1	Misfit-dislocation induced stop-and-go kinetics of interfacial
2	transformations
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16	Despite the ubiquitous presence at heterophase boundaries, directly probing the
17	dynamic action of misfit dislocations has been unachievable due to their buried nature.
18	Using the example of $Cu_2O \rightarrow Cu$ interfacial transformation, we demonstrate the unique
19	role of misfit dislocations in modulating oxide/metal interfacial transformations in an
20	intermittent manner, by which the lateral flow of interfacial steps is pinned at the core
21	of misfit dislocations until the dislocation climbs to the new oxide/metal interface
22	location. Together with atomistic calculations, we identify that the pinning effect is
23	associated with the non-local transport of metal atoms to fill vacancies at the dislocation
24	core. These results provide mechanistic insight into solid-solid interfacial
25	transformations and have significant implications in utilizing structural defects at
26	buried interfaces to modulate mass transport and transformation kinetics.
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Most engineering materials are based on multiphase microstructures produced either 28 through the control of phase equilibria or by the fabrication of different materials as in thin 29 30 film processing. In both processes, the microstructure relaxes toward equilibrium by interactions across internal interfaces. Different from isolated dislocations in the bulk that 31 increase the energy of a system, it is thermodynamically favorable to introduce misfit 32 33 dislocations at heterointerfaces to release some lattice mismatch strain and the associated strain energy. These misfit dislocations are accommodated by localized compressive and 34 tensile strain fields around the interface and have significant consequences for the functional 35 and structural properties of the heterophase systems that range from interfacial adhesion and 36 mass transport to interfacial charge modulation¹⁻⁷. Therefore, fundamental understanding of 37 misfit dislocations and their dynamic coupling to the interface structure, chemistry, 38 functionality and phase transformations has been a longstanding topic of study¹⁻¹⁸. 39 Unfortunately, directly probing misfit dislocation dynamics has been a major challenge due 40 to their buried nature and the difficulty of direct experimental measurements at the atomic 41 scale. Transmission electron microscopy (TEM) is one of the few tools capable of accessing 42 43 buried interfaces and has demonstrated its versatility and atomic precision in elucidating the location and configuration of misfit dislocations^{1,8,11,19,20}, but all these studies were of static 44 structures. A natural development is to understand the dynamic action of misfit dislocations at 45 46 moving interfaces during interfacial phase transformations. In-situ TEM based on diffraction contrast imaging has been widely employed to observe dynamic dislocation motion under 47 stress and during deformation^{14,21-23}. However, directly probing the dynamic action of misfit 48 dislocations at moving interfaces during interfacial phase transformations has been 49 unachievable because it requires not only a capability to capture the fast, real-time dynamic 50 51 evolution of an interface at the atomic scale and in real time but also to apply thermal and chemical stimuli to drive the interface transformation. 52

Here we report direct visualization of the dynamic action of misfit dislocations during an actual interface transformation process. This is performed with the use of in-situ environmental TEM to flow hydrogen gas in the sample area to activate the Cu₂O/Cu interface reaction at elevated temperature while at the same time temporally and spatially resolving the Cu₂O \rightarrow Cu interface transformation in bright-field HRTEM mode. We use the

Cu₂O/Cu interfaces as a model system because it plays a prominent role in many 58 technological fields such as heterogeneous catalysis, gas sensing, solar energy conversion, 59 and emission control²⁴⁻²⁸. We capture a stop-and-go interface transformation behavior 60 regulated by misfit dislocations, a phenomenon that has not been recognized due to the 61 difficulty of probing the fast dynamics of the local atomic configurations at buried interfaces. 62 63 By combining these in-situ atomic-scale observations with density-functional theory (DFT) simulations, we identify a mechanism by which the misfit dislocations delay the interfacial 64 transformation as a result of the required long-range mass transport to replenish missing 65 atoms at dislocation cores. The phenomenon reported here has wide relevance and is of 66 considerable practical importance, as misfit dislocations represent an important and 67 ubiquitous class of structural defects at heterophase boundaries and the associated interfacial 68 transformations play a pivotal role in the microstructural evolution for a wide range of 69 materials systems, properties and reactions, such as metallurgy, thin film processing, 70 71 heterogeneous catalysis and corrosion, among others.

Our in-situ TEM experiments (Extended Data Fig. 1) include the in-place Cu₂O/Cu 72 73 interface formation via oxidizing single-crystal Cu(100) thin films in O₂ gas flow, followed by the subsequent switching to H₂ flow that results in the reduction of Cu₂O to Cu at the 74 Cu₂O/Cu interface. Fig. 1a shows a typical high-resolution (HR) TEM image of a Cu₂O/Cu 75 interface formed in-situ by the oxidation of a faceted edge of the Cu film at pO₂=0.67 Pa and 76 T=623 K (Extended Data Fig. 2). Measurements of the periodicity and interplanar spacings 77 of the substrate and the oxide show the cube-on-cube epitaxial growth of a Cu₂O layer on the 78 79 Cu(110) substrate. This is also confirmed by the inset diffractogram, where the relative orientation between the Cu₂O and Cu is Cu₂O(200)//Cu(200), Cu₂O(020)//Cu(020), and 80 Cu₂O[001]//Cu[001] (Extended Data Fig. 3). The location of the Cu₂O/Cu interface is 81 marked by the green dashed line in Fig. 1a and four misfit dislocations along the Cu₂O/Cu 82 interface are identified, showing both the 7×6 and 8×7 coincidence-site-lattice (CSL) 83 84 configurations in which six and seven Cu spacings in the Cu₂O overlayer match seven and eight Cu spacings in the Cu substrate, respectively. The natural lattice misfit, f, between Cu 85 and Cu₂O, defined by $f = (a_{Cu_2O} - a_{Cu})/a_{Cu_2O}$ is ~ 14.48%, where the lattice constants of 86

bulk Cu₂O and Cu are 0.4275 nm and 0.3656 nm, respectively, with the lattice thermal 87 expansion taken into consideration (Extended Data Text 1). This large lattice misfit makes the 88 formation of a coherent interface energetically unfavorable, thereby resulting in an array of 89 misfit dislocations at the Cu₂O/Cu interface to release the misfit strain. Based on the 90 minimum CSL misfit criterion²⁹, the 7×6 CSL configuration results in a smaller strain 91 (0.226%) than both the 8×7 (2.26%) and 6×5 (2.62%) CSL configurations at 623 K 92 (Extended Data Text 1). This is also confirmed from the geometrical phase analysis (GPA) of 93 the HRTEM image to determine local strain fields based on the atomic position 94 displacements that use the bulk Cu lattice as the reference. As illustrated in Fig. 1b, the ε_{xx} 95 map shows that most of the in-plane strains concentrate at the core region of the misfit 96 97 dislocations. That is, the Cu₂O lattice adjacent to the core region of the misfit dislocations is under tension whereas the Cu lattice is under compression in the core region. The GPA results 98 99 also indicate that a larger maximum of strains in the core region of the misfit dislocations are associated with the 8×7 and 6×5 CSL segments rather than those with the 7×6 CSL segments 100 (Extended Data Tables 1-2). As illustrated later from our in-situ TEM observations, the 8×7 101 and 6×5 CSL configurations are transient and tend to transform to the more stable 7×6 CSL 102 upon the Cu₂O \rightarrow Cu interfacial transformation. Fig. 1c is a zoom-in HRTEM image of a 103 typical misfit dislocation, showing that the misfit dislocation has a Burgers vector of b =104 $d_{Cu(110)}$. This is further confirmed by HRTEM image simulations (Fig. 1d) using the 105 Cu₂O(110)/Cu(110) interface structure (Fig. 1e) obtained from DFT total energy 106 minimization (Extended Data Texts 2-3 and Extended Data Figs. 4-5) and high-angle annular 107 108 dark-field image (Fig. 1f).

The Cu₂O/Cu interfaces formed from the in-situ oxidation serve as an ideal platform to 109 visualize the dynamic action of misfit dislocations by switching the atmosphere from O₂ to 110 H₂ gas flow that induces the reduction of Cu₂O to Cu. Fig. 2a-d presents a time sequence of 111 in-situ HRTEM images (Supplementary Movie 1), seen edge-on at $pH_2 \sim 5.3$ Pa and T=623 K, 112 113 which show the Cu₂O \rightarrow Cu transformation along the Cu₂O(110)/Cu(110) interface for a large 114 Cu₂O island, where only the corner region is imaged. As indicated by yellow dashed lines in Fig. 2a-d, the Cu₂O/Cu interface is initially flat within the field of view and is observed to 115 migrate toward the Cu₂O side as the Cu₂O is transformed to metallic Cu along the Cu₂O/Cu 116

interface. The interface is measured to migrate by an amount of ~ 1.8 nm toward the Cu₂O 117 side within a time elapse of 102 s. As indicated by the blue and red arrows in Fig. 2b-c, the 118 Cu₂O \rightarrow Cu transformation occurs via the lateral flow of atomic steps along the Cu₂O/Cu 119 interface. The epitaxial Cu₂O/Cu interface is maintained through the step-flow transformation 120 that results in the homoepitaxial growth of metallic Cu along the (110) interface. However, 121 the in-situ TEM observation shows a striking stop-and-go manner of the Cu₂O→Cu 122 interfacial transformation, by which the lateral propagation of the Cu₂O/Cu interface steps is 123 regularly interrupted with short pauses that range from 2 s to 6 s, as shown in the 124 distance-time plot (Fig. 2e) of the lateral propagation of steps 1 and 2 marked in Fig. 2a to d. 125 Meanwhile, the Cu₂O surface undergoes some decay during the stop-and-go Cu₂O Cu 126 transformation at the Cu₂O/Cu interface, as indicated by the detailed tracing of the temporal 127 evolution of the oxide in Fig. 2d (Extended Data Text 4). 128

The discrete nature of the interfacial transformation dynamics is not tied to the (110) 129 interface only and is also observed along the (100) interface. Fig. 2f-i illustrates another 130 example of the Cu₂O \rightarrow Cu interfacial transformation, where the in-situ TEM observation 131 (Supplementary Movie 2) is made at a relatively low magnification in order to visualize the 132 dynamic evolution of the entire interface of a small supported Cu₂O island formed from the 133 oxidation of a Cu(100) facet. The inset HRTEM image in Fig. 2f shows that the Cu₂O island 134 135 and the Cu substrate have the (100)-type interface. The Cu₂O \rightarrow Cu transformation occurs via the lateral flow of steps along the $Cu_2O(100)/Cu(100)$ interface, as indicated by the arrows in 136 Fig. 2f-i. Similarly, the step-flow transformation shows the stop-and-go movement of steps 137 with regular interruptions of short pauses, as illustrated in the distance-time plot (Fig. 2j) of 138 the lateral propagation of steps 3 and 4 marked in Fig. 2f-i. The in-situ TEM observations 139 shown above also illustrate that the stop-and-go interfacial transformation is independent of 140 the oxide island size. Note that electron beam irradiation effects on the Cu₂O \rightarrow Cu 141 transformation are negligible (Extended Data Text 5). 142

Fig. 3 illustrates in-situ HRTEM imaging that demonstrates that the stop-and-go interface transformation is regulated by misfit dislocations. That is, the step flow pauses at the core location of dislocations and then, a few seconds later, resumes its lateral propagation.

