Engineering Cu surfaces for the electrocatalytic conversion of CO₂: Controlling selectivity toward oxygenates and hydrocarbons

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In this study we control the surface structure of Cu thin-film catalysts to probe the relationship between active sites and catalytic activity for the electroreduction of CO₂ to fuels and chemicals. Here, we report physical vapor deposition of Cu thin films on large-format (<6 cm²) single-crystal substrates, and confirm epitaxial growth in the <100>, <111>, and <751> orientations using X-ray pole figures. To understand the relationship between the bulk and surface structures, in situ electrochemical scanning tunneling microscopy was conducted on Cu(100), (111), and (751) thin films. The studies revealed that Cu(100) and (111) have surface adlattices that are identical to the bulk structure, and that Cu(751) has a heterogeneous kinked surface with (110) terraces that is closely related to the bulk structure. Electrochemical CO₂ reduction testing showed that whereas both Cu(100) and (751) thin films are more active and selective for C-C coupling than Cu(111), Cu(751) is the most selective for 2e⁻ oxygenate formation at low overpotentials. Our results demonstrate that epitaxy can be used to grow single-crystal analogous materials as large-format electrodes that provide insights on controlling electrocatalytic activity and selectivity for this reaction.

Significance

Anthropogenic global warming necessitates the development of renewable carbon-free and carbon-neutral technologies for the future. Electrochemical CO₂ reduction is one such technology that has the potential to impact climate change by enabling sustainable routes for the production of fuels and chemicals. Whereas the field of CO₂ reduction has attracted great interest, current state-of-the-art electrocatalysts must be improved in product selectivity and energy efficiency to make this pathway viable for the future. Here, we investigate how controlling the surface structure of copper electrocatalysts can guide CO₂ reduction activity and selectivity. We show how the coordination environment of Cu surfaces influences oxygenate vs. hydrocarbon formation, providing insights on how to improve selectivity and energy efficiency toward more valuable CO₂ reduction products.


The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1618935114/-/DCSupplemental.
have shown that the surface structure is often related to the bulk crystallographic orientation (12–14), indicating that epitaxial growth can be used for engineering the surface structure of electrocatalysts. In particular, researchers have used physical vapor deposition (PVD) and molecular beam epitaxy to successfully grow Cu epitaxially on Si and Al₂O₃ (12, 13, 15–17). It is worth noting that Si has garnered interest as a cathode in photo-electrochemical (PEC) cells (18, 19), and developing synthetic methods to engineer the surface structure of Cu on Si could be advantageous for controlling the performance and selectivity of PEC CO₂R devices. In this study, we use electron-beam (e-beam) deposition to epitaxially grow large-format single-crystal analogous Cu thin films on Si and Al₂O₃ single crystals. After growth, a combination of X-ray pole figures and electrochemical scanning tunneling microscopy are used to correlate the bulk and in situ surface structures. After physical characterization, we use our previously reported electrochemical flow cell design with high product detection sensitivity to examine the dependence of CO₂R on large-format (27 mm × 42 mm) Al₂O₃(0001), Si(100), and Si(111) substrates in a three-source PVD chamber according to the procedures outlined in the Supporting Information. On Al₂O₃(0001), a Ti layer was used to increase adhesion of Cu to the oxide substrate. These procedures allow for the synthesis of Cu thin-film electrodes that are ~2–3 orders of magnitude larger in geometric area than those used in typical single-crystal electrochemistry studies. X-ray diffraction (XRD) symmetrical scans were used to determine whether the single-crystal substrates impact the out-of-plane growth orientation of Cu thin films. As shown in Fig. 1, samples grown on Ti/Al₂O₃(0001) show only the face-centered cubic (fcc) Cu(111) peak (black), indicating that the Cu thin films are strongly textured in the <111> orientation out-of-plane with the relationship Cu{111} || Al₂O₃(0001). To confirm the role of the single-crystal substrate interface, Cu thin films were also grown directly on Al₂O₃(0001). The almost identical X-ray diffractograms (Fig. S1) show that the Ti binding layer does not influence the out-of-plane texture induced by the Al₂O₃(0001) substrate. These similarities in out-of-plane growth on Ti and Al₂O₃(0001) are analogous to a previous report showing that hexagonal close-packed (hcp) Ti grows in the <001> orientation on Al₂O₃(001), allowing for growth offcc Cu(111) on the similarly close-packed Ti(001) (12).

