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THE OXIDATION OF THIN SINGLE CRYSTALS OF COPPER

Lawrence O. Brockway

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INTRODUCTION

The subject under investigation was primarily the influence of the physical state of metal surfaces on their chemical behavior. Thin films were chosen to allow the use of transmission electron microscopy and diffraction for observing the structure and texture of the metal as well as for observing in situ the oxide formed when the metal is treated with oxygen. Single crystal films were used to avoid the varying influence of different crystallographic planes in a single specimen.

Copper was first selected because of interesting structural imperfections observed in preliminary experiments, and later experiments have included work on zirconium and iron films.

This report presents a review of the preparation and structural properties of thin single crystals of copper, of the treatment of copper films with oxygen both in a chemical vacuum line and in a reaction chamber mounted inside an electron microscope, and of preliminary work on zirconium and iron. The work carried out during the final stage of the contract (October 1966-September 1967) is included in the appropriate sections of the review.

COPPER FILMS

PREPARATION

Copper films were prepared by condensation from the vapor onto heated single crystal substrates. Most of the films used in systematic oxidation experiments were condensed at a rate of about 6Å/sec onto (001) sodium chloride surfaces at 330°C to a final average thickness of about 700Å. The residual pressure was most often in the range of 10^{-5} to 10^{-6} torr. Micrographs and diffraction patterns of such films were obtained by floating them off the substrate onto water and mounting on microscope specimen grids; the mounted films were treated in hydrogen at 420°C for 10 min to reduce oxide formed during the contact with water. Such films show single crystal patterns of copper with the (001) plane parallel to the film surface. The texture is uneven with grains about 0.1 micron in diameter separated by narrow thinner regions; some twin boundaries appear.

Annealing of the copper films for 10 min in hydrogen at 630°C produced two distinct results. With the film still mounted on the substrate the annealing produced a smooth background texture interrupted by wide complex stacking faults oriented on (111) planes (up to 2 microns wide with 5×10^4 cm^2 of faulted area per cm^3 of copper) and isolated dislocations at a density

of about 10^7 cm^{-2}. When the original films were mounted on grids and then annealed, no stacking faults were formed while the density of isolated dislocations was a hundred-fold greater.

Extensive experiments were conducted on substrate-annealed films because the wide stacking faults were a new observation in copper. Micrographs of surface replicas and of platinum-shadowed copper films showed that terraces ranging up to 150Å in height coincide with the stacking faults. The origin of the stacking faults and associated terraces was traced to the thermal effects of the annealing process rather than to any influence of the hydrogen gas or of the mechanical working of the film during the subsequent removal from the substrate. It is now believed that the copper has a much higher mobility on the substrate at 630°C than at the condensing temperature of 330°C; at the high temperature the 0.1 micron grains move together producing the smooth texture (a process which has been observed directly in annealing experiments carried out inside an electron microscope). During the subsequent cooling the film adheres once more to the substrate and further cooling compresses the film because of the two-fold greater contraction of the substrate. The stresses are not wholly accommodated by elastic strains and these stresses are responsible for slip on the (111) planes and the formation of faults.

Substrates tested other than sodium chloride include potassium chloride and lithium fluoride. For all three, extensive observations by carbon replicas were made on plain substrate surfaces heated to the various temperatures used in the deposition and annealing of films. Even at the low temperature of 330°C enough material was lost by evaporation to produce some thermal etching and to make it apparent that the surface prepared by cleaving and polishing at room temperature was appreciably altered before it received the metal film. At the high annealing temperatures (630°C for NaCl and KCl, and 745°C for LiF) the rate of evaporation was high enough to allow no firm attachment of the metal film during the high temperature anneal. The results obtained with copper deposited on potassium chloride were essentially the same as on sodium chloride ((001)-oriented films with stacking faults when substrate-annealed and only dislocations when grid-annealed). Copper deposited on freshly cleaved lithium fluoride showed several orientations (including (001), (110), and (111) parallel to the substrate); annealing up to 745°C caused an increase in size of individual grains but no predominance of a single orientation and no occurrence of stacking faults even in the (001) grains. Preheating of the lithium fluoride to 700°C and cooling again prior to cleaving followed by the deposition of copper did produce films having only the (001) orientations and having (111) stacking faults after substrate-anneal. These and related observations helped to establish the conditions mentioned above for the occurrence of wide stacking faults in copper.

