Electron-Microscopic Study of the Structure of a Metastable Oxide Formed in the Initial Stage of Copper Oxidation. I. Cu₄O

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Abstract

In an early stage of oxidation of copper, a metastable copper oxide with the chemical composition Cu₄O has been observed by an atomic-resolution electron microscope. The atomic positions of Cu and O have been studied using electron-microscope images and diffraction patterns interpreted by calculations based on the dynamical theory of electron diffraction. The unit cell of the new oxide Cu₄O belongs to the orthorhombic system with space group Pmm2. The lattice parameters are a = 4.02, b = 5.66 and c = 5.94 Å. The volume is approximately two times larger than that of Cu₂O. It is pointed out that at a certain thickness the images of O atoms appear bright and those of Cu atoms do not.

1. Introduction

In the early stages of oxidation of nickel single crystals, Garmon & Lawless (1966) found the existence of an induction period prior to the formation of nickel oxide, which was confirmed by structural changes in the nickel films. They observed a superlattice diffraction pattern similar to that found by Alessandrini & Freedman (1963) for the ordered structures of oxygen in nickel. Shibahara & Hashimoto (1980) observed a tungsten oxide crystal with a smaller content of oxygen than in WO₂, formed when WO₃ crystals were evaporated in a vacuum of 10⁻⁴ Pa.

In order to study the non-stoichiometric copper oxide structure observed by Ishii & Hashimoto (1967), the present authors have carried out further observations of the initial stages of copper oxidation and found a new type of copper oxide containing less oxygen than Cu₂O. In this observation, the copper oxide is sometimes found together with its superstructure. The atomic structure has been analysed using a high-resolution transmission electron microscope with interpretation based on the many-beam dynamical theory of electron diffraction. The present paper is concerned with the atomic structure of an oxide having the chemical composition Cu₄O.

2. Specimen preparation and observation

Specimens were prepared in a way similar to that described by Ishii & Hashimoto (1967). A block of pure copper (purity about 99.99%) was rolled into a sheet 70 μm thick. The sheet was annealed at about 923 K in a vacuum of 2.66 Pa for 30 min, and was then electrolytically thinned by a window method in
nitric acid and methyl alcohol. The thin films were then oxidized at 770–820 K in a vacuum of 2–2.4 Pa for about 2 min. The observations of the atomic structure of the oxidized films were also carried out in a vacuum of $10^{-1}$–$10^{-3}$ Pa in the electron microscope at 770–820 K under electron-beam irradiation. During the *in situ* observation of oxidation, when the oxide film was formed on the surface of the copper specimen, some parts of the copper were evaporated together with the oxide layer but other parts of the oxide layer remained. This phenomenon is similar to that observed by Ishii & Hashimoto (1967). The evaporation of copper may be due to the elevation of the specimen temperature during oxidation. A low-magnification electron-microscope image from such a film is shown in Fig. 1. The dark part in this figure is the copper matrix probably covered with copper oxide with a thickness of several hundred Å. The copper oxide crystal which is indicated by a circular mark at the center of Fig. 1 has a ribbon shape of thickness 100–200 Å and with other dimensions about 2000 × 7000 Å. The crystals are connected by a thin amorphous layer less than 50 Å thick. Fig. 2 shows high-magnification images of a ribbon-shaped oxide film. As can be seen in Fig. 2(a) and the interpretation given in Fig. 2(b), the oxide film consists of regions A and B which are separated by a grain boundary (G.B) and superstructure (S.S) as seen in region B. Figs. 2(c), 2(d) and 2(e) are magnifications of the regions indicated by (C), (D) and (E) in Fig. 2(b), respectively; here the grain boundary and superstructure are shown in (c), region B in (d) and region A in (e).

