Catalysis and Electrocatalysis at Nanoparticle Surfaces

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State-of-the-Art Characterization of Single-Crystal Surfaces: A View of Nanostructures

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SUMMARY

Atomic level characterization of solid surfaces is important for understanding and tailoring properties of nanoparticles. In the past 30 years, numerous electron and ion spectroscopic techniques, in addition to microscopic or imaging techniques, have been established to provide this information. In this chapter, we briefly describe several techniques that provide state-of-the-art characterization of the structure and morphology of single-crystal surfaces. Such surfaces serve as models to understand and predict the behavior of nanoparticles or are directly relevant as supports (substrates) for nanoparticles. The basis for X-ray photoelectron diffraction (XPD) and holography and low energy ion scattering (LEIS) is discussed, along with several examples of applications in structure determination including adsorbate structure
and adsorbate-induced restructuring at metal surfaces, ultrathin metal films and bimetallic surfaces, and oxide surfaces. Scanning probe microscopy (SPM), including scanning tunneling microscopy (STM), atomic force microscopy (AFM), and near-field scanning optical microscopy (NSOM) is discussed, and examples of results obtained by utilizing these techniques are given that illustrate their applications. These include ultrahigh vacuum experiments with STM, high-pressure STM studies, and STM investigations in electrolyte solutions.

4.1 INTRODUCTION

Advances in the characterization of solid surfaces have an important role to play in understanding and tailoring catalysis and electrocatalysis at nanoparticle surfaces. This is because of the strong “surface”–“nanoparticle” connection. There are two aspects to this: (1) surface properties of nanoparticles, and (2) nanoparticles on surfaces. By necessity, nanometer scale objects have a large part of their material present at the surface. Also, nanoparticles and nanometer-scale devices and structures are often deposited or constructed at a solid interface, and thus the surface properties and chemistry of that interface can control the construction, stability, and properties of the particle or device. This is important, because 30 years of surface science research has taught us that surface behavior is not that in the bulk. New thermodynamic variables for the surface must be specified. Abrupt termination of the bulk phase at the surface leads to changes in coordination (nearest neighbors) and charge distribution, and the existence of “dangling bonds,” electronic surface states, and other properties that are different from the bulk. Relaxation and reconstruction of the atoms in the top layer(s) occurs, causing new lattice structures (e.g., pseudo-morphic crystalline films templated by the substrate structure) and altered equilibrium shapes of nanoclusters due to the importance of the interface energy. Nanocluster geometries and properties of the gas phase are not the same if those clusters are deposited on a surface. Equilibrium bulk compositions and phase diagrams are not predictive and must be reevaluated, e.g., two metals that are immiscible in the bulk may alloy in the topmost layer to relieve strain at the interface. Surfaces generally are less stable than the bulk and, for example, have lower melting temperatures, higher vapor pressures, and greater reactivity.

It is also important to remember that all surfaces in ambient environments are covered with at least a monolayer of adsorbed water or other material. This means that experiments performed in vacuum or ultrahigh vacuum (UHV) conditions study different surface interactions. The structure of a surface is strongly influenced by adsorbed layers (surfactants), which can be used to control the surface structures present or the morphology of film growth. Even in UHV, the presence of gaseous adsorbates can cause large changes in alloy composition at the surface, because of chemisorption-induced segregation, and in the 2D and 3-D structure at the surface because of adsorbate-induced reconstruction, faceting, or massive step-bunching.

Thus, characterization of surfaces is important to the field of catalysis and electrocatalysis of nanoparticles. In the past 30 years, numerous electron and ion spectroscopic techniques, in addition to microscopic or imaging techniques, have been established to provide this information. Figure 1 provides high-resolution transmission electron microscopy (TEM) images of a practical (real), high-surface-area, Au/anatase−TiO₂ heterogeneous catalyst that show the small Au nanoparticles
that are thought to be responsible for the remarkable catalytic activity of these supported Au catalysts [1]. These images also illustrate the preferred orientational relationship between the crystalline Au nanoparticles and crystals of the TiO₂ support.

In this chapter, we briefly describe several techniques that provide state-of-the-art characterization of the structure and morphology of single-crystal surfaces. Such surfaces serve as models to understand and predict the behavior of nanoparticles or are directly relevant as supports (substrates) for nanoparticles. It is beyond the scope of this chapter to provide a comprehensive review of work in this field, but rather we provide a number of examples of results obtained by utilizing these surface characterization techniques which illustrates their applications.

4.2 PHOTOELECTRON DIFFRACTION AND ION SCATTERING

4.2.1 Introduction

Numerous spectroscopic techniques, such as x-ray photoelectron spectroscopy (XPS) [2], Auger electron spectroscopy (AES) [3], ultraviolet photoelectron spectroscopy (UPS), soft x-ray absorption spectroscopy (SXAS) [4], high-resolution electron energy loss spectroscopy (HREELS) [5], and Fourier transform infrared
spectroscopy (FTIR) [6] can be used to characterize surfaces and adsorbed films. These techniques probe different aspects of surfaces, and a multitechnique approach is usually necessary to get a complete picture.

The most powerful techniques commonly used to determine structure at single-crystal surfaces include low-energy electron diffraction (LEED) [7], x-ray photoelectron diffraction (XPD) [8–10], and low-energy ion scattering (LEIS) [11,12]. Herein, we focus on the latter two. These are element-specific tools for determining the local geometric structure around a probed atom at the surface. XPD and LEIS are highly surface-sensitive and can provide a direct determination of surface structure. In this section, we briefly describe some essential features of XPD, photoelectron holography, and LEIS, as they relate to determining the geometric structure of ordered, single-crystal surfaces. We then describe some recent examples of applications of these techniques to investigate adsorbate structure and adsorbate-induced restructuring at metal surfaces, thin films, and bimetallic surfaces, and oxide surfaces. This list is obviously not comprehensive but was chosen to illustrate the usefulness of these techniques and indicate the state-of-the-art in experimental and theoretical developments related to these methods.

4.2.2 X-ray Photoelectron Diffraction (XPD) and Holography

XPS is a quantitative, element-specific analytical probe that provides information on the chemical nature of atoms in the near-surface region of a solid. In XPS, x-rays photoionize atoms in a target, producing photoelectrons, and the kinetic energy of electrons emitted from the surface is analyzed. The focus is typically on photoelectrons produced by photoionization of deep, atomic-like core levels, because core-level binding energies are characteristic of each element and photoabsorption cross sections for these levels are independent of the chemical environment. Furthermore, these have relatively narrow linewidths and chemical shifts in the core-level binding energies can be related to changes in valence electronic state (i.e., oxidation state) of the probed atom.

For single-crystal substrates, there is additional information about the geometric structure of the surface contained in the intensity angular distribution (IAD) of the photoemitted electrons. This information is obtained in XPD measurements that often directly indicate bond directions at surfaces. A Fourier transform of the XPD data can also be used to determine element-specific surface structure in a method known as photoelectron holography. This approach can be used to directly determine surface structures without any starting model.

**X-Ray Photoelectron Diffraction (XPD)**

X-ray photoelectron diffraction is the coherent superposition of a directly photoemitted electron wave with the elastically scattered waves from near-neighboring atoms. This gives element-specific structural information about the near surface atoms in a single crystal [8–10]. The short inelastic mean free path of the electron waves at the kinetic energies of interest (15 to 1000 eV) leads to surface sensitivity and determination of the atomic geometry of the emitting atom. The known energies of narrow XPS core-level peaks lead to element specificity. The resolution of surface peaks and chemical shifts may even sometimes lead to a chemical state-specific structure determination.
One classification scheme for XPD uses the kinetic energy regime of the photo-emitte electrons. At sufficiently high kinetic energies (above 500 eV), the scattering factor is highly forward-peaked, which leads to a direct interpretation of bond angles from the angular intensity oscillations using single scattering theory. The interpretation of the data is particularly simple because there are substantial intensity enhancements along interatomic directions. At lower kinetic energies, the scattering factor is more isotropic, which leads to more complex XPD patterns because of increased multiple scattering. Therefore, at low energies, extensive numerical simulations including multiple scattering calculations have to be used to determine the structure.

Experimentally, XPD data are obtained by one of two approaches that are distinguished by the scanning parameter: angle-scanned mode and energy-scanned mode. Angle-scanned XPD is more common because it can be performed using any available, lab-based x-ray source typically used for XPS, and collecting the diffracted intensity over a wide range of angles. Energy-scanned XPD is performed using a synchrotron light source and an appropriate monochromator so that the photon energy can be scanned while keeping the photoelectron kinetic energy fixed for a few high-symmetry orientations of the crystal.

A schematic of the XPD experiment is shown in Figure 2. X-rays incident on the sample create photoelectrons detected by an electron-energy analyzer. Angular intensity modulations are created by elastic scattering of the photo-emitted electrons from the neighboring atoms. In angle-scanned XPD, these angular distributions are obtained by rotating either the sample or the analyzer to scan different exit angles for the photo-emitted electrons and then used to determine the surface structure.

![Figure 2](image_url)  
Figure 2 Schematic for photoelectron diffraction. Photo-emitted electrons are energy-analyzed at different exit angles. Direct photo-emitted electron waves interfere with the scattered waves to give angular intensity variations. These angular variations contain element-specific information about the near-surface structure.
Figure 3 illustrates the use of angle-scanned XPD data to determine the near-surface structure of a single-component metal, single-crystal sample. Figure 3a shows an XPD pattern for a face-centered cubic (fcc) Pt(111) single crystal using the Pt 4f core-level peak (at 1183 eV kinetic energy using Mg Kα excitation). The diffraction pattern is plotted with the center corresponding to the surface-normal direction and the edges corresponding to grazing exit angles for photoelectrons. The radial distance is proportional to the polar angle, as measured with respect to the surface normal. This diffraction pattern is representative of any fcc(111) surface. The angular intensity enhancements can be understood according to a simple forward-scattering model, denoted by Egelhofer [13] as the “searchlight effect,” by looking at the schematic drawing in Figure 3b. This shows a vertical cut along a high-symmetry azimuth of the fcc(111) crystal. The angular position of each high-intensity feature in the Pt(111) XPD pattern corresponds to a direction between a pair of near-surface atoms. For example, if we take a line scan along the [121] azimuth in the XPD pattern (i.e., a polar angle scan), the main feature is a strong peak near 35° that corresponds to the [101] direction. This angular peak originates from an emitter atom located one layer below the scattering atom. Similarly, in the radially opposite azimuth [121] three peaks correspond to the [112], [114], and [001] directions from emitters located at the 3rd, 4th, and 2nd layers, respectively, considering that the scattering atom is in the 1st layer. The intensity at the center corresponds to the normal direction [111] and originates from 4th-layer emitters.

Figure 3c shows an XPD pattern for the fcc Ni(100) surface using the Ni LMM Auger peak (at 841-eV kinetic energy) in XPS. This pattern is representative of fcc(100) single crystals. Figure 3d shows a vertical cut through the fcc(100) crystal along the [100]-like azimuths corresponding to a vertical or horizontal line in the XPD pattern. The three main features along this azimuth are in the [001], [103], and [101] directions, originating from emitters in the 3rd, 4th, and 3rd layers, respectively, considering the scattering atoms to be in the 1st layer. Similarly, the main features along the [110]-like azimuth in the XPD pattern, i.e., along a line oriented 45° from the horizontal or vertical direction in the XPD pattern, can be explained by viewing the schematic in Figure 3e of a vertical cut along the [110] azimuth. The [114], [112], and [111] directions correspond to emitters in the 5th, 3rd, and 3rd layers if the scattering atom is in the 1st layer. In general, in these diffraction patterns the intensity enhancements are inversely proportional to the interatomic distances involved, i.e., angular intensity modulations from scattering of a 4th layer emitter by a 1st-layer scatterer is weaker than that for a 2nd layer emitters (see, for example, [101] versus [111] in Figure 3a).

