Supporting Information

Direct Evidence of Subsurface Oxygen Formation in Oxide-Derived Cu by X-ray Photoelectron Spectroscopy
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Supplementary Information

EXPERIMENTAL METHODS

OD-Cu preparation
The oxide-derived (OD) Cu sample was prepared by H$_2$ thermal reduction according to the method reported by Arnau et al.\textsuperscript{1} The polycrystalline Cu was purchased from a commercial retailer, Surface preparation laboratory (SPL, the Netherlands), and directly used for the sample preparation as received. After rinsing with iso-propanol and DI-water for several times and drying under pure N$_2$ stream gas, the crystal was placed in a muffle furnace (Thermo Scientific) under the air atmosphere at 500 °C for 30 min with a heating rate of 10 °C/min. After this air oxidation process, visual inspection of the specimen revealed it to be dark in color and had a rough appearance, as shown in Figure S1a. The specimen was allowed to cool down slowly to the room temperature inside the furnace over several hours. The as-prepared Cu oxide precursor was then mounted on a custom designed sample holder (the specimen, as seen in Figure S1, is hat shaped to fit the sample holder) and subjected into the experimental vacuum chamber, the POLARIS end-station. The vacuum chamber was first pumped down to high-vacuum pressure regime (< 1x10$^{-6}$ mbar) and then the crystal was mildly cleaned by argon ion sputtering (voltage: 1 keV) for 30 min. The sample was then reduced inside the vacuum chamber by back-filling with 300 mbar pure H$_2$ and keeping the sample at a temperature of 140 °C for 2 hours. After H$_2$ thermal reduction process, the sample surface showed a shining reddish color (Figure S1b, image taken post XPS study) and the chamber pressure was pumped down to the high vacuum pressure regime again, yet the sample was still kept at 140 °C to avoid water and/or other gas adsorption on the surface that can obscure the XPS study. Throughout the OD-Cu preparation, XPS survey spectra, containing the core-levels from about 2500 eV binding energy, Cu 2p is located at ~930-960 eV region not considering satellites, to Fermi level, were collected under vacuum for multiple times to track appearance of possible contaminations.
Figure S1. The hat-shaped polycrystalline copper specimen, top view. (a) After oxidation in ambient air atmosphere at 500 °C for 30 min. (b) OD-Cu after thermal reduction in 300 mbar H₂ in the analysis vacuum chamber. The brown circle, indicated by the dashed red arrow, is the Cu₂O film that was prepared by oxidation in O₂ gas flow in front of XPS analyzer. Note: Small exfoliation on the surface is formed during removing the sample from the holder.

Cu₂O preparation
Thanks to the special front cone design of POLARIS, small amounts of pure O₂ could be dosed directly onto the hot OD-Cu surface inside the vacuum chamber while keeping the sample in XPS measurement position. The O₂ gas flow was set as 0.16 L/min and the valve was opened for only 1 sec, and at the same time the sample surface was still kept at 140 °C. The optical photo of the surface post oxygen gas exposure (Figure S1b) clearly shows the color difference between metallic Cu surface (reddish) and cuprous oxide surface (brown) where the circle size is comparable to the dimensions of the front cone apex.

XPS measurements
The XPS measurements were carried out using the POLARIS endstation at the P22 beamline[2] at the Petra III synchrotron radiation facility at DESY, Hamburg, Germany. The endstation is equipped with a modified ScientaOmicron HiPP-2 electron analyzer. The experimental geometry was X-ray incident angle of ~1.5° (=88.5° with respect to surface normal) and normal emission. The gap between the front cone and the sample surface was kept at around 500 μm through the whole experiment. Using hard X-rays, the surface X-ray reflectivity can be neglected due to the surface roughness and the 1.5° incident angle. Due to the front cone design,[2b] only electrons from a small area of the irradiated spot on the surface are recorded. In practice this means accurately estimating the actual photon flux on the area being measured is impossible. Therefore, this study relies on relative intensities of species present in the specimen for each photon energy. Comparisons between photon energies are only in terms of changes in the relative intensities. The electron scattering of gas molecules in the high-vacuum between the sample and the electron analyzer’s front cone is neglectable at the used photon energies and scanned core-levels, i.e. the photoelectrons’ kinetic energies. Spectral information as function of depth from surface was acquired by varying the probing depth by using
a series of different X-ray photon energies: 3266, 4600, 6000, 8000, and 9030 eV. These photon energies were selected out by using the beamline’s double crystal monochromator, which is housing Si(111) crystals for 3266 eV and Si(311) crystals for the other energies.

