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Flat-surface-assisted and self-regulated oxidation resistance of Cu(111)

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The formation of an ultraflat surface on copper thin films is important for suppressing the oxidation process, but the formation of multi-atomic steps and terraces is a result of the basic atomic stacking process and difficult to avoid. Here, we develop an innovative strategy for fabricating copper thin films with a semi-permanently oxidation-resistant surface. Comprehensive atomic-resolution microscopy reveals that our thin film consists mostly of flat surfaces and occasional mono-atomic steps. Our first principles calculations show that a mono-atomic step edge is as impervious as a flat surface to oxygen consistent with our experimental observations. Furthermore, the first principles calculations exhibit self-regulated oxidation resistance at the top surface layer: when the oxygen coverage of fcc sites of the surface exceeds 50%, the adsorbed oxygens on the top layer suppresses further adsorption of additional O atoms and renders the ultraflat Cu surface to be more oxidation resistant.

The oxidation resistance of copper is particularly important because unwanted oxidation can cause the deterioration of properties that are critical to a vast range of applications, including nanocircuitry in the semiconductor industry and transparent conducting electrodes using nano-patterning or nano-wiring in the field of electro-optics¹⁻⁷. Recent *in situ* atomic-resolution electron microscopy studies uncovered that oxides grow by oxidation through stepped Cu surfaces and that oxidation occurs via direct growth of Cu₂O on flat terraces with Cu adatoms detaching from steps and diffusing across terraces⁸⁻¹⁰. Although there are numerous studies on the oxidation of copper, the fact that a flat copper surface itself can be free of oxidation has been ignored, except for the phenomenon that single-crystalline copper is more resistant to oxidation than polycrystalline copper. Given that the step edge is vulnerable to oxidation because surface steps act as the dominant source of Cu adatoms for oxide growth on surface terraces^{2,10}, endowing the copper surface with oxidation resistance properties may be realized if the surface step edges are avoided^{6,11,12}. The close-packed Cu(111) surface is superior to other Cu surfaces^{13,14}.

In this work, we experimentally demonstrate that a tightly coordinated flat surface of a single-crystal Cu(111) film (SCCF) grown by atomic sputtering epitaxy (ASE)¹⁵ is free of oxidation and even remains stable against oxidation semipermanently. Theoretical calculations reveal the atomic-scale oxidation-resistant mechanism of the flat copper surface from the perspective of the likely pathways for oxygen atoms into the viable structures of the copper surface with a discovery of the self-regulated protection layer at elevated oxygen coverages. The implication is that the atomically flat surface of the SCCF shows oxidation-resistant properties due to the high energy barrier for oxygen infiltration and self-regulation due to high oxygen coverages.

Flatness of Cu(111) surface

The surface and structural characteristics of a 110-nm-thick SCCF with an ultraflat surface (see Extended Data Fig. 1 for a large-scale characterization) are examined using high-resolution (scanning) transmission electron microscopy (HR(S)TEM) combined with geometrical phase analysis (GPA)^{16,17} (Fig. 1). The cross-sectional (S)TEM images (Figs. 1a, e) show that the copper film grew along the [111] direction, thus creating an exposed surface (111) plane with mono-atomic step edge structures. Typical multi-atomic step edges and intrinsic defects such as grain boundaries and stacking faults are rarely detected. It is remarkable that the outermost copper surface layer has the same atomic configuration as the interior copper without evidence of surface relaxation or structural changes by surface oxidation even at the step edge positions. To examine the local strain behavior near the surface

region, lattice distortions along the in-plane (x) and out-of-plane (y) directions relative to the inside of the SCCF were measured by the GPA technique (Figs. 1b, c). The resulting strain field maps (E_{xx} and E_{yy}) clearly show that no noticeable change in lattice strain is observed throughout the entire surface region. This means that the SCCF has a nearly perfect atomic structure up to its outermost surface layer without any structural defects such as vacancies or dislocations. The simulated HRTEM image using an amorphous carbon/flat copper surface model matches well with the experimental HRTEM image (Fig. 1a). By comparing the layer spacings of the (111) stacking planes ($d_{(111)} = 0.21$ nm) between the simulated and experimental images (Fig. 1d), it is evident that the Cu surface is undistorted and ultraflat and has the same structure as bulk Cu. Annular dark field (ADF) and annular bright field (ABF) STEM images of the SCCF surface are complementary to the HRTEM observation results (Fig. 1e). We can discriminate this remarkable ultraflat surface structure of the SCCF from that of the conventional polycrystalline Cu thin film (PCCF) and the Cu(111) surface of a bulk Cu single crystal with a notable oxidised copper layer on top of them (Extended Data Fig. 2 and Fig. 3). Strikingly, we found that the SCCF sample maintained its ultraflat and pristine surface even after more than a year of air exposure (Fig. 2a–d), suggesting that our SCCF has exceptional oxidation-resistant properties. (also see Extended Data Fig. 4 for a large-scale scanning tunneling microscope (STM) topography)