In a theoretical description for the angle-dependent photoelectron-intensity variation, one considers the wave nature of the photoelectrons. The photon-emitted electron is scattered by the surrounding atoms. The interference of the photoelectron wave with its scattered waves results in an intensity modulation that depends on the geometrical arrangement of the scatterers (lattice atoms) and the atomic scattering factor. This ultimately is responsible for the angle dependency of the photoelectron intensity and is therefore directly related to the structure of the surface layers. For a
Figure 3 XPD patterns from $fcc(111)$ and $fcc(001)$ single-crystal surfaces showing the correspondence between enhanced intensity and near-neighbor directions. The center of the pattern corresponds to the direction normal to the surface and the radial distance is proportional to the polar angle with respect to the surface normal. (a) XPD pattern for $fcc$ Pt(111). (b) Vertical cross section of an $fcc(111)$ crystal along a high-symmetry direction. (c) XPD pattern for $fcc$ Ni(100). (d) Vertical cut of the $fcc(001)$ crystal along the [100] azimuth. (e) Vertical cut of the $fcc(001)$ crystal along the [110] azimuth.
plane incident wave $\phi_0$ (photoelectron), the scattered wave $\phi_j$ can be written as

$$\phi_j = \phi_0 f_j(\theta_j) e^{i\mathbf{k}r_j}$$

(1)

where $f_j(\theta_j)$ is the atomic scattering factor (complex number), $\theta_j$ is the scattering angle, $k$ is the electron wave number, and $r_j$ is the emitter-scatterer distance. In the small atom approximation, the scattering factor can be calculated using the partial wave method:

$$f_j(\theta_j) = \frac{1}{k} \sum_{l} (2l+1) e^{i\theta_j} \sin \delta_l^j P_l(\cos \theta_j)$$

(2)

where $\{\delta_l^j\}$ is a set of phase shifts for the $j$th scatterer, and $\{P_l(\cos \theta_j)\}$ are Legendre polynomial functions. This approximation is accurate in general for all but nearest-neighbor distances of $\leq 5 \, \text{Å}$ from the emitter. At smaller distances where the distance between the emitter and the scatterer is not large compared to the size of the scatterer, or the wave number of the electron is small, corrections have to be implemented [14–17] for the curved wavefront. When the emitted electron wave is other than a simple $s$ wave, the atomic scattering factor can be calculated using a high-energy approximation [14]. The total diffracted intensity is then given by the interference of the photoelectron wave with the scattered waves. This intensity can be expressed by the square of the sum of the waves. [9]:

$$I(\mathbf{k}) = \left| \phi(\mathbf{k}) + \sum_j \left( f(\mathbf{k}, r_j) e^{i(kr_j - \mathbf{k} \cdot r_j)} \phi(r_j) \right) \right|^2$$

(3)

The variation with the electron wave vector $\mathbf{k}$ is associated with an intensity variation in the experimentally observed polar and azimuth angles. (In order to include vibrational attenuation of interference effects, each scattered wave has to be multiplied by the temperature dependant Debye–Waller factor.)

At relatively high kinetic energies (above a few hundred eV), single scattering theory gives the position of diffraction features quite accurately. However, it overestimates the intensity of diffraction features [18] along low-index directions, because the theory does not consider the defocusing effect along chains of atoms. For lower energies, the errors are much more severe. This can be seen from the shape of the scattering factor. At high energies, the scattering factor is highly forward-peaked and most of the diffraction intensity lies along low-index internuclear directions. At low kinetic energies, the scattering factor is much more isotropic and, hence, multiple scattering becomes important in all directions. Hence, multiple scattering effects must be included in the theory and analysis to accurately interpret the intensity modulations.

**X-Ray Photoelectron Holography**

Gabor [19] first proposed holography in 1948 as a means to overcome barriers in doing “lensless” electron microscopy and avoiding inherent spherical aberrations. He proposed that if a known wave is allowed to interfere with an unknown wave, the resulting interference pattern can be stored as a “hologram,” which contains most of
the information needed to restore the original unknown wave. In his two-step model, a known spherical wave called the “reference” wave first interferes with a wave scattered by the object, called the “object” wave, and the interference modulations are recorded on film. Then, the reconstruction is done by illuminating the film by a similar reference wave to generate a three-dimensional holographic image of the object.

The large field of optical holography [20] emerged with the advent of laser sources. This technique is illustrated in Figure 4. A laser source, required for its large coherence length, which has to be of the order of the object to be imaged, is used as a reference wave. A beam splitter splits the laser beam in order to illuminate the object and allow for a direct wave to propagate to the film as the reference wave. Beams reflected from the object back to the film are the object waves, and the film records the interference patterns between the reference and object waves. Subsequently, a laser beam incident on the film gives a three-dimensional reconstructed image.

In 1986 Szöke [21] suggested that a photoelectron diffraction pattern from a single crystal may be treated as a hologram. In photoelectron holography the direct

![Optical Holography Diagram](image)

**Figure 4** Analogy between the principles of optical and photoelectron holography. In optical holography (top), the incident laser beam is the reference wave, the reflected waves are the scattered waves, and a film is used as a detector. In photoelectron holography (bottom), the direct, photo-emitted waves are reference waves that interfere with the scattered waves from neighboring atoms, and a hemispherical, electron energy analyzer is used as a detector.
wave can be considered as the reference wave. The scattered wave is similar to the object wave, and the photoelectron diffraction pattern can be used for holographic reconstruction. In 1988 Barton [22] proposed a computer algorithm based on the Helmholtz–Kirchoff principle of optics that directly inverts the XPD data to obtain a three-dimensional image of the local environment around the emitter atom. In order to suppress multiple scattering and twin images, an algorithm using holograms taken at different energies has been proposed [23].

A holographic transformation was first used successfully by Harp et al. [24] on high-energy, single x-ray, photoelectron patterns. In the case of the backscattering (low energy), which is needed to study adsorbate or thin layers, Zharnikov et al. [25] demonstrated the validity of the method. Here we show, using the backscattering geometry, that a simple and direct transformation of x-ray photoelectron data, without any corrections requiring a previous knowledge of the structure, can lead to a determination of the surface structure.

Barton [26] suggested that one may use a Fourier transform formula to convert the intensity modulation into an image function, $A(r)$:

$$A(r) = \int \int I(k) e^{-i k \cdot r} \, dk \, dl \quad (4)$$

where $k = (k_x, k_y, k_z)$ is a wave vector, $k_l = (k_x, k_y)$ is its component parallel to the surface, and $k_z$ is given by $k_z = \sqrt{k^2 - k_x^2 - k_y^2}$. The intensity $I(k)$ in single scattering is given by Eq. (3).

By expanding Eq. (3) and inserting it in Eq. (4), we get four terms. Of these four terms, the first term ($|\phi(k)|^2$) is the direct term, the cross terms are the image term and a twin image term, and the last term is the self-interference term. Assuming that the first term $|\phi(k)|^2$ does not vary very much with $k$, i.e., $f(k, r)$ is a smoothly varying function of $k$, and assuming that the self-interference term is negligible (true for backscattering geometries), it can be seen that the $A(r)$ has a maximum for $r = r_j$ due to the image term and at $r = -r_j$ due to the twin image term. Thus the intensity of $A(r)$ directly gives the emitter–scatterer distance and orientation and therefore the crystallographic structure.

Including multiple energy diffraction patterns, Barton’s algorithm can be rewritten as

$$A(r) = \int \int \int \chi(k_x, k_y, k) \exp(i k \cdot r - ik r) \, dk_x \, dk_y \, dk \quad (5)$$

where $k$ is the wave vector inside the crystal, $k_x$ and $k_y$ its components parallel to the surface directions, and $k$ its modulus (the z-axis is normal to the surface, $z$ is positive out of the surface). The advantage of including energy integration is that it removes the twin image completely. This improves the interpretation of the results because the twin-image intensities are located at positions different from atomic positions.

### 4.2.3 Low-Energy Ion Scattering (LEIS)

Ion scattering spectroscopy (ISS) was introduced by Smith [25] using noble gas ions and has become a powerful tool for surface analysis. In low-energy ion scattering (LEIS), a monoenergetic beam of low-energy ions in the 0.2–5-keV range is directed...
toward a surface and the backscattered incident ions are energy-analyzed at a known scattering angle [11,12]. Inert gas ions (e.g., $^4$He and $^{20}$Ne) are often used in typical applications. Mean free paths of ions in solids at low energies are extremely short such that only the topmost layer composition is probed normally in LEIS (in contrast to XPS and AES).

The process of ion scattering is illustrated schematically in Figure 5. Because collision times are very short ($10^{-15}$ to $10^{-16}$ s), the interactions can be approximated as elastic binary collisions [28] between the incident ion and a single surface atom (i.e., with an effective mass equal to the atomic mass). Diffraction effects are negligible. The basic equation in ISS, using energy and momentum conservation, is

$$\frac{E_1}{E_0} = \left( \frac{\cos \theta \pm \sqrt{m_2^2/m_1^2 - \sin^2 \theta}}{1 + m_2/m_1} \right)^2$$

where $E_0$ and $E_1$ are the initial and final energies of the incident ion of mass $m_1$ scattered through an angle $\theta$ by a target atom of mass $m_2$. Since the final energy $E_1$ depends only on the mass ratio $m_2/m_1$ for a fixed scattering angle $\theta$, the energy spectrum gives a direct picture of the surface composition. Only the plus sign applies for those cases in which the target atom is heavier than the incident ion ($m_2/m_1 > 1$) and each target mass can be identified by a single peak in the spectrum. If $m_2/m_1 < 1$, both signs apply and each target mass gives rise to two peaks at different energies [Detection of forward-scattered, recoil ions in elastic recoil spectrometry (ERS) has been particularly important for analysis of surface hydrogen.]

In addition to elemental analysis, LEIS can be used to provide information about the local surface structure at the probed atom. This application of LEIS was improved by using alkali ions (e.g., $^7$Li and $^{23}$Na) and large scattering angles (near $180^\circ$) in so-called impact-collision ISS (ICISS) [29] Alkali ions have strong trajectory-dependent neutralization cross sections and give relatively intense

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**Figure 5** Schematic of a binary, elastic collision in LEIS. An incident ion of mass $m_1$ and energy $E_0$ gets scattered by a stationary target atom of mass $m_2$ in a crystal. The final energy $E_1$ of the scattered, incident ion only depends on the mass ratio $m_2/m_1$ for a fixed geometry.
angular-dependent signals in alkali ion scattering (ALISS) studies of surface atomistic structure. Most of the results discussed in this section are based on ALISS experiments in which the scattered alkali ions are energy-analyzed for a range of incidence angles while monitoring the scattered intensities.

For structural analysis, the interaction potential between the incident and target atoms must be considered to calculate the trajectory of the ions during the scattering process. The interaction between two charged particles (here, the incident ion and target nuclei) is given by the Coulomb potential. At low energies (∼1 keV), screening due to the electrons has to be considered also. Thus, a screened Coulomb potential is used to describe the scattering

\[ V(r) = \frac{Z_1 Z_2 e^2}{r} \phi \left( \frac{r}{a} \right) \]  

where \( Z_1 \) and \( Z_2 \) are the atomic numbers of the incident ion and target atom, respectively, and \( r \) is their instantaneous separation. An analytical approximation, called the Thomas–Fermi–Moliere [30] (TFM) screening function of the form

\[ \phi(x) = 0.35e^{-0.3x} + 0.55e^{-1.2x} + 0.1e^{-6.0x} \]  

is the most commonly used screening function. The screening length \( a \) suggested by Firsov [31] is

\[ a = C a_F = \frac{C(0.8853)a_B}{\left(\frac{Z_1}{2} + \frac{Z_2}{2}\right)^{-2/3}} \]  

where \( a_B = 0.529 \text{ Å} \), the Bohr atomic radius. The adjustable parameter \( C \) was introduced to improve agreement with experimental results.

The concept of a “shadow cone,” i.e., a region behind the target atom where no ion can penetrate, is useful in surface-structure determination using ISS. This region is created by the repulsive potential between the incident ion and target atom. Figure 6a illustrates the shadow cone region behind a target atom. When a parallel beam of mono-energetic ions interact with an atom at varying impact parameters, the envelope of the ion trajectories creates a region behind the target atom that is inaccessible to any of the incident ions. A universal, empirical relation for this shadow cone at a distance \( l \) from the target atom was given by Oen [32] as

\[ \frac{r(l)}{2\sqrt{bl}} = 1 - 0.12\alpha + 0.01\alpha^2 \quad \text{for} \ 0 \leq \alpha \leq 4.5 \]  

\[ \frac{r(l)}{2\sqrt{bl}} = 0.924 - 0.182\ln\alpha + 0.0008\alpha \quad \text{for} \ 4.5 \leq \alpha \leq 100 \]  

where \( b = Z_1 Z_2 e^2 / E_0, \alpha = 2 \sqrt{bl} / a \), and \( a \) is the screening length. The shadow cone can also be calculated by solving the scattering integrals numerically with an appropriate scattering potential. Figure 6b illustrates the determination of local surface structure using the shadow cone concept. At a sufficiently low angle of incidence \( \psi \) (polar angle) of the ion beam relative to the surface, all the surface atoms are hidden in the shadow cones of the preceding atom in the “chain” of scatterers. As the angle of incidence is increased above a critical angle \( \psi_c \) adjacent, top-layer atoms
Figure 6  (a) Trajectories of a parallel flux of ions impinging on an atom with varying impact parameters. The envelope of these trajectories creates a region behind the target atom which is inaccessible to the incoming ions. This region is called the shadow cone. (b) With increasing incidence angle, a critical angle $\psi_c$ is reached where nearest-neighbor atoms emerge from the shadow cone of the preceding atom. This causes a sharp increase in the ion scattering intensity, and thus a measurement of $\psi_c$ can be used to determine unknown surface structures.

emerge out of these shadow cones and there is a sharp increase in the ion scattering signal at the detector. Simple geometry relates $\psi_c$ to the shadow cone radius $r$ at a distance $l$ from its apex and at a distance $d$ between two neighboring atoms:

$$\begin{align*}
    r &= d \sin(\psi_c) \\
    l &= d \cos(\psi_c)
\end{align*}$$

These relationships can be used to obtain the shadow cone radius and interaction potential for known distances (structures) as a calibration. Then, unknown distances and structures can be solved using the known shadow cone radius.

