Elucidating metal oxide growth mechanisms is essential for precisely designing and fabricating nanostructured oxides with broad applications in energy and electronics. However, current epitaxial oxide growth methods are based on macroscopic empirical knowledge, lacking fundamental guidance at the nanoscale. Using correlated in situ environmental transmission electron microscopy, statistically-validated quantitative analysis, and density functional theory calculations, we show epitaxial Cu$_2$O nano-island growth on Cu is layer-by-layer along Cu$_2$O(110) planes, regardless of substrate orientation, contradicting classical models that predict multi-layer growth parallel to substrate surfaces. Growth kinetics show cubic relationships with time, indicating individual oxide monolayers follow Frank-van der Merwe growth whereas oxide islands follow Stranski-Krastanov growth. Cu sources for island growth transition from step edges to bulk substrates during oxidation, contrasting with classical corrosion theories which assume subsurface sources predominate. Our results resolve alternative epitaxial island growth mechanisms, improving the understanding of oxidation dynamics critical for advanced manufacturing at the nanoscale.
Advanced manufacturing of nanostructured metal oxides (MOs) is essential for myriad applications including energy, electronics, sensors, photocatalysts, bio-medicine, and recently for quantum computing. Thus, precise, scalable synthesis and processing of nanostructured MOs are in much demand. Microfabrication methods, such as thermal oxidation, reactive sputtering, and atomic layer deposition, are promising approaches for preparing large batches of epitaxially nanostructured MOs. However, current nano-oxide fabrication methods, for which oxidation is a vital step, are empirically based. To better predict and control the shape of nanostructured MOs, a fundamental understanding of the oxide nanocrystal growth process is essential. Established oxidation theories of Wagner and Cabrera–Mott treat the oxidation process exclusively from a macroscopic viewpoint assuming simplified, continuous uniform layers. While these models have been successful in guiding fabrication of amorphous oxide films—such as SiO2—and corrosion mitigation, they have little predictive power for describing nanostructured MOs due to their lack of atomic crystalline considerations. This shortcoming greatly hinders the industrial manufacturing of nanostructured MOs.

Borrowing from thin-film growth theories, MO nanocrystals that attach to a metal substrate epitaxially during the growth of three-dimensional (3D) oxide islands are explained using the Stranski–Krastanov (layer-plus-island) growth mode. However, this model is defined from an interfacial energy viewpoint, leaving the kinetic process of how these nanostructures form uncertain. One well-accepted kinetic process is the multilayer growth mechanism, which explains the formation of 3D islands as the simultaneous growth of multiple layers stacked parallel to the substrate surface, forming “wedding cake”-shaped islands. For example, islands on (100) substrates form by the concurrent growth of multiple stacked layers along the (100) planes. However, 3D islands with faceted crystal surfaces are also widely observed, such as pyramidal Ge and Si islands in quantum dots and nano-wedge-shaped Fe islands, and 3D Cu2O islands on Cu(100). While these faceted crystal surfaces are at variance with the multilayer growth mechanism, it remains unclear whether the deviations are due to the early or the later stages of the island growth. The lack of direct observation of the growth dynamics at the atomic scale has hindered establishing a fundamental mechanistic explanation for the growth of the 3D epitaxial islands. Recent developments in in situ environmental transmission electron microscopy (ETEM)—with which material systems can be examined under relevant reaction conditions—offer a solution to this problem, enabling the direct observation of growth dynamics. However, the results here-tofore have been qualitative at best. Extracting statistically meaningful quantitative atomic-scale growth kinetics from the in situ movies, which is critical for understanding atomic-scale growth mechanisms, has become the new challenge.

Herein we perform in situ ETEM oxidation experiments on copper—the most well-studied model material for oxidation that forms epitaxial oxide islands—to provide direct, atomic-scale observations of the growth dynamics of 3D epitaxial oxide islands during oxidation. Quantitative atomic-scale information was extracted using advanced image analysis techniques. By correlating the experimental observations and statistical validation of growth kinetics with density functional theory (DFT) modeling, we present an unusual epitaxial layer-by-layer growth mechanism for the oxide island along a preferred surface facet, unforeseen by previous crystal growth theories.

