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Initial Oxidation of Cu(*hkl*) Surfaces Vicinal to Cu(111): A High-Throughput Study of Structure Sensitivity

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ABSTRACT: The initial stage in the oxidation of Cu single crystal surfaces has been studied on a surface structure spread single crystal (S⁴C) exposing a continuous distribution of all Cu(*hkl*) surface orientations lying within 10° polar angle of the (111) plane, Cu(111) \pm 10°-S⁴C. The uptake of oxygen across the Cu(111) \pm 10°-S⁴C during exposure to O₂ at 300 K has been measured using spatially resolved X-ray photoelectron spectroscopy (XPS), and the resulting Cu₂O surface oxide layer has been imaged using scanning tunneling microscopy (STM). Uptake of oxygen is dependent on surface step density and increases with increasing polar angle relative to the (111)



pole. In contrast, the oxygen uptake does not depend on the crystallographic orientation of the step edge or, in other words, the kink density along the step edge. STM images reveal that once oxidation of the step edges begins, all of the boundaries of the Cu₂O step oxide layer are oriented along (100) step edges in the Cu(111) terrace independent of the initial orientation of the step. In other words, the oxidizing step edges have no memory of their original orientation, and thus, the step growth depends only on step density and not on the kink density along the step edge. The combined use of both spatially resolved XPS and atomic scale imaging with STM on a Cu(111) \pm 10°-S⁴C has provided unique insight into the origins of structure-sensitive surface chemistry.

1. INTRODUCTION

Many metal-catalyzed surface reactions are structure sensitive in the sense that their rates and selectivities depend on the atomic structure or crystallographic orientation of the surfaces on which they occur. Catalysis may be the best known example, but numerous surface chemical processes are structure sensitive. Although the concept of surface-structure sensitivity dates back to the earliest studies of catalysis, the clear and unequivocal demonstration of structure-sensitive surface chemistry is perhaps one of the greatest achievements of modern surface science.¹ In fact, the 2007 Nobel Prize in Chemistry was awarded in a large part for the demonstration that the rates of catalytic ammonia synthesis from nitrogen and hydrogen are vastly different on the three low Miller index planes of Fe.² In general, the origin of structure sensitivity in a multistep catalytic surface reaction lies in the structure sensitivity of the rate constants for the elementary steps in the process. Understanding and predicting the structure sensitivity of these elementary rate constants is one of the most fundamental problems in surface chemistry.

Demonstration of surface-structure sensitivity relies on the study of surface chemistry on isolated single crystal planes of a material. Very often this is done by preparing several flat single crystal surfaces of unique crystallographic orientation and by

systematically comparing reactivity on each. This methodology preludes systematic study of structure sensitivity across all possible surfaces because the orientations of crystal surfaces span two continuous degrees of freedom. The set of all possible crystal surfaces is typically represented using a stereographic triangle such as the one shown for a face-centered cubic (fcc) crystal in Figure 1A.³ All points in or on the stereographic triangle uniquely represent one of all possible surfaces that can be exposed by an fcc crystal. The ideal structures of these surfaces are formed of atomically flat terraces, straight monatomic steps, and atomic kinks in those step edges, where the differences among the surfaces lie in the crystallographic orientations and widths of the terraces, the straight step edges, and the kinks. Preparation, characterization, and study of single crystal surfaces of a unique orientation is the basic methodology of much of surface science; however, it is not amenable to systematic study of structure sensitivity across the continuous space of surface orientations. This requires the use of a high-throughput approach that allows parallel preparation,

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Figure 1. (A) The stereographic triangle used to enumerate all possible surfaces that can be exposed by an fcc crystal such as Cu. The solid green, blue, red, and purple vectors around the (111) pole are $[\overline{112}]$, $[1\overline{10}]$, $[11\overline{2}]$, and $[\overline{110}]$, respectively. (B) Schematic illustration in cross section and plan view of a S⁴C oriented along the [111] direction. The concentric circles illustrate the increase in density of monatomic steps as the radial distance (polar angle) from the [111] direction increases. (C) A Cu(111) $\pm 10^{\circ}$ -S⁴C. The crystal diameter is ~10 mm, and the thickness is ~2 mm at the center. The directions indicated with the arrows are the high-symmetry directions drawn onto the stereographic triangle. The steps running perpendicular to the direction of the [112] vector (red) are close-packed with (111) structure. Those running perpendicular to the direction of the [112] vector (green) are close-packed with (100) structure. The steps running perpendicular to the [110] and [110] vectors are not close-packed.

characterization, and study of a large library of surface orientations.

This paper reports the results of a high-throughput study of the oxidation of Cu(hkl) single crystal surfaces that are vicinal to the Cu(111) plane. The high-throughput library is a curved single crystal that has been prepared such that its surface exposes all possible planes lying within 10° of the (111) orientation (Figure 1B). We refer to this library as a Surface Structure Spread Single Crystal (S⁴C), and the nomenclature for the library shown in Figure 1B is $Cu(111) \pm 10^{\circ}-S^{4}C$. Given the orientation of the bulk crystal lattice and the coordinates of any point on the S⁴C relative to the (111) point, one can determine its local crystallographic orientation. The advantage of studying surface chemistry on this S⁴C library is that the use of one sample ensures that all points on the surface have been treated and prepared identically. The value of such a library is that it allows the study of structure sensitivity across a continuous distribution of surface orientations provided that one can spatially resolve the surface-sensitive measurements that are needed to characterize the local surface structure and the surface properties of interest.

