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The Epitaxial Relationships of Cuprous Oxide Formed on Copper Single Crystals Immersed in an Aqueous Solution of Copper Sulfate

By Kenneth R. Lawless and G. Tyler Miller, Jr.*

Cobb Chemical Laboratory, University of Virginia, Charlottesville, Virginia, U.S.A.

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The epitaxial relationships of cuprous oxide formed on copper single crystals which had been immersed in an aqueous solution of copper sulfate were determined by means of electron diffraction and electron microscope techniques. The copper surfaces were carefully prepared by electropolishing and were found to be free of facets or irregularities down to the limit of resolution of the electron microscope and replica techniques (~ 20 Å). On the five faces studied, the (001), (011), (111), (012) and (113), four different orientation relationships were found. In all cases at least one closest packed direction of the oxide was parallel to a closest packed direction of the metal. The shapes of the oxide growths and the particular faces present were determined. Only the three most densely packed faces occurred on the oxide.

Introduction

In order to understand more thoroughly the mechanism of the growth of oxide films on metals it is necessary to know the details of the initial growth of the oxide and its relationship to the structure of the metal surface. It is now well known that under certain conditions there is a definite orientation relationship between a metal and the oxide formed on it. The particular orientations observed depend on the preparation of the surface, the structure of the metal face exposed, and on the conditions of the reaction.

If a metal surface consists of several different types of facets, more than one orientation of an oxide will often occur, corresponding to growth on various crystal planes. If experiments on epitaxy are to have any meaning it is obviously important to know not only the relative orientation of the metal and the oxide, but also the specific plane of the substrate on which a particular orientation of oxide occurs. Many epitaxial relationships reported in the literature are subject to doubt because the submicroscopic structure of the substrate surface was not known. It is necessary, therefore, that particular attention be paid to the preparation and characterization of the metal surface. Copper single crystals have been used in these studies since the techniques for the preparation of satisfactory reproducible surfaces have been previously developed (Young *et al.*, 1956; Lawless *et al.*, 1956; Miller *et al.*) and under the conditions used in this study only one oxide forms.

This paper will report the results of a study of the epitaxial relationships of cuprous oxide formed on copper single crystals which were immersed in an aqueous solution of $CuSO_4$. It is part of a more complete study of the formation of oxide on copper single crystals under varying conditions, including, oxidation in oxygen gas (Lawless *et al.*, 1956), oxidation in pure water, and oxidation in solution. Further results on the epitaxial relationships of the oxide formed under other conditions will be reported in a later paper. The mechanism of the formation of oxide on copper crystals immersed in aqueous $CuSO_4$ solution has been discussed elsewhere (Miller *et al.*).

Several workers (Thomson, 1931; Meyer, 1908; Dony-Henault, 1910) have reported that Cu_2O was formed on copper when it was immersed in an aqueous solution of $CuSO_4$. Thomson (1931) during an experiment on the electrodeposition of copper from aqueous $CuSO_4$ solution onto etched (100) and (111) surfaces of copper observed electron diffraction spots which were apparently due to Cu_2O. A parallel orientation of the oxide was observed on both the (100) and (111) surfaces. An additional orientation in which the oxide (111) face was parallel to the (100) face of copper was also observed. A complete study of this oxide formation was not carried out.

Experimental procedure

The experimental procedure can be divided into three parts: first, the preparation of suitable surfaces on copper single crystals; second, the oxidation of the specimens; and third, the examination of the surfaces.

Single crystal spheres of $\frac{5}{8}''$ and $\frac{3}{4}''$ diameter were prepared from 99·999% copper. Flat faces parallel to specific crystallographic planes were machined on some of these spheres. The flat faces varied in size from $\frac{3}{8}''$ to $\frac{1}{2}''$ diameter. The surfaces of these crystals were carefully polished mechanically and electrolytically, then washed and dried, and finally annealed in hydrogen at 500 °C. The techniques of specimen preparation prior to oxidation have been previously described (Young *et al.*, 1956; Lawless *et al.*, 1956;

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* Present address: Hampden-Sydney College, Hampden-Sydney, Virginia.

Miller *et al.*). Five faces were studied, the (001), (011), (111), (012) and (113).

The copper crystals were oxidized by immersing them in an aqueous solution of 50 g./l. of $CuSO_4 . 5 H_2O$ at a pH of 3·8 and a temperature of 25 °C. After a definite period of immersion the crystals were removed from the solution, washed with distilled water and dried in a jet of nitrogen.

The surfaces of the specimens were examined initially by means of reflection electron diffraction at 60, 80 or 100 kv. The specimens could be examined at all azimuths and at varying angles of inclination to the electron beam. In some cases the oxide film was stripped from the metal surface using a modification of the technique described by Harris, Ball & Gwathmey (1957). It was then examined by transmission electron diffraction and electron microscopy.

After reflection diffraction studies were completed, the surfaces were examined with the optical microscope. Carbon replicas of the surfaces were then prepared (Miller *et al.*; Bradley, 1954) and examined with the RCA EMU-3B electron microscope at 50 or 100 kv. Both prepared flat faces and faces on the spherical surface were examined by electron diffraction, but the replicas for electron microscopy were made from the flat surfaces only. The spherical surfaces exposed all possible planes and it was possible to utilize this feature for an initial survey of all the crystal faces and to decide which faces to study in more detail.

The condition of the metal surfaces after electropolishing and annealing was investigated for representative crystals by means of X-ray and electron diffraction of the specimens and by electron microscopy of replicas of the surfaces.