Fig. 3a-e show in-situ HRTEM images (Supplementary Movie 3) of the intermittent flow of 146 the interfacial atomic step along the Cu₂O(110)/Cu(110) interface. Fig. 3a shows three misfit 147 dislocations with the 8×7 CSL lattice matching along the Cu₂O/Cu interface, where the 148 atomic columns around the dislocation cores are marked by red crosses to trace the exact 149 location of the misfit dislocations. As marked by the yellow arrow in Fig. 3b, a step enters the 150 151 field of view from the right side. This results in a step-and-terrace interface configuration, where the two terraces are separated by a double-atomic-height step (i.e., $2d_{Cu(220)}$) on the 152 Cu₂O/Cu interface, as marked by the yellow dashed lines in the HRTEM image of Fig. 3b. 153 Correspondingly, the lateral flow of the step results in the growth of two atomic layers of 154 Cu(220) by consuming the Cu₂O lattice in front of the step. The in-situ HRTEM observation 155 156 shows that the step flow does not sweep across the Cu₂O/Cu interface unimpeded. Instead, the lateral propagation of the step is regularly interrupted at the core of the dislocations, 157 158 where the step is pinned for about 2-6 s (Fig. 3f) and then resumes its lateral migration. After the step passes through the core of the dislocations, the dislocation core is observed to climb 159 by two atomic layers to the upper terrace of the Cu₂O/Cu interface, followed by the lateral 160 glide on the interface by one lattice spacing. This results in the transformation from the 8×7 161 CSL to 7×6 CSL, as shown in Fig. 3c-e. 162

This intermittent step flow is also observed atomically at the Cu₂O(100)/Cu(100) 163 164 interface. Fig. 3g-k illustrates in-situ HRTEM images (Supplementary Movie 4) of the Cu₂O \rightarrow Cu transformation along the (100) interface. Fig. 3g shows four misfit dislocations, 165 apart by segments of the 6×5, 8×7, and 7×6 CSL lattice matching along the Cu₂O/Cu 166 interface. The Cu₂O/Cu interface has a step-and-terrace configuration, where the two terraces 167 are separated by a monatomic step (i.e., d_{Cu(200)}), as marked by arrow 1 in Fig. 3g. This 168 interfacial step sits right above the core of the misfit dislocation. After ~ 2 s of dwelling on 169 the dislocation core, the step is seen to propagate quickly toward the right side and then stay 170 at the core location of the next dislocation, as shown in Fig. 3h. Meanwhile, another 171 monatomic step enters the field of view from the right side and sits right above the 172 dislocation core, as marked by arrow 2 in Fig. 3h. After ~ 0.5 s of dwelling on the dislocation 173 core, step 2 resumes its lateral propagation toward the left side and becomes pinned at the 174 core location of the adjacent dislocation, as shown in Fig. 3i. It can be noted that step 1 is still 175

pinned at the dislocation core during this time period. After another ~ 0.5 s of dwelling on the 176 dislocation core, steps 1 and 2 are observed to propagate in the opposite direction and meet 177 up with each other, thereby resulting in the annihilation of the two interfacial steps, as shown 178 in Fig. 3j. Same as the Cu₂O(110)/Cu(110) interface, the stop-and-go flow of the interfacial 179 step along the (100) interface has also concurrently driven the rearrangement of the misfit 180 dislocations along the interface, for which the 8×7 and 6×5 CSL segments on the right side 181 transform to the energetically more favorable 7×6 CSL by climb and glide of the dislocation 182 core upon the sweeping of the step. As shown in Fig. 3k, a new step (marked by arrow 3) 183 enters from the left side into the field of view and repeats the same stop-and-go step flow 184 with a dwell time ranging from 0.5 s to 1.5 s at the core of each dislocation (Fig. 31). It can 185 also be noted that the interfacial steps are pinned for a longer period (2 s to 6 s) at the core of 186 the misfit dislocations along the $Cu_2O(110)/Cu(110)$ interface than that (0.5 s to 1.5 s) along 187 188 the $Cu_2O(100)/Cu(100)$ interface. This indicates that the dwell time depends on the height of the interfacial steps, where the step along the (110) interface is two atom layers high, whereas 189 the step along the (100) interface is mono atomic layer high. Meanwhile, the sweeping 190 191 velocity of the step motion along the Cu₂O/Cu interface can be calculated using the dwell time at the misfit dislocation core and the distance between adjacent misfit dislocations, 192 which are 1.28 nm/s and 0.43 nm/s, respectively, for the (100) and (110) interfaces (Extended 193 Data Text 6). The microscopic sweeping velocity of the step motion can be also translated 194 into the thickening rate of the underlying Cu layer, which can be measured macroscopically 195 (Extended Data Text 6 and Extended Data Fig. 6). 196

Our in-situ TEM observations described above demonstrate that the $Cu_2O \rightarrow Cu$ 197 interfacial transformation is temporarily delayed at the core of misfit dislocations. 198 Microscopically, the Cu₂O \rightarrow Cu interfacial transformation is induced by the removal of 199 lattice oxygen in the Cu₂O adjacent to the Cu₂O/Cu interface, for which Cu atoms in the 200 oxide are directly displaced to the interfacial ledges of the Cu lattice, thereby resulting in the 201 202 step-flow dynamics. During the H₂ exposure, hydrogen can easily react with lattice oxygen at 203 the Cu₂O surface to form H₂O molecules that desorb from the surface at elevated temperature. Accompanying the surface desorption of H₂O molecules is the concomitant formation of 204 oxygen vacancies at the oxide surface, as evidenced by the observed surface decay in Fig. 205

2a-d (Extended Data Text 4). Oxygen vacancies produced from the H₂O formation can 206 readily migrate into the subsurface and then toward the Cu₂O/Cu interface due to the counter 207 diffusion of lattice oxygen from the Cu₂O/Cu interface to the oxide surface with low energy 208 barriers (Extended Data Text 7 and Extended Data Figs. 7-8). Furthermore, H₂ adsorption at 209 the Cu₂O surface results in chemically dissociated H atoms that may enter the bulk of Cu₂O 210 as interstitial protons^{30,31} and further promote the vacancy-assisted diffusion of O atoms 211 (Extended Data Text 7 and Extended Data Fig. 7). Thus, the Cu₂O overlayer serves as the O 212 source to sustain the surface reaction and Cu₂O is reduced to Cu at the Cu₂O/Cu interface due 213 to this counter diffusion of lattice oxygen and vacancies. Therefore, the step-flow rate may be 214 related to degrees of easiness to remove lattice oxygen in front of the Cu₂O/Cu interfacial 215 216 ledge. One would expect that oxygen atoms that surround the core of the dislocations are more prone to departure due to the lattice distortions around the dislocation core. Indeed, our 217 218 density-functional theory (DFT) calculations indicate that the oxygen vacancy formation energies for the interfacial step located at two representative sites, i.e., at the dislocation core 219 and away from the dislocation core, are 2.1 eV and 2.6 eV, respectively (Extended Data Fig. 220 221 8). Using nudged elastic band (NEB) calculations, we further identify that the energy barriers for the vacancy-assisted oxygen diffusion in front of the interfacial ledge decrease as it moves 222 to the misfit dislocation (Extended Data Text 7 and Extended Data Fig. 7). The smaller 223 224 oxygen vacancy formation energy and the lower O diffusion barriers at the dislocation core implies more favorable $Cu_2O \rightarrow Cu$ transformation at these defect sites. However, on the 225 contrary, our in-situ TEM observations (Fig. 3) show that the $Cu_2O \rightarrow Cu$ interfacial 226 transformation is actually impeded by the core of the misfit dislocations, which thereby 227 points strongly to the effect from the supply of Cu atoms on the interfacial growth of Cu upon 228 229 the departure of lattice oxygen.

DFT calculations are further employed to elucidate the step-flow growth of Cu using the (7×6) Cu₂O/Cu interface configuration. That is, lattice oxygen in front of the interfacial step is sequentially removed, as illustrated in Fig. 4a, where the newly formed oxygen vacancies in the Cu₂O lattice are marked as red circles. Upon the departure of the lattice oxygen, neighboring Cu atoms in front of the interfacial step undergo spontaneous lateral relaxation toward the oxygen vacancy sites, as indicated by the black arrows in Fig. 4a. The

DFT-optimized structure (Fig. 4b) shows that the lateral relaxations of the Cu atoms upon the 236 sequential departure of the lattice oxygen result in their perfect matching with the underlying 237 238 Cu lattice, a process similar to the homoepitaxial growth of Cu adatoms on a Cu substrate. As seen from Fig. 4b, the cyan Cu atom above the dislocation core shifts toward the right side by 239 one atomic spacing to match the underlying Cu lattice. In turn, the misfit dislocation line 240 shifts from the red dashed "T" site to the pink solid "T" site, consistent with the in-situ 241 HRTEM observations that show the $(8 \times 7) \rightarrow (7 \times 6)$ transformation in the CSL lattice matching 242 in front of the interfacial step (Fig. 3b and c). Another revealing feature noted in the DFT 243 relaxed structure (Fig. 4b) is related to the dislocation core region, where the lateral 244 relaxations of Cu atoms toward the oxygen vacancy sites result in two Cu vacancy columns 245 246 in front of the interfacial step, as marked by the dashed blue circles in Fig. 4b. The presence of the Cu vacancy columns in front of the interfacial ledge is also confirmed by high-angle 247 248 annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging, as shown in the inset of Fig. 4b. As marked by the red intensity profiles, the larger atomic 249 spacing in front of the interfacial ledge compared to neighboring atomic columns of both the 250 Cu₂O and Cu lattices, indicating the presence of atomic vacancies in the atom columns 251 adjacent to the double-atomic-height interfacial ledge (more detail in Extended Data Text 8 252 and Extended Fig. 9). The formation of these Cu vacancy columns is due to the decreased 253 254 lattice spacings from Cu₂O to Cu and the (7×6) CSL interface configuration, in which the Cu₂O side has a smaller number of Cu atoms to match the Cu side. The dislocation core is the 255 preferred region to develop these Cu vacancy columns due to concentrated displacements of 256 atoms in the core region (Fig. 1). By contrast, the smaller displacements of interfacial Cu 257 atoms located away from the dislocation core undergo spontaneously small displacements to 258 develop the one-on-one matching of Cu atoms upon the departure of interfacial lattice 259 oxygen, as seen in the DFT relaxed structure (Fig. 4b). 260

The pinned step flow at the core of misfit dislocations is therefore attributed to the presence of Cu vacancy columns in front of the interfacial step. The ledge resumes its lateral flow only after the Cu vacancy columns are completely filled with extra Cu atoms. The ledge flow that does not fill up the Cu vacancy columns will transform the misfit dislocations into isolated edge dislocations in the bulk of Cu, this will significantly increase the energy of the

system due to the required presence of many broken bonds along the dislocation lines 266 (Extended Data Fig. 10). Therefore, the climb of the entire misfit dislocation line to the new 267 location of the Cu₂O/Cu interface is essential before the sweeping of the dislocation core by 268 the ledge flow. The resumed ledge propagation after the misfit dislocation climb is like 269 synchronized movements of atoms in front of the interfacial ledge, by which the interfacial 270 271 ledge maintains straight between its two end points defined by the interface size of individual grains (Extended Data Text 9 and Extended Data Fig. 11). For the Cu₂O/Cu(110) interface as 272 shown in Fig. 3a-e, this dislocation climb process requires extra Cu atoms to fill the two Cu 273 vacancy columns. As demonstrated in our DFT calculations shown in Fig. 4c, the misfit 274 dislocation is observed to climb by two atomic layers from the site marked with pink dashed 275 "T" to the black solid "T" site and the system energy decreases by 0.44 eV after the two 276 vacancy columns are filled up with extra Cu atoms. This confirms the in-situ TEM 277 278 observations (Fig. 3a-e) that show the dislocation core climb by two atomic layers to the new Cu₂O(110)/Cu(110) interface to accompany the sweeping of the dislocation core by the 279 interfacial step. By contrast, the interfacial step along the Cu₂O(100)/Cu(100) interface is 280 only one-atomic layer high (Fig. 3g-k), and thus the misfit dislocation climbs by one atomic 281 layer to the new Cu₂O/Cu interface by filling up only one Cu vacancy column above the 282 dislocation core. Therefore, the step-flow of the Cu₂O \rightarrow Cu transformation at the (100) 283 interface shows a shorter dwell time at the core of the dislocations compared to that along the 284 (110) interface (Fig. 3f and l). 285

