Simple X-Ray Standing-Wave Technique and Its Application to the Investigation of the Cu(111) $(\sqrt{3}\times\sqrt{3})R30°$-Cl Structure

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A new variant of the usual x-ray standing-wave experiment, scanning the Bragg reflection in energy at normal incidence, is shown to be applicable to metal crystals without special precautions being taken to ensure high crystalline perfection. The structure of the Cu(111)$(\sqrt{3}\times\sqrt{3})R30°$-Cl chemisorption phase is found to be compatible with the results of a previous surface extended x-ray-absorption fine structure and photoelectron diffraction study.

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There have been several demonstrations recently of the application of x-ray standing waves,[1,2] to the elucidation of surface structural problems.[3-9] In particular, the spacing of an adsorbate layer relative to substrate atom planes can be determined by monitoring the x-ray fluorescence yield from the adsorbate as the crystal is rocked through a Bragg reflection. The width of these Bragg reflections is, however, typically only a few seconds of arc so that the experiment is not only instrumentally demanding but can only be applied to highly perfect crystals, usually of semiconductor materials. This makes the technique very limited in its range of applicability. Here we demonstrate an alternative version of the same experiment applicable to "normal" samples used in many surface-science studies which also uses more widely available instrumentation. Specifically we investigate the structure of the Cu(111)$(\sqrt{3}\times\sqrt{3})R30°$-Cl chemisorption phase.

Our experiment differs from the usual x-ray standing-wave method in two ways; of greatest importance is the fact that the Bragg reflection is studied at normal incidence to the relevant scattering planes [in this case (111)] but in addition the Bragg reflection is scanned in photon energy rather than scattering angle. This photon-energy scan has also been used, as a matter of convenience, in recent synchrotron radiation experiments,[9] but at near-normal incidence it also greatly simplifies the analysis.[10] At normal incidence the Bragg-reflection condition becomes very insensitive to the exact-incidence angle; if we define the incidence angle, θ, relative to the surface normal, the Bragg condition depends on the cosine of this angle and $\cos\theta$ is a very weak function of θ or $\theta \simeq 0°$. Thus the width in angle (rocking curve) is order 1° or in energy order 1 eV. Crystal imperfections leading to mosaicity of a few tenths of a degree therefore have little effect on the line shape, while an energy resolution of order 1 eV is also acceptable. Similarly, convergence or divergence of the incident x-ray beam of a few tenths of a degree is not a problem. It was therefore possible to perform these experiments on a synchrotron radiation beamline on the Synchrotron Radiation Source at Daresbury, England[11] developed for surface extended x-ray-absorption fine structure (SEXAFS) and also used to study the Cl/Cu(111) adsorption system with both SEXAFS and photoelectron diffraction.[12] This beamline uses a double crystal monochromator [in our case Ge(111)] and has a prefocusing mirror with a horizontal acceptance of up to 5 mrad (typically reduced by apertures to reduce aberrations). In fact, the idea of exploiting the standing x-ray wave method at near-normal incidence and using rather soft x-ray energies has been highlighted very recently by Ohta *et al.*,[13] who have provided a preliminary indication of its potential by a study of a clean Si(111) surface.[14] They have stressed its application to semiconductor surfaces, however, and do not appear to have recognized its potential for the study of normal metal crystals which are usually much less perfect.

The Cu(111) crystal was prepared, in the usual way for surface studies, by spark machining, mechanical polishing, and cycles of argon-ion bombardment and annealing in the UHV chamber on the SEXAFS beamline. *In situ* characterization was performed with use of LEED and Auger-electron spectroscopy, and chlorine dosing was performed from an electrochemical source.[15] The x-ray standing-wave experiment was performed by our monitoring the Auger-electron emissions (collected with a cylindrical mirror analyzer) at 2370 and 910 eV associated with ionization of the Cl 1*s* and Cu 2*p* levels. These signals were recorded as the photon energy was scanned through the (111) Bragg reflection which occurs, at normal incidence, at a photon energy of approximately 2975 eV. Similar measurements were also made with the analyzer set to collect electrons of 50-eV higher energy than each Auger peak and these data were used to subtract an inelastic- and secondary-electron background. In previous studies of x-ray standing waves the x-ray absorption profile (usually monitored by fluorescence) has been compared with the x-ray reflectivity profile to establish an exact (relative) angle (or energy) calibration. In our case the absorption in the substrate material, monitored by the Cu Auger feature, provides the reference. Note that the use of a reasonable mean free path for this Auger electron[16] indicates that the contribution from the surface layer is only 16%; as no substantial surface rearrangement is expected for this surface this signal should therefore be rather exactly representative of the bulk. The insensitivity of the measurements to the angular spread of the crystal and x-ray beam at normal incidence is illustrated by the data in Fig. 1. Here the measured Cu 2p Auger yields close to the Bragg peak at incidence angles of 0° (along the surface normal), 10°, and 20° are compared with theoretical line shapes which include Gaussian angular spreads (standard deviations) of 0.01° and 0.1°. At 0° the two theoretical curves are indistinguishable, but the marked broadening and attenuation of the standing-wave profile as the angle is moved away from the surface normal indicates the true angular spread is close to 0.1°. Note that a major theoretical complication for near-normal incidence, that the resonance displacement parameter y is not a linear function of the angular displacement,[10,17] is circumvented in our calculations because y remains linear in the energy displacement. The angular spreads are handled by numerical integration. The theoretical curves also incorporate an incident energy spread, also represented by a Gaussian with a full width at half maximum of 1.7 eV. This Gaussian representation was found to give a much better fit than a Lorentzian and can be attributed to the influence of source size and beam convergence from the focusing optics.[11] Note that the smaller negative excursions in the experimental curves of Fig. 1 relative to the theoretical curves are due to the assumption of perfect coherence of all absorbers and this discrepancy is rectified in the more important comparisons which follow. We attribute this loss of coherence in the near-surface copper, relative to the deeper substrate in which the standing waves are established, to structural damage.

