Normal photoelectron diffraction of O/Cu(001): A surface-structural determination

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The two systems $c(2\times2)$O/Cu(001) and $(\sqrt{2}\times2\sqrt{2})R45°$ O/Cu(001) have been studied by normal photoelectron diffraction (NPD), with the use of O(1*s*) line. In the $c(2\times2)$ structure oxygen occupies the fourfold hollow site, with $d_\perp=0.80(5)$ Å. The $\sqrt{2}\times2\sqrt{2}$ structure has a similar NPD curve, indicating the same local site geometry for the $c(2\times2)$ sublattice.

Oxygen adsorbs on Cu(001) with difficulty, producing a $c(2\times2)$ structure at low exposures and a $(\sqrt{2}\times2\sqrt{2})R45°$ structure at higher exposures [Fig. 1(b)]. Recent studies of the $c(2\times2)$ structure by azimuthal photoelectron diffraction,[1] angle-resolved secondary-ion mass spectroscopy,[2] and low-energy ion scattering plus low-energy electron diffraction (LEED),[3] have yielded conflicting results: hollow site [$d_\perp=0.0(1)$ Å $=0.0\pm0.1$ Å], hollow site [$d_\perp=1.2$–1.5 Å], and bridge site ($d_\perp=1.4$ Å), respectively. In this Communication we report oxygen (1*s*) normal photoelectron diffraction (NPD) studies[4] on both structures that rule out all the above geometries for the $c(2\times2)$ structure.

Two of the above experiments[1,2] did not employ *in situ* LEED analysis, which creates ambiguities because of the propensity of the $c(2\times2)$ structure to develop additional $(\sqrt{2}\times2\sqrt{2})R45°$ spots. In our experiments, extremely weak $(\sqrt{2}\times2\sqrt{2})R45°$ spots were observed after the completion of NPD data collection on each of our $c(2\times2)$O/Cu(001) samples, 30–70 h after sample preparation. This sample evolution was contrary to our experience with all other samples studied with NPD.[4] This led us to perform NPD measurements on deliberately prepared $(\sqrt{2}\times2\sqrt{2})R45°$ O/Cu(001) samples. Beam dosing exposures of 400 L (1 L $=10^{-6}$ Torr sec) were used to obtain the $c(2\times2)$ structure and 4000 L for the $(\sqrt{2}\times2\sqrt{2})R45°$ structure, each being followed by annealing to 375 K for 4 min.

These experiments were performed at the Stanford Synchrotron Radiation Laboratory on beam line I-1 using an apparatus described elsewhere.[5] Auger spectroscopy, photoemission, and LEED were used to check surface cleanliness and ordering. Any S and O impurities were below detectable levels and C-Cu Auger intensity ratios were less than 0.005. The purity of the oxygen exposures was monitored by a residual gas analyzer. Excellent internal agreement was

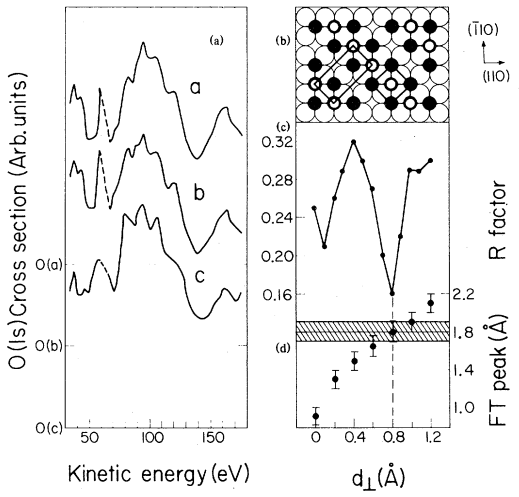

FIG. 1. (a) Experimental O(1*s*) cross-section measurements: curve *a*, $c(2\times2)$O/Cu(001) in which the photon intensity normalization is made using the I_0 measurement from a gold grid-channeltron assembly; curve *b*, same as curve *a* but with an internal photon intensity measurement made by sampling electrons at a kinetic energy above the O(1*s*) peak; curve *c*, $(\sqrt{2}\times2\sqrt{2})R45°$ O/Cu(001), with normalization done as in curve *b*. The dashed sections are interpolated values. The photoemission peaks at 61 and 64 eV were obfuscated by the Cu *MVV* Auger line. (b) Model of the Cu(001) surface (light circles) with the $c(2\times2)$ oxygens in the fourfold hollows (filled circles) and the additional $(\sqrt{2}\times2\sqrt{2})$ oxygens also in the hollows (dark circles). Note the differences in the unit cells. Only one of two orthogonal domains is shown for the $(\sqrt{2}\times2\sqrt{2})$ structure. (c) *R* factors (R_N) of the hollow site, normalized to the Zanazzi-Jona *R* factor, showing a relative minimum at 0.1 Å and an absolute minimum at 0.8 Å ($V_0=10$ eV). (d) The position of the theory Fourier-transform (FT) peak, plotted against $d_\perp$, using no scattering-atom phase shifts. The experimental FT peak position is 1.8(1) Å: The theoretical FT peak has this value for $d_\perp=0.8(2)$ Å, in agreement with the position of the absolute minimum in (c).