The climb of the misfit dislocations requires the supply of extra Cu atoms either from the 286 Cu_2O side or the Cu substrate side to join the extra Cu plane at the Cu_2O/Cu interface. This 287 leaves the Cu vacancy columns above the dislocation core to diffuse away. Using DFT and 288 NEB computations, we first investigate the barriers for Cu atom-vacancy exchanges in the 289 bulk of the Cu₂O side. Two crystallographically nonequivalent pathways for atom-vacancy 290 diffusion exchanges between adjacent layers can be identified (Extended Data Fig. 12a), and 291 our NEB calculations give the energy barriers of 1.42 eV and 1.76 eV, respectively. These 292 values are in good accordance with the experimental result of the energy barrier ($\sim 1.73 \text{ eV}$) 293 of the lattice diffusion of Cu in Cu₂O³². Furthermore, in the case of the presence of interstitial 294 H in the Cu₂O lattice (pink balls in Extended Data Fig. 12b), our calculations indicate that the 295

diffusion barriers for the two Cu atom-vacancy pathways decrease to 1.27 eV and 1.55 eV, 296 respectively. Therefore, penetration of H into the Cu₂O lattice enhances the Cu transport for 297 298 the dislocation climb at the Cu₂O/Cu interface. Similarly, the barriers for atom-vacancy exchanges in the Cu bulk of the Cu side are evaluated to assess the kinetic feasibility for the 299 supply of Cu atoms from the Cu side for the dislocation climb. Our NEB calculations 300 301 (Extended Data Fig. 12c) show that the energy barriers for bulk diffusion in Cu are 0.57 eV along [110] and 0.64 eV along [100], respectively. Therefore, extra Cu is supplied more 302 favorably from the Cu side for the dislocation climb, where the dwelling of the interfacial step 303 flow at the core of misfit dislocations is induced by the long-range diffusion of Cu from the Cu 304 bulk to fill up the vacancies in the misfit dislocation core. This corroborates well with our DFT 305 calculations, showing the increasingly lowered system energy as the vacancies diffuse deeper 306 into the Cu bulk and the higher energy barriers (0.57 eV \sim 0.64 eV) for the vacancy-assisted 307 diffusion in the Cu bulk than the energy barriers ($0.22 \text{ eV} \sim 0.31 \text{ eV}$) for the interfacial jumps 308 of metallic Cu atoms to the vacant site of the dislocation core (Fig. 4d-e, Extended Data Text 10 309 and Extended Data Figs. 13-14). Edge dislocations in the Cu bulk can provide a convenient 310 311 sink for vacancies diffusing away from the misfit dislocations, conversely, Cu atoms are emitted by the recession of the extra half-plane of the edge dislocation and diffuse to the misfit 312 dislocation core, as schematically shown in Fig. 4f. This process is also confirmed by the 313 314 time-sequence HRTEM images in Fig. 4g and Extended Data Fig. 15 (Supplementary Movie 5), showing that edge dislocations in the Cu bulk acts as a vacancy sink and experiences the net 315 positive climb in the Cu bulk. Similar stop-and-go Cu₂O \rightarrow Cu interfacial transformation along 316 with the coordinated positive climb of edge dislocations in the Cu bulk is also observed for 317 high-index Cu₂O/Cu interfaces (Extended Data Text 11, Supplementary Movie 6 and 318 Extended Data Fig. 16). The long-distance diffusion required for the interfacial dislocation 319 climb is further confirmed by our calculations using the classic dislocation model, which give 320 the misfit dislocation climb velocities of 0.067 nm/s for the (110) interface and 0.233 nm/s 321 322 for the (100) interfaces, respectively (Extended Data Text 12 and Extended Data Fig. 17). 323 These values agree well with our experimentally measured dislocation climb velocities of $\frac{d_{Cu(110)}}{t_{dwell(110)}} = \frac{0.2585 \, nm}{4 \, s} = 0.065 \, nm/s \text{ for the (110) interface and } \frac{d_{Cu(100)}}{t_{dwell(100)}} = \frac{0.1828 \, nm}{1 \, s} = 0.065 \, nm/s$ 324

0.183 nm/s for the (100) interface (Fig. 3), respectively.

It should be borne in mind that the misfit dislocations form an orthogonal network at the 326 327 Cu₂O/Cu interface, as illustrated schematically in the left model in Fig. 4h (Supplementary Movie 7). In our in-situ TEM experiments shown above, the Cu₂O/Cu interfacial 328 transformation is visualized along the direction parallel to the interfacial steps. Clearly, the 329 330 pinning effect on the interfacial transformation is associated with the climb of the dislocation lines parallel to the interfacial step (middle model in Fig. 4h). The step-flow interfacial 331 transformation is paused once the step encouters the dislocation lines. As described above, 332 the interfacial step resumes its lateral propagation only after the entire dislocation line climbs 333 to the new location of the Cu₂O/Cu interface (right model in Fig. 4h), which requires 334 long-range diffusion of a large number of Cu atoms to fill up Cu vacancies along the entire 335 dislocation line and therefore resluts in the observed dwelling of the interfacial step flow at 336 337 the core of the dislocation lines. By contrast, the other set of the dislocation arrays with their dislocation lines perpendicular to the interfacial step has a negligible contribution to the 338 observed dwelling of the interfacial step. This is because those dislocation lines intersect with 339 340 the step all the time (Fig. 4h) and their climb to the new Cu₂O/Cu interface happens instantaneously by replenishing just one Cu atom for monoatomic steps (along the 341 Cu₂O(100)/Cu(100) interface) or two Cu atoms for double-atomic-height steps (along the 342 Cu₂O(110)/Cu(110) interface) (Extended Data Text 2 and Extended Data Fig. 4). 343

With in-situ TEM imaging in plan view, we further identity that the similar stop-and-go 344 interfacial transformation can also occur along the other orthogonal direction, albeit not 345 concurrently at the same place of the two perpendicular directions (Extended Data Text 13, 346 Supplementary Movie 8 and Extended Data Figs 18 and 19). The non-coexistence of 347 perpendicular interfacial ledges at the same place is because the ledges are the sink of oxygen 348 vacancies in the oxide (as shown in our DFT modeling, Fig. 4b and Extended Data Fig. 7), 349 suggesting that an active zone of oxygen vacancy capture exists around an interfacial ledge 350 351 and nucleating new ledges either parallel or perpendicular to the existing one in the close 352 vicinity is unlikely. This corroborates well with our in-situ TEM observations, showing that all the interfacial ledges are well separated without bunching during their motion. As shown 353 by the observed climb motion of the misfit dislocations at the Cu₂O/Cu interface in 354

conjuction with the positive climb of edge dislocations in the Cu bulk, the interfacial ledge along with its intersection with the misfit dislocations serves first as a sink for capturing oxygen vacancies produced originally at the oxide surface and then act as the source for dumping the captured vacancies to the Cu side, thereby resulting in the eventual annihilation of the vacancies by edge dislocations in the Cu bulk (Fig. 4d-f).

360 Misfit dislocations are well recognized as accommodating the crystal lattice structure phase transformations^{5,6}. both diffusional and martensitic Taking 361 changes in oxidation/reduction as examples, the lattice parameter of an oxide is usually significantly 362 larger than that of the metal from which it is formed. This large lattice misfit makes the 363 formation of coherent metal-oxide interface energetically unfavorable although many oxides 364 are nonetheless observed to grow crystallographically-aligned with the metal substrate. A 365 classical model describing the occurrence of epitaxy in such large-misfit systems is the 366 367 coincidence site lattice (CSL) interface that requires the presence of an equilibrium array of misfit dislocations with a spacing given by the difference in lattice parameters of the given 368 epitaxial relation^{15,17}. Therefore, Cu and Cu₂O actually form a semi-coherent interface in 369 370 which the mismatch is periodically taken up by misfit dislocations that can be considered as extra half planes of Cu ending in the interface. 371

Kinetically, the dynamic role of misfit dislocations during boundary migration associated 372 with a solid-state transformation is a subject of general interest^{6,15,17}. For oxidation induced 373 phase transformations, the oxide growth rate is assumed to follow Wagnerian parabolic 374 kinetics controlled by vacancy-assisted diffusion of ions through the oxide, where misfit 375 dislocations are required as sinks/sources of vacancies for ionic diffusion. A difficulty in 376 vacancy annihilation or creation arising from blocking the misfit dislocations by segregated 377 378 impurities would result in reduced oxidation rate from Wagnerian scaling kinetics. In contrast to the extrinsic (impurity) cause of the interface control by segregant pinning^{3,7,17}, here we 379 show that the misfit dislocation array itself exerts important intrinsic interface control by 380 pinning lateral propagation of interfacial steps at the misfit dislocation core. The large crystal 381 382 lattice changes accompanying the oxide growth typically lead to equilibrium misfit dislocation spacings of about 1-3 nm. This high density of the misfit dislocations leads to the 383 expected importance for interface control of the reaction kinetics at the metal/oxide interface. 384

The semi-coherent interphase boundary containing terraces and ledges is a common feature 385 for interface-mediated phase transformations^{5,18}. This is because the atomically flat interface 386 is typically associated with higher interfacial energies due to the lattice mismatch between a 387 pair of parallel adjoining planes. Introducing regular step risers that connect adjacent terraces 388 can effectively increase the area of good matching (coherency), thereby minimizing the 389 interfacial energy. The retardation of global transformation kinetics by diffusion through the 390 pinning action of intrinsic misfit dislocations on the interfacial step flow was not yet known 391 for inclusion in recent reviews of the role of interface structure in phase transformations^{5,6}. 392 Given the ubiquitousness of semicoherent interfaces and the ledge mechanism in many 393 technologically relevant material systems and solid-solid transformations^{5,6}, the insight 394 developed from the dynamic, real-time observations showing the important role of the misfit 395 dislocations in mediating the interfacial step propagation during the oxide reduction may be 396 directly applicable to scaling reactions (i.e., oxidation, nitridation, sulfidation, silicidation, 397 hydridation), precipitation reactions, solid-state displacement reactions, and layer formation 398 by interdiffusion, where the prototypes of basic processes governing the interfacial 399 400 transformation exhibit great similarity to the oxide reduction including semi-coherent interfaces, ledges and vacancy-assisted diffusion. 401

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Figure 1 | Formation of misfit dislocations at the Cu₂O/Cu interface. a, HRTEM image of 478 a Cu₂O/Cu interface formed by in-situ oxidation of a Cu(110) facet at $pO_2 = 0.67$ Pa and T 479 =623 K. The core regions of four misfit dislocations along the Cu₂O/Cu interface (green 480 dashed line) are marked with crosses. Inset: diffractogram of the HRTEM image, yellow and 481 red circles mark the (200) spots of Cu and Cu₂O, respectively. **b**, Strain maps of ε_{xx} obtained 482 by GPA of the HRTEM image in a. c, d, Experimental and simulated HRTEM micrographs 483 showing the dislocation core structure, where the Burgers circuits are marked by white lines. 484 e, DFT-relaxed Cu₂O(110)/Cu(110) interface structure used for HRTEM simulations in d. f, 485 486 HAADF image of a typical misfit dislocation. Parameters of the HRTEM image simulations: accelerating voltage: 300 keV, the spherical aberration: 0.001 mm, defocus: -2 nm, thickness: 487 30 nm. Yellow balls: Cu atoms; Red balls: O atoms. Scale bar, 1 nm (a), 0.5 nm (c, d, f). 488



Figure 2 | In-situ TEM visualization of the $Cu_2O \rightarrow Cu$ interfacial transformations via 491 the stop-and-go step flow at 623 K and 5.3 Pa of H₂ gas. a-d, Time-sequence HRTEM 492 images showing the Cu₂O \rightarrow Cu transformation along the Cu₂O(110)/Cu(110) interface 493 (Supplementary Movie 1). Arrows 1 and 2 mark the Cu₂O/Cu interfacial steps. Between c 494 and **d**, the e-beam was blanked for ~ 60 s to examine possible electron beam irradiation 495 effects on the interfacial transformation and then unblanked for TEM imaging. The dark red, 496 497 red, orange, and yellow dashed lines show the traces of the surface position and contour of the oxide at 0 s, 10.5 s, 21 s, and 102 s, respectively. e, Distance-time plot measured from 498 Supplementary Movie 1 showing the lateral flow of steps 1 and 2 in a stop-and-go manner. f-i, 499 Time-sequence TEM images (Supplementary Movie 2) showing the $Cu_2O \rightarrow Cu$ 500 transformation along the Cu₂O(100)/Cu(100) interface. Arrows 3 and 4 mark the lateral flow 501 of the Cu₂O/Cu interfacial steps. j, Distance-time plot measured from Supplementary Movie 502 2 showing the stop-and-go flow of steps 3 and 4. Scale bar, 2 nm (a-d), 5 nm (f-i). 503



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Figure 3 | In-situ atomic-scale observations of the intermittent step-flow regulated by misfit dislocations during the Cu₂O \rightarrow Cu interfacial transformations at 623 K and 5.3 Pa of H₂ gas flow. a-e, Time-sequence of HRTEM images (Supplementary Movie 3) showing the regular interruption of the lateral flow of a double-atomic-height step along the Cu₂O/Cu(110) interface, where the step is pinned for about 2-6 s at the core of each dislocations and then resumes its lateral migration. **f**, Plot showing the dwell time of the interfacial steps at the core of dislocations along the Cu₂O(110)/Cu(110) interfaces. **g-k**, Time

sequence of HRTEM images (Supplementary Movie 4) showing the periodic pauses of monoatomic steps at the core of the misfit dislocations along the Cu₂O(100)/Cu(100) interface, where the step is pinned for about 0.5-1.5 s at the dislocation cores and then resumes its lateral migration. Dashed yellow lines mark the Cu₂O/Cu interface and yellow arrows point to the location of the interfacial steps. **I**, Plot of the dwell time of the interfacial steps at the core of dislocations along the Cu₂O(100)/Cu(100) interfaces. Scale bar, 1 nm (**a-e, g-k**).