In contrast, samples grown on Si(100) show only the fcc Cu(200) peak, indicating that the Cu thin films are textured in the <100> orientation out-of-plane with the relationship Cu{100} || Si(100). The difference in growth direction on Si(100) compared with growth on Al₂O₃(0001) clearly demonstrates that the single-crystal substrates guide the growth direction, likely due to differences in interfacial energy. The results on Si(100) are similar to previous reports that have shown Cu grows in the <100> orientation from hydrogen-terminated Si(100) surfaces (13, 20, 21). These reports show that Cu thin-film growth on Si(100) proceeds through the formation of a silicide due to diffusion at the interface (21). Unlike Cu thin films on Al₂O₃(0001) and Si(100), samples grown on Si(111) show no peaks within the range of the X-ray diffractogram, indicating that samples are not oriented out-of-plane in a low Miller index direction. Although it might be expected that Cu grows in the <111> direction on Si(111) due to similarities in the fcc and diamond (111) plane, researchers have demonstrated radically different textures for growth of Cu on Si(111) depending on the growth conditions (13, 15, 21). A previous report showed that the strain from the large lattice mismatch at the interface between Si(111) and Cu can cause the Cu thin film to grow in the high Miller index <531> orientation (15). Therefore, whereas XRD symmetrical scans show that low Miller index films are textured out-of-plane with the relationships Cu{111} || Al₂O₃(0001) and Cu{100} || Si(100), a different XRD analysis is necessary to determine this relationship for Cu thin films on Si(111).

Results and Discussion

Out-of-Plane Thin-Film Texture. Thin films of Cu were synthesized on large-format (27 mm × 42 mm) Al₂O₃(0001), Si(100), and Si(111) substrates in a three-source PVD chamber according to the procedures outlined in the Supporting Information. On Al₂O₃(0001), a Ti layer was used to increase adhesion of Cu to the oxide substrate. These procedures allow for the synthesis of Cu thin-film electrodes that are ~2–3 orders of magnitude larger in geometric area than those used in typical single-crystal electrochemistry studies. X-ray diffraction (XRD) symmetrical scans were used to determine whether the single-crystal substrates impact the out-of-plane growth orientation of Cu thin films. As shown in Fig. 1, samples grown on Ti/Al₂O₃(0001) show only the face-centered cubic (fcc) Cu(111) peak (black), indicating that the Cu thin films are strongly textured in the <111> orientation out-of-plane with the relationship Cu{111} || Al₂O₃(0001). To confirm the role of the single-crystal substrate interface, Cu thin films were also grown directly on Al₂O₃(0001). The almost identical X-ray diffractograms (Fig. S1) show that the Ti binding layer does not influence the out-of-plane texture induced by the Al₂O₃(0001) substrate. These similarities in out-of-plane growth on Ti and Al₂O₃(0001) are analogous to a previous report showing that hexagonal close-packed (hcp) Ti grows in the <001> orientation on Al₂O₃(001), allowing for growth of fcc Cu(111) on the similarly close-packed Ti(001) (12).

