Temperature-Dependent Phase Evolution of Copper-Oxide Thin-Films on Au(111)

(Supplementary Information)

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I. Computational settings

DFT calculations were carried out with standard GGA (PW91) or hybrid (HSE03) exchange-correlation functionals, as implemented in VASP. The interaction between valence electrons and ionic cores was treated with the projector augmented wave method. Standard copper and gold, and soft oxygen (energy cutoff of 270 eV) pseudopotentials provided by VASP were used, enabling a complete structural relaxation at the hybrid level of all supported infinite films as well as GGA calculations on a large variety of supported oxide configurations. GGA results obtained with soft and full (energy cutoff of 400 eV) oxygen pseudopotentials were confronted and showed very satisfactory agreement (difference of bulk Cu₂O lattice parameter smaller than 0.01 Å, difference of (1×1) -Cu₂O(111) surface energies below 0.002 eV/Å²).

Bulk Cu₂O: Reference calculations of bulk Cu₂O were performed with a (111)-oriented unit cell, composed of six Cu₂O formula units. The Brillouin zone was sampled with a (4×4×3) Monkhorst-Pack k-point grid. The equilibrium bulk Cu₂O lattice parameter was found equal to 4.31 Å and 4.29 Å in HSE and GGA, respectively, compared to the experimental value of 4.27 Å. The calculated HSE gap width (1.96 eV) is significantly larger than the GGA one (0.4 eV), and close to the experimental value of 2.15 eV.

Infinite Cu₂O(111) films: The bulk-cut Cu₂O(111) surface can be seen as a stacking of O-4Cu-O trilayers. Successive Cu planes are fcc-stacked such that each oxygen atom forms three O-Cu bonds with the copper atoms from the Cu plane within the trilayer and a single bond with a Cu atom from the following trilayer. Ultra-thin Au-supported cuprous oxide films were modeled by slabs composed of 1, 2, and 3 trilayers (labeled 1ML, 2ML, and 3ML) in contact with an Au(111) slab composed of three atomic planes. Slabs were separated by at least 10 Å of vacuum and dipole correction was applied to eliminate the effect of periodic conditions in the direction perpendicular to the slab surface. A (1×1)-Cu₂O(111)//(2×2)-Au(111) coincidence unit cell with the in-plane lattice parameter of bulk Au (a = 2.88 Å) was used. Atomic coordinates of all ions in the oxide film were relaxed until residual forces dropped below 0.01 eV/Å, while the in-plane coordinates of the Au atoms were kept fixed. We have verified that, with the above settings and a (4×4×1) Monkhorst-Pack k-point grid, the results show very satisfactory agreement with those obtained for thicker, six-layer Au slabs and a much denser (18×18×1) Monkhorst-Pack k-point grid (difference of O-Cu, O-Au, and Cu-Au bond lengths smaller than 0.02 Å, difference of oxide/metal separation energies smaller than 0.01 eV/Å²).

Given the low coordination of the outermost copper and oxygen atoms in the multilayers, configurations with missing anions at the gold interface (O_{int}) and/or missing coordinately unsaturated copper atom at the surface (Cu_{CUS}) were considered. Formation energies were then estimated as a function of the oxygen chemical potential $\Delta\mu_0$ with the usual ab-initio thermodynamics expression:

$E(\Delta\mu_O) = (E_{film+substrate} - E_{bulk} - E_{substrate} - n_O(\Delta\mu_O + E_{O2}/2))/S.$

Here, $E_{film+substrate}$, E_{bulk} , $E_{substrate}$, and E_{O2} are the total energies of the supported oxide film, of the same number of formula units in bulk Cu₂O, of the bare Au(111) support, and of a free O₂ molecule, respectively. S is the area of the surface unit cell and n_O represents the oxygen excess in the film with respect to the bulk Cu₂O stoichiometry. A similar approach was used to compare the stability of infinite CuO_x monolayers with different connectivity and stoichiometry.

