Study of Cuprous Oxide formed in Air at 0.5 mm of Hg between 200° C and 1030° C and its rectification

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Oxides of copper formed at an air pressure 0.5 mm of Hg in the temperature range 200° C to 1030° C and for a time of formation of one hour have been studied. Their composition structure by the method of electron diffraction and X-ray reflection, rectification, and magnetic susceptibility — all these as a function of the subsequent heat treatment and the thickness of the film — have been investigated. The films formed at 500° C just begin to show rectification, it becomes appreciable at 800° C and then increases rapidly with the temperature of formation of the film. The rectifying films are all Cu_2O films but with a peculiar structure. The appearance of an appreciable amount of rectification is accompanied by changes in the surface structure, body structure and the susceptibility of the films. For a rectifying film the surface layer consists of large Cu_2O crystals showing 111 orientation. Below this small crystallites of Cu_2O, including an excess of oxygen, and showing a zinc blende structure, are present. The effect of the subsequent heat treatment is to reduce the amount of oxygen and increase the diamagnetic susceptibility. A maximum rectification is obtained, when the Cu_2O crystallites are fairly small and contain on an average an excess of one atom of oxygen per crystallite. A plausible mechanism for the changes is suggested.

We have already reported the properties of oxides of copper formed at atmospheric pressure[1] and also at low pressures[2]. In the present work the oxides of copper formed at an air pressure 0.5 mm of Hg in the temperature range 200° C to 1030° C and for a time of formation of one hour have been studied. Their composition structure by the method of electron diffraction and X-ray reflection, rectification and magnetic susceptibility – all these as a function of the subsequent heat treatment and the thickness of the film – have been investigated.

Experimental and Results

The copper blocks (except those used for magnetic susceptibility measurements) were prepared and oxidised at a given temperature in the same manner as described earlier[2]. In the first series the oxide was formed by keeping the block at a temperature of 1030° C for 60 minutes in air at a pressure of 0.5 mm of Hg. The blocks of oxide so formed were subsequently cooled in vacuum from 1030° C to 200° C in different intervals of time; and their resistances R_1 and R_2 in the two directions and rectification was determined (see Fig. 1 and 2). In the second series of experiments the oxide

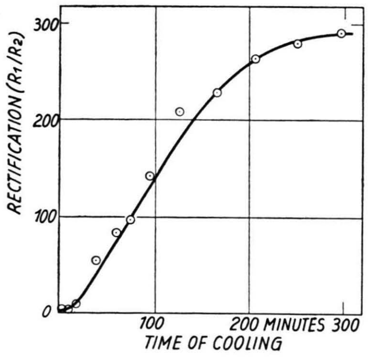

Fig. 1. Shows the manner in which the rectification R_1/R_2 changes as a function of the time of cooling in the temperature range 1030° C to 200° C.

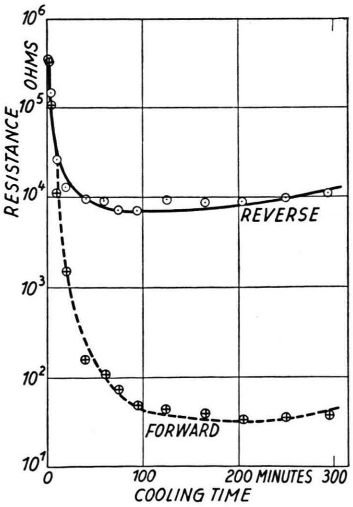

Fig. 2. Shows the manner in which the resistances R_1 and R_2 measured at 1.5 volts (D.C.) change as a function of the time of cooling in the temperature range 1030° C to 200° C.

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[1] K. R. Dixit and V. V. Agashe, Z. Naturforschg. **10 a**, 152 [1955].

[2] K. R. Dixit and V. V. Agashe, Z. Naturforschg. **11 a**, 41 [1956].