DATA ANALYSIS AND INTERPRETATION

XPS data analysis
A representative survey XPS spectrum is shown in Figure S2, it contains the binding energy region from 2500 eV to 0 eV and was measured using 3266 eV photons, giving the most shallow probing depth of all used photon energies. In the Figure, the Cu and O core-levels in this region are indicated as well as the Cu LMM Auger electrons. In addition, the 3rd harmonic light (3×3266 eV = 9798 eV) brings the deep Cu 1s core-level into this binding energy window. No peaks in binding energy regions of common contaminants are resolved, meaning the level of contaminants is small, if present.

Figure S2. XPS survey measurement with 3266 eV photons of the as prepared OD-Cu sample. The expected XPS Cu and O components are visible as well as Auger Cu LMM electrons. The Cu 1s is reached owing to the 3rd harmonic of the light. Traces of common contaminants are not seen.

In Figure S3, X-ray photoelectron spectra of the Cu 2p-region are presented at different photon energies together with a reference signal from a prepared Cu₂O film. Separating metallic copper from Cu₂O is notoriously difficult relying on Cu 2p, especially in system where both are present. The difficulty to separate the peaks stems from that both 2p₃/₂ and 2p₁/₂ components overlap and the satellite features of Cu₂O are weak. Residing to the Auger Cu LMM (see main text for spectra) peaks provide support in the discrimination as metallic copper and Cu₂O provide strong differences. The Auger electrons have the same kinetic energy independent on the photon energy leading to the inability of depth profiling (compare Fig. S8). The Cu LMM electrons have, in comparison to the XPS Cu 2p electrons, much lower probing depth
because of their lower kinetic energy, meaning shorter electron IMFP. This provides the ability of determining the state of copper in the near-surface region.

The Cu 2p$_{3/2}$ peak was fitted, after a Shirley background was removed, using a Doniach-Sunjic line profile convoluted with a Gaussian line profile. For all photon energies, the same Lorentzian full-width half maximum (LFWHM), life-time broadening, was used while the Gaussian FWHM (GFWHM) was permitted to vary in order to account for the light’s energy band width and the resolution of the electron analyzer. The recorded variations in GFWHM was used for the fitting of O 1s.

![Figure S3](image)

**Figure S3.** XP spectra for the Cu 2p region for OD-Cu recorded using different photon energies and Cu$_2$O reference sample. The spectra have all been normalized to the background intensity on the low-binding energy side of the 2p$_{3/2}$ spin-orbit component. A constant offset is added for clarity. The stars point out the binding energy positions for the Cu$_2$O satellites.

![Figure S4](image)

**Figure S4.** O1s XPS spectra
Fitting procedure of O 1s XPS

The binding energy scale of O 1s was corrected to the peak position of Cu 2p_{3/2} for each photon energy, not considering the recoil effect[^3], which will cause an apparent peak shift towards higher binding energies with higher photon energies. It should be mentioned that the significant difference between X-ray attenuation length and photoelectron IMFP tentatively could ionize an insulating oxide layer buried deeper into the specimen than what can be probed by XPS, causing an electric field. However, no effects on the peaks positions from charging effects could be observed. The small shifts observed are within what is expected to be caused by the recoil effect.

