angles, the overall scattering angle thus remains small giving rise to a sufficiently high elastic scattering cross-section. In the plane of observation the reciprocal lattice rods are not intersected perpendicularly as in LEED but obliquely, giving rise to "streaks" rather than spots. Since there is no complete quantitative theory for RHEED, the method has so far only been used for the determination of surface periodicity. In this respect LEED and RHEED provide identical information for a smooth surface. Since, however, the sample in RHEED must be turned azimuthally to establish the full two-dimensional periodicity, LEED is in fact the simpler technique. On the other hand, RHEED can provide structural information on rough surfaces for which LEED might be ineffective.

Photoelectron diffraction (PED) See 17.2.1.6.

Recalling the technique of X-ray photoelectron spectroscopy described in section 17.7.2 we note that the kinetic energy of the photoemitted electron, E_k , is given by the difference between the photon energy and the binding energy of the level concerned. In photoelectron diffraction the photoelectron current from a core level of an adsorbed species is measured as a function of either emission angle or photon energy. The coherent interference between the directly emitted electrons and those elastically scattered from the surrounding, (mainly) substrate atoms means that information is obtainable on the position of the emitting atom relative to the substrate i.e. on the adsorption site.

X-ray absorption (SEXAFS) See 17.2.1.4.

SEXAFS has proved particularly successful in determining adsorption sites for atomic adlayers on metal surfaces. As in photoelectron diffraction, no ordered overlayers are necessary. Where LEED and SEXAFS have been applied to the same adsorption systems agreement is good. Data analysis is particularly simple: for energies higher than 50 eV

above the edge EXAFS can be normally described by single scattering. In most cases Fourier transform techniques using known or calculated phase shifts deliver the information on the distance of the emitter atom to the neighbouring substrate atoms. Very often, however, this is not sufficient to determine the adsorption site and a so-called amplitude analysis has to be performed. This entails measuring the amplitude of the SEXAFS modulation for various angles of the polarisation vector relative to the surface.

Helium diffraction

The collision of an atomic beam with a solid surface gives rise to both elastic and inelastic scattering. Since the de Broglie wavelength of a helium atom is of the order of 0.05 nm depending on temperature, elastic collisions are expected to give rise to diffraction phenomena. The repulsive part of the interaction potential between a rare gas atom and a solid arises from the overlap of the electron charge distribution of the surface with that of the incoming atom. Theory shows that a plot of the classical turning point for a scattered He atom corresponds to a constant electron density contour, some tenths of a nm in front of the surface. It is thus clear that He atom diffraction can be used for structural determination of single crystal surfaces. The dimensions of the unit cell can be determined from the angular position of the diffractions peaks, whilst the arrangement of atoms in the unit cell and the resulting surface electronic structure determine their relative intensities. To calculate the intensities of the He diffraction beams a particular structural model is taken and approximated by a periodically modulated hard wall (corrugation function). The model parameters are varied until there is agreement between theory and experiment.

Ion scattering spectroscopy (ISS) See 17.3.

Ion scattering spectroscopy (ISS) is based on the conservation of energy and momentum during the collision of ions with individual surface atoms. If the initial and final energies and momenta of the projectile are known, the mass of the surface atom from which the ion has been inelastically scattered can be calculated.

Grazing incidence X-ray diffraction (XRD), X-ray standing waves

X-ray diffraction has always been the most important technique for determining the three-dimensional structure of bulk materials. The main limitations in using it for surface studies have been the lack of surface sensitivity and the low brightness of conventional X-ray sources. By using a grazing incidence geometry, at an angle close to the critical angle for total reflection, however, the penetration depth of the X-rays is minimised and the surface signal enhanced. The use of synchrotron radiation can provide orders of magnitude more brightness, giving substantially more flux per unit area of surface and a strongly collimated beam. The measured Bragg intensities can simply be evaluated with kinematic scattering theory because of the absence of multiple scattering as in LEED.

X-ray standing wave analysis has also become a viable tool for surface structural studies due to the availability of synchrotron radiation. When an X-ray beam is Bragg diffracted by a perfect crystal, a standing wave field is generated inside the crystal due to the interaction of the coherently related incident and diffracted waves. The nodal and anti-nodal planes of the standing wave field are parallel to and have the same periodicity as the diffraction planes. By varying the angle of incidence it is thus possible to modulate the electric field strength to which an atom at a particular location in the crystal is subjected. If the intensity of a secondary process such as fluorescence is measured, it is then possible to establish the position of the atom relative to the lattice plane.

Field ion microscopy (FIM) and related methods See 7.3.

In a high electrostatic field of 20 to 50 V nm⁻¹ atoms or molecules can be field ionised. Field ionisation occurs in front of a nearly hemispherical field emitter tip with an apex radius of ≈ 100 nm, where the required field strength is produced by applying a few kV potential difference against a counter electrode. Field ionisation consists in electron tunnelling from atoms or molecules into empty energy levels above the Fermi energy of the solid. A minimum distance X_c is required (establishing a forbidden ionisation zone) which is determined by the ionisation potential I , the work function Φ and the field strength E :

$$X_c = \frac{I - \Phi}{E}$$

Field desorption and field evaporation are achieved with an even higher electrostatic field strength. They are thermally activated processes.

Related methods are: *Field Ionisation Mass Spectrometry (FIMS)* for the measurement of the charge to mass ratios of the ions generated at the field emitter surfaces; *field ion appearance potential spectroscopy* involves measurement of the energy distribution of the ions, i.e. the high energy onset in the integral kinetic energy distribution (produced by field ionisation, field desorption or field evaporation) establishes the minimum energy for the ionisation process; *electron-stimulated field desorption* and *pulsed laser field desorption* or *photon-induced field desorption*.