Over the past 50 years, there have been several studies that have employed the concept of a S⁴C without necessarily considering it to be a high-throughput library. Although the use of S⁴C samples is commonly attributed to Gwathmey⁴⁻⁶ in the 1940s, the first reference of which we are aware is a study in 1927 by Linder⁷ of the photoelectric effect in a cylindrical Zn single crystal oriented with the $[1\overline{2}10]$ axis along its length and prepared to expose a continuous distribution of surface orientations about its perimeter. The photoelectric current showed periodic variations around the perimeter of the crystal. Gwathmey used spherical single crystals of Cu, much like those used in this study, to observe the influence of crystallographic orientation on oxidation, corrosion, and other phenomena originating at the surface.⁴⁻⁶ Since that time, there have been many other uses of curved single crystals to elucidate structure sensitivity in various surface processes. However, in spite of the apparent simplicity of the S⁴C as a platform for study of structure-sensitive surface chemistry, past studies have been hampered by experimental limitations. It is only recently that the continued evolution of surface analysis tools; the improvements in their spatial resolution; and the recent developments in automated sample manipulation, data acquisition, and data analysis have eliminated many of the barriers to fully realizing the potential of S⁴C surface libraries for detailed and comprehensive study of structure-sensitive surface chemistry.

This paper presents the results of a study of the surfacestructure sensitivity of the initial oxidation of Cu(hkl) surfaces. The oxidation of Cu single crystals, specifically Cu(111), has been studied experimentally⁸⁻¹³ and with theory^{14,15} for decades. Scanning tunneling microscopy (STM) studies by Matsumoto et al. showed that upon room-temperature exposure to O_{2} , step edges on the Cu(111) surface were faceted into three directions that were aligned with the closepacked directions of the Cu(111) terrace.⁹ The faceted step edges appeared to be decorated with a rim of step oxide having a thickness equivalent to the monatomic Cu step height. Wiame et al. presented STM images before and after oxidation suggesting oxide film growth along two fronts: accumulation at the lower terrace side of the step edge and growing into the upper terrace.¹³ They also identified the oxide as $Cu_2O(111)$ on the basis of atomic resolution images. This is in agreement with the stoichiometry previously proposed by Jensen and coworkers^{16,17} who performed STM studies of high coverage ordered oxide structures. In addition to oxide film growth at the step edges, the oxide film can grow on the flat terraces. The terrace oxide is nucleated at defect sites in the Cu(111) terrace and grows such that the boundaries between the terrace oxide and the Cu(111) terraces run along close-packed directions. With increasing O₂ exposure, the terrace oxide islands grow resulting in the displacement of Cu atoms out of the terrace layer and onto the terrace. There, the Cu atoms are oxidized to form shapeless added oxide islands. The added oxide islands are shapeless because they are on top of the terrace and are not bounded by the topmost Cu(111) layer like the triangular terrace oxide islands. Density functional theory (DFT) calculations performed by Xu and Mavrikakis described the O_2 dissociation pathway on the (111) terrace as going through a bridge-hollow-bridge transition state yielding atomic O atoms adsorbing in adjacent fcc hollow sites.¹⁴ They also predicted that there should be an enhancement in the dissociation rate at step edges.¹⁵ These results indicate that O₂ dissociation kinetics and the formation of Cu oxide layers are sensitive to the structure and orientation of the Cu surface.

In 1982, Armitage and Woodruff published a highthroughput study of the initial stages of oxidation of Cu single crystals.¹⁸ Their surface-structure library was a Cu cylinder orientated along the $[1\overline{10}]$ direction. The perimeter of the cylinder exposed surfaces on the (110) to (111) and the (111) to (100) edges of the stereographic triangle shown in Figure 1A. These surfaces expose (110), (111), and (100) terraces separated by straight, close-packed step edges. Armitage and Woodruff used Auger electron spectroscopy to study the initial uptake of oxygen following various exposures to O_2 at 300 K as a function of position around the edge of the cylinder. This was accomplished by rotating the cylinder underneath the electron beam and by obtaining Auger spectra at different angles. Following a 5 L exposure to O_2 , the oxygen coverage on the (110) surface was ~5–10 times higher than on the (111) surface and varied smoothly as a function of the angle between the two. This pioneering work demonstrated unequivocally that the rate of dissociative O_2 adsorption on Cu is structure sensitive with the dissociative adsorption rates on the low Miller index surfaces varying in the order (110) > (100) > (111).