obtained among two NPD curves from two $c(2\times2)$ samples and three NPD curves on two $\sqrt{2}\times2\sqrt{2}$ samples.

The three NPD curves in Fig. 1(a) show normalized O(1s) peak intensities plotted against kinetic energy. Curves a and b represent the same data for $c(2\times2)$O/Cu(001), normalized to photon intensities in two different ways. In the conventional *external* method (curve a), the relative photon intensity is determined by a gold grid-channeltron assembly.[4] A preferred new *internal* method (curve b) was developed that employs the background electron intensity at a kinetic energy above the O(1s) peak, normalized to secondary electron cross sections.[6] The latter method is preferred because the photon intensity and cross-section measurements are made simultaneously by the same detector observing a single section of the photon beam. The two curves show very good agreement. Curve c, for the sample $(\sqrt{2}\times2\sqrt{2})R45°$ O/Cu(001), is based on the internal method.

The $c(2\times2)$ curves were compared with theoretical results[7,8] in three ways. The first and most orthodox comparison with theory consists of matching theoretical and experimental curves, with special attention to peak positions. This was done exhaustively, with the use of theory curves computed for a wide range of possible structures, including the coplanar hollow geometry. Particular emphasis was placed upon the results of the previous experiments.[1–3] With the exception of the hollow site, $d_\perp=0.8$-Å case, no other structure gave an NPD curve in even remotely acceptable agreement with experiment. The curve for the adopted structure shows excellent agreement for every peak position, even at the highest and lowest energies (Fig. 2, curves a and b), with the exception of the features near 75 eV. A detailed comparison of experimental peak positions with theoretical curves was made at closely spaced $d_\perp$ intervals around 0.8 Å. This yielded consistent results for all features, with the conclusion that $d_\perp=0.80(5)$ Å. This $d_\perp$ corresponds to a Cu-O distance of 1.97(3) Å, in good agreement with the bond length of 1.95 Å in CuO. This binding site and bond distance match closely with that for $c(2\times2)$O/Ni(001): hollow, 1.95(2) Å (Ref. 9) and 1.96(3) Å (Ref. 10).

The short range of the data set precludes a quantitative analysis from a Fourier transform (FT)[4,11] solely of the experimental data. Nevertheless, the FT, over this same energy range, of theoretical curves for a series of $d_\perp$ values, yields a single strong peak at a position that varies monotonically with $d_\perp$. When this peak position is treated semiempirically, the FT can be regarded as a compact parametrization of the NPD curve and compared to the experimental FT curve. This approach yields $d_\perp=0.8(2)$ Å [Fig. 1(d)] in agreement with the above result.

As a check of the objectivity of our comparisons, an R factor[9,12] analysis, normalized to the Zanazzi-Jona R factor,[13] was performed. The absolute minimum at $d_\perp=0.8$ Å ($R_N=0.16$) and a sharp relative minimum at $d_\perp=0.1$ Å ($R_N=0.21$) were observed in the hollow site geometry. For the bridge site, a broad relative minimum between $d_\perp=1.5$ Å ($R_N=0.23$) and $d_\perp=1.4$ Å ($R_N=0.24$) was present: Owing to the similarity of these two curves and the previous result,[3] the 1.4-Å curve will be used for comparison with experiment. The sensitivity of the method is borne out by the tremendous difference in the quality of the fits, as is shown in Fig. 2, curves a–d. The only suitable match is for the 0.8-Å hollow site, which is also the only curve with R_N less than 0.20, the value proposed by Zanazzi and Jona as an upper limit on a good fit. This is evidence to support the emphasis placed upon this value and suggests that it may be the method of choice for such comparisons.