Fig. 1 | Surface of a single-crystal copper thin film (SCCF) grown by atomic sputtering epitaxy (ASE). **a**, Cross-sectional HRTEM image of the surface part of the copper thin film observed in the $[1\bar{1}0]$ orientation. The simulated HRTEM image and the corresponding model of the carbon-copper supercell are presented alongside the experimental HRTEM image. **b-c**, In-plane (E_{xx}) and out-of-plane (E_{yy}) strain field maps obtained by geometrical phase analysis (GPA) for the experimental HRTEM image. The reference area of Cu chosen for

GPA is marked by the white square boxes in each map. Note that complex patterns for parts of the carbon film are shaded by a gray color for clarity, as those are not relevant for the strain behavior of the SCCF. **d**, Comparison of the experimental and simulated intensity profiles obtained along the out-of-plane direction for (111) layer spacings ($d_{(111)} = 0.21$ nm). **e**, Simultaneously acquired ADF- and ABF-STEM images for the surface part of the copper thin film. Scale bars are 2 nm.

The low-magnification BF-TEM image (Fig. 2a, top) and the cross-sectional HRTEM image (Fig. 2a, bottom) show that the mono-atomic step edge structure is maintained even after a year. The two intensity profiles for the (111) plane between the as-deposited (red) and the 1-year-old (blue) samples (Fig. 2b) show a change in the planar spacing of the (111) planes up to the uppermost surface layer, and they agree well with each other, suggesting that no notable oxidation has occurred even in the SCCF under long-term exposure to air. The electron backscatter diffraction (EBSD) map (Fig. 2c) and inverse pole figure (IPF) (Fig. 2d) show that no misalignment of crystal lattices deviating from the (111) plane has occurred after a year. Oxidised portions were rare on the 3-year-old SCCF sample oriented along $[1\bar{1}0]$ in the HRTEM image although they were found on the sample edge where the sample was cut (Fig. 2e, top). The resulting strain field maps (E_{xx} and E_{yy}) prepared using the GPA technique (Fig. 2e, middle and bottom) show that the overlayer (region 1) has a new lattice structure that is mismatched with the SCCF. The fast Fourier transform (FFT) patterns of region 1 (Fig. 2f, top), region 2 (Fig. 2f, middle) and both regions (Fig. 2f, bottom) indicate that the two regions belong to the Cu_2O and Cu phases, respectively, and suggest that part of the surface is oxidised. However, the oxidised surface only reaches a few Cu_2O layers, which is thin compared with the thickness of natural oxide layers in polycrystalline Cu (Extended data Fig. 2). Comparative thermogravimetric analysis (TGA) of PCCF and SCCF samples having different surface roughness clearly demonstrates that the SCCF with mono-atomic step edges exhibits exceptional resistance to initial oxidation at elevated temperatures compared with the other samples (Fig. 2g).

Fig. 2 | Long-term oxidation resistance and structural stability of the SCCF surface. **a**, Low-magnification bright field TEM (BF-TEM) image of the SCCF sample exposed to ambient air at room temperature for approximately 1 year (top). The result shows that the atomically flat surface morphology over the entire SCCF film has remained almost unchanged. HRTEM image of the surface part (marked by a red rectangle in A) of the 1-year-old SCCF sample (bottom). The sample was oriented in the $[1\bar{1}0]$ direction. **b**, Comparison of the intensity profiles for the (111) plane between the as-deposited (red) and 1-year-old (blue) samples. **c**, EBSD map showing perfect alignment along the (111) plane. **d**, IPF with a sole spot associated with the (111) plane. The inset image is the enlarged image of the sole spot area. **e**, HRTEM image of the surface part of the 3-year-old SCCF sample observed in the $[1\bar{1}0]$ orientation (top) and in-plane (E_{xx} , middle) and out-of-plane (E_{yy} , bottom) strain field maps obtained by geometrical phase analysis (GPA) for the HRTEM image of the 3-year-old SCCF sample. **f**, FFT patterns of region 1 (top), region 2 (middle) and both regions (bottom). **g**, Thermogravimetric analysis for the PCCF and SCCF samples with different surface roughness. Scale bars of e are 2 nm.

