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Surface Structure Spread Single Crystals (S⁴C): Preparation and characterization

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ABSTRACT

A set of six spherically curved Cu single crystals referred to as Surface Structure Spread Single Crystals (S⁴Cs) has been prepared in such a way that their exposed surfaces collectively span all possible crystallographic surface orientations that can be cleaved from the face centered cubic Cu lattice. The method for preparing these S⁴Cs and for finding the high symmetry pole point is described. Optical profilometry has been used to determine the true shapes of the S⁴Cs and show that over the majority of the surface, the shape is extremely close to that of a perfect sphere. The local orientations of the surfaces lie within $\pm 1^{\circ}$ of the orientation expected on the basis of the spherical shape; their orientation is as good as that of many commercially prepared single crystals. STM imaging has been used to characterize the atomic level structure of the Cu(111) $\pm 11^{\circ}$ -S⁴C. This has shown that the average step densities and the average step orientations match those expected based on the spherical shape. In other words, although there is some distribution of step-step spacing and step orientations, there is no evidence of large scale reconstruction or faceting. The Cu S⁴Cs have local structures based on the ideal termination of the face centered cubic Cu lattice in the direction of termination. The set of Cu S⁴Cs will serve as the basis for high throughput investigations of structure sensitive surface chemistry on Cu.

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1. Introduction

Many phenomena occurring on the surfaces of materials are sensitive to the atomic level structure of the surface. Such processes include catalysis, corrosion, etching, adsorption, etc. As a consequence, understanding the influence of surface structure on surface chemistry is one of the central problems of surface science. In fact, one of the great achievements of modern surface science has been the unequivocal demonstration of structure sensitivity in catalysis [1,2]. Much of the work on this problem has been accomplished through the careful and painstaking study of adsorption and surface reaction kinetics on small sets of single crystal surfaces. Most commonly these are the high symmetry, low Miller index planes of metal crystals. These studies have been complemented by studies on high Miller index surfaces that expose monoatomic steps and kinks which, in many cases, are sites of high reactivity [3–5]. The study of structure sensitive surface chemistry has been limited by the fact that surface structure spans two continuous degrees of freedom. Comprehensive study of structure sensitive surface chemistry across broad continuous regions of surface structure space requires a high throughput methodology

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that provides access to all possible single crystal surfaces, coupled with spatially resolved methods for surface analysis.

The orientations of single crystal surfaces are enumerated using their Miller indices, (*hkl*), and the complete set of surfaces that can be cleaved from a crystal lattice is represented using the stereographic triangle, as shown in Fig. 1 for a face centered cubic lattice. The points on the vertices of the triangle represent the high symmetry. low Miller index planes. The points on the perimeters represent lower symmetry surfaces that expose straight step edges. Those in the interior of the triangle are often referred to as kinked surfaces and lack mirror plane symmetry. Fig. 1 also illustrates the ideal structures of a number of these surfaces, giving some impression of the variety of different structures that can be exposed. A detailed account of these surface structures and their symmetry can be found in the work of Jenkins et al. [6]. The key point in Fig. 1 is that it makes apparent the fact that the space of all possible surface structures is continuous and two dimensional. It is important to point out, however, that the structures of metal single crystal surfaces are not always well represented by the types of ideal structures that derive solely from the cleavage of the bulk crystal lattice. They can be further complicated by phenomena such as atomic relaxation, reconstruction, and thermal roughening [2,6,7].

High throughput methods are ideally suited to study problems such as structure sensitivity in which the important independent variables span multiple, continuous degrees of freedom and are not

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Fig. 1. The stereographic projection of planes through a face centered cubic lattice. The vertices represent the high symmetry low Miller index planes. Points along the edges are surfaces with straight step edges separating low Miller index terraces. Points in the interior of the triangle are high Miller index planes with ideal structures based on kinked step edges separating low Miller index terraces. Model representations are shown of select surfaces with structures based on different combinations of (111), (110) and (100) terraces, steps and kinks.

easily explored using traditional experimental methods. A high throughput study of structure sensitivity requires the use of surface structure libraries; samples that expose continuous distributions of single crystal surface orientations. It also requires the use of spatially resolved surface analysis methods that can quantify surface composition or measure surface reaction kinetics at different surface orientations within the library. The most common approach to creating a surface structure library is to prepare a curved surface from a single crystal sample, such that each point on the surface represents a different local crystallographic orientation that can be determined from the shape of the curved crystal and the orientation of its bulk lattice vectors [8–13]. By analogy with Composition Spread Alloy Films (CSAFs) [14] which are commonly used as high throughput libraries that span composition space, we refer to surface structure libraries as Surface Structure Spread Single Crystals (S⁴Cs).

