

Solving the Long-Standing Cu(111) “8” Surface Oxide Puzzle

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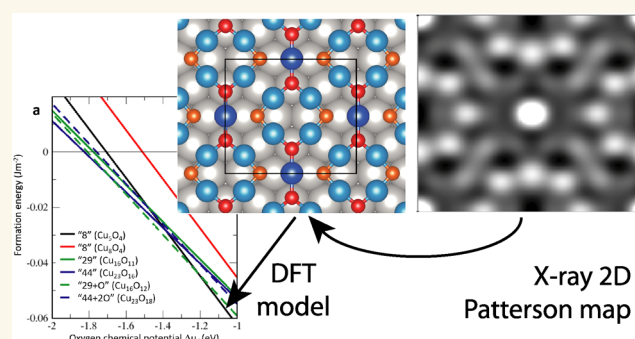
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ABSTRACT: Due to the interesting properties of copper oxides, in particular for catalytic applications, ultrathin oxide layers formed by Cu oxidation have attracted sustained interest. Experimental observations of several surface phases, including the so-called “5–7”, “8”, “29” and “44” structures, have sparked ongoing debate. However, their precise atomic configurations remain incompletely resolved. Among these, the “8” phase is particularly challenging, as existing structural models rely on limited experimental evidence. Here, we combine surface X-ray diffraction, direct fitting of experimental data, and density functional theory (DFT) calculations, to determine both the composition and atomic structure of this phase. The resolved structure reveals a dense, interwoven network of four-membered Cu–O rings, comprising two distinct Cu cation species with markedly different structural and electronic characteristics. DFT results show that a substantial electron transfer from the Cu(111) substrate stabilizes its relatively oxygen-rich composition, Cu_5O_4 . This “8” phase is energetically more stable than the most recent Cu_8O_4 model [Kim, H. J. et al. *ACS Nano* 2024, 18, 4559–4569] across the full range of oxygen chemical potential and is structurally and electronically distinct from the “29” and “44” surface oxides. Its bonding motifs and charge distribution resemble those of Pd_5O_4 and Ag_5O_4 , formed on oxidized (111) surfaces of palladium and silver, but its formation requires less oxygen-rich conditions, reflecting the stronger affinity of Cu for oxygen.

KEYWORDS: ultrathin surface oxides, surface X-ray diffraction, density functional theory, Cu oxide surface reconstruction, thermodynamics of surfaces



INTRODUCTION

Thanks to their unique surface chemistry and tunable oxidation states, thin copper oxide films (e.g., CuO and Cu_2O) exhibit remarkable catalytic activity in several key reactions, including low-temperature CO oxidation,¹ CO_2 reduction,² water–gas shift reaction (WGS),³ or methanol reforming.⁴ Compared with bulk oxide surface terminations, thin copper oxide films display a broader range of accessible Cu oxidation states, which is directly linked to their catalytic performance. In particular, ultrathin copper oxide layers formed by oxidation of Cu(111) have been widely studied and extensively employed as model catalytic systems.^{5,6}

Various periodic motifs have been identified by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM),^{7,8} including the so-called “5–7”, “8”, “29” and “44” configurations.^{9,10} Their nomenclature reflects their surface unit cell area relative to that of the (1×1) substrate. Determining their atomic structure has been the subject of extensive debate since their discovery, owing to the large

number of atoms involved and the stringent preparation conditions required for their stabilization. Despite significant efforts, key questions remain regarding their composition and detailed atomic arrangements. For instance, tentative structural models for the phases with the largest unit cells have only recently been proposed.¹¹

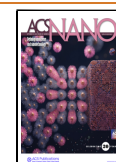
Regarding the “8” phase which is the focus of the present work, its first atomic model was proposed by Judd et al.,¹² assuming that it corresponds to a stretched Cu(001) plane where O atoms occupy half of the 4-fold hollow sites, corresponding thus to a Cu_2O surface composition. This

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model was later refined by Moritani et al.,¹³ to include a possible buckling of the Cu atoms, and was further relaxed by density functional theory (DFT) by Richter et al.¹⁴ It was found mechanically stable but having a higher Gibbs free energy of formation than the other oxide structures known to exist on Cu(111). Kinetic limitations were thus invoked to explain its observation at an oxygen pressure $p_0 = 1$ atm, and for temperatures $T > 500$ K. In 2021, X-ray photoemission spectroscopy (XPS) measurements have evidenced the existence of two species of oxygen atoms, with nearly equal concentration,¹⁵ whereas their chemical environment was nearly the same as in the previous models. This observation led to a new model in which half of the O atoms were located in subsurface position.¹⁵ However, this model was recently found unstable by DFT.¹⁶ Using machine-learning-accelerated *in silico* global optimization, the authors identified a more stable structure featuring two distinct oxygen species while still preserving the Cu₂O stoichiometry. However, its formation energy remained higher than those of the other known surface oxide reconstructions, namely the “5–7”, “29”, and “44” phases.

In this work, we combine surface X-ray diffraction (SXRD) and DFT calculations to unambiguously determine the composition and resolve the structure of the “8” phase. We propose a structural model that consistently accounts for all experimental observations reported to date and is energetically more stable than the most recent model¹⁶ across the full range of oxygen chemical potentials. Furthermore, its stability is comparable to that of other known surface copper oxide phases, supporting their observed coexistence under oxygen-rich conditions. Its Cu₅O₄ stoichiometry naturally gives rise to two distinct types of Cu atoms with different local environments and oxidation states, which may act as key active sites in complex catalytic reactions. Finally, we highlight both the similarities and differences in bonding patterns and charge distributions relative to the Pd₅O₄ and Ag₅O₄ phases formed on oxidized Pd(111) and Ag(111) surfaces.