Results

When an electropolished crystal sphere of copper was immersed in an aqueous $CuSO_4$ solution, a striking oxidation pattern formed on the surface within a few seconds showing the symmetry of the crystal. Fig. 1 shows such a pattern after an immersion time of 5 minutes. These patterns were useful for locating particular faces on the spherical crystal. They were also helpful in orienting the crystal in the diffraction apparatus. The formation of these patterns is discussed elsewhere (Young *et al.*, 1956).

Electron micrographs and electron diffraction patterns from representative flat (001), (011), (111), (012), and (113) faces are shown in Figs. 2–6. The electron micrographs were made from replicas of surfaces immersed in aqueous $CuSO_4$ for periods of 24–60 hours. Micrographs of earlier stages of the oxidation have been published in another paper (Miller *et al.*). These micrographs show both the well defined shapes of the oxide polyhedra and the various orientations of oxide present on the different faces of the copper crystal. Table 1 shows the particular crystallographic faces present on the oxide polyhedra after different times of oxidation. Only the three most densely packed planes of the oxide developed to an appreciable extent.

Electron diffraction of the crystals after immersion times varying from 15 sec. to 90 hr. showed well defined single crystal patterns which corresponded to cubic Cu_2O. The diffraction patterns shown in Figs. 2(*b*)–6(*b*), and 7(*a*), were obtained from specimens oxidized 1–5 min. Many of the diffraction patterns, particularly those patterns from the large oxide polyhedra present after 24–60 hr. of oxidation, showed complex refraction effects. The topography of the

Table 1. *Crystallographic faces on the oxide polyhedra*

Parallel planes		Crystallographic faces on oxide			
Cu	Cu_2O	30 sec. immersion	5 min. immersion	24 hr. immersion	60 hr. immersion
(001)	(111) or 2°–4° from (111)	$(111), (\bar{1}11)$ $(1\bar{1}1), (11\bar{1})$	Same as 30 sec. plus (001), (010) (100)	Same as 5 min.	Same as 5 min.
(011)	(011)	$(111), (\bar{1}11)$ $(\bar{1}\bar{1}1), (\bar{1}1\bar{1})$ $(1\bar{1}1), (11\bar{1})$	Same as 30 sec. plus (001), (010)	Same as 5 min. plus (011)	Same as 24 hr. but increased development of (011)
(111)	(111)	$(111), (\bar{1}11)$ $(1\bar{1}1), (11\bar{1})$	Same as 30 sec. plus (001), (010) (100)	Same as 5 min.	Same as 5 min.
(012)	(012)	$(111), (\bar{1}11)$ $(1\bar{1}1), (\bar{1}\bar{1}1)$	Same as 30 sec. plus (001), (010) (100), (100)	Same as 5 minutes plus few small (011)	Same as 24 hr.
(113)	(110)	$(111), (11\bar{1})$ $(\bar{1}11), (\bar{1}1\bar{1})$ $(1\bar{1}\bar{1}), (1\bar{1}1)$	Same as 30 sec. plus (010), (100)	Same as 5 min. plus (110)	Same as 24 hr. but larger (110)'s

Table 2. *Epitaxial relationships*

Parallel planes		Parallel axes		% Misfit*	Class designation	Remarks
Cu	Cu_2O	Cu	Cu_2O			
(001)	(111)	$[1\bar{1}0]$	$[1\bar{1}0]$ *a*	2	I	*a* and *b* have a twin relationship
		$[1\bar{1}0]$	$[\bar{1}10]$ *b*			
		[110]	$[1\bar{1}0]$ *c*			*c* and *d* have a twin relationship
		[110]	$[\bar{1}10]$ *d*			
(001)	2°–4° from (111), clockwise rotation about *a*	$[1\bar{1}0]$	$[1\bar{1}0]$ *a′*		I*a*	The amount of rotation varied from 2°–4° in separate experiments, but was constant for a given experiment
	2°–4° from (111), counter clockwise rotation about *b*	$[1\bar{1}0]$	$[\bar{1}10]$ *b′*			
	2°–4° from (111), clockwise rotation about *c*	[110]	$[1\bar{1}0]$ *c′*			
	2°–4° from (111), counter clockwise rotation about *d*	[110]	$[\bar{1}10]$ *d′*			
(011)	(011)	$[1\bar{1}0]$	$[1\bar{1}0]$ *e*	18	II	
(111)	(111)	$[1\bar{1}0]$	$[1\bar{1}0]$ *f*	18	II	Parallel
		$[1\bar{1}0]$	$[\bar{1}10]$ *g*		III	Anti-parallel†
(012)	(012)	$[12\bar{1}]$	$[12\bar{1}]$ *h*	18	II	Parallel (111(Cu_2O || (111) Cu $[1\bar{1}0]$ Cu_2O || $[1\bar{1}0]$ Cu
		$[1\bar{2}1]$	$[12\bar{1}]$ *i*		III	Anti-parallel $(1\bar{1}1)$ Cu_2O || (111) Cu $[0\bar{1}1]$ Cu_2O || [110] Cu
		$[12\bar{1}]$	$[1\bar{2}1]$ *j*		III	Anti-parallel (111) Cu_2O || $(\bar{1}11)$ Cu $[0\bar{1}1]$ Cu_2O || $[\bar{1}10]$ Cu
(113)	(110)	$[1\bar{1}0]$	$[1\bar{1}0]$ *k*	0·5	IV	

* The misfit indicated in this column is that between closest packed rows of atoms in the interface plane. In all cases a direction of the type [110] of the oxide is parallel to a direction of the same type in the metal with an 18 % misfit in this direction.

† The anti-parallel orientation in each case bears a twin relationship to the parallel orientation; *f* and *g*, *i* and *h*, *j* and *h* all have a twin relationship.

oxide polyhedra could be determined at least partially from these refraction effects. These effects will be discussed in another paper. So-called forbidden reflections were common in the diffraction patterns. In general, these could all be explained on the basis of secondary reflections, the primary diffracted beams acting as sources for secondary reflections.