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In-Plane Thin Film Texture. Whereas XRD symmetrical scans establish the out-of-plane texture relationships, both out-of-plane and in-plane texture analyses are necessary to determine whether the Cu thin films grow epitaxially on Al₂O₃ and Si. To this end, X-ray pole figure analysis was conducted on Cu thin films on Ti/Al₂O₃(0001), Si(100), and Si(111) (Fig. 2). An X-ray pole figure for Cu(111) on Ti/Al₂O₃(0001) shows sixfold symmetry for the Cu(200) Bragg reflections, indicating both strong out-of-plane and in-plane texture and thus epitaxial growth on the Ti/Al₂O₃(0001) substrate (Fig. 24). There are six diffraction spots in the pole figure instead of three because there are two discrete sets of crystallographies from twinning with an azimuthal angle of 60° apart. Twinning defects are common in the epitaxial growth of Cu metals due to both growth accidents and grain encounters (16, 17). Similar to the Cu(200) pole figure for Cu(111) growth on Ti/Al₂O₃(0001), the Cu(111) pole figure for Cu(100) growth on Si(100) shows discrete Bragg reflections, indicating cube-on-cube epitaxial growth of Cu on the Si(100) substrate (Fig. 2B). Fourfold symmetry is observed for the Cu(111) Bragg reflections with an azimuthal angle of 90° apart, which is expected for a Cu(100) single crystal. Whereas Cu thin films on Si(111) exhibit no diffraction intensity in symmetric scans, a Cu(111) pole figure clearly shows strong out-of-plane and in-plane texture indicating epitaxial growth of Cu on Si(111) (Fig. 2C). The Cu(111) Bragg peaks have threefold symmetry with an azimuthal angle of 120° apart. To better understand the out-of-plane growth orientation of Cu thin films on Si(111), we constructed an orientation distribution function (ODF) with three X-ray pole figure scans sequentially collected on the same sample for the Cu(111), (200), and (022) Bragg reflections (Fig. S2). Using the ODF, an inverse pole figure was calculated, demonstrating that the majority of diffraction intensity parallel to Si(111) comes from the (751) plane (Fig. 2D). Therefore, Cu films on Si(111) grow predominantly in the <751> direction with the growth relationship Cu(751) || Si(111).

![XRD symmetrical scans of Cu thin films on Al₂O₃(0001) and Si(100) compared with the Joint Committee on Powder Diffraction Standards Cu reference pattern #00-004-0836.](image_url)
These results demonstrate that PVD can be used to epitaxially grow large-format electrodes in both low and high Miller index orientations.

Comparison of Ideal Surface Structures. To investigate structure–activity relationships for CO$_2$R, it is important to correlate the growth orientation of Cu thin films with the expected surface structure. According to XRD results, Cu thin films are epitaxially grown in the <111>, <100>, and <751> orientations on Al$_2$O$_3$(0001), Si(100), and Si(111), respectively. These samples will henceforth be discussed as Cu(111), (100), and (751) for simplicity. As shown in Fig. 3, the epitaxial Cu films are expected to have either a flat (Fig. 3 A and B) or kinked (Fig. 3C) surface structure depending on the growth direction of the film. The flat Cu(111) and Cu(100) surfaces (Fig. 3 A and B) are expected to have ninefold and eightfold coordination for all atoms on their surfaces, respectively. Unlike Cu(111) and Cu(100), Cu(751) is kinked, so microfacet notation is used to determine the ratios of the low Miller index facets (111), (110), and (100) present in a (751) unit cell (Fig. S3). With this notation, Cu(751) can be described as CuS-[111] + 4(110) + 2(100)], indicating that there are one (111), two (110), and one (100) unit cells in a (751) unit cell (22). Using these ratios, Cu(751) can be visualized as a kinked surface with narrow (110) terraces and a high density of (100) and (111) step sites. The presence of all fcc low Miller index facets suggests a high degree of site heterogeneity on the Cu(751) surface. This heterogeneity is clearly observed in Fig. 3C, where the kinks in Cu(751) are shown to have sites with six-, seven-, and eightfold coordination. Although there are additional sites with 10- and 11-fold coordination, these atoms are expected to be subsurface and have a minimal impact on electrocatalysis. In summary, the different copper surfaces can be placed in the order Cu(751) < Cu(100) < Cu(111) in terms of coordination number.

