

THE STRUCTURE OF SOLID SURFACES AND OF ADSORBATES BY LOW-ENERGY
ELECTRON DIFFRACTION

by

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Low-energy electron diffraction (LEED) is one of the powerful techniques to study the atomic structure of surfaces. The theory has developed to the point where the diffraction beam intensities can be computed using the locations of surface atoms as the only adjustable parameters. The position of atoms in many clean monatomic solid surfaces and the surface structures of ordered monolayers of adsorbed atoms have been determined this way. Surface crystallography studies are now being extended to small hydrocarbon molecules that are adsorbed on metal surfaces. The physical picture of the surface chemical bond emerges from these studies.

A. Experimental system and procedure to obtain the surface structure.

Ultrahigh vacuum conditions (UHV), base pressure approximately 10^{-9} torr are maintained to insure surface cleanliness. The backscattered electrons are postaccelerated to a fluorescent screen, and the diffraction pattern so produced is observed through a glass viewport. Sharp spots are indicative of long-range order, i.e., the ordered domain sizes on the surface are larger than the lateral coherence length of the electrons (~ 100 Å). Extra diffraction spots, meaning those not expected on the basis of

simple termination of the bulk lattice structure along the surface plane, indicate either reordering (reconstruction) of the lattice in the surface region or the presence of ordered impurity structures.

There are several auxiliary techniques that are available in the diffraction chamber to analyze surface cleanliness and to prepare surfaces that are clean and ordered. These include the popular Auger electron spectroscopy which is routinely used to identify impurities that may be present with about 1% of a monolayer sensitivity. It also includes ion bombardment capability using 300 volt inert gas ions that remove by direct impact impurities which may have segregated at the surface. Other techniques of surface analysis include X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS). Recently high resolution electron loss spectroscopy (HRELS) that excites vibrational modes of surface atoms and molecules is being developed to analyze the surface structure, to complement the structural information available from LEED.

The energy range of 15-200 eV ^{of the} / incident ^{electrons} provides optimum surface sensitivity. The electrons are rather strongly scattered in an elastic fashion by the attractive Coulomb forces of the atomic nuclei and may traverse very complex trajectories (multiple or dynamical scattering) before exiting from the crystal. These considerations are, of course, quite general and also have some bearing on quantitative interpretation of Auger electron spectroscopy and photoelectron spectroscopy.

The two-dimensional unit cell vectors are readily found from observation of the diffraction pattern geometry. We cannot in this manner, however, discover the arrangement of atoms or molecules in the basis of the unit cell, nor information concerning spacings of the atom in the

direction perpendicular to the surface plane. This essential information can be extracted from analysis of the dependence of the intensity I of the diffraction spots on incident beam energy V -- so-called I - V profiles. These profiles exhibit pronounced peaks and valleys which are indicative of constructive and destructive interference of the electron waves scattered from planes parallel to the surface as the electron wavelength is varied. The combination of intensity features, single and multiple scattering, serve as the basis of the surface crystallography analysis. The presence of well-defined peaks and valleys, of course, indicates that LEED is actually not a purely two-dimensional surface diffraction technique. There is a finite penetration and diffraction takes place in the first 3 to 5 atomic layers. This, of course, allows one to study the structural properties in the near surface region that includes atoms below the top-most layer of atoms.

The diffraction beam intensities are measured by photographing the fluorescent screen or by using other means of detection of the elastically scattered electron flux. Future developments will most likely include image intensification and cathode ray tube display methods that are so well advanced in other technologies.

There have been a number of formulations of low-energy electron diffraction which take proper account of multiple scattering and inelastic scattering from crystalline solid surfaces. Few approximations are made; the important ones concern the construction of the crystal potential. The resulting formulas transform to computationally more efficient expressions currently in use which are based upon reflection and transmission matrices from individual surface layers.

Even with the most efficient computational procedures presently developed, a complete dynamical LEED intensity analysis is still feasible only for systems with relatively small surface unit cells containing up to ~5 atoms in a unit cell.

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B. The structure of metal surfaces.

The surface unit cell of a low-index face of a clean metal surface has generally been found to be that expected from the projection of the bulk (X-ray) unit cell to the surface [referred to as (1x1)], and the uppermost layer z-spacing is equal to the bulk value within the estimated accuracy of about 5%. However, the Al(110) (5-15%), Mo(100) (11-12%) and W(100) (6%) surfaces seem to show substantial contraction in the upper-layer z-spacing with respect to the bulk, while retaining the (1x1) surface unit cell. A simple contraction or expansion of the interplanar z-spacing of this kind is usually termed a relaxation. More dramatically, the (100) and (110) faces of Ir, Pt and Au and the (100) surfaces of Mo

and W are reconstructed, i.e., the two-dimensional surface unit cell is different from that given by the termination of the bulk structure along the plane of interest.