RESULTS AND COMPARISON WITH EXISTING MODELS

Figure 1a shows the in-plane diffraction map obtained on the oxidized Cu(111) surface, measured for $q_z = 0.1$ Å^{−1}. Diffraction rings, corresponding to the intersection of a diffraction sphere with the plane are clearly visible. The projection of the scattering intensity along the q coordinate in Figure 1c reveals that these rings arise from diffraction by Cu₂O crystallites. Indeed, Cu₂O has a cubic structure (space group: Pn $\bar{3}$ m) with a lattice constant of 4.27 Å, and peaks corresponding to the diffraction by Cu₂O {110}, {111}, {200}, {211} and {220} families of planes are clearly visible at $q = 2.08, 2.55, 2.94, 3.60$ and 4.16 Å^{−1} respectively. The two other peaks in Figure 1c correspond to the diffraction by Cu {111} and {200} families of planes. The first one is particularly intense and is mainly due to the presence of a Bragg reflection for $H = 1, K = 0, L = 1$ diffraction conditions in the integrated volume of the reciprocal space considered.

Apart from these circular features in Figure 1a, diffraction spots, corresponding to the intersection of diffraction rods with the $q_z = 0.1$ Å^{−1} plane are also visible. They can be indexed using a centered rectangular lattice. The corresponding rect. $c(4 \times 2\sqrt{3})$ reconstruction of Cu(111) exhibits three equivalent rotational domains, related by 120° rotations, which are indicated by the blue, red, and green circles in

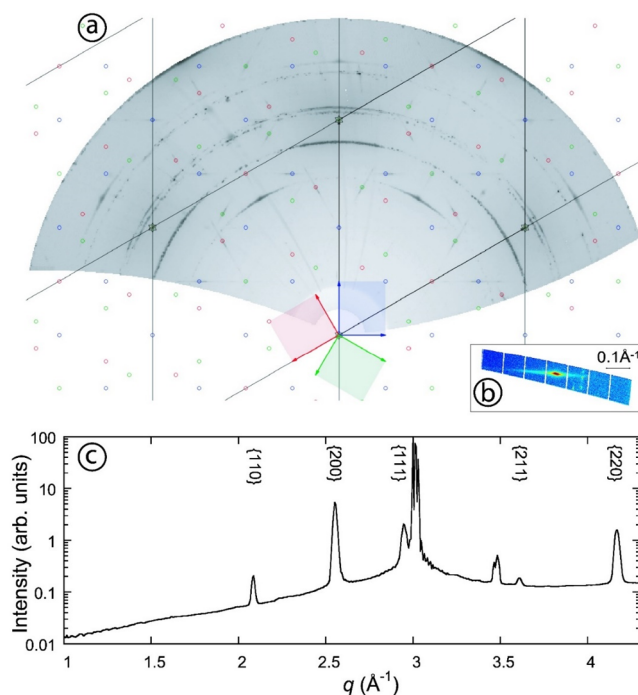


Figure 1. (a) Diffracted intensity for in-plane conditions (measured at $q_z = 0.1$ Å^{−1}) on the oxidized Cu(111) surface. The surface unit cell is indicated by the black lattice and black stars. Blue, red and green lattices and dots correspond to the three different orientations of the rect. $c(4 \times 2\sqrt{3})$ reconstruction and their diffraction spots. (b) detailed view of the (4, 0) spot of the blue domain of the reconstruction. The intensity scale is logarithmic. (c) Diffracted intensity as a function of q integrated for $0 < q_z < 1.43$ Å^{−1} and $0.60 < q_{\parallel} < 4.17$ Å^{−1}.

Figure 1a. This reconstruction is equivalent to the $\begin{bmatrix} 3 & 2 \\ -1 & 2 \end{bmatrix}$ O/Cu(111) reconstruction first observed by Judd et al. by LEED.¹² In Figure 1a, the streaks in the direction of the large side of the unit cell (small size in reciprocal space) may be related to the presence of domain walls along this direction. We have restricted our analysis to the well-defined spots corresponding to the rect. $c(4 \times 2\sqrt{3})$ phase. An example of such a spot is shown in Figure 1b. The width of the spot is 0.04 Å^{−1} along q_x and 0.016 Å^{−1} along q_y , which corresponds to domains of size around 16×40 nm². The width of the spots associated with crystal truncation rods (CTR) is 0.012 Å^{−1}, corresponding to an average terrace size of 50 nm. Apart from the features already mentioned, no additional spots that could be associated with another reconstruction are observed.

From the measured in-plane structure factors, we have computed the 2D Patterson map for the rect. $c(4 \times 2\sqrt{3})$ reconstruction, shown in Figure 2a. It is given by¹⁷ $P(x,y) = 2 \sum_{HK} |F(H,K)|^2 \cos(2\pi(Hx + Ky))$, where $F(H,K)$ are the structure factors specific of this reconstruction, and measured for $L = 0.1$ ($q_z = 0.1$ Å^{−1}). Since it approximates the electron density autocorrelation function, the Patterson map is much more sensitive to Cu atoms than to O ones.

We initially benchmarked our findings against the structural models previously proposed in the literature, which are illustrated in Figure 2e,f. As can be seen in Figure 2b, the Patterson map calculated from the “8”@2014t model¹⁴ does not reproduce the experimental ones (Figure 2a). This is not surprising as it corresponds in fact to a smaller rect. $p(2 \times \sqrt{3})$

