

3.2.6 Secondary-Electron Imaging

Secondary-electron imaging (SEI) is a method to investigate the arrangement of atoms in real space. This method involves the excitation of the surface with electrons of energy near 2000 eV and 2DIM imaging of the quasi-elastically backscattered electrons. SEI probes the immediate environment of a particular atomic site. Individual atomic species need not possess LRO, but the local environment must be in the same orientation around each atom. Therefore, SEI is ideally suited for the study of structures that only possess orientational LRO, e.g., quasicrystals.

![Figure 3.19: Atomic scattering amplitude $|f(\theta)|$ of electrons at Ni atoms having different energies. With increasing energy, electron intensity is concentrated predominantly in the forward-scattering direction, defined as $\theta = 0$. From M. Fink and A.C. Yates, At. Data 1. 385 (1970).](image)

The processes involved in imaging the surface atomic structure of solids by SEI can be visualized in a two-step model: (1) the excitation of the surface by primary electrons having an energy near 2000 eV, and (2) subsequent 2DIM spherical recording of the backscattered secondary electrons. In the first step, primary electrons penetrate the solid and are diffracted at atoms in a surface layer. This process localizes the electron wave field at atoms below the surface. In the second step, these atoms are considered to be point sources of secondary electrons which emanate as spherical waves from localized atomic sites, and are subsequently scattered by the atoms surrounding the source atoms.

At energies above a few hundred eV, elastic forward scattering is the dominant process and the scattered intensity is focussed in the forward direction, as shown in Fig. 3.19. Therefore, the intensity of secondary electrons are concentrated into internuclear directions with respect to the source atoms. Electrons which can escape the solid are predominantly those scattered by atoms around and near the source.
Figure 3.20: Secondary electrons are emitted from an atomic source localized at a lattice site. The scattering intensity is concentrated in forward-scattering directions.

Figure 3.20 shows schematically one such source of secondary electrons below the surface. By virtue of this process, a spherical recording of these electrons represents a central projection of the internuclear directions in a near-surface region of the sample.

Since energy-loss processes are involved in the production of secondary electrons, scattering events around different atomic sites contribute incoherently to the total emitted current, and, therefore, successful imaging is possible even in the absence of LRO. This is not a coherent process. Electrons at around 2 keV have longer mean free path, and therefore penetrate several atomic layers into the solid. Hence, one does not only observe the arrangement of atoms at the surface, but multiple atomic layers can be analyzed simultaneously. An additional advantage of the SEI technique compared to other methods is that images can be recorded, while the sample is rotated through an appropriate axis. These images provide 3DIM views of the structure. Consequently, all symmetry elements of the sample can be observed with equal precision, and the angles between the symmetry axes can exactly be determined. Further, since the patterns are mostly produced by forward scattering along atomic chains and contain real-space features, time-consuming data transformation is no longer needed. This advantage together with the high signal-to-noise ratio markedly accelerates the acquisition of structural information.
Figure 3.21: (Top panel) SEI image from the pentagonal surface of an icosahedral quasicrystal Al-Pd-Mn. The electron gun used for the excitation of secondary electrons and its holder appear in the middle of the figure. Structural details become visible as the sample is tilted in one direction. (Lower panel) A wire-frame model of an icosidodecahedron in the same orientation as the sample. Ref. [10]

Figure 3.21 shows an SEI pattern obtained from a quasicrystalline AlPdMn alloy. There are bright bands of increased electron intensity which connect each adjacent bright patch. Five bright patches positioned on a small circle with a radius of $\theta = 32^\circ$ form an equal-sided pentagon, which clearly reveals the presence of fivefold symmetry in the structure. Other bright spots appearing halfway between the two main patches are probably generated by additional atoms in the quasicrystal structure. By rotating the sample through polar and azimuthal angles we can experimentally determine the angles between the major symmetry axes and prove that the specimen possesses icosahedral (53m) point-group symmetry.$^{10}$

Some electromagnetic forces try to establish order between particles, while thermal motion tends the opposite. The state of order is a universal phenomenon in 3DIM and is described by phase transitions. There are phenomenological methods to describe phase transitions. They rely on concepts like symmetry or order, while almost no microscopic ideas have been used so far. Phase transitions occur because all systems in thermodynamic equilibrium try to minimize their free energy $F = U - TS$. $U$ is the internal energy and $S$ the entropy. A certain phase

dominates the other at a given temperature because different states distribute their energy differently between $U(T)$ and $S(T)$.