Figure 7 illustrates the appearance of critical angles in LEIS data. As described above, the locations of the critical angles are directly related to the atomic geometry and can be utilized in solving surface structures. Figure 7a gives a polar scan in ALISS using 1-keV Na$^+$ ions incident on the fcc Pt(111) surface along the [211] direction. At incident angles below $\psi_1$, all atoms are in the shadow cone of their preceding atoms and hence no ALISS signal can be observed. As the angle reaches
$\psi_1$, the atoms emerge out of the shadow cone of the preceding atom, leading to a sharp rise in intensity corresponding to the $\psi_1$ peak in the ALISS scan. Similarly, as the polar scan is increased further to $\psi_2$, the second-layer atoms emerge out of the shadow cone of the first-layer atoms, giving rise to the $\psi_2$ peak. Figure 7b shows an azimuthal ALISS scan for 5-keV Na$^+$ ions incident on a fcc Ni(111) surface at a grazing polar angle of 12°. When the angle of incidence is along a low-index azimuth direction, like [110] or [112], the shadow cone of the preceding atom prevents the incident ions from reaching the target atoms for polar angles below the critical angle. This causes the dips in ion scattering intensity along the [110] and [112] azimuthal directions. Such azimuthal scans can provide the structure, orientations, and symmetry of the neighboring atoms for a surface-layer target atom.

### 4.2.4 Applications to Structure Determination at Single-Crystal Surfaces

Studies of single-crystal surfaces under UHV conditions have allowed us to quantify fundamental interactions at surfaces, and the majority of surface-science studies have been conducted in this manner. Utilization of XPD and LEIS techniques require the studies to be conducted under high vacuum, and studies of clean surfaces or precisely controlled adsorbate layers require UHV conditions. Here we discuss a few examples of the use of these two techniques in studies of single-crystal surfaces, illustrating their power and limitations. The surfaces discussed are metal surfaces that contain controlled amounts of adsorbates, ultrathin metal films, two-component metal alloy surfaces, and oxide surfaces.
Figure 7  (a) ALISS polar scan for an fcc Pt(111) crystal along the [−211] azimuth. The peak at ∼20° originates from scatterers in the surface layer. The peak at ∼60° originates from second-layer scatterers. (b) ALISS azimuthal scan at a low polar angle for an fcc Ni(111) surface. At low polar angles, there are dips in the [110] and [112] directions because of the shadow cone effect.

Adsorbate Structure and Adsorbate-Induced Restructuring at Metal Surfaces

Formation of a surface always requires energy. However, the surface free energy can often be minimized by interplanar relaxation or, more severe by reconstruction of atoms at the surface to positions that deviate greatly from those expected from an ideal termination of the bulk lattice. The presence of adsorbates can alter or induce such reconstructions, and adsorbates themselves can form a variety of structures in the adlayer as well. In the past, LEED and other surface-science techniques have been employed to characterize the structure of these reconstructed surfaces and
ordered adsorbate layers. The chemical specificity of XPD and extreme surface sensitivity of LEIS are particularly useful in this regard.

*Adsorbate-Induced Surface Reconstruction of Ag(110)–(2 × 1)–O*

Atomic and molecular adsorbates that form chemical bonds to surface atoms may cause a restructuring of the surface in order to minimize the total energy of the system. Such adsorbate-induced surface reconstructions have been observed for many reactive adsorbates, e.g., H, C, N, O, and S adatoms. In the particular case of O/Ag(110), LEED studies on the Ag(110)–(2 × 1)–O surface concluded that O adatoms were adsorbed on long-bridge sites, but reconstruction of the Ag(110) surface was not considered. Later, LEIS and STM studies indicated a “missing-row” reconstruction for the Ag(110)–(2 × 1)–O structure in which alternating rows of Ag were removed. Scanned-energy mode XPD was used to unambiguously confirm this missing-row structure [33].

Figure 8 shows the environment of the O atoms at the surface of the (2 × 1) reconstruction. This result was obtained using the “projection method” to get the approximate atomic geometry without a starting model. The vertical and horizontal cuts near the surface establish the position of O atoms to be at the long bridge sites.

Figure 9 shows the comparison between theory and experiment for the missing-row model of the Ag(110)–(2 × 1)–O system. After consideration of all possible (2 × 1) reconstructions, the missing-row model has the lowest (best) R-factor, i.e., a one-parameter expression for the quality of fit between two curves.

The locations of the O atoms deduced from XPD are consistent with previous studies on this system using LEIS, STM, and surface-enhanced x-ray absorption fine-structure spectroscopy (SEXAFS). Similar (2 × 1)–O phases on Cu(110) and Ni(110) also have missing-row reconstructions.

![Figure 8](image)

Figure 8  Intensity plot for the projection-method calculation. (a) Vertical cut through the [−110] azimuth. (b) Horizontal cut 1.61 Å below the oxygen atom emitter, which is at (0,0,0). (From Ref. 33.)
Figure 9  Comparison of results from theoretical simulations (thin lines) with energy-scanned, O 1s XPD data (thick lines) for the Ag(110)-(2 x 1)-O system. (From Ref. 33.)

Orientation of Adsorbed C\textsubscript{60} Molecules Determined by XPD

XPD has been used to determine the structure of C\textsubscript{60} molecules chemisorbed on single crystal metallic substrates [34]. The origin of the XPD pattern from a chemisorbed C\textsubscript{60} molecule is schematically illustrated in Figure 10a. All 60 carbon atoms act as photo-emitters. The photo-emitted electrons are scattered by neighboring carbon atoms, and this gives enhanced intensity along the C-C bond directions, as shown in Figure 10b due to “forward focusing.” Analyzing the position and symmetry of the high-intensity spots therefore gives a direct determination of the relative locations of the carbon atoms. Figure 10c shows a calculated diffraction pattern for the orientation of the C\textsubscript{60} molecule, as shown in Figure 10a. The dark spots correspond to interatomic directions.

Figure 11 shows the C 1s diffraction patterns observed in experiments on C\textsubscript{60} monolayers on Cu(111), Al(111), Cu(110), and Al(001) surfaces. Figures 11a and b have sixfold symmetry, which shows that a six-carbon ring is “facing” the Cu(111) and Al(111) surfaces. The diffraction patterns between the two are quite similar except for a 30° azimuthal rotation. This shows that the C\textsubscript{60} molecules are rotated by 30°. None of the groups has fivefold symmetry, suggesting that the 5-ring is not
Figure 10  (a) Schematic depiction of a C₆₀ molecule adsorbed on a substrate showing the relative orientation of the 60 carbon atoms. (b) Schematic drawing of the enhanced intensity in XPD along interatomic directions caused by forward focusing. (c) Calculated XPD pattern for a C₆₀ molecule adsorbed on a substrate with a 6-ring directed toward the substrate. The dark spots correspond to C–C bond directions with the size of the spots inversely proportional to the interatomic distance. (From Ref. 34.)

facing the surface in any of the cases. The orientation of the C₆₀ molecules adsorbed on different substrates is illustrated schematically in Figure 12. The atoms closest to the surface are shown in black. In each of the four cases, theoretical single scattering cluster (SSC) simulations of the rigid C₆₀ cage structure closely reproduce the corresponding diffraction patterns in Figure 11 after domain averaging. The twofold symmetry in Figure 11c can be reproduced well by considering that the two C atoms from a 6-ring and 5-ring (5–6 bond) face the surface. The fourfold symmetry in Figure 11d can result from a single edge atom adsorption (between two 6-rings and one 5-ring).

Ultrathin Metal Films and Bimetallic Surfaces

The interest in the morphology of ultrathin (monolayer, bilayer, etc.) metal films on metal substrates has been fueled partly by the possibility of growing novel materials with unique chemical and physical properties. For example, giant magnetoresistance (GMR) structures are built by alternating thin nonmagnetic and ferromagnetic layers, and the intermixing in the interface region has a large effect
Characterization of Single-Crystal Surfaces

Figure 11  C 1s XPD pattern, using a Mg Kα source, from monolayer films of C₆₀ adsorbed on (a) Cu(111), (b) Al(111), (c) Cu(110), and (d) Al(001). The patterns have been azimuthally averaged by considering the appropriate rotational symmetry. (From Ref. 34.)

on the strength of the GMR effect. XPD and LEIS are both well suited to studying such structures since both of these techniques can directly probe aspects of the composition and structure of individual layers at and near the interface.

Bimetallic alloy surfaces are also of great importance. Most metallic materials used commercially, and in particular metal-based, heterogenous catalysts, have multicomponent alloy phases. Despite their obvious importance, alloy single-crystal surfaces have not been studied so extensively in the past. A first step in understanding the chemistry of these surfaces is a thorough characterization of the structure of such surfaces. These attempts are part of efforts to overcome the “material gap” between commercial catalysts and surface-science studies.

Fe/Ni(001) Studied by XPD

The fcc phase of Fe (γ-phase) at low temperature is of interest to understand the effects of magnetic properties on atomic volume. While the γ-phase in bulk, solid Fe is only stable at high temperatures (above 910°C), epitaxial growth of Fe thin films on suitable substrates can stabilize the γ-phase at room temperature. Thin films of Fe on Ni(001) are of interest because of lattice matching and the possibility of novel magnetic phases that may arise from the influence of the structure and magnetism of the substrate.

The growth mode of Fe on Ni(001) was studied using forward-scattering photoelectron diffraction [35]. Figure 13 shows the IAD along the [110] azimuth for
the Fe/Ni(001) surface with Fe coverages of 0–14 ML. The presence of forward-scattering features from Fe emitters at 0.5-ML and 1-ML coverage shows that the Fe film growth mode is not “layer by layer.” The position of the forward-scattering features of Fe[112] shifted by −1.4° from clean Ni(001)) and the corresponding Ni 3p IAD (not shown here) strongly suggest that the growth mode is one of island formation, rather than intermixing (alloying). The shift in the Fe[112] peak position from 0–2 ML can be explained by elastic strain. The Fe[112] peak at 1 ML coverage shifts by −1.4°, which compares to −1.3° expected from the vertical expansion required to retain the atomic volume of bulk Fe. As the Fe film thickness increases, the [112] peak shifts to even lower angles, reaching a final value of 31.7°, which far exceeds values from elastic strain calculations. The IAD features for the thicker films can be explained by a strain relief transition of Fe to a body-centered cubic (bcc) (110) phase (with a bcc(111) || fcc(001) in-plane orientation) between 2- and 3-ML coverage. The in-plane lattice constant between the bcc(110) and fcc(001) surface unit cell is within 0.1%. Along the bcc[111] azimuth, the forward-scattering features
Figure 13  IAD curve from XPD data for 0-14-ML Fe on Ni(001). Angular scans from the Fe 3p core level are shown and compared with those from the Ni 3p core level. The scans were taken along the [110] azimuth of the Ni substrate. The inset shows the position of the [112] peak and the anisotropy function. Cross sections of the bcc(110) azimuth [111] and fcc(001) azimuth [110] are shown at the right, along with an in-plane schematic diagram of the fcc(100) and bcc(110) surface cells. (From Ref. 33.)

are expected to be at 31.5° and 50.8°, which match quite well with the features denoted as “b” (31.7°) and “c” (51°) for the 14-ML Fe coverage. The in-plane angular rotation between the bcc(110) and fcc(001) surface can be explained by including the sum of the four possible (110) domains leading to the same symmetry as the (001) surface.