The two most common forms of S⁴Cs used in past studies of structure sensitive surface phenomena are cylinders and lenses (spherical sections). The first use, of which we are aware, of a single crystal cylinder is by Linder in 1927 to study the influence of surface structure on the photoelectric effect [15]. In the 1940's, Gwathmey used spherical single crystal samples to study a variety of surface chemical processes [9–13]. In the 1980's, Woodruff used Auger electron spectroscopy to study the surface structure sensitive oxidation of Cu and Ni by using cylindrical single crystals oriented with the 110 direction along their axes [8,16–20]. More recently, Ranke used single crystal cylinders of semiconductors such as GaAs, Si, and Ge to look at the structure sensitivity of H₂O, NO, NH₃, and O₂ adsorption [21–25]. The surface of a cylindrical S⁴C traces a one dimensional path through the stereographic projection. For example, a cylinder of an fcc crystal oriented with the [$\bar{1}$ 10] direction along its axis traces a path from the (110) to the (111) to the (100) points on the stereographic triangle (Fig. 1). This path includes the three low Miller index planes and all possible surfaces with structures based on low Miller index terraces separated by close-packed step edges. It does not, however, include any of the surfaces represented by the line connecting the (100) and (110) points directly, and are formed of (100) or (110) terraces separated by straight but non-close-packed step edges. The lens shaped or spherical S⁴Cs have local structures that span continuous regions of the stereographic triangle. There is a long history of the use of S⁴Cs to elucidate the surface structure sensitive properties of crystalline materials [10,15]. Unfortunately, most efforts have been hampered by the limited availability and capability of spatially resolved surface analysis tools for characterization of their shapes, surface structures and surface chemistry. However, the past decade has seen a proliferation of such tools, and the rapid data collection and data analysis systems needed to take full advantage of the use of S⁴Cs for high throughput study of structure sensitive surface chemistry and the structure sensitive physical properties of surfaces.

The work described herein, has prepared a set of six Cu S⁴Cs that collectively span the entire stereographic projection and thus, expose all possible single crystal surfaces of Cu. The method of preparation is quite simple and readily repeated. We describe a method based on the combined use of Laue X-ray diffraction and optical reflection for locating particular planes such as the high symmetry, low Miller index surfaces on these S⁴Cs. We have used optical profilometry to provide careful measurements of the shapes of these S⁴Cs and to demonstrate that they are indeed very close to perfectly spherical; sufficiently close that their local surface normals are within $\pm 1^{\circ}$ of those of a perfect sphere. Most importantly, scanning tunneling microscopy (STM) has been used to study the atomic level structure

of the surfaces vicinal to the (111) pole. This has shown that the surface structures have the monoatomic step densities and step orientations that one would expect based on the ideal termination of the Cu crystal lattice. The step spacing is not uniform and the step orientations vary about the expected direction. However, there is no evidence of large scale surface reconstruction, step bunching, or faceting. This represents the first systematic, macroscopic and atomic resolution analysis of the real structure of a spherical S⁴C to be used for high throughput study of structure sensitive surface chemistry.

