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TRANSFORMATIONS IN THIN FOILS OF CUPROUS OXIDE AS OBSERVED IN AN ELECTRON MICROSCOPE

L. TERTIAN, D. HOKIM and J. P. RIVIÈRE
Laboratoire de Physique des Matériaux, C.N.R.S. Bellevue, 92190 Meudon, France

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Résumé. — En examinant dans un microscope électronique conventionnel des lames minces monocristallines de Cu2O orientées (001) et (011) on a observé, dans certaines conditions d’irradiation, soit la formation de précipités de cuivre en épitaxie sur Cu2O soit une transformation partielle en CuO polycristallin sans orientation préférentielle. Ces transformations sont interprétées comme résultant d’un échauffement local sous le faisceau d’électrons, dû à la faible conductibilité thermique de l’échantillon.

Abstract. — Investigating (001) and (011) oriented monocrystalline thin foils of Cu2O in a conventional electron microscope enabled us to observe, depending on the irradiation conditions, either the formation of Cu precipitates oriented on Cu2O, or a partial transformation into polycrystalline unoriented CuO. These transformations are interpreted as the result of a local heating under the electron beam, caused by the low thermal conductivity of the sample.

1. Introduction. — When investigating thin foils of various oxides by means of a transmission electron microscope (TEM), transformations induced by the electron beam have been reported by several authors. Thus, Das and Mitchell [1] examining thin foils of quartz observed either the appearing of black spots and dislocation loops or a crystalline-to-amorphous transition; this electron irradiation damage was studied as a function of the accelerating voltage from 50 to 650 kV. Shimomura et al. [2] observed the decomposition of nickel oxide under a 100 kV electron beam and studied the orientation relationships between the Ni precipitates and NiO in (001) oriented flakes of NiO. Kuzel, Cann and Weichmann [3] investigating thin foils of cuprous oxide Cu2O characterized crystalline copper precipitates but did not consider the relation to the electron beam. Martinez-Clemente and Schmidt-Whitley [4] while examining (111) oriented thin foils of Cu2O detected the presence of Cu and CuO precipitates in the Cu2O matrix and regarded them as the result of the eutectoid decomposition of Cu2O, which takes place below 375 °C [5]. Finally, Barrio et al. [6] observed the presence of Cu precipitates in thin samples of Cu2O that had been subjected (before examining in a TEM) to a 700 keV a-radiation beam, at temperatures ranging from 200 to 800 °C.

The present work concerns the study of monocrystalline, (001) and (011) oriented, thin foils of cuprous oxide Cu2O which were irradiated in a TEM under various conditions. The selected areas, chosen close to a hole, were initially transparent, homogeneous and well oriented and provided, before irradiation, an electron microdiffraction pattern of pure Cu2O. We observed that depending on the irradiation conditions, transformations took place under the electron beam and that Cu spots or CuO rings appeared on the corresponding microdiffraction patterns.

Consequently, a systematic study was made and our purpose here is to specify the experimental factors that determine the irradiation level of the selected areas, then to report results from numerous experiments and suggest an interpretation of the observed facts.

2. Experimental. — 2.1 Specimen Preparation. — Samples were cut from Cu2O monocrystalline bars (grown from copper of 99.999 % purity) normally to the growth axis (100) or (110); then they were mechanically thinned down to 0.1 mm. Some of the samples were subsequently thinned through ion bombardment in a « IMMI » apparatus by two 8 kV argon ion beams impinging on the two faces of the foil under a 30° incidence angle (with respect to the surface of the specimen) for 5 to 6 hours and then under a 10° angle until a hole appeared in the centre of the foil. Other specimens were chemically thinned in a (10 % NO3H + 90 % PO4H3) bath and then subjected to a shorter ion bombardment (incidence 10°) in order to clean up the surfaces. The thinned samples were deposited on large mesh copper grids.
2.2 Irradiation parameters. — The specimens were studied by using a « Jeol 100 C » microscope and the following parameters varied in order to modify irradiation intensities:

a) The accelerating voltage could be adjusted to 100, 80, 60 or 40 kV.

b) The current in the electron gun. — For each voltage \( V \), the intensity \( I_0 \) as provided by the high voltage without heating the filament as well as the saturation intensity \( I_s \) can be read on a microammeter. Varying the wehnelt bias allows to alter \( I_s \) and then the gun current which is proportional to \( (I_s - I_0) \). Samples were irradiated with the following sets of conditions:

\[
\begin{array}{ccc}
V & I_0 & I_s \\
100\, kV & 70\, \mu A & 85, 90, 100\, \mu A \\
& 120 and 140\, \mu A \, (for \, short \, times) \\
80\, kV & 80, 55, 50\, \mu A & \\
60\, kV & 50-40, 50\, \mu A & \\
40\, kV & 25-30, 40\, \mu A & \\
\end{array}
\]

c) The excitation of the first condenser. — When the electron beam is focused on the sample by means of the second condenser, the lens current in the first condenser, selected by one of the three spot size positions SS 1 to 3 acts mainly on the size of the illuminated area; but it does not substantially change the electron current density on the sample. In fact, in SS 2 and SS 3 the second condenser is used to enlarge the illuminated area so that the current density and consequently the irradiation of the sample decreases from SS 1 to SS 3.

d) The condenser lens aperture (\( \varnothing_c \)). — This aperture can be either inserted (on) or removed (off). In the second case the electron flux is much larger and, for identical conditions of focus, the current density on the sample is strongly increased (see § 4).