Table 1 shows the results of fitting quantitative multiple scattering calculations to the XPD data for clean Ni(001) and Fe coverages of 3 and 7 ML. The calculations for 8-ML fcc Ni(001) give a “best fit” for a Ni lattice constant of 1.75 Å and lattice parameter of 2.50 Å, which agrees well with the known, bulk values of 1.76 and
Table 1  Best-Fit Structural Parameters for Ni(001), 3-ML Fe/Ni(001), and 7-ML Fe/Ni(001)

<table>
<thead>
<tr>
<th>Experimental structural</th>
<th>Ni(001)</th>
<th>3-ML Fe/Ni(001)</th>
<th>7-ML Fe/Ni(001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best-fit structure</td>
<td>8-ML fcc</td>
<td>2-ML bcc/3-ML fcc</td>
<td>4-ML bcc/3-ML fcc</td>
</tr>
<tr>
<td></td>
<td>(R = 0.050)</td>
<td>(R = 0.038)</td>
<td>(R = 0.030)</td>
</tr>
<tr>
<td>Best-fit</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parameters (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_{1-2,2-3} =$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_{1-2} =$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1.75 \pm 0.01$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{1,2,3} =$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_{2-3} =$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2.01 \pm 0.03$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_{3-4,4-5}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1.85 \pm 0.03$</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$a =$</td>
<td></td>
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</tr>
<tr>
<td>$2.49 \pm 0.02$</td>
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</tbody>
</table>

Source: Ref. [35].

2.49 Å, respectively. Best fits for the 3-ML Fe coverage data indicate a structure of 2-ML bcc/3-ML fcc Fe. The spacing corresponds well with the expected spacing of 2.04 Å for the bcc phase and 1.84 Å for the tetragonally expanded fcc phase. The thickness indicated by the best fit in the calculation is greater than the nominal coverage (5 ML versus 3 ML), and this is consistent with an island-formation growth mode. Calculations for the 7-ML Fe film show a best fit for a 4-ML bcc/3-ML fcc Fe structure. The Fe lattice parameter was relatively unchanged in both Fe films. The consistently low R-factor values for all three structures show a very reliable goodness of the fit for the fcc to bcc phase transition above 3-ML Fe thickness on Ni(001).

$c(2 \times 2)-Mn/Ni(001)$

MnNi and MnCu binary alloys are found to have ordered surface reconstructions. Theoretical arguments based on total energy calculations suggest that the magnetic properties of these surfaces are the reason for the existence of the unusual surface structures. Indeed, novel magnetic properties of these alloys have been found using X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD), showing an enhanced magnetic moment of Mn of 4 $\mu_B$.

LEED studies showed an outward corrugation or “buckling” of Mn atoms out of the surface. Photoelectron holography and quantitative XPD [36] was used to unambiguously determine the element-specific structure of these surface alloys. Photoelectron holography was used to get an initial estimate of the structure. Figures 14a and b compare a model structure with the 3-D perspective view of the holographic reconstruction. The reconstruction was performed using Barton’s algorithm [Eq. (5)] on 14 full-hemisphere diffraction patterns equispaced in momentum space. In the model structure, the Mn emitter atom is at the origin and the neighboring atoms are all chosen to be Ni from the observed $c(2 \times 2)$ symmetry of the surface. The Mn emitter is located at the origin also in the holographic reconstruction. This determines the structures to be a surface alloy from the relative position of the holographic intensities along the substrate crystallographic directions. The difference in height between the top-layer holographic intensities from the origin is assigned to a large, outward buckling of Mn atoms.
Figure 14  Comparison of a 3D projection for (a) a model structure and (b) a holographic reconstruction for the MnNi surface alloy produced using XPD data. The model structure is a substitutional alloy with Mn atoms buckled out of the surface plane by 0.4 Å. All of the nearest neighbors around Mn atoms can be seen in the holographic transformation, and these are located close to the position of atoms expected from the model structure. A large buckling (0.5 Å) for Mn is also observed in the holographic reconstruction.

To get better quantitative accuracy, simulations were then performed using multiple-energy diffraction patterns and calculating R-factors over four different kinetic energies. The kinetic energies selected were 60, 66, 80, and 94 eV, where the backscattering intensities were strong and the experimental patterns varied considerably. Comparisons between experiment and theory for the Mn diffraction patterns are shown in Figure 15. The simulations reproduce the main features in each of the distinct diffraction patterns.

A two-dimensional R-factor is shown in Figure 16 with the top-layer Mn-height $d_{Mn}$ varied from 1.6 Å to 2.4 Å, while the Ni height $d_{Ni}$ is varied from 1.4 Å to 2.2 Å. The R-factor is plotted in a reverse intensity scale where the maximum intensity corresponds to the minimum in R-factor. We observe the presence of a global minimum of the R-factor corresponding to $d_{Mn} = 2.1$ Å and $d_{Ni} = 1.7$ Å. This shows the structure where the Mn atoms are buckled out of the surface by 0.4 Å with respect to the top-layer Ni atoms. This is also accompanied be an inward buckling of the Ni atoms by 0.06 Å.

Buckling in Bimetallic Alloys of Pt Determined by ALISS

Bimetallic Pt–Sn catalysts are useful commercially, e.g., for hydrocarbon conversion reactions. In many catalysts, Pt–Sn alloys are formed and play an important role in the catalysis. This is particularly true in recent reports of highly selective oxidative dehydrogenation of alkanes [37]. In addition, Pt–Sn alloys have been investigated as electrocatalysts for fuel cells and may have applications as gas sensors. Characterization of the composition and geometric structure of single-crystal Pt–Sn alloy surfaces is important for developing improved correlations of structure with activity and/or selectivity of Pt–Sn catalysts and electrocatalysts.

While bulk, single-crystal samples of alloys or intermetallic compounds can sometimes be obtained, another approach is to anneal films prepared by depositing
Figure 15 Comparison between theoretical (left) and experimental (right) results for diffraction patterns obtained at four different kinetic energies: 60, 66, 80, and 94 eV. The diffraction patterns are from Mn emitters in a $c(2 \times 2)$ MnNi surface alloy. The model structure used for the theoretical results was a substitutional alloy with the Mn atoms buckled out of the surface layer.

one metal on a second metal, single-crystal substrate. It is particularly important to know whether the deposited metal forms an adlayer or is incorporated into the surface layers to form an alloy structure. The $c(2 \times 2)$–Sn/Pt(100) structure provides a good example of this situation, as shown in Figures 17a and b. Ordered Sn adlayers and intermixed, alloy-surface layer models can both account for this structure. Using most surface science techniques, it is quite difficult to distinguish between such structures. However, the large difference in the critical angles for Sn scattering in ALISS polar scans for the two structures can immediately determine the actual structure. At low-incidence angles, Sn ad-atoms are shadowed by other Sn adatoms that are located at relatively large distances compared to the situation for incorporated Sn atoms, which are shadowed by closer-in, neighboring Pt atoms. Figure 17c shows that incorporation of Sn into the surface layer increases $\psi_c$ by about $6^\circ$.

Sn has been shown to form ordered ($\sqrt{3} \times \sqrt{3}$) R30$^\circ$ surface alloys at the (111) surfaces of several late-transition metals upon annealing. Because of the lattice
Figure 16  Two-dimensional, R-factor calculation for variations in the height of Mn and Ni atoms above the first subsurface layer in a c(2 × 2) MnNi surface alloy. The R-factor was calculated as the square of the difference between experiment and theory, summed over all points in the diffraction patterns that were obtained at four different energies. The bar on left shows the intensity scaling of the R-factor, and the plot shows that a global minimum is present.

mismatch between Sn and substrate atoms (the atomic diameters of Sn, Ni, Cu, Rh, and Pt are 2.81 Å, 2.49 Å, 2.56 Å, 2.69 Å, and 2.77 Å, respectively), Sn atoms “buckle,” i.e., are displaced outward from the surface plane, to relieve the strain. ALISS has been used to determine the geometric location of Sn atoms in these bimetallic alloys for the Sn/Ni(111) [38] Sn/Cu(111) [38] Sn/Rh(111) [39] Sn/Pt(111) [38]. Figure 18 shows that a linear relationship exists between the buckling of the Sn atoms and the lattice mismatch with the substrate atoms.

Oxide Surfaces

Although oxides are of increasing industrial importance for a large number of applications, structural studies on oxide surfaces are still relatively rare compared to those on metals and semiconductors. Oxides have a variety of chemical compositions and structures, and a wide range of properties. For instance, perovskites range from insulating to superconducting, range from transparent to opaque, and exhibit dielectric constants between 30 to 30,000 within a relatively small variation of composition. In chemical applications, oxides are used as gas sensors or support
Figure 17  Two possible structures for the \(c(2 \times 2)\) Sn–Pt(100) surface. (a) Overlayer model with the Sn atoms located above the Pt(111) surface plane in threefold hollow sites. (b) Surface alloy model with the Sn atoms replacing every second Pt atom in the surface plane. (c) ALISS is ideally suited to distinguish between these two structures with high accuracy, as indicated by the shift in the critical angle for Sn-scattering upon alloying between 720–760 K. (From Ref. 73.)

materials for nanodispersed catalysts. XPD and LEIS can be used to study oxide surfaces, even those that are insulating, and problems due to charging at insulating surfaces can be overcome. These are powerful structural tools because XPD and LEIS determine the element-specific real space structures, which break down the structure of complex oxide surfaces into simpler building blocks.

Anatase TiO\(_2\) Surface Using XPD
Rutile and anatase are two phases of TiO\(_2\). High-quality rutile single crystals can be found in nature as it is the more stable polymorph. Naturally occurring anatase minerals usually contain impurities. Single-crystal anatase phase with few impurities can be grown on SrTiO\(_3\)(001) single crystals due to its close lattice match with the anatase phase. XPD has been used to characterize the anatase phase grown on SrTiO\(_3\)(001) and check the ordering of O and Ti in the crystal [40].
Figure 18  A linear correlation exists between the Sn-buckling distance $d_p$ and the lattice constants of late-transition metal, fcc(111) substrates. (From Refs. 38 and 39.)

Figures 19a and b show the experimental XPD patterns of O 1s and Ti 2p core levels from anatase TiO$_2$ grown on an SrTiO$_3$(001) single crystal. Figures 19c and d and Figures 19e and f show the corresponding single-scattering cluster (SSC) simulations for the anatase and rutile phase, respectively. We can see that the experimental results match very closely to the anatase phase, whereas it is quite different from the rutile phase. Hence, we can conclude that the TiO$_2$ phase grown on SrTiO$_3$ is a high-quality anatase single crystal.

**Rutile TiO$_2$ Surface Using ALISS**

Studying the titanium dioxide surfaces are of fundamental importance in understanding heterogeneous catalysis. High-quality rutile phase TiO$_2$ are easy to obtain and prepare. The TiO$_2$(110) surface has been studied extensively, as it has the highest thermodynamic stability, but widely different structural models have been proposed using experiment and theory.

Recently ALISS experiments and simple classical theory have been used to directly get the surface structure of TiO$_2$(110) [41]. Figure 20 shows an unrelaxed stoichiometric TiO$_2$ surface with bridging oxygen rows.
Figure 19  Experimental and theoretical results for XPD patterns from TiO₂ surfaces. (From Ref. 40.)
Figure 21 shows the Li$^+$ ALISS polar scans obtained along the [001] and [−110] azimuths of the TiO$_2$(110)−p(1 × 1) surface and the corresponding theoretical simulations. Peaks I through VI have been reproduced in the theoretical simulations, and the difference with bulk structure is illustrated in Figure 21b. The structure determined from the critical angles shows that the bridging oxygens are located at 1.2 ± 0.1 Å above the sixfold titanium atoms at the surface. A large relaxation of about −18 ± 4% (−0.6 ± 0.1 Å) was observed between the first and second titanium layers.