2. Experimental

The Cu single crystals used for the preparation of S⁴Cs were purchased from Monocrystals Inc. and had nominal orientations of Cu(111), Cu(100), Cu(110), Cu(432), Cu(821) and Cu(861). Each was a disk of ~10 mm diameter and ~2 mm thickness. In order to prepare a set of S⁴Cs that spanned the entire stereographic projection, the orientations were chosen such that the three high Miller index orientations were spaced as far from the low Miller index orientations and from one another as possible. Their positions in the stereographic projection are shown in Fig. 2. The angles subtended by the S⁴Cs were roughly $\pm 10^{\circ}$ or $\pm 15^{\circ}$ from the nominal orientation, chosen to span the entire stereographic projection as shown by the circles in Fig. 2. The S⁴Cs are denoted Cu(*hkl*) $\pm \phi^{\circ}$ -S⁴C where (*hkl*) is the nominal orientation at the center of the sample (orientation of the original single crystal) and φ° is the subtended angle from the center to edge. The data presented in the main text of this paper was obtained from an S⁴C prepared from a Cu(111) single crystal with an angular spread of $\pm 11^{\circ}$; it is referred to as Cu(111) $\pm 11^{\circ}$ -S⁴C. The data for the other five S⁴Cs prepared in the course of this work is presented in the Supplementary data section. The samples were prepared and examined using Laue backscattering and optical profilometry at Carnegie Mellon University. Atomic scale structural characterization was performed using STM at Tufts University.



Fig. 2. Stereographic projection showing the regions spanned by the six S⁴Cs prepared in the course of this work. The set of six spans the entire stereographic projection with significant overlap. The three S⁴Cs centered in the interior of the stereographic triangle all have S-chirality. The three low Miller index S⁴Cs span regions of alternating R- and S-chirality.

2.1. Optical profilometry

The height profiles of the S⁴Cs were measured using a ZYGO NewView 7000 Optical Surface Profiler based on non-contact white-light technology. A 3D map of the surface height, h, versus lateral position, (x, y), was obtained by comparing the optical path differences due to height variances between the sample surface and a reference surface. A map of the entire S⁴C surface was obtained by stitching together individual scans of 1 mm², obtained at a lateral resolution of 4.4 μ m. The raw data files containing over 10⁶ data points were filtered for noise, and approximately 4% of the data points were used in constructing the height profiles h(x, y). These were then fitted numerically to a spherical function to determine the true spherical radius of curvature and the deviation from sphericity as a function of radial position, r, from the center. At each point on a $22 \times 22 \ \mu m^2$ square grid the orientation of the surface normal was computed by fitting a plane to all points within a 50 µm radius in the full data set and then finding the normal to that plane. This was then used to calculate the angle between the surface normal and the normal to a sphere.

2.2. Scanning tunneling microscopy

The surface of the Cu(111) \pm 11°-S⁴C was imaged with atomic resolution using an Omicron Nanotechnology variable-temperature ultrahigh vacuum (VT-UHV) STM. The base pressure in the STM chamber was approximately 1×10^{-10} mbar. The S⁴C surface was cleaned in a sample preparation chamber by cycles of Ar⁺ ion bombardment using a current of 60 µA at 1500 eV and a final anneal at 1000 K for 10 min. After cleaning, the sample was transferred in vacuum into the STM chamber. STM images were acquired with either Omicron or Veeco etched W tips.

In order to reproducibly approach predetermined points on the $Cu(111) \pm 11^{\circ}$ -S⁴C 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 11°-S⁴C. This grid accounted for the 3D shape of the Cu(111) \pm 11°-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 in mm from the (111) pole and the angle in degrees from the $[\bar{1}\bar{1}2]$ 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 further misalignment caused by its subsequent preparation, both of which lead to positioning of the (111) pole slightly off the center of the $Cu(111) \pm 11^{\circ}-S^{4}C.$

3. S⁴C shaping and orientation

The procedure for shaping the S⁴C started with an ~10 mm diameter by ~2 mm thick Cu single crystal disk and resulted in the shape shown in Fig. 3 with one side remaining flat and the other side being ground and polished into a nearly perfect spherical section. Once the nominal desired angular spread of the S⁴C had been decided, the necessary spherical radius of curvature was determined; 28.8 mm to achieve $\pm 10^{\circ}$ and 19.3 mm to achieve $\pm 15^{\circ}$. Polished stainless steel spheres (ball bearings) of the appropriate radii were then used to create concave spherical molds from epoxy. A 3 cm diameter by 3 cm long glass or polycarbonate tube was placed on a



Fig. 3. Photograph of a Cu(111) \pm 11°-S⁴C. The original Cu(111) single crystal was ~2 mm thick and ~10 mm in diameter.