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was formed on blocks kept at various temperatures in the range 200° C to 1030° C, and at each temperature air at a pressure of 0.5 mm of Hg was allowed to remain in contact with the blocks for 60 minutes. The oxide blocks formed at each temperature were divided into two groups. One group was suddenly cooled (500° C/min) and the other was slowly cooled (10° C per min) in vacuum. The resistance, rectification, the growth of oxide and its crystal structure (by the method of weighing on a microbalance combined with electron reflection) was determined as before. This time the structure of the films was studied in addition by X-ray reflection. For comparison X-ray photographs of chemically pure Cu_2O were also taken. The results are shown in Tab. 1 and 2. The average rectifier formed at 1030° C is about 90 microns thick. The manner in which its structure changes with depth is shown in Tab. 3.

The magnetic susceptibility was determined by a Guoy balance, with an accuracy in weight determination of 0.01 mg. The rods were rectangular cylinders (75 mm × 5 mm × 4 mm) prepared by melting electrolytic copper in vacuum. The oxide layer was formed on these rods at the given temperature, pressure and time. The oxide formed on the two smallest faces and the surface in contact with the holder was removed. The oxide block so prepared, with the oxide layer on three faces, was weighed with and without the magnetic field (6500 Gauss). The oxide film present on the three faces was now removed by slow etching with sodium cynide. The copper rod (without the oxide film) was also weighed with and without the magnetic field. These four weights, together with the linear dimensions of the block, enable us to determine the weight of the oxide film and its susceptibility. Further if we assume that the film contains Cu_2O and traces of oxygen in solid solution and that the susceptibility of the solid solution is the sum of the susceptibilities[3] of the two components. It will be possible for us to calculate the amount of oxygen present per 100 molecules of Cu_2O (vide Fig. 4).

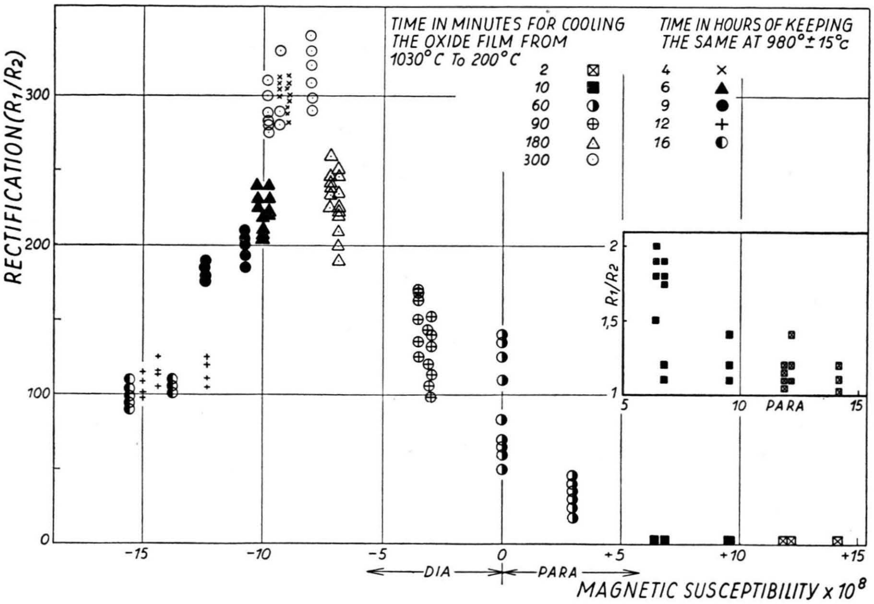

Fig. 3. Shows the relation between the magnetic susceptibility and the rectification for the Cu_2O films prepared at 1030° C followed by different heat treatments.

The susceptibility measurements were carried out with the two series of oxides already mentioned. In addition they were carried out with blocks prepared at 1030° C, 0.5 mm Hg air pressure and 60 minutes but subjected to subsequent heat treatment. The oxide layer was cooled from 1030° C to 980° C in 18 minutes, it was then kept at this temperature 980° C for various intervals of time (4, 6, 9, 12, 16 and 36 hours); it was subsequently cooled from 980° C to 200° C in 282 minutes. This procedure enabled us to have films with a reduced content of oxygen, increased diamagnetic susceptibility (see Fig. 3 and 4). Fig. 3 shows that the suddenly cooled films are paramagnetic. Heat treatment in the form of slow cooling ejects oxygen atoms making the film less and less paramagnetic and that the maximum rectification (about 300) occurs in a given range of diamagnetic susceptibility (about minus 11 to $7 \cdot 10^{-8}$) or a given oxygen content.