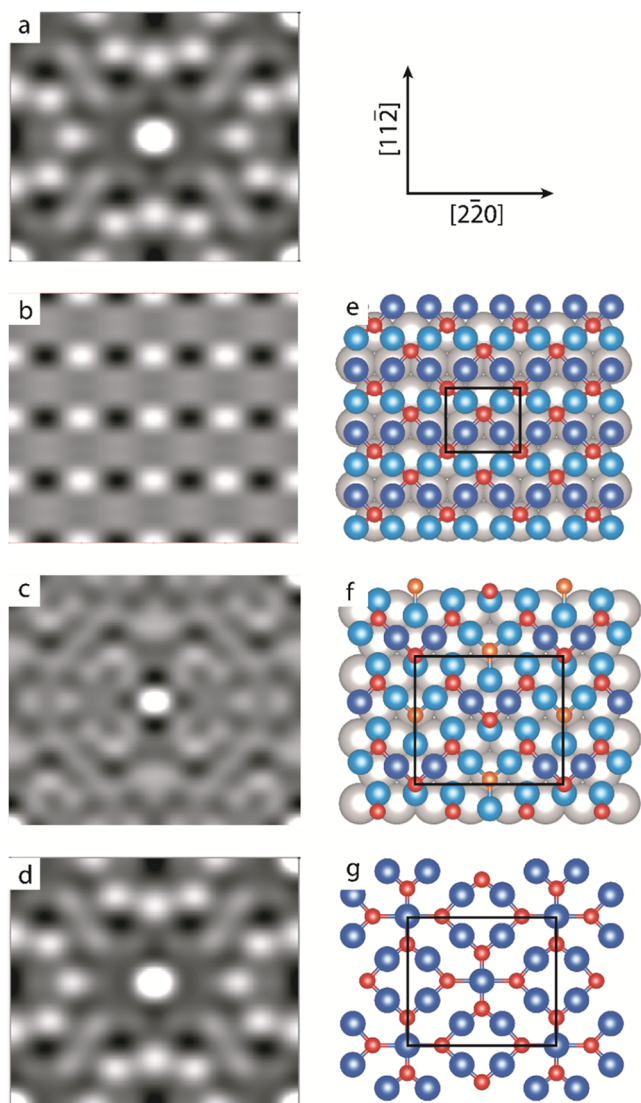


Figure 2. (a) experimental Patterson map of the rect. $c(4 \times 2\sqrt{3})$ unit cell. (b–d) theoretical Patterson maps corresponding to the surface oxide models shown in (e–g). (e) “8”@2014t Cu_8O_4 .¹⁴ (f) “8”@2023t.¹⁶ (g) Cu_5O_4 present model. The corresponding unit cells are drawn in black. O atoms are represented by red and orange spheres. Gray spheres correspond to Cu substrate atoms. Blue and light-blue spheres denote the topmost and other surface Cu atoms, respectively.

unit cell, in complete disagreement with the experimental LEED pattern. The agreement with the theoretical Patterson map (shown in Figure 2c) derived from the “8”@2023t¹⁶ model shows only a slight improvement, even though the unit cell matches the experimental one. Considering that the highest maxima visible in Figure 2a correspond to Cu–Cu interatomic distance vectors, since the Patterson map reflects the electron density autocorrelation function, we established a minimal model with 10 Cu atoms per unit-cell. From this observation, such a minimal model is enough to reproduce all the features of the Patterson map, while adding 8 O atoms allowed us to obtain a very good agreement between experimental and in-plane structure factors (details of the procedure are given in the Supporting Information). Our proposed Cu_5O_4 model is shown in Figure 2g together with the corresponding Patterson map in Figure 2d.

As a further refinement step of the model, the Cu_5O_4 layer has been put on top of the Cu(111) substrate, modeled with two atomic planes. The entire system was relaxed to reproduce both in-plane and out-of-plane structure factors along the different measured rods. For this purpose, Debye–Waller (DW) factors along x , y , and z directions were added, with the constraint that all the atoms in one of the two substrate planes have the same set of DW factors. Moreover, we used a specific scaling factor for the in-plane structure factors to account for the increased transmission coefficient of the diffracted beam as the exit angle approaches the critical angle for total reflection.¹⁸ A perfect fit of the data, corresponding to a reduced chi-squared $\chi^2 = 0.8$, is obtained after relaxation. Corresponding parameters are given in Table S1.

The atomic positions obtained by this procedure were further relaxed by DFT, using alternative exchange–correlation functionals (HSE06, PW91, PBE+U, and PBEsol). For comparison with the experiments, a similar procedure was used, except that all atomic positions were fixed to their DFT relaxed values, so only the DW and scale factors were fitted. As the number of free parameters is highly reduced (from 53 to 20), the agreement is inherently poorer. χ^2 values ranging from 3.7 for HSE06 to 10.0 for PBEsol were obtained.

Figure 3 shows the comparison between experimental and simulated in-plane and out-of-plane structure factors. Consistent with the calculated χ^2 values, the HSE06-simulated structure accurately reproduces all features of the experimental rods. The best agreement obtained with the HSE06 functional is in line with conclusions reported in previous studies on $\text{Cu}_2\text{O}(111)$ surfaces by some of the present authors.^{19,20}

Table 1 summarizes the main characteristics of the structural models derived either from a direct fit to the experiment (best-fit) or from DFT calculations using different exchange–correlation functionals (HSE06, PW91, PBE+U, and PBEsol). In all cases, the oxide film forms a network of entangled chains composed of four-membered Cu–O rings that align along the $[1\bar{1}0]$ direction of the Cu(111) surface (Figure 4). Each ring comprises four Cu cations occupying surface hollow sites (h ; $d_{\text{Cu–O}} = 1.86\text{--}1.89$ Å in the best-fit model) and four O anions located at either bridge (b) or top (t) sites. Successive rings are interconnected by Cu cations at substrate bridge positions (b; $d_{\text{Cu–O}} = 1.80$ Å). Cu cations in both hollow and bridge sites are 2-fold coordinated. The four O anions split into two groups: O at bridge sites reside closer to the substrate, whereas O at top sites — bonded to bridging Cu — are positioned about 0.7 Å higher relative to the Cu(111) surface ($d_{\text{O–Cu(111)}} = 2.35$ Å). This pronounced buckling of the oxygen sublattice effectively accommodates the preferred quasi-linear geometry of all O–Cu–O units within the monolayer, thereby facilitating commensurability with the underlying substrate. The distance between a bridging Cu and the nearest O in neighboring chains is much longer ($d_{\text{ch–ch}} = 2.63$ Å), and the corresponding bond is not drawn in Figure 4. All DFT-derived models reproduce adequately this structural pattern; however, only the HSE06 and PW91 ones simultaneously capture three key quantitative characteristics of the best-fit structure: (i) the relatively small hollow vs bridge anisotropy of $d_{\text{Cu–O}}$, (ii) the relatively large buckling of the oxygen sublattice, and (iii) the large interchain separation $d_{\text{ch–ch}}$.

