

A SHORT REVIEW OF METHODS FOR STRUCTURAL STUDIES OF SURFACES AND THIN FILMS

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Abstract

Interest in structural features on surfaces has been gradually increasing during last decades. Many different methods for studies of surface structures have been developed. In this short review, specific features of surface structure are mentioned and then the methods for studies of surface structures are characterized. They can be divided into several groups - diffraction methods (LEED, XRD, GIXRD, SWXRS, atomic diffraction), spectroscopic techniques (EXAFS, NEXAFS, SEXAFS), scattering (ISS) and microscopies (FEM, FIM, STM, AFM).

1. Surface crystallography

There are several sources of information on surface crystallography, in addition to International Tables of Crystallography. A nice survey can be found for example at site [1] from which also some illustrative pictures were taken for this review. Books [2-4] can also be useful for first reading on surface crystallography.

Structural effects on surfaces

The main aim of structural studies of surfaces consists in the identification of surface atoms and their positions as well as the length and character of bonding. 2D surface structures are usually different than in the bulk. Several effects are studied:

Relaxation is a small and subtle rearrangement of the surface layers which may nevertheless be significant energetically. It involves adjustments in the layer spacings perpendicular to the surface, there is no change either in the periodicity parallel to the surface or to the symmetry of the surface.

The *reconstruction* of surfaces is more often observable effect, involving larger displacements of the surface atoms. It occurs with many of the less stable metal surfaces, but is much more prevalent on semiconductor surfaces.

Unlike relaxation, the phenomenon of reconstruction involves a change in the periodicity of the surface structure.

The effect of *adsorption* of foreign atoms can often be observed. The adsorbed atoms usually create a new (reconstructed) structure.

The stability of surface depends on the surface energy. Dense, closely packed crystallographic planes are quite stable but if the crystal is cut in a general high index direction then other surface structures can appear - *facets* and *steps* with low index planes.

Artificial surface structures like *quantum dots* and *quantum wires* are of increasing interest nowadays.

Crystallography

In 2D there are only five lattice cells - oblique, hexagonal, square, rectangular and centered rectangular. For description of the surface structures two notations have been introduced - matrix and Woods notation. The former is rigorous scheme relating the unit cell lattice vectors of the surface 2D structure - b to basis vectors a of substrate (bulk) 2D structure (Fig. 1) in matrix form. However, the latter is much more frequently used since it is quite clear.

General form is the following

$$M(hkl) - p/c \begin{pmatrix} m & n \end{pmatrix} R \quad E$$

where M is the substrate (element, phase), (hkl) is substrate orientation - plane parallel to the surface, p or c means primitive or centered cell of the surface structure, m and n

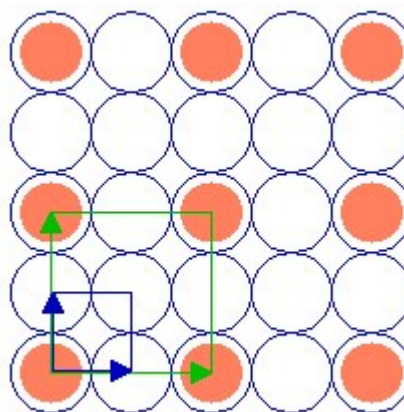


Figure 1. Example of surface structure (dark atoms). Matrix notation $\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$, Woods notation (2 2)

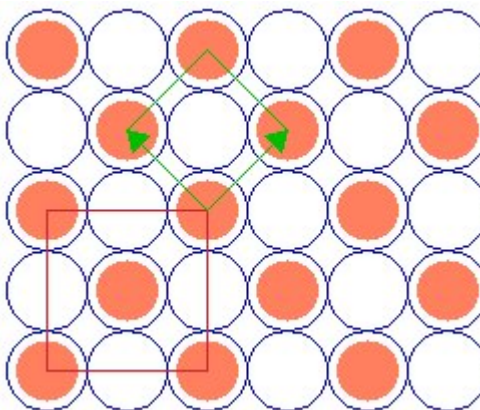


Figure 2. Example of surface structure (dark atoms). Two unit cells can be chosen - centered (left bottom) which would be marked as $c(2 \ 2)$ or primitive but rotated (upper) which should be marked as $\begin{pmatrix} 2 & 2 \\ 0 & 0 \end{pmatrix} R45$.