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[3] W. Klemm and W. Schüth, Z. Anorg. Chem. **203**, 104 [1932].

Temp. °C	Weight of oxide films in mg	Thickness of oxide films in microns	Resistance of oxide films at 1.5 volts D.C.				Electron Reflection		X-ray Reflection Suddenly and slowly cooled Cu_2O
			Suddenly cooled		Slowly cooled		Topmost layer of suddenly cooled Cu_2O	At a depth of 1000 Å for both, suddenly and slowly cooled Cu_2O	
			R_1	R_1/R_2	R_1	R_1/R_2			
200	0.015	0.025	—	—	—	—	(110)	—	—
250	0.035	0.058	—	—	—	—	(110)	—	—
300	0.075	0.125	—	—	—	—	(110 & Traces of 111)	—	—
350	0.186	0.310	9	1	9	1	(110 & 111)	—	—
400	0.277	0.462	12	1	12	1	(110 & 111)	—	—
500	0.877	1.46	25	1	22	1.37	(110 & 111)	Normal Cu_2O rings (F.C.)	—
550	1.58	2.63	30	1	25	1.25	(110 & 111)	Normal Cu_2O rings (F.C.)	—
600	2.55	4.25	110	1.57	37	1.37	Traces of orientation	Normal Cu_2O rings (F.C.)	Normal Cu_2O
650	6.015	10.0	400	2	52	1.53	(111) and spots on rings	Normal Cu_2O rings (F.C.)	Normal Cu_2O
700	8.5	14.2	2000	1.19	80	2.1	,,	222 broad & very strong at centre	Normal Cu_2O
800	14.52	24.2	10000	2	400	10.8	,,	222 broad & very strong at centre	200 weak
900	19.22	32.0	42000	1.4	1250	30.5	,,	4 arc pattern	220 stronger & 200 nearly absent
950	26.69	44.5	72000	1.3	3360	54.2	Weak (111) & strong spots on rings	4 arc pattern	,,
1000	38.65	64.4	100000	1.1	6600	75	,,	4 arc pattern	,,
1030	55.69	92.8	150000	1.1	8080	94	,,	4 arc pattern	,,

($h\ k\ l$) denote preferred orientation h, k, l.

Table 1. Properties of the oxide formed in air at a pressure of 0.5 mm of Hg for 60 minutes.

Specimen	Treatment	Intensity of X-ray reflection							Resistance		
		110	111	200	211	220	311	222	R_1 ohms	R_2 ohms	R_1/R_2
Pure Cu_2O Tablet	Prepared with a little gum tragacanth	20	100	61	(<5)	32	25	5	—	—	—
Cu_2O formed at 550° C	Slowly cooled in vacuum	20	100	60	(<5)	31	25	5	22	11	2
700° C	Slowly cooled in vacuum	20	100	61	(<5)	33	26	3	80	38	2.1
900° C	Slowly cooled in vacuum	15	100	(<5)	(<5)	50	30	5	1250	42	30.5
1030° C	Slowly cooled in vacuum	13	100	(<5)	8	50	35	(<5)	6600	88	75
1030° C	*Suddenly* cooled in vacuum	20	100	(<5)	8	50	35	(<5)	($\sim 10^5$)	(10^5)	1.1
Diamond	A. W. Hull, Phys. Rev., **10,** 66 [1917]	0	100	0.5	0	50	40	0			
Zinc blende	W. Gerlach, Phys. Z. **23,** 114 [1922]	0	V, S	W	0	S	S	W			

Table 2. The relative changes in X-ray reflection intensities.