The parameters b, c, d allow to change in a gradual way the irradiation level which mainly depends on the current density on the sample and varies in the same way. In our microscope we cannot measure the current density directly but we have been able to estimate it in a microscope of same model in which we could measure the electron flux impinging on the fluorescent screen. The measurements have been made in two particular cases reported in the discussion.

The vacuum in the microscope was about \( 10^{-5} \) torr so that the partial pressure of oxygen was likely not very different from \( 2 \times 10^{-6} \) torr.

3. Results. — The transformations we observed in our thin samples of \( \text{Cu}_2\text{O} \) are reported in table I, schematically, as a function of the experimental parameters. The following points must be emphasized:

1) Under a heavy irradiation (for example with 100 kV, 100 \( \mu A \), SS 1 and \( \varnothing_c \) off) we have always recognized a very quick precipitation of copper and the formation, within a few seconds, of monocrystalline areas that are particularly large along the edge of the foil. With initially (001) oriented samples Cu is very often oriented on \( \text{Cu}_2\text{O} \) with the epitaxial relationships:

\[ (001)_{\text{CuO}}//\langle001\rangle_{\text{Cu}_2\text{O}} \text{ and } [100]_{\text{Cu}}//[100]_{\text{Cu}_2\text{O}} \text{.} \]

### Table I

Transformations of \( \text{Cu}_2\text{O} \) depending on the irradiation conditions

<table>
<thead>
<tr>
<th>( \varnothing_c ) ((\text{On}))</th>
<th>100 kV</th>
<th>80 kV</th>
<th>60 kV</th>
<th>40 kV</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>85-90 ( \mu A )</td>
<td>100 ( \mu A )</td>
<td>120-140 ( \mu A )</td>
<td>70 ( \mu A )</td>
</tr>
<tr>
<td>1</td>
<td>Cu (immed.)</td>
<td>Cu (immed.)</td>
<td>Cu</td>
<td>Cu</td>
</tr>
<tr>
<td>2</td>
<td>Cu or nothing or CuO</td>
<td>Cu or nothing or CuO</td>
<td>CuO</td>
<td>CuO</td>
</tr>
<tr>
<td>3</td>
<td>nothing</td>
<td>nothing</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>Cu (1 h) or nothing or CuO (1 h)</td>
<td>Cu (1/2 h-1 h) or nothing</td>
<td>Cu (a few seconds) or nothing</td>
<td>CuO or nothing</td>
</tr>
<tr>
<td>2</td>
<td>nothing or CuO (1 h)</td>
<td>nothing</td>
<td>Cu (a few seconds)</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>nothing</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
Figure 1a, b shows the electron micrograph of a selected area before irradiation with only very small defects likely caused by the thinning method, and the associated microdiffraction pattern of (001) oriented pure Cu$_2$O. Figure 2a shows, after a few second irradiation, the presence of Cu precipitates in Cu$_2$O; on the corresponding diffraction pattern (Fig. 2b) we can see not only (001) spots of Cu and Cu$_2$O but also {111} twin spots in Cu as well as double diffraction spots between both crystalline lattices of Cu and Cu$_2$O.

Let us recall that Cu crystallises in f.c.c. system ($a = 3.60$ Å) and that in Cu$_2$O the copper atoms are at the nodes of a f.c.c. lattice ($a = 4.25$ Å) while the oxygen atoms are inserted at the nodes of a b.c.c. lattice with the same parameter.

When Cu is not oriented on Cu$_2$O, then the crystallites are generally fairly large and give rise to dotted rings on the microdiffraction patterns. It can happen that in some limited areas the transformation into Cu is complete so that Cu$_2$O is no longer visible on the patterns.

2) Under a lower irradiation (for example with 100 kV, 100 μA, SS 1 and $\varnothing_s$ on), copper generally appears in a gradual way, sometimes after about half an hour or even one hour. Then the transformation is only partial and sometimes does not occur at all. By increasing the gun current or removing $\varnothing_s$ a quicker precipitation of Cu can be obtained.

3) Under a moderate irradiation (for example with 80 kV, 70 μA and either SS 1 and $\varnothing_s$ on or SS 2 and...
(\(\varnothing_e\) off) copper does not appear. Sometimes nothing occurs after one hour or more and sometimes very small precipitates appear after 30 to 45 minutes, while the main rings of unoriented polycrystalline cupric oxide CuO become visible on the microdiffraction pattern. Figure 3a shows a selected area after one hour irradiation and figure 3b the corresponding diffraction pattern with the initial spots of (001) Cu\(_2\)O and the characteristic rings of monoclinic CuO (\(a = 4.68\) Å, \(b = 3.42\) Å, \(c = 5.13\) Å, \(\beta = 99^\circ 28'\)). We noticed that CuO is not very stable and we were able to see its rings appear and then disappear in the course of the experiment, though we did not change anything as to the irradiation conditions. Commuting to heavy irradiation conditions when CuO has become visible always caused CuO to vanish and Cu to appear.

