Surface Structure from Angle-Resolved Secondary-Ion Mass Spectrometry: Oxygen on Cu(001)

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Measured angular distributions for O^- and Cu^+ ejected by 1500-eV Ar^+-ion bombardment of chemisorbed oxygen on Cu(001) exhibit anisotropies which vary by greater than a factor of 2. Molecular-dynamics calculations of the ion-impact event agree well with experiment if the oxygen atom is placed in a fourfold coordination site 1.2–1.5 Å above the Cu(001) plane. Angle-resolved secondary-ion mass spectrometry is proposed as a powerful new method for the determination of adsorbate positions.

An analysis of the angular distributions of particles ejected from ion-bombarded single crystals has been predicted to be a sensitive measure of the registry of the surface layer. Specifically, molecular-dynamics calculations have shown that those for the model system of $c(2\times 2)$O on Cu(001) that ejected Cu and O atoms should exhibit intensity variations which are uniquely ascribable to a particular bonding site of the O atom.[1] The anisotropies associated with these distributions can be maximized by appropriate selection of polar angle and kinetic energy of the ejected particle. For example, the ejected particles with kinetic energy greater than 10 eV are particularly well channeled by the surface since they are ejected soon after the primary-ion impact and before the surface order is significantly disrupted.

An experimental test of this idea is most easily accomplished by a detection scheme sensitive to the ejected ions, Cu^+ or O^-. The trajectories of these species should be nearly identical to the neutral atoms since, for a 20-eV particle, the image force will increase the polar deflection angle by less than 2°.[1] In this work, then, we present the first angle-resolved secondary-ion mass-spectrometric (SIMS) measurements on a well-defined substrate obtained under low-dose bombardment (static) conditions. The experimental results for O^- and Cu^+ ejection agree well with quantitative calculations using the molecular-dynamics procedure for O placed in the fourfold hole of the Cu(001) surface.[1,2]

The angle-resolved SIMS experiments were performed with use of a previously described apparatus.[3] Angle selection was accomplished by placing a cylindrical shield around the Cu(001) crystal as shown schematically in Fig. 1(a). The polar angle, θ, for ejected species was fixed at 45° with two appropriately placed apertures while the azimuthal angle, φ, was varied over 360° by rotation of the crystal. These angles are defined in the illustration in Fig. 1(b). The Ar^+-ion beam always struck the crystal at normal incidence. From an analysis of the geometry of the shield and the size of the apertures, we estimate that the angular resolution is ~8°–10°. The energy selector for the ejected ions is a 45° electrostatic sector[3] with a bandpass of ~± 20 eV at the approximate pass energy of 30 eV utilized in these experiments. The kinetic energy of the Ar^+ beam was held to between 900 and 1500 eV while the total dose of ions was kept below 10^{13} ions/cm^2 to avoid significantly altering the surface structure.[4] The crystal was cut and polished to within 1° of the (001) face, etched and cleaned *in situ* by cy-

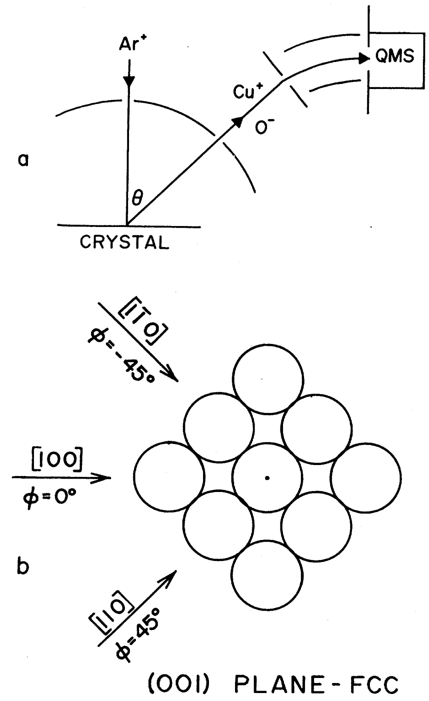

FIG. 1. (a) Schematic representation of the angle-resolved SIMS experiment. (b) The azimuthal angle, φ, defined for the (001) plane.

cles of ion bombardment, exposure to O_2 at 200°C, reduction in H_2 at 150°C, and annealing at 800°C. The cleanliness of the surface was verified by the lack of C^- and O^- peaks in the SIMS spectrum. The oxygen overlayer was prepared by exposure to 1200 L (1 L = 10^{-6} Torr sec) of O_2 at 25°C.[5] Low-energy electron diffraction (LEED) has shown that this procedure results in a $c(2\times 2)$ structure on the Cu(001) surface.[6]

The observed azimuthal plots for Cu^+ and O^- ejection from these samples are shown in Fig. 2(a). The fourfold symmetry of the (001) orientation is clearly evident for both species. The Cu^+ intensity is maximized at $\varphi = 0°$, 90°, 180°, and 270°, while the 0^- maxima are shifted by 45°, occurring at $\varphi = 45°$, 135°, 225°, and 315°. Note that the observed anisotropy is quite large, changing by more than a factor of 2 between minimum and maximum values. The measurement required ~ 160 sec for each azimuthal plot and a total of 10^{13} Ar^+ ions/cm^2. The signal intensities are clearly sufficient to demonstrate this anisotropy and to provide data of sufficient quality for comparison to the calculations.