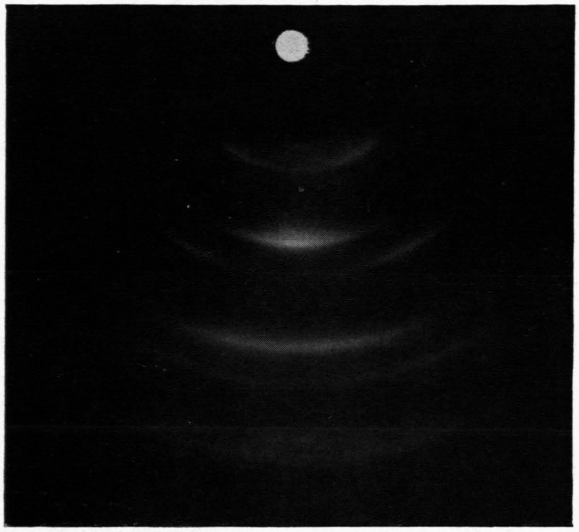

Fig. 5. Shows oriented rings of Cu_2O with 110 orientation. The rings strong at the centre are $\sqrt{2}$ (near the shadow edge), $\sqrt{8}$ and $\sqrt{18}$.

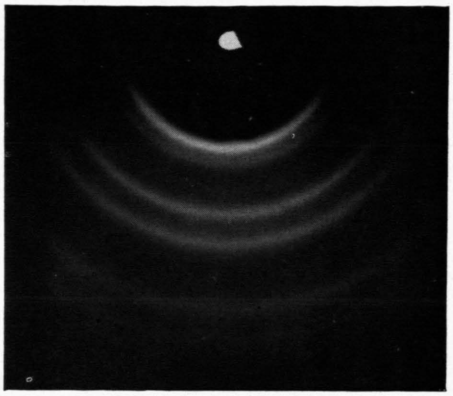

Fig. 7. Shows the rings of normal Cu_2O. They give the impression of a face centred configuration. The following rings are seen. $\sqrt{3}$, $\sqrt{4}$, $\sqrt{8}$, $\sqrt{11}$ $\sqrt{12}$, $\sqrt{19}$ $\sqrt{20}$ and $\sqrt{24}$.

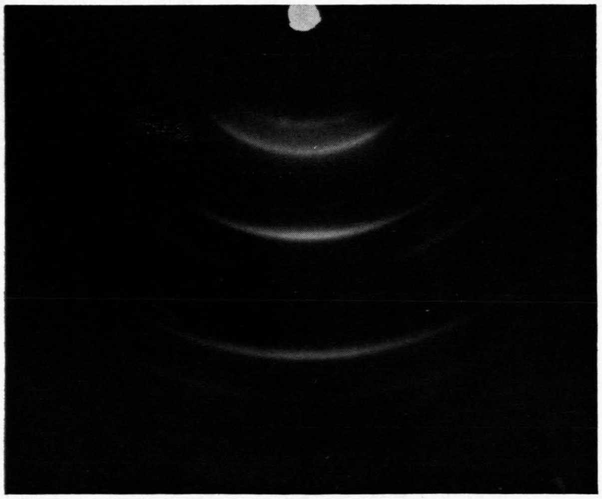

Fig. 6. Shows oriented rings of Cu_2O with a double orientation 110 and 111. The rings strong at the centre are $\sqrt{2}$, $\sqrt{3}$, $\sqrt{8}$ and $\sqrt{18}$.

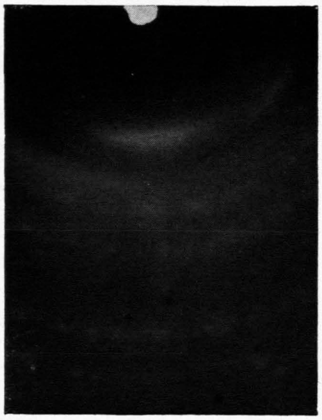

Fig. 8. Shows rings of Cu_2O with spots on them. The signs of 111 orientation ($\sqrt{3}$ strong at the centre and $\sqrt{4}$ weak at the centre) are still there.

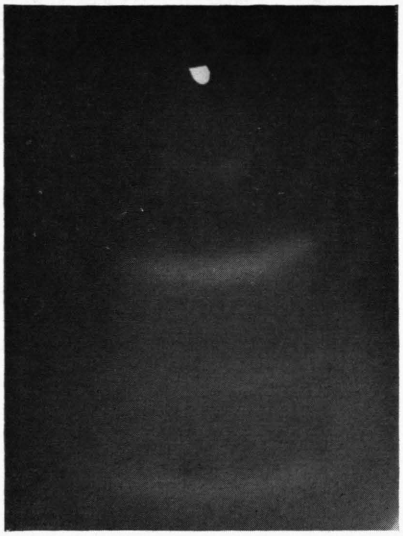

Fig. 9. Shows the four arc pattern, which approximately corresponds (vide Tab. 4) to 111, 222, 333 and 444 arcs of Cu_2O.