flat glass and filled with epoxy (Devcon 10210 Plastic Steel Liquid and Devcon 0202 Epoxy Hardener). The ball bearing was then placed on the top of the cylinder and the epoxy was allowed to harden to create the concave spherical mold of the desired curvature. The concave surface of the mold was then lined with 200 grit abrasive Emery cloth that was glued into place. The mold was then mounted onto the center of a rotating plate of a polisher that can spin at 150-300 rpm. The single crystal disk was bonded to the end of a cylindrical steel rod of the same diameter as the crystal (10 mm). A soap solution was sprayed onto the surface of the Emery cloth and the crystal was then ground in the spinning concave mold to a spherical shape after ~10 min. The grinding procedure was then repeated with 400, 600, and 1200 grit Emery cloth for ~1 h at each stage. Polishing of the Cu crystal in the spherical concave mold was continued using diamond and alumina polishing compounds (6, 2, and 0.3 µm) on appropriate polishing cloths glued into the concave mold. Each polishing step required ~10 min. The result was a Cu-S⁴C with a highly polished and curved surface (Fig. 3).

Having prepared the S⁴C, it is necessary to determine its orientation and to find the location of one point on the surface, such as a low Miller index plane, that can be used as a reference for determination of the orientations of all others. Single crystal surfaces are not perfectly aligned along the nominal crystallographic orientation direction and most are provided with stated orientational uncertainties in the range $\pm 0.1-1^{\circ}$. Furthermore, the preparation procedure described above also contributes to some degree of misorientation and so, some method must be used to identify the crystallographic orientation of a reference point on the surface.

In the case of S⁴Cs that are vicinal to low Miller index planes, the best method for finding the reference point is to use STM to find the large, flat terraces of the low Miller index surface. The orientations of the atomic rows in the low Miller index plane provide the necessary orientational information, although this can also be determined from Low Energy Electron Diffraction or any X-ray diffraction technique. STM and X-ray diffraction have been used to find the (111) pole and the orientation of the Cu(111) \pm 11°-S⁴C characterized in Section 4 below. Of course, the use of STM is a somewhat cumbersome method for finding a reference point and is not well suited to determining the orientation of Laue X-ray backscattering and optical laser reflection can be used to find the reference point on the S⁴C surface.

Orientation of a S⁴C using Laue backscattering and laser reflection requires that the S⁴C be mounted on a goniometer that allows rotation about two orthogonal axes, (x, y), that are orthogonal to the

sample normal, z, and also allows translation of the sample in (x, y)as shown in Fig. 4. The goniometer must be mounted on the optical rail of the Laue backscattering apparatus. In addition, the laser must be mountable on the optical rail such that the beam is parallel to the X-rays. Initially, the S⁴C sample mounted on the optical rail will diffract X-rays in directions determined by the orientation of the bulk crystal lattice vectors and will reflect the laser beam in another direction determined by the orientation of the surface (Fig. 4, left). The rotational motion of the goniometer can be used to orient the bulk lattice vectors, as determined by Laue backscattering, such that the desired bulk crystal plane is perpendicular to z (Fig. 4, middle). Finally, the sample can be translated in (x, y), while preserving the rotational orientation, until the laser beam is reflected along z. Given that the S⁴C is spherical, the point of reflection must be the reference plane with the crystallographic orientation determined from the Laue back diffraction.

4. S⁴C characterization

This work has used optical profilometry to determine the macroscopic shapes of the six S⁴Cs and, in particular to determine their true radii of curvature and deviations from sphericity. This has been combined with the use of STM to examine the atomic scale structure in regions vicinal to the (111) plane on the Cu(111) \pm 11°-S⁴C. Note that, the optical profilometry and STM imaging were done on two different Cu(111) \pm 11°-S⁴C samples prepared using identical procedures.

4.1. $Cu(111) \pm 11^{\circ}$ -S⁴C shape from optical profilometry

Optical profilometry was used to create maps of the shapes of the S⁴Cs. These are measurements of h(x,y) obtained with 4.4 µm resolution in x and y and the standard deviation in the height measurements is $\sigma_h = 0.5$ µm. These height maps are then converted into a polar coordinate system $h(r,\theta)$ to be compared with a numerical fit to a sphere.