FIG. 3. — After about one hour under moderate irradiation : a) Very small precipitates of CuO in Cu\(_2\)O matrix ; b) Corresponding (80 kV) diffraction pattern : (001) Cu\(_2\)O spots and unoriented CuO rings.

4) As shown by table I, no transformation at all was observed under low irradiation (for example with SS 3 and \(\varnothing_e\) off, or with SS 2 and \(\varnothing_e\) on) even after two hour irradiation.

5) Finally, it is important to point out that in our experiments we were never allowed to characterize a simultaneous presence of Cu and CuO in the Cu\(_2\)O matrix.

4. Discussion. — The above mentioned formation of crystalline copper in Cu\(_2\)O foils and the precipitation of crystalline nickel in NiO flakes as observed by Shimomura [2] appear as very similar phenomena, likely induced by the electron beam. On the contrary, we cannot interpret our results as a consequence of the eutectoid decomposition of Cu\(_2\)O [5] since we never detected Cu and CuO simultaneously. Moreover this decomposition is questioned by Yund and Kullerud [7] whose experiments have shown the stability of Cu\(_2\)O far below 375 °C.

If we consider the Cu-O diagram (Fig. 4) drawn by Schmidt-Whitley et al. [8] after O’Keeffe and W. J. Moore [9] as a function of temperature \(T\) and oxygen pressure \(P(0_2)\), our results can be qualitatively explained as a consequence of a local temperature increase as caused by the electron beam passing through an insulating material, this increase depending on the irradiation level.

With \(P(0_2) \approx 2 \times 10^{-6}\) torr, at room temperature the kinetics of transformation of Cu\(_2\)O to CuO is frozen. No transformation is to be expected when the irradiation level is too low to accelerate the kinetics; with a moderate irradiation, if the temperature reaches about 500 °C, the equilibrium reaction :

\[
\text{Cu}_2\text{O} + \frac{1}{2} \text{O}_2 \leftrightarrow 2 \text{CuO}
\]
could explain the partial and unstable formation of CuO and, with a higher irradiation level, liable to increase the temperature up to about 800 °C or more, the decomposition of Cu₂O with copper precipitation can be expected. An estimate has been made in order to appreciate the possibility of reaching such a high temperature. Since the thermal conductivity of ceramics is low, we suppose that we can neglect the thermal losses by conductivity especially when the illuminated area is large and situated on the edge of the sample.

We can then write that the energy absorbed in the sample i.e. :

\[ dW_s = \Delta V \cdot i \cdot dS \]

is mainly radiated by the two faces of the foil according to the Stefan law :

\[ dW_r = 2 \cdot \sigma \cdot T^4 \cdot dS \]

where \( \Delta V \) (in volts) corresponds to the energy lost by an electron within the sample,

\[ i = \text{the current density through the sample, in nA} \mu \text{m}^{-2}, \]

\[ \sigma = \text{(Stefan-Boltzmann constant) = 5.67 \times 10^{-8} W \text{ m}^{-2} \text{ K}^{-4}}, \]

\[ T = \text{the absolute temperature being reached}. \]

Thus, when \( T \) reaches 1 100-1 200 K, the energy lost by thermal radiation is about \( 20 \times 10^{-8} \text{ W/μm}^2 \). Supposing \( \Delta V = 10 \text{ V} \), it should be necessary in order to compensate this energy loss, to irradiate the specimen with a current density \( i \) of about 20 nA/μm². In fact, in SS 1 position, \( i \) as measured with \( \varnothing_e \text{ on} \) was 28 nA/μm² and with \( \varnothing_e \text{ off} \) 1 800 nA/μm². In the latter case such a high value can explain the rapid precipitation of copper we always observed.

5. Conclusion. — Cuprous oxide Cu₂O is probably a material as sensitive to irradiation as alkali halides [10] and SiO₂ [1] are; its non-compact lattice suggests rather low displacement energies (a few electron-volts) with a maximum of 4 eV and 15 eV respectively transferred to copper and oxygen in a 100 keV electron beam. Ionization may also be important in Cu₂O, which is a semiconductor with complicated electronic behaviour [11]. These two mechanisms may be important at lower current densities.

However, the preceding estimation suggests that, at higher current densities our results can be qualitatively interpreted as a consequence of a local heating of the sample under the electron beam. We cannot propose a quantitative interpretation because in these experiments, it is very difficult to know the temperature actually reached under various current densities. Moreover, many factors, namely the initial treatments, thinning method, purity and shape of the sample are liable to alter the reproducibility of the results.

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References