4.3 SCANNING PROBE MICROSCOPY

4.3.1 Introduction

The invention of the scanning tunneling microscope (STM) by Binnig and Rohrer at the IBM Research Laboratory in Zürich in 1981 has revolutionized the science of surface imaging and characterization. STM laid the basis for numerous scanning probe microscopy (SPM) techniques now successfully employed in many surface-science experiments. Today modern surface science is difficult to imagine without SPM techniques to provide structural information that is either complimentary to other techniques or unique observations of local defect structures on an atomic scale. In this section we briefly review the physical principles of some of the most important SPM techniques. Then we discuss the use of STM. We describe results obtained for single-crystal surface characterization on metal and metal oxide surfaces under UHV conditions in some detail. The reader interested in the enormous number of STM studies on semiconductor surfaces is referred elsewhere [42]. Although most single-
Figure 21  ALISS polar scans of a TiO$_2$(110)–p(1 × 1) surface taken along the (a) [001] direction and (b) [110] direction using 1-keV Li$^+$ ions backscattered at 160°. The solid circles are experimental data points and the solid curve is the result of theoretical calculations. Dotted lines demonstrate simulations for an error in critical angle by ±1.0°. The dashed line shows the simulations for the bulk structure shown in Figure 20. (From Ref. 41.)
crystal characterization is done under UHV conditions, SPM techniques do not rely on those conditions for their operation. Thus, we also describe results obtained on surface structures in other controlled environments, in particular under high-gas-pressure conditions and in electrolyte solutions.

4.3.2 Scanning Probe Microscopy (SPM)

All SPM techniques have in common that a sharp probe is raster-scanned across the surface, utilizing piezoelectric transducers to control the position of the probe relative to the surface with sub-Ångström precision. The various SPM techniques exploit different interactions between the probe and the surface to obtain locally resolved information about the surface. This information can be presented as a two-dimensional map (image) of the properties of the probed surface. Depending on the technique, various physical and chemical properties of the surface can be imaged. To illustrate the versatility of scanning probe microscopes, we briefly describe three commonly used SPM techniques utilizing different probe-surface interactions to obtain surface-sensitive information: STM, atomic force microscopy (AFM), and near-field scanning optical microscopy (NSOM). There are numerous variations of these techniques and other techniques utilizing different physical phenomena to image the surface [43–50].

Scanning Tunneling Microscopy (STM)

The operation of an STM and the resulting resolution are very simple conceptually. A schematic diagram illustrating this is shown in Figure 22. An atomically sharp metal tip (commonly W, Pt, PtIr, or Au) is brought in close proximity to a conducting sample, only separated by a few Ångstroms. A bias voltage applied

![Diagram](image)

**Figure 22** (a) Schematic diagram of a scanning tunneling microscope. An applied bias voltage between the tip and the surface causes a tunneling current to flow, which can be measured and used as an input signal for a feedback loop. During raster-scanning the tip across the surface, the tunneling current is kept constant by changing the z-position of the tip by applying a voltage (feedback output) to a piezoelectric transducer. An image of the surface is generated by monitoring the feedback signal at different positions of the tip. (b) Tunneling mechanism under the influence of an applied bias voltage between tip and sample. Electrons tunnel from occupied states in the tip to empty states in the sample. The tunneling barrier is defined by the separation between tip and sample and workfunctions of the tip \( \Phi_t \) and sample \( \Phi_s \).
between the sample and the tip can cause electrons to tunnel through this gap, which acts as a barrier, from occupied electronic states in the tip to empty states in the sample, or vice versa, depending on the polarity of the applied bias voltage. This tunneling current depends exponentially on the width of the barrier (i.e., the distance between the tip and the surface) and directly on the electronic structure of the surface. Thus the change in the tunneling current caused by scanning the tip across the surface gives an image that is a convolution of the topography and the electronic structure of the surface. In most STM experiments the tunneling current is kept constant by means of a feedback loop. A voltage applied to a piezoelectric transducer adjusts the tip–sample separation to maintain a constant, preset tunneling current.

A more detailed description of the tunneling current between the tip and the surface can be derived from Bardeen’s tunneling-current formalism [51] and expressed as

\[ I = \int_{0}^{eV} \rho_s(r, E)\rho_t(r, E - eV)T(r, E, eV)dE \]  

(13)

where \( \rho_s(r, E) \) and \( \rho_t(r, E) \) are the electronic density of states of the sample and the tip at location \( r \) and energy \( E \), respectively, \( V \) is the applied bias voltage, and \( T \) is the tunneling transmission probability. This is given by

\[ T(E, eV) = \exp \left( -\frac{2\sqrt{2m_e}}{\hbar} \sqrt{\frac{\varphi_s + \varphi_t}{2} + \frac{eV}{2} - E} \right) \]  

(14)

where \( \varphi_s \) and \( \varphi_t \) are the workfunctions of the sample and tip, respectively, and \( z \) is the tip–sample separation. Thus in “constant-current” mode, the STM tip follows a complex contour line dictated by the surface density of states and the transmission probability, which critically depends on the workfunction of the sample.

Each atom is sensed locally in STM, and in contrast to most surface-science techniques, data are not generated by an average over ensembles of many atoms. The electrons involved in STM have energies of a few electron volts, often smaller than chemical bond energies, and this allows nondestructive, atomic-resolution imaging.

**Atomic-Force Microscopy (AFM)**

STM relies on a conducting sample for its operation. This restriction inspired the invention of a new scanning probe microscope, the atomic-force microscope (AFM). In contrast to the STM, which senses tunneling current, the AFM probes the force between the tip and sample. To sense the force over a small area, a sharp tip with a radius of curvature of a few nanometers is mounted at the end of a fine cantilever micromachined out of silicon. These tips are usually etched from Si or SiN₂. Carbon nanotubes have been either attached or grown at the end of a tip, in order to create tips with even-higher aspect ratios, and various tips have been functionalized to add chemical sensitivity to the AFM. Bending of the cantilever is proportional to the applied force (Hook’s law) and can be monitored and used as a feedback signal to keep the force on the tip constant.
The AFM can be utilized in various operational modes, with the most popular ones being contact, noncontact, and tapping modes.

In contact mode the tip is "touching" the surface and is hindered from penetrating the surface by repulsive forces. These repulsive forces are mainly Coulomb repulsion due to incomplete shielding of nuclear charges of atoms in the tip and the surface and the Pauli exclusion principle for the electrons. Scanning is a dynamic process, and because the tip is in mechanical contact with the sample, frictional or lateral forces can act on the tip in addition to the surface-normal forces. These lateral forces result in a twisting of the cantilever. By separating the twisting and bending of the cantilever one can simultaneously obtain information about normal and lateral forces (lateral force microscopy).

In noncontact mode, attractive forces or force gradients between the tip and surface are sensed. These attractive forces mainly arise from van der Waals interactions between the tip and the surface. Since these interactions (~10^{-11} N) are smaller than the forces encountered in contact-mode AFM, they must be detected by some resonance-enhancement technique. This is commonly done by vibrating the cantilever just above its mechanical resonance frequency. Force gradients encountered by the tip in close proximity to the surface shift the resonance frequency of the cantilever. This causes a change in the amplitude and/or a change in the time lag (phase shift) between the driving oscillation and vibration of the cantilever. These shifts can be monitored and used as feedback signals to keep the tip-sample separation constant. Thus an image of the topography of the surface can be obtained. Samples with ferromagnetic or electrostatic components can be probed by special tips that are sensitive to those interactions and used to image magnetic domains or electrostatic charges. Because the interaction forces in noncontact-mode AFM are considerably smaller than for contact-mode operation, the risks of "accidentally" manipulating the surface by the measurement are reduced. This allows for imaging soft (e.g., biological) materials by using noncontact AFM that would be otherwise altered by contact-mode AFM.

Some operational limitations of noncontact-mode AFM, in particular trapping of the tip in a water layer that is omnipresent on samples under ambient conditions, can be overcome by utilizing a tapping mode of operation that retains a low impact rate of the tip on the surface. In this mode the tip is vibrated at higher amplitude than in noncontact-mode AFM. The tip makes contact with (i.e., taps on) the sample, and the change in amplitude of the oscillating cantilever due to this contact is measured. The force exerted by the tip on the sample can be very small because small changes in the amplitude can be measured. Furthermore, lateral (shear) forces on the sample are virtually zero. This allows delicate samples to be examined without altering their surfaces.

Near-Field Scanning Optical Microscopy (NSOM)

The resolution in conventional optical microscopy is limited to (\lambda/2) by the diffraction limit. This limitation can be avoided by using near-field microscopy. A small light source brought close to the sample (<10 nm) interacts with the sample in the "near field" of the light. Imaging the surface is accomplished by measuring the interaction of the light with the surface, by reflection, refraction, or by absorption and fluorescence mechanisms, and by detection of the light in the far field.
The light source in this subwavelength optical probe is usually a nanofabricated optical fiber or a metal-coated micropipette. Raster-scanning of the probe in close proximity to the surface is usually controlled by combining the NSOM with an AFM feedback loop. This means that the contact of the probe with the sample is controlled in the same way as in an AFM, but the image is generated from the detected light.

4.3.3 UHV Experiments with STM

As mentioned before, the bulk of surface-science studies have been conducted under UHV conditions. Most atomic-scale STM studies have been performed also in UHV, even though STM itself does not require vacuum conditions, because it is necessary to prepare and keep clean a well-defined surface (often highly reactive) in order to obtain meaningful, reproducible results. Also, STM is used under UHV conditions so that complementary electron- or ion-based analytical techniques can be used to characterize the same surface.

In this section we discuss a few illustrative examples of the use of STM in studies of single-crystal surfaces. Given the large and increasing number of STM studies in recent years we have made no attempt at completeness. The contributions and limitations of STM for the characterization of different single-crystal surfaces are demonstrated. The surfaces discussed are low Miller-index, clean metal surfaces, two-component metal alloy surfaces, metal surfaces that contain controlled amounts of adsorbates, ultrathin films that have been epitaxially grown on single-crystal substrates, oxide surfaces, and finally nanoclusters on single-crystal supports.

STM of One-Component, Single-Crystal Metal Surfaces

As discussed above, STM is primarily sensitive to the electronic structure of surfaces. Thus, on an atomic scale, protrusions may not necessarily correspond to the positions of atomic nuclei, even if the measured periodicity corresponds to the anticipated atomic lattice. However, in contrast to semiconductor surfaces, studies on clean metal surfaces have shown that this caution can generally be ignored and protrusions can be assigned to atom-nuclei positions. Furthermore, while large corrugations are observed on semiconductor surfaces due to the presence of dangling bonds, the atomic corrugation on metal surfaces is smaller by a factor of 50 to 100 than on semiconductor surfaces. Thus a higher resolution is needed for imaging metal surfaces with atomic corrugation compared to semiconductors.

An unknown factor in the imaging of surfaces is usually the state of the tip. It is generally believed that a single-atom tip, i.e., a tip with a single atom protruding farther than all the others, is required in order to achieve a well-resolved, atomic corrugation image of the surface. Since no reliable, reproducible way exists to product such a tip and the shape and even chemical state of the tip frequently change during the acquisition of an STM image, the resolution and even the measured electronic structure of the “surface” can change with the tip. Even though this appears at first to be a great disadvantage, different tip geometries may allow additional fitting parameters for calculated, theoretical STM images to compare to experimental results. Usually only a few feasible tip geometries have to be considered for the different appearances of the experimental STM images. Thus, the change of the appearance of the surface with different tip geometries allows a more accurate
picture of the surface to be obtained. Such procedures have been successfully applied for more complex surfaces where the electronic structure of the surface did not allow the simple assignment of protrusions to atomic sites [52].

Surface Reconstructions

“Broken” bonds at the surface give surface atoms a lower coordination number compared to bulk atoms, and this causes the position of surface atoms to be altered. In some cases this results in a relaxation of the interatomic spacing between the atoms in the surface layer and the second layer compared to the bulk lattice spacing. In other cases the surface reconstructs, i.e., surface atoms occupy completely different positions, giving rise to a larger surface unit cell than that for an ideal termination of the bulk at the surface. In principle, STM can be used to determine the atomic arrangement of the surface layer. However, although STM has been successful in elucidating surface structures of reconstructed surfaces and discriminating between different surface structures proposed by using other experimental techniques and theoretical calculations, STM has rarely been used alone to identify the structure of a reconstructed surface. Other techniques (e.g., I-V LEED, XPD, and LEIS) still have the edge over STM for quantitatively determining exact atomic positions within the surface layer. Nevertheless, “real-space” images of surface reconstructions provided by STM uniquely provide information on domain sizes, defects, and interactions of reconstructions with other surface irregularities, e.g., step edges.