Growth condition for the flat surface

The flatness of a surface is decisively influenced by the interface structure between the film and substrate^{18,19}, which can be relaxed by structural defects such as dislocations. The interface structure between the Cu film and Al₂O₃ substrate is characterized by HR(S)TEM (Fig. 3). The overall interface structure viewed at the [11 $\bar{2}$] orientation of the Cu film and the FFT pattern of the image reveal that the crystallographic orientation relationship (OR) is (111)_{Cu}[11 $\bar{2}$]_{Cu}/(001)_{Al₂O₃}[110]_{Al₂O₃} (Figs. 3a, b). The copper lattices appear to flawlessly adjoin with the Al₂O₃ substrate without interfacial misfit defects, suggesting that the Cu film grows metamorphically on the substrate²⁰ (Extended data Fig. 5). The enlarged image of the interface (Fig. 3c) reveals a detailed lattice mismatch between the two materials. The atomic distance mismatch $f((d_{O-O}^{[\bar{1}20]}_{Al_2O_3} - d_{Cu-Cu}^{[\bar{1}10]})/d_{O-O}^{[\bar{1}20]}_{Al_2O_3})$ between Cu and Al₂O₃ is estimated to be 6.9%. However, considering the extended atomic distance mismatch (EADM)^{21,22}, the large mechanical misfit strain can be relieved if the match for a relatively long period is extremely small. The EADM is defined as $(ID - I'D')/I'D'$, where D and D' are the two atomic distances of the epilayer and substrate, respectively, and I and I' are determined by the relation $D:D' \sim I:I'$. Given the D_{Cu-Cu} ($14 \times d_{Cu-Cu}^{[\bar{1}10]}$) interatomic spacing (3.578 nm) of Cu and the D_{O-O} ($13 \times d_{O-O}^{[\bar{1}20]}$) interatomic spacing (3.575 nm) of Al₂O₃, the EADM of the Cu/Al₂O₃ interface is about 0.1% (Fig. 3c). The light element-sensitive ABF-STEM imaging²³ (Fig. 3d) reveals that the interface model of Cu grown on the oxygen-terminated Al₂O₃ surface matches well with the experimental heterostructure. The inverted intensity profile obtained across the interface (Fig. 3e) clearly corroborates the presence of an oxygen layer between the Cu and Al layers, thus indicating the existence of Cu–O interactions at the interface, which can be stabilized on a typical Al₂O₃ surface terminated with oxygen²⁴. Owing to the in-plane lattice mismatch, a large-scale interference pattern, i.e., a moiré pattern²⁵, can be observed in the plane view of the Cu/Al₂O₃ heterostructure (Fig. 3f). Indeed, the hexagonal moiré pattern with a dimension (d_m) of 1.83 nm is observed due to the different in-plane lattice periodicities in the vertical OR of [111]_{Cu}/[001]_{Al₂O₃}, which is confirmed by the FFT pattern analysis (inset in Fig. 3f). The simulated moiré pattern generated by the epitaxy model of Cu/Al₂O₃ with the same OR is consistent with the experimental moiré pattern showing the repeating large-scale contrast feature (Figs. 3g and h). This vertical OR observation corroborates our EADM analysis and indicates that the growth mechanism of the SCCF on the Al₂O₃ substrate can be understood based on the large-scale mismatch epitaxial relationship rather than the atomic-scale lattice interrelation. The detailed chemical nature of the SCCF at the surface and the interface regions are investigated by the combined spectroscopic

approaches of energy dispersive X-ray spectroscopy (EDX), electron energy loss spectroscopy (EELS)
in ADF-STEM imaging mode, and X-ray photoelectron spectroscopy (XPS) (Extended data Fig. 6)^{26,27}.

Fig. 3 | Interface structure and crystallographic relation. **a**, Cross-sectional HRTEM image of the Cu/Al₂O₃ heterointerface having the orientation relation of (111)_{Cu}[11 $\bar{2}$]_{Cu}/(001)_{Al₂O₃}[110]_{Al₂O₃}. **b**, A composite pattern of FFTs for the regions of Cu and Al₂O₃ in the HRTEM image. **c**, Enlarged HRTEM image for the region marked by the dotted box in **a**. **d**, ABF-STEM image and superimposed atomic model of the Cu/Al₂O₃ heterointerface. **e**, Inverted intensity profile obtained across the interface between Cu and Al₂O₃ in **d**. **f**, Plan-view HRTEM image of the Cu/Al₂O₃ heterointerface. **g-h**, Side view and plan view of the deduced epitaxy model of Cu grown on an Al₂O₃ substrate.