522 Figure 4 | DFT modeling of the stop-and-go Cu₂O/Cu interfacial transformations. a-b, Upon the sequential departure of lattice oxygen (small red circles) at the Cu₂O/Cu interface, 523 adjacent Cu atoms shift spontaneously toward the vacated oxygen sites, resulting in two Cu 524 vacancy columns (blue dashed circles) above the dislocation core. In turn, the misfit 525 dislocation glides to the pink solid "T" position from the original position (red dashed "T" in 526 **b**). The inset in **b** is a HAADF-STEM image of the Cu₂O/Cu(110) interface, showing the 527 pinning of a double-atomic-height interfacial ledge at the misfit dislocation core. The 528 intensity profile along the red dashed rectangle shows the larger atomic spacing in front of 529 530 the interfacial ledge due to the presence of atomic vacancies. c, Upon filling up the two Cu vacancy columns with extra Cu atoms (blue balls), the dislocation climbs spontaneously from 531 the pink dashed "T" position to black solid "T" position. d, Atomic model for evaluating the 532 system energy changes as a function of the distance of a Cu vacancy from the Cu₂O/Cu 533 interface by one (site 1), three (site 2) and five atomic layers (site 3) in the Cu bulk, 534 respectively. e, System energy plot as a function of the Cu vacancy site shown in d. f, 535 Schematic showing an edge dislocation in the Cu bulk acting as a source of Cu atoms to fill 536

up the Cu vacancies for the misfit dislocation climb in front of the interfacial ledge. g, 537 Time-sequence HRTEM images (Supplementary Movie 5) showing the glide and positive 538 climb of an edge dislocation in the Cu bulk during the Cu₂O reduction at 623 K and 5.3 Pa of 539 H₂ gas flow. **h**. Schematic showing the stop-and-go transformation kinetics induced by the 540 dislocation lines parallel to the interfacial step, the lateral flow of the interfacial step is 541 pinned at the dislocation core until the dislocation line climbs to the upper terrace 542 (Supplementary Movie 7). The dislocation lines perpendicular to the interfacial step intersect 543 544 with the step all the time and have no contribution to the intermittent propagation of the step. Blue, cyan and yellow balls: Cu; small red balls: O; blue dashed circles: Cu vacancies; red 545 circles: O vacancies. Scale bar: 0.5 nm ((inset, b) and g). 546

547 Methods

548 Sample preparation

549 Cu(100) thin films with a nominal thickness of ~ 50 nm were deposited on NaCl(100) at 573 550 K using an ultrahigh vacuum e-beam evaporation system. The Cu films were then removed 551 from the substrate by dissolving NaCl in deionized water, washed, and mounted on a TEM 552 specimen holder. Plasma cleaning of the specimen holder and specimen was performed prior 553 to insertion in the environmental TEM (E-TEM).

554

555 Procedure for the in-situ environmental TEM (ETEM) experiments

In-situ E-TEM experiments were conducted in a dedicated field-emission environmental TEM (FEI Titan 80–300) equipped with an objective-lens aberration corrector capable to deliver spatial resolution of 0.08 nm at 300kV and a gas manifold to control the pressure of various gases in the sample area^{33,34}. The procedure for the E-TEM experiments is schematically shown in Extended Data Fig. 1 and include the following steps:

- 5611) As-loaded Cu films were deliberately annealed at ~ 873 K and ~ 0.13 Pa of H2 gas562flow to remove native oxide and generate tears and holes with faceted edges.563These freshly created facets are oxide-free and ideal for in-situ TEM observations564made in cross-sectional views of oxidation and reduction along the faceted edges565(Extended Data Fig. 1). The cleanliness of the sample was confirmed by in-situ566electron diffraction and electron energy loss spectroscopy (EELS).
- 567 2) The specimen was then cooled down to 623 K and H₂ gas was pumped out. The 568 freshly cleaned Cu was oxidized at 623 K to form epitaxial Cu₂O islands along the 569 edges of faceted holes in the Cu film by flowing O₂ gas at $pO_2 = 0.67$ Pa 570 (Extended Data Fig. 1).
- 571 3) O₂ gas was then pumped out and the epitaxial Cu₂O on Cu was reduced to Cu in 572 place at 623 K by flowing H₂ gas at the pressure of $pH_2 = 5.3$ Pa.
- 573 4) In-situ HRTEM imaging was performed to visualize the Cu₂O \rightarrow Cu interfacial 574 transformations and the resulting dynamic motion of misfit dislocations at T=623 575 K pH₂=5.3 Pa. In-situ time-sequence HRTEM images were recorded along the

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Cu₂O(100)/Cu(100) and Cu₂O(110)/Cu(110) interfaces in an edge-on position, respectively.

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579 Excluding the electron beam effect

Potential TEM electron beam irradiation effects on the observed stop-and-go interfacial 580 581 transformations were evaluated carefully to ensure that an intrinsic behavior of the interfacial transformation was studied. We performed comparison experiments by un-blanking and 582 blanking the electron beam. As shown in Fig. 2 (Supplementary Movie 1), the electron beam 583 was intentionally blanked for 60 s in the course of the in-situ TEM observation, and no 584 noticeable difference in the Cu₂O reduction rate was noted (in terms of the Cu₂O/Cu interface 585 migration distance), confirming the negligible effect of electron beam on the interfacial 586 transformations. Conducting such comparative TEM observations to understand the effect of 587 588 electron irradiation is part of experimental protocol and in this case ensured that the electron beam effect has a negligible effect on the interfacial transformation, and the stop-and-go flow 589 of interfacial steps that we see is inherent. 590

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592 High-resolution TEM image simulations

593 Density functional theory (DFT) optimized Cu₂O/Cu interfacial configurations were used as 594 input files for HRTEM simulations. HRTEM image simulations were performed using the 595 multi-slice method with the parameters carefully matched to the experimental conditions 596 (accelerating voltage: 300 keV, the spherical aberration: 0.001 mm, defocus: $-8 \sim 8$ nm, 597 thickness: $5 \sim 50$ nm).

598

599 Geometrical phase analysis (GPA) procedures

Geometric phase analysis was performed to identify the core of misfit dislocations along Cu₂O/Cu interfaces and quantify strain distribution around the misfit dislocation core based on the high resolution TEM images using the GPA tool³⁵. The HRTEM images were filtered using the Wiener filter code with a noise-to-signal ratio of 0.2 in order to reduce the noise levels before conducting GPA procedures. Cu lattice taken in a zone of the image far away from the interface was considered as the structure reference.

607 Ab initio calculations

The total energy calculations were carried out within DFT^{36,37} using the plane wave 608 pseudopotential method³⁸ embodied in the VASP code with ultra-soft pseudopotentials³⁹. 609 PBE generalized gradient approximation (GGA)⁴⁰ and projector augmented-wave (PAW)⁴¹ 610 potential were performed to describe the electron-electron exchange and core-electron 611 potential separately. The plane-wave cutoff energy cut-off energy was set to be 400 eV, and 612 the k-point sampling of $4 \times 2 \times 1$ based on the Monkhorst-Pack grids was used for the 613 interface model. In modeling the Cu/Cu2O interface, we used periodically repeated 614 eight-layer slabs with their top and bottom layers fixed. To minimize the strain induced by 615 the lattice misfit, we used the coincidence-site-lattice (CSL) structure of the 7×6 interface 616 configuration, in which 6 Cu spacings in Cu₂O match 7 Cu spacings in the Cu substrate, 617 resulting in a minimum strain of 0.226%. Considering the strong correlation effect among Cu 618 3d electrons, DFT+U is employed in our simulations. According to the previous study⁴², the 619 values of 7.5 eV and 0.98 eV were adopted for parameter U and J, respectively. All our 620 calculations were spin-averaged, except for isolated molecular and atomic oxygen. The 621 622 calculation of vacancy formation energies is defined as,

 $E_f = E_{slab/vac} + E_{atom} - E_{slab},$

where E_f is the vacancy formation energy, $E_{slab/vac}$ is the free energy of the slab with one vacancy, E_{atom} is the free energy of one single atom in the pure substance, E_{slab} is the free energy of the slab without the vacancy. All the atomic structures are visualized using the Visualization for Electronic and Structure Analysis (VESTA).

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629 Methods references:

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Author contributions G.Z. conceived the experiments and supervised the project. X.S., L.Z.,
S.H. and X.C. conducted experiments. D.W. conducted DFT calculations. M.L. developed the
codes for TEM image alignment. D.Z. and J.Y. contributed experimental platform. X.S. and
G.Z. analyzed data and wrote the paper. All the authors commented on the manuscript.

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669 **Competing interests** Authors declare no competing interests.