In this work, the initial oxidation of Cu(hkl) surfaces has been studied on a Cu(111) \pm 10°-S⁴C using a combination of spatially resolved X-ray photoelectron spectroscopy (XPS) to measure oxygen uptake and scanning tunneling microscopy (STM) to image the structures of the oxidized surfaces. The advantage of the spherical S⁴C library used in this work over the cylinder used by Armitage and Woodruff is that the spherical S⁴C library exposes surfaces with structures that span a continuous 2D region of the stereographic triangle rather than just a 1D path along the perimeter. The area spanned by the Cu(111) \pm 10°-S⁴C is illustrated by the dashed oval in Figure 1A. From a surface-structure perspective, the surfaces in this region have (111) terraces separated by all possible orientations of step edges, close-packed and kinked. The density of step edges increases with polar angle away from the (111) pole. The kink density along the step edges varies smoothly with azimuthal angle around the (111) pole. XPS measurements show that the initial uptake of oxygen depends on the step density on the surface but that it does not depend on the kink density along the step edges. The STM images clearly reveal the faceting of step edges that occurs during initial oxidation and provide insight into the origins of the fact that the initial uptake of oxygen depends on step density but not on kink density. Equally importantly, these results highlight the potential value of the combination of spatially resolved surface analysis by XPS, spatially resolved atomic scale imaging using STM, and S⁴C libraries for understanding the origins of structure-sensitive surface chemistry.

2. EXPERIMENTAL SECTION

The work presented in this paper was conducted in two laboratories. Two Cu(111) \pm 10°-S⁴C's were prepared at Carnegie Mellon University, and one was shipped to Tufts University. The Cu(111) \pm 10°-S⁴C at Carnegie Mellon University was used for quantitative study of oxygen uptake using XPS measurements made in a Thermo-Fisher Theta-Probe. Atomic resolution STM imaging of the other Cu(111) \pm 10°-S⁴C was performed using an Omicron VT-STM at Tufts University.

The details of the $Cu(111) \pm 10^{\circ}$ -S⁴C preparation method and the analysis of their shapes will be described elsewhere. Briefly, they were prepared by starting with commercially available 10 mm diameter and 2 mm thick Cu(111) single crystals (Monocrystals Co.). The crystals were mechanically curved by grinding against a series of spherically shaped abrasive templates of the appropriate curvature. Once curved and polished, the shapes of the S⁴C surfaces were mapped using optical profilometry and were very close to spherical across the inner 90% of their diameter (~80% of their area). The local orientation of these S⁴C surfaces is within $\pm 0.5^{\circ}$ of the perfect sphere out to a radius of ~4.5 mm from the center of the 10 mm diameter crystal. The polar angular orientation of the S⁴C surfaces was determined using Laue back diffraction. This is critical to unequivocal determination of the crystallographic orientation of the steps on the surface. Once mounted in the ultrahigh vacuum (UHV) chambers, the surfaces of the Cu(111) \pm 10°-S⁴C's were cleaned by consecutive cycles of Ar⁺ sputtering (1.50 keV/20 μ A) and annealing (1000 K). Sample cleanliness was verified in both apparatuses using XPS.

Scanning tunneling microscopy experiments were performed using an Omicron Nanotechnology variable-temperature ultrahigh vacuum (VT-UHV) STM. The base pressure in the STM chamber was approximately 1×10^{-10} mbar. For imaging of oxidized surfaces, the Cu(111) $\pm 10^{\circ}$ -S⁴C was exposed to 168 L of O₂ while in the analysis chamber and at 300 K. O₂ was introduced into the analysis chamber through a leak valve connected to a collimated doser. After exposure, the sample was transferred in vacuum into the STM chamber. STM images were acquired with either Omicron or Veeco etched W tips. All biases refer to sample voltage.

To reproducibly approach predetermined points on the crystal for STM imaging, a grid was constructed to map the image seen by the STM alignment camera with the polar coordinates used to describe the points on the Cu(111) \pm 10°-S⁴C. This grid accounted for the 3D shape of the Cu(111) \pm 10°-S⁴C surface and gave an accurate perspective that accounted for the distance and angle from the camera used for coarse approach of the STM tip to the surface. The camera had line-of-sight to the crystal and provided an image on a computer screen that was used during approach of the STM tip to the surface. The transparent grid was superimposed on the computer screen to overlap with the perimeter of the crystal. Polar coordinates were used for this grid, and all STM images are referenced in polar coordinates; the radius is in millimeters from the (111) pole and the angle is in degrees from the $[\overline{112}]$ direction. Minor adjustments to the grid alignment were made by positioning the center of the grid in the area determined by STM to have the widest (111) terraces (typically >1 μ m²). This adjustment was necessitated by the slight and unavoidable miscut of the original crystal and its subsequent preparation both of which lead to positioning of the (111) pole slightly off the center of the Cu(111) \pm 10°-S⁴C.

The ThetaProbe used for spatially resolved XPS analysis is equipped with a sample preparation chamber that was used for sample cleaning by Ar⁺ sputtering and annealing. The sample was then transferred into the analysis chamber. Prior to exposure to O_2 , the Cu $2p_{3/2}$ signal was measured from the clean surface along the $[11\overline{2}]$ and $[1\overline{10}]$ directions. The surface was analyzed using an X-ray spot size of 100 μ m diameter and an analyzer pass energy of 100 eV. This corresponds to an angular spread of surface orientations of $\sim 0.2^{\circ}$ under the X-ray spot. During these measurements, the lateral position of the sample is changed while the X-ray spot and the analysis position are kept fixed. The vertical position of the sample can be varied automatically to compensate for the curvature of the S⁴C and to keep the analysis point on the surface at the focal point of the analyzer. Needless to say, the curvature of the surface also resulted in some variation of the Cu $2p_{3/2}$ signal across the clean surface simply because there is some variation of the takeoff angle as the analysis point is moved across the S⁴C.