Calculation of oxidation-resistance

We can understand the exceptional oxidation resistance of our films using a microscopic model of copper oxidation based on first principles density functional theory (DFT) calculations²⁸⁻³⁰. The main reason for the suppression of oxidation is that our atomically flat film is free of one critical feature, namely, multi-atomic step edges, as shown in Fig. 4. The energy profile in Fig. 4a shows that the penetration of an O atom through a pristine Cu(111) surface needs an activation energy of more than 1.4 eV (Fig. 4b), and the O atom becomes stable only in the second subsurface interlayer space with an additional energy barrier of 1.3 eV (Fig. 4c). One of the main reasons for the strong resistance of a flat surface to oxidation is that when Cu atoms are oxidised, the out-of-plane distance between Cu layers increases from 2.10 to 2.48 Å, and the volume expands by 18% (Extended data Fig. 7). The volume increase is even more pronounced in the early stage of oxidation: the Cu layer distance in the monolayer of Cu₂O on the Cu surface is 3.26 Å, and the volume is greater by 55% (Extended data Fig. 7). Given that one exposed Cu surface is insufficient to initiate the oxidation process, we examine a structure wherein two crystallographically different planes meet, namely, the edge of a multi-atomic step. Notably O₂ molecules physisorbed on a Cu(111) surface readily dissociate into O ions with a small activation energy of 0.027 eV (Extended data Fig. 8). Figure 4d-f shows the initiation of oxidation on the edge of such multi-atomic steps according to our DFT calculation; Fig. 4a shows that there is a critical difference between a mono-atomic step and a multi-atomic step in terms of the oxidation resistance. While the penetration of O atoms at a bi-atomic and tri-atomic step is an exothermic reaction ($\Delta E = -0.90$ and -0.86 eV, respectively) with smaller activation energies ($E_a = 0.97$ and 0.71 eV, respectively), the penetration of O at the edge of a mono-atomic step is highly endothermic ($\Delta E = +0.80$ eV), requiring a much larger activation energy ($E_a = 1.56$ eV), and shows strong oxidation resistance. Our DFT calculation indicates that, as the coverage of oxygen increases, the incremental adsorption energy for the next O atom becomes smaller and eventually becomes negative beyond 50% of oxygen coverage, rendering the adsorption process energetically unfavorable (Fig. 4g). This self-regulation of oxygen suppresses further adsorption of O atoms on an ultraflat Cu surface at elevated oxygen coverages and increasingly enhances the oxidation resistance of the surface. Our microscopic model of oxidation is well supported by HRTEM images, which show that atomically flat Cu thin films with occasional presence of mono-atomic steps are highly resistant to oxidation over an extended period (≥ 3 years) (Fig. 2), while Cu films with multi-atomic steps show substantial oxidation (Extended data Figs. 2 and 3). The oxidation resistance of a Cu(111) surface is significantly affected by the type of surface defects³¹⁻³⁴, which suggests that an atomically flat Cu(111) surface without multi-atom steps is essential to achieve strong oxidation resistance.

Fig. 4 | Theoretical analysis and a model of oxidation of the Cu surface. **a**, Energy profile of the O atom along various penetration paths: **b**, from the Cu(111) surface into the first Cu substrate interstitial layer (black solid circle ●); **c**, from the first to the second Cu substrate interstitial layer (black open circle ○); **d**, from the outside to the inside of the mono-atomic step edge (red solid circle ●); **e**, from the outside to the inside of the bi-atomic step edge (blue open square □); and **f**, from the outside to the inside of the tri-atomic step edge (purple open square □). Blue spheres represent Cu atoms in the bulk or substrate, green spheres represent Cu atoms in the steps, and dark blue spheres represent Cu atoms on the step edge. Orange spheres represent adsorbed O atoms, whereas red spheres represent O atoms infiltrating into the interstitial region. Panel **f** also shows the initiation of oxidation on the edge of a multi-atomic step: (1) given a pristine step edge and ambient oxygen conditions, (2) two O atoms (orange spheres) adsorb on each side of the Cu on the edge (Cu-1, dark blue sphere); (3) the third adsorbed O atom (O-2, red sphere) causes the local structure of Cu-1 to be similar to that of Cu in a monolayer of Cu_2O , and the expansion of volume causes Cu-1 to move upward and open a pathway for O-2; and (4) O-2 passes through the opening and binds with Cu atoms in the next row to push those Cu atoms upward to sustain the oxidation process; **g**, Incremental adsorption energy of O-atom as a function of oxygen coverage of the fcc sites on the Cu(111) surface.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, statements of data availability and associated accession codes are available at <https://doi.org/>

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Methods

Preparation of the single-crystal Cu thin film via the atomic sputtering epitaxy (ASE) technique. Cu thin films were grown as nearly defect-free and grain boundary-free single crystals using the ASE technique achieved by addressing the problems of conventional sputter systems¹⁵. The ASE was realized by an improved RF magnetron system equipped with single-crystal sputtering target. Electrical and mechanical noises were effectively reduced by replacing conventional electric conductors with single-crystal ones and by employing a mechanical noise reduction (MNR) system. Employing the single-crystal target prevented particulate sputtering, which is mainly caused by the presence of grain boundaries in a conventional poly-crystal target. This resulted in improved film quality. The electric signal noise usually caused by the scattering of electrons due to grain boundaries in conductors^{35,36} was reduced by replacing the conventional Cu wires (including the power, ground, power supply network, and various interconnection cables) with grain-boundary-free single-crystal wire³⁷. Environmental mechanical noise was also reduced through the introduction of the MNR system. These electrical and mechanical improvements effectively suppressed the extrinsic and environmental factors that can hinder atomic-level deposition and facilitated the generation of homogeneous and high-quality plasma gases. Ar gas (99.9999%, 6 N) was used for the deposition atmosphere. The relationship between the deposition time and the thickness of the thin film (or the average growth rate) was determined from the average deposition time of a 200-nm-thick film grown under the optimum conditions. The determined average growth rate of ~4.3 nm/min

349 is fairly reliable above a film thickness of 10 nm.