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677	Supplementary Information
678	for
679	Misfit-dislocation induced stop-and-go kinetics of interfacial
680	transformations
681	
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695	This file includes:
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697	Extended Data Texts 1 to 13
698	Extended Data Figures 1 to 19
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700	Captions for Supplementary Movies 1 to 8
701	References
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703	Other Supplementary Materials for this manuscript include the following:
704	Supplementary Movies 1 to 8

705 Extended Data Text 1. Calculations of the lattice mismatch of different Cu₂O/Cu CSL 706 configurations

According to the Powder Diffraction Files from JCPDS (Joint Committee on Powder 707 Diffraction Standards), the lattice constants of Cu₂O (JCPDS No. 65-3288) and Cu (JCPDS 708 No. 04–0836) are 0.4267 nm and 0.3615 nm, respectively, at room temperature. Considering 709 the thermal expansion of the specimen at 623 K (the temperature of our in-situ TEM 710 experiments), the thermal expansion coefficients of Cu₂O and Cu are 3.1×10⁻⁶ K⁻¹ and 18×10⁻⁶ 711 K⁻¹, respectively,⁴³ and the lattice constants of Cu₂O and Cu at 623 K are calculated to be 712 $a_{Cu_2O} = (3.1 \times 10^{-6} \text{K}^{-1} \times 623 \text{K} + 1) \times 0.4267 = 0.4275 \text{ nm and } a_{Cu} = (18 \times 10^{-6} \text{K}^{-1} \times 623 \text{K} + 1) \times 0.3615$ 713 = 0.3656 nm, respectively. For m×n CSL configuration, the lattice mismatch, f_{1} is defined as 714 $(na_{Cu_2O} - ma_{Cu})/na_{Cu_2O}$. Thus, the 8×7, 7×6, and 6×5 CSL configurations have the lattice 715 mismatch of 2.26%, 0.226%, and 2.624%, respectively. Thus, the 7×6 CSL configuration is 716 the most stable interfacial configuration, in which 7 Cu spacings in the Cu substrate match 6 717 Cu spacings in Cu₂O. This is in agreement with our in-situ TEM observations, showing that 718 the 8×7 and 6×5 CSL configurations have the tendency to transform into the 7×6 CSL 719 configuration during the Cu₂O Cu interfacial transformation. 720

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722 Extended Data Text 2. Identification of the Cu₂O/Cu interface

Fig. 1c shows a typical HRTEM image of a misfit dislocation at the 723 Cu₂O(110)/Cu(110) interface. HRTEM image simulations were used to compare the 724 experimental HRTEM images for actually identifying the Cu₂O/Cu interface location. Since 725 the Cu₂O(110) surface can be terminated by pure Cu or Cu-O, there are two possible 726 interface terminations, i.e. Cu-terminated and Cu-O terminated Cu₂O(110)/Cu(110), as 727 shown in Extended Data Fig. 4. Our DFT calculations indicate that the Cu-O terminated 728 Cu₂O(110)/Cu(110) interface results in a structurally stable interface (Extended Data Fig. 729 4a-b), whereas the Cu-terminated interface is unstable and spontaneously transforms into the 730 Cu-O terminated interface (Extended Data Fig. 4c-d), where the interfacial Cu atoms on the 731 Cu₂O side spontaneously transform into metallic Cu of the Cu substrate. This also result in a 732 Cu vacancy column in the Cu substrate due to the 7×6 CSL interface configuration. 733

Therefore, the Cu-O terminated Cu₂O(110)/Cu(110) interface configuration (Fig. 1e and 734 Extended Data Fig. 4b) is chosen in the DFT modeling and HRTEM image simulations. Fig. 735 1d shows a simulated HRTEM image using the Cu-O terminated interface model (Fig. 1e), 736 matching well with the experimental HRTEM image (Extended Data Fig. 1c). The combined 737 DFT and HRTEM image simulations confirm the Cu₂O(110)/Cu(110) interface location as 738 marked by the green dashed lines in Fig. 1, which is consistent with the identified misfit 739 dislocations located at the Cu₂O/Cu interface. The required Cu-O interface termination also 740 explains why the experimentally observed Cu₂O \rightarrow Cu transformation along the (110) 741 interface occurs via the lateral flow of double-atomic-height steps that consist of one pure Cu 742 and one Cu-O layers (Fig. 3). 743

This is in contrast to the interfacial transformation along the Cu₂O(100)/Cu(100) 744 interface that is controlled by the lateral propagation of monoatomic interfacial steps (Fig. 745 3g-k). For the Cu₂O(100) the surface, it can be terminated by pure Cu or O layer and the 746 vertical separation between the adjacent Cu and O layers is ¹/₄ of the edge length of the Cu₂O 747 unit cell (i.e., O atoms reside in the tetrahedral holes formed by neighboring Cu atoms ⁴⁴). 748 Therefore, there are two possible interface terminations, i.e., Cu-terminated and O-terminated 749 Cu₂O(100)/Cu(100) interfaces. Our DFT calculations indicate that the O-terminated 750 Cu₂O(100)/Cu(100) interface results in a structurally stable interface, whereas the 751 Cu-terminated interface is unstable and spontaneously transforms into the O terminated 752 interface (Extended Data Fig. 4e-f), where the interfacial Cu atoms on the Cu₂O side 753 spontaneously transform into metallic Cu of the Cu substrate. This also results in a Cu 754 vacancy column in the Cu substrate due to the 7×6 CSL interface configuration. The O atoms 755 in the interface reside in the tetrahedral holes between two adjacent Cu layers, which 756 757 corresponds to the height of a monoatomic interfacial step formed by Cu atoms. This explains why the experimentally observed $Cu_2O \rightarrow Cu$ transformation along the (100) 758 interface occurs via the lateral flow of monoatomic interfacial steps (Fig. 3). 759

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761 Extended Data Text 3. HRTEM image simulations

HRTEM image simulations were performed to identify the interface location usingthe multi-slice method with the parameters carefully matched to the experimental conditions

(accelerating voltage: 300 keV, the spherical aberration: 0.001 mm, defocus: $-8 \sim 8$ nm, 764 thickness: 5 ~ 50 nm). Based on the Cu₂O(110)/Cu(110) interface structure model in 765 Extended Data Fig. 4b (Fig. 1e), simulated HRTEM images are shown in Extended Data Fig. 766 5 with specimen thickness increasing from bottom (5nm) to top (50 nm) and defocus 767 increasing from left (-8 nm) to right (8 nm). By comparison of the simulated images with the 768 experimental HRTEM image in Fig. 1c, it is found that a simulated HRTEM image with 769 simulated parameters of 30 nm thickness and -2 nm defocus outlined by the red rectangle in 770 Extended Data Fig. 5 reproduces the experimental results. 771

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773 Extended Data Text 4. Cu₂O surface decay during the Cu₂O Cu interfacial 774 transformation

775 It is also observed that the Cu₂O surface undergoes slow decay during the Cu₂O Cu transformation at the Cu₂O/Cu interface. This is shown by tracing the temporal evolution of 776 the surface profile of the oxide in Fig. 2d. The reaction between adsorbed H₂ and lattice 777 oxygen at the Cu₂O surface results in the formation of H₂O molecules that desorb from the 778 surface at the elevated temperature. Accompanying the surface desorption of H₂O molecules 779 is the concomitant formation of oxygen vacancies at the oxide surface. The surface decay is 780 induced by the overpopulation of oxygen vacancies that induce the collapse of the Cu₂O 781 lattice at the surface. The observed surface decay confirms the presence of a high 782 concentration of oxygen vacancies at the oxide surface, where the vacancy concentration 783 gradient between the surface and the Cu₂O/Cu interface results in the inward diffusion of 784 oxygen vacancies toward the Cu₂O/Cu interface via the counter diffusion of lattice oxygen 785 from the Cu₂O/Cu interface to the oxide surface. The observed surface decay also indicates 786 that the rate for the loss of lattice oxygen at the oxide surface is faster than that of the oxygen 787 supply via the counter diffusion of lattice oxygen from the Cu₂O/Cu interface to the oxide 788 surface, thereby resulting in the overpopulated oxygen vacancies at the surface and thus 789 inducing the surface decay of the oxide. As also shown in Fig. 2a-d, the surface decay does 790 not result in the in-place buildup of metallic Cu on the oxide surface, indicating that Cu 791 atoms freed from the Cu₂O surface decay migrate to the Cu substrate via surface diffusion 792

across the oxide surface because Cu adatoms are energetically more favorable to stay on theCu substrate than on the oxide surface.

795

796 Extended Data Text 5. Excluding the electron beam irradiation effect

Electron beam irradiation effect was carefully considered for TEM observations in 797 order to ensure that the observed stop-and-go interfacial transformations were an intrinsic 798 behavior. On one hand, we collected TEM images (Fig. 2f-i, Supplementary Movie 2) at the 799 dose rate as low as possible via lowering the image magnification, spreading beam, and 800 increasing image acquisition rate. As shown in Fig. 2f-i (Supplementary Movie 2), the 801 stop-and-go interfacial transformation still occurred under the low electron beam dose rate, 802 suggesting negligible electron beam irradiation effect on the interfacial transformations. On 803 another hand, comparison experiments by blanking and un-blanking the electron beam was 804 805 conducted to further examine possible beam effects on interfacial transformations. As shown in Fig. 2a-d (and Supplementary Movie 1), 4 layers of the Cu₂O(110) lattice transformed into 806 Cu at the interface within 26 s under the electron beam irradiation. Similarly, 10 layers of the 807 808 Cu₂O(110) lattice transformed into Cu when beam was blanked for 60 s (Supplementary Movie 1). The similar transformation rate from the Cu₂O lattice to the Cu lattice with and 809 without the presence of the electron beam irradiation confirms its negligible effect on the 810 observed stop-and-go interfacial transformations. 811

812

813 Extended Data Text 6. Thickening of the Cu substrate via the ledge propagation along 814 the Cu₂O/Cu interface

The sweeping velocity of the step motion between two adjacent misfit dislocations is dominated by the dwell time at the misfit dislocation core and can be calculated as L/t, where L is the distance between two adjacent misfit dislocations (i.e., 7 lattice spacings of the Cu substrate for the 7×6 CSL interfacial configuration), and t the average dwell time at the misfit dislocation core. For the Cu₂O/Cu(100) and (110) interfaces, the sweeping velocities of the step motion are calculated as 1.28 nm/s and 0.43 nm/s, respectively.

821 In addition to the Cu₂O \rightarrow Cu interfacial transformation, the oxide is also reduced at 822 the surface by surface decay during the H₂ exposure. Therefore, the microscopic interface

growth velocity (i.e., the sweeping velocity of the step motion) does not amount to the total 823 reduction rate of Cu₂O to Cu. However, the microscopic interface growth velocity can be 824 translated into the thickening rate of the underlying Cu layer, which can be measured 825 macroscopically. As shown schematically in Extended Data Fig. 6, the relationship between 826 the microscopic interface growth velocity (u) and thickening rate (v) of the underlying Cu 827 layer can be easily shown as $v = \frac{uh}{d}$, where d is the distance between adjacent steps and 828 h is the step height. For the Cu₂O/Cu(100) interface, the thickening rate, v, is calculated to be 829 0.0512 nm/s using the value of u=1.28 nm/s, d=4.5 nm (from Supplementary Movie 2) and 830 h=0.18 nm (monoatomic step height), which is very close to experimentally measured 831 velocity (0.0514 nm/s) of the Cu₂O/Cu(100) interface migration along the vertical direction. 832 833 Similar calculations for the Cu₂O/Cu(110) interface give a thickening rate of 0.022 nm/s using the value of u=0.43 nm/s, d=4.9 nm (from Supplementary Movie 1) and h=0.25 nm 834 (double-atomic-height step height), which is also in good agreement with the experimentally 835 measured velocity (0.018 nm/s) of the Cu₂O/Cu(110) interface migration. 836

837

838 Extended Data Text 7. Energy barriers for vacancy-assisted oxygen diffusion in Cu₂O 839 during the Cu₂O Cu interfacial transformation

NEB calculations are employed to evaluate the energy barriers for the vacancy-assisted 840 841 oxygen migration for the surface/subsurface exchanges, in the bulk and at the Cu₂O/Cu interface. As illustrated Extended Data Fig. 7, we show two values for each diffusion pathway, 842 where the first value is calculated using the pristine lattice (in the absence of interstitial H) and 843 the second one (given in the square brackets) is obtained in the presence of interstitial H in the 844 Cu₂O lattice. Extended Data Fig. 7a, e shows the surface/subsurface exchanges by the 845 migration of an O atom in the second layer to a vacant lattice site in the surface layer with an 846 energy barrier of 0.55 eV [0.41 eV]. By the surface/subsurface exchanges, the O vacancies 847 produced at the surface thus diffuse through the bulk toward the Cu₂O/Cu interface. Extended 848 Data Fig. 7b, f shows the two crystallographically nonequivalent pathways (i.e., interlayer and 849 intralayer migration) of the vacancy-assisted diffusion in the bulk with the energy barrier of 850 1.22 eV [0.77 eV]. At the Cu₂O/Cu interface, two representative interfacial locations are 851

considered for the ledge flow, i.e., at the misfit dislocation core and away from the dislocation 852 core. Extended Data Fig. 7c, g corresponds to the situation that the interfacial ledge flow is 853 854 pinned at the dislocation core, where three nonequivalent pathways can be identified for the migration of the O atom at the dislocation core to the adjacent vacant lattice sites with the 855 energy barriers of 0.81 eV [0.75 eV], 0.89 eV [0.8 eV] and 0.47 eV [0.31 eV], respectively. 856 857 Extended Data Fig. 7d, h illustrates the interfacial ledge flow to the location that is away from the dislocation core by two Cu lattice spacings, where the energy barriers for the migration of 858 the O atom in front of the interfacial ledge to its adjacent, nonequivalent O vacant sites are 0.91 859 eV [0.79 eV], 1.13 eV [0.97 eV], and 1.34 eV [1.12 eV], respectively. 860