The structural nonequivalence of Cu cations directly correlates with their distinct electronic properties, as consistently predicted by all DFT calculations. According to HSE06 data, hollow-site and bridge-site Cu atoms exhibit

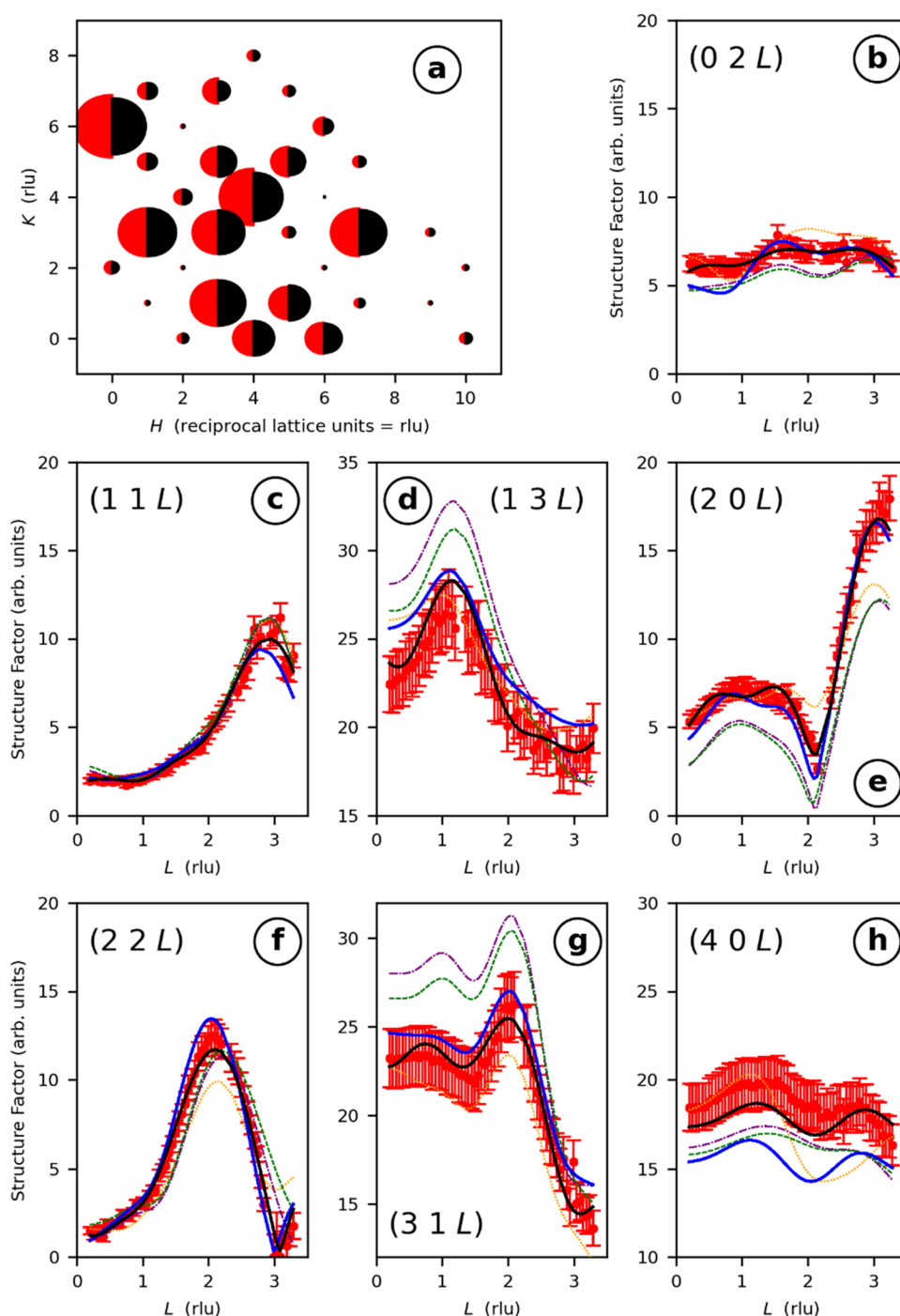


Figure 3. (a) Nonequivalent in-plane reflections of the rect. $c(4 \times 2\sqrt{3})$ superstructure. The measured and simulated (best fit, i.e., before DFT relaxation) structure factor amplitudes are shown by the radius of the red and black half circles, respectively. (b–h) Rod profiles. The indices are given with respect to the rect. $c(4 \times 2\sqrt{3})$ unit cell. Red dots: measured structure factors; black solid lines: structure factors from the best fit; blue solid lines: HSE06; orange dotted lines: PW91; purple dotted lines: PBE+U; green dash lines: PBEsol.

different Bader charges of +0.61 e and +0.70 e, respectively. This charge difference aligns with the upward shift in the local density of states (LDOS) observed at bridge-site Cu atoms and the corresponding larger depletion of their valence band (below -2 eV), as illustrated in Figure 4(b). Comparison with the Bader charge of bulk Cu_2O (+0.57 e) suggests a formal +1 oxidation state for hollow-site Cu atoms. Bridge-site Cu exhibits a slightly larger oxidation state, intermediate between +1 and +2 (the Bader charge of bulk CuO is +1.18 e). The combined structural and electronic nonequivalence results in a

notable shift of the calculated Cu core-level binding energies: bridge-site Cu core levels lie approximately 1 eV above those of hollow-site Cu, reflecting the relative LDOS shifts in the valence band.