Au-supported Cu₃O₂ honeycomb stripes:

Following the experimental evidence, the periodicity along oxide stripes was assured by aligning the stripes with the Au[110] direction and imposing a matching of the two lattices with a short period of $a = 2 \times 2.88$ Å = 5.76 Å. A large cell parameter *b* in the perpendicular direction (*a*±*b*) of $6 \times \sqrt{3} \times 2.88$ Å = 29.93 Å enables us to simulate a variety of stripes, with different widths, edge structures, and in different registries with the gold substrate.

Since alternative edge structures display different stoichiometry, their relative stability was estimated from the edge energy $E_{edge}(\Delta\mu_O) = \frac{1}{2}(E_{stripe+substrate} - E_{film+substrate} - n_O \cdot (\Delta\mu_O + \frac{1}{2}E_{O2}))$. Here, $E_{stripe+substrate}$, $E_{film+substrate}$, and E_{O2} are the calculated total energies of the supported oxide stripe, of the same number of oxide formula units in the supported honeycomb monolayer, and of a free O_2 molecule, respectively. Factor two accounts for the two equivalent stripe edges and n_O represents the oxygen excess in the stripe with respect to the Cu_3O_2 stoichiometry.

The relative stability of Cu-terminated stripes of different widths (configurations A, see text), having a $Cu_{3n+1}O_{2n}$ composition per unit cell, was estimated from their formation energy $E_{form}(n) = E_{stripe+substrate} - E_{film+substrate} - (E_{Cu+substrate} - E_{substrate})$. $E_{stripe+substrate}$, $E_{film+substrate}$, and $E_{substrate}$ hereby depicts the calculated total energies of the supported oxide stripe, of the same number *n* of Cu_3O_2 formula units in the infinite monolayer with $a = 2 \times 2.88$ Å, and of the bare Au(111) substrate, respectively. The energy of a single Ausupported Cu atom ($E_{Cu+substrate} - E_{substrate}$) was systematically used to account for copper excess with respect to the infinite honeycomb layer.

All STM-image simulations are obtained with the Tersoff-Hamman approach, based on the state density in an energy range between 0-2eV above E_{Fermi} (bias +2V) and plotted 5 Å above the Au surface.

II. Results: Au-supported infinite Cu₂O ultrathin films

In order to understand the transition from the semi-infinite $Cu_2O(111)$ surface to the Cu_3O_2 honeycomb monolayer, we present a stability analysis of Cu_2O films composed of 1, 2 and 3 ML with and without under-coordinated O_{int} and Cu_{Cus} as a function of oxygen chemical potential, and compare the results obtained with the GGA and the HSE approach (Fig S1 and S2).

At the stoichiometric surface, the main structural elements are six-membered Cu-O rings, interconnected by four-fold coordinated O ions. The Cu-ions locate at the sides of the hexagon and coordinate the corner oxygens by linear O-Cu-O bonds, specific to the Cu₂O lattice. The center of each ring contains Cu₃-O-Cu tetrahedrons from the layer below. The presence of the terminal Cu ions of these tetrahedrons, termed Cu_{Cus} , ensures charge compensation of the entire structure. The dangling-bond state of the exposed Cu_{Cus} ions is expected to play a major role for the chemistry of $Cu_2O(111)$, but also governs the contrast observed in empty-state STM images.