Prior the peak deconvolution of the O 1s region, a Shirley background was removed from each spectrum using the Fityk 1.3.1 software. The components in the XPS O 1s region was fitted using Doniach-Sunjic line profiles convoluted with Gaussian line profiles as implemented in the FitXPS 3 software. The aim of the peak fitting is to explain the observed spectral changes with varying the photon energy. To do this, a need of four components was identified. One component for Cu_{2}O and one for CuO. The remaining two components are permitted to be broader as they model oxygen species in an unordered copper film, where many similar but equal sites are contributing to each peak. Two assumptions were made to simplify the peak fitting: (i) the Cu_{2}O and CuO peaks will have the same LFWHM and GFWHM. (ii) The two broad components (representing O_{int} and O_{Cu,vac}, see main text) will have the same LFWHM and GFWHM. The relative energy position of the peaks were kept fixed while the entire region was permitted to move to compensate for the recoil effect.[^3] Restrictions for energy position of the region had to be added for some photon energies to prevent unphysical peak shifts.

To compensate unknown energy broadening from the light and the electron spectrometer in the fitting, the Cu_{2}O and CuO peaks’ GFWHM were mimicked those of Cu 2p_{3/2} while the same LFWHM was kept for all photon energies. In Table S1, the fitting parameters for the oxygen components are listed, where the GFWHM are for hv = 3266 eV.

[^3]: Restriction for energy position of the region had to be added for some photon energies to prevent unphysical peak shifts.

Table S1. Fitting parameters for O 1s-region. ∆BE = Shift in binding energy relative the Cu_{2}O component. LFWHM = Lorentzian Full-Width Half-Maximum, GFWHM = Gaussian Full-Width Half-Maximum (for hv = 3266 eV), FWHM = Peak’s total Full-width half-maximum.

| Peak   | ∆BE [eV] | LFWHM | GFWHM | Asymmetry | FWHM |
|--------|----------|-------|-------|-----------|------|
| Cu_{2}O | 0.00     | 0.14  | 0.76  | 0.002     | 0.83 |
| CuO    | -0.80    | 0.14  | 0.76  | 0.002     | 0.83 |
| O_{Cu,vac} | 1.02   | 0.30  | 1.60  | 0.002     | 1.77 |
| O_{int} | 2.95     | 0.30  | 1.60  | 0.002     | 1.77 |
Estimation of fitting sensitivity

The sensitivity of the peak intensity to the fitting is tested by using the optimized peak fitting and varying the intensities of $O_{\text{int}}$ and $O_{\text{Cu,vac}}$ components by ±10 % and ±20 %. Here, the XPS O 1s spectrum collected with 6000 eV photons is used as it is an intermediate between strong and weak components. After varying the intensity of one peak, the others were permitted to get re-optimized. The results are shown in Figure S5. As can be determined, ±10 % does not provide any greater impacts on the results, neither in spectrum line-shape nor in relative intensities. For ±20 %, the line-shapes are noticeably affected as well as the relative intensities when varying the $O_{\text{Cu,vac}}$ component. This shows the accuracy of the peak-fitting results are good enough for the purpose of this study.

Figure S5. Investigation on the stability by altering the intensity of $O_{\text{Cu,vac}}$ and $O_{\text{int}}$ by ±10 % and ±20 % from the optimized values as obtained from the peak fitting. The top panels illustrate the impact on the reproduction of the line shape of the experimental data and the lower panels illustrate the impact on relative coverage estimation. (Left) Varying the $O_{\text{Cu,vac}}$ component. (Right) Varying the $O_{\text{int}}$ component.
Estimation of relative oxygen coverage and atomic ratio O/Cu
The relative coverage of the different oxygen species for each photon energy was calculated from the integrated area under each component from the peak fitting without taking the IMFP into consideration. This is refined in the calculation on the atomic ratios. To estimate how the distribution changes with depth, the increased probing depth with photon energy is utilized. The result is shown in Figure 3b in the main text.