The calculated O 1s core-level splitting is much smaller, with top-site O core levels lying less than 0.1 eV above those of bridge-site O. Similar small separation is also predicted by the PW91 functional (0.1 eV), for which film atomic structure is closest to that obtained with HSE06. In contrast, while the splitting remains comparably small in the PBE+U and PBEsol

Table 1. Quality of Matching (χ^2) and Structural Characteristics of $\text{Cu}_5\text{O}_4/\text{Cu}(111)$ Monolayers from the Best Fit to the Experimental Data and from DFT Calculations with Alternative Exchange-Correlation Functionals (HSE06, PW91, PBE+U, and PBEsol)^a

	best fit	HSE06	PW91	PBE+U	PBEsol
χ^2	0.8	3.7	6.1	9.5	10.0
$d_{\text{Cu-O}}$ hollow/bridge (Å)	1.86–1.89/1.80	1.84–1.85/1.85	1.85–1.86/1.85	1.86–1.87/1.92	1.84–1.86/1.89
buckling (Å)	0.74	0.53	0.82	0.26	0.27
rumpling (Å)	−0.03	−0.14	+0.03	−0.03	+0.01
d_{interf} (Å)	2.04	2.09	2.17	2.11	2.05
$d_{\text{O-Cu}(111)}$ (Å)	2.35	2.21	2.64	2.16	2.15
$d_{\text{ch-ch}}$ (Å)	2.63	2.61	2.67	2.40	2.46

^a Cu-O bond-lengths $d_{\text{Cu-O}}$ of cations at hollow and bridge sites of the $\text{Cu}(111)$ surface; buckling of oxygen sublattice (Å); average film rumpling $\langle z_{\text{O}} \rangle - \langle z_{\text{Cu}} \rangle$ and interface distance $d_{\text{interf}} = (\langle z_{\text{O}} \rangle + \langle z_{\text{Cu}} \rangle)/2 - \langle z_{\text{Cu}(111)} \rangle$; Cu-O distance between oxygen at top site and the $\text{Cu}(111)$ surface $d_{\text{O-Cu}(111)}$ and distance between the neighboring chains $d_{\text{ch-ch}}$.

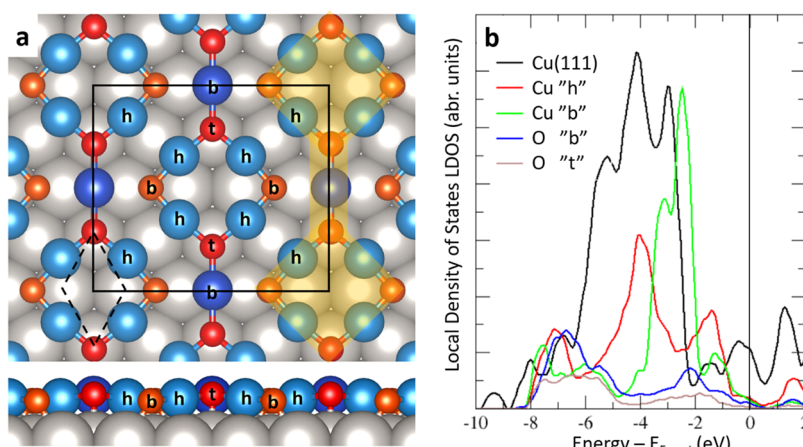


Figure 4. Atomic and electronic structures of the “8” / rect.c($4 \times 2\sqrt{3}$) $\text{Cu}_5\text{O}_4/\text{Cu}(111)$ monolayer, obtained with the HSE06 functional. (a) Top and side views of the fully relaxed atomic structure, composed of entangled lines of distorted 4-membered rings (highlighted in orange). Oxygen, copper, and $\text{Cu}(111)$ substrate atoms are represented by red/orange, light/dark blue and large gray balls, respectively. Positions of oxide ions in top (t), bridge (b) and hollow (h) sites of the $\text{Cu}(111)$ surface are indicated. Surface rect.c($4 \times 2\sqrt{3}$) and (1×1) unit cells are plotted with black solid and dashed lines, respectively. (b) LDOS of the $\text{Cu}(111)$ substrate and of the nonequivalent anions and cations in the monolayer.

calculations (−0.1 eV and −0.2 eV, respectively), the level ordering is reversed, likely because of more pronounced structural differences.

Most importantly, the calculated O 1s core levels are consistent with the measured spectrum,¹⁵ where the two peaks have nearly identical integrated intensities, indicating that the two oxygen species are present in approximately equal amounts. The absence of any pronounced photon-energy dependence in the reported line shape further suggests that both oxygen atoms occupy surface sites, where attenuation of the O 1s signal is minimal. Although final-state effects are not included, the calculated small difference in core level positions of the two oxygen species is consistent with the experimentally observed peak separation of 0.4 eV only. The overall negative charge of the supported Cu_5O_4 monolayer is compensated by significant positive charging of the underlying $\text{Cu}(111)$ substrate. Without the substrate, the freestanding monolayer exhibits increased cation charges (+0.80 e and +1.02 e for the two types of cations), corresponding to approximate oxidation states of +1.5 and +2, respectively, thereby maintaining charge neutrality within the monolayer.

To the best of our knowledge, no STM observations of the “8” phase have been reported in the literature. We have simulated the STM images at both negative and positive bias

voltages for future comparison with experimental observations. The simulated images are shown in Figure S2.

In summary, the atomic structure of the observed “8” phase has been consistently resolved through direct fitting of experimental data and through DFT calculations. The newly identified structure features a dense interwoven network of four-membered Cu-O rings, in which substantial electron transfer from the $\text{Cu}(111)$ substrate stabilizes the relatively oxygen-rich composition and preserves overall charge neutrality. Pronounced buckling within the oxygen sublattice accommodates the quasi-linear geometry of all O-Cu-O units and maintains film commensurability with the substrate lattice, with hollow- and bridge-site Cu cations displaying quite distinct structural and electronic characteristics.