For 3DIM, first-order phase transition is characterized by an abrupt change in the order parameter at the critical temperature, while in a second-order phase transition, two equivalent phases do coexist and become indistinguishable. The order parameter changes continuously with temperature and near $T_c$ as $(T - T_c)^\beta$. These cases are schematically shown in Fig. 1.9.

Cobalt is known to exist in two allotropic phases, a low-temperature hexagonal close-packed (hcp) phase and a high-temperature fcc phase. The hcp – fcc transformation is reversible and weakly first order. The hcp and fcc phases are in equilibrium at $T_{eq} \approx 422^\circ C$, but there is considerable thermal hysteresis between the heating and cooling transformations. Because of these characteristics, together with the diffusionless nature of the phase change, this transformation is designated as martensitic. There is no difference in the corresponding coordination numbers between the hcp and fcc phases, there is a substantial change in the stacking sequence, as seen in Fig. 3.22. Both the fcc and hcp structures can be represented by stacking planes with atoms in sixfold symmetry, the (111) planes. The difference in stacking sequence leads to fcc or hcp structures. Layers with alternating AB planes result in the hcp structure, while a sequence alternating ABC gives the fcc structure. Figure 3.22 shows this structural assembly in top and side view. For
the fcc structure, [111] is normal to the sixfold-symmetry planes, it is the [0001] for the hcp structure. Thus, characteristic modifications in microscopic properties, e.g., the electronic structure, and macroscopic properties, e.g., the electrical resistivity and the work function, have been observed to accompany the martensitic transformation.

![Graph showing electrical resistivity and surface spot intensity](image)

Figure 3.23: The electrical resistivity $\rho$ and the surface spot intensity $A$ as a function of $T$. $\rho$ and $A$ are both normalized to unity for the hcp phase and zero for the fcc. The resistivity is used to record the bulk phase transitions. The inset shows $\rho(T)/\rho(RT)$. $A$ is the intensity of backscattered electrons along an hcp-characteristic direction divided by the intensity along an fcc-characteristic direction. Ref. [11].

The change in the stacking sequence in the near-surface region is observed directly with SEI because the depth of the imaging is given by the mean free path of 1750-eV electrons ($\simeq 15$ Å), which corresponds approximately to 5 – 6 layers. The resistance of the specimen was measured continuously for temperatures between 300 and 870 K with the SEI patterns recorded simultaneously. Since the lateral arrangement of atoms on the (0001) surface of hcp Co is the same as that on a (111) surface of fcc Co, observing the hcp $\rightarrow$ fcc phase change on the surface is not straightforward. The change in the structure can be detected only by surface
methods that are sensitive to at least the top three layers of atoms.\textsuperscript{11}

Figure 3.23 shows the temperature dependence of the ratio $A = I_{\text{hcp}}/I_{\text{fcc}}$. $A$ is normalized to unity at RT and to zero at the high-temperature end. Each $A$ point represents an individual SEI measurement such that large (low) values of $A$ are associated with the hcp (fcc) structure at the surface. The arrows show the direction of the temperature change. Also shown is the bulk resistivity $\rho$ of the Co crystal, which has been transformed by subtracting a parabolic background and normalized to unity for the hcp phase and zero for the fcc phase. The inset shows the raw resistivity data. The temperature dependence of $A$ shows a hysteresis, but one that is distinctly broader in temperature than that of the bulk.

The origins of the transformation occurring at different temperatures on the surface than in the bulk remain unclear. One possibility is that the thermal equilibrium transition temperature of the surface is effectively higher than that in the bulk. A second possibility is that the sliding of the planes is better pinned at the surface than in bulk, giving rise to a more stable metastable state.

Figure 3.24: (left) The sample holder allowing for polar and azimuthal rotations of the sample. (middle) The energy analyzed electrons are recorded as a function of the polar and azimuthal angles and are plotted in an arbitrary fashion. Here, the pattern represents a stereographic projection. Schematic drawing of the principal crystallographic properties of a cubic lattice in the same representation. Ref. [12].