The Cu(111) \pm 10°-S⁴C was exposed to O₂ introduced into the analysis chamber of the ThetaProbe through a leak valve.

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Figure 2. STM images obtained at five positions along the $[\overline{112}]$ vector direction (0°) and the $[11\overline{2}]$ vector direction (180°) from the (111) pole of the Cu $(111) \pm 10^\circ$ -S⁴C. The image from the center of the crystal (0 mm) shows a flat (111) terrace. The inset in this image is a high-resolution image of the hexagonal lattice of Cu atoms in the (111) terrace. STM images obtained from points along the $[11\overline{2}]$ direction and $[\overline{112}]$ direction and $[\overline{112}]$ directions and separating (111) terraces. The density of steps increases with distance from the (111) pole. Image conditions V = -0.2 V, I = 100 pA. Images are 88×90 nm². The inset is atomic resolution of Cu atoms taken from the center of the crystal. Image conditions -0.2 V, 100 pA, 1×1 nm².

An exposure of 30 L with the sample at 300 K was used to restrict the oxygen uptake to levels that are fairly low (<20% of saturation) and, therefore, sensitive to the structure of the clean surface. Under these same conditions, exposures of >300 L were needed to approach saturation of the surface with oxygen. Once exposed to O₂, the uptake of oxygen was determined from the relative intensities of the O 1s and Cu $2p_{3/2}$ XPS signals measured at 40 points equally spaced along the [112] and [110] directions and passing through the (111) center point of the Cu(111) $\pm 10^{\circ}$ -S⁴C. The reported oxygen concentrations were obtained from the areas under the O 1s and Cu $2p_{3/2}$ XPS peaks scaled using the sensitivity factors for each.

3. RESULTS

Structure sensitivity of the oxidation of Cu surfaces vicinal to the (111) plane has been studied using XPS to measure the uptake of oxygen across the Cu(111) \pm 10°-S⁴C following exposure to O₂ at 300 K. The local structure of the surface has been studied using STM to image the Cu(111) \pm 10°-S⁴C surface before and after O₂ exposure.

3.1. Structure of the Clean Cu(111) \pm 10°-S⁴C. The Cu(111) \pm 10°-S⁴C is spherical, and thus, the tangent planes at each of the points across its surface represent different crystal planes of the fcc crystal lattice. Near the center of the Cu(111) \pm 10°-S⁴C lies a point whose tangent plane is the (111) plane. Using the STM, it has been possible to find this point, and it is imaged in the middle panel of Figure 2. At this point, the surface is atomically flat across the entire image and the atomic resolution inset reveals the hexagonal close-packed array of Cu atoms in the (111) plane. The (111) pole of the Cu(111) \pm 10°-S⁴C is not at its exact center simply because of slight misorientation of the original Cu(111) single crystal and because of additional misorientation that occurred during curving and polishing of the Cu(111) \pm 10°-S⁴C.

The ideal structures of the surfaces at different points across the Cu(111) \pm 10°-S⁴C surface consist of (111) terraces separated by monatomic steps. Ideally, the steps increase in density with distance from the (111) pole and form concentric rings around the pole as implied by the schematic in Figure 1B. Along high-symmetry directions of the crystal such as [112] and its symmetry equivalent directions, the step edges will be atomically close-packed and straight. At other angles around the (111) pole, the monatomic steps will have structures based on close-packed rows separated by kinks.

STM images were acquired at several points on the Cu(111) $\pm 10^{\circ}$ -S⁴C to demonstrate how the step direction and step

density vary because of the varying orientation of the local surface. In Figure 2, the middle image labeled $(0 \text{ mm}, 0^\circ)$ is taken from the (111) pole of the crystal where large scale images (>10,000 nm²) reveal flat terraces with few step edges. Additional images were collected at radii of 1 mm and 2 mm from the (111) pole and angles of 0° and 180° , that is, in the $[\overline{112}]$ and $[11\overline{2}]$ directions. These directions are the green and red lines in Figure 1C, respectively. The images shown in Figure 2 reveal monatomic steps running roughly perpendicular to the $[\overline{112}]$ and $[11\overline{2}]$ directions. The expected increase in step density with increasing radial distance from the (111) pole is evident. In the (2 mm, 180°) image in Figure 2, the bright spots are most likely artifacts from the STM tip scanning over multiple step edges at a higher scan speed. The orientation of the steps at different azimuthal angles is illustrated in the montage of images in Figure 3. STM images have been taken at a radius of 1 mm from the (111) pole and at angles from 0° through 360° in 30° increments. It is evident that as one moves

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Figure 3. Montage of STM images obtained from points at 1 mm radius from the (111) pole of the Cu(111) \pm 10°-S⁴C and azimuthal angles from 0° to 360°. The images reveal monatomic steps with orientations that rotate through 360° around the (111) pole. The monatomic steps separate (111) terraces. V = -0.2 V, I = 200 pA. Images are 88 × 90 nm².

around the (111) pole, the orientation of the step directions rotates through 360° as expected. Thus, qualitatively, the local structure of the surfaces at different points across the Cu(111) $\pm 10^{\circ}$ -S⁴C is representative of the ideal structure.