Several key conclusions can be drawn from these NEB modeling results. (1) The stop 861 862 of interfacial ledge lateral motion at the misfit dislocations is not caused by oxygen diffusion in front of the ledge. This is because the energy barriers for the vacancy-assisted oxygen diffusion 863 864 decrease as the interfacial ledge moves to the misfit dislocation (this means that the ledge flow becomes even faster at the dislocation core). This also corroborates well with our DFT results 865 showing the smaller oxygen vacancy formation energy at the misfit dislocation core than that 866 away from the dislocation (Extended Data Fig. 8). (2) The relatively smaller energy barriers for 867 the surface/subsurface exchange process compared to those for the vacancy-assisted diffusion 868 in the bulk and at Cu₂O/Cu interface indicate that oxygen vacancies produced at the oxide 869 870 surface can easily migrate into the oxide lattice. (3) The presence of interstitial H in the Cu₂O lattice further promotes the vacancy-assisted diffusion in the bulk for the inward migration of 871 oxygen vacancies toward the Cu₂O/Cu interface. 872

873 It is worth mentioning that faster diffusion along misfit dislocation lines at the Cu₂O/Cu interface may occur along the oxide island perimeter, which is defined as the 874 875 contact line between the three phases of the metal, oxide and hydrogen gas, their relative contributions to the total diffusion flux also depend on the area fraction. Because the area 876 fraction for hydrogen adsorption and vacancy-assisted lattice diffusion is much larger than 877 878 that for the pipe diffusion, the contribution from the lattice diffusion can be significantly 879 larger over the pipe diffusion. Furthermore, our DFT calculations show that the interfacial ledge serves as the sink to capture oxygen vacancies in the oxide (Extended Data Fig. 7) and 880 the oxygen vacancies captured by the interface ledges subsequently diffuse into the Cu bulk 881

882 (Fig. 4d-g).

883 Extended Data Text 8. HRTEM and HAADF imaging of atomic vacancy columns in 884 front of interfacial ledges

Both HRTEM and STEM-HAADF are employed to confirm the presence of Cu 885 vacancies at the misfit dislocation core right in front of the interfacial ledges. Extended data 886 887 Fig. 9a shows a HRTEM image obtained from an interfacial ledge that is pinned at the misfit dislocation core along the Cu₂O/Cu(110) interface. As marked by the intensity profiles, the 888 larger atomic spacing in front of the interfacial ledge compared to neighboring atomic 889 columns of both the Cu₂O and Cu lattices, indicating the presence of atomic vacancies in the 890 atom columns adjacent to the double-atomic-height interfacial ledge. Similarly, the larger 891 atomic spacing in front of the monoatomic ledge along the Cu₂O/Cu(100) interface 892 (Extended data Fig. 9b) suggests the presence of vacancies in the atom column. 893

894 The above HRTEM analysis is further complemented by STEM-HAADF imaging. HAADF is capable of providing more conclusive evidence of Cu vacancies because only Cu 895 contributes directly to the Z contrast of atomic columns. Extended data Fig. 9c illustrates a 896 897 HAADF image obtained from the Cu₂O/Cu(110) interface, showing the presence of a double-atomic-height ledge pinned at a misfit dislocation. As shown by the intensity profiles, 898 the larger atomic spacing in front of the interfacial ledge indicates the presence of atomic 899 900 vacancies. Extended data Fig. 9d shows a HAADF image obtained from the Cu₂O/Cu(100) interface, showing the presence of a monatomic ledge pinned at a misfit dislocation. The 901 larger atomic spacing in front of the interfacial ledge is induced by the presence of atomic Cu 902 903 vacancies.

904

905 Extended Data Text 9. Interfacial ledge flow by cooperative displacement of atoms

As shown from our in-situ TEM observation (Fig. 3), the interfacial step stops only at the misfit dislocation core during its stop-and-go propagation. The distance between successive stops is seven Cu lattice spacings for the 7×6 Cu/Cu₂O coincidence-site-lattice (CSL) configuration. Assuming that the Cu vacancies in a segment of the interfacial step are filled up and the segment of the interfacial step then propagates to the next misfit dislocation core, it results in large geometric kinks with their side lengths of seven Cu lattice spacings, as

shown schematically in Extended Data Fig. 11. This unsynchronized ledge flow will lead to a 912 highly kinked ledge with significantly increased ledge lengths (and thus ledge energies) and 913 914 therefore is energetically unfavorable compared to the lateral propagation of a straight ledge that happens only after all the Cu vacancies in front of the entire interfacial ledge are filled up. 915 In analogy to the different types of phase transformations in materials, the former can be 916 917 equivalent to the civilian transformation in which atom movements from the parent to the product lattice sites occur by random diffusional jumps, whereas the latter is similar to the 918 military transformation that involves cooperative movements of large numbers of atoms in 919 front of the interfacial ledge. The observed stop-and-go propagation of the interfacial ledges 920 shown here is more like the military-type movements of atoms in front of the interfacial 921 ledges, during which the interfacial ledge tends to maintain straight (thereby minimizing the 922 ledge energy) between its two points defined by the interface size of individual grains (not 923 924 the outer dimensions of a macroscopic crystal).

925

926 Extended Data Text 10. DFT modeling of long-range diffusion of Cu atoms from the Cu 927 substrate to the misfit dislocation core

Thermodynamically, we evaluate the system energy changes by the swap of a Cu 928 vacancy at the misfit dislocation core with a Cu atom at different lattice sites of the Cu 929 930 substrate. As shown in Extended Fig. 13a, the system energy becomes increasingly lowered by placing the Cu vacancy deeper toward the Cu bulk. The similar trend can be noted for the case 931 with the presence of two Cu vacancies, where the system energy drops even more significantly 932 933 as the two vacancies move deeper into the Cu bulk (Extended Data Fig. 13b). These DFT results show the thermodynamic tendency for the migration of Cu vacancies in the misfit 934 935 dislocation core in front of the interfacial ledge toward the Cu bulk. This in turn corresponds to the long-range diffusion of Cu atoms (via atom-vacancy exchanges) from the Cu bulk to fill up 936 the vacancies at the misfit dislocation core, thereby resulting in the misfit dislocation climb. 937

Kinetically, we then use the NEB method to evaluate the energy barriers for the vacancy diffusion from the misfit dislocation core to adjacent lattice sites of metallic Cu. As shown in Extended Data Fig. 14, three non-equivalent types of atom-vacancy diffusion pathways around the misfit dislocation core are identified with the resulting diffusion barriers in the range of 0.22 to 0.31 eV. These energy barriers are much lower than the barriers for vacancy-assisted diffusion in the Cu bulk, i.e., $0.57 \text{ eV} \sim 0.64 \text{ eV}$ (Extended Data Fig. 12c). Consequently, the supply of Cu atoms via the long-range diffusion in the Cu bulk, instead of the interfacial jumps of Cu atoms around the misfit dislocation core, is the rate-limiting step for the misfit dislocation climb. These DFT modeling results confirm that the long-range vacancy-assisted diffusion is not only kinetically required but also thermodynamically favored.

949

950 Extended Data Text 11. Stop-and-go propagation of ledges along high-index Cu₂O/Cu 951 interfaces

Extended Data Fig. 16 illustrates a relatively high-index and rough Cu₂O/Cu interface 952 consisting of narrow terraces and multiple ledges during the Cu₂O reduction at 623 K and 953 954 0.021 Pa of H₂ gas flow, showing that the interfacial ledges are constantly pinned at the misfit dislocations during the Cu₂O/Cu interface propagation toward the Cu₂O side. As shown in 955 Supplementary Movie 6, the stop-and-go propagation of the interfacial ledges is accompanied 956 with the glide and climb of the misfit dislocation in front of the ledges. Meanwhile, an edge 957 dislocation in the Cu bulk is observed to glide and climb deeper toward the Cu substrate 958 during the Cu₂O→Cu interfacial transformation. The net positive climb of edge dislocations 959 in the Cu bulk in coordination with the stop-and-go propagation of the interfacial ledges 960 indicates that the edge dislocation serves as a source of supplying Cu atoms from the Cu bulk 961 to the Cu₂O/Cu interface. Conversely, vacancies diffusing away from the core region of the 962 misfit dislocations at the Cu₂O/Cu interface are adsorbed by the extra half-plane of edge 963 dislocations in the Cu bulk, which results in the recession of the extra half-plane of the edge 964 dislocations. This is consistent with the in-situ TEM observation of the low-index 965 Cu₂O/Cu(110) interface, showing the similar net positive climb of edge dislocations in the Cu 966 bulk during the stop-and-go propagation of the interfacial ledges in the course of the Cu₂O 967 reduction at 623 K and 5.3 Pa of H₂ gas flow (Fig. 4, Supplementary Movie 5 and Extended 968 969 Data Fig. 15). Extended Data Figs. 15 and 16 also show evidently that the higher H₂ gas pressure results in the faster Cu₂O reduction, which corresponds to the faster propagation of 970 the interfacial ledges and faster climb of the edge dislocation in the Cu bulk. 971

973 Extended Data Text 12. Calculations of dislocation climb velocity by the classic 974 dislocation model

975 The classical thermodynamic stability of a microstructure is determined by the system976 Gibbs free energy (G),

977
$$G = \sum_{i=1}^{p} V_i g_i + \sum_{i=1}^{q} S_i r_i + \sum_{i=1}^{m} L_i E_i^d + E_{elec} + E_{elast} + E_{mag} , \qquad (1)$$

where the first term is the bulk chemical free energy, g_i is bulk chemical free energy density of *i*th phase with volume V_i ; the second term is the interfacial energy (grain boundary, surface), r_i is the specific interfacial energy of *i*th interface with interfacial area S_i ; the third term is dislocation energy, E_i^d is the dislocation core energy per unit length of *i*th dislocation with length L_i ; the fourth, fifth, and sixth terms are the electrostatic, elastic, and magnetic energies, respectively, which have negligible contribution to free energy change in this study as no external field is applied.

The phase transformation of Cu₂O to Cu is driven by the minimization of bulk 985 986 chemical free energy (the first term in Eq. (1)) in H₂ at elevated temperature. As a result of the Cu₂O \rightarrow Cu transformation, the Cu phase grows through the Cu₂O/Cu interface motion 987 from the Cu side to the Cu₂O side (Fig. 2a-d, Fig. 3) to reduce the total Gibbs free energy 988 together with the interfacial misfit dislocation glide and climb (Fig. 3) via lattice diffusion to 989 990 reduce dislocation energy (the third term of Eq. (1)). Our in-situ TEM observations show that the climb of the misfit dislocation to the new location of the Cu₂O/Cu interface is essential 991 before the sweeping of the dislocation core by the step flow. Our DFT modeling in Extended 992 993 Data Fig. 12c has confirmed that extra Cu is supplied more favorably from the Cu side for the dislocation climb, which requires long-range diffusion of Cu that results in the dwelling of 994 the interfacial step flow at the core of misfit dislocations. According to a Frank network 995 model ⁴⁵, the Cu diffusion aided dislocation climb velocity, *v*, is given by relation 996

997
$$v = \frac{D_{SD}Gb^3c_j}{rkT},$$
 (2)

where *G* is shear modulus of copper with a value of 4.1×10^{10} Pa ⁴⁶; *b* is Burgers vector, it equals to $b = \frac{\sqrt{2}}{2} \times a_{cu} = 2.585$ Å ($a_{cu} = 3.656$ Å) for the (110) interface (Extended Data Fig. 17a) and $b = 1/2a_{Cu} = 1.828$ Å for the (100) interface (Extended Data Fig. 17b); c_j represents jog concentration; r is the distance between neighbouring dislocation lines, which is equal to $7d_{Cu(110)}=7\times0.2585=1.809$ nm for the (110) interface and $7d_{Cu(200)}=1.279$ nm for the (100) interface; k is Boltzmann's constant (8.62×10^{-5} eV/(atom·K)); T is experimental absolute temperature of 623 K. D_{SD} represents the coefficient of self diffusion of Cu, which is calculated through the following equation,

$$D_{SD} = D_0 \cdot \exp\left(-E_{SD}/kT\right),\tag{3}$$

1007 where $D_0 = 11 \ cm^2 \cdot s^{-1}$ for copper ⁴⁷; E_{SD} is the activation energy of self diffusion of Cu 1008 with the value of 0.57 eV along Cu[110] and 0.64 eV along Cu[100] based on our DFT 1009 calculations in Extended Data Fig. 12c; k is Boltzmann's constant (8.62×10⁻⁵ eV/(atom·K)); 1010 thus, $D_{SD} = 27.39 \ cm^2 \cdot s^{-1}$ for the (110) interface and $D_{SD} = 74.69 \ cm^2 \cdot s^{-1}$ for the 1011 (100) interface.