The electron diffraction pattern corresponding to the area shown in Fig. 2(a) is shown in Fig. 3(a) together with an explanation in Fig. 3(b). The diffraction pattern suggests that a crystal with a unit cell similar to that of Cu₂O is arranged in two orientations, *i.e.* (011) and (001) are parallel to the crystal surface as shown in Fig. 3(c). It seems reasonable that the oxide formed is parallel to planes (011) and (001), because the substrate copper was rolled into a sheet and hence planes (011) and (001) of copper are parallel to the specimen surface and the Cu₂O crystal will grow epitaxially on the surface of the copper crystal, *i.e.* (011) and (001) of the Cu₂O crystal are parallel to the specimen surface. Since the intensity of the electron diffraction spots cannot be completely explained by a Cu₂O crystal, there may be some anomalies in the composition of the atoms, and hence we tentatively name this crystal Cu₂O'. Determination of the position of the Cu and O atoms in the Cu₂O' crystal was carried out by comparing the observed intensity distribution of the electron-microscope images and the electron diffraction pattern with the theoretical calculation by the many-beam dynamical theory of electron diffraction. The procedure for atomic structure determination is described in § 3. The details of the superstructure are not discussed in this paper.

### 3. Crystal structure

The perspective view of a unit cell of Cu₂O is given in Fig. 4(a) and the (110) projection is shown in Fig. 4(b). Figs. 4(c) and 4(d) are the calculated intensity...
distributions of electron waves at the bottom face of Cu$_2$O in the orientation shown in (b) with film thicknesses of 120 and 150 Å, respectively. The calculated contrast does not change with a change of thickness of ±10 Å. In Fig. 4(c), the large white discs represent the images of O atoms, while the images of Cu atoms are represented by small white discs. In Fig. 4(d), however, only the images of the O atoms can be observed and the images of the Cu atoms disappear. Carrying out the calculation of the theoretical intensity distribution at the bottom face of the Cu$_2$O crystal with various thicknesses up to 500 Å, we noted that though the images of O atoms are always observed clearly, the images of Cu atoms are very sensitive to the film thickness and often disappear. By comparing the electron micrograph shown in Fig. 2(e)

Fig. 2. (a) Larger magnification of part of Fig. 1. (b) Explanation of (a). Regions A and B on either side of the grain boundary (G.B) show atomic structure. A superstructure (S.S) is seen in region B.

Fig. 2 (cont.). (c), (d), (e) Magnifications of the regions indicated by (C), (D), (E) in (b).
and the calculated image shown in Fig. 4(d), it is seen that the bright spots in Fig. 2(e) correspond to every other bright spot in Fig. 4(d). Therefore, it is assumed that the projection of the atomic structure shown in Fig. 5(a) and (b) is that for the Cu$_4$O crystal in [110] and [100] orientations of the Cu$_2$O lattice. One of the O atoms in the unit cell of Cu$_2$O is eliminated and the position of the other O atom is changed, which can be seen by referring to the positions of atoms in Cu$_2$O shown in Fig. 5(c). In this model, the oxide has the chemical composition Cu$_4$O and can no longer be described by the unit cell of Cu$_2$O, and thus a new unit cell is constructed as shown by the full lines in Fig. 5(a) and (b). The relation between the unit cell of Cu$_2$O and that of the new model of Cu$_4$O is shown in Fig. 6(a) which corresponds to Fig. 3(c). The axes of the unit cell of Cu$_4$O which are projected in the planes shown in Fig. 3(b) are shown in Fig. 6(b) together with the reciprocal nets projected on to (001) and (100).

In the unit cell of Cu$_4$O, there are eight Cu atoms with the coordinates (0, 0, 0), (0, ½, 0), (0, 0, ½), (0, ½, ½), (½, ½, ½), (½, ½, ½), (½, ½, ½), and two O atoms with the coordinates (¼, ¼, 0), (3, 3, ½). This crystal of Cu$_4$O belongs to the orthorhombic system with lattice constants $a = 4.02$, $b = 5.66$ and $c = 5.94$ Å. The space group is assigned as $Pmnm2$ from crystallographic consideration of the proposed structure model.
4. Comparison of the calculations with the observations

The model of Cu₄O has been confirmed by a comparison of the image observations with the intensity distribution of electron waves at the bottom face of the crystal or with the electron diffraction pattern calculated using the multislice method of the dynamical theory of electron diffraction.

First, amplitudes and intensities of diffracted waves from the various lattice planes of the Cu₄O crystal in [001] and [100] orientations with various thicknesses were calculated and the thickness dependence of the amplitudes of several main diffracted waves from the crystal in the [001] orientation is shown in Fig. 7(a). As can be seen in Fig. 7(a), though the amplitudes from (100), (110), (101), (020) and (002) increase gradually with increasing thickness, the amplitudes from (000), (120), (102) and (200) oscillate with a period of about 100 Å.