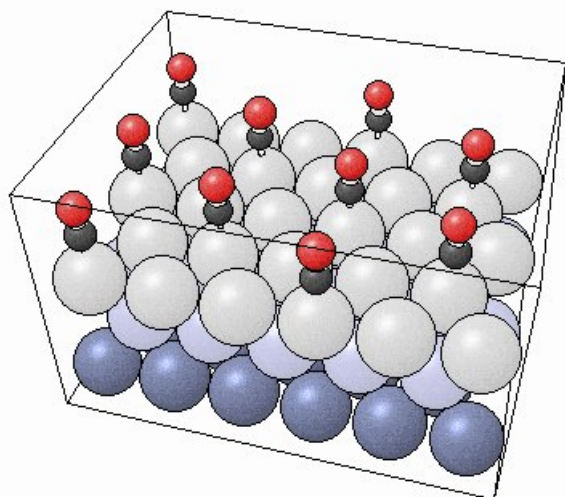


Figure 3. Example of surface structure Ru(0001) - (3×3) R30-CO

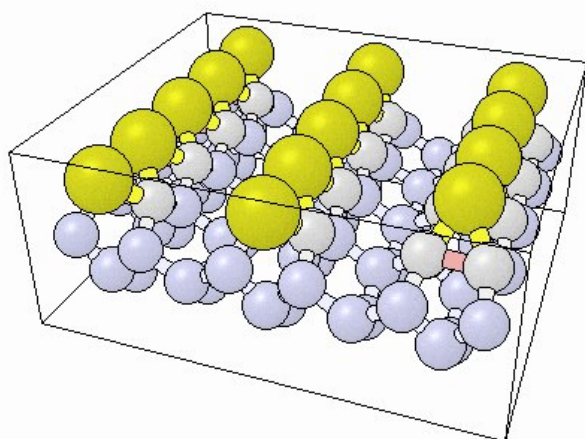


Figure 4. Example of surface structure Si(100) - (2×1) - Na

are equal to the ratio of corresponding unit cell vectors of the surface and substrate structure, respectively (b_1/a_1 and b_2/a_2), R stands for possible rotation of the surface unit cell with respect to the substrate unit cell, E is used for the specification of adsorbate atom or molecule. Examples are shown on Fig. 2-4

Steps and facets have a little more extended notation.

$$M(S) - (m(hkl) \quad n(h'k'l'))$$

where S stands for substrate, m is number of atoms in the terrace plane of the orientation (hkl) and n the number of atoms in the step of the orientation ($h'k'l'$).

NIST distributes database of surface structures. Many pictures can be found at [5]. Surface planes can be visualized by Surface Explorer [6].

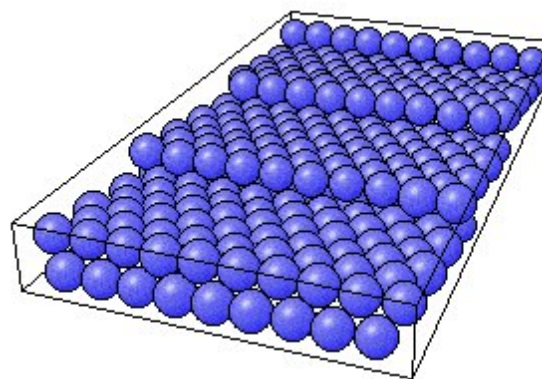


Figure 5. Example of surface step structures fcc(775)

2. Methods for studies of surface structures

The methods can be divided into several groups - diffraction, scattering, spectroscopic and microscopic. There are numerous books and articles on the methods [e.g. 7 - 15].

2.1 Diffraction methods

Low energy electron diffraction

This is the traditional method of study of surface structures. It was discovered by Davisson, Kunsman and Germer in 1924-27. Diffraction of electrons of energy in the range 30 - 500 eV is suitable for study of surface because the penetration depth is only a few atomic planes in general. The general scheme of experiment arrangement can be seen on schematic picture (Fig. 6).

Analysis of the geometry of LEED diffraction patterns can give 2D surface structures. However, it must be taken into account that the Ewald construction looks differently than for 3D because reciprocal lattice points are replaced by reciprocal lattice rods (Fig. 7).

This approach is insufficient for 3D surface structure determination, i.e. the position of the 2D surface layer with respect to the substrate. In this task, intensities of diffraction spots must be measured. The corresponding theory is much more complicated than for X-ray diffraction. It includes dynamic theory and quantum theory of scattering on muffin-tin potential. Actually, the so-called I vs E (intensity vs energy) is used.