The data for the shape of the Cu(111) \pm 11°-S⁴C is shown in Fig. 5. The left hand panel of Fig. 5 shows the height measurements in black, collapsed from the polar coordinate system to generate h(r) for all values of θ . The height from center to edge spans about 600 µm, which is expected given the nominal radius of spherical curvature and the 5.2 mm radius of the original crystal disk. Note that the data in black includes > 100,000 points. It is obvious that the quality of the S⁴C deteriorates towards the outer 0.5 mm annulus of the sample as it becomes over-curved at the edges during polishing. This is readily visible at the very edges of the sample in the photograph in Fig. 3. One idea for minimizing this over curving of the sample is to encircle the initial Cu single crystal disk before shaping and polishing with a ring of Cu that is 0.5–1 mm thick. The over curvature would then be borne by this disposable Cu ring, leaving the S⁴C shape almost perfectly spherical from center to edge.

Superimposed on the h(r) measurements shown in the left panel in Fig. 5 is the fit in red of the data to a perfect sphere. The fit to the sphere indicates that while the nominal spherical radius of curvature for this Cu(111) ± 11°-S⁴C was 28.6 mm (dictated by the radius of curvature of the mold) the true spherical radius of curvature determined by the fit to the data was 23.1 mm within a radius of 2.5 mm from the center. The fit of the true heights to the sphere is extremely good out to a radius of 4.5 mm, at which point the deviation between the normal to the sphere and the normal to the true surface starts to exceed 1°.

More important than the height profiles of the S^4C are the surface orientations and their deviations from those of a perfect sphere. The local orientations of the surface have been calculated from the tangent planes determined using the height measurements in a region of 50 μ m radius about points distributed on a 22 μ m grid. The right



Fig. 4. Identification of the high symmetry point on the $Cu(111)\pm 11^{\circ}-S^4C$ is accomplished by placing the S^4C in the path of co-aligned X-rays for Laue back diffraction and laser photons for simple reflection from the surface. In the first step the S^4C is rotated about axes orthogonal to the incident X-rays until the bulk lattice vectors are aligned with the X-rays and the high symmetry back diffraction beam is reflected back into the incident beam. In the second step the S^4C is translated perpendicular to the laser until the reflected beam reflects back into the laser. Because the surface is spherical, the point of reflection from the surface must be the high symmetry point.

hand panel in Fig. 5 shows the deviations of the true normals from those of the perfect sphere of radius 23.1 mm, plotted from the center of the S⁴C to a radius of 4.5 mm. Over all but the very outermost edge of this region the local orientations of the surfaces lie within $\pm 1^{\circ}$ of the perfect sphere. While the nominal angular spread of this S⁴C was $\pm 10^{\circ}$ it is in reality $\pm 11^{\circ}$ within a circle of radius 4.5 mm from the center.

Profilometry data for all six of the Cu(*hkl*) S⁴Cs have been obtained and analyzed using the same procedure as for the Cu(111) \pm 11°-S⁴C (Supplementary data S1–S5). In all cases, the true spherical radius of curvature was somewhat larger than the nominal spherical radius of curvature, however, the majority of the sample area (to 90% of the full radius) is a curved surface with surface normal that lie within 1° of perfectly spherical. For all future work, we plan to make use of only this inner 80% of the S⁴C sample area.

4.2. $Cu(111) \pm 11^{\circ}$ -S⁴C surface structure from STM

Optical profilometry shows that the $Cu(111) \pm 11^{\circ}-S^4C$ is shaped to within 1° of perfectly spherical across the majority of the surface, within 4.5 mm of the center. In principle, this means that all possible Cu single crystal planes within $\pm 11^{\circ}$ of the (111) pole are exposed within this region of the $Cu(111) \pm 11^{\circ}$ -S⁴C surface. Of course, the resolution of the local orientation determination is only 22 µm and insensitive to surface orientation fluctuations that can occur on the nanometer length scale. Using STM we have examined the local structure of the surfaces vicinal to the (111) plane with atomic resolution to look for phenomena such as step bunching, reconstruction, faceting, etc. that might cause the atomic level surface structure to differ from ideality. Fig. 6 shows representative STM images over scales of ~100 \times 100 nm² taken from five regions of the Cu(111) \pm 11°-S⁴C surface. STM image 6a is taken from the region near the center of the Cu(111) \pm 11°-S⁴C which has been identified as the (111) pole, based on the fact that it exposes very large flat terraces as wide as 1 um with no steps. The atomic resolution 1×1 nm² image 6b shows the hexagonal close packed array of atoms in the (111) terraces. Image 6c has been taken from a point that is 1 mm from the (111) pole along the $[\overline{1}\overline{1}2]$ direction. It shows the expected presence of monoatomic step edges running roughly parallel to one another and roughly perpendicular to the $[\bar{1}\bar{1}2]$ direction. Not surprisingly,



