Adsorption Sites of Oxygen on Cu(001) and Ni(001) Determined from the Shape of the Low-Energy Electron-Diffraction Spots

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The low-energy electron-diffraction patterns of the oxygen structures on the (001) pole of spherical Cu and Ni surfaces show characteristic differences: For Cu the $(\frac{1}{2}\frac{1}{2})$ and the (10) spots are elongated along $\langle 11 \rangle$, while only the half-order spots are broadened for Ni. These unusual spot profiles are caused by antiphase scattering from neighboring domains, with the oxygen in the bridge position for Cu and in the fourfold hollow site for Ni.

The registry of adsorbed atoms with respect to a single-crystal substrate has often been a controversial subject in surface physics. A case in point is the $c(2\times2)$ structure formed by oxygen adsorption on both Cu(001) and Ni(001). In the case of Cu, the comparison of the measured and calculated low-energy electron-diffraction (LEED) intensities favors the bridge position,[1] while a recent normal photoelectron diffraction study (NPD)[2] claims that "the only suitable match is for the 0.8-Å hollow site" position. The more universally accepted fourfold hollow site position in the case of Ni has been most recently called into question by evidence for "pseudo-bridge" bonding, derived again from the comparison of measured and dynamically calculated LEED intensities.[3]

In this paper we analyze the shape of the LEED spots which show characteristic differences for the two cases, as seen in Figs. 1 and 2. The surfaces of the samples were prepared by elec-tropolishing, with the final cleaning done in the usual way by repeated cycles of argon-ion bombardment and annealing in the LEED chamber capable of a base pressure of 2×10^{-10} Torr. The elongation, broadening, or splitting of certain LEED spots is caused either by antiphase scattering from atomic steps on surfaces misaligned with respect to the vicinal high-symmetry plane,[4] or by antiphase domains of an adsorbate, with the adsorption site determining for which spot this antiphase scattering occurs.[5,6] We avoid atomic steps in our experiments by using spherical surfaces ($r = 61.5$ mm) containing the (001) pole. The electron beam is adjusted onto the (001) pole by shifting the sample at right angles to the beam until a perfect fourfold rotational symmetry of the LEED pattern is observed. Any remaining elongation or broadening of the LEED spots must then be caused by antiphase domains
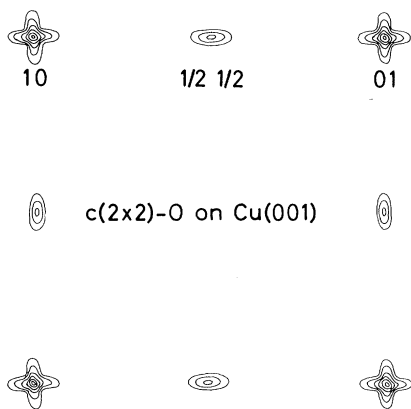

FIG. 1. The LEED pattern of Cu(001) at 61.3 eV, with the sample exposed to 1.2×10^{-3} Torr sec oxygen at 300 K. The solid lines roughly indicate contours of equal intensity.
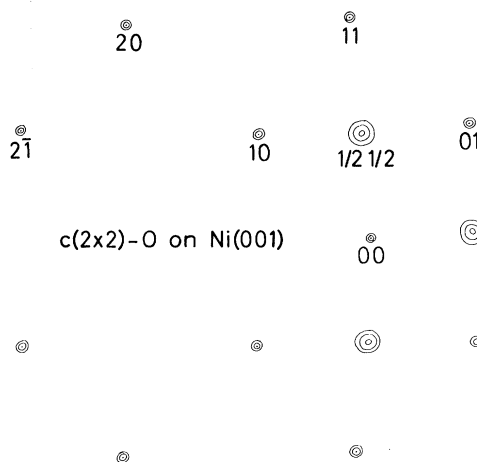

FIG. 2. The LEED pattern of Ni(001) at 129.8 eV, with the sample exposed to 3×10^{-5} Torr sec oxygen at 300 K. The solid lines again roughly indicate contours of equal intensity.

of the adsorbate only.