The calculated azimuthal plot for oxygen adsorbed in a fourfold bridge configuration is indicated by the dotted line in Fig. 2(b) and was determined with use of our previously described molecular-dynamics treatment.[1,2] The potential parameters used in the calculations are the same as those reported previously except for the Cu-O pair potential which is adjusted so that the oxygen position is at the minimum of the interaction. The calculated curves are remarkably close to the experimentally obtained data shown in Fig. 2(a) except for the fact that the predicted anisotropy is somewhat larger than the measured anisotropy. The reasons for this deviation are unclear at the moment, but could arise from crystal imperfections. Following the procedure used in angle-resolved photoemission studies[5,7] we have subtracted the minimum intensity and have employed fourfold averaging as $I = I(\varphi) + I(\varphi + 90°) + I(\varphi + 180°) + I(\varphi + 270°)$. The resulting data are also plotted in Fig. 2(b) where the shape of the anisotropy is compared to the calculated values. The only deviation in the two sets of curves is that the experimental peaks are about 5°–10° wider than the calculated peaks.

Of particular note is that other possible adsorbate geometries produce calculated angular distributions vastly different than those shown in Fig. 2. For example, our calculations for O-atom ejection show that only the fourfold bridge position yields a sharply peaked maximum intensity shifted 45° from the substrate Cu atom.[1] In Fig. 3, the vertical or z position of the adsorbate is varied while keeping its x-y location over the fourfold hole constant. All the different O-atom placements are easily distinguishable.

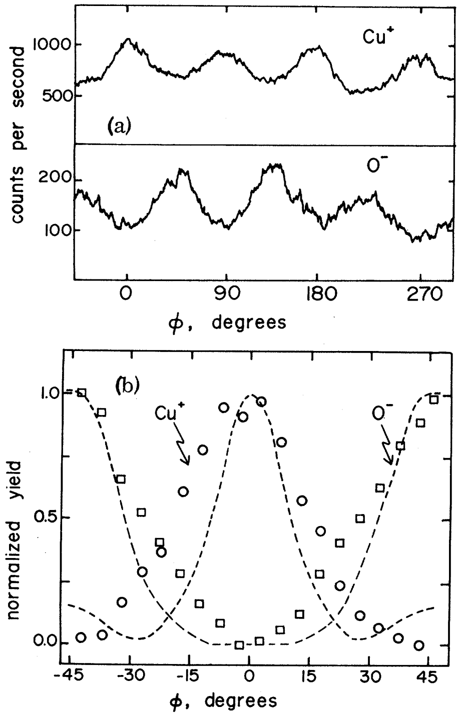

FIG. 2. (a) The Cu^+ and O^- azimuthal plots as recorded from the spectrometer. (b) A fourfold average of the data in (a) with the minimum intensity subtracted from each curve. The dashed lines represent the calculated curve for O placed in a fourfold hole 1.2 Å above the Cu plane. The circles represent the Cu^+ intensities and the squares represent the O^- intensities. The primary ion is 1500 eV Ar^+ at a total dose of 10^{13} ions/cm^2.

These calculations were performed for $c(2\times 2)$O using Ar^+ at 600 eV as the primary ion since prohibitively large model microcrystallites are required for higher-energy projectiles. However, preliminary experiments and calculations[8] performed with projectiles up to 2000 eV indicate that the shapes of these curves do not change significantly with primary-ion kinetic energy. In addition, calculations performed for a $p(2\times 2)$ overlayer and for a full monolayer coverage of O yield similar azimuthal plots. The calculations for the ejected Cu angular distributions predict results which are rather insensitive to the O-atom placement. The Cu azimuthal plots all maximize at $\varphi = 0°$ (for $\theta = 45°$) although the width of the peak