350 **Structural and chemical characterizations.** XRD θ - 2θ measurements were performed using a PANalytical
351 Empyrean Series 2 instrument equipped with a Cu- $K\alpha$ source (40 kV, 30 mA). Data were collected within the
352 range of $20^\circ < 2\theta < 90^\circ$, with a step size of 0.0167° and a dwell time of 0.5 s per point in all cases. AFM
353 measurements were carried out using an XE-100 system (Park Systems, Inc.). Scanning electron microscopy
354 (SEM), EBSD, pole figure (PF) and IPF measurements were performed with a Zeiss SUPRA40 VP with a
355 scanning electron microprobe. An STM surface analysis was conducted using a custom-built STM system
356 installed in University of Ulsan, Korea. Electron-transparent cross-sectional TEM samples were prepared by
357 the Ga ion beam milling and lift-out method in focused ion beam systems (FIB, Helios NanoLab 450, FEI and
358 Auriga CrossBeam Workstation, Carl Zeiss), and the possible damaged surface layers on the samples were
359 removed by subsequent low-energy Ar ion beam surface milling at 700 eV for 15 min (Model 1040 NanoMill,
360 Fischione). The plan-view TEM specimen was prepared by mechanical polishing and dimple grinding followed
361 by ion milling with Ar ions. Double C_s -corrected (S)TEM systems (JEM-ARM200CF, JEOL) equipped with
362 EELS (Quantum ER965, Gatan) and EDX (JED-2300T, JEOL) were used for atomic-scale structure imaging
363 and chemical analysis of the samples at an accelerating voltage of 200 kV. The inner and outer angle ranges for
364 ADF- and ABF-STEM imaging were 45–180 and 12–24 mrad, respectively. The HRTEM, ADF- and ABF-
365 STEM images were denoised by a local 2D difference image filter that is implemented in commercial software
366 (HREM Filters Pro, HREM Research Inc.). The HRTEM simulation was carried out for the amorphous
367 carbon/copper $[11\bar{2}]$ supercell structure ($4.8 \times 4.8 \text{ nm}^2$) using the multislice method, which is implemented in
368 the commercial software MacTEMPAS (Total Resolution LLC, USA), with the following microscope and
369 imaging parameters: accelerating voltage ($V = 200 \text{ kV}$), spherical aberration coefficient ($C_s = 0.4 \text{ }\mu\text{m}$), chromatic
370 aberration coefficient ($C_c = 1.1 \text{ mm}$), convergence semi-angle ($\alpha = 0.5 \text{ mrad}$), sample thickness ($t = 20.5 \text{ nm}$),
371 and defocus ($\Delta f = +14 \text{ nm}$). The simulated HRTEM image was estimated to have a correlation of 0.98 with the
372 experimental HRTEM image as a cross-correlation factor. For the quantitative analysis of local strain
373 components in the copper thin film, the GPA technique was employed, which allows mapping two-dimensional
374 local displacement fields by analyzing the phase shift between noncolinear Fourier components of the lattice
375 vectors g_1 and g_2 . For EELS measurements of the Cu/ Al_2O_3 interface and the Cu surface, the core-loss EELS
376 spectra of the Cu L edge were obtained from the interface to the Cu surface using the line scan function of the
377 scanning step (0.72 nm) for a 37.83 nm length with an energy dispersion of 0.5 eV/pix and a dwell time of 2.0
378 s/pix. For core-loss EELS spectrum imaging for the comparison of surface structures between the SCCF and
379 the PCCF samples, surface parts of both samples were selected by 20×16 pixels that can be translated as 9.87
380 $\times 7.9 \text{ nm}^2$ and scanned with the step size of 0.493 nm to obtain EELS SI dataset. The selected range of energy
381 loss was set to be 477–988 eV including O K and Cu $L_{2,3}$ edges. Nanoscale STEM-EDX maps of the constituent
382 elements of the Cu/ Al_2O_3 heterostructure were obtained for a 256×256 pixel resolution with a high-efficiency

383 dual silicon drift detector (SDD) X-ray detector system having a wide collection window of 100 mm² for each
384 detector, and the sample drift during the acquisition was corrected by tracking the reference area assigned at the
385 acquisition setup.