The STM images in Figures 2 and 3 do reveal differences between the atomic level structure of the surfaces and the ideal structures of planes cleaved from an ideal fcc lattice. For example, it is clear that the spacing of steps is not uniform, and similarly, their orientations are not aligned perfectly perpendicular to the radial vector from the (111) pole. In part, these are the result of local misorientations of the surface observable only when examining them on the ~100 nm scale. The wandering of the steps and the varying widths of terraces within an image can also be due to thermal roughening by diffusion of atoms resulting in a distribution of terrace structure and orientation.

Finally, it is important to discuss the ideal structures of the step edges on the Cu(111) \pm 10°-S⁴C. As noted earlier, these step edges separate (111) terraces. Our measurements of oxygen uptake have been made along lines passing through the (111) pole and lying in the [$\overline{112}$], [$1\overline{10}$], [$11\overline{2}$], and [$\overline{110}$] directions. In Figure 1, these are indicated by the green, blue, red, and purple lines, respectively. The steps along these directions have different structures as indicated in Figure 4. The



Figure 4. Ideal structures of the step edges vicinal to the (111) pole. The step edges oriented perpendicular to the $[\overline{112}]$ direction are close-packed and separate (111) terraces. These have the square structure of a (100) microfacet projecting from the (111) terrace. The step edges oriented perpendicular to the $[11\overline{2}]$ direction have the structure of a (111) microfacet projecting from the terrace, and these are referred to as (111) step edges. This can also be thought of as the projection of a (110) microfacet from the (111) terrace. The step edges oriented perpendicular to the $[11\overline{2}]$ direction are kinked. The kinks are formed by the intersection of (100) and (110) microfacets.

steps oriented perpendicular to the $[\overline{11}2]$ direction are closepacked and have the local structure of a (100) plane or microfacet projecting out of the (111) terrace. We refer to these as (100) step edges. Moving in the opposite direction, $[11\overline{2}]$, from the (111) pole of the Cu(111) $\pm 10^{\circ}$ -S⁴C one also finds close-packed step edges, however, the local structure of the step edges is different. These have the local structure of a (110) microfacet projecting from the (111) terrace. These step edges are sometimes considered to be (111) microfacets because they can also be considered to have the close-packed structure of a (111) plane as illustrated by the triangle. We refer to these as (111) steps. The step edges oriented perpendicular to the $[1\overline{1}0]$ direction are not close-packed. They are kinked step edges with the kinks being formed by the intersection of (100) and (110) microfacets. As such, they are chiral and the clockwise orientation of the (111) to (100) to (110) sequence in the step edge shown in Figure 4 makes this an R-step edge.^{3,19–21} Going in the opposite, $[\overline{1}10]$, direction through the (111) pole of the Cu(111) $\pm 10^{\circ}$ -S⁴C, one finds surfaces with steps that have a counterclockwise orientation of the (111) to (100) to (110) sequence of microfacets, and these are S-step edges. The structures of the step edges are emphasized because, in principle, one might expect the differences in the atomic structures of the step edges around the (111) pole of the Cu(111) $\pm 10^{\circ}$ -S⁴C to influence the kinetics of surface oxidation.

3.2. Oxidation of the Cu(111) \pm 10°-S⁴C. The structure sensitivity of the oxidation of Cu surfaces vicinal to the (111) plane has been studied by exposing the Cu(111) \pm 10°-S⁴C to oxygen at 300 K and then by using spatially resolved XPS to measure the uptake of oxygen along the [112], [110], [112], and [110] directions. The X-ray spot was ~100 μ m in diameter and was used to measure the O 1s and Cu 2p XPS signals at ~20 points spaced by ~200 μ m along each of the four directions from the (111) pole. The concentration of oxygen was determined from the O and Cu XPS sensitivities and represents the O atom concentration in the near surface region that contributes to the XPS signal. The 30 L exposure to O₂ was chosen to be well below the 300–500 L exposure needed to saturate the surface. Thus, the oxygen concentration is a measure of the initial rate of surface oxidation.

