Supporting Information: Formation a 2D meta-stable oxide by differential oxidation of AgCu alloys

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Figure S1 Preparation of AgCu(111) single crystal. (left) This shows the Cu2p and Ag3d peak area profiles during annealing in H\textsubscript{2} of an Ag(111) single crystal coated with 50 nm of Cu. (middle) This spectrum stack shows the Cu2p signal during the annealing process. (right) This spectrum stack shows the Ag3d spectra during the annealing process.

Figure S2 (A) LEEM image (E\textsubscript{kin} = 16 eV) of AgCu(111) surface after loading into the SMART microscope and treating the sample with one sputter-anneal cycle. The diameter of the field of view is 12.4 μm. (B) LEEM image (E\textsubscript{kin} = 4 eV) of AgCu(111) after 23 sputter-anneal cycles. The diameter of the field of view is...
12.4 μm. (C) and (D) are LEED patterns ($E_{\text{kin}} = 42$ eV and 52 eV, respectively) corresponding to the field of views shown in (A) and (B).

**Figure S3** Structure of the analysis using a network diagram

There are four different types of experiments:
1. in-situ epoxidation
2. XPEEM
3. DFT
4. NAP-XPS of single crystal

Experiment types 1: in-situ epoxidation and 3: DFT provide links to function (i.e. epoxide selectivity) and structure (i.e. atomic coordinates), respectively. Experiment type 1: in-situ epoxidation provides the link to function via the measurement of catalytic performance and the correlation to spectroscopic features.

Each type of experiment has a set of useful attributes that can be used to link the experiments together. These are noted in parentheses:
1. in-situ epoxidation (XPS, NEXAFS, valence band, conditions)
2. XPEEM (Valence band, LEED, conditions)
3. DFT (Valence band, LEED, conditions)
4. NAP-XPS of single crystal (Valence band, XPS, NEXAFS, conditions)

For experiments where some data might be possible, but are not listed here, it was found that the quality of the data was not sufficient for the data to be useful, due to instrument artefacts, noise or inaccuracy. For instance, NEXAFS was measured in XPEEM, but the signal quality was insufficient. Or NEXAFS can be calculated with DFT but the accuracy of the results was not sufficient for comparison with experiment.
By networking commonly observed data sets among different experiments, we draw a link between atomic structure and function.

In B) we see that valence band connects all experiment types. In C) we have a connection between experiment types 1: in-situ epoxidation and 4: NAP-XPS of crystal. Nodes that have no connection are greyed out. Thus here we see that this combination of data only gives us correlation between spectroscopic fingerprints and functional performance.

In D. we have links between experiment types 2: XPEEM and 3: DFT. This link provides correlation between experimental data and atomic structure. In E we have a connection between experiment types 1: in-situ epoxidation and 4: NAP-XPS of crystal. This link provides a connection between a spectroscopic signature and a correlation with functional performance.
In F. we have links between experiment types 1: in-situ epoxidation, 2: XPEEM, 3: DFT and 4: NAP-XPS of crystal. These links provide confidence that what was observed in each experiment is the same as the experiment it is linked to.

Panel G. shows a complete connectivity graph, where the colors of the lines represent the type of data or attribute that gives rise to the link. Panel H. shows a complete connectivity graph, where the thickness of the line represents the number of links that exist.
Figure S4 schematically illustrates the XPS and NEXAFS process in the case of Cu$_2$O and the p2 structure. The excitation of a core level electron (i.e. from the Cu 2p level) lead to a formation of a core-hole in both cases. While in XPS the excited electron is removed from the system, in NEXAFS the electron remains in the system, bound as an exciton to the core-hole. Generally, in metallic systems, core-hole screening effects are similar for XPS and NEXAFS processes, since there is a vast availability of valence electrons in the Fermi sea of metallic systems. Consequently, XPS binding energies (Cu 2p) and NEXAFS absorption edge positions (Cu L-edge) are the same in metallic systems.