Even with the thinnest films studied (15 sec. immersion), it was not possible to obtain electron diffraction patterns from the metal substrate. The specific orientation relationship of the oxide and the metal substrate was readily obtained, however, since the orientation of the metal could be determined from the oxidation pattern on the spherical part of the specimen. The analysis of the diffraction patterns was carried out by means of reciprocal lattice projections. The epitaxial relationships which were determined are summarized in Table 2, the first two columns showing the plane of oxide which was parallel to the prepared copper plane, and the third and fourth columns giving the directional relationships necessary to define completely the orientation. In all cases at least one [110] direction of the oxide was parallel to a [110] direction of the metal.

On the (001) face of copper two distinct types of orientation were observed and are designated as Class I and Class I*a* in Table 2. In Class I two pairs of twin related oxide orientations occurred, giving four completely equivalent orientations. In each of these Class I orientations the (111) plane of the oxide was accurately parallel to the (001) plane of copper. Fig. 2 shows an electron micrograph and an electron diffraction pattern of an oxide having this orientation.

The Class I*a* orientation was similar to Class I except that the (111) planes of each of the four equivalent orientations were not parallel to the (001) face of copper but were tilted at an angle of 2–4° to the (001). Each of the four orientations of Class I*a* can be derived from one of Class I by the proper rotation about the parallel axis indicated in Table 2. Fig. 7*a* shows a typical diffraction pattern from a Class I*a* orientation and the analysis is indicated in Fig. 7(*b*). The orientation in each case was well defined, giving sharp spots in the diffraction pattern. The angular spread of 2–4° was observed in separate experiments, but the angle of tilt was very specific for a given oxidation. The twin relationships of Class I no longer held true for the Class I*a* orientations.

Orientations of Classes I and I*a* did not occur together on a (001) face, but either one type or the other was present after a given experiment. A given crystal of copper would give orientation I in one

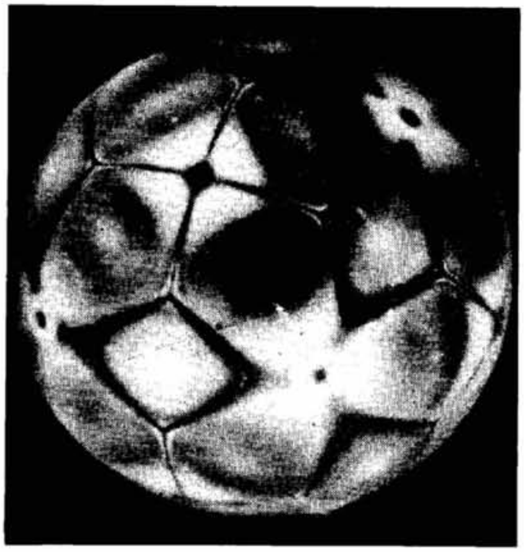
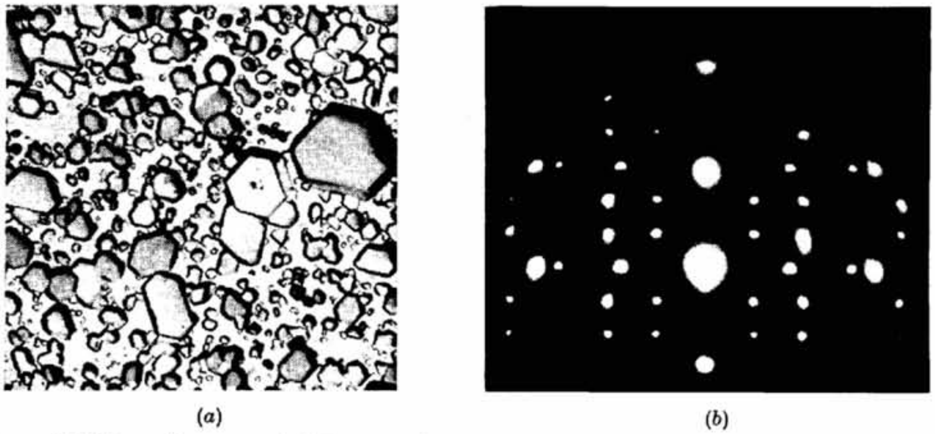
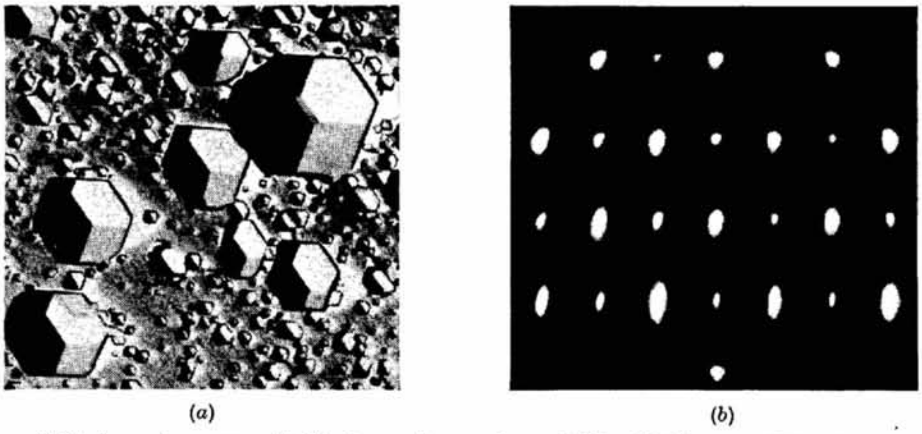


Fig. 1. Oxidation pattern on copper single crystal. 5 minutes immersion in $CuSO_4$ solution at 25° C. pH = 3·8.