The spatially resolved uptake of oxygen by the Cu(111) \pm 10°-S⁴C is illustrated in Figure 5. Two independent sets of



Figure 5. Oxygen uptake on the Cu(111) \pm 10°-S⁴C as a function of distance from the (111) pole and along the [112], [110], [112], and [110] directions. The open and closed circles for the data taken along the [112] and [112] were obtained from two repetitions of the experiment. The squares are data taken along the [110] and [110] directions. The 30 L exposure to O₂ was performed at 300 K and was ~10% of the exposure needed to saturate the surface with adsorbed oxygen. The oxygen uptake was measured using O 1s and Cu 2p XPS signals to determine the atomic O concentration in the near surface region that contributes to the XPS signal.

measurements obtained along the $[11\overline{2}]$ and $[\overline{112}]$ are shown using the open and closed circles. A set of measurements taken along the $[1\overline{10}]$ and $[\overline{110}]$ directions is shown with the squares. It is clear from the data in Figure 5 that the oxygen uptake is minimal in the center of the Cu(111) \pm 10°-S⁴C and increases by a factor of ~4 toward the edges. The key points revealed by the data in Figure 5 are that the uptake of oxygen on the



Figure 6. STM images showing the (111) pole of the $Cu(111) \pm 10^{\circ}$ -S⁴C (a) before and (b) after oxidation. The exposure to O_2 in the STM chamber was 168 L at 300 K. The image of the clean Cu(111) surface before O_2 exposure reveals a perfectly flat (111) terrace with no steps. After exposure to O_2 , the STM image reveals the presence of oxidized regions of the surface. The dark triangular pits in b are terrace oxide islands formed in the top (111) terrace. The edges of these islands are aligned along high symmetry directions. The boundaries of the terrace oxide islands create (100) step edges in the Cu(111) terrace. The lighter features are shapeless islands of added oxide formed on the Cu(111) terrace. Image conditions: bare Cu images were obtained at -0.2 V and 200 pA, oxidized Cu images were obtained at 0.2 V and 300 pA. Images are 176 × 180 nm². The graph is a line scan taken along the white line in b.

Cu(111) \pm 10°-S⁴C depends on the distance from the (111) pole but does not depend significantly on the orientation around the pole. In other words, the uptake of oxygen depends on the step density but not on the step structure (or kink density).

3.3. STM of Oxygen Growth on Cu(111) \pm 10°-S⁴C along (hhl) Direction. The initial stages of the oxidation of Cu(111) have been studied in the past by Matsumoto et al.⁹ and by Wiame et al.¹³ Their work revealed the existence of two types of oxide islands formed after exposure of the surface to O_2 at room temperature. One is a terrace oxide layer that grows within the top layer of the Cu(111) surface. The second is an added oxide layer that is formed by the Cu atoms ejected from the top layer during formation of the terrace oxide. Figure 6 illustrates our images of the (111) pole of the Cu(111) \pm 10°-S⁴C before and after exposure to 168 L of O₂ at 300 K. The image of the clean surface reveals the flat (111) terrace with no step edges. Once exposed to O_{2} , the image of the surface reveals two types of features separated by flat clean Cu(111) terraces. The dark features that appear to be pits correspond to the terrace oxide islands. Their edges are regular and run along the three equivalent $[\overline{1}10]$, $[\overline{1}01]$, and $[0\overline{1}1]$ directions. These are close-packed (100) steps between the Cu(111) terrace and the terrace oxide. We used Laue X-ray diffraction to determine the absolute orientation of the crystal and, thus, the step orientation. The contrast between the terrace oxide and the surrounding Cu terrace arises because STM images are a convolution of topographic and electronic information. The topographic height of the bare Cu terrace is lower than the terrace oxide; however, they have different electronic properties. Specifically, the oxide has a lower electrical conductivity than the surrounding Cu terrace; therefore, it images as a depression with STM. The lighter features on the Cu(111)

terrace are the added oxide layer formed by oxidation of the Cu atom ejected from the top (111) layer by formation of the terrace oxide. The edges of the triangular terrace oxide islands are oriented because they are in the surface layer and, hence, are surrounded by the hexagonal lattice of Cu atoms. The added oxide islands assemble on top of the surface and are not surrounded by Cu, hence, their irregular shape. Topographic height measurements seen in the line scan in Figure 6 reveal that the added oxide sits 0.21 nm above the terrace oxide. These images are largely consistent with the results of Matsumoto et al.⁹ and Wiame et al.¹³ In Figures 6-8, the added oxide islands were imaged as depressions in the Cu(111)terrace, but they were imaged as protrusions in these previous studies. This difference in contrast could be explained by different states of the STM tip. Molecules adsorbed at the end of the STM tip can cause surface features to be imaged differently than with a bare metal tip.²² Very occasionally, we observed the added oxide islands imaging as protrusions. However, as the added oxide islands were predominantly imaged as depressions, we represent them with the images selected.

On the high Miller index planes vicinal to Cu(111), oxidation tends to occur at the step edges. This is entirely consistent with the results of the XPS measurements of oxygen uptake across the Cu(111) \pm 10°-S⁴C which revealed that oxygen uptake is strongly dependent on step density, although not on step orientation. Figure 7 includes three STM images of the Cu(111) \pm 10°-S⁴C surface after an oxygen exposure of 168 L at 300 K. The two lower images come from points at a 1 mm radial distance from the (111) pole and along the [112] and [112] directions. The third has been obtained from a point 60° from the [112] direction. All three reveal the formation of oxide as a dark band running along the downstairs side of the step

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Figure 7. STM images of three high Miller index planes on the $Cu(111) \pm 10^{\circ}$ -S⁴C surface following exposure to 168 L of O₂ at 300 K. The triangles superimposed on the images indicate the directions of the close-packed, (100) step edges facing the interior of the triangle. The oxide layer grows from the step edges onto the terraces. As indicated by the triangles superimposed on each of the images, the Cu step edges facet to create boundaries with (100) step edges.