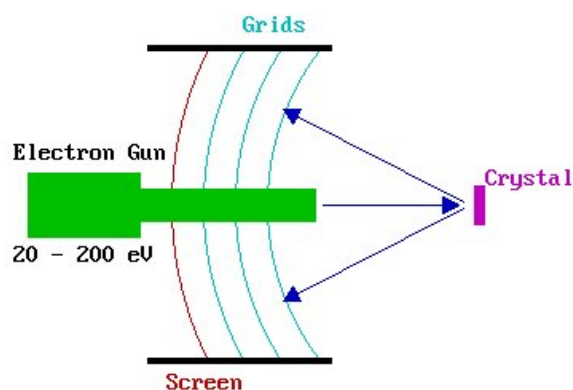


Figure 6. Schematic picture of LEED experiment. The grids placed in front of the screen because of energy filtering, direct path of the electrons and shading of field of collector, respectively.

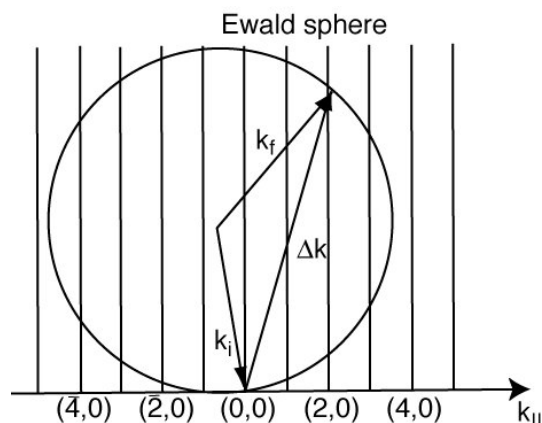


Figure 7. Ewald construction for 2D surface structure. Instead of reciprocal lattice points, reciprocal lattice rods must be considered.

sity vs. energy) curves are measured for different Bragg diffraction spots (hk). The experimental data are then compared to theoretical calculations made for different surface structure models. More sophisticated criteria for estimation of the agreement than usual R -factor must be constructed. Kinematical theory is only sometimes used for particular problems like steps and facets on the surface. For more, see e.g. [3, 4]

Reflection High Energy Electron Diffraction

The method is used at low angles of incidence ($1-3^\circ$) and energy range of electrons 1 - 10 keV. Corresponding penetration depth is 3 - 10 nm. In the arrangement, the radius of the Ewald sphere is very large. The method is in particular used for the in-situ studies of thin films growth. Two basic modes can be distinguished - layer-by-layer growth (circles on diffraction pattern) or bulk-like with nucleation centers (spots on the pattern - diffraction in transmission).

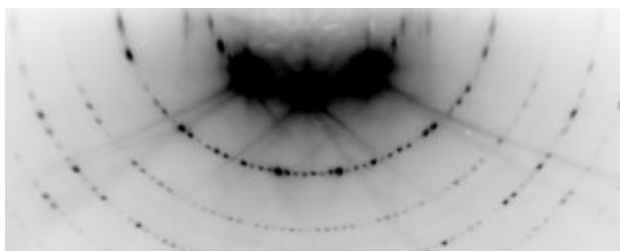


Figure 8. Example of RHEED picture.

Atom scattering and diffraction

This method was suggested already in 1929 by Stern but since it is experimentally not that simple, it has been developed only after 1970. It uses the beam of neutral He or Ne atoms with rather low energies - 20 - 300 meV corresponding to wavelength of about 1 Å. This is the most surface sensitive method as the atoms feel only periodic surface atomic potential and do not penetrate into the film. The simplest model of the surface is called corrugated hard-wall model and the surface potential is described by