Electrochemical Scanning Tunneling Microscopy. To understand the correlation between bulk orientation and surface structure in electrolyte solution, electrochemical scanning tunneling microscopy (ECSTM) was used to examine the in situ surface structure of Cu(111), (100), and (751) thin films. For the ECSTM study, the Cu(111) thin film was grown on Si(110) instead of Al$_2$O$_3$(0001) to allow for electrical back-contact to the sample. The different single-crystal substrates yielded Cu films that are identical in texture (Fig. S4). Each sample was immersed in 0.1 M HClO$_4$ and scanned from the open-circuit potential to −0.76 V vs. reversible hydrogen electrode (RHE) at 50 mV s$^{-1}$ to reduce the surface oxide into Cu metal. Afterward, ECSTM images were collected at −0.24 V vs. RHE. Additional details about these experiments can be found in Supporting Information. Low-magnification ECSTM images show the morphological similarities of the three Cu thin-film orientations (Fig. S5). A large-scale view of the Cu(111) surface (Fig. S5A) depicts multiple stacks of Cu layers that are randomly interspersed from each other. The hexagonal topographic unit in each stack shares similar corner internal angles, although a few edges appear irregular and almost rounded. A similar magnification view of the Cu(100) surface (Fig. S5B) shows stacks that are more interconnected than those of Cu(111). A large number of Cu layers still appear stacked on top of each other, but, unlike their Cu(111) counterpart, the constituent units form a spiral ramp that implies the formation of screw dislocations during growth. For Cu(751), only a nondescript film terrain is observed with grains of various sizes that range from 20 to 60 nm (Fig. S5C). Similarly, all samples show evidence that epitaxy likely proceeds through either a Volmer–Weber or Stranski–Krastanov growth mechanism. This is consistent with previous studies that show epitaxy of Cu on Si proceeds through 3D growth (13, 16).

At higher magnification, atomically resolved ECSTM images (Fig. 4) show the in situ surface structures of Cu(111), (100), and (751) thin films. A high-resolution image of the Cu(111) surface (Fig. 4A) shows a threefold rotational symmetry that is indicative of a well-ordered close-packed Cu(111) structure. Imaging of Cu(100) at various points in the spirals unveiled a square Cu(100) net with an interatomic distance of 0.27 ± 0.01 nm (Fig. 4B). These ECSTM results demonstrate that for Cu(111) and (100) thin films, the majority of the in situ surface structure is identical to the bulk orientation (Fig. 2B and Fig. S4) and the ideal atomic models (Fig. 3A and B). Throughout the several-hour duration of the measurements, the surface structure of the epitaxial Cu thin...
filaments remains stable. Cu(111) and (100) electrodes have been shown to be impervious to surface reconstruction in alkaline solution (23); polycrystalline Cu surfaces, however, tend to restructure, initially into (111) and later into (100) (24). This highlights the importance of using surface-sensitive in situ tools to investigate the relationship between the surface and bulk structures.

In contrast to Cu(111) and (100), an atomically resolved ECSTM image of the surface of the Cu(751) thin film shows more heterogeneity in structure (Fig. 4C). This image is marked by color-coded stippled circles to serve as a visual guide for the geometric relationship of the Cu surface atoms. The terraces delimited by blue and white circles are relatively wide and narrow, respectively. Noteworthy features include: (i) the presence of bright and dark regions that are indicative of a highly stepped surface, (ii) the prevalence of (110) terraces, defined by interatomic distances of 0.36 nm and 0.26 nm ± 0.01 nm along the [001] and [110] directions, respectively, (iii) the variable width of the (110) terraces; in terms of the number of atoms, the span ranges from 2 (e.g., white circles at the bottom left of Fig. 4) to 7 (e.g., blue circles found at the top), and (iv) the interruption, by a kink, of 2–4 atoms along every 20-atom edge; that is, about 10–20% of the steps are kinked.