Electron microscopies (TEM, SEM, STEM) See 17.3.

Although a wide variety of diffraction methods and spectroscopic techniques is available for the structural characterisation of surfaces, only direct microscopic methods are able to provide real space information about local inhomogeneities such as surface steps, terraces, domains and defects. Although direct imaging of surfaces with electrons has been

somewhat overshadowed by the invention of the scanning tunnelling microscope, considerable progress has been made in recent years in conventional electron microscopy following the belated introduction of ultra high vacuum (UHV) into electron microscopes.

Scanning tunnelling microscopy (STM)

The scanning tunnelling microscope is able to directly probe surface structure and electronic properties down to the atomic scale. In the experimental set-up a sharp metal tip (atomically sharp in the ideal case) is scanned across the surface at distances in the order of typically 1 nm or less. Scanning is usually performed by means of piezoelectric translators (tripods or single tubes which allow motion in all three directions of space, from atomic dimensions up to several μm). Coarse approach of the tip to the surface can be performed by means of fine-threaded screws, differential spring systems or electrostrictive devices. As the tip is scanned across the surface a bias voltage of typically a few millivolts is applied between the tip and the sample leading to a tunnelling current in the order of a few nanoamperes. Since there is an exponential relation between the tunnelling current and the tip-surface separation, the tunnelling current is an extremely sensitive measure for controlling that separation. For example a variation of the separation by 0.1 nm will change the tunnelling current by a factor of approximately 10. This means that in principle variations in the separation of 0.001 nm can be monitored by keeping the current constant (through vertical repositioning of the tip by a feedback loop) within a few percent. Thus, surface topography can be obtained with an extremely high resolution (resolutions of better than 0.2 nm laterally and 0.01 nm vertically have been achieved). It should be pointed out, however, that the tunnelling current is also influenced by the electronic structure of the surface. Since electrons can only tunnel from occupied states in the tip to unoccupied states in the surface or vice versa depending on the polarity of the bias, in general for small voltages the STM images represent contours of the local density of states near the Fermi level (LDOS_{EF}). A great advantage of the method is the fact that information is obtained in real space, which allows local defects like e.g. atomic steps or dislocations to be resolved. Furthermore, measurements can also be made under ambient conditions and are not restricted to ultra high vacuum. Finally, it should also be mentioned that spectroscopic information is obtainable by measuring the tunnelling current as a function of the tip-sample separation or the bias voltage.

Atomic force microscopy (AFM)

In AFM a sharp tip mounted on a soft lever is scanned across the sample surface by means of piezoelectric translators while the tip is in contact with the surface. The force acting on the tip changes according to the sample topography resulting in a varying deflection of the lever, which in commercial instruments is measured by means of laser beam deflection off a micro fabricated cantilever and subsequent detection with a double segment photo diode. Cantilevers (with integrated tips, e.g. silicon or silicon nitride) with extremely low force constants of less than 10^{-1} Nm^{-1} and resonance frequencies of more than 100 kHz can be produced which allow imaging with forces in the nN and sub-nN range. In AFM the tip is

always touching the sample surface, which we call the contact mode. As a consequence there is always an interatomic repulsive force at the contact area owing to penetration of the electronic shells of the tip and substrate atoms. In addition to this short range force long range forces (e.g. Coulombic forces between charges, dipole-dipole-interactions, polarisation forces, van der Waals dispersion forces, capillary forces due to adsorbate films between tip and substrate), which can be attractive or repulsive, are also encountered. However, high resolution imaging is only possible by utilising the short range interatomic forces, because only these are confined to a small area. The great potential of AFM for surface analytical studies mainly arise because surfaces can be imaged from the μm range down to the atomic scale, images contain direct depth information, both conductors and insulators can be imaged and measurements can be performed under ambient conditions under liquids and in gases.

A further development is tapping mode AFM. In this technique the tip is vibrated above the sample surface in such a way that it just slightly taps the sample surface. The corresponding change in the amplitude of the signal can be used to monitor the surface topography. The advantage of this technique is the fact that lateral shear forces are eliminated and vertical forces can be reduced significantly. This is advantageous when looking at soft and sensitive surfaces.

Besides AFM there are a number of other scanning force microscopic techniques (e.g. electrical force microscopy, magnetic force microscopy, van der Waals force microscopy), which operate in the non-contact mode and make use of long range forces. Finally it should be mentioned that scanning force microscopic techniques have also been used to access other material properties like elasticity by force modulation, friction phenomena by friction force microscopy and adhesion by force-distance measurements.

Electronically stimulated desorption (ESD)

Electronically stimulated desorption is the surface analogue of electron impact dissociation or photodissociation in free molecules. Ions or neutral species are desorbed from an adsorbate-covered surface as a result of an electronic transition into a repulsive state induced by electron impact or photon absorption. The internal bond concerned will then be broken as long as the excitation remains localised. On surfaces the number of channels for energy transfer i.e. for charge delocalisation will be very large so that the desorption cross-sections are in general very small compared to dissociation cross-sections in isolated molecules. They also vary over several orders of magnitude. Although the effect was discovered many years ago there has been renewed interest lately owing to the possibilities offered by synchrotron radiation allowing investigation of the primary excitations in some detail. In fact, the technique should really be designated as a probe of electronically excited states at surfaces. A display apparatus enables the desorption patterns to be photographed directly. There is still some controversy as to whether the patterns can be interpreted.