(*a*) (*b*)

Fig. 2. Oxide on (001) face of copper. (*a*) Electron micrograph—× 3500. (*b*) Electron diffraction pattern—$[1\bar{1}0]$ Cu.



(*a*) (*b*)

Fig. 3. Oxide on (011) face of copper. (*a*) Electron micrograph—× 3500. (*b*) Electron diffraction pattern—$[0\bar{1}1]$ Cu.

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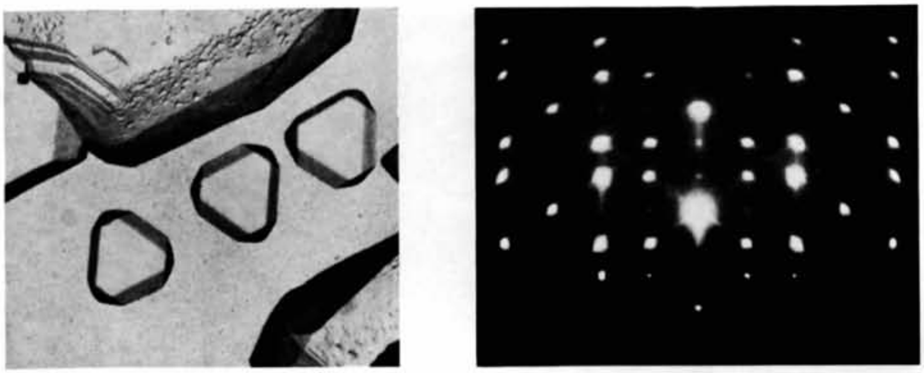
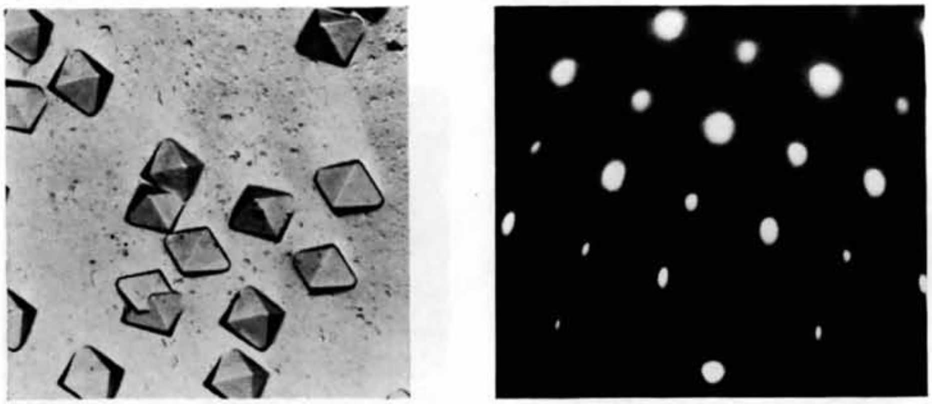


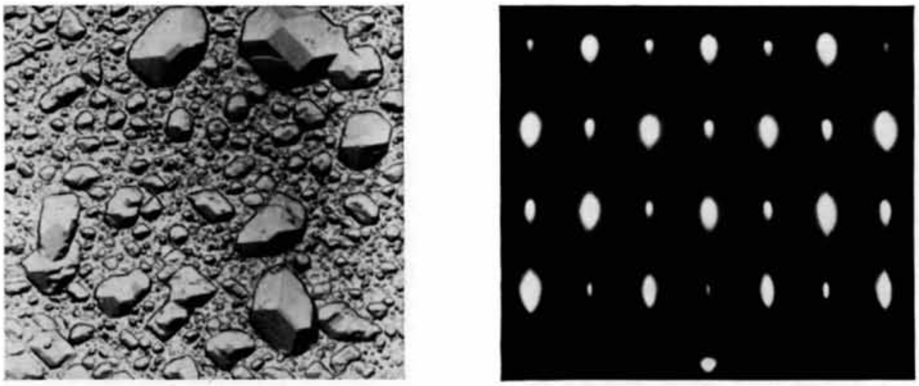
(*a*) (*b*)

Fig. 4. Oxide on (111) face of copper. (*a*) Electron micrograph—× 7000. (*b*) Electron diffraction pattern—[$1\bar{1}0$] Cu.



(*a*) (*b*)

Fig. 5. Oxide on (012) face of copper. (*a*) Electron micrograph—× 7000. (*b*) Electron diffraction pattern—[100] Cu.



(*a*) (*b*)

Fig. 6. Oxide on (113) face of copper. (*a*) Electron micrograph—× 3500. (*b*) Electron diffraction pattern—[$1\bar{1}0$] Cu.