In general, one observes that crystal planes having relatively less dense packing of atoms will be more prone to relaxation or reconstruction as compared to the most densely-packed plane of a given crystal structure. In order to minimize the surface free energy in these cases a rearrangement (perhaps a subtle one such as a slight buckling of the surface) of surface atoms from the bulk positions may, therefore, be quite favorable.

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C. The structure of semiconductor surfaces.

Several elemental (Si, Ge) and compound (GaAs, InSb, etc.) semiconductor surfaces have been studied by LEED and in some cases diffraction beam intensities have been analyzed. Whereas surface reconstruction is certainly rare for metals it seems to be very common for semiconductors. Competing models for the reconstruction of cleaved silicon surfaces involve either periodic displacements of the surface atoms from bulk positions or the formation of ordered surface vacancies.

The essence of Haneman's model for the Si(100) surface is as follows. In the bulk material the Si atoms are tetrahedrally coordinated with an sp^3 hybrid bonding scheme. The surface atoms, however, have only three nearest neighbors and the remaining "dangling bond" may have a tendency to become more p-like. If this happens the back bonds will tend towards sp^2 hybridization or trigonal bonding which is essentially planar. These considerations suggest a movement of the surface atom towards the second plane of atoms (contraction of the back bonds), but this will in turn give rise to lateral forces on the second layer atoms, forces which can be released if other atoms in the upper layer are slightly raised. The net result is a slight buckling or rumpling of the surface caused by the raising and lowering ($\sim 0.1-0.2 \text{ \AA}$) of alternate rows of surface atoms, thereby producing a (2x1) periodicity. A number of theoretical calculations for the electronic structure of the idealized Si(111)-(1x1) surface have been reported.

Non-stoichiometry is apparently a major factor in the observed reconstruction of the polar faces of the III-V semiconductors such as GaAs (zinc blende structure). The $(\bar{1}\bar{1}\bar{1})$ surface has been found to lose As at elevated temperatures and this is associated with a $(\sqrt{19} \times \sqrt{19})$ surface structure, while the low temperature (2x2) structure is arsenic-stabilized. Similarly, phosphorous is found to preferentially desorb at high temperatures from the GaP($\bar{1}\bar{1}\bar{1}$) surface. On the other hand, GaAs(110) surface which has an equal number of Ga and As surface atoms does not exhibit reconstruction but LEED intensity analysis does favor outward (inward) movement of As (Ga) surface atoms.

A LEED intensity analysis has been reported for the layered metal

dichalcogenide compound MoS_2 .

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D. The structure of alkali-halide surfaces.

Definitive studies of the surface atomic structure of ionic materials have not yet been made by electron-diffraction techniques. However, McRae and Caldwell did find LEED evidence for a distortion of the (100) surface of LiF indicating that the top Li and F sublayers do not lie in the same plane, i.e., the surface is periodically buckled. This result is qualitatively consistent with the theoretical predictions.

A number of studies have pointed to possible non-stoichiometry of alkali-halide crystal surfaces upon cleavage. These surfaces may also become charged or damaged under electron beam exposure. In general there is preferential desorption of the halogen atom from the surface.

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E. The structure of oxide surfaces.

The interaction of oxygen with metals to produce various surface oxides is of considerable chemical and technological interest, but relatively few structural studies have been carried out by LEED. Changes in chemical composition have been related to the formation of new surface unit cells as evidence for the (0001) surface of α -alumina (Al_2O_3) where reconstruction at elevated temperatures in vacuum was associated with loss of oxygen. The observed transformation from a (1x1) to a ($\sqrt{3}T \times \sqrt{3}T$) unit cell could be reversed by oxidation of the surface in 10^{-4} torr of oxygen at 1000° - $1200^\circ C$. The reconstructed surface has been interpreted in terms of a reduced oxide surface layer containing Al^{1+} or Al^{2+} ions. Reconstruction of V_2O_5 and TiO_2 surfaces has also been very recently reported.

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F. The structure of organic crystal surfaces.

A very large group of materials, including most organic solids, can be classified as molecular crystals. Although it has been widely recognized that the surface properties of these molecular crystals are important in many fields of science and technology, they have not been studied by the various electron or atom scattering techniques on the atomic scale. One of the reasons is that most of these molecules are electrical insulators, and thus they can build up surface space-charge under electron bombardment to interfere with the electron scattering. Furthermore, electron bombardment can stimulate chemical changes in the molecules. However, we have recently surmounted these obstacles and obtained surface structural information on over 50 of these molecular crystal surfaces using low-energy electron diffraction (LEED). The electron radiation damage can be minimized by preparing the organic crystals sufficiently thin (less than 1000 Å).