**Cu2O monolayer growth kinetics.** To better understand the growth kinetics of each monolayer, we performed quantitative analysis on the boxed area in Fig. 1d on the atomically aligned movie to measure the size evolution of each layer over time (Fig. 1f, Supplementary Note 3). As illustrated in Fig. 1e, each new layer is a 2D flake that grows in both planar directions. Although TEM images only provide 2D thickness projections of the growing new layer, given that the two directions are equivalent, the projected length evolution in one dimension can be used to estimate the growth in both directions. The nucleation sites of each Cu2O monolayer (Fig. 1g and Supplementary Fig. S6) were randomly distributed on the previously grown layer, indicating identical nucleation energetic favorability across all sites. Despite that the layer edges typically proceeds in stairs (Fig. 1g), the total projected lengths (l) all exhibited a similar smooth growth trend following a cube root relationship with time (t): \( \bar{P} = \bar{A}t \) (referred to as cubic relationship for short hereafter, Fig. 1h, Supplementary Fig. 14, and Supplementary Note 3). As a result, the growth rate of the island size is quasi-linear along the [110] direction and cubic along [100] and [010] directions. Interestingly, typical oxide thickness curves found in bulk Cu oxidation experiments in this temperature range also follow cubic rates, which were explained based on classical oxidation theory due to the formation and diffusion of cation vacancies through an oxide layer that fully covers the metal surface. However, this explanation does not apply to our sample, since the metal surface near the oxide island is still exposed. Instead, we argue that the cubic growth rate of each oxide monolayer could be explained using the diffusion-limited 2D growth kinetics of F–M thin-film growth. In this growth mode, a full layer forms by coalescence of several single-monolayer-thick 2D flakes, where each flake grows with \( \bar{P} = \bar{A}t \) scaling. The main difference with the thin-film F–M growth is that the observed growth of the oxide monolayer in our samples is due to the nucleation of a single “flake”, rather than many flakes as in thin-films. This difference is likely because the effective substrate for the growth of the oxide layer is relatively small compared to typical thin-film substrates. Presumably, as the MO islands grow in size, layer formation through the coalescence of more than one flake would occur. Hence, the observed \( \bar{P} = \bar{A}t \) growth kinetics of each monolayer indicates a diffusion-limited process, possibly due to surface diffusion of Cu and O atoms to form adatoms at the Cu2O monolayer edge.

The growth trajectories also exhibited coordinated increments and oscillations between multiple layers (Fig. 1g–i). To substantiate
Fig. 1 Layer-by-layer growth of Cu2O island along Cu2O(110) during Cu(100) oxidation. a–c Snapshots from Supplementary Movie 1 showing adatom growth of the 2nd Cu2O new layer at 300 °C and pO2 = 0.3 Pa. The layer nucleation site (triangle) and growth direction (arrow) are indicated. Scale bar: 5 nm. d The island top forms a flat Cu2O(100) plane over time. e Schematic 3D model of the Cu2O island with a growing new layer. f The boxed area from d, reoriented for growth trajectory measurement, with a corresponding schematic defining the measured data plotted in g–i. g Growth trajectory coordinates of the left (x+) and right (x−) ends of each layer with time, namely when measuring from the right side of the image defined in f. Nucleation sites on each layer, marked by gray arrows, indicate a random site distribution. These two ends show stepwise growth with oscillations marked by triangles of matching colors. h The projected length (l) of each layer shows a similar trend with smoother curves. i Statistically defined breakpoints in growth rates indicate nucleation events (N) and interlayer atom diffusion events (P).