### 3.2.7 X-Ray Photoelectron Diffraction

X-ray photoelectron diffraction (XPD) relies on the interaction of photoexcited electrons with the atoms of the sample during the escape process. The heart of the experiment is the fact that the core levels of an atom have a well-defined binding energy $E_B$, as seen for the $4f$ electrons of a gold sample in Fig. 3.6, and the x-ray photoemission process leads to excited electrons with a similarly well-defined

kinetic energy \( E_{\text{kin}} = h\nu - E_{B} - \Phi \). Thus the photoemission process produces sources of electrons below the surface localized at atomic sites. These electrons scatter elastically at atoms during the escape process. For large values of \( h\nu \) and shallow core levels, \( E_{\text{kin}} \) is sufficiently large that scattering of emitted electrons can be taken as travelling in forward-scattering directions, as shown in Fig. 3.20. Like it is done in SEI, one collects these electrons for a real-space image of the surface atomic symmetry. Compared to SEI, XPD has the advantage that the core levels are element specific and one maps the structural symmetry around each constituent atom in a multi-component alloy, like it is done in EXAFS.\(^\text{12}\)

Data are obtained by tuning the pass energy of the energy analyzer on the core level at a given emission angle and rotating the sample through polar and azimuthal angles, while recording the intensity [cf. Fig. 3.24(left)]. The entire pattern is constructed by using the angular collection of discrete measurement points. The disadvantage of XPD is that data collection time is too long that the sample surface has to be cleaned frequently; one only obtains static pictures, while in SEI video recording of the symmetry properties allows observations during structural phase transitions.

### 3.2.8 Scanning Microscopes

In far-field microscopy, the distance between the specimen and the radiation source is large. 2DIM spatial information is obtained either by scanning the source beam on the surface or the emitted particles are imaged with spatial resolution (cf. Fig. 3.7). In either case, physical laws prevent atomic resolution. This limitation is circumvented in near-field microscopy by keeping the distance between the object and the light source much smaller than the wavelength \( \lambda \). The ability to meet this condition marks the advent of scanning techniques with atomic resolution.

Historically, \textit{stylus profilometer} represents the principles of near-field microscopy. The idea is sensing some surface details while scanning the probe. The precision of scanning and the method of sensing both are the main factors that limit the spatial resolution. The idea of imaging with microscopic resolution came with \textit{topografiner} as shown in Fig. 3.25.\(^\text{13}\)

The topografiner is based on the revolutionary idea of utilizing piezo-electricity to attain \textit{picometer} resolution in three directions. Quartz crystal is piezo-electric, namely it shows charge separation under mechanical stress. If the crystal is cut in the proper direction, we observe that the polarity changes for tension or compression and its magnitude depends linearly on mechanical stress. Conversely, if an external voltage \( U \) is applied, e.g., in the \( x \)-direction, the dimensions of the crystal change by \( \delta_{x} = \delta_{11}U \) in the \( x \)-direction and \( \delta_{y} = -\delta_{11}Ul_{y}/l_{x} \) in the \( y \)-direction keeping \( \delta_{z} = 0 \). This situation is illustrated in Fig. 3.26. The polarity of \( U \) changes the sign


\(^{13}\text{R. Young et al., Rev. Sci. Instrum. } \textbf{43}, \text{999 (1972)} \)
of $\delta_x$ and $\delta_y$. The piezo-electric coefficient $\delta_{11}$ is as large as 2.3 pm/V allowing the required atomic resolution by applying voltages in a practical range. $\delta_{11}$ is linear and has a large dynamical range. These properties are also found in inexpensive piezo-ceramic material. The principle of moving the probe and the specimen using the piezo-electric effect applies to all scanning techniques.

Figure 3.25: The experiment is performed in vacuum by scanning a fine tip in $x$- and $y$-directions and sensing structural details in the $z$-direction using piezo-electric components. Ref. [13].