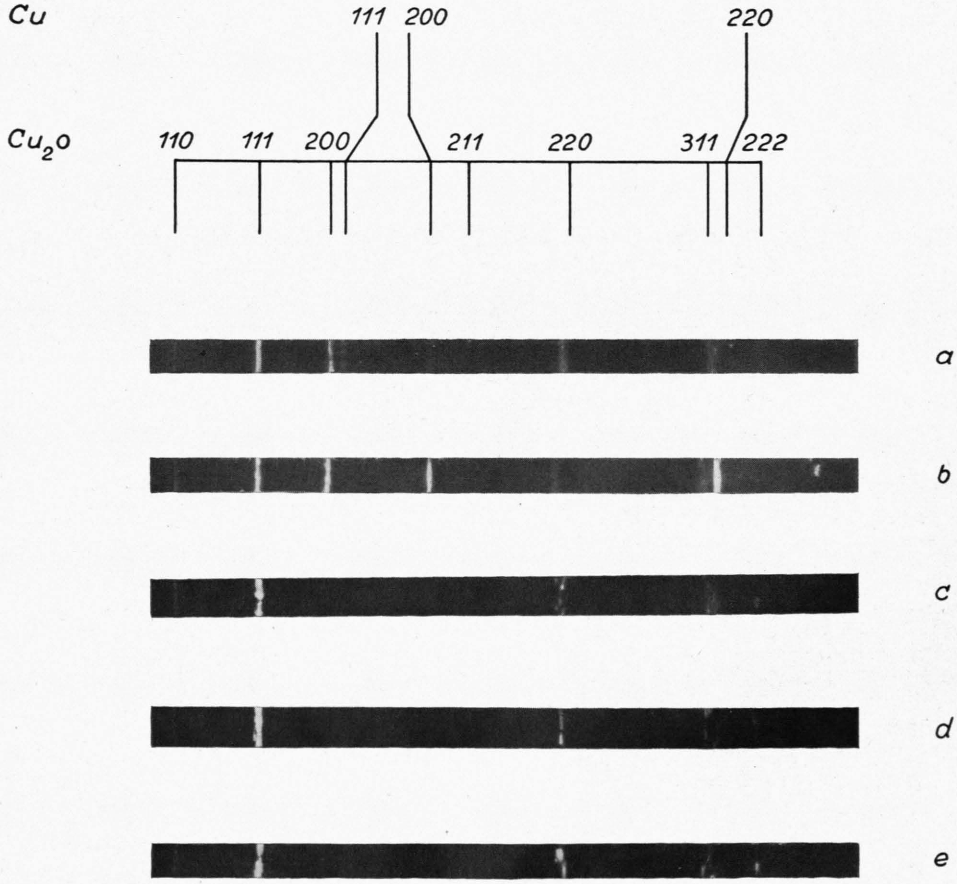

Fig. 10. Shows X-ray reflection from: (a) Cu_2O powder with small copper impurity. (b) Cu_2O film formed at 700° C, 0.5 mm Hg air pressure and slowly cooled. (c) Cu_2O film formed at 900° C at the same pressure and slowly cooled. (d) Cu_2O film formed at 1030° C at the same pressure and slowly cooled. (e) Cu_2O film formed at 1030° C at the same pressure but suddenly cooled.

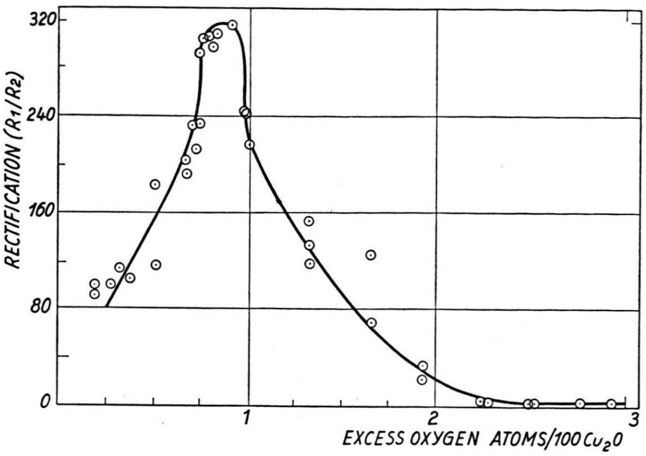

Fig. 4. Shows the relation between the rectification and the percentage excess of oxygen atoms present for all films in Fig. 3.