They generally differ in cases where there is a band gap (e.g. Cu$_2$O in Figure 13a). In such cases, the NEXAFS process requires the core electron not only to be excited to the Fermi energy ($E_f$), but beyond by an amount equal to conduction band minimum (CBM) – $E_f$. Furthermore, the core-hole screening in semiconductors is generally more effective in NEXAFS than in XPS because the final state in the NEXAFS process contains one more electron than the final state in the XPS process.

The observed difference between the Cu L$_3$-edge of the Cu$_x$O$_y$ structure and Cu$_2$O is not trivial to explain. Both materials have very similar initial-state energies (as calculated by DFT), and both have essentially identical Cu 2p binding energies. DFT also shows that both have very similar charge densities. However, NEXAFS shows that Cu$_x$O$_y$ is substantially different from Cu$_2$O. The observed difference can be explained if one assumes the Cu$_x$O$_y$ structure has no band gap (i.e. has a finite density of states at the Fermi level). If this is the case, then the band gap term plays no role in the NEXAFS process, and the electron only needs to be excited from the Cu 2p state to the Fermi level for X-ray absorption to occur at the Cu L-edge.

S4. Schematic illustration of the XPS and NEXAFS process in the case of (a) a semiconductor exhibiting a band gap (Cu$_2$O) and (b) a system without bandgap (well coupled p2 structure).
Figure S5 Projected density of states (PDOS) of the CuO-1ML/Ag(111) structure, illustrating the contribution of O states over a wide energy range.

Table S6 Table of calculated surface energies for different expansions of the p2 layer.

| Overlayer | Area (Å²) | E_{ads} (eV) | E_{form} (meV/Å²) | E_{form, vdw} (meV/Å²) |
|-----------|-----------|--------------|------------------|----------------------|
| 12x2      | 180.06    | -8.60        | -47.80           | -68.87               |
| 13x2      | 195.06    | -9.59        | -49.15           | -71.67               |
| 14x2      | 210.07    | -9.50        | -45.21           | -62.84               |

To investigate the relative stability of p2 structures in different unit cells, we compute the formation energy per unit area $E_{\text{form}}$ defined as:

$$E_{\text{form}} = \frac{1}{A} [E(p2/Ag) - E(p2) - E(\text{Ag})]$$

where $E(p2/Ag)$ is the total energy of the adsorption system, $E(p2)$ is the total energy of an isolated layer of the p2 oxide layer with its optimized lattice parameter, $E(\text{Ag})$ is the total energy of the Ag slab and $A$ is the surface area. We consider three unit cells, where the p2 overlayer is accommodated in a 12×2, 13×2 or 14×2 Ag(111) surface unit cell. In the 12×2 unit cell, the p2 overlayer, with a stoichiometry Cu$_{18}$O$_{12}$, has a 2×2 periodicity. In the 13×2 unit cell, the same p2 overlayer is stretched along one
direction (by 1/12 ~ 8%) and in the 14×2 unit cell it is stretched even further. Given the large size of these unit cells, HSE06 calculations would be extremely expensive; the total energies reported above were therefore computed using the PBE exchange and correlation functional. Table S.5 shows that the 13×2 unit cell provides the lowest formation energy, in agreement with the experimental findings showing that the p2 structure is stretched by ~8% with respect to a commensurate structure with 2×2 periodicity with respect to the Ag substrate. We also tested the effect of including van der Waals (vdW) interactions, using the exchange dipole model (XDM) of Becke and Johnson\(^5\). We find that, while significant in magnitude (-21.1, -22.6 and -17.6 meV/Å\(^2\) for the 12x2, 13x2 and 14x2 unit cells, respectively), dispersion interactions do not show a strong variation with the registry of the oxide with the substrate. The 13x2 unit cell provides the lowest formation energy even in this case.