DISCUSSION

Comparison with Other $\text{Cu}(111)$ Surface Oxide Models

To provide broader context, the newly characterized “8” / rect.c($4 \times 2\sqrt{3}$) phase is compared with an alternative model derived from machine learning–accelerated global optimization¹⁶ and with other prototypical $\text{Cu}(111)$ surface oxides, notably the “29” and “44” phases, for which refined atomistic structures were recently established via element-specific STM with functionalized tips.¹¹ To enable efficient optimization of

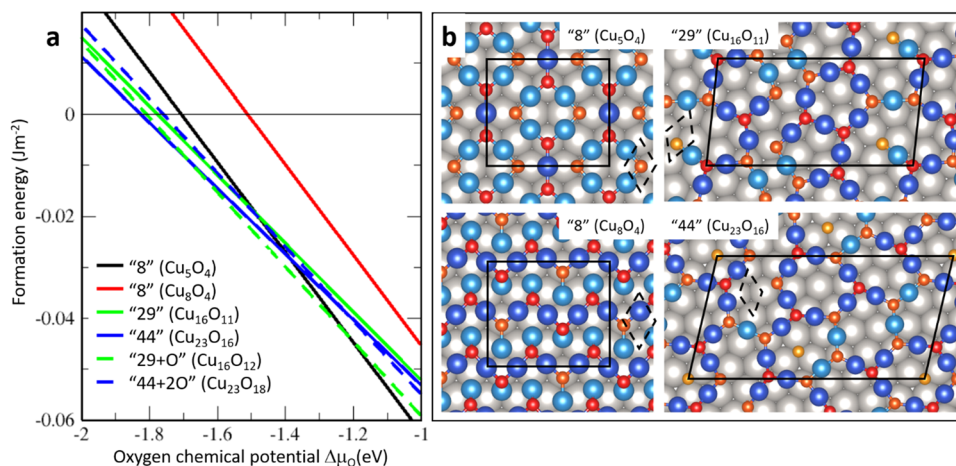


Figure 5. (a). Formation energies of the alternative surface oxides as a function of oxygen chemical potential $\Delta\mu_{\text{O}}$ and (b) top views of the corresponding atomic structures, obtained with PW91 exchange-correlation functional: Cu_5O_4 ("8", present study), Cu_8O_4 ("8"@2023t,¹⁶), $\text{Cu}_{16}\text{O}_{11}$ and $\text{Cu}_{16}\text{O}_{12}$ ("29" and "29+O",¹¹), $\text{Cu}_{23}\text{O}_{16}$ and $\text{Cu}_{23}\text{O}_{18}$ ("44" and "44 + 2O",¹¹). Oxygen and copper atoms in the film, and Cu(111) substrate atoms are represented by red/orange, light/dark blue, and large gray balls, respectively. Reconstruction and (1×1) -Cu(111) unit cells are indicated with full and dashed lines, respectively.

Table 2. Calculated (PW91) Structural and Electronic Characteristics of $\text{X}_5\text{O}_4/\text{X}(111)$ Monolayers ($\text{X} = \text{Ag}, \text{Pd}, \text{Cu}$)^a

	Ag	Pd	Cu
$d_{\text{X-O}}$ hollow/bridge (Å)	2.11/2.16	2.05–2.09/2.24	1.85–1.86/1.85
q_{X} hollow/bridge (e) (bulk $\text{X}_2\text{O}/\text{XO}$)	+0.48/+0.70 (+0.46/+0.83)	+0.44/+0.72 (+0.42/+0.84)	+0.58/+0.77 (+0.54/+0.96)
buckling (Å)	0.36	0.10	0.82
rumpling (Å)	−0.10	−0.09	+0.03
d_{interf} (Å)	2.34	2.26	2.17
$d_{\text{O-X}(111)}$ (Å)	2.43	2.14	2.64
$d_{\text{ch-ch}}$ (Å)	2.75	2.26	2.67
Δ_{WF} (eV)	+0.3	−0.4	−0.0
$\Delta\mu_{\text{O}}$ (eV)	−0.6	−0.9	−1.7

^a X-O bond-lengths $d_{\text{X-O}}$ (Å) and cation Bader charges q_{X} at cations at hollow and bridge sites compared to the corresponding values calculated for bulk X_2O and XO oxides; X-O distances between oxygen at top site and the $\text{X}(111)$ surface $d_{\text{O-X}(111)}$ and between the neighboring chains $d_{\text{ch-ch}}$; average film rumpling $\langle z_{\text{O}} \rangle - \langle z_{\text{X}} \rangle$ and buckling of the oxygen sublattice; film-induced change of substrate work function Δ_{WF} ; thermodynamic oxygen conditions $\Delta\mu_{\text{O}}$ of oxide monolayer formation on the $\text{X}(111)$ substrate.

these larger systems, we systematically employ the second-best PW91 functional in the following comparison.

The recently proposed "8"@2023t model¹⁶ features a markedly more Cu-rich stoichiometry, Cu_8O_4 ($\text{CuO}_{0.50}$). Its structure comprises entangled chains of zigzagging, quasi-linear O-Cu-O motifs aligned along the $[110]$ direction of Cu(111), as seen on Figure 5. Their apparent linearity arises from pronounced oxygen buckling with O atoms positioned either close to or far from the substrate. As shown in Figure 5, this Cu_8O_4 model is significantly less stable than the present Cu_5O_4 phase across the full range of oxygen chemical potentials under consideration. This reduced stability correlates with its much lower average Cu coordination number: 1.5 Cu–O bonds per cation in Cu_8O_4 versus 2.0 in Cu_5O_4 .

The recently resolved "29" and "44" phases¹¹ form buckled monolayers with stoichiometries of $\text{Cu}_{16}\text{O}_{11}$ ($\text{CuO}_{0.69}$) and $\text{Cu}_{23}\text{O}_{16}$ ($\text{CuO}_{0.70}$), respectively, both only slightly more O-poor than the present Cu_5O_4 "8" phase ($\text{CuO}_{0.80}$). As shown in Figure 5, these oxides are somewhat less stable than the Cu_5O_4 structure under the oxygen-rich conditions of this study ($\Delta\mu_{\text{O}} \approx -1.3$ eV), but become thermodynamically competitive already for $\Delta\mu_{\text{O}} \lesssim -1.4$ eV. Adsorption of additional O atoms ("29+O" and "44 + 2O" models from ref 11) further stabilizes

them at higher oxygen chemical potentials, their stability matching closely that of the "8" phase. These subtle variations in stability can be attributed to distinct ring topologies: the "8" phase is composed of compact four-membered rings, whereas the "29" and "44" phases consist of edge- or corner-sharing five-membered rings and extended networks of edge-sharing six-membered rings, respectively. This yields different Cu–O bond densities: $0.22 \text{ \AA}^{-2}$ for "8", versus $0.19 \text{ \AA}^{-2}$ for both "29" and "44". Electronically, the "29" and "44" phases exhibit lower average Cu oxidation states than the "8" one, with only two Cu atoms (out of 16) in "29" and none in "44" approaching the somewhat higher oxidation state found for 2 among 8 cations in the "8" phase. Consistently, calculated electron transfer from the Cu(111) substrate to these films is roughly twice smaller.