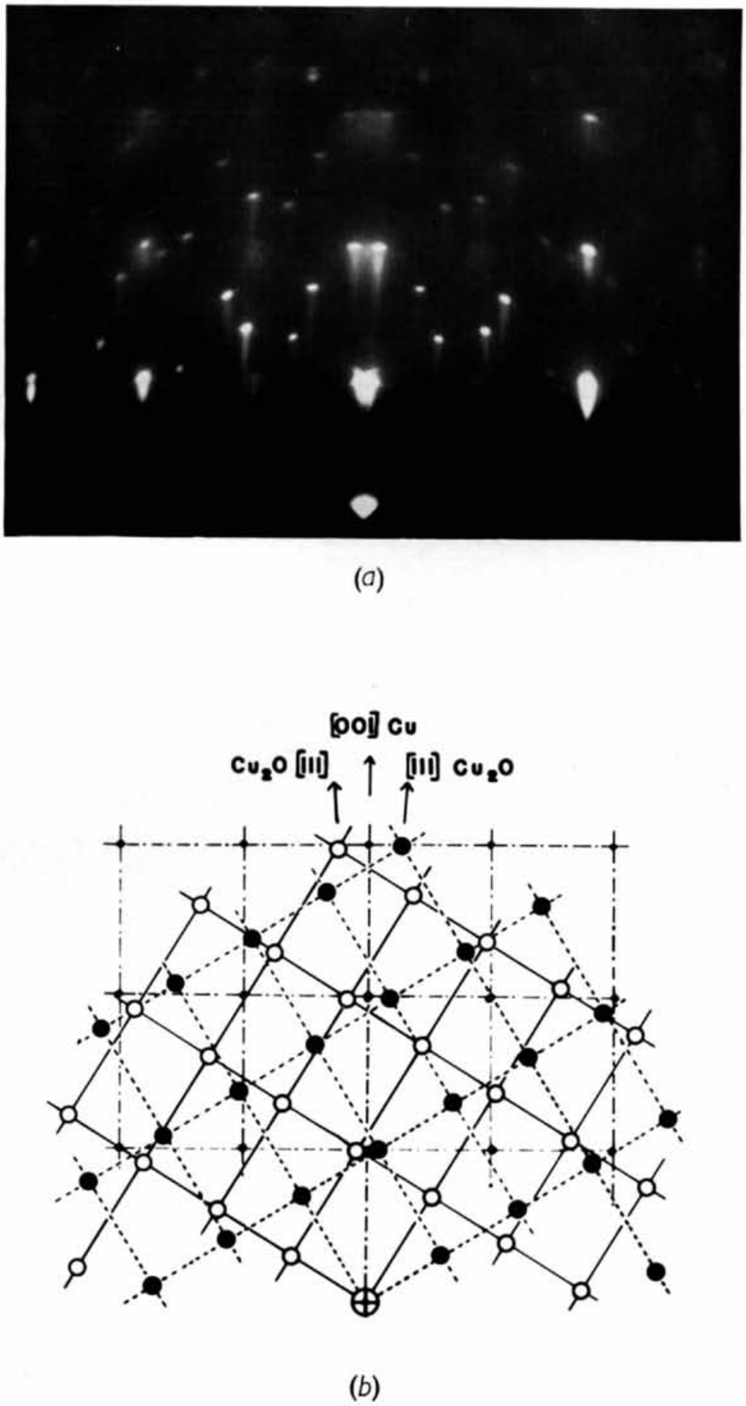


Fig. 7. Oxide on (001) face of copper. Class I*a* orientation. (*a*) Electron diffraction pattern—[1$\bar{1}$0] Cu. (*b*) Reciprocal lattice projection of oxide. ● points correspond to [1$\bar{1}$0] projection. ○ points correspond to [$\bar{1}$10] projection. • points correspond to [11$\bar{2}$] projection. These latter points are actually 4° out of the plane of the drawing.

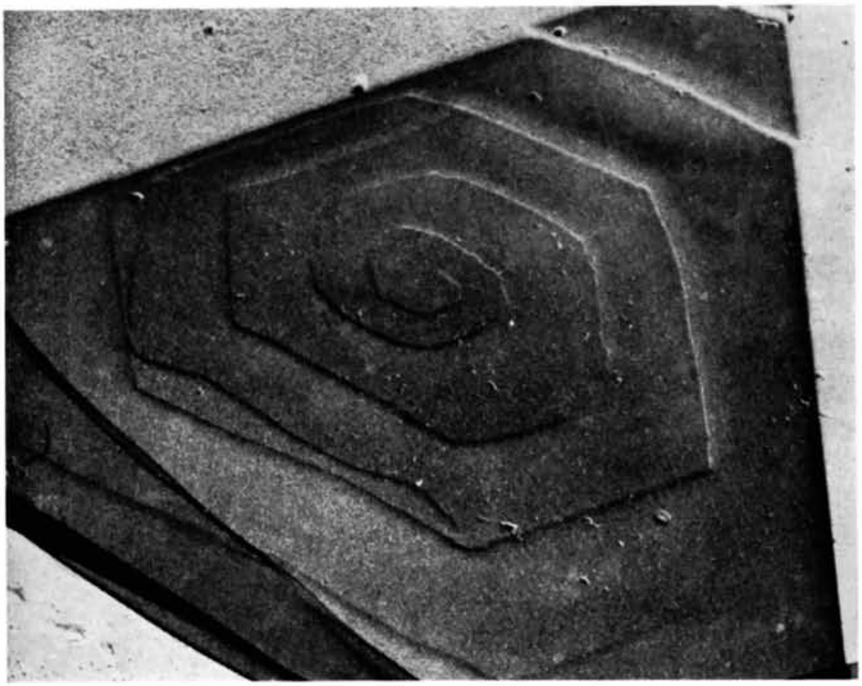


Fig. 9. Growth spiral on (111) face of Cu_2O crystal formed on the (012) face of copper. ×13,000.

experiment and I*a* in another apparently identical experiment.

Only one orientation was found for the oxide on the (011) and (113) faces of copper. This can be seen in Figs. 3 and 6. In each case a (110) plane of the oxide was parallel to the metal surface plane. On the (011) face the oxide had a completely parallel relationship to the metal. On the (113) face, however, the only parallelism of major faces was that of

$$(110)\mathrm{Cu_2O} \parallel (113)\mathrm{Cu}\ .$$

Oxide on the (111) face showed two twin related orientations with $(111)\mathrm{Cu_2O} \parallel (111)\mathrm{Cu}$. These are evident in Fig. 4. One of these orientations is designated in Table 1 as parallel since all planes of the oxide were parallel to like planes of the metal. The other which was related to the first by a rotation of 180° about the [111] axis is designated as anti-parallel. The anti-parallel orientation was observed in all experiments on the (111) face, but the parallel orientation did not occur in all cases. When present, the parallel orientation occurred in both thin and thick oxide films and was not related to the thickness of the growth.