An analysis of the diffraction contrast effects observed in electron micrographs of copper films shows that stacking fault images are most often associated with a (200) reflection. Dark-field micrographs and selected area diffraction patterns showed that both extrinsic and intrinsic stacking faults occur in films prepared in this way, in approximately equal proportions.

The most recent experiments on preparation of copper films have been directed toward two points. One is the attempt to alter the density of dislocations in grid-annealed films in order to test for a correlation between the density of dislocations and the density of oxide nuclei on subsequent treatment with oxygen. Such a correlation would indicate a role of dislocations in determining the sites of nucleation of the oxide grains. A thermal gradient has been applied to grid-mounted films by supporting one edge of the specimen grid in a relatively massive clamp as a heat sink and bringing a hot wire close to the opposite edge of the grid. These experiments are not complete but the preliminary results are promising.

The other point of recent experiments is testing the effect of altering the composition and pressure of the residual gas during the deposition of the metal film. Such experiments in other laboratories have been concerned only with the epitaxy of the films, but our interest lies also in structural imperfections and in the consequences on the nucleation and growth of oxide. An ultrahigh vacuum chamber consisting of a 4 in. diameter Pyrex tee closed by stainless steel plates with Viton gaskets was mounted on a 4 in. Granville-Philips pumping station. In spite of the limitation of the baking temperature to 150°C by the use of Viton, pressures of 10^{-9} torr can be reached in a few hours. The substrate support and heater has a new design; 0.002 in. molybdenum sheet is used to form a box for supporting the substrate crystals (3 x 8 x 25 mm) with a window on the bottom for admitting the metal vapor. It is heated by radiation from a tungsten grid mounted just above and both the grid and the substrate box are surrounded (except for an appropriate window) by another molybdenum box as a radiation shield. Rapid cooling back to room temperature is achieved by admitting purified hydrogen gas. The composition and pressure of the residual gas are adjusted by admitting small amounts of hydrogen, nitrogen, water, ammonia or dry air. The composition is measured on a bakeable Varian partial pressure gauge of the permanent magnet type. Good single crystal films of copper have been prepared in this unit; preliminary tests on the effect of residual gases are in progress.

Some polycrystal copper films have been prepared for observations of the effect of grain boundaries on oxidation. The films were prepared by electro-thinning of annealed rolled sheet; grains of 2 or 3 microns with well-defined boundaries were obtained with a wide range of orientations among the grains.

OXIDATION OF (001) COPPER FILMS

Most of the experiments in which the copper films were treated with oxygen were carried out at oxygen pressures ranging from 10^{-1} to 10^{-4} torr and at temperatures of 525°C and 425°C. Some early experiments were done at higher pressures and lower temperatures but these conditions are not suitable for observing the nucleation and growth of the individual oxide grains characteristic of the early stages of oxidation.

The treatment with hydrogen for annealing and for chemically reducing the surface and subsequently with oxygen was given in two types of systems. The first was a Vycor or quartz tube mounted through a tubular furnace and continuously pumped against a controllable leak through which the purified gases were admitted. The second was a small metal chamber supporting the metal film in the correct specimen position in an electron microscope. The construction of the chamber provided heating of the specimen and treatment with hydrogen or oxygen during the electron exposure so that the history of a fixed area often including one or more oxide grains could be followed on the fluorescent screen or recorded on a series of frames in a movie sequence.

The general results of oxidation under the conditions mentioned above may be described as follows. There is an induction period of contact with oxygen prior to the first appearance of oxide grains in transmission micrographs; the period is roughly inversely proportional to the pressure with a constant of 0.01 torr-min at 525°C. At the end of the induction period there is the simultaneous occurrence of oxide grains of the same size (about 0.2 micron) and at a nearly uniform surface distribution which is roughly proportional to pressure with a constant of 5×10^{-5} grains cm^{-2} $torr^{-1}$ at 525°C.