Au(110) Surface Reconstruction

Examples of simple reconstructions with a small unit cell are the “missing-row” (2 × 1) reconstructions of Pt, Ir, and Au(110) surfaces. The Au(110) reconstruction was one of the first structures studied by STM. The STM results confirmed the (2 × 1) reconstruction determined earlier by other techniques and allowed further studies of domain sizes and the order-disorder phase transition that LEED found to occur at ~700 K. Annealing the sample within 10 K of this transition temperature and then suddenly quenching the sample caused the half-order LEED spots to almost disappear. STM revealed that (2 × 1) domains still existed, but with small domain sizes of the order of 2–4 nm, far less than the usual coherence length required for sharp spots in electron diffraction. Furthermore, STM showed that the domains were separated by (1 × 3) and (1 × 4) missing-row structures, in addition to steps. This illustrates how STM can provide important information about “local” atomic structure, even when the ordered domains are too small (smaller than the coherence length) to provide a signal in diffraction techniques.

Pt(100)—Hex Reconstruction

More complex reconstructions are formed on Ir, Au, and Pt(100) surfaces. These surfaces form quasi-hexagonal overlayers on the square substrate lattice. This results in a large surface-unit cell. On the Pt(100) surface, two reconstructions are known to exist. There is a metastable Pt(100)-hex reconstruction that forms by annealing the crystal to ~1000 K, and a stable reconstruction that is rotated by 0.7°, i.e., the Pt(100)-hexR0.7°, that forms upon annealing to above 1200 K. The exact structure of the surface-unit cell of the reconstruction is still disputed. LEED studies suggest a unit cell of [√5 \ 1]/2, which would give a fivefold symmetry in approximately the [011] direction. However, more sensitive He-scattering experiments show a splitting of the
one-fifth-order diffraction peak and thus indicates a much larger unit cell of \([111]\).

High-resolution STM images exhibit a clear modulation of the surface atoms with a periodicity of 30 atoms in \(~[01\overline{1}]\) and 6 atoms in the \(~[011]\) direction, as shown in Figure 23. This corresponds to 29 and 5 atoms on the \((1 \times 1)\) lattice, and thus a \((29 \times 5)\) unit cell. However, Figure 23 shows that there is also a less well-pronounced, long-range modulation visible along the \([011]\) direction. While rows 3 and 5 appear equally bright in cell A in Figure 23, the same rows of the “unit” cell in cell B are different in appearance. This implies that the surface is not described by a \((29 \times 5)\) unit cell but by a very large unit cell in the \([011]\) direction, or it may even be incommensurate in this direction. A thorough inspection of the modulation in such STM images suggests that the whole period of the unit cell consists of 26 \((29 \times 5)\)-cells in the \([011]\) direction, i.e., 156 surface atoms or 129 substrate atoms. This result agrees closely with the He-scattering data.

**Standing Electron Waves**

Apart from the determination of topography and atomic structure of surfaces, the STM also has a unique capability to image the local electronic structure of surfaces. Delocalized surface states of electrons, so called Shockley states, behave very much like a two-dimensional free-electron gas. These electrons are scattered at step edges and point defects at the surface. Reflected electron waves from step edges can interfere with incident waves, leading to an oscillation in the local density of states. It is possible to image these surface states by STM [53]. The formation of standing waves by the scattering of surface states at defect sites was first observed on a

![Figure 23](image)

**Figure 23** High-resolution STM image of a reconstructed Pt(100) surface. A \((29 \times 5)\) cell with \((30 \times 6)\) surface atoms is indicated. The differences between cells A and B are highlighted in the schematic drawings at the right. These inequalities between the \((29 \times 5)\) cells indicate a larger unit cell for the reconstruction. (From Ref. 62.)
Cu(111) surface at low temperatures. The constant-current images clearly show standing electron waves at step edges and around point defects in Figure 24. It was found that the oscillation wavelength is energy-dependent. The wavelength increases as the energy is lowered with respect to the Fermi energy. Similar surface-state oscillations have been observed on other metal surfaces such as Au(111) and Ag(111) that exhibit Shockley states.

**Adsorbate-Induced Surface Restructuring**

STM can be used to study this restructuring on an atom-by-atom basis, but it also allows studies of the dynamics of this process, i.e., the nucleation and growth of reconstructed domains and the mass transport that is involved.

**Oxygen on Cu(110)**

The oxygen-induced reconstruction of a Cu(110) surface has been studied by recording consecutive STM images of the same surface area during oxygen exposure. Some of these images are reproduced in Figure 25. It was found that the nucleation and growth of the (2 × 1) reconstruction proceed via the release of Cu atoms from step edges to combine with adsorbed oxygen atoms, forming Cu–O “added rows” on top of terraces running in the ⟨001⟩ directions [54]. These added rows tend to

![Figure 24](image-url)  
*Figure 24* Constant-current STM image of a Cu(111) surface measured at 4 K (\(V_t = 0.1\ V\) and \(I_t = 1.0\ nA\)). Spatial oscillations with a periodicity of 15 Å are clearly emanating from monatomic step edges and point defects. (From Ref. 53.)
agglomerate with increasing oxygen exposure to form \((2 \times 1)\) islands. Once most of
the step edges of the \(\text{Cu}\) surface are pinned by \((2 \times 1)\) islands, another reaction
channel becomes competitive. \(\text{Cu}\) atoms also can be expelled from flat terraces to
form rectangular troughs of missing first-layer \(\text{Cu}\) atoms. If the amount of oxygen
exceeds the saturation coverage for the \((2 \times 1)\) reconstruction \((0.5 \text{ ML})\), a more
complex reconstruction evolves and a \(c(6 \times 2)\) structure is formed. STM images
reveal that this structure preferentially nucleates and grows from step edges and
appears to form on top of the coexisting \((2 \times 1)\) structure. STM shows protrusions
situated in short bridge sites of the underlying \(\text{Cu}(1 \times 1)\) lattice forming the
\(c(6 \times 2)\) superstructure. These protrusions are associated with \(\text{Cu}\) atoms sitting on
top of the \((2 \times 1)\) \(\text{Cu--O}\) rows. A structural model for the \(c(6 \times 2)\) surface is depicted
in Figure 26.

**Lifting of the Pt \((100)\)–Hex Reconstruction by CO Adsorption**

Adsorption of various molecules (CO, NO, \(\text{O}_2\), and \(\text{C}_3\text{H}_4\)) onto the reconstructed
\(\text{Pt}(100)\) surface causes a lifting of the surface reconstruction and the formation of a
\((1 \times 1)\) Pt surface covered by an adsorbed layer. The driving force for lifting the
reconstruction is the higher heat of adsorption of the molecules on an
Figure 26 STM images of Cu(110) showing (a) coexistence of a (2 × 1)O structure with a c(6 × 2)O structure (5.1 × 5.0 nm² scan), and (b) heterogeneous nucleation of a c(6 × 2) structure at step edges and its subsequent anisotropic growth (15.7 × 17.1 nm² scan). Panels (c) and (d) show perspective and top-view atomic models for the c(6 × 2) structure, respectively. (From Ref. 54.)

unreconstructed surface layer compared to that on a quasi-hexagonal, reconstructed overlayer.

The hexagonal, platinum top layer of the reconstructed surface is more densely packed than the square (1 × 1) Pt(100) lattice. As a consequence, lifting the reconstruction causes platinum atoms to be expelled from the surface layer. These platinum adatoms rapidly nucleate to form Pt islands at 300 K. Lifting of the reconstruction and formation of Pt islands can be directly observed by STM at room temperature. Figure 27 shows a series of STM images that were taken as the Pt (100)–hex surface was exposed to CO gas. With increased CO adsorption, the areas covered with Pt islands increase until the reconstruction has been removed from the whole surface. The nucleation and growth of the Pt islands appear to be rather anisotropic. Once islands have formed, these regions grow rather than nucleating new areas. The islands have an elongated shape in the long-periodicity direction of
Figure 27  Series of STM images of a Pt(100) surface at 300 K exposed to CO gas. Lifting of the hex-reconstruction of the clean surface and formation of Pt ad-islands can be observed.
the hex-reconstruction, indicating that adatom diffusion and/or lifting of the reconstruction proceeds preferentially along this direction. Annealing such a surface to ∼450 K causes the islands to assume a compact, square shape (Figure 28), as one would expect for an equilibrium island shape. The absorbed CO molecules on this surface can also be imaged by STM. The CO molecules form $c(2 \times 2)$ domains (Figure 28), both on top of the islands as well as on the region between the islands. The $c(2 \times 2)$ structure is also observed by LEED.

**Metal Alloy Surfaces**

In order for STM to be a useful tool to characterize surfaces with multiple (here we limit ourselves to two) components, it has to be able to discriminate between the different elements present at the surface. Such a sensitivity of the STM to different chemical elements is not obvious a priori and cannot be expected generally. Such a discrimination, however, has been observed for many systems. The mechanism for such “chemical contrast,” a discrimination between two different elements, is not yet completely understood. In a few cases the state of the tip appears to be critical, and it was proposed that “trapping” of an adsorbate atom at the end of the tip may be critical. This tip-adsorbate atom may then form chemical bonds preferentially with one element in the surface. Such a precursor of a chemical bond may increase the

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*Figure 28*  Annealing the surface probed in Figure 27 to 450 K causes the Pt ad-islands to assume a compact, square shape. Adsorbed CO forms a $c(2 \times 2)$ adlayer on top of the unreconstructed Pt(100) islands and surface regions between the islands. (Inset 10 × 9.3 nm²)
local density of states (LDOS) between the adsorbate and the surface and/or move the adsorbate closer to the surface. Both mechanisms result in higher tunneling probability and thus increased contrast. In such a case, frequent “tip changes” are usually observed that cause alterations of the chemical contrast as atoms are picked up and dropped by the tip. A more controlled contrast has been observed on surfaces that exhibit large variations in the LDOS between the two elements in the surface. This is the case for PtRh alloys, for instance. In this case, the density of states near the Fermi level is significantly larger above Rh than above Pt atoms. This results in a larger corrugation of the Rh compared to Pt atoms in the STM images.

Chemical contrast on alloy surfaces is a direct way of determining the composition of the surface layer. For example, the image shown in Figure 29 of a

![Figure 29](image_url)  
**Figure 29** STM image of a Pt$_{33}$Rh$_{67}$ (111) surface showing chemical contrast (30 x 30 nm$^2$). A histogram of the centers of the atoms results in two separate peaks and the concentration of the components can be determined by a Gaussian fit. (From Ref. 55)
Pt$_{72}$Rh$_{23}$(111) crystal surface shows 69% Pt and 31% Rh atoms in the surface layer [55]. Furthermore, information on the short-range order of the atoms can be extracted from atomically resolved images. From Figure 29, a small but significant increase in the number of hetero-neighbor atoms compared to a random distribution was deduced.

STM images of alloyed surfaces may also show a contrast difference between the same element with different numbers of hetero-neighbor atoms due to the effects of alloying, like charge transfer between atoms and rehybridization. This arises from changes in the LDOS around the Fermi level. Such an effect was observed for Au atoms alloyed in Ni(111) (Figure 30, top) and also for Sn/Pt(111) surface alloys (Figure 30, middle). Two ordered surface alloys can be formed for Sn alloyed into the top layers of a Pt(111) crystal, i.e., the (2 × 2) and the (√3 × √3)R30° structures. The two structures have two and three Sn-neighbor atoms per Pt atom, respectively. On a surface that exhibited domains of both surface structures, it was found that Pt ensembles with fewer Sn-neighbor atoms per Pt atom appeared brighter than Pt ensembles with more Sn-neighbor atoms (Figure 30, middle and bottom). This effect was explained by a depletion of the DOS of the Pt atoms near the Fermi level due the effect of alloying with Sn.

Metal-on-Metal Epitaxy

STM has greatly contributed to obtaining a better understanding of the nucleation and growth of metals deposited on metal substrates. Traditionally three growth modes are distinguished: 2D layer-by-layer growth (Frank–van der Merwe), 3-D island growth (Volmer–Weber), and 3-D island growth on top of a 2D wetting layer (Stranski–Krastanov). These growth modes are only valid in the limit of thermodynamic equilibrium. Depending on the temperature and concentration (e.g., supersaturation) of metal adatoms at the surface, growth modes deviate from the thermodynamic equilibrium and kinetic effects play an important role. The dynamic range of the STM to image surfaces from an atomic scale to micron-sized areas allows direct information to be gathered on atomic processes governing the growth kinetics, such as the size of the critical nucleus, motion of individual adatoms and clusters, and shape and branch thickness of individual dendritic islands. Information on island densities, morphological defects, and step densities can be obtained as well.

