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Substrate surface relaxation for Cl and S on Cu(001)

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Using a combination of x-ray standing waves and surface extended x-ray-absorption fine structure, we have determined the interlayer relaxation of a metal surface in the presence of an adsorbate. The Cu(001) surface was studied with Cl $c(2\times2)$ and S $p(2\times2)$ overlayers using a back-reflection diffraction geometry from (111) planes at 2.9 keV. For the Cl-covered surface we find a 0.07 ± 0.04 Å outward relaxation while for the S-covered surface the relaxation is more difficult to determine because of possible substract reconstruction.

One of the more challenging problems in surface physics is the determination of surface relaxation and an understanding of how it depends on submonolayer chemisorption. Studies on this subject have included techniques such as medium-energy ion scattering (MEIS),[1] surface extended x-ray-absorption fine structure (SEXAFS),[2] and angular resolved photoemission fine structure (ARPEFS).[3] Complementary to MEIS, SEXAFS and ARPEFS can offer a straightforward measurement of the relative distance between the two outermost surface planes, provided the data quality allows for a reliable determination of the higher-neighbor shells around the chemisorbed atom. Further requirements for using SEXAFS are high-symmetry chemisorption sites and negligible substrate reconstruction.

In this work, we demonstrate the utility of combining SEXAFS measurements with the x-ray standing-wave method[4] to determine the out-of-plane relaxation of the Cu(001) surface plane in the presence of chemisorbed Cl. For S, the determination is complicated by the possible presence of substrate reconstruction. Although it is widely believed that x-ray standing-wave measurements are applicable only to perfect-crystal substrates, it has been known for some time that at Bragg angles near 90°, Bragg's law is satisfied over a large angular range.[5-8] Therefore, the reflection width at $\theta\approx90^\circ$ can be up to more than an order of magnitude larger than the width under the usual diffraction conditions. The important virtue of this feature is that the width of reflections near 90° is insensitive to certain crystal imperfections such as small-angle mosaic boundaries or dislocations. As pointed out by Woodruff *et al.*,[9] this opens up the applicability of the standing-wave method to a wide variety of crystals, e.g., metals, which are difficult to obtain in perfect-crystal form. The imperfection limits on the usefulness of this method have not yet been established, but we demonstrate here that a promising start has been made in exploiting near-normal reflections for atom location studies. The aim of this work is to show that the x-ray standing-wave method, which measures impurity-atom positions with respect to the bulk crystal planes, combined with SEXAFS, which measures the distance of the absorbate atom from the substrate surface plane, gives a reliable determination of the surface-plane relaxation along a specific crystallographic direction. This information can then be used for determining out-of-plane relaxation and, in principle, in-plane reconstruction.