The sites of nucleation of oxide grains are uniformly distributed at 10^{-1} and 10^{-2} torr of oxygen; at 10^{-3} and 2×10^{-4} torr the stacking faults and their associated surface terraces on substrate-annealed films are favored as nucleation sites by a factor four times larger than expected for random distribution.

Three distinct epitaxies and shapes of oxide grains occur. Diffraction patterns confirm the Cu_2O phase for all grains and identify (100), (110), and (111) as the oxide planes which are parallel to the copper film in the three different types of grains. No other orientations are ever observed. Grains of the first are square, those of the second are right isosceles triangles, and those of the third are equilateral; the first are more rare while the second and third occur with equal frequency.

Each type of grain has its own growth pattern. The (110) right triangles grow into needles by extension of the hypotenuse with some twinning while maintaining $Cu_2O(110)||Cu(001)$. The (111) triangles retain the equilateral shape at first but frequently change into distorted diamond shapes with twinning. The square shapes also grow in two dimensions but quickly lose their straight edges and finally develop an octagonal shape with longer edges at 45° to the sides of the original square; no twinning is noted here.

Oxidized films were treated with dilute hydrochloric acid solutions to remove the oxidized copper. Micrographs then showed holes reproducing the size and shape of the oxide grains; such holes appeared in all acid-treated films which had been exposed to oxygen for times longer than the induction period.

The rates of growth have been observed both in terms of individual grains and of the fraction of the metal surface converted to oxide. The growth rates for individual grains are more readily observed at pressures below 10^{-1} torr, since at this pressure the density of nuclei and their rate of growth is so great that the grains coalesce in a minute or less. Five rates have been observed at fixed lower pressures with the following order of decreasing magnitude: (110) grains lying with the hypothenuse extended along a stacking fault—a linear extension of 1000Å sec^{-1} is observed here at 10^{-3} torr and 525°C; (110) grains lying across or away from stacking faults; (111) grains on stacking faults; (111) grains away from stacking faults; and (100) grains, which were not observed frequently enough to test the influence of stacking faults. Some typical rates observed in movie sequences for which the measurement of oxygen pressure is uncertain are shown in the table.

GROWTH RATE OF AREA OF INDIVIDUAL GRAINS AT 525°C
In Units of $cm^2\ sec^{-1} \times 10^{17}$

Sequence	(110)	(111)	(100)
1	243	126	---
2	---	65	50
3	47	36	25
4	26	19	7

Over a period of several minutes marking the duration of one sequence the rates are constant, and each type of grain grows by its own mechanism.

Growth rates have also been measured in terms of the rate at which all grains in a given field of view convert the metal to oxide. From these experiments in the chemical line the pressure dependence of the overall rate is determined. Typical results at 525°C are:

Oxygen pressure, torr	10^{-1}	10^{-2}	10^{-3}	2×10^{-4}
Rate, $cm^2 Cu_2O/cm^2 Cu$-min	0.426	0.091	0.013	0.0004

For the first three pressures, the rate is proportional to $p^{0.8}$, but it should be noted that this is a composite for two (and sometimes three) types of grains. This relation gives a rate at 2×10^{-4} torr which is ten times greater than observed.

Observations made with a reaction chamber mounted inside a microscope provide very graphic movie records of the annealing of the metal film (including the motion of imperfections under thermal stresses) and of the nucleation and growth of individual oxide grains but the duration of the observation of a single grain is limited to about 1 min. One of the most interesting

observations by this technique is the sudden appearance of oxide nuclei between successive movie frames separated by 1/6 sec where the earlier frame shows no particle bigger than the microscopes resolving power of 20Å while the succeeding frame shows an oxide grain of 0.2 micron diameter.

Oxidations at 2 x 10^{-4} torr produce nuclei so widely spaced that individual grains can grow to several microns (some 30 times the original diameter) without mutual interference. The later stages of growth represented here involve a surface diffusion of copper as shown by the removal of copper from a half-micron wide moat which appears around each oxide grain in micrographs of carbon replicas of the films treated for several hours.