In summary, the newly identified "8" phase on Cu(111) is significantly more stable than the previous Cu_8O_4 "8"@2023t model of this phase in the whole range of oxygen chemical potential. It is also structurally and electronically distinct from the previously characterized "29" and "44" surface oxide phases. Structurally, the "8" phase consists predominantly of more compact four-membered Cu–O rings, which results in somewhat higher Cu–O bond density and correlates with its enhanced thermodynamic stability under oxygen-rich conditions. Electronically, the "8" phase displays a larger ratio of

Cu cations with somewhat higher oxidation state, while the “29” and “44” phases exhibit mainly Cu^{1+} cations, associated with a weaker electron transfer from the Cu(111) substrate.

Comparison with Similar “8” Phases at Oxidized Ag(111) and Pd(111) Surfaces

This Cu_5O_4 model for the “8” surface oxide on Cu(111) is similar to that proposed for the $c(4 \times 8)$ Ag surface oxide on Ag(111).^{21,22} Indeed, the $c(4 \times 8)$ unit cell reduces to a rect. $c(4 \times 2\sqrt{3})$ one, twice as small in size. This Ag surface oxide can be obtained by exposing the sample to ~ 100 L atomic oxygen at 500 K.²¹ The Cu_5O_4 structure is also similar to the Pd_5O_4 incommensurate phase found after exposure of Pd(111) at 300 °C under 5×10^{-6} mbar of atomic oxygen.²³

This suggests a broader structural stability of this type of oxide monolayer across late-transition and noble metals and raises the question of whether analogous motifs may also emerge for e.g., Ni and Pt. Our computational results for the corresponding $\text{Ag}_5\text{O}_4/\text{Ag}(111)$ and $\text{Pd}_5\text{O}_4/\text{Pd}(111)$ films, given in Table 2, confirm that they share several key structural features with $\text{Cu}_5\text{O}_4/\text{Cu}(111)$. Moreover, from an electronic standpoint, while hollow-site cations systematically tend to display +1 oxidation states close to those calculated for the corresponding X_2O bulks, the bridging ones are similarly characterized by higher oxidation states, approaching bulk XO values. In all cases, the underlying metal substrates also carry a positive charge.

However, beyond these similarities, the three systems exhibit several structural differences. While the quasi-linearity of the O–X–O entities is consistently preserved, the degree of oxygen buckling varies markedly (Table 2): it is the largest for Cu and the smallest for Pd. The shortest interfacial bond — the O–X bond between the metal substrate and the top-site oxygen atom, $d_{\text{O-X}(111)}$, also follows a systematic trend, with the longest value for Cu, followed by Ag and Pd. These structural differences lead to distinct average rumpling amplitudes and interface separations d_{interf} for the three supported monolayers and drive pronounced variations in surface work functions Δ_{WF} . Specifically, the work function is essentially the same for $\text{Cu}_5\text{O}_4/\text{Cu}(111)$ as for the bare substrate, it increases noticeably for $\text{Ag}_5\text{O}_4/\text{Ag}(111)$, and it is significantly reduced for $\text{Pd}_5\text{O}_4/\text{Pd}(111)$. Finally, owing to the markedly different Ag, Cu, and Pd affinities to oxygen ($\text{Ag} < \text{Pd} < \text{Cu}$), as estimated, e.g., from the corresponding Ellingham diagrams,²⁴ the thermodynamic stability of the X_5O_4 surface oxides is highly system dependent. Cu_5O_4 phase can be stabilized already under relatively oxygen-poor conditions (from $\Delta\mu_{\text{O}} \sim -1.7$ eV), whereas the analogous films on Pd — and particularly on Ag — form only under substantially more oxygen-rich environments ($\Delta\mu_{\text{O}} \geq -1.0$ eV).

Lastly, it is worth mentioning the case of Pt, for which an analogous $\text{Pt}_5\text{O}_4/\text{Pt}(111)$ phase could have been expected but, to the best of our knowledge, has never been observed experimentally. Interestingly, DFT calculations predict that $\text{Pt}_5\text{O}_4/\text{Pt}(111)$ monolayer, exhibiting structural and electronic characteristics closely resembling those described above, corresponds to a well-defined energy minimum for the $\text{PtO}_{0.8}$ film stoichiometry. Nevertheless, from a thermodynamic perspective, more oxygen-rich phases — such as the recently reported PtO_3 –Pt one²⁵ — are significantly more stable under the full range of oxygen chemical potentials relevant to surface oxide formation.

In summary, although the “8” phases on Ag(111) and Pd(111) exhibit analogous bonding patterns and charge distributions, their interfacial properties diverge significantly. Differences in oxygen buckling amplitudes and interface separations induce qualitatively distinct surface work function modifications, ranging from an increase in Ag_5O_4 to a strong reduction in Pd_5O_4 . Moreover, their thermodynamic stability is highly metal-dependent; while Cu_5O_4 phase stabilizes under relatively oxygen-poor conditions, the formation of Pd_5O_4 and especially Ag_5O_4 requires substantially higher oxygen chemical potentials.