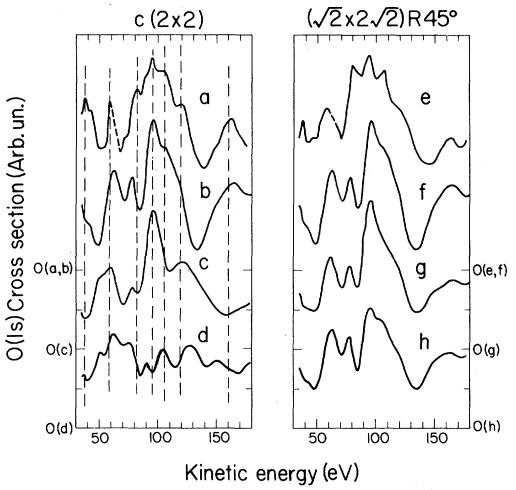

FIG. 2. NPD experiment and theory for $c(2\times2)$O/Cu(001); Curve a, experiment, same as Fig. 1, curve a; curve b, theory, $d_\perp=0.8$ Å, hollow, $R_N=0.16$; curve c, theory, $d_\perp=0.1$ Å, hollow, $R_N=0.21$; curve d, theory, $d_\perp=1.4$ Å, bridge, $R_N=0.24$. $V_0=10$ eV. NPD experiment and theory for $(\sqrt{2}\times2\sqrt{2})R45°$ O/Cu(001): Curve e, experiment, same as Fig. 1, curve c; curve f, theory, $d_\perp=0.8$ Å, hollow for $c(2\times2)$, $R_N=0.17$; curve g, theory, $1{:}\frac{1}{2}$ weighted sum of 0.8-Å hollow and 0.1-Å hollow, $c(2\times2)$ calculations, $R_N=0.18$; curve h, theory, $1{:}\frac{1}{2}$ weighted sum of 0.8-Å hollow and 1.4-Å bridge, $c(2\times2)$ calculations, $R_N=0.15$. $V_0=10$ eV.

The hollow site R factors are depicted in Fig. 1(c). The raw R-factor values were stable against variations in the inner potential (V_0) over the range of $V_0=8$ to 13 eV. The slope of the R factors near the absolute minimum, as well as the R factor values at 0.7 and 0.9 Å, permits an error estimate of $d_\perp=0.80(5)$ Å.

Addition of more oxygen to convert the $c(2\times2)$

structure to the $\sqrt{2}\times 2\sqrt{2}$ structure added the expected new spots to the LEED pattern while sharpening those of the $c(2\times 2)$ sublattice. The NPD curve showed little change, except at the lowest kinetic energies. It is therefore likely that the $\sqrt{2}\times 2\sqrt{2}$ structure is formed by adding something less than 50% more oxygen to the $c(2\times 2)$ lattice without otherwise substantially changing it. Figure 1(b) represents one of two orthogonal domains that can be formed in this way. Steric effects would appear to preclude any but the empty fourfold hollow sites for the new oxygen atoms. Electrostatic repulsion would hinder an arrangement with all of the oxygens in the same plane above the surface. Perhaps the new oxygens occupy positions at lower $d_\perp$ values, and the $\sqrt{2}\times 2\sqrt{2}$ structure represents the initiation of the nucleation involved in surface oxidation. This might explain the low $d_\perp$ value found by Kono *et al.*,[1] particularly in light of the special sensitivity of azimuthal photoelectron diffraction to near coplanar species.[14]

Because local scattering effects dominate in NPD, we attempted to simulate the $\sqrt{2}\times 2\sqrt{2}$ experimental curve by adding to the $c(2\times 2)$ hollow, $d_\perp = 0.8$-Å curve (taken to represent the "old" oxygens) various other $c(2\times 2)$ theoretical curves (for the "new" oxygens) with relative weights 2:1. Two such composite curves are depicted in Fig. 2, for the 0.1-Å hollow site and the 1.4-Å bridge site. The first composite curve shows about the same agreement as the 0.8-Å curve and the second improves slightly, but because of the overall similarity of the four curves (Fig. 2, curves *e*–*h*) and the foregoing discussion, our only firm conclusion about the $\sqrt{2}\times 2\sqrt{2}$ structure is that it is *dominated by the* $c(2\times 2)$ *sublattice,* in the hollow site, $d_\perp = 0.8$-Å geometry.

Bauschlicher *et al.*[15] recently completed a self-consistent-field calculation of the interplanar spacing in a Cu_5O model cluster, with the result of $d_\perp = 0.9$-Å, hollow. Moreover, they argue that $d_\perp = 0.8$ Å is the optimum prediction.

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