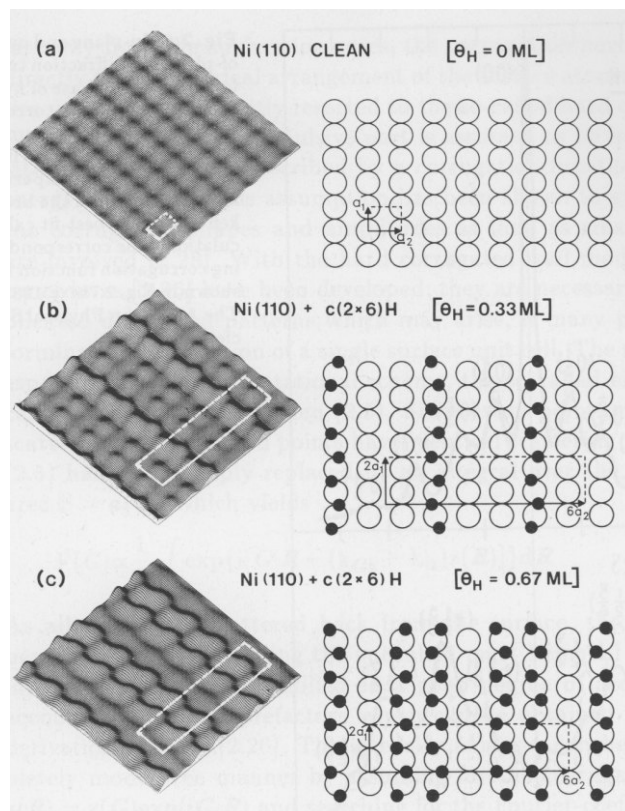


Figure 9. Evolution of H surface structure on Ni(110) surface.

periodic corrugation function which is to be determined from the experiment. Main advantage is strong scattering on the atoms with low Z so that it is suitable for study of hydrogen chemisorption, insulating surfaces, surface reconstruction and vibrational characteristics. It is a complementary method to LEED and unlike LEED it is not sensitive to interplanar spacing. On Fig. 9, a part of quite famous picture is shown - evolution of hydrogen surface structure on Ni(110) surface with hydrogen coverage. In left parts the corrugation functions, and in right parts corresponding models are shown, respectively. See e.g. [14] for more.

X-ray diffraction

XRD methods for study of *polycrystalline thin films* consist first of all in phase analysis, determination of crystallite size, strain, stress and texture. Depth profiling can also be done by using of different radiation and angles of incidence (varying penetration depth) or by specimen etching.

In the field of *single crystal films* the highest interest is usually in studies of epitaxial films where the misfit, tilt and strains are determined and also in implanted films for which the strain profile is determined.

Reflectivity measurement of all amorphous, single crystalline and polycrystalline thin films can give information on electron density and surface roughness.

Special techniques of surface diffraction are *grazing incidence diffraction* and *standing wave method*. Application of both methods for biological materials has been described in this journal recently [16]. The former method is a non-coplanar geometry close to the critical angle of total reflection when lattice planes perpendicular to the surfaces



are diffracting. The latter method consists of measurement of secondary radiation or particles (fluorescent radiation, photoelectrons, Auger electrons, Compton radiation) coming from the surface layers or adatoms during diffraction. The appearance of secondary radiation is related to the standing waves generated in the substrate under the diffraction phenomenon. The method is extremely sensitive to the position of surface atoms and it is chemically selective.

2.2. Spectroscopic methods

There are a number spectroscopic method for study of surfaces. They are usually used first of all for elemental analysis and also for studies of electronic structures, however, structural features can also be derived for example from the information on bonding. This concerns the methods like *XPS* - *X-Ray Photoelectron Spectroscopy*, *UPS* - *Ultraviolet Photoelectron Spectroscopy* and *AES* - *Auger Electron Spectroscopy*. The generated photoelectrons can be a local source for diffraction inside the material. The method of *Photoelectron Diffraction* is used for study of local environment of a selected (chemical) atom in the material.

Extended X-Ray Absorption Fine Structure - EXAFS

The method consists in measurement of absorption coefficient in dependence on the energy of incoming beam. The coefficient can be measured simply in a transmission as attenuation of the beam but for the purpose of thin film studies, it is measured indirectly through the secondary effects connected with the absorption process - photoelectrons, Auger electrons. Since absorption edges of particular atoms are studied, the method is chemically selective. Sur-

roundings of the selected atom can significantly modify the absorption edge and leads to oscillations (Fig. 10).

The surface sensitive alternatives of the method are called *SEXAFS* - *Surface Extended X-Ray Absorption Fine Structure* and *NEXAFS* - *Near Edge X-Ray Absorption Fine Structure* (*XANES*). The NEXAFS is usually considered about 50 eV from the edge. Quite complicated processes with multiple scattering are connected to this region which is sensitive to the detailed distribution of electron density. The method is mainly used for study of molecules on surfaces where the intramolecular processes are dominating.

The methods are suitable for study of local surroundings of the atom selected. Maxima in the oscillations correspond to the effective coordinate number in a specific distance from the atom. As the processes are given by the dipole selection rule there is a strong dependence on the orientation of the electric field vector with respect to the important direction in the structure (from the atom studied) for example significant molecule axis. The direction of the electric vector can be changed by the direction of the beam. Usually two beam directions are used - perpendicular to the surface (electric vector is in the surface plane) and at small angle of incidence (electric vector is nearly perpendicular to the surface). Example is shown on Fig. 11.

