Role of Multiple Scattering in X-Ray Photoelectron Spectroscopy and Auger-Electron Diffraction in Crystals

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The angular anisotropies of x-ray photoelectron and Auger peak intensities from Cu in epitaxial Ni-Cu-Ni(100) sandwich structures allow, for the first time, the breakdown of the observed diffraction from a crystal into the contribution from each layer of atoms. These data show that the primary role of multiple scattering of the outgoing electron wave is to deflect electron trajectories, thereby removing intensity from the strong forward-scattered beams which form upon the initial scattering events, i.e., scattering by nearest-neighbor and next-nearest-neighbor lattice atoms.

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It has been known for some time that the intensities of x-ray photoelectrons and Auger electrons emitted from single crystals exhibit pronounced angular anisotropies.[1] The most pronounced anisotropies generally take the form of enhanced intensities along principal crystal axes.[1,2] As a result of an apparent similarity with Kikuchi bands seen in electron microscopy, it was long thought that these enhancements were a consequence of electrons channeling along bulk planes of atoms.[2] However, recent studies of the development of these enhancements as a function of crystal thickness during epitaxial growth have demonstrated that a quantum-mechanical channeling mode was ill suited to describe the data at least for kinetic energies of several hundred electronvolts.[3-7] Instead, the source of the enhancements was forward scattering, by overlying lattice atoms, of the outgoing electron waves which originated around two to four atomic layers into the surface. Theoretical modeling of these data by Tong and co-workers[4] suggested that multiple scattering played an important role in preventing enhancements (along principal crystal axes) in the emission from atoms deeper than the top few layers.[4] Atoms deeper than the top few layers should tend to make a rather more isotropic contribution to the intensity.

The purpose of the present work is to present, for the first time, experimental data which reveal the layer-by-layer breakdown of the origin of the x-ray photoelectron spectroscopy (XPS) and Auger diffraction features from a single crystal. Such knowledge combined with the insights of the theoretical modeling by Tong and coworkers can provide a clearer picture of the basic physics of XPS and Auger diffraction in crystals.[4] Moreover, this understanding can (by the reciprocity relation) provide insights into the behavior of electron beams incident upon crystals. These insights in turn can contribute to the wider class of problems concerning electron propagation in solids at kinetic energies around several hundred electronvolts.

Figures 1(a) and 1(b) show the angular dependence of the Cu $2p_{3/2}$ XPS and *CVV* Auger peak intensities for epitaxial sandwich structures consisting of one monolayer (ML) of Cu on Ni(100) with various subsequent Ni overlayer thicknesses. The epitaxial sandwich structure for a 2-ML Ni overlayer is illustrated in Fig. 1(c). An extensive temperature-dependent study of Cu surface

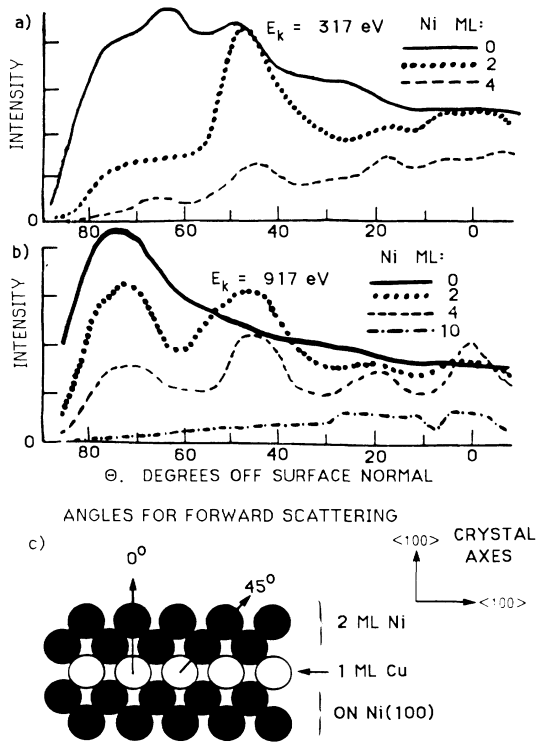

FIG. 1. The angular dependence of the intensity of (a) the Cu $2p_{3/2}$ and (b) *CVV* Auger peaks for 1 ML of epitaxial Cu on Ni(100) and for subsequent deposition of epitaxial Ni overlayers on the 1-ML Cu. (c) A typical such sandwich structure.

segregation in these structures was conducted to establish conditions for structural integrity.[8] For further experimental details, see Ref. 3.