DFT calculations on Cu2O monolayer growth mechanism. To better understand why the oxide grows along the Cu2O(110) plane in disagreement with classical theories, DFT calculations were performed to study the earlier-stage atom-by-atom oxide growth events. Gas–solid interfacial energies (γ) were calculated for the (100) and (110) Cu2O surface planes that are predominantly observed in our experiments. As shown in Fig. 2a and detailed in Supplementary Note 5, Cu2O surface units were sequentially added to these planes to simulate layer growth. For flat Cu2O surfaces (column i in Fig. 2a), Cu–O terminated Cu2O(110) had the lowest γ. Upon adding Cu2O5 surface units, Cu2O(110) surfaces with exposed Cu–O layers invariably had the lowest γ. These surfaces include structures i and iii for Cu–O terminated Cu2O(110) and structure ii for Cu-terminated Cu2O(110), and their favorability is attributable to their terminal, ionically bonded O–Cu–O chains (Supplementary Figs. 21–23). In contrast, O-terminated Cu2O(100) had the highest γ, regardless of the number of Cu2O5 surface units added to it. Such instability coincides with the undercoordination of exposed O atoms (Supplementary Fig. 20). Since Cu2O(100) structures must produce less-stable O terminations during its growth, oxide growth along Cu2O(110) is preferable to Cu2O(100). Simulated adatom adsorption events forming Cu2O5 surface unit ii (hollow data points in Fig. 2a and Supplementary Note 6) further support this conclusion. Therefore, γ trend comparisons show that Cu2O(110) forms thermodynamically more favorable flat surfaces, grown Cu2O monolayers, and single adatom interfaces than Cu2O(100), in agreement with the experimental results.

Nudged elastic band simulations of the diffusion events along the oxide island surface further verified the experimentally observed layer-by-layer growth kinetics along the Cu2O(110) plane (Supplementary Note 7). Figure 2b compares the preferred
Cu source for Cu$_2$O island growth. The source of Cu during Cu$_2$O growth also warranted investigation. Traditional oxidation theory\textsuperscript{12} argues that Cu is supplied from the metal|oxide interface through diffusion across the oxide, leading to an interface shift toward the metal side. However, as seen in Figs. 1 and Supplementary Fig. 6, the Cu|Cu$_2$O interfaces predominantly remained unchanged during the oxidation process, particularly during the initial period of oxidation when there are few nucleated Cu$_2$O islands. This indicates that there must be other sources for Cu instead of the substrate Cu. A recent study found Cu$_2$O island growth with gradual height decreases of the surrounding Cu surface steps\textsuperscript{45}, inferring that Cu detaching from step edges might be the source. However, direct evidence for this claim has been lacking. Figure 3 and Supplementary Movie 5 show that during oxidation of Cu(100) facets with several one-atomic-layer-high surface steps, these steps retreated when Cu$_2$O grew, while the Cu|Cu$_2$O interface remained unchanged. Due to the diffusion mechanisms required to make an oxide layer on Cu terminated Cu$_2$O(110) and Cu$_2$O(100) surfaces. The most favorable rate-limiting diffusion process for forming Cu–O layers on Cu-terminated Cu$_2$O(110) is single O diffusion with inter-channel endpoints (diffusion barrier of $\Delta = 0.35$ eV), and the matching Cu diffusion process to place Cu on top of that O is barrierless with favorable adsorption energy ($E_{\text{ads}} = -2.58$ eV). In comparison, the most favorable rate-limiting O diffusion process on a Cu-terminated Cu$_2$O(100) surface is in-channel single O diffusion ($\Delta = 0.75$ eV). The matching Cu diffusion process places Cu on top of that O, yielding a large barrier ($\Delta = 1.02$ eV) and less-favorable adsorption energy ($E_{\text{ads}} = -0.24$ eV). The corresponding process for forming Cu layers on Cu–O terminated Cu$_2$O(110) is in-channel single Cu diffusion ($\Delta = 0.42$ eV, Supplementary Fig. 29). Rate-limiting step comparisons favor Cu$_2$O(110) over Cu$_2$O(100) not only across the initial and final states of the oxide layer formation process (0.42 eV vs. 1.02 eV) but also for each transient diffusing atom composition. Therefore, Cu and O prefer to diffuse to Cu$_2$O(110) island growth fronts over Cu$_2$O(100) fronts, further validating prior experimental outcomes.