To get a crude estimation of the atomic ratio of oxygen and copper in the specimen, both the photoionization cross-section and IMFP for the electrons have to be taken into consideration, both depend on the photon energy and the core-level. Here, the O 1s and Cu 2p$_{3/2}$ core-levels will be resorted. As the distribution function w.r.t. the depth is unknown, each specie is here treated as a uniform distribution in a Cu(100) crystal. The impact of the IMFP is estimated according to the equation below, where I is the intensity leaving the surface and $I_0$ is the initial intensity at all depths.

$$I = \int_0^{\infty} I_0 \exp\left(-\frac{x}{\lambda}\right) dx = \lambda I_0$$

The integrated intensity of each component from the XPS O 1s and Cu 2p$_{3/2}$ core-levels are normalized to the photoionization cross-section and the IMFP before the ratio is calculated. In Table S2, the photoionization cross-sections and IMFPs for the different core-levels and photon energies are collected. The obtained atomic percentage oxygen coverages are presented in Figure 3c in the main text.

Estimations of the probing depth.
To facilitate the oxygen depth distribution estimations, the probing depth for each photon energy needs to be estimated. In Figure S5, it is seen that 10 % variations in the intensity of the components have no significant impact of the result. Therefore, the information depth is here defined as the depth from which and above 90 % of the total intensity is obtained. For comparisons, also the probing depth for IMFP and 3×IMFP are included.

The X-ray photoelectron spectra depend on multiple variables that are photon energy dependent, the interesting parameters for this study are the photoionization cross-section ($\sigma$), photoelectron inelastic mean-free path ($\lambda_{\text{IMFP}}$), and the X-ray attenuation length ($\lambda_{\text{hv}}$). In the calculations, even distribution of the oxygen is assumed in a perfect Cu(100) crystal, which has an atomic plane distance of about 1.81 Å. This of course is crude considering the specimen where heavily distorted copper layer is on top of Cu$_2$O. In Table S2, literature data are collected for the relevant parameters mentioned above. As can be seen in the table, the
photoionization cross-section ratio of O 1s and Cu 2p\textsubscript{3/2}-regions remain reasonable constant for all photon energies.

**Table S2.** Values taken from published sources for photoionization cross section (\(\sigma\)), photoelectron inelastic mean-free path (IMFP), and X-ray attenuation lengths in copper. Photoionization data is obtained from interpolation of reported numbers.\[^4\] The X-ray attenuation length was obtained from the X-ray attenuation length calculator at the web open source (The Center for X-Ray Optics, Berkeley lab, \texttt{https://henke.lbl.gov/optical_constants/}) for 1.5\(^\circ\) incidence light.\[^5\] The IMFP in copper were calculated using NIST Electron Inelastic Mean-Free Path database.\[^6\]**

| hv [eV] | Peak         | Photoelectron kinetic energy [eV] | \(\sigma\) \[10^{-3} \text{ kb}\]** | \(\sigma_o/\sigma_{Cu}\) | IMFP [Å] | X-ray attenuation length [Å]** |
|---------|--------------|----------------------------------|----------------------------------|--------------------------|-----------|-------------------------------|
| 3266    | O 1s         | 2736                             | 3.8                              | 0.23                     | 36.3      | 360                           |
|         | Cu 2p\textsubscript{3/2} | 2336                             | 16.6                             |                          | 32.0      |                               |
| 4600    | O 1s         | 4070                             | 1.4                              | 0.24                     | 50.0      | 1094                          |
|         | Cu 2p\textsubscript{3/2} | 3670                             | 5.8                              |                          | 46.0      |                               |
| 6000    | O 1s         | 5470                             | 0.6                              | 0.25                     | 63.6      | 2405                          |
|         | Cu 2p\textsubscript{3/2} | 5070                             | 2.6                              |                          | 59.8      |                               |
| 8000    | O 1s         | 7470                             | 0.3                              | 0.26                     | 81.9      | 5530                          |
|         | Cu 2p\textsubscript{3/2} | 7070                             | 1.1                              |                          | 78.3      |                               |
| 9030    | O 1s         | 8500                             | 0.2                              | 0.26                     | 91.0      | 1016                          |
|         | Cu 2p\textsubscript{3/2} | 8100                             | 0.7                              |                          | 87.5      |                               |