For molecules on the surfaces, the method can give orientation of the molecule on the surface (accuracy about 10°), bond length and hybridization.

In some cases, the method can also give orientation of surface atoms with respect to the substrate atoms, atomic distances in clusters.

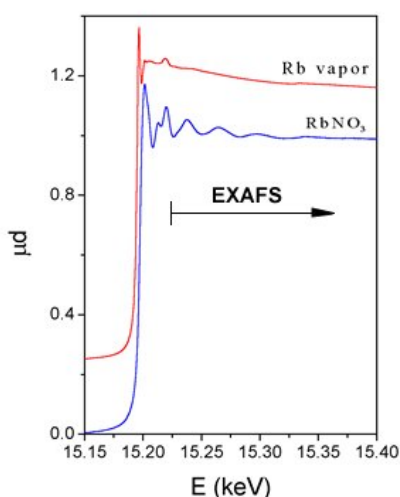


Figure 10. Comparison of the absorption edge for Rb atom in vapor and Rb atom in RbNO_3 . More significant oscillations are found for the latter case.

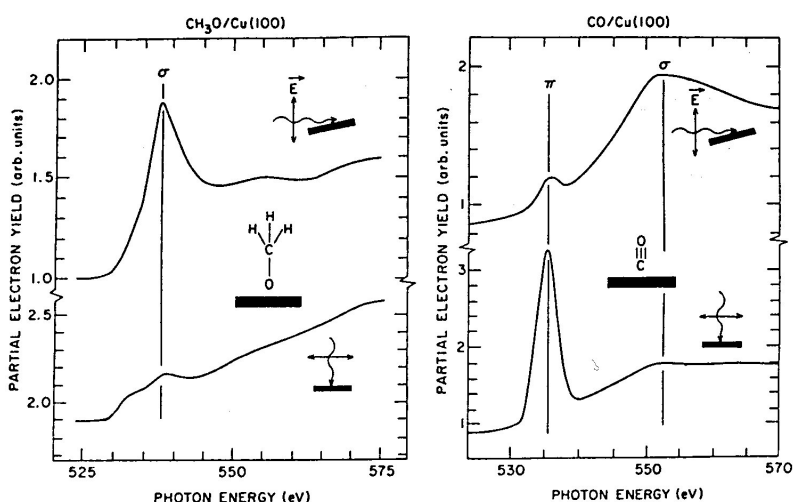


Figure 11. Example of NEXAFS spectra for CH_3O and CO on $\text{Cu}(100)$ for two different orientations of electric field vector. Orientation of molecule on the surface can be estimated as well as the triple bonding in CO and bond length.

2.3 Scattering

The most important method in this group of methods is ion scattering, *ISS - Ion Scattering Spectroscopy*. It can be divided into three groups according energy - LEIS, MEIS, HEIS (low, medium, high). Usually ions of He or Ne are used in the energy range 100 eV - 10 keV. High energy ions are used in the well-known Rutherford Back Scattering - RBS (500 keV- 2 MeV).

RBS is used mainly for chemical elemental analysis which can be depth sensitive. The method was well characterized for example in [17]. If the surface has crystalline structure, the so-called surface peak can appear in the signal dependence on energy. The peak is related to the mass of scatterers but can also be used for characterization of the structure because its intensity is related to the direction of incoming ions with respect to the crystallographic directions (the so-called channeling) and of course to all the surface structural effects - relaxation if the beam is inclined to the surface, reconstruction and adsorption. The method is quite simple and can also be used for separation of effects of enhanced surface atom vibrations from the relaxation effects by angular measurements. It is a very suitable as a complementary method to previous techniques also in study under non-ambient conditions.

2.4 Microscopy

The first microscopical studies were performed by *FEM (Field Emission Microscope)* which cannot in principle reach atomic resolution and *FIM (Field Ion Microscope)* which was the first microscopic method able to visualize individual atoms. However, both method has severe limitations in the shape of sample which must be a sharp tip.

After discovery of *STM (scanning tunneling microscopy)* very fast development in this field lead to appearance of different variants of surface microscopies with atomic resolution, first of all *AFM (atomic force microscopy)*. However, a special contribution [18] will be devoted to the topics.

Acknowledgement

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