1012 At termperature *T*, the misfit dislocation in equilibrium will have a concentration of 1013 jogs, c_i , which is calculated by the following relation ⁴⁵,

1014
$$c_j = A_j \cdot \exp(-E_j/kT),$$
 (4)

where A_j is of unity; E_j represents the energy of thermal jog formation with the values of 0.8 eV along [110] and 0.75 eV along [100] ⁴⁵; thus, $c_j = 3.38$ for the (110) interface and 8.57 for the (100) interface.

Based on Eqs. (2-4), the velocities of the misfit dislocation climb can be calculated to be 0.067 nm/s for the (110) interface and 0.233 nm/s for the (100) interfaces, respectively. These values predicted by the classic dislocation model agree reasonably well with our experimentally measured dislocation climb velocities of $\frac{d_{Cu(110)}}{t_{dwell(110)}} = \frac{0.2585 nm}{4 s} = 0.065 nm/$ s for the (110) interface and $\frac{d_{Cu(100)}}{t_{dwell(100)}} = \frac{0.1828 nm}{1.0 s} = 0.183 nm/s$ for the (100) interface (Fig. 3), respectively.

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1025 Extended Data Text 13. Stop-and-go interfacial transformation viewed along the 1026 fore-and-aft direction parallel to the incident e-beam

1027 The misfit dislocations form an orthogonal network at the Cu_2O/Cu interface. Figs. 2 1028 and 3 show the stop-and-go interfacial ledge flow along the direction that is perpendicular to

the e-beam direction. Using the in-situ HRTEM imaging in plan view and HRTEM image 1029 simulations, we further identify that the stop-and-go interfacial ledge flow of the $Cu_2O \rightarrow Cu$ 1030 1031 transformation also occurs in the orthogonal direction that is parallel to the e-beam direction. Extended Data Fig. 18a-d (Supplementary Movie 8) depicts the time-sequence HRTEM 1032 images, showing the intermittent attenuation in the image intensity of the atomic columns in 1033 the Cu₂O/Cu(100) interface (as marked by the red, cyan, blue, and green rectangles in 1034 Extended Data Fig. 18a, b, c, and d, respectively). This is evident by monitoring the temporal 1035 1036 evolution of the image intensity profiles from the Cu₂O/Cu(100) interface layer, as shown in Extended Data Fig. 18e. In first 0-1 s, the intensity profiles consist of alternate strong and 1037 weak peaks and their average intensity ratio stays relatively unchanged at ~1.15. The 1038 intensity ratios of the strong and weak peaks then stay at ~1.12, ~1.09 and ~1.05 in the 1039 subsequent time periods of 1.5 s to 2.5 s, ~3 s, and 3.5 s to 4.5 s, respectively, as depicted in 1040 red, cyan, blue, and green in Extended Data Fig. 18e. The intensity profiles from the four 1041 time periods show a dwell time of $0.5 \text{ s} \sim 1.5 \text{ s}$ for each image group, which is the same as the 1042 dwell time (0.5 s to 1.5 s) of the interface ledge flow in the direction that is perpendicular to 1043 1044 the e-beam direction (Fig. 3i). For comparison, the image intensity profiles from the pure Cu₂O and the Cu substrate regions are also given in Extended Data Fig. 18f, showing that 1045 their intensity profiles stay nearly unchanged throughout the entire time period. It is also 1046 1047 worth noting that no interfacial steps enter the field of view along the direction perpendicular to the e-beam direction within the time period of the TEM observation. 1048

Interfacial ledges and their motion parallel to the e-beam direction cannot be 1049 visualized readily because of the projection of the overlapped crystal lattices of Cu₂O and Cu 1050 1051 in the interface. However, the intermittent attenuation of the image contrast of the interfacial 1052 atomic columns provides important clues to the stop-and-go interfacial ledge flow nature of the Cu₂O \rightarrow Cu transformation in the fore-and-aft direction that results in the overlapping of 1053 1054 the Cu₂O lattice and the transformed Cu lattice in the interface viewed along the e-beam 1055 direction. Qualitatively, this is consistent with the different image contrast of the pure Cu_2O 1056 and Cu substrate regions, showing that the metallic Cu lattice appears constantly dimmer than the Cu₂O lattice (see Extended data Fig. 18a-d). That is, the Cu₂O \rightarrow Cu transformation results 1057 in more metallic Cu in the interface and thus makes dimmer image contrast of the interfacial 1058

1059 atomic columns in the projection view. Quantitatively, this is also confirmed with HRTEM 1060 image simulations. As shown in the side and front views in Extended data Fig. 19a, b, we construct a Cu₂O/Cu(100) interface slab (30 nm in thickness) consisting of a monoatomic 1061 interfacial ledge that separates two interface terraces (the interfacial ledge and terraces are 1062 invisible in the front view). By placing the interfacial ledge at the core of different misfit 1063 dislocations along the (100) interface, we can simulate the HRTEM image contrast evolution 1064 induced by the stop-and-go $Cu_2O \rightarrow Cu$ interfacial transformation that results in the stepwise 1065 1066 increase in the L1/L2 ratio, where L1 and L2 correspond to the lengths of the upper and lower interfacial terraces, as marked in Extended Fig. 19a. Extended Fig. 19c-f show 1067 simulated HRTEM images based on the front-view model (Extended Fig. 19b) with 1068 L1/L2=0.15, 0.175, 0.2 and 0.225, respectively. Extended data Fig. 19g illustrates the 1069 1070 intensity ratios of the strong and weak peaks in the intensity profiles of the interfacial atomic columns from the simulated HRTEM images with the four L1/L2 ratios, which show the 1071 stepwise attenuation and are in good accordance with the values measured from the 1072 experimental HRTEM images (Extended data Figs. 18e and 19h). 1073



Vaccum, 298 K 📥 H₂ (0.13 Pa), 873 K 📥 O₂ (0.67 Pa), 623 K 📥 H₂ (5.3 Pa), 623 K



Extended Data Fig. 1 | Experimental procedure for in-situ TEM observations. a-b, 1076 Pictorial illustrations and corresponding characteristic TEM images showing the morphology 1077 evolution of the Cu thin film under different experimental conditions. Annealing at 873 K in 1078 H₂ gas flow results in the removal of native and generation of tears and holes with faceted 1079 edges. The freshly created facets are oxide-free and can be oxidized to form epitaxial Cu₂O 1080 1081 islands at 623 K by flowing O₂ gas. The epitaxial Cu₂O is reduced to Cu at 623 K by switching to H₂ gas flow. In-situ TEM observations of the redox reactions can be made in 1082 cross-sectional views along the faceted edges. Scale bar, 50 nm in the left two images in **b**, 5 1083 nm in the right two images in **b**. 1084



1086

Extended Data Fig. 2 | Clean Cu(110) surface in flow of H₂ gas and the formation of Cu₂O/Cu interfaces in the flow of O₂ gas. a, [001] HRTEM image showing a clean (110) surface of the Cu thin film at 873 K and 0.13 Pa of H₂ gas flow. b, HRTEM image showing the formations of epitaxial Cu₂O on Cu(110) from the oxidation at T =623 K and pO₂= 0.67 Pa of O₂ flow. The Cu₂O/Cu interface is marked by the green dashed line and the interfacial misfit dislocations are marked by crosses. Scale bar, 1nm.



1093

Extended Data Fig. 3 | Identification of the epitaxial relationship of the Cu₂O layer with the Cu substrate. a, Experimental diffractogram obtained after the oxidation at T =623 K and 0.67 Pa, showing the composite electron diffractions of Cu₂O and Cu with the epitaxial relationship of Cu₂O(200)//Cu(200), Cu₂O(020)//Cu(020), and Cu₂O[001]//Cu[001]. b, Simulated [001] diffraction patterns using the Cu₂O/Cu epitaxial relationship identified in **a**. Red and yellow spots represent the superimposed diffraction spots from Cu₂O and Cu, respectively.



Extended Data Fig. 4 | Structural stability comparison of the Cu₂O/Cu interface 1102 terminations. a, Cu-O terminated Cu₂O/Cu(110) interface viewed along the [001] direction. 1103 1104 Red dashed line represents the Cu₂O/Cu interface location. After DFT structural optimization, the interface is stable without noticeable changes in atom positions in **b**. **c**, Cu 1105 terminated $Cu_2O(110)/Cu(110)$ interface viewed along the [001]. DFT relaxation in **d** reveals 1106 that the Cu terminated interface spontaneously transforms into the Cu-O terminated interface, 1107 1108 which is accompanied by the spontaneous transformation of the interfacial Cu atoms on the Cu₂O side into the metallic Cu of the Cu substrate with the resultant 7×6 CSL interface 1109 matching and a Cu vacancy column (blue circle in the relaxed structure) in the Cu substrate. 1110 This process induces the shift of the initially Cu terminated interface location (marked by the 1111 dashed red lines) by one lattice spacing toward the Cu-O terminated interface location 1112 (marked by the dashed light blue line). Similarly, Cu terminated (100) interface in e also 1113

- 1114 transforms spontaneously into O terminated (100) interface in **f** after structural optimization,
- 1115 revealing O terminated (100) interface is more stable. Yellow and red spheres represent Cu
- 1116 and O atoms, respectively.



1118

1119 Extended Data Fig. 5 | Simulated HRTEM images of the $Cu_2O(110)/Cu(110)$ interface 1120 along the [001] direction. Simulations are based on the Cu-O terminated Cu₂O/Cu 1121 interface shown in Extended Data Fig. 4b. Specimen thickness increases from bottom to top 1122 and defocus increases from left to right. The panel marked by the red rectangle shows the 1123 simulated HRTEM image that matches well with the experimental HRTEM image. 1124





1126 Extended Data Fig. 6 | Thickening of the underlying Cu layer by the ledge propagation

1127 along the Cu₂O/Cu interface.

1128



Extended Data Fig. 7 | NEB calculations of energy barriers for vacancy-assisted 1131 diffusion of oxygen atoms with the absence (upper panel) and presence (lower panel) of 1132 interstitial H in Cu₂O. a, surface/subsurface: migration of an O atom in the second layer to a 1133 1134 vacant lattice site in the topmost layer. **b**, bulk: interlayer $(1 \rightarrow 0)$ and intralayer $(2 \rightarrow 0)$ O-vacancy exchanges. c, Cu₂O/Cu interfacial ledge pinned at the misfit dislocation core: 1135 1136 migration of the O atom at the misfit dislocation core to its adjacent, nonequivalent vacant lattice sites. d, Cu₂O/Cu interface ledge away from the dislocation core by two Cu lattice 1137 spacings: migration of the O atom in front of the ledge to its adjacent, nonequivalent vacant 1138 1139 lattice sites. e-h, vacancy-assisted O diffusion along the same pathways as (a-d) with the presence of interstitial H in the Cu₂O lattice. 1140



Extended Data Fig. 8 | DFT calculations of oxygen vacancy formation energy at the interfacial step and terrace. a-b, Atomic models with oxygen vacancies formed at the interfacial step and terrace, respectively, viewed along the [100] zone axis. The oxygen vacancy formation energies at the interfacial step and terrace are 2.1 eV and 2.6 eV, respectively, indicating that the Cu₂O \rightarrow Cu transformation occurs preferentially from the interfacial step resulting in step flow. Yellow, red balls and red circles represent Cu, O, and O vacancies, respectively.



