XSW

A standing X-ray wave is set up by using a Bragg reflection from the crystal surface. The incident and reflected beams create the standing wave which will extend out of the surface. The intensity of the standing wave at a particular position can be changed by altering the reflection angle, or the photon energy. The intensity of an Auger (seeAES) or fluorescence (see EDX) peak from a molecule attached to the surface is then monitored. The variation of the intensity of the peak can provide information regarding the adsorption site and thus provides information complementary toSEXAFS and XPD). XSW has the advantage of being able to work in non-UHV conditions and to investigate buried interfaces, but a high degree of crystal perfection is necessary. Changing the photon energy means that a synchrotron radiation source is required.

According to dynamical diffraction theory, when an x-ray plane wave is Bragg diffracted from a perfect single crystal, a standing wave will be created above and below the crystal surface as a result of the interference between the incident and the reflected beams, as the figure shows. This standing wave is characterized as having the same period as the d-spacing of the corresponding diffraction planes. When a scan of the incident angle is performed within the angular range of a rocking curve (typically <50 micro-rad), the nodes and the antinodes of the standing wave move inward by half a d-spacing with the increase of the angle. On the low angle side, the nodes line up perfectly with the diffraction planes; while on the high angle side, the antinodes line up with the diffraction planes.
When interaction of photons with impurity atoms occurs on the surface or in the bulk, if the incident x-ray has the energy above the lowest absorption edge of the impurity atoms, the electric field of the standing wave will stimulate the photoelectric effect, which leads to the emission of Auger electrons and x-ray fluorescence photons with characteristic energies. By dipole approximation for the photoelectric effect, the intensity of the fluorescence yield is proportional to the electric field intensity of the standing wave at the center of the impurity atoms.
By combining the absorption of the crystal, the reflectivity, the phase difference between the incident and the reflected plane waves, we could obtain the coherent fraction and coherent position. They are directly related to the phase and amplitude of the Hth Fourier component of the electron density of the impurity atom. Coherent position is the relative position of impurity atom with respect to the diffraction plane. And coherent fraction is a number between 0 and 1. A random distribution of the impurity atoms would give a value of zero, and it is unity only when all the atoms are in the same position.