The essentials of this effect are most easily appreciated by considering a periodic arrangement of domains in *one* dimension which produce antiphase scattering for the first-order spot. This means that the scattering amplitude of the adsorbate is zero for the momentum transfer $\Delta k = G_1 = 2\pi/a$ but has extremal values ($\gtrless 0$) for $\Delta k = G_1 \pm \pi/d$, where d is the size of one domain and a is the lattice constant of the substrate surface. The first-order spot is thus transformed into a doublet, with its components separated by $2\pi/d$. A statistical variation in the size of the domains will result in an elongation of the spot, corresponding to a superposition of doublets with various splittings. The *total* scattering amplitude is of course nonzero for $\Delta k = G_1$ since it contains the in-phase contributions of the substrate. In *two* dimensions, an antiphase spot will be broadened uniformly if the domain boundaries have no preferred directions or show elongations perpendicular to domain boundaries running parallel to some specific directions. Antiphase and in-phase scattering for the spot (hk) will occur whenever $\vec{G}_{hk} \cdot \vec{I}$ is an odd or even multiple of π, respectively, where $\vec{I}$ connects two representative adsorption sites across the domain boundary considered, with the sharpness of an in-phase spot limited by the LEED system only. We emphasize that the above considerations remain valid if multiple scattering is included since it affects only the intensity but not the geometry of the LEED pattern.

As pointed out by Park,[6] a broadening of both the $(\frac{1}{2}\frac{1}{2})$ and the (10) spots is compatible with an adsorption site of twofold symmetry only. The LEED pattern observed for $c(2\times2)$– O on Cu(001) (Fig. 1) thus definitely establishes the bridge position as the adsorption site in this case. At lower coverages (e.g., 10^{-4} Torr sec at 100 C) similar but weaker adsorbate-induced features are observed. In addition, the spots are not uniformly broadened but show elongations perpendicular to the $\langle11\rangle$ directions. This means that $\langle11\rangle$ domain boundaries dominate, probably because the oxygen atoms in mutually perpendicular bridge positions can arrange themselves along $\langle11\rangle$ in such a way that their surface concentration is continuous across such a boundary, while they are either too close or too far apart for $\langle01\rangle$ boundaries. For example, the boundaries $[11]$ and $[1\bar{1}]$ with $\vec{I} = a(\frac{3}{2}, \mp \frac{1}{2})$, respectively, give $\vec{G}_{1/2\,1/2} \cdot \vec{I} = \pi$ for the $[11]$ boundary but 2π for $[1\bar{1}]$. This explains why the $(\frac{1}{2}\frac{1}{2})$ spot is elon-

gated perpendicular to $[11]$. On the other hand, the (10) spot suffers antiphase scattering for both the $[11]$ and the $[1\bar{1}]$ boundary, which gives rise to the crosswise elongations observed for this spot (Fig. 1).

As mentioned above, the bridge position is also favored as the adsorption site for $c(2\times2)$–O on Cu(001) by the LEED intensity investigations of Onuferko and Woodruff (OW).[1] As additional evidence, OW cite a LEED pattern somewhat similar to Fig. 1, showing also elongations of both the $(\frac{1}{2}\frac{1}{2})$ and the (10) spots, but with the elongations parallel to one of the $\langle11\rangle$ directions only, i.e., with some deviation from the fourfold symmetry expected for the (001) surface. This indicates some misalignment of the sample surface and thus the presence of steps which in turn can give rise to a preferred direction of the domain boundaries and even faceting in the presence of oxygen.[7] These complications in the interpretation of the LEED pattern might have been the reason why OW did not base any firm conclusions on their observation.

OW also point out that the fourfold symmetry observed in the angular dependence of x-ray photoemission (XPS) for oxygen adsorbed on Cu(001)[8] might be caused by the presence of the rectangular $(\sqrt{2}\times2\sqrt{2})$–45° structure which readily develops for higher coverages, higher temperatures,[1,2] and in particular for slightly misaligned surfaces, i.e., with the electron beam slightly off the (001) pole. In order to explain the XPS results and the initial increase and subsequent decrease of the work function of Cu(001) with oxygen coverage,[9] OW propose a unit cell for the rectangular structure containing one oxygen in the bridge position and two oxygens in fourfold hollow site positions essentially coplanar with the first Cu layer. It seems likely that the NPD results refer also to a mixture of the square and the rectangular structures, in particular since the sample had been heated after oxygen adsorption. In fact, the NPD spectra measured for the samples with the "square" and the "rectangular" structure show little difference, and the best fit between experiment and theory is obtained if a weighted average of the fourfold hollow site and the bridge position is used (curves e and h of Fig. 2 in Ref. 2, $R_N = 0.15$). This also favors the OW model of the rectangular structure, as does our observation that the spot elongations for this structure are qualitatively similar to that of the $c(2\times2)$ structure.