Discussion

It will be seen from Tab. 1 and 2, that the films formed at 500° C just begin to show rectification, it becomes appreciable at 800° C and then increases rapidly with the temperature of formation of the film. The rectifying films are all Cu_2O films but with a peculiar structure. The appearance of an appreciable amount of rectification is accompanied by changes in the surface structure and the body structure of the film. For a rectifying film the surface layer consists of large Cu_2O crystals showing 111 orientation. Below this small crystallites of Cu_2O including an excess of oxygen and showing a zinc blende structure are present. The changes in structure are indicated in the X-ray picture by an increase in the intensity of the 220 ring and a decrease in the intensity of the 200 ring. In the arrangement used by us 311 and 222 are rather broad and these lines do not definitely tell us whether the change in intensity is due to a change in the orientation or structure. This was settled by taking a few back reflection photographs, and studying rings of higher orders like $\sqrt{24}$, $\sqrt{27}$. They show that the change in the intensity is due to a change in the crystal structure. The electron reflection from the surface of the film shows oriented rings of Cu_2O with 111 orientation and spots. The electron picture of the layer at a depth of 1000 Å (and lower) shows four broad rings which are really arcs, 30° wide and strong at the centre (Fig. 9) *. This indicates (Tab. 4 and 5) that a large number of small crystallites of Cu_2O are so oriented that the 111 face is parallel to the substrate. Normally with such an orientation (111 of Cu_2O) many other rings are

Depth from the free surface in microns	Electron reflection pattern
0.0	No pattern
0.1	No pattern
1.0	The 222 arc of the four arc pattern visible
5.0	The four arc pattern
25.0	—do—
50.0	—do—
60.0	Four arc pattern but 222 strong and others weak
75.0	The 222 arc of the four arc pattern only
80.0	222 arc and elongated spots on normal Cu_2O rings
85.0	—do—
88.0	222 arc not visible, rings of Cu and normal Cu_2O with elongated spots on normal Cu_2O
90.0	Rings of Cu and normal Cu_2O but with elongated spots on Cu and not on Cu_2O

Table 3. The changes of crystal structure with depth for a cuprous oxide rectifier film formed at 1030° C, and *slowly cooled*. Film thickness about 90 microns. The table gives average values from 7 films.

Arc No.	Intensity	*d* in Å observed	Comparable values for normal Cu_2O			
			h	*k*	*l*	*d* in A
1	30	2.4 ± 0.08	1	1	1	2.47
2	100	1.26 ± 0.05	2	2	2	1.24
3	10	0.8 ± 0.03	3	3	3	0.82
4	20	0.6 ± 0.03	4	4	4	0.618

Table 4. The intensities and the '*d*' spacings of the four arc pattern.

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* Fig. 5, 6, 7, 8, 9, 10 on p. 98 a, b.

Nature of the post oxide treatment	R_1/R_2	Width of 2nd arc in the 4 arc pattern in mm	Average thickness τ of a crystallite in Å $\tau = \lambda L/W$
Suddenly cooled 1030° C–200° C/2 min	1.1	1.8 ± 0.1	11.7 ± 0.7
Slowly cooled 1030° C–200° C/75 min	95	1.6 ± 0.1	13.1 ± 0.8
Very slowly cooled 1030° C–200° C/300 min	290	1.4 ± 0.1	15.0 ± 1.0
Stored for 16 hours at 980° C and slowly cooled	104	1.5 ± 0.1	14.0 ± 0.9
Stored for 36 hours at 980° C and slowly cooled	25	1.7 ± 0.1	12.5 ± 0.7