Figure 2 presents several classical electron trajectories which can be very instructive for visualizing the single- and multiple-scattering processes which are responsible for the data in Fig. 1. Tong and co-workers have noted how useful such classical analogies can be for translating the obscurities of partial-wave-expansion treatments of multiple scattering into useful physical pictures that provide an intuitive feeling for how the diffraction events occur.[4] For example, the intensity enhancement associated with forward scattering is closely associated with the deflection of the electron trajectory by the neighboring attractive potential, as shown in Fig. 2(a). This "focusing" in the forward direction is immediately apparent in Fig. 1(a) in which intensity which appeared at, say, 60° and 30° for the clean Cu ML is deflected to $\approx 45°$ for the 2-ML Ni case, offsetting the general signal attenuation by the overlying Ni. This offsetting effect is even more pronounced at higher kinetic energies, as in Fig. 1(b), in which 2-ML Ni actually produces an increase in the Cu signal at 45°.

These enhancements at 45° are approximately as strong for 1 ML of overlying Ni as for the 2-ML case presented in Fig. 1. The reason for this similarity can be seen by comparison of Fig. 2(a) with 2(b). Trajectories deflected into the forward direction by the first scattering atom are deflected out of the forward direction by the second scattering atom. However, other trajectories, initially at larger angles, can compensate by being deflected into the forward direction by two scattering events.

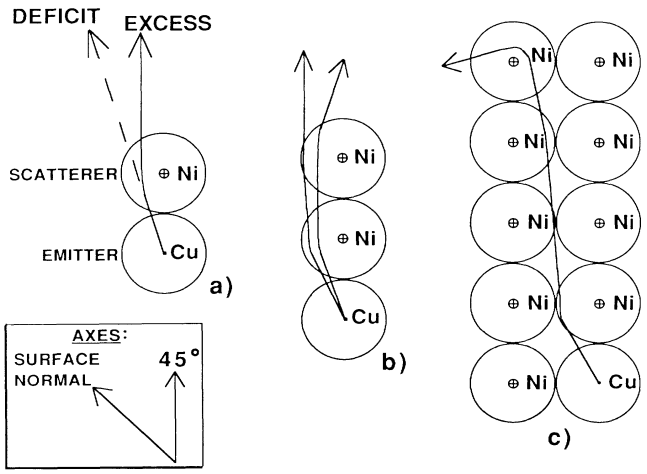

FIG. 2. Several classical electron trajectories that can help in understanding some of the basic processes contributing to XPS and Auger diffraction. Although this model is obviously not complete, it is important because it depicts the basic process at work in the quantum-mechanical description, namely electrostatic deflection of trajectories.

The crucial point here about multiple scattering is that the forward-direction enhancements cannot be maintained for steadily larger overlayer thicknesses by going to steadily larger initial trajectory angles, as in Fig. 2(b), to compensate for the multiple-scattering events. This is because, in a lattice, these larger angles would eventually lead the trajectory into adjacent rows of atoms as illustrated in Fig. 2(c). Of course, there will be an initial trajectory angle for which multiple scattering (or deflection) will allow the trajectory to converge on the line exactly between rows of atoms and this will indeed escape in the forward direction, but the solid angle for this process will shrink rapidly with increasing overlayer thickness.

It may be of interest to point out here that these "channel-axis trajectories" with $k=0$ (perpendicular to the axis) correspond to classical channeling, of which XPS and Auger forward focusing is a manifestation.[9] Quantum-mechanical channeling, for which $k=\pm 1/2g$ (in the two-beam dynamical theory), plays a very limited role in XPS and Auger diffraction since the penetration length generally is not long enough for the different scattering of type 1 and type 2 waves to become manifest.[10]

In addition to the simple channel-axis trajectories there are many other more complicated trajectories which can also produce some intensity in the forward direction, but no special enhancements would be expected since this variety of complex trajectories would have random phases. The importance of trajectories cylindrically symmetric about a row of atoms, as in Fig. 2, is that they have the same phase so that the square of the sum of amplitudes potentially can give large intensity enhancements. It is important to recognize that it is this phase coherence that allows the classical description to be so useful. Moreover, the classical scattering amplitude $[d\sigma(\theta)/d\Omega]^{1/2}$ versus angle agrees quite well with the quantum $[f(\theta)]$ result.[11]

The reduction of the forward-direction enhancements by multiple scattering, termed "defocusing" by Tong and co-workers in their theoretical prediction of this effect,[4] is directly observable in Fig. 1(a) at 45° in comparing the 2- and 4-ML Ni cases. The 45° peak is greatly reduced in prominence relative to the rest of the curve in going from 2 to 4 ML of overlying Ni. At the higher kinetic energies of Fig. 1(b), it takes more layers to achieve defocusing, e.g., 10-ML Ni at 45° (higher kinetic energies require closer encounters with the core for a given angular deflection; i.e., cross sections become smaller). It is interesting to note that 10-ML Ni does not fully defocus the 0° enhancement in Fig. 1(b) as it does the 45° enhancement. This important result is a direct consequence of there being only five Ni atoms along the 0° path in contrast to ten Ni atoms along the 45° path. The major result of this work is thus that Fig. 1 permits for the first time direct experimental observa-