Diffusion-Controlled Island Morphology—Ag on Pt(111)

Information on island morphologies can provide details about atomistic diffusion processes. For the growth of Ag on Pt(111), island growth proceeds via anisotropic branching after reaching a critical size. Two types of ramified island structures were observed as shown in Figures 31a and b. A fractal structure, i.e., a randomly ramified island, results when ad-atoms “hit and stick” to the growing island, and a dendritic structure, i.e., symmetrically branched islands, results if the growth rate is lowered. Anisotropic ad-atom diffusion around the perimeter of the islands has been identified as an important process for the formation of dendritic islands. There are two types of close-packed island edges, so-called “A” and “B” steps, on an fcc(111) surface. It is apparent from simple geometric reasoning that diffusion from a corner site to the A step can occur via an hcp-hollow site while diffusion to the B step has to
Figure 30 (top) Au atoms alloyed randomly into the Ni(111) surface appear as “holes.” Ni atoms surrounding an alloyed Au atom appear brighter than Ni atoms without Au-neighbor atoms. This may be explained by a change in the electronic structure of the Ni atoms due to the effect of alloying. (From Ref. [63].) (middle and bottom) Mixed domain surface of the ordered (2 × 2) and ($\sqrt{3} \times \sqrt{3}$)R30° Sn/Pt(111) surface alloys. The brightness of Pt ensembles depends on the number of Sn-neighbor atoms. This is interpreted as increasing depletion of the Pt electronic states close to the Fermi level with increasing number of Sn neighbors. This results in a lower tunneling probability and thus a decreased contrast in STM. (From Ref. 64.)
Figure 31  STM images (120 × 120 nm²) showing (a) fractal (randomly ramified) and (b) dendritic Ag aggregates grown on Pt(111) at rates of 1.6 × 10−5 ML/s in (a) and 1.1 × 10−3 ML/s in (b). For both cases, the total Ag coverage was Θ = 0.12 ML. (From Ref. [65].) (c) Schematic diagram illustrating the A and B directions for the diffusion of an Ag ad-atom along the edges of an Ag heptamer on Pt(111). (d) Calculated total energy of an Ag ad-atom diffusing along the edges of an Ag heptamer. The diffusion path with the lowest barrier from a corner site (C) to the A step site is via the hcp site close to it. Diffusion to a B step site from the C-corner site is hindered by a larger diffusion barrier associated with diffusion over an atop site. (From Ref. 66.)

occur via an on-top site. This results in different diffusion barriers and thus anisotropic diffusion rates as illustrated in Figures 31c and d.

Surfactant-Influenced Growth—Homoepitaxial Growth of Pt
Ad-atom diffusion, in particular diffusion across step edges, can be influenced by the presence of “impurity” atoms on the surface, or so-called surfactants. The positive influence that surfactants can have on crystal growth has long been known and exploited. However, new microscopic insight was obtained from recent STM studies. Figure 32 shows how the presence of oxygen ad-atoms decisively influences the homoepitaxial growth of Pt on Pt(111) surfaces, producing a “flatter” surface.
Figure 32  STM topographs of 5-ML Pt deposited on a (a) clean and (b) oxygen precovered Pt(111) surface at 400 K. The imaged area is (220 x 220 nm²) for both images. The percentage of completion of the deposited layers versus the layer number \( n \) is plotted as histograms below each topograph. For the oxygen precovered surface, a completion of layers is favored before new layers nucleate, indicating a reduced interlayer diffusion barrier. (From Ref. 67.)

Oxygen reduces the diffusion barrier for interlayer diffusion of Pt and a more perfect, layer-by-layer growth is achieved.

*Strain Relief due to Misfit Dislocations—Cu on Ru(0001)*

Lattice mismatch between the adlayer and substrate material in heteroepitaxy can have pronounced effects on the morphology of the grown film. Pseudomorphic films, in which the adlayer adopts the substrate lattice spacing, can be significantly strained. There are several ways for this stress to be relieved. One way is to form islands instead of forming a continuous film. This can be done by forming either compact or elongated island structures or by forming islands on top of a strained wetting layer (Stranski–Krastanov growth). STM is an ideal tool for characterizing island density, shape, and size. Another strain-relief mechanism available for the film is the formation of dislocation networks. Ultrathin Cu films grown on Ru(0001) [56], for instance, grow pseudomorphically in the first monolayer, but form domains with fcc and hcp atom-stacking, similar to the Au(111) surface reconstruction, if a second layer forms in order to uniaxially relieve the stress in the film. These domains are separated by misfit dislocations where the Cu atoms occupy slightly higher, bridge sites. Since the domains are anisotropic, with the misfit dislocations running in (120) directions, the Cu atoms are still in registry with the substrate along this direction and consequently under tensile stress. This anisotropy is lifted for the third Cu layer, where the misfit dislocations are arranged in a pseudoisotropic triangular pattern. For a fourth Cu layer, the in-plane stress is relieved by rotation of the Cu overlayer.
with respect to the Ru(0001) substrate by $\sim 1^\circ$, forming a Moiré pattern. The small differences in the topography in the dislocation lines or in the Moire pattern can be imaged by STM (Figure 33), and this allows the most direct determination of the surface morphology.

Figure 33  STM images of Cu grown on Ru(0001) substrates. (a) Fully strained, 1-ML-thick pseudomorphic Cu layer in registry with the Ru substrate. (b) Relaxation of the lattice strain for different layer thicknesses: 2 ML (top), 3 ML (middle), and 4 ML (bottom right). The film in (b) had a nominal film thickness of 3 ML. (From Ref. 56.)
Oxide Surfaces

For STM and many other surface-science techniques, conductive samples are needed. However, many oxides with perfect stoichiometry are insulators. This problem has been addressed by studying thin oxide films grown on metal single-crystal substrates. Epitaxial, thin oxide films can be grown for the right choice of metal substrates, which exhibit surfaces with structures similar to those for bulk oxide samples.

Thin Oxide Films on Metal Supports—\( \text{Al}_2\text{O}_3 \) on \( \text{NiAl}(110) \)

\( \text{Al}_2\text{O}_3 \), one of the most important support materials for dispersed metal catalysts, can be grown in continuous films that are only a few Ångströms thick by oxidizing a NiAl alloy. Figure 34 shows an example of an \( \text{Al}_2\text{O}_3 \) film on \( \text{NiAl}(110) \) [57]. The film is atomically flat but exhibits line defects (antiphase and reflection domain boundaries). The line defects are a consequence of strain in the oxide film resulting from the lattice mismatch between the substrate and oxide film. The formation of these defect lines can partially relieve the strain in the oxide layer. Although these oxide films are very thin, they can possess properties similar to bulk oxide surfaces, and thus they are often used as substitutes for bulk oxide samples. These films allow for the use of STM and other surface-science techniques that rely on conducting samples. As one example, such oxide films have been used as supports to grow metal nanoclusters, which can then be used as model systems for nanodispersed metal, heterogeneous catalysts.

Bulk Oxide Crystal Surfaces—\( \text{TiO}_2(110) \)

Bulk oxides can also be studied by STM if the sample has a sufficiently high electrical conductivity. This may be achieved for some oxides by simply annealing the sample in vacuum in order to create oxygen defects. An oxygen deficiency of 0.1% alters the

![Image](image.png)

**Figure 34** STM image (45 × 45 nm²) of an \( \text{Al}_2\text{O}_3 \) film formed on \( \text{NiAl}(110) \) by oxidation. A step edge (S), reflection-domain boundary (R), as well as an antiphase boundary (A) are indicated. (From Ref. 57.)
electrical conductivity of SrTiO₃ from <10⁻⁸ (Ωcm)⁻¹ to 10⁻² (Ωcm)⁻¹. However, such annealing procedures may change the surface stoichiometry, because oxide surfaces accommodate variations in composition relatively easily. Consequently, a large variety of surface compositions and structures are expected and observed. Furthermore, transition metal cations have multiple valence states and concomitant variations in local bonding geometries. Thus, various surface-science techniques have been used to show numerous stable surface structures of oxides and the sensitivity of the surface structure to the thermal and chemical history of the sample.

Ambiguities arise in the interpretation of STM images of oxide surfaces from the convolution of electronic and topographic information in the STM data. Electronic effects at oxide surfaces are much more pronounced than on metal surfaces. Oxygen-deficient oxides are n-type semiconductors, i.e., the Fermi level is at the top of the band gap. Therefore, tunneling should probe the d-derived states of the cation. STM images should show cation sites as bright protrusions and oxygen sites as dark depressions. However, this assignment of cation and oxygen sites is disputed, and opposite assignments can be found in the literature.

The rutile TiO₂(110) surface has been extensively studied by STM, and Figure 35 shows one image from the (1 x 1) TiO₂(110) surface. There is now accumulated evidence from both theoretical calculations and studies of adsorbed molecules that

**Figure 35** STM image (14 x 14 nm²) of a stoichiometric 1 x 1 rutile TiO₂(110) surface. Dark rows on the terraces correspond to bridging oxygen rows, while the bright rows are due to titanium rows. The inset shows a ball-and-stick model of the rutile TiO₂(110)-(1 x 1) surface. Large balls represent oxygen atoms, and small balls represent titanium atoms. (From Ref. 68.)
are assumed to bind to the Ti sites at the surface that the bright rows in the STM image correspond to Ti rows along the (001) direction and the dark rows correspond to bridging oxygen rows.

Figure 36 STM topographs of Pd clusters grown on an Al₂O₃ thin film on a NiAl(110) substrate. (a) Image (65 × 65 nm²) recorded after deposition of ~2-ML Pd at room temperature. Pd clusters have preferentially nucleated at a step and along domain boundaries. (b) and (c) Atomic-resolution images of nanosize, crystalline Pd clusters. The top of the clusters are (111)-terminated. The side facets are (100)- or (111)-terminated. (From Ref. 57.)
Nanoclusters on Single-Crystal Supports

STM is ideally suited to characterize the morphology of nanostructures grown on single-crystal substrates. The self-organization of nanoclusters with a preferential size distribution on semiconductor surfaces is being exploited to form quantum dots, and a huge number of studies in this technologically important field have been conducted. Here, however, we provide two examples that relate to catalysis and electrocatalysis.

**Metal Clusters on Oxide Supports—Pd on Al₂O₃**

Metal clusters on single-crystal oxide substrates have been studied with an aim to better understand metal/oxide interfaces and to create model systems for supported, nanodispersed metal catalysts for surface-science studies. Growth of metal deposits on oxide crystal surfaces proceeds via nucleation and ad-atom incorporation into existing clusters. Initial nucleation can occur by trapping of an ad-atom at a defect site (heterogenous nucleation) or by fluctuations that form a critical cluster size or nucleus during recombination of ad-atoms (homogenous nucleation). For homogenous nucleation, the density of nuclei is dependent on the ad-atom diffusion coefficient and the deposition flux of ad-atoms. Both parameters can be varied easily experimentally and thus one can control the density of nanoclusters and their sizes. For heterogenous nucleation, the saturation cluster density is independent of the incident atom flux and surface diffusion coefficient. In this case, only a change in the density of defect sites (nucleation sites) on the substrate allows for an adjustment of the nanocluster distribution. STM is a powerful probe of the cluster-size distribution for different preparation conditions.

Pd deposits on thin Al₂O₃ films grown on an NiAl(110) substrate have been studied by STM. Since Al₂O₃ is an insulator with a wide band gap of \( \approx 8 \) eV, tunneling at low-bias voltages takes place from, or to, states in the underlying metal substrate. Determining the real height of metal clusters on the surface requires a subtraction of the oxide film thickness from the apparent height measured with STM at low bias. Islands preferentially nucleate along line defects like surface steps and antiphase or reflection boundaries of the Al₂O₃ thin film as shown in Figure 36a. Atomic-resolution STM images of these Pd nanoclusters were achieved for clusters with a width larger than \( \sim 40 \) Å (Figures 36b and c). The top faces of the Pd islands were found to be (111)-terminated. The facets on the side of the islands were also predominantly (111) faces and only small (100) facets were exposed. Quantitative information about the work of adhesion could be derived from the observed shape of the islands and a Wulff construction based on calculated surface energies [57].

**MoS₂ Islands on Au(111)**

Atomic-scale, structural information has also been obtained on MoS₂ nanoclusters grown on a Au(111) substrate [58] STM results for these single-layer, MoS₂ nanoclusters showed that the S-terminated step edges are preferred to Mo-terminated step edges. This results in a triangular-shaped island. A reconstruction of the sulfur atoms along the step edges was also observed. This can be seen by using the grid superimposed on the STM image in Figure 37a. S atoms at the edges are shifted by onehalf of a lattice constant along the edge compared to the hexagonal lattice of the basal plane. Exposing the surface to atomic hydrogen “strips off” sulfur atoms from the step edges due to chemical reactions and forms defect sites with
Figure 37 Atom-resolved STM images of MoS₂ nanoclusters on Au(111). (a) A superimposed grid shows the registry of edge atoms relative to those in the basal plane of the MoS₂ triangle. The inset shows the Wulff construction for the MoS₂ crystal. Eₘ₀ and Eₙ denote the free energy for Mo and S edges, respectively. (b) An MoS₂ nanocluster after it was exposed to atomic hydrogen at 600 K. S vacancies were formed at the edges (indicated by circles). (From Ref. 58.)

undercoordinated Mo atoms, as shown in Figure 37b. It is believed that such sites are catalytically active for hydrodesulfurization reactions. This approach makes it possible to directly image active sites for catalysis with STM.