Whereas ex situ XRD pole figure measurements reveal the predominance of the (751) structure in the bulk (Fig. 2D), in situ ECSTM data show that the (751) structure populates a minor fraction of the film surface (Fig. 4C). The step notation of Cu(751) is $\text{Cu}(S)^2(110) \times (311)$, a designation more instructive for structure visualization than the condensed (hkl) notation; it expresses the fact that the surface is characterized by 4-atom-wide (110) terraces separated by kinked (311) steps. The vestiges of the kinked (311) steps that could be associated with the (751) adlattice are marked by the broken-line arrow aligned with the vector drawn on the schematic model on the right. The Cu(110) terraces demarcated by the white circles are only either 2- or 3-atom-wide along the [110] direction. The missing atoms are most likely highly undercoordinated kink sites that are rendered unstable in the presence of the acidic 0.1 M HClO$_4$ electrolyte. Because steps of (100) and (110) orientations and their respective fourfold and twofold rotational symmetries are more easily discerned than the (111) steps, the overall highly stepped surface is better described as a composite of Cu(S)–$n$(110) × (100), where $n$ varies from 2 to 7. A comparison with an ideal (751) surface (Fig. 4 C and D) where $n = 4$ shows that this heterogeneity in terrace length leads to a difference in the overall distribution of six-, seven-, and eightfold-coordinated sites. Nevertheless, in situ ECSTM confirms the existence of a kinked Cu surface with (110) terraces that is undercoordinated in comparison with Cu(111) and (100). Henceforth, the bulk structure Cu(751) will continue to be used to refer the kinked Cu sample unless details about the in situ surface structure are discussed.

The aforementioned conclusions show that PVD can be used to control the surface structure of large-format Cu electrodes, to gain deeper insights into the activity and selectivity of Cu surfaces for CO$_2$ electroreduction. Below, we describe our measurements of catalytic activity and selectivity for CO$_2$ electroreduction for these three different surfaces with distinct coordination environments and site motifs.

**Electrochemical CO$_2$ Reduction Selectivity and Activity.** After bulk and surface-structure characterization, Cu(111), (100), and (751) were tested for their CO$_2$ reduction selectivity and activity within our previously described electrochemical cell (7). The Cu thin films have an exposed geometric electrode area of 5.9 cm$^2$, allowing for electrochemical testing of samples that are ~2 orders of magnitude larger in area than those used in typical single-crystal studies. Each epitaxially grown Cu sample is tested using chronoamperometry (CA) at a single potential for 1 h in CO$_2$-purged 0.1 M KHCO$_3$ electrolyte. The gas- and liquid-phase products were quantified using a combination of gas chromatography and NMR spectroscopy, respectively. Current efficiencies for detected products (Fig. S6) indicate that Cu(111), Cu(100), and Cu(751) thin films all make $>2e^-$ reduction products in the tested potential range between −0.89 and −1.10 vs. RHE. These products include hydrocarbons such as CH$_4$ and C$_2$H$_6$, and various oxygenates such as carboxyls and alcohols that are typical products for both single-crystal and polycrystalline Cu within this potential range (7, 8). A plot comparing the total CO$_2$ reduction rate as a function of applied potential confirms that CO$_2$ mass transport is not limited within this potential range for the three Cu surfaces (Fig. S7).

To examine the C–C coupling selectivity of the different Cu surfaces, the current efficiencies for $>2e^-$ products are grouped by the number of carbons within a given product into the categories C1, C2, and C3 (Fig. 5). The $2e^-$ CO$_2$R products, CO and HCOO$^-$, are excluded from the analysis because on Cu surfaces CO is an intermediate for all $>2e^-$ C1, C2, and C3 products, and HCOO$^-$ is considered to be a terminal $2e^-$ pathway formed through a different mechanism than that of CO (8, 25). At −0.89 and −0.97 V vs. RHE, Cu(100) and Cu(751) are clearly more selective for C2 and C3 products than Cu(111), indicating that flat (100) and kinked surfaces are more selective for C–C coupling at lower overpotentials. In addition, larger partial current densities (20 and C3 products from Cu(100) and Cu(751) demonstrate that this improvement in selectivity over Cu(111) is primarily due to an increase in the absolute rate of C–C coupling rather than simply a decrease in C1 activity (Fig. S8). These conclusions are similar to those drawn from single-crystal electrochemistry experiments that showed higher C$_2$H$_6$/CH$_4$ ratios for surfaces with (100) facets and/or step sites with any microfacet orientation (8). Also, a recent report shows the same trends in C–C coupling selectivity for CO electroreduction on Cu(111) and Cu(100) single crystals (9). Theoretical studies indicate that this difference in selectivity could be due to a lower kinetic barrier for CO dimerization on Cu(100) compared with Cu(111) (10). Our results suggest that there is a strong correlation between C–C coupling selectivity and the coordination number of the surface, because Cu(111) is more coordinated than Cu(100) and Cu(751) (Figs. 3 and 4). Although it is clear that C–C coupling is favored on more
undercoordinated surfaces, further work will be necessary to elucidate how the geometry of kinked surfaces affects kinetic barriers. Nevertheless, these results demonstrate that PVD can be used to surface-structure-engineer large-format electrodes that have analogous electrocatalytic properties to Cu single crystals.