386 **Thermogravimetric analysis for the PCCF and SCCF samples with different surface roughness.** The
387 thermal mass change was measured using thermogravimetric measurement system (TG-DTA 2000S, MAC
388 Science). We prepared samples of two SCCF samples with different values of surface roughness and PCCF
389 sample. The gravimetric changes of the three samples were measured in the temperature range of RT–700°C at
390 a heating rate of 20°C/min under air atmosphere. Two SCCF samples with different values of RMS roughness,
391 i.e., 0.3 (SCCF-0.3, corresponding to a mono-atomic step) and 0.7 nm (SCCF-0.7, corresponding to a bi- or tri-
392 atomic step), were tested to ascertain the effect of the surface steps on oxidation in comparison to the PCCF
393 sample (blue) (RMS roughness: ~10 nm). While the SCCF sample with a roughness of 0.3 nm (red) was
394 synthesized by ASE and had an ultraflat surface with occasional mono-atomic steps, the SCCF with the
395 roughness of 0.7 nm (green), which was synthesized by using a single-crystal target in a conventional sputtering
396 system, had occasional multi-atomic steps of 2 or 3 atomic layers in height.

397 **Theoretical calculations.** All *ab initio* total energy calculations and geometry optimizations were performed
398 with DFT in the generalized gradient approximation (GGA) Perdew–Burke–Ernzerhof functional²⁸ and with the
399 projected augmented plane-wave method²⁹, as implemented by Kresse *et al.*³⁰. The Cu substrate was represented
400 by slabs of six layers with the theoretical equilibrium lattice constant. A vacuum length of 15 Å was used, and
401 the bottom two layers of the slab were fixed in their bulk positions. The electron wave functions were expanded
402 in a plane-wave basis set with a cutoff energy of 400 eV. The Brillouin zone for the slabs was sampled using *k*-
403 point sets equivalent to at least a (5×5×1) Monkhorst-Pack grid³⁸ for the primitive face-centered cubic (fcc) unit
404 cell. The climbing image-nudged elastic band method³⁹ was used to calculate activation energies. The local
405 atomic charge was computed using Bader’s charge decomposition method⁴⁰, which divides the total volume into
406 individual atomic volumes for each atom as the one containing a single charge density maximum and separated
407 from the other volumes by a zero-flux surface of the gradients of the charge density magnitude. The incremental
408 adsorption energy of an oxygen atom as a function of oxygen coverage $\theta = n/n_0$ for *n* O atoms on *n*₀ fcc
409 sites on a Cu(111) substrate is calculated as the energy change when an additional O atom is adsorbed on the
410 substrate, $E_{\text{ad}}(n) = E[\text{Cu}+(n+1)\text{O}] - E[\text{Cu}+n\text{O}] - \frac{1}{2}E[\text{O}_2]$, where $E[\text{Cu}+n\text{O}]$ is the total energy of *n*
411 oxygen atoms on the Cu substrate and $E[\text{O}_2]$ is the total energy of an isolated oxygen molecule.

412

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Author contributions

S.-Y.J., Y.-M.K., and S.G.K. conceived this work and wrote the manuscript. S.-Y.J. and Y.-M.K. supervised the experiments. S.J.K. and Y.L. prepared the SCCF samples. Y.-M.K., Y.I.K., Y.-H.K., J.C. Kim, and H.Y.J. performed TEM analyses and sample preparations. J. K. conducted the STM analysis. S.J.K. and Y.L., T.H., C.R.C., and M.C. performed EBSD and AFM experiments and assisted with the data analyses. S.-Y.J. and S.G.K. established the theoretical model, and S.G.K., and B.L. carried out first-principles calculations. S.-Y.J. and Y.H.L. supervised and coordinated this work. All authors contributed to the discussion and analysis of the results.

Competing interests

The authors declare that there are no competing interests.

Additional information

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Extended data figures

Extended Data Fig. 1 | Pristine SCCFs grown by ASE. **a**, Photo of a 2-inch SCCF grown on Al_2O_3 . **b**, θ - 2θ X-ray diffraction (XRD) data taken at different positions marked in **a**. **c**, Surface morphologies at 20-nm (upper) and 1.5-nm (lower) vertical scale of atomic force microscopy (AFM) images with a root-mean-square (RMS) surface roughness of 0.28 nm. **d**, EBSD map showing perfect alignment along the (111) plane. **e**, IPF with a sole spot associated with the (111) plane. **f**, [100] PF revealing the six-fold symmetry of the {100} PF. The inset images in **e** and **f** are the enlarged images of the sole spot areas. **g**, SEM images of the sample at different magnifications. **h**, Low-magnification cross-sectional bright field TEM (BF-TEM) image of the SCCF sample.