For Ni(001)-O as specified in Fig. 2, the in-

tegral-order spots are as sharp as the zero-order spot at all energies, while a uniform broadening of the half-order spots is seen whenever these spots are observable, indicating a random orientation of the domain boundaries. We determine the spot size photoelectrically as the width of the radial intensity distribution with an accuracy of $\pm 7\%$. At 44.3 eV we find the same width for (00), (01), and (11), namely, 0.031 of the (00)-(01) separation. In comparison, the widths of $(\frac{1}{2}\frac{1}{2})$ and $(0\frac{1}{2})$ are larger by a factor of 2.1 and 3.1, respectively. The occurrence of the weak $(0\frac{1}{2})$ spots at low energies means that the $p(2\times 2)$ structure coexists with the $c(2\times 2)$, while the difference in the spot width reflects the difference in the domain size for the two structures. The sharpness of the integral-order spots suggests an adsorption site of fourfold symmetry[6] for both structures, i.e., the hollow site, but we also have to investigate the compatibility of the observed LEED patterns with the pseudobridge bonding proposed recently,[3] for which the oxygen is displaced from the hollow site by about 0.3 Å towards the bridge site. This means that the phases produced by this displacement have to be added to the antiphase or in-phase scattering produced by the ideal fourfold hollow site domains only.

We have investigated this effect by optical simulation.[6] The pattern which we have used consists of eight in-phase and eight antiphase fourfold hollow site domains of roughly equal area and roughly random orientation of the domain boundaries, with the domain size adjusted to give the same broadening for the $(\frac{1}{2}\frac{1}{2})$ spot in the optical diffraction pattern as in the LEED pattern. The scattering centers within one domain, however, occupy one of the four possible types of pseudobridge sites, corresponding to the 0.3 Å shift, with four domains for each possible site. The optical diffraction pattern shows an increase in the width of the integral-order spots with the order of diffraction, with the (11), (20), and (21) spots roughly as large as the $(\frac{1}{2}\frac{1}{2})$ spot. We have not detected any indication of such a broadening of the high integral-order spots in the LEED pattern even when scanning the energy of the primary beam. On the other hand, a domain pattern prepared as described above but with the scattering centers in the ideal fourfold hollow site positions produces an optical diffraction pattern very similar to the LEED patterns, with all the integral-order spots as sharp as the (00) spot. The pseudobridge site is thus compatible with the size of the observed LEED spots only if the shift from

the ideal fourfold hollow site is much less than 0.3 Å, a situation which is probably not distinguishable from the true fourfold hollow site position by any of the current methods.

Analyzing the shape of the LEED spots thus establishes that oxygen is adsorbed at the bridge position for the $c(2\times 2)$ structure on Cu(001), and at or very near to the hollow site position for both $p(2\times 2)$ and $c(2\times 2)$ on Ni(001). This difference probably correlates with the different bonding of oxygen in the Cu_2O and the NiO crystals.[1] This method to attack the registry problem has not been used extensively up to now, probably because of the difficulties in separating antiphase domain scattering from the scattering at atomic steps which produce similar changes in the shape of the LEED spots. In order to avoid atomic steps, the deviations in the orientation of the sample surface from that of the low-index plane under investigation have to be minimized, which can be achieved by the *in situ* method described above. Investigating the shape of the LEED spots should generally be a useful starting point for more sophisticated procedures like LEED intensity analysis or NPD which try to determine the adsorption site and the bond length by minimizing the deviations between the measured and the calculated spectra. These methods are hampered by the fact that it is often difficult to know whether one has really reached the absolute minimum in the multidimensional parameter space involved.

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