Figure 3.26: Piezo-electric effect in a quartz crystal showing polarization charges produced by stress and strain.
3.2.8.1 Scanning Tunnelling Microscope

The principles of imaging in the *scanning tunnelling microscope* (STM) is based on a fine metallic tip, like in FEM or FIM, through which an imaging current tunnels to the specimen. For tunneling the required separation $s$ between the sample and the tip is adjusted by an additional piezo-ceramic unit. When $s$ is made sufficiently small there is an overlap of the wave functions of the tip and the sample. As a result, there is a tunnelling current through vacuum $J_T \propto \frac{V}{s} e^{-A\Phi s}$, if a voltage $V$ is applied across the tunnel junction. This is the Fowler-Nordheim equation with an average work function $\Phi$ of the sample and the tip. A variation $\Delta s$ in the tunnelling gap by 1 Å results in a change of current $J_T$ by $\times 10$. The tip is scanned across the surface at a fixed bias voltage $V$ and a piezo-electric feedback mechanism regulates the vertical motion of the tip so that the tunnelling current is kept constant. Thus the tip traces the contours of constant wave function overlap, namely the surface topology. In the topografiner the tip is used as an electron source. The distance $s$ is kept so large that the experiment is not performed in the tunnelling mode and the current does not depend critically on $s$. The success of STM is achieved by bringing the tip near to the sample ($\approx 5$ Å) in a tunnelling position (G. Binning and H. Rohrer, Nobel Prize 1986).

![Figure 3.27: The working principle of STM showing electron tunnelling at the tip. From Wikipedia.org.](image)

In STM, the tip can be represented by a spherical potential well, for which we have to solve the Schrödinger equation. If we only keep the spherically symmetric solutions, the expression for the tunnelling current reduces to $I \propto eV\rho(r_o, E_F)$ for low applied voltages. $\rho(r_o, E_F)$ is the so-called local density of states at the Fermi energy $E_F$ and at the site $r_o$ of the surface. Therefore, the surface is scanned while the current is kept constant, so that the contours of the constant charge density
One of the first experiments are performed on the Si(111) surface, because this surface provides the most interesting reconstruction, namely $7 \times 7$ that was discovered many years ago in LEED experiments, but the real-space visualization of the atomic arrangement was not complete yet. This surface shows metallic behavior.

On Fig. 3.28 we see the line scans of the STM in two surface directions. The tunnelling current, i.e., surface topology, is represented in the third direction. We can make up rhombic unit cells on the surface, each edge of which is approximately 27 Å wide. This cell is called the $7 \times 7$, because each edge is as long as 7 atomic distances. Thus, the surface unit cell is $\times 49$ larger than the not reconstructed cell. We further see 12 hills which can be grouped into 2 each with 6 hills. Probably these hills represent individual atoms.

The revolutionary idea in STM is the possibility of spectroscopy at the surface, which comes about by scanning the surface using different applied potentials, as illustrated in Fig. 3.29. If the tip is biased positively current flows from the occupied states of the sample to unoccupied states of the tip (left panel). This provides information on the occupied states below $E_F$, these are the bonding orbitals. In contrast, if we bias the tip negatively, current will flow into the unoccupied antibonding orbital states of the sample (right panel). Thus all the states below and above $E_F$ can be recorded.

The lowest intensity of the wave functions for the antibonding states $|\psi_A - \psi_B|^2$ is located just between the atoms $A$ and $B$ in agreement with the STM image on the left-hand side of Fig. 3.30. This fact renders the best atomic resolution.

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contrast, the shape of the bonding orbitals does not allow to resolve individual atoms, because $|\psi_A + \psi_B|^2$ represents just an enhanced intensity.

Figure 3.30: On the left we see the image of empty states, on the right it is the image of the filled states of the reconstructed Si(001) surface. Ref. [15].

STM is limited to metallic samples. In other materials, the local density of states near $E_F$ is negligibly small and we have vanishing tunnelling current. Further, one has to work with one magnification value. There are some instances where lower magnification would help to better visualize the surface geometry. This possibility is not applicable to STM.

3.2.8.2 Atomic Force Microscopy

If the tip is brought near the surface, the surface atoms exert a force on the tip. This force is $\propto 1/s^2$ and constitutes the principle of atomic force microscopy (AFM) operation. The tip is mounted on a flexible cantilever and scanned over surface. The force acting on the cantilever will be directly related to the deflections of the cantilever. This situation is illustrated schematically in Fig. 3.31. The deflections can be registered by directing a laser beam on the cantilever and recording the
variations in the reflected beam as the cantilever changes its position slightly. This technique is known as AFM and allows lateral resolution on the atomic level. The vertical resolution is below 0.1 nm.

![Diagram of atomic force microscope](image)

Figure 3.31: Operating principle of the atomic force microscope. From Wikipedia.org.