On the (012) face of copper either two or three orientations were present. Fig. 5 illustrates the case in which three orientations were present. In every case the (012) planes of oxide and metal were parallel. The two orientations designated as anti-parallel in Table 2, were always present, but the parallel orientation was only present in part of the experiments. It should be noted that in each of these orientations a (111) plane of the oxide was parallel to one of the two adjacent (111) planes of the copper and bore the same parallel or anti-parallel relationship to the copper as the oxide on a prepared (111) face.

The transmission electron diffraction patterns of stripped oxide films indicated the same orientations as those shown by reflection diffraction. There was, however, one important result which was not apparent from the reflection patterns. In addition to the sharp spots from well-oriented single crystals of $\mathrm{Cu_2O}$, a pattern of rings corresponding to polycrystalline $\mathrm{Cu_2O}$ was present. It was, therefore, apparent that a base film of polycrystalline oxide was present at the surface of the metal. This did not show up in reflection experiments since the electron beam was passing through the tops of the oxide polyhedra and did not reach the surface layer. Electron micrographs of the stripped film also showed the presence of the polycrystalline layer (Miller *et al.*).

The orientations indicated in Table 2 were confirmed

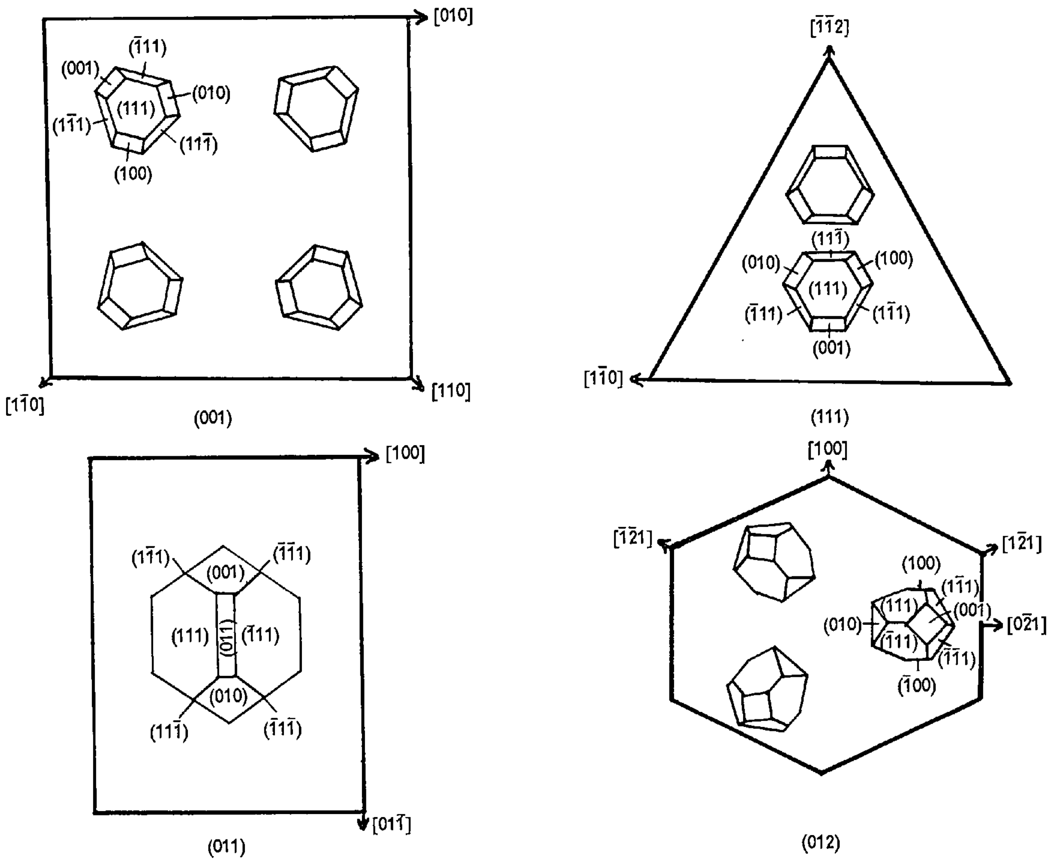


Fig. 8. Schematic drawing showing the oxide orientations on four copper faces and the shapes of the oxide crystals.

by the electron micrographs. It was not possible, however, to distinguish between Class I and Class I*a* orientations in the micrographs. Both the electron diffraction and electron microscope studies showed that the orientation relationships observed for the oxide polyhedra were the same after 60 hr. oxidation as those obtained after 15 sec. oxidation. Fig. 8 is a schematic diagram showing both the observed orientations and the faces developed on the oxide crystals.

Many of the micrographs showed well defined spirals on the oxide polyhedra. An example of this is shown in Fig. 9 for a spiral formed on the (111) face of an oxide polyhedron grown on the (012) face of copper. In general, all the larger oxide polyhedra showed spiral or step features on their (111) faces. In a few cases spirals were present on the (100) faces, but these were rare. The step height of the spirals was of the order of 100–200 Å.