The experiments were carried out on well-ordered Cu(001)-Cl $c(2\times2)$ and Cu(001)-S $p(2\times2)$, prepared as described elsewhere.[3,10] The standing-wave data were taken at a fixed angle of incidence by scanning the Si(111) double-crystal monochromator of the X-24 National Institute of Science and Technology beam line[11] at National Synchrotron Light Source and measuring (i) the $K\alpha$ fluorescence yield of the adsorbate ($S_{K\alpha}$: 2.307 eV; $Cl_{K\alpha}$: 2.618 eV) as the standing-wave field moves through the adsorbate atom position, (ii) the total electron yield of the sample from the standing-wave field present in the Cu substrate, and (iii) the total electron yield of a 90% transmission mesh (placed in the incident beam at ~40 cm from the sample) as the photon energy was scanned through the Cu(111) back-reflection Bragg condition. The yield from the mesh shows an additional signal from diffracted intensity superimposed on the incident intensity. Since the x-ray standing-wave position must be derived solely from the adsorbate signal, care must be taken to decouple it from any substrate-dependent signal and to obtain the best possible discrimination against background. The adsorbate fluorescence signal was measured with a custom-made ultrahigh-vacuum-compatible soft x-ray proportional counter,[12] placed with its axis along the polarization direction, and operated with an angular acceptance restricted to ±5° to minimize the Compton background to $\leq 1\%$ of the adsorbate fluorescence yield. The signal-to-background ratio obtained with this geometry, ~200%, is illustrated in Fig. 1(a), where the main peak is due to S $K\alpha$ fluorescence. The elastic scattering peak, indicated by the arrow, is seen to be negligible. The choice of monitoring the S $K\alpha$ fluorescence yield, rather than the relatively more intense and surface-sensitive Auger yield, is dictated by the better discrimination with respect to the background substrate signal. This is shown in Fig. 1(b), where the electron energy distribution in the photon range of the Cu(111) standing wave is characterized by a S KLL peak whose intensity is only ~10% relative to the underlying background of the substrate's secondary-electron yield. The small peak to the left of the S $K\alpha$ fluorescence peak [Fig. 1(a)] is due to trace silicon and can be easily removed from the main peak. The bandpass of the X-24 monochromator[11] is substantially narrower than that previously used,[9] with a full width at half maximum value of $\Delta E = 0.7$ eV at the Cu(111) Bragg reflection ($E = 2.978$ eV). The SEXAFS data were taken on the JUMBO monochromator at Stanford Synchrotron Radiation Laboratory, as previously described.[10]

Rotating the (001) surface normal ~54° with respect to the incident beam places the (111) plane at a Bragg angle $\theta \sim 89°$ and allows optimal detection of x-ray fluorescence from the crystal face. Figure 2 shows the reflectivity and S $K\alpha$ fluorescence yield for a (111) reflection from Cu(001)-S $p(2\times2)$. The points represent experimental data and the solid line the theoretical fit. Since the customary approximations in the dynamical theory of x-rays for usual Bragg diffraction conditions are no longer valid for $\theta_B \sim 90°$, we have used an (8×8) matrix formulation,[13] which is a direct solution of Maxwell's equations and is free from assumptions about the shape of the dispersion surfaces. The fluorescence-yield data are fitted to the theory by varying two parameters, P and F. The first (P) represents the atomic position in units of Cu(111) d spacing ($d_{111} = 2.087$ Å), shown in the inset of Fig. 2. The second (F) represents the coherent fraction, which is defined as the fraction of adsorbate atoms at the identical lattice position (P). In our experiments a value of $F = 1$ for the (111) reflection indicates that all the S atoms are in a single-plane position on the Cu(001) surface. The reflectivity curve shown in Fig. 2 has a peak reflectivity of 0.72, compared to the theoretical unconvoluted value of 0.85. The half-width is 1 eV compared to the theoretical unconvoluted width of 0.8 eV for Cu(111) at 2970 keV. The resolution of our monochromator was high enough to observe a small but measurable narrowing of the reflection width, following successive anneals performed during the course of several preparations of the surface. Good fits to the experimental points were obtained with a monochromator Gaussian smearing function (half width at half maximum = 0.7 eV). The data for the bulk Cu-atom position, measured from the total electron-yield signal, are shown as filled squares. They fit well the position for bulk Cu planes and give a coherent fraction within 5% of $F = 1$.

The results for Cu(001)-Cl $c(2\times2)$ are comparable to those in Fig. 2. A coherent fraction $F = 1$ was obtained and indicates that the Cl overlayer is very well ordered and occupies a single-plane position. Fitting the dynamical theory prediction to the total electron-yield spectrum indicates that, as for Cu(001)-S $p(2\times2)$, the Cu atoms occupy bulk sites. This is in agreement with the bulk sensitivity of this method, where the signal originating from many Cu bulk planes dominates the (possibly different) signal from the surface Cu atoms. Extinction effects due