Using standard GGA, Cu-deficient surface structures are energetically favored for films of 1-3 ML thickness (red and blue lines) at all oxygen chemical potentials at which bulk Cu₂O is stable ($\Delta\mu_0 > -1.8$ eV, Fig. S2). While HSE reproduces this overall trend, the stoichiometric surface termination (black line) becomes thermodynamically preferred at oxygen-lean conditions in the 3ML film. We have previously shown that the same is true for thicker Cu₂O films, both Au-supported and unsupported, as well as for the Cu₂O(111) surface (Ref. 29). The discrepancy in predicting relative stabilities with either GGA or HSE has been assigned to an incorrect GGA energy associated with hole-gas formation at polar, non-stoichiometric surfaces. Indeed, while stoichiometric terminations are non-polar, due to the absence of a dipole moment in the O-4Cu-O repeat unit, Cu-deficient surfaces are polar with a Fermi level shifted into the valence band in order to produce a charge-compensating hole gas. The associated formation energy is too low at the GGA level due to an underestimation of Cu₂O band gap and ionization potential, being inherent to this type of calculation. Below 3ML thickness, polarity remains uncompensated and no hole-gas is formed so that differences between both approaches become unimportant.



Figure S1. Top and side views of 1ML, 2ML and 3ML Cu_2O films. Copper and oxygen ions are depicted by small blue and large red balls, respectively. Low-coordinated interface anions (O_{int}), missing in (1x1)- O_{int} and (1x1)- $O_{int}-Cu_{CUS}$ configurations, and coordinately unsaturated surface cations (Cu_{CUS}), missing in (1x1)- Cu_{CUS} and (1x1)- O_{int} - Cu_{CUS} configurations, are highlighted in pink and green, respectively.

Figure S2: Variations of the film formation energies for various stoichiometries with respect to bulk Cu₂O shown as a function of the oxygen chemical potential $\Delta\mu_O$, as obtained with the GGA and HSE. The corresponding limits of the Cu₂O bulk stability are indicated by vertical lines. For 1ML thickness, the (1×1)-Cu_{CUS} label represents the Cu₃O₂ honeycomb layer. The stability of Cu_{cus} ions is additionally affected by the thickness of the $Cu_2O/Au(111)$ films. With decreasing thickness, the depolarizing role of the gold metal gains importance and the charge imbalance inherent to the Cu-deficient termination loses impact. As a consequence, Cu_{Cus} ions become energetically unfavorable in mono- and bilayer films, which renders Cu-deficient structures particular relevant for the interpretation of ultrathin copper oxide films. Additionally, while in 2-3 ML thick films the gold substrate systematically destabilizes the interfacial low-coordinated anions (O_{int}), the latter remain stable at 1ML and assure connectivity between the surface Cu_3O entities. The resulting honeycomb Cu_3O_2 monolayer is predicted to be thermodynamically preferred over the entire range of relevant oxygen conditions, both in GGA and HSE approximations. In the light of this good agreement between the two approaches, all subsequent calculations were performed at the GGA level.

III. Results: Alternative structures in CuO_x monolayers on Au(111)

Figure S3 displays the relative stability of various infinite CuO_x monolayer films built from linear O-Cu-O elements in the form of triangles (T), squares (S), hexagons (H), distorted octagons (O) or a combination of hexagons and distorted squares (1H1S). We find that, due to its stoichiometry, the Cu₃O (T) layer is only stable at extremely oxygen-poor conditions ($\Delta\mu_0 < -4.5 \text{ eV}$), while stability of the unsupported Cu₂O (S) layer requires somewhat higher oxygen chemical potentials ($-4.5 < \Delta\mu_0 < -2.0 \text{ eV}$). At the oxygen-lean conditions of the experiment ($-2.0 < \Delta\mu_0 < -1.5 \text{ eV}$), the honeycomb layer (H) is thermodynamically preferred over the square layer, and this preference increases progressively with increasing oxygen chemical potential. The presence of the Au(111) substrate stabilizes both the S and H layers by a similar amount of about 0.6-0.7 J/m², and thus does not considerably alter their relative stability as a function of the oxygen chemical potential. Different local environments of the anions in the two types of films (O-Cu bonds at 120° in Cu₃O₂ and at 90° in Cu₂O) make the mixing between the two structural motifs energetically unfavorable. However, the existence of square, point or line defects in a perfect honeycomb layer cannot be excluded under oxygen-lean conditions, especially if they enable a better matching with the gold substrate.