4.3.4 High-Pressure STM Studies

Most surface-science techniques use electrons or ions to probe surfaces and thus require vacuum conditions for their operation. STM does not involve free electrons. This allows STM to be used in various ambient environments, such as air, liquid, or a pressurized cell with a well-defined background gas. The latter situation is described in this section. High-pressure STM studies are designed to close the “pressure gap” between the conditions for surface-science studies and those encountered in industrial catalytic processes. Studies of adsorption of molecules on surfaces under UHV conditions are necessarily carried out at low temperatures (often below 300 K) to create high coverages of molecules similar to those that might form at high pressures and elevated temperatures, i.e., those conditions under which most catalytic processes take place. However, adsorbate structures formed at low temperatures are not necessarily in equilibrium with the gas phase and thus may correspond to kinetically trapped structures that have little resemblance to the thermodynamically stable structures formed at high pressures and temperatures. The use of low temperatures also severely limits observations of surface reactions that occur via activated processes.

High-pressure STM apparatuses are now available in a few laboratories. This allows one to scrutinize the low-temperature results, identify new, ordered adsorbate structures, and study activated processes such as adsorbate-induced, surface reconstruction, and reactions that only occur in the presence of adsorbates at high
temperatures. These studies may shed new light on mechanisms of catalytic reactions under industrial conditions.

Although these measurements are taken at elevated pressures, an UHV chamber is still normally used to prepare a clean, well-defined surface prior to exposing the surface to gases. In practice this is often achieved by having a two-chamber design with sample transfer between the chambers. One chamber includes sample preparation and standard surface-science analysis techniques, while the second chamber contains the STM and can be pressurized conveniently.

**Molecular Adsorbates at High Pressures—CO on Pt(111)**

An example of an adsorbate structure identified at high pressure that is different from those observed under UHV conditions comes from studies of CO adsorption on Pt(111). An STM image of a Pt(111) surface in a background pressure of 150 Torr CO and 50 Torr O₂ is shown in Figure 38a. The surface exhibits an ordered, hexagonal superstructure with a uniform spacing of 12 ± 1 Å. A comparison with (110)-type step edges of the Pt(111) surface indicates that the close packed rows of the hexagonal superstructure are aligned along this crystallographic direction. Thus, the hexagonal structure shows only one rotational domain, in contrast to the CO structures observed under UHV conditions. The structure observed in STM at high pressure is a Moiré-type structure, due to an ordered, close-packed layer of CO that is incommensurate with the Pt(111) substrate. The observed orientation of the Moiré structure indicates that rows of CO molecules are formed that are parallel with rows of the Pt lattice. The 12 ± 1 Å Moiré structure is most likely explained by a model for the CO overlayer in which CO molecules are separated by 3.7 Å, with three CO molecules spanning approximately four Pt atoms, as shown in Figure 38b. Such a structure corresponds to a coverage of 0.60 ML.

This surface structure is different from those formed at high-CO coverage under UHV conditions and stabilized by low temperatures. Under UHV conditions,
these adlayers always exhibit several domains due to different angular epitaxies with the Pt substrate. Thus, even though the detailed model for the CO overlayer structure can be disputed, it is apparent that CO molecules adopt a different surface order at high pressures than under low-temperature, UHV conditions. It is likely that this structure is relevant for catalytic processes occurring at elevated pressures and temperatures.

**Surface Reconstruction—Pt(110) under High Pressures of H₂, O₂, and CO**

Topographical changes due to massive surface reconstructions may occur if surfaces are exposed to high pressures. This can be illustrated by the example of a Pt(110) surface. In one experiment, a clean Pt(110) surface was exposed to hydrogen, oxygen, and CO at pressures of above 1 bar and annealed to 425 K for several hours. The surface was imaged in situ by using a high-pressure STM before, during, and after gas exposure.

Hydrogen exposure causes rows running in the (110) direction with separations varying by multiples of the lattice spacing (Figure 39a). Corrugation of the rows increased with their separation. It was concluded from these observations that the

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**Figure 39** STM images of Pt(110) surfaces exposed to different gases at high pressures. (a) Pt(110) surface in 1.6-atm H₂ after heating to 425 K for 5 h, showing a randomly nested, \((n \times 1)\) missing-row reconstruction. Image size: 73 × 70 nm². (b) Pt(110) surface in 1-atm O₂ after heating to 425 K for 5 h, showing a faceted “hill and valley” surface structure. Image size: 90 × 78 nm². (c) Pt(110) surface in 1-atm CO after heating to 425 K for 4 h, showing flat terraces separated by multiple-height steps. Image size: 77 × 74 nm². (From Ref. 70.)
surface consists of missing rows with \((n \times 1)\) unit cells, where \(n\) is an integer between 2 and 5. This surface reconstruction was unchanged by annealing to 425 K or evacuating the STM chamber.

Oxygen exposure causes a different surface morphology. Instead of the moderately corrugated, missing-row reconstruction, the surface was dominated by 10–30 nm structures as shown in Figure 39b. These features were identified as \((111)\) microfacets resulting in a larger “hill and valley” surface topography compared to the same surface exposed to hydrogen.

CO exposure causes yet another surface morphology. The surface appears to be atomically flat with no missing-row reconstructions on a small length scale. This is in agreement with UHV studies that showed that CO lifts the missing-row reconstruction. On a larger length scale, steps of multiple-layer heights can be identified in Figure 39c. Thus, this surface consists of flat terraces separated by multiple-height steps.

### 4.3.5 STM in Electrolyte Solutions

STM is one of only a few techniques that can be used to obtain detailed structural information at the solid/liquid interface. Surface x-ray scattering (SXS) can be used and probes the local order of the surface with higher resolution than STM, but the information is averaged over an extended area of the surface. STM has the advantage that it can image lighter atoms that do not scatter x-rays well, but it is fairly insensitive for distinguishing between atomic or molecular species. Thus, as usual, a combination of the two techniques can provide a more detailed description of the solid–liquid interface.

The potential of the surface (which acts as an electrode) has to be controlled independently of the tunneling tip potential in STM studies in electrolyte solutions. This is commonly done by using a four-electrode configuration such as that depicted in Figure 40. The potential of the substrate and tunneling tip relative to a reference electrode can be controlled independently by using a bipotentiostat. Electrochemical current flowing through the substrate and counter electrode can be monitored and the tunneling current \(I_t\) can be measured by using another amplifier. The tunneling wire has to be insulated because it is immersed in solution and could generate a Faradaic background current approaching several milliamps. This can be achieved by completely coating the tunneling wire, except at its very end, using a variety of coating materials, e.g., soft glass, polyethylene and other polymers, Apiezon® wax, or even nail polish.

Preparing a clean surface is often a prerequisite for surface-science studies. UHV-based methods of sample preparation and characterization are established, and these may be exploited for studies of surfaces immersed in solution by interfacing an electrochemical cell with an UHV chamber. Samples can then be transferred from UHV and immersed into electrolyte solution under a purified-Ar atmosphere. However, even under these “clean” conditions, some metals oxidize or get contaminated prior to immersion. Other techniques for the preparation of clean surfaces that do not require UHV techniques are available for some metals. For example, flame annealing and quenching have been successfully used, but this procedure is probably limited to Au, Pt, Rh, Pd, Ir, and Ag substrates. In this technique, substrates are annealed in an oxygen flame and quenched in pure water.
Iodine adlayers can provide a protective layer against oxidation and contamination while single-crystal surfaces are handled in ambient atmospheres. Also, the adsorbed iodine can be replaced by CO, which in turn can be electrochemically oxidized in solution to yield a clean metal surface. Anodic dissolution of various metals occurs at step edges under carefully adjusted electrochemical conditions, and this is a promising method for in-situ preparation of atomically flat terraces. Such layer-by-layer dissolution has been demonstrated for Ni, Ag, Co, and iodine-modified Pd and Cu surfaces.

Below, we describe two examples that illustrate electrochemical applications of STM. Other topics that can be studied by solution-phase STM include surface reconstructions of single crystals, adsorption of molecules, and anodic dissolution [59,60].

**Adsorbed Anions—Iodide (I⁻) on Au(111)**

The adsorption and structure of anions such as bromide, cyanide, sulfate/bisulfate, and iodide on metal electrodes have been extensively studied by in-situ STM in electrolyte solutions. Figure 41a displays a cyclic voltammogram for an Au(111) electrode in 1-mM KI solution. The anodic/cathodic peaks below 0 V versus Ag/AgI are associated with adsorption/desorption of iodide at the surface. The smaller peaks at ~0.5 V are due to a phase transition in the adsorbed iodine layer, as can be observed by STM images taken at various electrode potentials. STM images shown in Figure 41b taken at a potential of ~0.2 V show a periodic structure with perfect
threefold symmetry, and a 0.50-nm periodicity. This corresponds to a $(\sqrt{3} \times \sqrt{3})R30^\circ$-iodine adlayer. A shift of the electrodes more positive potential results in a more densely packed ad-atom arrangement with an uniaxial compression of the unit cell, as shown in Figure 41b. At an electrode potential of 0.5 V, the surface exhibits a true sixfold symmetry. In this structure, the iodine interatomic spacing is smaller than in the $(\sqrt{3} \times \sqrt{3})R30^\circ$-iodine adlayer, and the lattice appears to be rotated by several degrees with respect to the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. This type of adlattice has been denoted as a “rot–hex” structure. The additional periodic features that can be clearly identified in the STM images are associated with a Moiré pattern due to the mismatch between the iodine adlattice and the Au(111) substrate lattice.

In addition, ex-situ LEED measurements were also performed. Samples immersed at a potential of $-0.2$ V exhibited a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. Samples immersed at a more positive potential exhibited a more complex LEED pattern that
can be associated with a rectangular $c(n \times \sqrt{3} R30^\circ)$ structure, with $n$ a rational number less than 3 (for $n = 3$ the structure is $(\sqrt{3} \times \sqrt{3})R30^\circ$). This describes the uniaxially compressed unit cell that was observed in STM. However, samples immersed at potentials more positive than 0.5 V still exhibited a $c(n \times \sqrt{3})R30^\circ$ structure in the ex-situ LEED studies, even though a rotated hexagonal structure was observed in the STM data. This discrepancy was interpreted as arising from the instability of the rot-hex structure under UHV conditions, and thus this serves as a demonstration of the limitations of ex-situ techniques.

**Underpotential Deposition—Cu on Au(111)**

Cyclic voltammograms of an Au(111) electrode in 0.05-M H$_2$SO$_4$ and 1-mM CuSO$_4$ solutions, as shown in Figure 42, show an anodic peak at 1.25 V and a cathodic peak.
Characterization of Single-Crystal Surfaces

at 0.82 V due to oxidation and reduction of the Au(111) surface, respectively.
In the potential region between 0 and 0.35 V versus SCE, two clear Cu underpotential
deposition waves were observed. High-resolution STM images of the surface under
underpotential deposition conditions revealed \((\sqrt{3} \times \sqrt{3})R30^\circ\) domains covering
the surface almost entirely. Coulometric curves obtained simultaneously indicate
that the ratio of charges consumed during the first and second underpotential deposition
waves was roughly 2:1. This implies a surface Cu coverage of about 2/3 after the first
underpotential deposition peak. Therefore, the observed \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure,
which corresponds to a surface coverage of 1/3 for a primitive unit cell, cannot be
explained by Cu ad-atoms only. SXS examinations of this surface [61] lead to a
model where Cu ad-atoms located at threefold-hollow sites of the substrate form a
"honeycomb" lattice. Sulfate ions are adsorbed in the honeycomb centers, with the
three oxygen atoms of the sulfate ion bound to Cu atoms. Thus, the sulfate ions form
a \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure, and it is likely that this is the structure observed in STM
images. STM is not very sensitive for distinguishing between different chemical
species, and this is a serious limitation. Once again, this illustrates the importance of
a multitechnique approach to nanostructure determination.

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