**Fig. 2** DFT-calculated interfacial energies and diffusion energies for Cu$_2$O (110) and (100) surfaces. **a** Most favorable structure $\gamma$ during Cu$_2$O monolayer growth for Cu$_2$O(110) with Cu (green) and Cu–O (blue) terminations, and Cu$_2$O(100) with Cu (orange) and O (red) terminations. The corresponding atomic structures are shown to the right of the plot, with matching border colors. Hollow data points between events forming the first Cu$_2$O$_x$ surface unit. **b** Most-favorable Cu and O diffusion events on Cu$_2$O surfaces linking diffusion barrier ($\Delta$) and adsorption energy ($E_{\text{ads}}$). Insets with matching border colors show top-down views of the corresponding atomic structures. Cu and O atoms are colored in orange and red, respectively. Brighter/darker colors indicate a higher/lower $z$ position.

**Fig. 3** Cu sources for Cu$_2$O nano-island growth. **a** Cu$_2$O grows while surface steps (1–3, marked by triangles) retreated and the Cu|Cu$_2$O interface (dashed lines) remained unchanged. (Scale bar: 5 nm). **c** When surface steps were far from the Cu$_2$O island, Cu$_2$O continued to grow and the Cu|Cu$_2$O interface started to migrate towards Cu. **d** A plot of the measured distance ($d$) between the Cu$_2$O island and step edge “1” with time. $d$ suddenly increased at ~31 s, leading to the transition from step edge Cu to bulk Cu consumption.
thickness difference between the Cu film and the Cu$_2$O island, the amount of Cu lost from the surface steps is comparable to the amount of Cu added to Cu$_2$O. This indicates that Cu detaching from step edges is the source of Cu for Cu$_2$O growth in the early oxidation stage. Later, the Cu$|$Cu$_2$O interface migrates toward the Cu substrate, indicating that in later stage oxidation, the substrate serves as the Cu source. The transition between Cu sources is determined by the distance from the nearest step edge (Fig. 3d), which is explainable by Cu diffusion. When the oxide island is near a step edge, Cu detached from surface steps can easily diffuse to the oxide island via surface diffusion. However, when there are very few surface steps or the oxide island is far away from the surface steps, bulk Cu diffusion from the Cu substrate to the gas$|$oxide interface becomes more efficient. As shown in Supplementary Note 8, even on reconstructed Cu surfaces, the diffusion barrier of Cu surface diffusion is still lower than that of bulk diffusion, leading to less-faceted oxide shapes during the interfacial Cu sourcing stage.

**Mechanism of 3D Cu$_2$O island growth.** Based on the above discussion and the energetic data summarized in Supplementary Table 7, the mechanism of the unusual epitaxial oxide island growth processes during Cu oxidation, summarized in Fig. 4, is:

a. Due to surface reconstruction, O$_2$ dissociation on the Cu surface is inhibited, so O adatoms are provided by O$_2$ dissociative adsorption on Cu$_2$O surfaces. The preferred diffusion barriers and adsorption energies of O on Cu$_2$O (110) over those on Cu$_2$O(100) suggest more diffusing O atoms will be present on the Cu$_2$O(110) surface.

b. When there are Cu surface steps nearby, Cu adatoms detached from Cu step edges diffuse to Cu$_2$O surfaces via surface diffusion. Because of the preferred diffusion barriers and adsorption energies of Cu on Cu$_2$O(110), more Cu atoms will diffuse on Cu$_2$O(110) than Cu$_2$O(100). Due to the lower surface energy of Cu$_2$O(110) and more favorable adsorption energies of Cu and O on the Cu$_2$O(110) step, Cu$_2$O nuclei will form on Cu$_2$O(110). This is followed by the growth of Cu$_2$O monolayers in an atomic adsorption process directed toward the growth front of the new layer. The vapor deposition process to grow oxides can be viewed as an extreme case of this scenario, where there are sufficient mobile Cu atoms present to directly react with O atoms.