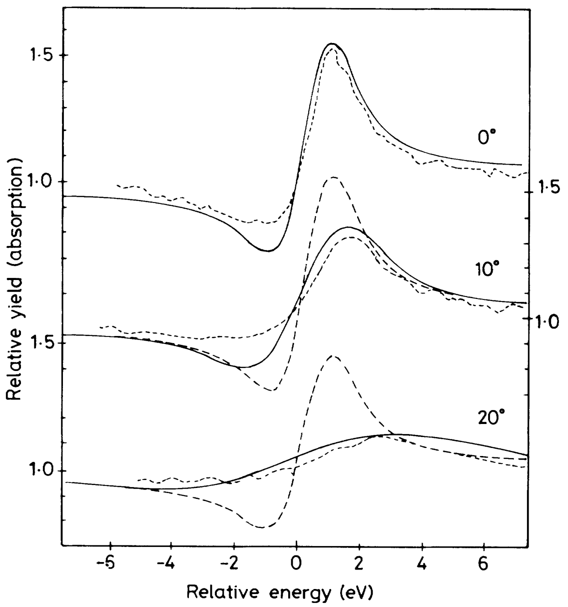

FIG. 1. Relative Cu 2p-derived Auger-electron yield (short dashed lines) from Cu(111) as the photon energy is scanned through the (111) Bragg reflection for incidence angles of 0° (normal incidence), 10°, and 20° compared with theoretical absorption profiles at the atomic planes incorporating random angular standard deviations of 0.01° (long dashed lines) and 0.1° (solid lines). For 0° incidence the two theoretical lines are indistinguishable.

Figure 2 compares the Auger-electron yield profiles obtained at normal incidence from the Cl and Cu absorptions. In this case only 80% of absorbers (both species) are assumed coherent. The clear energy shift and change in line shape are well represented by the theoretical curve based on a Cl layer positioned 1.81 Å above the top layer of an ideal substrate. Comparison with calculations at other spacings (Fig. 2) indicates an error of ±0.05 Å in this value. Reducing the coherent fraction of Cl atoms led to no improvements in the fits and so does not modify this error. Studies of the same adsorption structure (which use the same instrument) by SEXAFS and photoelectron diffraction[12] show that the

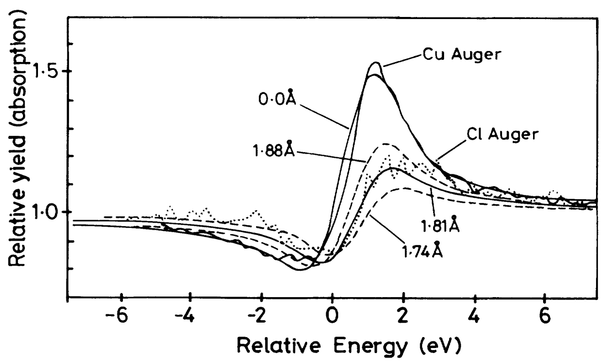

FIG. 2. Relative Cu 2p-derived and Cl 1s-derived Auger-electron yields from Cu(111)$(\sqrt{3}\times\sqrt{3})R30°$-Cl as the photon energy is scanned through the (111) Bragg reflection at normal incidence. Also shown are theoretical absorption curves for absorption on the Cu atom planes and at 1.7, 1.8, and 1.88 Å above the last Cu atom plane of a perfect substrate. In these theoretical curves only 80% of the Cu or Cl absorbers are assumed to be coherently positioned relative to the substrate lattice.

Cl atoms are adsorbed in the "fcc" threefold hollow site with a Cu-Cl top-layer spacing of 1.88 ± 0.03 Å. The standing-wave measurements are therefore generally in agreement with these previous studies. We note, however, that the standing-wave measurements determine the Cl-layer position relative to the continuation of the bulk copper atom planes, while the SEXAFS determines the position relative to the nearest Cu layer. The two results could therefore be taken to indicate that the top substrate layer has a slight contraction in spacing relative to the bulk undistorted crystal. However, this effect lies within the combined uncertainty of the two measurements of ± 0.06 Å. It is interesting to note that there have been suggestions[18] that the top-layer spacing of *clean* Cu(111) may be contracted by as much as 0.08 Å although other studies find no such contraction.[19]

In summary, therefore, we have demonstrated that the x-ray standing-wave technique can be applied to study the structure of adsorbed phases on typical metal single-crystal surfaces as well as highly perfect crystals. Moreover, the experiment can be performed by use of synchrotron radiation-beamline instrumentation developed for SEXAFS, which is therefore designed for high-flux output rather than high resolution and narrow angular spread. The key requirement of these studies is the use of normal incidence relative to the Bragg-reflecting planes (which need not be parallel to the surface plane). It is interesting to note that Bragg-reflection features such as those seen in Figs. 1 and 2 have been seen in SEXAFS spectra previously.[20] Indeed, Ohta *et al.*[13] first observed them in this way but also recognized their potential utility. For the special case of the Cu(111)$(\sqrt{3}\times\sqrt{3})R30°$-Cl structure we also show that the standing x-ray wave data support the conclusions of SEXAFS and photoelectron data on this system; any discrepancy which could be related to a change in the spacing of the Cu(111) surface lies within the combined uncertainty of ± 0.06 Å.

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