Current experiments whose results are incomplete include oxidations performed in a bakeable ultrahigh vacuum line. The line was constructed from 1-1/2 in. stainless steel tubing and valves with a 1 in. quartz section passing through a tubular furnace. It is fitted with a variable leak for admitting oxygen at pressures ranging from 10^{-4} to 10^{-7} torr with a residual pressure of 10^{-9} torr; purified hydrogen can be supplied at pressures up to one atmosphere for removing oxide formed during the mounting of the copper film. The line is also fitted with a partial pressure gauge for monitoring the composition of the gas to which the specimen is actually exposed. The advantages of the line are its lower residual pressure and lower level of contaminants than is found in the glass and Vycor line, and the lower range of oxygen pressures which should afford extensive data on the surface diffusion of copper to the oxide grain as observed only at the lowest pressure obtainable in the glass line. The oxidation runs made with this line thus far have been at 2 x 10^{-4} torr and 525°C for comparison with the glass line; the results are comparable. The next runs will be with copper at pressure of 10^{-5} torr and with iron films.

DISCUSSION OF THE OXIDATION OF COPPER

Data of the sort reviewed above lead to suggestions on the mechanism of the reaction of oxygen with copper during the three stages represented by (a) the incubation period prior to the first appearance of oxide grains in transmission micrographs, (b) the early growth of oxide grains where the linear dimensions increase by a factor of no more than four or five times those of the first visible nuclei, and (c) the later growth stages where much larger individual grains can be observed. None of these involve a complete coverage of the metal surface nor any homogeneous oxide layer. The suggestions have not been completely developed but they do arise from the observations supplemented at some points with results from other laboratories.

The induction period certainly involves the absorption of oxygen as has been indicated at several other laboratories by the two-dimensional atomic arrays observed by low energy electron diffraction on copper surfaces exposed to oxygen. In addition there must be a volume diffusion of oxygen since the

first Cu_2O nuclei observed always involve the copper through the total thickness of the film as shown by the treatment with hydrochloric acid. The suddenness of the appearance of the relatively large nuclei (0.2 micron across and 800Å thick in less than 1/6 sec) indicates that the oxygen atoms must be already distributed through the metal prior to the reorganization of the two kinds of atoms into the known Cu_2O phase. This step in the process is not controlled by the arrival of gas at the metal surface since the 10^8 atoms of oxygen in the oxide grain is 10 times larger than the number of oxygen atoms reaching the surface in the 1/6 sec interval nor by diffusion of oxygen through copper over many atomic distances during this short interval. When the interstitial oxygen atoms diffusing through the copper during the incubation period have reached an adequate concentration, at some point in the volume or on the surface of the film a triggering process occurs which leads to the formation of the Cu_2O structure without involving movement of any individual atoms over distances in excess of a couple of atomic spacings. When the triggering occurs, the incubation period is brought to an end but this cannot happen before the concentration of interstitial oxygen has reached a critical minimum value. The time required to build up this concentration goes down with increased concentration of oxygen at the surface, and this accounts for the inverse relation between incubation time and oxygen pressure.

The nature of the triggering process must account for the uniform distribution of the oxide grains observed at the higher pressures. Each grain is surrounded by an area of copper surface which is inversely proportional to the pressure so that within the higher pressure range the rate of bombardment with gas on the area associated with one grain is constant. This suggests that a rapid surface diffusion mechanism is part of the triggering process. This would require that there be a series of centers on the surface which act as collecting stations for oxygen atoms and such clusters would provide the critical excess of concentration on the surface and perhaps also down through the copper for triggering or seeding the crystallization of Cu_2O. The collecting stations or sites must vary in the effectiveness of their collecting i.e., the captured atoms escape with capture times varying according to the activation energy for the escape process. The distribution of the sites for each degree of effectiveness must be nearly uniform over the surface. With increase in pressure even the poor collecting sites are able to achieve the critial concentration of atoms because of the greater availability of adsorbed gas. Some steady state is achieved of surface sites having the critial clusters before the end of the induction period so that when the volume diffusion has provided the concentration of oxygen in copper required by the stoichiometry of the oxide, the nucleation of oxide grains proceeds simultaneously at all sites.