**Table S7** Table of DFT calculated free energies for different p2 configurations relative to the substrate

| Structure | ΔE (eV) |
|-----------|---------|
| Hollow    | 0.00    |
| Bridge    | 0.08    |
| Top       | 0.28    |

Table S7 compares the total energy of structures obtained translating the p2 overlayer in the 2x2 unit cell with respect to the underlying Ag(111) substrate. The hollow structure refers to the most stable configuration, where Cu atoms of the p2 overlayer occupy hollow sites of the Ag(111) surface. The bridge and top configurations are only slightly less stable (0.08 and 0.28 eV respectively).
Figure S8 (a) LEEM image ($E_{\text{kin}} = 6$ eV) of AgCu(111) surface after cooling the sample from 300 °C to liquid nitrogen (LN$_2$) temperature in $1 \times 10^{-5}$ mbar O$_2$. There is no microscopic evidence that the surface oxide has morphologically changed upon cooling. We cooled down the sample in an attempt to stabilize (minimization of thermal drift) and enhance the contrast of the collected LEED pattern in order to perform a full LEED-IV analysis for the oxide structure determination. The survey spectrum at LN$_2$ temperature of the region shown in the LEEM image (b), shows that the most common contaminants carbon and sulphur, nor any other contaminants, are present on the surface. The absence of sulphur containing species can be seen from the missing S2p states in the survey with binding energies between 165 – 167.5 eV$^1$, as well as the absence of intensity of S-related states in the valence band (c), which would occur at binding energies between 6.5 – 8.5 eV$^1$. However, the valence band spectra stack collected at different photon energies in the area shown in the LEEM image (c), indicates the formation of an additional species on the surface upon cooling, with a binding energy of 1.7 eV. As the photon energy is swiped across the Cooper minimum (around 170 eV), one can see that those states scale with the Ag 4d states. We therefore interpret this additional species as adsorbed oxygen on Ag. A strong hybridization of the Ag 4d and O 2s states leads to the observed scaling of the two bands. (d) shows the direct comparison of the VB measured with a photon energy of $h\nu = 170$ eV at 350°C (red curve) and at liquid nitrogen LN$_2$ temperature (both at $5.5 \times 10^{-5}$ mbar O$_2$). By comparison of the O 1s spectra measured under the two temperatures, shown in (e), it becomes evident that an additional shoulder on the high binding energy side in the O1s spectrum appears. It is conceivable that, during cooling, additional oxygen atoms adsorb onto free fcc sites in-between the p2 structure, as depicted with the filled red circles in the inset of (f).

The calculated projected density of states of this structure show that, indeed, this oxygen species gives reason to expect a higher XPS intensity in the valence band at a binding energy of about 1.5 eV. However, the calculations also reveal that this structure is not particularly stable. The bond between the
extra O atom and the surface is approximately 0.2 eV less stable as compared to an O-O bond in an O₂ molecule. If the position of the adsorbed oxygen atom is moved closer to a Cu atom of the p2 oxide, the stability increases to a maximum of -0.1 eV, relative to an O₂ molecule. In summary, the identity of this additional mystery oxygen species at low temperature remains unknown for now, as a higher spatial resolution is required to identify the exact adsorption sites. A further complication that arises with the adsorption of this species is that fact that it contributes in an unknown way to the LEED spot intensities, that are of critical interest in a LEED-IV analysis. Hence, we were not able to use LEED-IV to fully describe the observed oxide surface structure of CuₓOᵧ.

Table S9 Calculated Cu 2p binding energies

| Calculated binding energies in eV (referenced to Cu metal) |
|-----------------------------------------------------------|
| P2 | -0.2 |
| Cu₂O | -0.9 |
| Cu | 0.0 |

| Calculated initial states in eV (referenced to Cu metals) |
|----------------------------------------------------------|
| P2 | -0.8 |
| Cu₂O | -1.3 |
| Cu | 0.0 |

| Calculated final state shifts (eV) |
|-----------------------------------|
| P2 | 0.6 |
| Cu₂O | 0.4 |
| Cu | 0.0 |

Table S10 Calculated atomic charges

| Bader (e) | Löwdin (e) |
|-----------|------------|
| p2/Ag(111) |            |
| Cu | +0.60 | +0.65 |
| O | -1.14; -1.04 | -1.07; -0.99 |
| Ag | 0.00 | +0.17 |
| p2 free standing |            |
| Cu | +0.73 | +0.79 |
| O | -1.14; -1.05 | -1.07; -0.99 |
| Cu₂O (bulk) |            |
| Cu | +0.56 | +0.62 |
| O | -1.18; -1.08 | -1.03; -1.03 |
| CuO (bulk) |            |
| Cu | +1.11 | +1.14 |
| O | -1.11 | -1.03 |
Table S10 reports atomic charges computed using both the Bader and the Löwdin methods for the p2 structure, in comparison to bulk CuO and Cu₂O. The numbers reported indicate the charge in units of the electrons, computed as difference with respect to neutral Ag, Cu and O. Clearly the charges on Cu and O in the p2 structures are closer to those found in Cu₂O compared with those found in bulk CuO, in agreement with the experimental spectroscopy results reported in the main text.