In Figure S6, the calculated signal attenuations for Cu 2p\textsubscript{3/2} (left panel) and O 1s (right) are shown. The solid lines take both X-ray attenuation in copper (squares) and IMFP (solid dots) into consideration. It is apparent that the impact of X-ray attenuation varies heavily between the photon energies. All the intensity numbers for the different depths are relative the intensity of the surface layer, which is 100 %. It is noticeable that for the 9030 eV, the X-ray attenuation is heavily impacted by the interaction with the Cu 1s (K-shell) core-level. The two horizontal lines indicate intensities for the IMFP and 3xIMFP for the photoelectrons.
**Figure S6.** The effects of X-ray attenuation and photoelectron IMFP in copper (left) Cu 2p$_{3/2}$ and (right) O 1s. The relative contribution is relative the surface-most layer, that is 100 %. The unfilled squares are the effect of X-ray attenuation, the filled circles are the photoelectron IMFP, and the solid lines are when considering both. The horizontal lines correspond to 5% and 37%, respectively.

Figure S7 show the integrated intensity from the surface to depth d for each photon energy. The upper panel show the XPS O 1s signal, the middle panel shows the XPS Cu 2p$_{3/2}$ signal, and the bottom panel shows the Auger Cu LMM signal. The three horizontal lines correspond to 95 % ($\sim$1/e$^3$, $\sim$3×IMFP if X-ray attenuation is not been considered), 90 %, and 63 % ($\sim$1/e, $\sim$IMFP if X-ray attenuation is not been considered) of the total signal. The depths for which these intensities are reached for the different photon energies and core-levels and Auger Cu LMM are presented in Table S3. It is observed that the short IMFP of the Auger Cu LMM electrons makes the impact of X-ray attenuation so low that depth profiling of the state of copper using Auger Cu LMM is not possible.

**Figure S7.** Percent of total signal from surface to depth d [Å] for different photon energies and electrons from O 1s, Cu 2p$_{3/2}$, and Cu LMM. These data assume even oxygen concentration with depth and a perfect copper lattice.
Table S3: Depths [Å] for different photon energies where 90 % and 95 % of the total signal from O 1s, Cu 2p$_{3/2}$, and Cu LMM for a uniform oxygen distribution is obtained. $\Delta$ is the difference between the deepest and narrowest probing depth. Also, the attenuation depth, 1/e of the signal, is added.

| Photon energy / eV | 3266 | 4600 | 6000 | 8000 | 9030 | $\Delta$ |
|-------------------|------|------|------|------|------|---------|
| Integrated intensity limit |      |      |      |      |      |         |
| XPS O 1s          |      |      |      |      |      |         |
| 90 %              | 74   | 108  | 141  | 185  | 190  | 116     |
| 95 % (1/e$^3$)    | 98   | 141  | 183  | 241  | 249  | 151     |
| 1/e               | 33   | 48   | 62   | 81   | 84   | 51      |
| XPS Cu 2p$_{3/2}$ |      |      |      |      |      |         |
| 90 %              | 67   | 100  | 132  | 176  | 183  | 116     |
| 95 % (1/e$^3$)    | 87   | 131  | 172  | 230  | 239  | 152     |
| 1/e               | 29   | 44   | 58   | 77   | 81   | 51      |
| Auger Cu LMM      |      |      |      |      |      |         |
| 90 %              | 33   | 33   | 33   | 33   | 33   | 0       |
| 95 % (1/e$^3$)    | 44   | 44   | 44   | 44   | 44   | 0       |
| 1/e               | 13   | 13   | 14   | 14   | 13   | 1       |

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