edge. In other words, the oxide grows in the form of the step oxide as illustrated in Figure 6. The STM images of Figure 7 also reveal that the oxidation of the step edges can lead to a drastically different step morphology because of the boundary between the step oxide and the upper terrace. Oxidation of the (100) step edges along the $[\overline{112}]$ direction does not cause any change in step orientation; the step oxide boundary runs parallel to the direction of the original (100) step. One can see that there are a few facets that have formed along the left most step edge and that the boundaries of these facets also lie along the high symmetry directions indicated by the triangle superimposed on the image. These directions are equivalent to those of the terrace oxide boundaries observed on the Cu(111) terrace in Figure 6. In contrast with the oxidation of the (100) step edges along the [112] direction, oxidation of the (111) step edges along the $[11\overline{2}]$ direction creates a more jagged boundary. The boundary between step oxide and the (111) terrace is sawtoothed. The directions of the oxide-Cu(111) boundaries also lie along the high symmetry directions as indicated by the superimposed triangle. In other words, these lie along directions that form (100) step edges at the boundary between the Cu(111) terrace and the step oxide. Finally, the image in Figure 7 taken at a point 60° from the $[\overline{112}]$ direction reveals the same qualitative behavior of the steps during oxidation; the resulting oxide/step edge boundary is faceted to create a sawtoothed boundary with facets formed by (100) step edges. In this image, one can see quite clearly that the boundary between the step oxide and the upper terrace is sawtoothed, while the boundary between the step oxide and the lower terrace is relatively smooth.

The oxide boundary at step edges on the Cu(111) \pm 10°-S⁴C formed by exposure to oxygen is observed at all points across its surface. Figure 8 presents a montage of 12 images taken at a radius of 1 mm from the (111) pole and at 12 azimuthal angles between 0° and 360° with respect to the [112] direction. Given the symmetry of the Cu(111) \pm 10°-S⁴C surface, the surfaces at 0°, 120°, and 240° expose (100)-type steps and the surfaces at 60°, 180°, and 300° expose (111)-type step edges. This is supported by the STM images in Figure 8 as the oxide boundaries at 0°, 120°, and 240° are not faceted to the same



Figure 8. Montage of STM images of the Cu(111) \pm 10°-S⁴C surface after oxidation. All images on the perimeter are taken at 1 mm radius from the (111) pole. Step edges at 0°, 120°, and 240° appear less faceted than step edges at 60°, 180°, and 300°. Bias = 0.2 V, *I* = 100 pA. Images are 88 × 90 nm².

extent as boundaries at 60°, 180°, and 300°. To quantify the extent of oxide boundary faceting along the $[11\overline{2}]$ and $[\overline{112}]$ directions, we measured the lengths of the oxide-terrace boundary and the original straight step edge. A ratio between these lengths of 1 would infer that the step edge had not been roughened at all. A value >1 signifies faceting of the boundary with a maximum faceting value of 2 indicating the complete faceting of a (111) step edge to (100) step edges. This analysis revealed that the oxidized (111) step edges at 180° have a ratio of 1.6 ± 0.1 while the oxidized (100) step edges at 0° have a ratio of 1.2 ± 0.1. During oxidation, the oxide boundaries at (111) step edges clearly become more highly faceted than the boundaries at (100) step edges.

4. DISCUSSION

The early work of Armitage and Woodruff¹⁸ clearly demonstrated the structure sensitivity of the initial stages in the oxidation of Cu single crystal surfaces, specifically those with orientations that lie along the (110) to (111) to (100)edges of the stereographic triangle as shown in Figure 1A. Their work demonstrated that the initial rate of oxidation is lowest on the (111) plane and increases monotonically along the two directions toward maxima at the (110) and (311) surfaces. The previous STM studies of this system^{9,13,16,17} revealed the formation of Cu₂O(111) terrace oxide and step edge oxide layers. Furthermore, they revealed the special nature of the boundaries between the Cu₂O(111) oxide layer and closepacked step edges in the Cu(111) terraces. The work presented here has used a Cu(111) \pm 10°-S⁴C library to expose single crystal surfaces that span a continuous region of the stereographic projection around the (111) pole, and it has combined the use of XPS and STM to demonstrate and understand the fact that the initial oxidation of surfaces vicinal to Cu(111) depends on step density but not on step orientation.

4.1. Structure Sensitivity of the Initial Oxidation of $Cu(111) \pm 10^{\circ}-S^4C$. The XPS measurements summarized in Figure 5 provide the core evidence that the initial oxidation of the Cu surfaces vicinal to Cu(111) depends on step density but not on the initial step orientation. This data is entirely consistent with the results of Armitage and Woodruff¹⁸ obtained with Auger spectroscopy but adds measurements made along the $[1\overline{10}]$ and $[\overline{110}]$ directions. In these directions, the step edges are kinked, rather than close-packed; however, this has no significant impact of the initial rates of surface oxidation.