Extended Data Fig. 2 | Structural and chemical characterizations of a conventional PCCF grown on a glass substrate. **a**, Low-magnification cross-sectional BF-TEM image of the PCCF sample showing a typical polycrystalline structure. **b**, Magnified image of the region marked by the yellow box in **a**, which shows the presence of a thick oxidised Cu layer on the surface of the PCCF. **c**, **d**, HRTEM images of oxidised Cu nanoparticles formed in the regions denoted by white boxes in **b**. The measured planar spacings of the (111) planes are 2.32 and 2.46 Å, which represent typical values of CuO and Cu₂O phases, respectively. **e**, ADF-STEM image of the surface part of the PCCF. **f**, **g**, STEM-EDX elemental maps of Cu (**f**) and O (**g**) in the surface region. **h**, Vertically averaged intensity profiles of Cu (blue) and O (red) across the surface. Note that the intensity of each element was normalized with respect to its intensity maximum. From this result, it is evident that the highly oxidised Cu surface layer (indicated by the pink shaded region in the graph) can be formed on the PCCF with a thickness of tens of nanometers.

465

466 **Extended Data Fig. 3 | Surface oxidation of bulk Cu single crystal.** **a, g**, Low magnification
 467 micrographs of the non-polished and polished Cu single crystal samples prepared by FIB milling. The
 468 insets show the two Cu single crystals sliced and cut to dimensions of $5 \times 5 \text{ mm}^2$. **b, h**, HRTEM images
 469 of the two Cu surfaces. Note that the yellow arrows indicate thin Cu_2O layer that formed on the two
 470 surfaces. **c, d, i, j**, FFT patterns of the two regions of Cu_2O (red box, labelled '1') and Cu (green box,
 471 labelled '2') depicted in each HRTEM image. **e, k**, Composite of the two FFT patterns for comparison.
 472 **f, l**, Measurements of the layer spacings across the interface between Cu and Cu_2O (red dotted arrows).

474 **Extended Data Fig. 4 | STM topography images of the clean Cu(111) single-crystal film at room**
475 **temperature. a,** Configuration of step edges for an imaging area of $200 \times 200 \text{ nm}^2$. **b,** Atomic-
476 resolution surface structure (image size $\sim 3 \times 3 \text{ nm}^2$). The arrows indicate the three corresponding
477 $\langle 110 \rangle$ orientations on the (111) plane. **c,** Profile of step height obtained from the line scan marked with
478 a black arrow in a, which shows a series of mono-atomic steps corresponding to the planar spacing of
479 the Cu(111).

Scale bars: 2 nm.

Extended Data Fig. 5 | Interface structure and strain distribution. a, Cross-sectional HRTEM image of the interface region of the Cu/Al₂O₃ heterostructure with an orientation relation of (111)_{Cu}[11 $\bar{2}$]_{Cu}/(001)_{Al₂O₃}[110]_{Al₂O₃}. **b,** Enlarged image showing an abrupt interface structure. **c, d,** In-plane (E_{xx}) and out-of-plane (E_{yy}) strain field maps obtained by a geometrical phase analysis (GPA) of the HRTEM image. Note that the region enclosed by the white dotted line indicates the strained interface region of ~1–2 nm in thickness. The color scale indicates the magnitude of the strain relative to the reference area marked by the white box. Scale bars are 2 nm.

489

490 **Extended Data Fig. 6 | Chemical analysis and electronic structure of the grown SCCF. a, b,**
 491 **Nanoscale STEM-EDX elemental maps of Al, O, and Cu in the regions on the surface and at the**
 492 **interface of the Cu/ Al_2O_3 heterostructure, respectively. c, Comparison of the Cu $L_{2,3}$ -electron energy**
 493 **loss near edge structure (ELNES) profiles obtained at four different positions (marked by the numbers**
 494 **1–4 in the ADF-STEM images) and the reference profiles obtained from copper metal and copper**
 495 **oxides, CuO and Cu_2O (lower graphs). d, ADF-STEM image, Core-loss EELS spectrum imaging data,**
 496 **the constructed elemental map of Cu and O for the surface region of the SCCF sample. The red and**

497 blue profiles on the right side are core-loss EEL spectra of O K and Cu $L_{2,3}$ edges extracted from the
498 white dotted rectangular denoted in the EELS map. **e**, Equivalent data arrangement for the PCCF
499 sample for comparison of surface oxidation. **f**, XPS depth profile depending on the etching time for
500 the SCCF sample.
501 _____

Extended Data Fig. 7 | Structural and electronic properties of Cu, Cu₂O, and Cu₂O monolayers on the Cu(111) surface. **a-c**, Structural model of Cu, Cu₂O, and Cu₂O monolayers on the Cu(111) surface. Cu and O atoms are represented by blue and red spheres, respectively. Only the bonds between O and Cu atoms are drawn explicitly for clarity. **d**, Structural parameters of Cu, Cu₂O, and Cu₂O monolayers on the Cu(111) surface. **e**, Degree of oxidation of atoms in various configurations. n_e is the electron charge of each atom (the number of valence electrons attributed to each atom computed using the Bader decomposition method⁴⁰), while n_0 is the number of valence electrons of the corresponding isolated neutral atom.