Among the \( >2e^- \) products, it is useful to compare selectivity toward oxygenates and hydrocarbons to help understand elements of the reaction mechanism, because oxygenates are less reduced than hydrocarbons with the same number of carbons. Examining the product distribution in this manner also assesses possibilities for developing catalysts with desired selectivity for a number of important chemical products. In particular, achieving greater selectivity toward oxygenates is of interest because hydrocarbons with the same number of carbons are typically less valuable (26). By grouping the current efficiencies for \( >2e^- \) products into the categories hydrocarbons and/or oxygenates (Fig. S6), it is clearly shown that Cu(111), (100), and (751) are all more selective for hydrocarbons than oxygenates across the measured range of potentials (Figs. S9 and S10). In particular, high selectivity for the hydrocarbons CH\(_4\) and C\(_2\)H\(_4\) has been commonly observed for Cu of any surface orientation (8). Whereas all epitaxial Cu thin films show higher selectivity toward hydrocarbons, examining the potential dependence of oxygenate/hydrocarbon ratios can aid in determining which active site motifs lead to greater oxygenate production (Fig. 6). At the highest potential of \(-0.89\) V vs. RHE, both Cu(751) and Cu(100) have higher oxygenate/hydrocarbon ratios than that of Cu(111), which makes only hydrocarbons at this potential. Whereas both Cu(751) and (100) are both selective and active at this potential for C–C coupling, the higher oxygenate/hydrocarbon ratio for Cu(751) than (100) indicates a clear distinction between the surfaces in oxygenate selectivity. A comparison of Cu(751) and (100) indicates that the primary distinctions in surface structure on the former are the step sites and narrow (110) terraces, which lead to differences in geometry and a lower average coordination number (Figs. 3 and 4). Therefore, these trends suggest that the geometry of undercoordinated sites on Cu surfaces can be engineered to guide selectivity toward greater oxygenate production.

To hypothesize why undercoordinated sites are more selective for oxygenates, it is useful to examine how the geometry and coordination of atoms will impact the surface coverage of intermediates during CO\(_2\)R. Online electrochemical mass spectrometry experiments demonstrate a strong correlation between the applied potentials for the hydrogen evolution reaction (HER) and reduction of possible oxygenated CO\(_2\)R intermediates on Cu electrodes (27). Recent theoretical studies indicate that C–C coupled product selectivity from Cu is strongly correlated to the coverage of CO* and H* simultaneously on the surface (28, 29). These reports suggest that the dominant mechanisms for C–C coupling and hydrogenation at lower overpotentials are chemical (hydride transfer) rather than electrochemical (proton-coupled electron transfer). Therefore, at lower overpotentials the selectivity for oxygenates or hydrocarbons could be determined by the ability of the surface to accommodate simultaneous coverages of CO* and H*.