Fig. 5. The shape of the $Cu(111) \pm 11^\circ$ -S⁴C as determined by profilometry. Left) the height versus radius from the center of the S⁴C. The black data points are taken at positions along full 360° azimuthal circles at each radius and compressed onto the radial plot. The red curve is the shape of a perfect sphere fit to those height measurements within 2.5 mm radius of the center. Beyond a radius of 4.5 mm the spherical fit (dashed blue line) deviated from the real surface shape. Right) the angular deviation between the local normal to the $Cu(111) \pm 11^\circ$ -S⁴C and the local normal to a perfect sphere plotted to a radius of 4.5 mm from the center of the $Cu(111) \pm 11^\circ$ -S⁴C. The angular deviation is within $\pm 1^\circ$ for ~99% of the surface. Similar data for the other five S⁴Cs are shown in the Supplementary data section.



Fig. 6. STM images of the $Cu(111) \pm 11^{\circ}$ -S⁴C. a) Image of the (111) pole of the S⁴C revealing an atomically flat surface. b) $1 \times 1 \text{ mm}^2$ image of the (111) pole revealing the hexagonal close packed array of Cu atoms. c) and d) STM images taken at two points along the $[\bar{1}\bar{1}2]$ direction at 1 mm and 2 mm from the (111) pole. These reveal the increasing density of monoatomic steps on the surface as the distance from the (111) pole increases. e) and f) STM images at points that are 1 mm from the (111) pole but angles that are $\pm 30^{\circ}$ from the $[\bar{1}\bar{1}2]$ direction. These reveal monoatomic steps that are rotated in positive and negative directions with respect to the $[\bar{1}\bar{1}2]$ direction, as expected.

the spacing between the steps is not perfectly uniform nor are they atomically straight. This is the result of the preparation procedure and the thermal roughening of step edges. In image 6d, taken at a radius of 2 mm from the (111) pole and along the $[\bar{1}\bar{1}2]$ direction, one can readily observe the expected increase in step density with the

increased angular deviation from the [111] direction. Finally, images 6e and 6f have been taken at radii of 1 mm from the (111) pole but at angles that are $\pm 30^{\circ}$ from the $[\bar{1}\bar{1}2]$ direction. They display the expected steps, but these are now running at angles that are roughly $\pm 30^{\circ}$ from perpendicular to the $[\bar{1}\bar{1}2]$ direction. Note that the low



Fig. 7. Step densities and orientations on the Cu(111) \pm 11°-5⁴C. Left) Step densities measured at radii in the range \pm 1.5 mm from the (111) pole. These show the expected increase in step density with distance from the pole. Middle) Step densities measured at azimuthal angles in the range 0–360° and at a constant radius of 1 mm from the (111) pole. The step densities are roughly constant about the (111) pole, as expected. Right) Deviations in step orientation from that expected measured at azimuthal angles in the range 0–360° and at a constant radius of 1 mm from the (111) pole. Large deviations in orientation observed at angles near 0° and 180° may arise from thermal drift during scanning in the slow direction along 0° and 180°.

symmetry orientations of these steps means that they are chiral with R- and S-handedness as indicated [26,27]. The images shown in Fig. 6 indicate that the surfaces vicinal to the (111) pole on the Cu(111) \pm 11°-S⁴C exhibit the expected structural phenomenology. Although there is clear evidence of thermal roughening and random step spacing there is no evidence of systematic deviations from ideality that might arise from surface reconstruction, step bunching or faceting.