All of these crystals were grown from their vapors using copper or platinum crystal surfaces as substrates. They were grown at suitable temperature ranges according to their vapor pressure -- the higher the vapor pressure, the lower the crystal growth temperature. The grown crystalline films were studied by LEED. From the LEED diffraction patterns, the surface unit cells of the crystals could be determined.

From these studies two main surface structural properties of these molecular crystals were uncovered:

1. The chemical bonding and the ordering of the molecular monolayer that condenses first is very sensitive to the structure of the substrate surface. This phenomenon becomes more dominant for the larger, more complex molecules.

2. The surface structure of the vapor-grown molecular crystal does not necessarily correspond to a simple plane in the bulk crystal structure of the material. Rather, the structure of the first layer that was deposited on the substrate surface is "reproduced" layer by layer in the growing crystal. This phenomenon is called pseudomorphism.

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G. The structure of high Miller Index surfaces.

High Miller Index surfaces have been studied less than low Miller Index crystal surfaces. The few studies that have been made using metal, semiconductor and oxide surfaces revealed that these surfaces are structurally heterogeneous. Many high Miller Index planes are characterized by atomic structures consisting of periodic steps of one atom height separated by terraces of several atoms wide. Both steps and terraces had low Miller Index orientations.

We have studied the high Miller Index surfaces of platinum in

ultrahigh vacuum, in the presence of oxygen and in the presence of hydrocarbons that deposited a layer of carbon on the metal surface. Some of the crystal faces were stable in all three ambients, some of them in two or one and some were unstable and faceted.

Stepped surfaces are particularly interesting because of the presence of step and kink sites having lower coordination number than terrace sites and, in fact, these surfaces often exhibit strikingly different chemical behavior from low index planes. Ibach and co-workers found an exponential increase with step density in the sticking coefficient for oxygen adsorption on cleaved silicon surfaces. Rowe et al. have reported UPS spectra showing strong dependence on step density for cleaved silicon. Somorjai and associates have found higher reactivity of stepped surfaces as opposed to nominally step-free surfaces in the hydrogen-deuterium exchange reaction and for several hydrocarbon reactions at low pressures. Some theoretical interpretations of the electronic properties of stepped surfaces have been given for metals and semiconductors. There may indeed be a correspondence in chemical properties between atoms in step and kink sites on single crystal surfaces and surface atoms on small metal clusters of importance in industrial catalysts, and for this reason alone it is probable that the properties of stepped surfaces will continue to be a topic of lively interest.

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H. The structure of adsorbed monolayers.

One of the exciting observations of low-energy electron diffraction studies of adsorbed monolayers on low Miller Index surfaces is the predominance of ordering within these layers. A listing of over 300 adsorbed gas surface structures, mostly of small molecules adsorbed on low Miller Index crystal surfaces, can be found in a recent review. In current LEED work the focus is on quantitative structure analysis, and in several cases the full surface crystallography has been reported using multiple scattering, LEED intensity calculations.

Several general observations appear to be emerging from this work. Chemisorbed atoms seek an adsorption site which allows them to maximize their coordination. The substrate-adsorbate bond length, at least for the strongly chemisorbed systems studied thus far, can be reproduced rather well by adding the metallic radius of the substrate and the single bond covalent radius of the adsorbate. There are other types of surface bonding, however, that are neither simple nor readily rationalized using

simple chemical arguments. There are surface structures where adsorbed atoms are located on sites of low symmetry or even under the surface plane. In some cases the substrate surface is reconstructed as a result of chemisorption.

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I. Structure of chemisorbed molecules.

The first quantitative structure determination of molecular chemisorption has been reported for the unsaturated hydrocarbon acetylene (C_2H_2) on the Pt(111) surface. The molecule adsorbs on the Pt(111) surface in at least two different undissociated chemisorption states which are separated by a thermal activation barrier. A dynamical LEED I-V analysis of both structures has been carried out recently.

One state involves coordination of C_2H_2 to essentially one Pt surface atom at a z-distance of $2.45 \pm 0.10 \text{ \AA}$ above the topmost plane of Pt atoms (a C-Pt bond length of 2.5 \AA). The bonding site for the other state is a triangular position at a z-distance of $1.95 \pm 0.10 \text{ \AA}$ (C-Pt bond lengths of 2.2 and 2.6 \AA). Unfortunately, very limited sensitivity is found to either C-C bond length or C-C-H bond angle variations under the present conditions of surface structure analysis. More recently Andersson

and Pendry reported on the surface structure of CO on the Ni(100) surface. It appears that CO is located directly above the Ni atoms with a Ni-C spacing of 1.80 Å. It is proposed that the C=O bond is at an angle of $34^{\circ} \pm 10^{\circ}$ with respect to the surface normal.

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