**Figure S11** PDOS of the p2/Ag(111)structure
Figure S12 PDOS of the Cu₄O₄/Ag(111) structure
Figure S13

The following panels outline the analysis done to arrive at the difference spectra used in Figure 1 of the main text.

**Step 1:** Raw data. Spectra collected as a time series. The spectral line-shape changes with time, which indicates there is more than one component in the data set.

**Step 2:** Principle Component Analysis (PCA) is performed to determine how many components are present. PCA shows two main components, with a small contribution from a third.

**Step 3:** The two most different spectra in the data set are taken (top and bottom spectra from step 1).

**Step 4:** A set of difference spectra are constructed from the two spectra of step 3. \( S_1 = xS_2 + (1-x)S_1 \) where \( S_1 \) and \( S_2 \) are the raw spectra, \( S_1 \) is the difference spectrum and \( x \) is a factor.

**Step 5:** Two spectra are subjectively chosen from the difference spectra to be used as basis vectors. The spectra were selected that 1) represent most closely the AgCu metal and 2) a Cu-oxide.

**Step 6:** The basis vectors are used to fit the original spectra, and a profile is constructed to show how contribution of each basis vector changes with time. The resulting trend is as expected from the interpretation of the basis vectors (i.e. transition from more metallic to more oxidic.)
Table S14 - Compilation of O1s binding energies

| Surface   | O1s BE       | citation |
|-----------|--------------|----------|
| Cu2O      | 530.15 (528.94 shoulder) | Greiner² |
| CuO       | 529.24       | Greiner² |
| Cu-(O)    | 529.6-529.8  | Greiner² |
| Ag(O-α₁)  | 528.1-528.4  | Rocha³   |
| Ag(O-α₂)  | 529.1-529.2  | Rocha³   |
| Ag(O-α₁)  | 530.1-530.4  | Rocha³   |
| Ag(O-β)   | 529.5-529.7  | Rocha³   |
| Ag(O-β)   | 530.8-531.0  | Rocha³   |
| SiO₂      | 531.5-532.4  | Rocha³   |
| SOₓ       | 530.7-530.8  | Jones⁴   |

Figure S14 - Ambiguity of non-spatially resolved O1s spectra

Figure S14 shows an O1s spectrum measured from AgCu (0.5 % Cu) in a 1:1 mixture of O₂ and C₂H₄ at 0.5 mbar and 350°C. The peaks binding energies used to fit this spectrum are taken from literature values of all common Cu-O and Ag-O surface species (as well as SiO₂, a common contaminant). One can see that there are at least 10 possible O1s species within a binding energy range of 3.3 eV, with each peak having a typical full-width-half-max of 1.1 eV. With so many free parameters, the ability to analyze the O1s spectrum from non-spatially resolved measurements is very unreliable, and conclusions are associated with a very high uncertainty.
**Figure S15** - Comparison of DOS for freestanding p2 and p2 adsorbed onto Ag(111) surface

Figure S.15 shows a comparison of calculated DOS for a p2 layer adsorbed to an Ag(111) surface, and a p2 layer, freestanding in vacuum. One can see that the adsorbed p2 layer has no band gap, while the freestanding p2 layer has a band gap.
Figure S16 shows a comparison of the ring dimensions for the strained Cu₄O₁₃x₂ structure and the (111) plane of the Cu₂O structure.

Figure S17 (top left) SEM image, (top right) O K EDX map, (bottom left) Cu L EDX map and (bottom right) Ag L EDX map of AgCu foil (0.5 at. % Cu) after being heated in 0.3 mbar ethylene and oxygen at 300 °C for eight hours.

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