The "collecting stations" which determine the nucleation sites might be no more than various step sites in the surface of the copper. At the low pressure studied where the high terraces (up to 150Å) associated with complex stacking faults in substrate-annealed films are favored as nucleation sites,

it is very probable that the profile of such a high terrace consists of a multitude of short steps which would act to provide an especially concentrated supply of adsorbed oxygen atoms. Not only are these terrace sites favored for nucleation but the most rapid growth of oxide occurs along the lines of these terraces. That these terraces are not equally favored at high pressures arises from the higher general availability of adsorbed gas allowing the more isolated step sites to achieve the critical collecting before the end of the period required for the critical volume diffusion. Another consideration is tempting in view of the approximate agreement between the surface density of oxide nuclei at the highest pressure and the density of dislocations observed in the substrate-annealed films. These dislocations might serve as collecting sites and provide pipes in the copper structure for funneling oxygen atoms down into the interior of the copper. Experimental tests of this hypothesis have not been completed whereby films with controlled variation of the dislocation densities are oxidized at a given pressure to see whether there is a correlated change in the nucleation site density.

The nucleation of (111) and (110) grains in approximately equal numbers at the higher pressures suggests a randomness in the nucleating organization of oxygen and copper atoms which does not clearly favor one over the other, although all other epitaxies are excluded (with the exception of an occasional (100) grain). The epitaxial differences in the subsequent growth, on the other hand, are quite marked. The (111) grains at their first appearance are as thick as the copper film and as they grow the copper available around all edges of the grain is involved and the extension is in two dimensions without appreciable increase in thickness. The (110) grains extend in only one direction, which is always a [110] direction for both the oxide and the metal film. The rate of linear extension (with a fixed width) is larger than the square of the linear rate for (111), since the area increase is faster for the (110) grains. It is not true that every (110) grain is as thick as the copper film since micrographs of films oxidized at 10^{-1} torr where the grain density is high show occasional overlaps of grains without coalescing; they appear to be growing on opposite surfaces of the film. At this high pressure the grain density and the (110) growth rate are so high that within 1 min after the induction period the (110) grains have engulfed the whole surface and the (111) grains have been incorporated and converted to (110). Attempts to discuss the differences in the detailed atomic arrangements of (110) and (111) oxide relative to (001) copper as a means of accounting for the differences in growth behavior lead to an expected difference in the nucleation frequency, which is not observed.

Observations on the growth at lower pressures (10^{-3} torr or lower) where the grain density is low enough to allow longer growth periods without interference between grains show the influence of the stacking faults and/or high surface terraces. In the same way that the multiple step sites of these terraces provide high concentrations of adsorbed oxygen for the nucleation of grains, they provide an enriched supply of oxygen for the grains whose epitaxy-

growth relation favors extension along the terraces. Since the terraces lie
in the [110] directions of the metal surface, the (110) oxide grains are
favored as indicated by the habit observed at higher pressures, and the
fastest of all growth rates observed is that of a (110) grain extending along
a stacking fault.

There is strong evidence for the diffusion of copper atoms to and through
the oxide grains in the later growth stages, where the lateral dimensions are
10 or more times larger than originally. These old grains have thickened and
distorted from their original position so that they stand well above the orig-
inal metal surface on one side and show a concave depression on the other side.
On the top (protruding) surface of the grain inverted growth steps appear,
i. e., the steps are highest at the outside edge of the grain and are lower in-
side. The growth proceeds by a raising of the outer edge and a filling in of
the center. All of this is shown in surface replicas and can be accounted
for only by the diffusion of copper through the outer edges of the oxide crys-
tal (where the contact with copper metal occurs) up to the upper surface where
the oxygen is supplied by bombardment from the gas phase. These replicas also
show a deep moat in the copper metal surrounding each grain; the outer edges
of the moat show the (100) faces of copper exposed by the migration of copper.
This surface diffusion of copper occurs only adjacent to the oxide grains and
only in the presence of oxygen gas. Here the process may be described as the
formation of a two dimensional phase of copper and oxygen with interactomic
distances differing from those of copper or of the two known bulk phases of
copper oxide (as shown by low energy electron diffraction) and with the copper
atoms having a higher surface mobility than they do on pure metal. Where
this sheet of copper and oxygen touches the oxide grain it is incorporated
in the oxide structure which grows larger while draining copper continuously
from the adjacent metal surface. As a result the surface drops below its
original position and develops the moat around the crystal. At this later
stage this process of diffusion of copper and associated oxygen over the
metal surface to the oxide evidently predominates over the alternative of
having oxygen diffuse into the metal and convert it to oxide adjacent to the
original grain. This is in contrast to the mechanism at nucleation and the
earliest growth stage. It should be noted that the appearance of moats has
been clearly observed only at an oxygen pressure of 2 x 10^{-4} torr, low enough
to give widely spaced grains which can grow for several hours without meeting
each other. This is one of the principal reasons for an ultrahigh vacuum
line where the oxidation can be observed at still lower pressures.