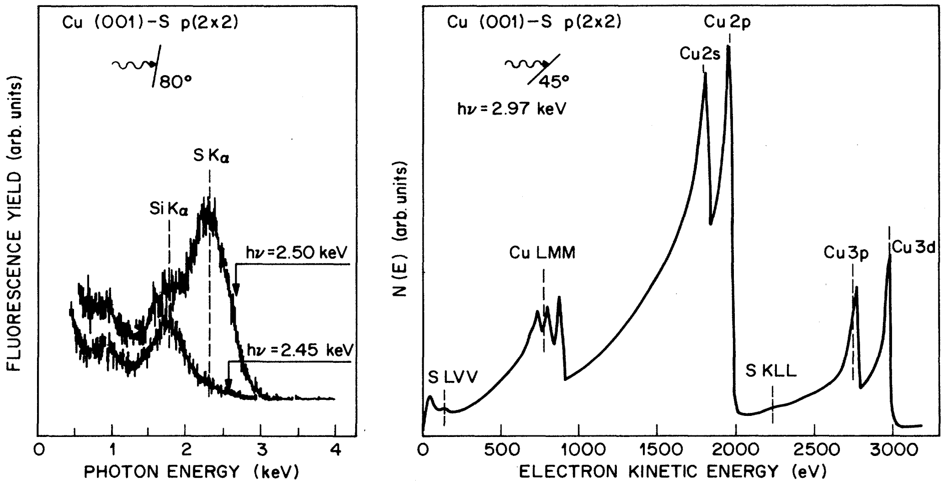

FIG. 1. Comparison of the fluorescence and electron yield for 0.25 ML S on Cu(001). The improved signal to background of the adsorbate fluorescence compared to the electron yield is illustrated.

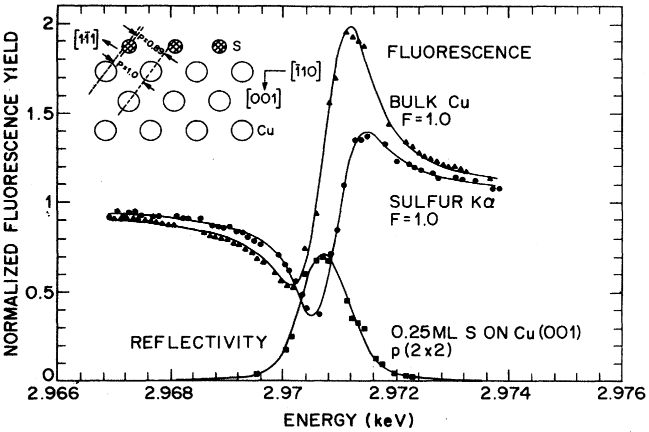

FIG. 2. Fluorescence yield and reflectivity for S on Cu(001) $p(2\times2)$ vs photon energy. Inset shows the sulfur position measured by the fluorescence signal. The bulk Cu standing-wave signal agrees exactly with bulk Cu(111) positions and was obtained using the total electron yield.

to the variation of the x-ray penetration depth in the region of total reflection are also negligible since extinction lengths are an order of magnitude larger than corresponding electron escape depths.

The x-ray standing-wave method measures the position of the impurity atom with respect to the bulk-extrapolated Cu surface plane, which is not the same as the actual crystal surface. SEXAFS, on the other hand, gives direct information on the local environment of the surface impurity atom. A high degree of accuracy with the latter technique is now routine, particularly for nearest-neighbor distances.[2,14] A reliable measure of the surface-plane relaxation can thus be obtained by considering the impurity distance from the surface plane derived from SEXAFS and comparing it to the x-ray standing-wave results. Any mismatch between the two measurements may then be ascribed to a relaxation of the surface atomic plane from its bulk-extrapolated position.