The calculated intensity of the electron diffraction patterns from the Cu₄O crystal in [001] orientation is shown in Fig. 7(b) for thicknesses of 216, 274 and 386 Å. The pattern from the crystal 216 Å thick agrees well with the observed diffraction pattern shown in Fig. 3(a), whose indices are shown in Fig. 6(b).

The calculated images at the bottom face of the crystals are shown in Fig. 7(c) for the thicknesses 110, 216, 274 and 386 Å. It should be noted that the calculated image for a thickness of 110 Å is the same as that for a thickness of 216 Å, and the image for 274 Å is the same as that for 386 Å. For the thicknesses 274 and 386 Å, the image of O (large white disc) and the image of Cu (small white disc) can be observed simultaneously, but for the thicknesses 110 or 216 Å only the image of O can be observed.

Since the amplitudes of the diffracted waves from (200), (102) and (120), which reflect the periodicity of the arrangement of copper, become minima at the thicknesses 110 and 216 Å, as can be seen in Fig. 7(a), the images of Cu atoms disappear at these thicknesses. On the other hand, the diffracted waves from (110) and (101) which contain O, always have some magnitude and above 150 Å the amplitudes become stronger than those of (200) and (120) within the thickness of 500 Å. Thus it is reasonable that the image of O can always be observed.

Figs. 8 and 9 show magnified images of Cu₄O as observed in the two orientations [001] and [100] respectively. The calculated images and models obtained using the experimental data with the model

Fig. 6. (a) Perspective view of the Cu₄O lattice (thick lines) in [001] and [100] orientations and relation to the unit cell of Cu₂O (thin lines). The [100], [010] and [001] axes of Cu₂O are parallel to the [001], [110] and [110] axes of Cu₄O, respectively. (b) Explanation of the electron diffraction patterns of Cu₄O crystals in [001] and [100] orientations, whose diffraction spots are represented by * and ○ respectively.

Fig. 7. (a) Thickness dependence of the amplitudes of diffracted electron waves from several atomic planes of Cu₄O. (b) Calculated intensity of electron diffraction patterns from Cu₄O crystals in [001] orientation for thickness values of 216, 274 and 386 Å. (c) Calculated intensity distribution of electron waves at the bottom surface of Cu₄O in [001] orientation and the projection of the atoms. Crystals of thickness 110 and 216 Å give identical images and only O atoms appear.
of Cu₄O are shown at the bottom. The agreement between the observed and calculated images is fairly good.

Fig. 8. Observed and calculated images of the Cu₄O crystal in [001] orientation and the projection of Cu and O atoms. Calculated conditions: Δf (defocusing) = 1700 Å, C₅ (spherical-aberration coefficient) = 0.67 mm, T (thickness) = 184 Å.

5. Discussion and conclusion
During the initial stage of oxidation of copper crystals at 770–820 K in a vacuum of 10⁻¹ ~ 10⁻² Pa, a very thin layer of a metastable oxide with the chemical composition Cu₄O has been observed.

During the oxidation process, O atoms go into the copper lattice interstitially. As can be seen in Figs. 4(a) and 5(c), if both positions (½, ½, ½) and (½, ½, ½) in the unit cell of the copper lattice are occupied by O atoms, the Cu₂O crystal structure is formed. If only one O atom occupies the position (½, ½, ½) or (½, ½, ½) in the unit cell of the copper lattice as shown in Fig. 5(b), the Cu₄O crystal structure is formed. In the Cu₄O crystal structure, the positions of the O atoms are not the same as those in the Cu₂O structure and thus Cu₄O cannot easily be changed to Cu₂O by heating to the temperature where Cu₂O crystals normally grow. Allowing for the difference in the unit cell, the Cu₂O crystals seem to grow on the surface of the copper epitaxially with a relation similar to that of the Cu₂O crystals grown on a copper substrate, i.e. the [001], [010] and [110] axes of the Cu₂O crystal are parallel to the [100], [010] and [001] axes of the Cu₂O crystal respectively which are parallel to the [110], [010] and [001] axes of the copper.

The formation mechanism of Cu₄O crystals may not be much different from that of Cu₂O crystals grown on a clean copper surface. However, the surface of an electropolished copper film may be contaminated with some materials which act catalytically and thus Cu₄O crystals seem to be formed instead of Cu₂O.

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