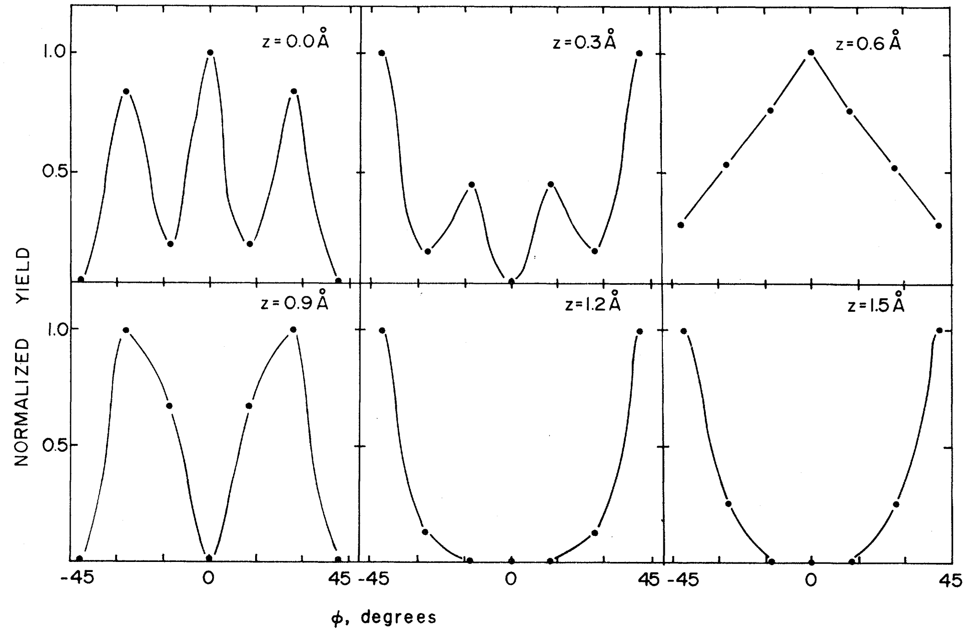

FIG. 3. Calculated azimuthal plots for different z values when oxygen is placed in the fourfold bridge configuration. All calculations are performed for 600-eV Ar^+ at normal incidence with oxygen in a $c(2\times2)$ coverage. Only those oxygen particles with kinetic energy between 10 and 50 eV and polar deflection angles of 45° ± 5° have been counted. The yields are normalized to the most intense peak for each curve. Note that if higher angular resolution could be obtained and more trajectories were computed, additional structure in these curves would probably appear. Since the calculated resolution matches our best estimate of the experimental resolution, their presence or absence would not affect the conclusions of this work.

may change by as much as 10°–20°.

At their current state, angle-resolved SIMS measurements provide results which contrast structure determinations deduced from azimuthal plots obtained by photoemission from the O 1s core level.[5] Although both techniques predict that the O atom resides in a fourfold coordination site, the photoemission results suggest that it lies in the plane of the Cu layer with $z = 0.00$ Å. From the calculations of Fig. 3 and the measurements shown in Fig. 2(b), it is not currently possible to fit our results to this atomic position. The z values between 1.2 and 1.5 Å are clearly in best agreement with experiment. To be sure of the precise atomic position and to be sure that a reneutralization of the ejected ion does not influence the results, however, SIMS measurements at other polar angles with better angular resolution would be desirable. For example, a z value of 0.3 Å is reasonably close to the experimental results, although it might be ruled out by examination of azimuthal plots at different polar angles. The calculations also suggest that similar considerations could be used to distinguish the structures with $z = 1.2$ Å and $z = 1.5$ Å. All of these variables should be easily reconcilable into a single structure.

The strong calculated variations of yield versus angle as the z value changes allow ultimate sensitivity to determination of atomic positions. The reasons for the variations are extractable from the dynamics, but represent a convolution of many different mechanisms. As the oxygen atom is lowered into the hollow site, for example, it can experience strong scattering from the surrounding Cu atoms. The scattering direction is clearly determined by the initial position of the oxygen atom. In any case, the plots do not arise as a matter of chance.

This approach provides a complementary tool to others currently available for the determination of adsorbate structures. For example, the registry problem is quite complicated to solve using LEED since the z value for the adsorbate must first be determined. From Fig. 2(a) and 3(a), it is clear that angle-resolved SIMS provides a simple, unequivocal answer to this question since the relative position of the substrate with respect to the adsorbate controls the ejection direction. In addition, the calculated angular distributions are rather insensitive to the exact form of the scattering potential, but very sensitive to the relative placement of the atoms. For those techniques involving electron scattering, however, a reasonably accurate electronic potential surface is required for the calculation.

In conclusion, angle-resolved SIMS has been shown to be readily applicable to the determination of the registry of chemisorbed oxygen on Cu(001) as being over the fourfold coordination site. More detailed analyses suggest that the z position is 1.2–1.5 Å above the Cu(001) plane. The generalization of this scheme to other atomic adsorbate-substrate systems, including those involving hydrogen, appears to be limited only by the sensitivity of the SIMS technique. The most sensitive adsorbates would be those involving highly electronegative (O^-, F^-, Cl^-) or electropositive (H^+, Na^+, K^+, Li^+) species. The scheme should also be amenable to the analysis of some molecular adsorbate geometries. Even when the recombination mechanism for cluster formation is dominant,[2] our calculations show that the anisotropy is still significant.[8]

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