The final description of the mechanism of oxidation must recognize two
distinct stages: an earlier one where the rates are faster and are clearly
distinct for the different epitaxies and a later one where the oxidation is
slower, the grains are heavily twinned, and a surface diffusion of copper is
clearly involved. The later stage marked by relatively large grains shows
some similarities to the oxidation process discussed very extensively in the
literature for metal covered with a homogeneous oxide layer where diffusion
of copper through the oxide is one of the principal steps, but it necessarily
has some distinctive differences due to the availability of copper only at
the edge of the grain.

IRON FILMS

Iron was selected for study in thin single crystal films because it has a body-centered structure and should occur with different structural imperfections from those formed in the cubic closest packed structures of copper and because information on the fundamentals of the early oxidation would have great interest in the field of corrosion.

Preparation of thin single crystal films by condensation from the vapor onto crystalline substrates has been reported to require traces of water in the residual gas or in a pre-exposure of the substrate. We now obtain good single crystal iron films on sodium chloride substrates in a vacuum chamber consisting of an unbaked 3 in. Pyrex tee evacuated to below 10^{-6} torr by a diffusion pump through a very efficient liquid nitrogen trap and without applying any special control on the composition of the residual gas. The substrate is cleaved in air on a (001) plane, then mounted in a molybdenum support in the evaporation unit where it is heated by radiation to 480°C. This temperature produces a fresh substrate surface by vaporization of substrate material; temperatures below 480°C do not lead to a single orientation of the deposited iron.

The iron (99.999%) is mounted on the water-cooled copper anvil of a small MRC electron beam evaporator for which an electron current of 50 mA at 1800 V leads to the condensation of a film at about 8Å/sec to a total of about 1000Å. The film and substrate are taken from the evaporator at room temperature, at which the film is removed on water and mounted on microscope specimen grids. The film as grown under these conditions shows the single crystal diffraction expected for a crystal extended on (001); the micrographs show an irregular texture with thickness variations.

Annealing in hydrogen at one atmosphere is effective only if the temperature is raised to 700°C and maintained for an hour. The annealed films are smooth with many dislocations (approximately 10^{10} cm^{-2}) and some boundaries about a micron long separating regions distinguished by a low-angle tilt. No stacking faults appear in films annealed either on the substrate or on the specimen grid.

Preliminary oxidations have been carried out at 450°C and 2 x 10^{-4} torr of oxygen. The only oxide formed is Fe_3O_4 and it occurs in a single orientation. The distribution on the surface and data on induction times and growth have not yet been observed.

ZIRCONIUM FILMS

Thin films of zirconium have been grown by vapor deposition at residual pressures of 10^{-5} torr onto both polished and as-cleaved surfaces of NaCl substrates heated to 400-450°C at deposition rates of 3 to 10Å/sec. The resulting films form individual crystallites about 0.1 micron across with three distinct orientations. Predominant are two orientations with the (0001) plane in the plane of the film and a 30° rotation between them. A third, less abundant orientation has been tentatively identified as having ($2\bar{1}\bar{1}0$) plane in the plane of the film. Some single crystalline grains as large as 3-4 microns have been found.

These films have been exposed to oxygen in the microscope reaction stage at temperatures up to 750°C and oxygen pressures of 10^{-3} to 10^{-2} torr. At these pressures the incubation period ranges from 10 to 30 min before oxide grains are detected. The nuclei grow at a rapid rate, and holes appear in the film as the reaction proceeds. Unlike cuprous oxide grains, which grow with quite definite epitaxial relations to the underlying copper, the zirconium oxide is randomly oriented under these conditions of growth.

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