The STM images of Figures 7 and 8 reveal that the step edges on the surfaces vicinal to Cu(111) form faceted oxide boundaries during the very earliest stages of oxidation such that the boundaries between the Cu₂O(111) step oxide and the Cu(111) terrace run along the three directions that form (100) step edges. Laue X-ray diffraction has been used to determine the orientation of the Cu(111) \pm 10°-S⁴C and shows that the step oxide grows from the (100) steps in the (111) terrace. This is shown schematically in Figure 9 which represents the



Oxidized Cu

Figure 9. Illustration of the alternate modes of oxide growth at the (111) and (100) step edges on the Cu(111) \pm 10°-S⁴C surface. Formation of the Cu₂O step oxide (blue) occurs preferentially at boundaries along (100) step edges of the Cu(111) terraces. The blue spheres represent the domains of Cu₂O step oxide but are not intended to represent the positions of the Cu atoms as the structure of this oxide layer is not well-known. The darker brown spheres represent Cu atoms in the (111) terrace at the edges of the Cu(100) step that forms the boundary with the Cu₂O step oxide.

 $Cu_2O(111)$ as the blue spheres, the (100) step edges as the dark brown atoms, and the Cu(111) terrace with light brown atoms. The blue spheres do not represent known positions of Cu atom or the structure of the observed oxide; they merely indicate domains of Cu₂O with as yet undetermined structure. The fact that the oxidation rate does not depend on step orientation is simply the result of the fact that all steps facet to form (100) boundaries with the step oxide, and thus, the growth rate is limited in all directions to the intrinsic growth rate of this boundary. The mechanism is probably one in which O₂ first adsorbs dissociatively on the clean Cu(111) terraces. Oxygen atoms then diffuse across the terrace to the Cu₂O(111)/Cu(100) boundary where they become incorporated into the step oxide that is growing into the Cu(111) terrace. This is the same process that results in the formation of

the terrace oxide islands imaged on the Cu(111) plane in Figure 6b. Cu atoms ejected onto the terrace in the process of surface oxidation can diffuse across the terrace and become incorporated into the ascending edge of the Cu₂O(111) step edge oxide. This growth of the Cu₂O(111) step edge oxide in both directions away from the original step has been documented by Wiame et al.¹³

It is not clear what characteristic of the close-packed (100) boundary between the Cu(111) terraces and the Cu₂O(111) step edge causes it to limit oxide growth. One might imagine that the slow kinetics of oxidation of the (100) step edges is related to their stability relative to other step orientations. However, (100) and (111) step edges on the clean Cu(111) surfaces have been shown to differ in energy by <1%.²³ Of course, the critical characteristic in this case is the relative stabilities of the (100) and (111) step edges as boundaries with a Cu₂O(111) oxide layer. These may be quite different in thermodynamic stability. For some reason, the (100) boundary grows most slowly, and as a result, all other boundaries oxidize rapidly to leave the oxide boundary with facets along the (100) steps of the Cu(111) terrace.

Ideally, the length of the step oxide boundary with the Cu(111) terrace should be twice as long in the $[11\overline{2}]$ as in the $[\overline{112}]$ direction because of the faceting of the boundary to form (100) step edges. In principle, this would imply that the oxide growth rate in the $[11\overline{2}]$ direction ought to be twice a fast as in the $[\overline{112}]$ direction if it is limited by oxygen incorporation into the boundary of the step oxide with the (111) terrace. This difference is not observed in the XPS data of oxygen uptake shown in Figure 5. However, our measurements of the boundary length show that the ratio of the faceted boundary lengths in the $[11\overline{2}]$ as in the $[\overline{112}]$ directions is closer to 1.6:1.2. This represents a real difference in boundary lengths of about 30%, and it is unlikely that our XPS measurement of oxygen uptake could resolve structure sensitivity at that level.

4.2. High-Throughput Study on S⁴C's. The work presented illustrates the potential power of the combination of spatially resolved surface analysis with atomically resolved imaging using STM to study and understand structure sensitive surface chemistry on high-throughput structure libraries such as surface structure spread single crystals. The S⁴C's are ideal samples for use with STM to study the roles of steps in surface chemistry. The only work of which we are aware that has combined the use of STM and a curved single crystal surface has focused on issues of surface structures exposed by a cylindrical Au single crystal oriented along the $[1\overline{10}]$ direction.²⁴ The obvious virtue of the use of S⁴C's as libraries with STM is that one has a continuous range of surface orientations within reach of a single STM tip. The added value from the point of view of studying structure-sensitive surface chemistry is that all points on the surface have been treated identically thus limiting the experimental variations in surface preparation from sample to sample.

5. SUMMARY

The rates of the initial oxidation of Cu surfaces vicinal to Cu(111) have been shown to depend on the step density because oxidation occurs by incorporation of oxygen atoms into the surface at the boundaries formed between the Cu(111) terrace and a growing $Cu_2O(111)$ film. The $Cu_2O(111)$ layer grows from the initial step edges. The oxidation kinetics are independent of the initial orientation of the step edges because the boundaries between the step oxide and the Cu(111) terrace

are faceted; the boundaries all form between the $Cu_2O(111)$ layer and the (100) step edges in the Cu(111) terrace independent of the initial orientation of the step.

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Notes

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