X-ray diffraction studies showed that all of the faces of copper prepared were within 1° of the desired crystallographic plane and in many cases were closer than $\frac{1}{2}$°. Sharp single spots were obtained in the X-ray diffraction patterns indicating a high degree of perfection in the crystals. Electron diffraction of the surface gave sharp Kickuchi patterns. The electron diffraction patterns of the electropolished and annealed surfaces were also characterized by a shifting of the diffraction spots in the direction of the metal surfaces and by a tailing of the spots in the direction of the shadow edge. Electron micrographs of carbon replicas of the electropolished and annealed surfaces showed the surfaces to be smooth, and at magnifications up to 140,000 (Miller *et al.*) there could be seen no pitting, facet development or large scale roughnesses. Both the diffraction and microscope results indicated a maximum waviness of the surface of the order of 2°.

Discussion

It is obvious from previous work (Lawless *et al.*, 1956; Pashley, 1956) that the particular orientation of a growth product which occurs on a given surface depends to a great extent on the initial preparation of the surface. When facets are present on a surface, the orientations observed will be characteristic of growth on those particular facets (Lawless *et al.*, 1956; Pashley, 1956). In these studies the electron microscope and diffraction results indicated a very smooth initial surface, free of facets, at least to the resolution of the microscope and the replica technique (~ 20 Å). A few small pits were usually present on each surface and were observed in a few of the replicas. These pits were of two types, pits with spherical sides (therefore exposing all possible planes of the metal) and pits made up of (111) facets only. The slight waviness of the electropolished surface indicated that undoubtedly some facets were present which were smaller than 20 Å and therefore not resolved. These facets, however, would be only a relatively small part of the surface. It is also important to realize that for planes such as the (012), (112) or (122), which are not as close packed as the (001), (011), (111) or (113), steps on an atomic scale which might not be observable by present day techniques could determine the orientations of an oxide growth. On the five faces examined in this study only the orientations of the oxide formed on the (012) face could be attributed to growth on planes other than those parallel to the prepared face. Previous studies of oxidation in dry oxygen gas (Lawless *et al.*, 1956) indicated that the orientations observed on the (012), (112), (122), and (133) faces could be interpreted in terms of the possibility that the orientation was determined by atomic scale steps. In general, however, the surface preparation used in this study did seem to be satisfactory for providing a known interfacial contact plane so that accurate epitaxial relationships could be determined.

The orientation relationships shown in Table 2 are the same as those previously reported and discussed by Lawless & Gwathmey for oxidation in oxygen gas at elevated temperatures. The Class I*a* orientation, however, was not previously observed with the X-ray diffraction techniques. The orientations observed in this study were well defined, and little or no disorientation was detected. Some electron micrographs showed occasional oxide crystals which were obviously disoriented from the rest of the oxide, but these could in most cases be explained in terms of growth on crystal facets in some of the few pits present on a surface.

In every case except for the orientation of Class I*a*, the oxide had a very specific relationship to the structure of the substrate contact plane, and a misfit value could be given. These misfits are given in Table 2. In all cases at least one direction of the type [110] in the oxide was parallel to a direction of the same type in the metal with a misfit of 18% along that direction. These are the closest packed directions in both the metal and the oxide and this parallel relationship is the only general relationship which held on all faces studied.

Completely parallel orientations of the oxide on the metal were present on the (011), (111) and (012) faces of the metal with a misfit of 18%. Non-parallel orientations occurred on the (001), (012) and (113) faces. With the exception of oxide on the (012), these non-parallel orientations gave a smaller misfit between the rows of closest-packed atoms in the interfacial plane than the parallel orientation would have given. The non-parallel orientations on the (012) face had an 18% misfit between the parallel close packed rows of atoms in the interface plane, as shown in Table 2. It was not possible on the (011) and (111) faces to obtain a smaller misfit between close packed directions with other orientations unless multiple fits were considered, and as Pashley (1956) has pointed out, this would be of dubious value. It seems likely, therefore, that a small misfit between the closest-packed rows of atoms in the oxide and the metal is an important factor in determining the orientation.

The three orientations observed on the (012) face of copper must be considered in greater detail. Of these three orientations, only the two anti-parallel relationships are equivalent. In these two orientations, the parallel close packed rows of atoms in the interface plane are $[12\bar{1}]\mathrm{Cu_2O}\|[1\bar{2}1]\mathrm{Cu}$ and $[1\bar{2}1]\mathrm{Cu_2O}\|[12\bar{1}]\mathrm{Cu}$. These directions are not as close packed as the parallel [100] directions which occur in the third orientation. As shown in Table 2, the misfits are 18% for each of these orientations. Since the misfits are the same, it might be expected that those orientations in which the most densely packed rows of atoms in the interfacial plane were parallel would be most likely to occur. This was not what was observed, since in some cases only the two anti-parallel orientations occurred. It seems unlikely, therefore, that a matching of close packed rows of atoms in the interface plane is a major factor in determining the orientation on the (012) face. It should be noted that the (012) face is not a close packed face and there are no rows of closest packed atoms (e.g., [110]) in the interface plane.

A possible interpretation of these orientations is that the (111) and $(\bar{1}11)$ facets which on an atomic scale make up the (012) plane structure are influencing the orientation. If parallel and anti-parallel orientations such as were observed on the prepared (111) face occurred on the (111) and $(\bar{1}11)$ facets, the three orientations observed on the (012) face would result. Occasionally only the two anti-parallel orientations were present, and this is in agreement with the fact that sometimes only the anti-parallel orientation occurred on the (111) face. This interpretation is also in agreement with previous results on the (112), (122) and (133) faces of coppper for oxidation in dry oxygen gas (Lawless *et al.*, 1956). This interpretation, therefore, seems to be a reasonable one. There was no electron microscope or electron diffraction evidence to indicate the presence of large scale (111) or $(\bar{1}11)$ facets on the (012) face of copper.