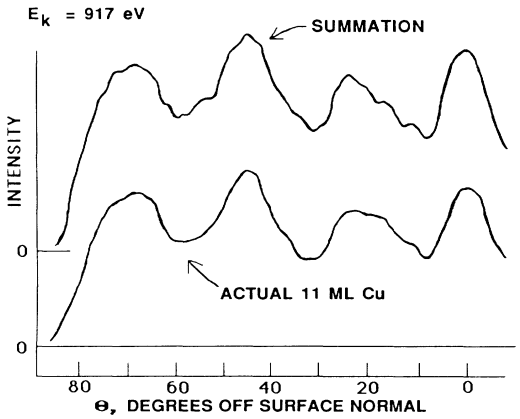

FIG. 3. A comparison of the summation of the layerwise contributions to the angular distribution of the Cu Auger intensity [e.g., Fig. 1(b)] with that obtained from an actual 11-ML Cu film.

tion of how the diffraction features depend on depth of origin: The first few atomic layers are forward focusing along rows of atoms; subsequent layers are defocusing. The number of layers required for either process is larger, the higher the electron kinetic energy.

Thus this very intuitively appealing picture explains much of the XPS and Auger diffraction data. However, the peaks in Fig. 1(b) at $\approx 20°$ and $\approx 70°$, although partly due to forward focusing,[3] also contain contributions which do not have a classical description. In the $\approx 20°$ peak this occurs because at 917 eV the phase happens to be the same at 20° for the wave scattered by the nearest-neighbor atom (at 45°) and the next-nearest-neighbor atom (at 0°).[4,5] The 70° peak has an analogous contribution from atoms at 45° and 90°.[4,5]

Since Cu and Ni atoms scatter electrons in a very similar manner, what Fig. 1 does, in effect, is to reveal the layerwise components of the XPS and Auger-diffraction features for a Cu(100) crystal. A consistency check on this is presented in Fig. 3 in which the layerwise components are summed, $\sum_{i=0}^{10}(i$ ML Ni), and compared with an actual 11-ML epitaxial film of Cu on Ni(100). The agreement is excellent.

Figure 4 presents a simple application of the reciprocity relation. If emission from the core of an atom is focused in the forward direction, then an electron beam (at the same kinetic energy) incident on the surface along this crystal axis will focus on the core of that atom. Small-impact-parameter encounters of this type are important because they dominate large-angle elastic scattering (or backscattering), and core ionization with its consequences, x-ray and Auger emission. The importance of the present work in this context is that angle-resolved emission data, such as in Fig. 1, provide a direct measure of how the cross section for hitting the core of atoms in a particular layer will vary with incident

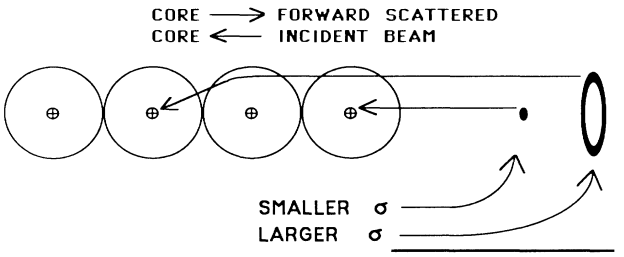

FIG. 4. An illustration of how the data in Fig. 1(b) provide insights, through the reciprocity relation, into the enhanced cross section for hitting the core of a third-layer atom with an incident electron beam.

electron-beam angle. Suggestions that such focusing of incident beams would occur have been made in the past,[12,13] but the present work reveals the depth scale and the angular anisotropy for such processes for the first time and in a readily observable form. For example, the 0-ML and 2-ML Ni cases in Fig. 1(b) show, as illustrated in Fig. 4, how the third-layer atoms have a larger cross section for core impact than surface atoms when a 917-eV electron beam is incident at 45° in the ⟨100⟩ azimuth. Data such as these clearly suggest the prospect for improved depth resolution in x-ray and Auger emission from crystal surfaces by variation of the incident-beam angle.

It is interesting to note in passing that, when an electron beam of a few kiloelectronvolts is incident on a crystal surface along a row of atoms, a maximum occurs in the total yield of elastically backscattered electrons and Auger electrons, and in x-ray emission.[12,14] This is a consequence of incident electrons tending to focus on the core more efficiently at these angles than at random angles before they dissipate their energy on inelastic losses to the valence electrons.

In summary, this work presents, for the first time, experimental data that reveal the layerwise dependence of XPS and Auger diffraction from a crystal. The data demonstrate clearly the level of importance of multiple scattering. Theoretical predictions are confirmed that for electron energies of several hundred electronvolts, multiple scattering defocuses the emission from atoms deeper than about four layers into the surface. Consequently, the observed diffraction features originate predominantly from the top two to four layers. A simple classical description provides much insight into both focusing and defocusing. By the reciprocity relation these data provide a direct measure of the depth scale for focusing incident electron beams on lattice atoms, and these insights can be applied to other types of electron propagation in solids at these energies.

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