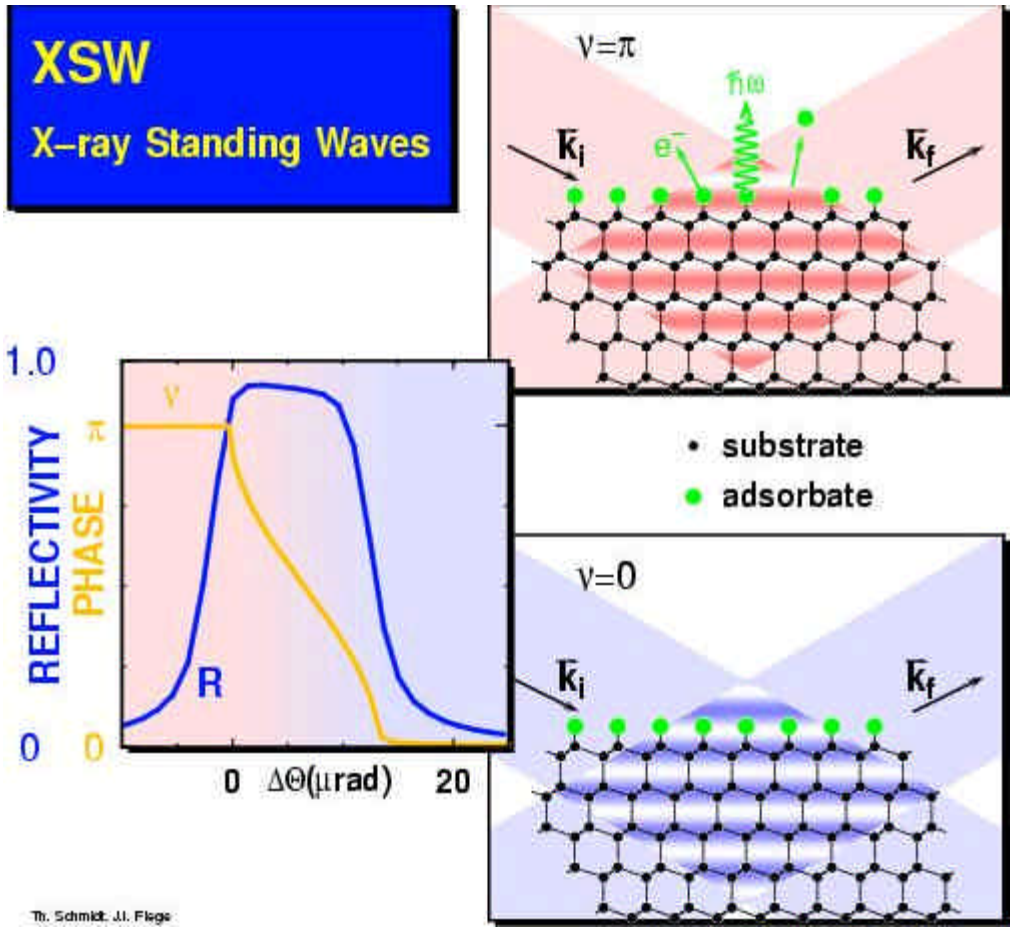
ABSTRACT

Research in this section of our group is focused on the structural aspects of thin films, adsorbate systems and growth phenomena. For a characterization various surface science techniques are used. However, most specialized we are in the use of x-ray standing wave fields (**XSW**), x-ray diffraction and x-ray reflectivity.These methods are non-destructive and the use of synchrotron radiation enables high accuracy measurements of doping profiles with less than monolayer sensitivity.

X-RAY STANDING WAVES

Measurements of x-ray standing waves (**XSW**) can be used to identify the lattice position occupied by the selected element, e.g. dopant or adsorbate atoms and the fraction of these atoms on lattice sites. An x-ray standing wave field is generated with a monochromatic x-ray beam and the sample is scanned in angle or wavelength through a Bragg condition. The interference of the incoming and Bragg reflected waves results in the formation of a x-ray standing wave field with the periodicity of the Bragg diffraction planes. The interference effects and the exact shape of the Bragg reflection are properly described by the dynamical theory of x-ray diffraction.
Briefly summarizing, the Bragg peak of a perfect crystal has a finite width of some 10 to 1000

microradians, depending on the Bragg reflection, the crystal material and the x-ray wave length. The phase of the x-ray standing wave field with respect to the diffraction planes changes when scanning through a reflection. For incidence angles below the exact Bragg condition, the antinodes of the x-ray standing wave field are located exactly between the diffraction planes, while for incidence angles above the exact Bragg condition, the antinodes coincide with the diffraction planes. The combination with an inelastic signal which is proportional to the intensity of the x-ray standing wave field results in an element specific method with extremely high spatial resolution. As inelastic signal the x-ray fluorescence yield, photoelectrons, Auger electrons and desorbing ions can be used. The latter combination of **XSW** and x-ray photon stimulated ion desorption (XPSID) also allows the investigation of the dominating desorption mechanisms induced by electronic excitations in the x-ray regime .The principle of **XSW** is schematically shown in the figure below for various secondary signals.