From previous SEXAFS work on Cu(001)-Cl $c(2\times2)$, it is known that Cl occupies fourfold hollow sites with first-neighbor bond lengths of 2.37 ± 0.02.[2,10] Since no lateral displacement of surface Cu atoms is expected, based on simple symmetry arguments, the vertical distance of Cl above the Cu surface can be calculated to be 1.53 ± 0.02 Å; see Fig. 3. Analysis of the x-ray standing-wave results give $P=0.94\pm0.02$, which, combined with the known site location, implies that the Cl atoms are vertically displaced 1.60 ± 0.04 Å relative to the bulk Cu plane; see Fig. 3. Comparison of these two different vertical distances shows that there is a net outward shift of the surface Cu plane by 0.07 ± 0.04 Å. This relaxation value can be compared to a SEXAFS measurement of the second-neighbor distance between Cl and the Cu atom directly below it in the second Cu plane, which gives a value of 3.43 ± 0.02 Å.[2] Assuming no relaxation of the second Cu plane, this implies a distance between the two outermost Cu planes of 1.90 ± 0.02 Å, or 0.09 ± 0.02 Å larger than the bulk value. This result, which is similar to that obtained from x-ray standing waves, leads us to conclude that Cl on Cu(001) induces a net outward expansion of the first surface Cu plane by 0.07–0.09 Å.

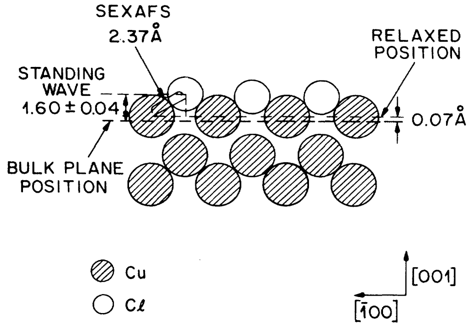

FIG. 3. Schematic of the [$\bar{1}$00] projection of the (001) planes for Cu, showing the Cl-Cu distance measured with x-ray standing waves and with SEXAFS. The corresponding upward relaxation of the surface Cu plane, obtained from the two measurements is shown as 0.07 Å.

For Cu(001)-S $p(2\times2)$, SEXAFS measurements indicate that the S atoms also occupy fourfold hollow sites with first-neighbor distances of 2.31 ± 0.02 Å.[10] The assumption of no reconstruction of the surface Cu atoms, which for this unsaturated coverage no longer follows from symmetry arguments, but if this assumption is made the vertical distance of S from the Cu surface is calculated to be 1.44 ± 0.02 Å. The standing-wave method yields a value of 1.40 ± 0.04 Å. This result suggests an inward relaxation of 0.04 Å of the first Cu plane. The relatively large error bar on the standing-wave result, however, precludes a definitive conclusion regarding the net surface-plane relaxation. A SEXAFS measurement of the S-Cu second-shell distance of 3.28 ± 0.02 Å, along with the assumption of no second-plane Cu motion, gives a net outward relaxation of 0.03 Å, which is within the error of the standing-wave measurement. The significance of this result is difficult to evaluate in view of the very different values reported previously which either assume or ignore reconstruction. In particular, ARPEFS data analyzed without[3] and with[15] reconstruction report S distances from the surface Cu planes of 1.39 Å and 1.42 Å, respectively. LEED data analyzed without[16] and with[17] reconstruction (of a sense opposite to that in Ref. 15) report corresponding values of 1.32 Å and 1.29 Å, respectively. Clearly, further study of this system is required.

In conclusion, a method for determining adsorbate-induced metal surface relaxation has been described which combines the techniques of x-ray standing waves and SEXAFS. An outward relaxation of the Cu(001) surface in the presence of a Cl $c(2\times2)$ overlayer has been observed whereas the same substrate in the presence of a S $p(2\times2)$ overlayer shows a smaller effect that may be influenced by absorbate induced reconstruction. A number of experimental and analytical improvements have been made over earlier work,[9] specifically, the measurement of the Bragg reflected intensity, theoretical treatment of the data, monochromator resolution, and fluorescence detection of the x-ray standing-wave signal. The uncertainty of the combined measurements has, accord-

ingly, been reduced considerably. Further refinements are still possible, suggesting that the use of x-ray standing waves in the back-reflected geometry may have more widespread applicability for determining adsorbate-induced substrate relaxation.

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