By examining structure models and atomically resolved in situ ECSTM images (Figs. 3 and 4), we can postulate how CO* and H* coverages depend on the geometry and coordination of atoms on Cu(111), (100), and (751). Whereas the Cu(111) and (100) surfaces have a high density of sites with eight- and ninefold coordination, respectively, the Cu(751) surface has a low density of sites with six-, seven-, and eightfold coordination (Fig. 3). A closer look at the structure models shows that Cu(111), (100), and (751) each have six, four, and two nearest surface neighbors, respectively. It was formerly noted that the in situ surface structure of Cu(751) is better described as Cu(S)–[n(110) × (100)], where \( n \) varies from 2 to 7, and that the surface heterogeneity changes the distribution of six-, seven-, and eightfold coordination sites. This heterogeneity does not affect the trend in nearest surface neighbors, because the main structural motif of (110) terraces, where each Cu atom will have two nearest surface neighbors, is present in both the composite Cu(S)–[n(110) × (100)] (Fig. 4C) and the ideal Cu(751) (Fig. 4D) surface structures. Since it is statistically less likely for a CO* dimer to be adjacent to H* atoms on a surface with fewer neighbors, Cu(751) could have greater oxygenate selectivity because it is more difficult to hydrogenate C–C coupled CO\(_2\)R intermediates on its surface. This trend in surface neighbors is corroborated by comparing the trend in oxygenate/hydrocarbon ratios at \(-0.89\) V vs. RHE, where Cu(751) \( > \) Cu(100) \( > \) Cu(111). At more negative potentials, all surfaces have similar oxygenate/hydrocarbon ratios, suggesting that CO* and H* coverages may be less important at high overpotentials. The aforementioned theory study predicts that at more negative potentials the barrier height for chemical hydrogenation increases, whereas the barrier height for electrochemical hydrogenation decreases (28). Therefore, these similarities in selectivity at higher potentials
overpotentials could be due to a shift in the hydrogenation mechanism from chemical to electrochemical. If the predominant mechanism for hydrogenation at these overpotentials is electrochemical, it is expected that the oxygenate/hydrocarbon ratio would be less sensitive to geometry and coverage on the surface because the proton and electron transfers are concerted. For polycrystalline Cu electrodes, the selective production of ethanol from the electrochemical reduction of CO₂ in alkaline solution was achieved by atomic-level surface modification via mild oxidation–reduction cycles (30). Results from the present work provide impetus for the exploration of advanced engineering strategies to design electrocatalytic surfaces with undercoordinated sites that can steer selectivity toward oxygenate formation.

Conclusions

We have investigated PVD as a growth method to structure-engineer large-format Cu thin films for electrochemical CO₂ reduction. X-ray pole figures indicate that the Cu thin films grow epitaxially with <111>, <100>, and <751> out-of-plane orientations on Al₂O₃(0001), Si(100), and Si(111), respectively. The XRD results show that Cu can be epitaxially grown in both low and high Miller index directions using different single-crystal substrate orientations. Analysis of the structure in situ using ESTEM confirmed the existence of three unique Cu surface structures from epitaxial growth. Electrochemical testing of these samples for CO₂ reduction led to a number of important observations. Thin-film orientations with more undercoordinated sites are more active and selective for C–C coupling, which is consistent with previous studies on small-format single crystals. This demonstrates that PVD can be used to grow large-format electrodes that have analogous electrocatalytic properties to single crystals. Furthermore, analysis of oxygenate vs. hydrocarbon selectivity reveals that at −0.89 V vs. RHE, Cu(751) has the highest oxygenate/hydrocarbon ratio of the three Cu orientations. We suggest that this improvement in oxygenate selectivity is related to the lower number of nearest neighbors on the Cu(S)–[0(110) × 100] surface, or the topmost layer of the Cu(751) film, because barriers for hydride transfer are predicted to be lower than those for proton-coupled electron transfer at lower overpotentials. Additional mechanistic details can be unveiled from future investigations that examine fine surface structural nuances under operando conditions, akin to the protocols that led to the discovery of Cu(511) as a selective ethanol-generating surface formed from polycrystalline Cu (30). Our results demonstrate that epitaxy can aid in the discovery of structure–activity relationships for CO₂R, providing insights into designing more active and selective electrocatalysts.

ACKNOWLEDGMENTS. We thank Dr. Jakob Kibsgaard and Dr. Karen Chan for their assistance in constructing the Cu surface structure models. Additional thanks go to the Stanford Nano Facility. Part of this work was performed at the Stanford Nano Shared Facilities (SNSF) and the Stanford Nanofabrication Facility (SNF), supported by the National Science Foundation under Award ECCS-1542152. This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a Department of Energy (DOE) Energy Innovation Hub, as follows: the development of electrochemical testing of Cu thin films was supported through the Office of Science of the US DOE under Award DE-SC0004993; the development of epitaxial growth was supported by the Global Climate Energy Project at Stanford University; the procurement of the physical vapor deposition chamber was supported by the DOE Laboratory Directed Research and Development under Award DE-AC02-76SF00515.