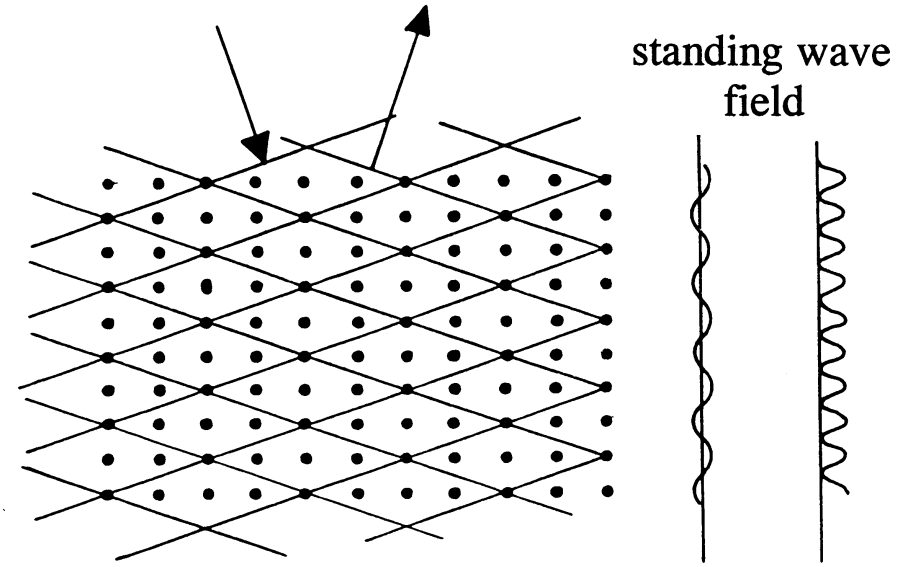


X-RAY REFLECTIVITY

The x-ray reflectometry is a well known nondestructive method to characterize thin films and multilayer structures. Most often the x-ray reflectivity data are to be analyzed by modelling the electron density profile of the investigated specimens. The technique has the potential to evaluate thickness, density and interfacial roughness of an ultrathin layer with very high accuracies. It has a good resolution (about 0.10 nm) in measuring the surface roughness parameter as well, and gives average results owing to relatively large surface area of the specimen examined. Although negative, a characteristic feature of this technique is that it is not sensitive to crystal structure, dislocations and defects. This is because the signal depends only on the electron density of the studied material.

However, as long as the x-ray scattering vector is always perpendicular to the surface, this technique is very sensitive to the vertical surface and interface roughness. In the case of solid surfaces the usual Descartes-Snell law of refraction applies, and there is very little penetration of the incident radiation for grazing angle of incidence inferior to the critical angle for total external reflection. The specularly reflected intensity ideally follows the Fresnel law of optics which, for larger angle of incidence, falls off rather rapidly with increasing the roughness parameter. In our laboratory we routinely use this x-ray reflectometry method to characterize thin films and ion-bombarded specimens

NIXSW - Normal Incidence X-ray Standing Wavefield Absorption



When an X-ray Bragg reflection is established in a crystal the incident and scattered waves interfere to produce an X-ray standing wavefield in the crystal which has a periodicity in intensity equal to the periodicity of the associated scatterer planes of the crystal. A full dynamical (multiple scattering) formulation of the X-ray scattering under these conditions shows that the range - in X-ray incidence angle or wavelength - over which the nominal total reflectivity of the Bragg condition is maintained is finite, and the standing wave thus exists throughout this range. However, the juxtaposition of the nodal planes of the standing wave relative to the scatterer planes - i.e. the phase of the standing wave - shifts in a systematic and predictable fashion within this range by one half of the scatterer plane spacing. This can be used to locate specific atomic species within the solid by monitoring the X-ray absorption of these species as a function of scattering condition within the total reflectivity range. If the absorber lies on the nodal planes of the standing wave no adsorption is detected, while if they lie on the antinodes, enhanced absorption is found. In this way XSW can be used to locate specific atoms, relative to the bulk scatterer planes, not only within a crystal, but also at the surface of a crystal, because the standing wavefield extends far above the surface. A key limitation of this general XSW method, however, is that under general conditions the angular range of the total reflectivity condition - the 'rocking curve width - can be very narrow (seconds of arc) so the experiment is only possible on samples which have a very high degree of crystalline perfection. Typically this restricts the method to semiconductor samples (especially Si) and a few materials grown with especial care.

In experiments in the 1980s the Warwick group, in collaboration with Rob Jones at Nottingham University, showed that this restriction can be overcome by working at Bragg conditions close to normal incidence to the scatterer planes [1]; in this case the Bragg condition goes through a turning point and the effective rocking curve width can be of order 1 degree or more. The resulting normal incidence XSW (**NIXSW**) method has now been applied successfully to many adsorbate systems (Cl, S, CH3S-, CH2ClCH2Cl, Na, O, Rb, CH3O-, PF3 etc.) on standard metal surfaces (especially

Cu, Ni, Al) [2] using the Daresbury Synchrotron Radiation Source (SRS). This is a continuing programme in which we are seeking to push the method to problems of increasing complexity and potential technical relevance. In addition to continued use of the SRS we are now making increasing use of the European Synchrotron Radiation Facility (ESRF) in Grenoble. The very significant improvement in both flux and resolution at the ESRF undulator stations an this third-generation X-ray source means that it is possible to exploit 'chemical shifts' in photoelectron binding energies to determine the structure of coadsorbed molecular fragments and reaction products, and the first such results have now been published [2,3]. It should also be possible to map the local adsorption structure through adsorbate phase diagrams and to make further progress on the **NIXSW** technique in the study of low atomic number adsorbate species - especially C, N and O.

Normal Incidence X-ray Standing Wave

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