CONCLUSION

By combining SXRD, direct fitting of experimental data, and DFT calculations, we have resolved the composition and atomic structure of the surface “8” phase. The structure consists of a dense interwoven network of four-membered Cu–O rings, with hollow- and bridge-site Cu cations displaying quite distinct structural and electronic characteristics. A substantial electron transfer from the Cu(111) substrate stabilizes its relatively oxygen-rich Cu_5O_4 composition.

This newly identified “8” phase is significantly more stable than the previously proposed Cu_8O_4 “8”@2023t model across the full range of oxygen chemical potentials. It also differs from the “29” and “44” surface oxides by a higher Cu–O bond density and by a larger ratio of Cu cations in higher oxidation state. Under oxygen-rich conditions, its stability is comparable to that of these large unit cell phases, thus rationalizing their observed coexistence.

The bonding patterns and charge distribution of the “8” phase are similar to those of Pd_5O_4 and Ag_5O_4 oxides formed on oxidized Pd(111) and Ag(111) surfaces. However, unlike these systems, the “8” phase induces only limited modifications of the substrate work function and forms under less oxygen-rich conditions, reflecting the stronger affinity of Cu for oxygen.

Resolving the structure of the “8” phase structure represents a key step toward the rational design of copper-based catalysts, enabling the controlled formation of Cu active sites to enhance the catalytic activity and selectivity in tailored reaction environments.

METHODS/EXPERIMENTAL

SXRD experiments were performed at the SIXS beamline of SOLEIL synchrotron. The Cu(111) sample was prepared by several cycles of Ar ion sputtering ($P = 4 \times 10^{-5}$ mbar, 2.5 keV) followed by annealing ($T = 670$ K). Prior to the experiment, the cleanliness of the sample surface was checked on another UHV setup by Auger Electron Spectroscopy (AES), and no trace of contamination was detected. Surface oxidation was performed by exposing the clean sample to 5×10^{-5} mbar of O_2 at 720 K during 40 min. The sample was cooled after oxygen exposure. After preparation, the sample was analyzed at room temperature with 18.46 keV X-rays at a grazing incidence angle of 0.3°. Scattered X-rays were detected with a 2D detector in continuous acquisition mode, and the detector was kept in its best dynamic range by constantly adapting the beam attenuation.²⁶ Diffracted intensity was measured by performing a series of wide rocking scans for in-plane conditions and narrow rocking scans for out-of-plane momentum transfers along given rods. Rocking scans performed on the Cu Bragg reflections exhibited a full width at half-maximum (fwhm) of 0.20°, indicating a good crystalline quality of the substrate. We used the “BINoculars” software to produce three-dimensional (3D) intensity data in the reciprocal space from the raw data.²⁷ The intensity was further integrated along the direction parallel to the

surface to obtain the structure factors, using the procedure detailed in.²⁸ We finally obtained a set of 32 nonequivalent in-plane structure factors and a set of 528 structure factors along 7 nonequivalent reconstruction rods. The (*H*,*K*,*L*) indices used for indexing a reflection in reciprocal space refer to the Cu(111) – rect. $c(4 \times 2\sqrt{3})$ reconstruction basis ($a = 10.219 \text{ \AA}$, $b = 8.499 \text{ \AA}$, $c = 6.258 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$). For fitting the structure factors, atomic factors for atoms and ions from the International Tables for Crystallography were used.²⁹

DFT calculations were carried out using the Vienna Ab-initio Simulation Package (VASP),^{30,31} the Projector Augmented Wave approximation^{32,33} to simulate the electron–core interaction, and a 400 eV energy cutoff in the expansion of Kohn–Sham orbitals on a plane-wave basis set. Copper (including 4d electrons) and oxygen pseudopotentials provided by VASP were used. The present spin-unrestricted calculations used either the PW91,³⁴ PBE+U³⁵ ($U_{\text{Cu}} = 4 \text{ eV}$), PBEsol,³⁶ or HSE06³⁷ exchange–correlation functionals to enable a more complete comparison with diffraction measurements. In the HSE06 case, soft oxygen pseudopotential provided with VASP and a 300 eV cutoff have been used to accelerate calculations. A comparison of the main structural and electronic characteristics of bulk, surface, and ultrathin film copper oxides obtained with GGA and hybrid exchange–correlation functionals can be found in refs 19,20,38,39. Atomic charges are estimated with the partition scheme proposed by Bader.^{40,41} Atomic configurations were plotted using VESTA.⁴²

The Cu substrate was approximated by a slab made up of four (111) atomic planes at the experimental in-plane bulk Cu lattice parameter (3.61 Å). The Brillouin zone of the (1 × 1) surface cell was sampled on a dense (12 × 12) Γ -centered Monkhorst–Pack mesh and the same density of k-point sampling was used in larger-cell calculations. The oxide film was placed on one side of the slab, slabs were separated by more than 10 Å of vacuum, and dipole corrections were applied. The atomic coordinates of all atoms were relaxed until forces dropped below 0.01 eV Å^{−1}, except for the bottom-most Cu layer, which was fixed in its bulk-like position.

Formation energies of the surface oxide phases were evaluated as a function of oxygen chemical potential $\Delta\mu_{\text{O}}$ and with respect to the bulk Cu crystal according to

$$E_{\text{form}} = [E(\text{Cu}_n\text{O}_m/\text{Cu}) - E(\text{Cu}^{\text{slab}}) - nE(\text{Cu}^{\text{bulk}}) - m(E(\text{O}_2)/2 + \Delta\mu_{\text{O}})]/S$$

Here, $E(\text{Cu}_n\text{O}_m/\text{Cu})$, $E(\text{Cu}^{\text{slab}})$, $E(\text{Cu}^{\text{bulk}})$, and $E(\text{O}_2)$ refer to total energies of the supported Cu_nO_m film, the bare Cu substrate, a bulk Cu atom, and an oxygen molecule, respectively. S is the area of the surface unit cell. Equivalent expressions have been used in the case of Ag and Pd surface oxides.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.6c11362>.

Details of the procedure used for determining the atomic structure of the $c(4 \times 2\sqrt{3})$ reconstruction from the structure factors measured. Simulated STM images of the "8" phase. (PDF)

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