The most unusual effect observed in this study was the occurrence of the Class I*a* orientations. Since the angle of tilt of the (111) faces of the oxide to the (001) face of copper varied from one experiment to another, it is not likely that the degree of misfit in the contact plane has any meaning. Evans & Wilman (1950) have explained a similar effect in terms of rotation about an axis due to epitaxial strain. Since the misfit for Class I orientations is quite small, and since oxide growths on the (011) and (111) faces of copper which have a greater misfit, do not show this tilt effect, this explanation does not seem to be satisfactory in this case. It has also not been possible to interpret these orientations in terms of growth on specific facets, or in terms of disorientation of the substrate. As yet, no satisfactory explanation of this peculiar orientation effect has been found.

It seems strange that the oxide polyhedra on all faces should show such a high degree of orientation in light of the observation of a thin polycrystalline layer of oxide at the metal surface. A possible explanation of this fact is that only those grains of oxide in the thin oxide film which have a certain preferred orientation relationship with the substrate continue to grow into large oxide polyhedra.

All of the oxide polyhedra in the early stages of growth showed only certain planes of the type {111} (Miller *et al.*) as shown in Table 1. This was true on all the faces of copper studied. Within a short period of time, however, a number of planes of the type {100} developed. (011) and (110) planes developed on the oxide on the (011) and (113) faces respectively of copper at a still later stage in the growth of the oxide. In general, the planes of the type {111} were the predominant planes, except that the (011) and (110) planes of oxide on the (011) and (113) faces of copper became of about equal predominance in some cases after 60–90 hr. oxidation. The particular habit planes which form would depend not only on the crystal structure of the oxide, but on the fact that the oxide is growing on a metal surface, and on the presence of impurities from the solution surrounding the crystal. The final shape of the oxide would also depend on the rate of growth of different crystal faces, which would in turn depend on the types of imperfections present in the oxide.

The presence of spirals on the (111) faces of some of the oxide indicated that these crystals were growing by means of a dislocation mechanism (Verma, 1953). It is probable, therefore, that these (111) faces are growing at a faster rate than either the (100) or the (110) faces. This would explain the development of larger (100) and (110) faces as the oxide continued to grow.

Summary

The epitaxial relationships of cuprous oxide formed on copper single crystals which were immersed in an aqueous solution of copper sulfate were studied by means of electron diffraction and electron microscope techniques. Particular care was taken in the preparation of the metal surfaces to insure known planes of contact between the metal and the oxide. The epitaxial relationships were determined for five crystal faces, the (001), (011), (111), (012) and (113). Four different classes of orientation were found, in agreement with previous studies on the oxidation of copper in dry oxygen gas (Lawless *et al.*, 1956). In each of these cases the oxide had a specific relationship to the structure of the substrate contact plane. An unusual orientation in which the oxide was tilted 2–4° from such a specific relationship occurred in some experiments on the (001) face. In all cases at least one closest-packed direction (a direction of the type [110]) of the oxide was parallel to a similar direction of the metal.

On one face, the (012), the orientations observed could be interpreted in terms of oxide growth on atomic scale (111) facets which make up the structure of the (012) plane.

The electron microscope pictures, in addition to confirming the orientations determined by electron diffraction, gave specific data on the shapes of the oxide growth and the particular faces present. Only the three most densely packed faces occurred on the oxide.

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To Fit a Plane or a Line to a Set of Points by Least Squares*

By Verner Schomaker, Jürg Waser, Richard E. Marsh and Gunnar Bergman

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A. and Department of Chemistry, The Rice Institute, Houston, Texas, U.S.A.

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The fitting of a plane or a line to a set of points by least squares is discussed, and a convenient numerical method is given.

In the description of a crystal structure, it is sometimes desired to fit a least-squares plane to the positions found for some approximately coplanar set of atoms. Because it seems that an incorrect method is often used for doing this, we would like to discuss the problem and recommend an alternative method that is both correct in principle and convenient in computation.

It becomes evident that the problem of the plane is essentially equivalent to the problem of finding the principal plane of least inertia for a set of point masses and that the problem of the best *line* is similarly equivalent to the very closely related problem of the least axis of inertia. The discussion therefore naturally covers line as well as plane and essentially recapitulates parts of a classical mechanical theory in deriving what is special to the present application. We first formulate the problem of the plane and present the recommended alternative method of solution, including a detailed numerical example, then discuss the prevalent incorrect method as well as various special cases, and finally consider the problem of the line and give a convenient method for handling it.

We find it convenient to use both ordinary vector notation, as in equations (1), (2), and (3), and matrix notation, as in equation (11), sometimes side by side. We also use two summation conventions: the Gaussian bracket [ ], to express summation over a set of points (cf., e.g., Whittaker & Robinson, 1940), and the convention of dropping the operator Σ whenever it applies to repeated alphabetic indices. Definitions we often express as identities.

The least-squares plane

What is desired is to find the plane that minimizes $S \equiv \Sigma_k w_k D_k^2 \equiv [wD^2]$, the weighted sum of squares of distances D_k of points k from the plane sought. These points are defined by the vectors

$$\mathbf{r} \equiv x^1\mathbf{a}_1 + x^2\mathbf{a}_2 + x^3\mathbf{a}_3 \equiv x^i\mathbf{a}_i \,. \quad (1)$$

The plane is defined by its unit normal

$$\mathbf{m} \equiv m_1\mathbf{b}^1 + m_2\mathbf{b}^2 + m_3\mathbf{b}^3 \equiv m_i\mathbf{b}^i \quad (2)$$

and by the origin-to-plane distance d, whereupon the distance from the plane to a point is

$$\mathbf{m}\,.\,\mathbf{r} - d \equiv m_i x^i - d \quad (3)$$

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