Figure S3. Possible building elements for simple regular 2D networks based on linear O-Cu-O entities (T, S, and H) and mixed networks (O and 1H1S) and their formation energies as a function of the oxygen chemical potential, calculated with respect to bulk Cu_2O .

IV. Results: Au-supported Cu₃O₂ stripes:

We present here more detailed results on the structure and relative stability of the five alternative edge structures of monolayer stripes supported on Au (Fig. S4). They involve either a different number of one-fold coordinated cations (compared to two-fold in infinite Cu_3O_2 honeycomb layers) [configurations A, C] or one- / two-fold coordinated anions (three-fold in infinite Cu_3O_2 honeycomb layers) [configurations E, B]. The edge depicted in D contains both, one-fold coordinated cations and two-fold coordinated anions.



Figure S4. Left: Au-supported copper oxide stripes with edges of various stoichiometry. Right: Stripes with A edges of various widths. The atomic structure and STM images are shown in the top and bottom panels, respectively.

We find that at all Cu-terminated edges [A,C and D], the edge anions undergo a strong outward relaxation. Interestingly, this edge effect affects equally anions located in hollow [A] and on-top positions [C and D]. Conversely, anions at O-terminated edges tend to move towards the Au substrate regardless their actual hollow/top site [B and E]. In configurations A and E, the resulting edge structure is consistent with the O_{up}/O_{dn} row sequence of the honeycomb layer. As a consequence, the edge effect enhances locally the existing contrast of the triangular STM pattern. In configurations B, C and D, this is not the case and the edge effect alters qualitatively the STM pattern in its vicinity. Indeed, edge anions in configuration B are not visible, elongated spots appear at the edges of configuration C, and the edge effect propagates deeper into the stripe in D.

When focusing on preferential Cu-terminated [A] stripes as a function of their width (configurations 1-5 in Fig. S4), we systematically find an O_{up} configuration of edge anions associated to a particularly strong STM contrast, in agreement with previous arguments. Interestingly, since the symmetric stripes are composed of an even number of oxygen rows, such symmetric edge effects are not consistent with the

 O_{up}/O_{dn} sequence of oxygen rows in the honeycomb structure. Thus, the finite stripe width introduces a structural frustration which mainly impacts the stripe center. The most paramount frustration occurs for width n = 2, with a clear $O_{up}/O_{dn}/O_{up}$ sequence of anionic rows. However, all other stripes are affected as well and the triangular STM pattern of the honeycomb monolayer is systematically distorted in the stripe centers. We note that the extent of the frustration-induced distortion reduces progressively with increasing stripe width. Indeed, in the case of the widest considered stripe with n = 5, the structural frustration is accommodated by a narrow linear defect (with respect to the structure of an infinite layer) localized in the very stripe center.

V. Experimental thickness of low- versus high-annealed cooper-oxide films

To substantiate our experimental conclusions on the thickness of low- and high-annealed Cu-O films, we display characteristic height profiles of oxide films exposed to different post-annealing conditions (Fig. S5). Films annealed to 600 K and above consist only of a single (2×2) Cu-O monolayer, and step heights to the adjacent Au(111) substrate are about 2.5 Å. Conversely, weakly annealed films, composed of either Au[112]- or Au[110]-oriented oxide stripes, are considerably thicker with topographic heights depending on the initial Cu exposure (10 Å in the present case). The dramatic height loss upon annealing is explained with the dissolution of Cu into the gold single crystal.



Figure S5. STM topographic images of copper oxide films annealed to (a) 725 K ($U_s = 0.5 V$, $45 \times 45 nm^2$) and (b) 450 K ($U_s = 1 V$, $25 \times 25 nm^2$) and corresponding height profiles taken along the dashed lines. While only monolayer (2×2) patches cover the Au(111) support, recognizable by its herringbone reconstruction (a), the film thickness in (b) is estimated from the depth of occasionally occurring holes in the thick oxide film.