AFM is an ideal complementation to STM, because it is sensitive to all electrons of the solid, the surface need not to be conductive. The resolution of AFM is improved if $s$ corresponds to just a few atomic distances. This mode is called the *contact mode*. For larger tip-to-sample distances we have the lower resolution *non-contact mode*.

The first known, but not recognized as such, self-organization phenomenon is the surface reconstruction. Si(111) is probably the most expensive surface so far, because the amount of research to explore the exact structure has been enormous. Figure 3.32 shows on the left-hand side an atomically resolved AFM image of the Si(111) $(7 \times 7)$ surface. On the right-hand side, the remarkable structural model of this reconstruction is shown. The key structural features of the model are: (a) 12 top layer adatoms, (b) a stacking fault in one of the two triangular subunits of the second layer, (c) nine dimers that border the triangular subunits in the third layer, and (d) a deep vacancy at each apex of the unit cell.\(^{16}\)

We identify a force between two objects as friction. This force can be in any lateral direction, and usually act to impede a movement. AFM senses forces normal to the surface. Lateral forces, on the other hand, give a clue on the friction between the tip and sample. Torsion at the cantilever, as seen on the left-hand side of the Fig. 3.33, can be plotted over the entire surface for performing tribology on nanometer scale. The polymer imaged here is a mixture of polyallylaminehy-

drochlorirde and polydiallyldimethylammoniumchloride.\textsuperscript{17} The micrograph suggest a cluster growth on the flat matrix. Similarly, biomolecules have successfully been detected, analyzed, and manipulated using AFM.\textsuperscript{18}

The strength of the scanning probes resides in the fact that they can operate under any ambient condition. \textit{Polarization-force microscope} is just one example. For a liquid with the dielectric constant $\epsilon$, the image charge is reduced by $(\epsilon - 1)(\epsilon + 1)^{-1}$. Therefore, the Coulomb force between a tip and the liquid will depend on the local changes of $\epsilon$. In this mode of operation, the electric field between the tip and the surface induces a polarization charge at the surface and hence the polarization


\textsuperscript{18}J. Fritz \textit{et al.}, Science \textbf{288}, 316 (2000).
Figure 3.34: Principle of the polarization-force microscopy. The induced polarization force is measured with the microscope. Ref. [19].

\[ F \approx \varepsilon_0 \frac{\varepsilon - 1}{\varepsilon + 1} \frac{R^2}{z^2} (V_{\text{tip}} + \Delta \phi)^2. \]  

Figure 3.34 shows schematically the ingredients of the experiment.

Figure 3.35: Time-resolved wetting of mica surface (mica is visible on dark areas, I, water on light regions, II) observed by polarization-force microscopy. The panels (a) – (d) illustrate the evaporation of water away from the mica surface. Ref. [19]
Wetting of mica (= aluminum silicate) is technologically important because it is widely used in cosmetic industry in facial powder, lip stick, or nail polish, as well as in electronic industry. It can withstand electric fields as large as 1500 V/mm. Fig. 3.35 shows microscopically the wetting process of a mica surface. Each frame is 5 µ × 5 µ large.\textsuperscript{19}

The magnetic force microscope (MFM) is a variation of AFM, where a sharp magnetized tip scans over a magnetic sample. The tip-sample magnetic interactions are detected and used to reconstruct the magnetic structure of the sample surface. Many kinds of magnetic interactions are measured by MFM, including magnetic dipole-dipole interaction. MFM is typically used in non-contact AFM mode.

Figure 3.36: Fe-atoms placed on Cu(111). Ref. \textsuperscript{20}.

Scanning techniques have also been used to manipulate surface atoms and molecules by simply dragging them on a flat surface. The success depends on the force between the tip and the atom pushed away which must be smaller than the force between the atom and the surface. Otherwise, the atom will stick to the tip and leaves the surface. Figure 3.36 displays progressive STM images of Fe atoms assembled in a circular ring on a Cu(111) surface.\textsuperscript{20} When the cage is closed, we observe interesting details like concentric water waves in a circular well. These details are produced by the conduction electrons, which are trapped in the cage, interfere and form standing waves. They move otherwise as Bloch waves.

\textsuperscript{20}M.F. Crommie et al., Science \textbf{262}, 218 (1993).