While the images in Fig. 6 illustrated expected behavior, statistics from numerous images have been obtained to quantify the local variations in surface structure from ideality. The left hand panel in Fig. 7 shows the step densities at $r=0, \pm 0.5, \pm 1$, and ± 1.5 mm from the (111) pole along the $[\overline{1}\overline{1}2]$ direction. Each point was measured from 4 sets of 4–5 images each of a 300×300 nm² area with sets spaced by ~20 μ m. The step densities on the Cu(111) \pm 11°-S⁴C increase as a function of distance from the (111) pole in the way expected. It should be pointed out that, in all cases, we have observed monoatomic steps predominantly, other than at a few points at which we observe step pinning that seems to be associated with the presence of residual surface contaminants. Fig. 7 (middle panel) shows the step density measured at r = 1 mm and 12 angles spaced by 30° around the (111) pole. The important point is that the step density is constant and independent of angular orientation at constant radius from the (111) pole. Again the step densities are in the range expected. Fig. 7 (right hand panel) illustrates the deviation of the average step normal, from the ideal direction as one goes around the (111) pole. The angular deviation of the step orientations is within $\pm 5^{\circ}$ of the expected direction for azimuthal angles within $\pm 30^{\circ}$ of 90° and 270°. In this regard, a positive angle is a clockwise rotation when viewed from above along the surface normal. However, we observed a larger than expected deviation from the step orientations at angles $\pm 30^{\circ}$ from 0° and 180° . Moreover, these deviations are all negative in sign rather than being randomly distributed about the expected angle. This cannot be rationalized in terms of the ideal surface structure. We suggest that, in part, this is due to the fact that the fast-scan direction of our STM is perpendicular to 0° and 180°. The direction of the fast-scan is relevant because images of the step edges perpendicular to the fast-scan direction are more susceptible to thermal drift during the scanning period of ~2 min.

4.3. Surface structures of Cu(hkl)-S⁴Cs

The primary result of our STM imaging is the demonstration that the local structures of the Cu surfaces vicinal the (111) pole are similar to those expected on the basis of the ideal structure but subject to some distribution of terrace widths and step directions around those values predicted from the ideal surface termination. The question is, what is known about the structures of clean Cu(hkl) surfaces exposed by other points on the set of Cu(hkl)-S⁴Cs? Of course, there are numerous STM images of the clean Cu(100) and Cu(110) single crystal surfaces showing that these are not reconstructed. By comparison, there are far fewer images of the high Miller index surfaces. In prior work, we have studied extensively the Cu(643) surface and demonstrated that its structure is guite similar to that expected for a Cu(643) single crystal surface that has been subject to thermal roughening [28]. The steps are all monoatomic but the distribution of kinks along the step edges show evidence of thermal roughening. This roughening is the result of atomic diffusion along step edges and results in the coalescence of kinks (kink bunching), thus reducing their numbers to below the density expected on the basis of the ideal Cu(643) termination [7,29]. Similarly, there have been STM and LEED studies of the Cu(531) surface which show that the real structure is quite similar to that expected but subject to thermal roughening rather than gross reconstruction [30]. Thus, all evidence to date indicates that the clean surfaces exposed by Cu S⁴Cs are not subject to reconstruction. Furthermore, within the constraints of thermal roughening of real atomic surface structure, the Cu S⁴Cs serve as good libraries of single crystal surface structure for high throughput studies of structure sensitive surface chemistry.

5. Conclusions

A fairly simple method for preparation of curved Cu single crystals has been developed and used to prepare a set of six Cu(*hkl*)-S⁴Cs that collectively span the entire stereographic projection of Cu surfaces. The shapes of these Cu(*hkl*)-S⁴Cs are very close to spherical, such that their local surface orientations lie within 1° of that expected. More importantly, the atomic scale surface structures of these Cu(*hkl*)-S⁴Cs have been shown to be representative of the ideal structure in terms of exposed step density and step orientation, but subject to local fluctuations resulting from surface preparation and thermal roughening. The set of Cu(*hkl*)-S⁴Cs serves as a surface structure library for comprehensive study of structure sensitive surface chemistry.

Disclaimer

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.susc.2012.09.015.

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