Extended Data Fig. 9 | HRTEM and STEM-HAADF imaging of atomic vacancy columns in front of interfacial ledges. a-b HRTEM and HAADF images of the Cu₂O/Cu(110) interfaces showing the presence of a double-atomic-height interfacial ledge pinned at the misfit dislocation core. c-d HRTEM and HAADF images of the Cu₂O/Cu(100) interface showing a monoatomic interfacial ledge pinned at the misfit dislocation. Plots on the right of each image are intensity profiles along the dashed rectangles in a-d. Scale bar: 0.5 nm.



Extended Data Fig. 10 | During the Cu₂O→Cu interfacial transformation, it is essential 1160 for the misfit dislocations to climb to the new Cu₂O/Cu interface location. a, The misfit 1161 dislocations (marked by red "T") are buried by the newly formed Cu and become isolated 1162 edge dislocations in Cu bulk, which will drastically increase their energies due to the required 1163 presence of many broken bonds along the dislocation lines. b, By contrast, it is 1164 thermodynamically more favorable for the misfit dislocations to climb to the new Cu₂O/Cu 1165 interface location, by adsorbing extra Cu atoms from the Cu substrate, to release some lattice 1166 mismatch strain and the associated strain energy upon the $Cu_2O \rightarrow Cu$ interfacial 1167 1168 transformation.



Extended Data Fig. 11 | Formation of geometric kinks by unsynchronized ledge flow 1171 along the Cu₂O/Cu interface. a, An initially straight ledge stops at a misfit dislocation core. 1172 **b**, **c**, The Cu vacancies in front of a segment (marked in red color) of the interfacial step are 1173 filled up and the segment then resumes its propagation to the next misfit dislocation core 1174 (marked by the blue dashed lines). This is a most unfavorable event because it will result in 1175 large geometric kinks with their side lengths of seven Cu lattice spacings for each 1176 1177 propagation (i.e., the distance between successive stops is seven Cu lattice spacings for the 7×6 CSL configuration of the Cu/Cu₂O interface). Such an unsynchronized ledge flow leads 1178 to a highly kinked ledge with significantly increased ledge lengths (and ledge energies) and 1179 therefore is energetically unfavorable compared to the propagation of a straight ledge that 1180 1181 happens only after all the Cu vacancies in front of the entire interfacial ledge are filled up, where the ledge length is defined by the interface size of individual grains. 1182



1184

1185 Extended Data Fig. 12 | a-b, Interlayer Cu-vacancy exchange barriers with and without the

- 1186 presence of interfacial H, respectively, along two nonequivalent pathways in Cu₂O. **c**, Atomic
- 1187 model for the calculation of Cu-vacancy exchange barriers within Cu.



1188

Extended Data Fig. 13 | Evaluation of the system energy changes as a function of the 1189 distance of the Cu vacancies from the Cu₂O/Cu interface. (a) The swap of one Cu 1190 1191 vacancy in the dislocation core with the Cu atom that is away from the Cu₂O/Cu interface by one, three and five atomic layers in the Cu bulk, respectively. (b) The swap of two Cu 1192 vacancies in the dislocation core with the Cu atoms that have increased distance from the 1193 Cu₂O/Cu interface. Yellow and red balls represent Cu and O atoms, respectively. Blue balls 1194 1195 and circles represent the swapped pairs between the Cu atoms in the Cu bulk and Cu vacancies in the misfit dislocation core in front of the interfacial ledge, respectively. 1196



Extended Data Fig. 14 | NEB calculations of the energy barriers for the interfacial jumps of metallic Cu to the vacant site of the misfit dislocation core in front of the interfacial ledge. Three non-equivalent types of atom-vacancy diffusion pathways are identified with the diffusion barriers in the range of 0.22 to 0.31 eV. Yellow and red balls represent Cu and O atoms, respectively, and the blue circle represents the Cu vacancy in the misfit dislocation core.

1205



Extended Data Fig. 15 | In-situ HRTEM observations of the positive climb motion of 1208 edge dislocations in the bulk of the Cu substrate during the stop-and-go $Cu_2O \rightarrow Cu$ 1209 transformation along the low-index Cu₂O/Cu(110) interface at 623 K and 5.3 Pa of H₂ 1210 gas flow. a, HRTEM micrograph showing the presence of edge dislocations (marked by 1211 yellow T) in the bulk of the Cu substrate. b, In-situ HRTEM images (Supplementary Movie 1212 5) showing the glide and positive climb of an edge dislocation in the region marked with the 1213 blue dashed square in **a**. The edge dislocation has a Burgers vector of $b = d_{Cu(200)}$ and is 1214 observed to glide (from yellow to cyan T positions) and climb (from cyan to red T positions) 1215 during the stop-and-go propagation of the interfacial steps. Scale bar, 0.5 nm (**a-b**). 1216

1217



Extended Data Fig. 16 | In-situ HRTEM observations of the stop-and-go $Cu_2O \rightarrow Cu$ 1220 transformation along a high-index Cu₂O/Cu interface during the H₂ exposure at 623 K 1221 and 0.021 Pa of H₂ gas flow. a-d, Time-sequence HRTEM micrographs (Supplementary 1222 1223 Movie 6) showing the presence of a high density of interfacial ledges that are constantly pinned at the misfit dislocations during the Cu₂O/Cu interface propagation toward the Cu₂O 1224 side. The propagation of the interfacial ledges is accompanied with the glide and climb of the 1225 misfit dislocation in front of the ledges. Meanwhile, an edge dislocation in the Cu bulk is 1226 1227 observed to glide and climb deeper toward the Cu substrate during the Cu₂O→Cu interfacial

- 1228 transformation. Scale bar, 2 nm
- 1229

1219



Extended Data Fig. 17 | Measurement of the Burgers vectors of misfit dislocations. a, Burgers circuit completed around a misfit dislocation at the Cu₂O(110)/Cu(110) interface, showing the Burgers vector $b=d_{Cu(110)}$. b, Burgers circuit completed around a misfit dislocation at the Cu₂O(100)/Cu(100) interface, showing the Burgers vector $b=d_{Cu(200)}$. Scale bar, 1 nm.



Extended Data Fig. 18 | In-situ TEM visualization (from Movie 8) of the intermittent 1239 attenuation of image intensity of the interface oxide layer at 623 K and 5.3 Pa of H₂ gas. 1240 1241 a-d, Time-sequence HRTEM images (in plan view) showing alternative bright and dim image contrast from interface Cu₂O (100) layer within the red, cyan, blue and green rectangles 1242 becomes dimer and dimer in an intermittent manner until transforming completely into 1243 homogeneous substrate Cu contrast (pink rectangle). e, Time-sequence intensity profiles 1244 along the interface Cu₂O (100) layer within the color rectangles, where the interface intensity 1245 keeps constant for about 0.5 to 1.5 s and then reduces in an intermittent manner. The similar 1246 intensity profiles are colored into the same color to stress the stopping effect. f, 1247

- 1248 Time-sequenced intensity profiles of Cu₂O and Cu from yellow and pink rectangle regions in
- 1249 TEM images, respectively. The intermittent attenuation of interface Cu₂O (100) layer image
- 1250 intensity reveals the Cu₂O \rightarrow Cu interfacial transformations could occur via the stop-and-go
- 1251 step flow along fore-and-aft direction. Scale bar, 0.5 nm (**a-d**).
- 1252
- 1253



1254

Extended Data Fig. 19 | HRTEM simulation and intensity profile analysis for interfacial 1255 stop-and-go ledge flow along the projection direction. a-b, Side view and front view of 1256 Cu₂O/Cu atomic models with interfacial step pinning at varied misfit dislocation cores, 1257 varying the length ratio of Cu₂O to Cu (L1/L2 length ratio). Yellow and red balls represent 1258 1259 Cu and O atoms, respectively. c-f, Simulated HRTEM images based on the front view model (b) with varied L1/L2 ratios. The inset intensity profiles are extracted from the interface layer 1260 marked by the dashed rectangle in the simulated HRTEM images. The HRTEM simulation 1261 parameters are carefully matched to the experimental conditions: 30 nm in the specimen 1262 thickness, -2 nm defocus, accelerating voltage: 300 keV, the spherical aberration: 0.001 mm. 1263 f, g, Intensity ratios of high/low peaks of the intensity profiles of the Cu₂O/Cu interface of the 1264 simulated HRTEM images as a function of length ratio (L1/L2) and of the experimental 1265

- 1266 HRTEM images as a function of the reaction time, respectively. The error bars represent
- 1267 standard deviation uncertainties based on multiple measurements of different atomic columns
- 1268 within the interface layer in the simulated and experimental HRTEM images.

1270 Extended Data Table 1

1271 The maximum Cu₂O/Cu compression/tension strains around four dislocation cores (from the 1272 left to right) in Fig. 1a, b. e_{xx} is in-plane strain. Negative and positive values denote 1273 compressive and tensile strains, respectively.

1274

Dislocation	1	2	3	4
Cu ₂ O/Cu in-plane strain	(left)			(right)
exx	-0.201/+0.190	-0.235/+0.241	-0.211/+0.220	-0.246/+0.270

1275

1277 Extended Data Table 2

1278 The average maximum Cu₂O/Cu compression/tension strains around dislocation cores 1279 associated with the 8×7, 7×6, and 6×5 CSL configurations. e_{xx} is in-plane strain. Negative 1280 and positive values denote compressive and tensile strains, respectively.

1281

CSL Cu ₂ O/Cu in-plane strain	8×7	7×6	6×5
e_{xx}	-0.230 ± 0.02	-0.191 ± 0.02	-0.265±0.02
	$+0.238\pm0.03$	$+0.195\pm0.01$	$+0.259\pm0.02$

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33 Captions for Movies
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1284

1285 Supplementary Movie 1

In-situ TEM imaging of the Cu₂O(110)/Cu(110) interfacial transformation during exposure to H₂ at T=623 K and ~ 5.3 Pa of H₂ gas flow. The e-beam was blanked for ~ 60 s to examine possible electron beam irradiation effects on the interfacial transformations and then unblanked for TEM imaging.

1290

1291 Supplementary Movie 2

1292 In-situ TEM imaging of the $Cu_2O(100)/Cu(100)$ interfacial transformation during 1293 exposure to H₂ at T=623 K and 5.3 Pa of H₂ gas flow.

1294

1295 Supplementary Movie 3

1296 In-situ HRTEM imaging of the $Cu_2O(110)/Cu(110)$ stop-and-go interfacial 1297 transformation regulated by misfit dislocations during exposure to H₂ at T=623 K and 5.3 Pa 1298 of H₂ gas flow.

1299

1300 Supplementary Movie 4

1301 In-situ HRTEM imaging of the $Cu_2O(100)/Cu(100)$ stop-and-go interfacial 1302 transformation regulated by misfit dislocations during exposure to H₂ at 623 K and 5.3 Pa of 1303 H₂ gas flow.

1304

1305 Supplementary Movie 5

In-situ HRTEM imaging of the isolated dislocation dynamics within substrate Cu
during exposure to H₂ at 623 K and 5.3 Pa of H₂ gas flow.

1308

1309 Supplementary Movie 6

1310 In-situ HRTEM observations of the stop-and-go Cu₂O \rightarrow Cu transformation along a 1311 high-index Cu₂O/Cu interface during the H₂ exposure at 623 K and 0.021 Pa of H₂ gas flow. 1312

1313 Supplementary Movie 7

1314 Schematic animation illustrating the stop-and-go interfacial transformation regulated1315 by misfit dislocations.

1316

1317 Supplementary Movie 8

In-situ TEM visualization of the intermittent attenuation of image intensity of the
interface oxide layer at 623 K and 5.3 Pa of H₂ gas.

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