Extended Data Fig. 8 | Relative energy per oxygen atom for the dissociation of the O₂ molecule approaching Cu(111) surface as a function of O-O bond length. Blue spheres represent Cu atoms, while red spheres represent O atoms. The insets show the side and top views of the configurations with corresponding letters on the curve. Configuration **b** corresponds to the physisorbed state, while configuration **c** corresponds to the transition state.

Figures

Figure 1

Surface of a single-crystal copper thin film (SCCF) grown by atomic sputtering epitaxy (ASE). a, Cross-sectional HRTEM image of the surface part of the copper thin film observed in the $[11\bar{1}0]$ orientation. The simulated HRTEM image and the corresponding model of the carbon-copper supercell are presented alongside the experimental HRTEM image. b-c, In-plane (E_{xx}) and out-of-plane (E_{yy}) strain field maps obtained by geometrical phase analysis (GPA) for the experimental HRTEM image. The reference area of Cu chosen for GPA is marked by the white square boxes in each map. Note that complex patterns for parts of the carbon film are shaded by a gray color for clarity, as those are not relevant for the strain behavior of the SCCF. d, Comparison of the experimental and simulated intensity profiles obtained along the out-of-plane direction for (111) layer spacings ($d(111) = 0.21 \text{ nm}$). e, Simultaneously acquired ADF- and ABF-STEM images for the surface part of the copper thin film. Scale bars are 2 nm.

Figure 2

Long-term oxidation resistance and structural stability of the SCCF surface. a, Low-magnification bright field TEM (BF-TEM) image of the SCCF sample exposed to ambient air at room temperature for approximately 1 year (top). The result shows that the atomically flat surface morphology over the entire SCCF film has remained almost unchanged. HRTEM image of the surface part (marked by a red rectangle in A) of the 1-year-old SCCF sample (bottom). The sample was oriented in the $[11\bar{1}0]$ direction. b, Comparison of the intensity profiles for the (111) plane between the as-deposited (red) and 1-year-old (blue) samples. c, EBSD map showing perfect alignment along the (111) plane. d, IPF with a sole spot associated with the (111) plane. The inset image is the enlarged image of the sole spot area. e, HRTEM image of the surface part of the 3-year-old SCCF sample observed in the $[11\bar{1}0]$ orientation (top) and in-plane (E_{xx} , middle) and out-of-plane (E_{yy} , bottom) strain field maps obtained by geometrical phase analysis (GPA) for the HRTEM image of the 3-year-old SCCF sample. f, FFT patterns of region 1 (top), region 2 (middle) and both regions (bottom). g, Thermogravimetric analysis for the PCCF and SCCF samples with different surface roughness. Scale bars of e are 2 nm.

Figure 3

Interface structure and crystallographic relation. a, Cross-sectional HRTEM image of the Cu/Al₂O₃ heterointerface having the orientation relation of (111)Cu[112]Cu // (001)Al₂O₃[110] Al₂O₃. b, A composite pattern of FFTs for the regions of Cu and Al₂O₃ in the HRTEM image. c, Enlarged HRTEM image for the region marked by the dotted box in a. d, ABF-STEM image and superimposed atomic model of the Cu/Al₂O₃ heterointerface. e, Inverted intensity profile obtained across the interface between Cu and Al₂O₃ in d. f, Plan-view HRTEM image of the Cu/Al₂O₃ heterointerface. g-h, Side view and plan view of the deduced epitaxy model of Cu grown on an Al₂O₃ substrate.

Figure 4

Theoretical analysis and a model of oxidation of the Cu surface. a, Energy profile of the O atom along various penetration paths: b, from the Cu(111) surface into the first Cu substrate interstitial layer (black solid circle $\bullet$); c, from the first to the second Cu substrate interstitial layer (black open circle $\circ$); d, from the outside to the inside of the mono-atomic step edge (red solid circle $\bullet$); e, from the outside to the inside of the bi-atomic step edge (blue open square $\square$); and f, from the outside to the inside of the tri-atomic step edge (purple open square $\square$). Blue spheres represent Cu atoms in the bulk or substrate, green spheres represent Cu atoms in the steps, and dark blue spheres represent Cu atoms on the step edge. Orange spheres represent adsorbed O atoms, whereas red spheres represent O atoms infiltrating into the interstitial region. Panel f also shows the initiation of oxidation on the edge of a multi-atomic step: (1) given a pristine step edge and ambient oxygen conditions, (2) two O atoms (orange spheres) adsorb on each side of the Cu on the edge (Cu-1, dark blue sphere); (3) the third adsorbed O atom (O-2, red sphere) causes the local structure of Cu-1 to be similar to that of Cu in a monolayer of "C" "u" "2" "O", and the expansion of volume causes Cu-1 to move upward and open a pathway for O-2; and (4) O-2 passes through the opening and binds with Cu atoms in the next row to push those Cu atoms upward to sustain the oxidation process; g, Incremental adsorption energy of O-atom as a function of oxygen coverage of the fcc sites on the Cu(111) surface.

Supplementary Files

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