c. The new Cu$_2$O layer grows in the adatom growth method until the edge of the layer reaches the ridge of the previous Cu$_2$O layer, then a new Cu$_2$O layer nucleates following the steps in (a) and (b). This leads to the observed layer-by-layer growth along Cu$_2$O(110). For each monolayer, the growth of a new Cu$_2$O layer on the Cu$_2$O(110) facet follows the diffusion-limited Frank–van der Merwe growth process with cubic growth rate $l^3$. However, due to the preference of Cu$_2$O(110) over Cu$_2$O(100) in both kinetics and energetics, the overall Cu$_2$O island follows the Stranski–Krusanov growth model. When the Cu surface steps are far away, substrate Cu will feed Cu$_2$O growth by interfacial diffusion via place exchange with Cu vacancies in Cu$_2$O islands.

**Discussion**

Using DFT, we have investigated the energetics of several most probable diffusion paths, and corresponding thermodynamic states, that are proposed to underlie studied experimental observations. However, a complete understanding of studied oxide growth dynamics is beyond the capabilities of DFT alone, especially when considering the many possible diffusion processes that induce concerted oxide nucleation and growth processes over multiple island layers. Comparisons between statistical conclusions and ETEM observations made in “Correlating Statistical Results with Experimental Observations” (Supplementary Note 4) demonstrate that limitations in Cu sourced from adjacent island layers contribute to observed island shapes and relative layer growth rates. Therefore, the combination of surface orientations and terminations predicted by simulation, island shape evolution by ETEM observations, and relative growth rates characterized by statistical conclusions, is needed to completely depict oxide growth dynamics.

Our results provide direct, atomic-scale growth dynamics of 3D epitaxial oxide island growth. Instead of multilayer growth along substrate surfaces to form wedding-cake shaped islands, we found the growth of 3D epitaxial oxide islands follows a layer-by-layer growth mechanism along a preferred facet. The growth kinetics of each oxide monolayer is consistent with predictions from the diffusion-limited 2D Frank–van der Merwe growth model for thin-films. To our knowledge, this is the first atomic-resolution
experimental proof of the atomic-level growth dynamics of 3D islands. Our study sheds new light on the epitaxial oxide growth mechanism and provides a deeper understanding of the dynamic processes involved in initial oxidation, which will ultimately help to precisely predict, design, and control nanostructured oxide growth. Our findings would apply to other metals—such as Al[15], Ni-Cr[4,6], Mo[29], Mg[49,50], and Ag[51]—where a similar layer-by-layer oxide growth was observed for the islands, though without confirmation on the early stages. Moreover, this work demonstrates that with meticulous in situ TEM experiments and advanced data analysis, statistically meaningful quantitative atomic-scale growth kinetics can be resolved. When complemented with correlated theoretical simulations, such work will promote the understanding of nanoscale dynamics to a new level.

Methods
Provided in Supplementary Information.

Data availability
All data is available in the main text or the Supplementary Materials (Supplementary Movies S1–S5, Methods, Supplementary Notes 1–8, Supplementary Tables 1–7).

Code availability
The code for in situ movie analysis and statistical analysis are available from the corresponding author on request.

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Author contributions

J.C.Y. and W.A.S. conceived and directed the project. M.L. conducted the experiments, data analysis, and drafted the manuscript. M.T.C. conducted D.F.T. simulations and statistical analysis. M.A.G. and S.D.H. assisted with the data analysis. All authors contributed to results discussion and manuscript refinement.

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Competing interests

The authors declare no competing interests.

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