Table 5. The average size of a crystallite in a film formed at 1030° C calculated from the formula given by A. R. STOKES and A. K. WILSON, Proc. Camb. Phil. Soc. **38**, 313 [1942].

seen (Fig. 4, Ref 2). In this case we do not see any other rings or the arrangement is a single crystal arrangement in two dimensions but not in the third. Such a pseudo single crystal structure or a layer structure tends to exhibit effects of surface reflection (RAETHER [4], DIXIT [5]) and also of multiple reflection (EHLERS [6], GÖTTSCHE [7]) of the electron beam. In the present case surface reflection makes the 222 ring broad and intense and the multiple reflection alters the intensity of the outer rings 333 and 444. Thus both, the X-ray pictures (directly) and the electron pictures (indirectly) show that the structure of the rectifying crystallites of Cu_2O is of the zinc blende type. Such a result is not entirely unexpected in the light of the work of WELKER [8] and of HOFFMANN and ROSE [9].

From Fig. 4 we note that at maximum rectification about 1 oxygen atom is associated with about 120 ± 25 molecules of Cu_2O. Assuming that these molecules are arranged in a small cube, the size of the cube comes out as 4 cell lengths of Cu_2O or about 17 Å. This is comparable with the average size of the crystallite deduced from the four arc pattern (Tab. 5). The actual number of oxygen atoms associated with a crystallite will be always integral. If we assume that the average size of our small Cu_2O crystallites present in the films is 17 Å and if we plot the average number of oxygen atoms associated with such a crystallite as a function of its rectification we get a curve very much similar to the curve in Fig. 4. Such a curve shows that maximum rectification occurs when the amount of oxygen associated with a crystallite is about one atom (1.0 ± 0.2).

Mechanism of the formation of the Rectifying Layers

When a block of copper heated to a sufficiently high temperature, is exposed to oxygen at low pressures (partial pressure of oxygen about 0.1 mm of Hg), we observe (Tab. 1) that a sort of instability sets in, in the crystallites of Cu_2O formed on the surface, either in the form of a change of orientation (up to 550° C) or in the form of an increase in the size of the crystallites (above 550° C). We assume as before [1] that such an instability will enable oxygen atoms or ions to diffuse through the interspaces between the crystallites of Cu_2O. This diffusion results in a layer of oxygen being formed below these oriented crystals of Cu_2O. Once such a layer of oxygen is produced it leads to the formation (according to the migration theory of MOTT and CABRERA [10]) of new crystallites of Cu_2O below the surface. If these new crystallites grow directly on the oriented crystals, we could expect from the laws of epitaxial growth that they have the same structure and orientation. The new crystals, however, are growing on a thin layer of oxygen formed on the oriented crystals of Cu_2O. The new crystals, therefore, have the same size, the same orientation, but have a few more oxygen atoms (about 3 per crystallite) virtually incorporated in the 111 system of planes. The 111 system of planes in Cu_2O includes copper and oxygen atoms in alternate planes and thus permits the inclusion of a few more oxygen or less copper atoms in this system of planes. This inclusion of a few more oxygen atoms in the 111 planes of a Cu_2O crystal changes its structure to that of the zinc blende type. During the process of annealing the oxygen gas dissolved in the film is gradually ejected out. This reduces the average number of oxygen atoms associated with a crystallite. The association

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[4] H. RAETHER, Z. Phys. **78**, 527 [1932].

[5] K. R. DIXIT, Phil. Mag. **16**, 980 [1933].

[6] H. EHLERS, Z. Phys. **136**, 379 [1953].

[7] H. GÖTTSCHE, Z. Naturforschg. **11 a**, 55 [1956].

[8] H. WELKER, Z. Naturforschg. **7a**, 744 [1952]; **8a**, 248 [1953].

[9] A. HOFFMANN and F. ROSE, Z. Phys. **136**, 152 [1953].

[10] N. CABRERA and N. F. MOTT, Rep. Progr. Phys. Vol. XII, 163, London 1949.

of one oxygen atom (of course as an average) with a crystallite gives maximum rectification. A further reduction in the amount of oxygen reduces rectification, till we reach the stage of zero oxygen. The substance is no longer a rectifier and the crystal structure of Cu_2O (as shown by electrons) reverts back from the zinc blende to the normal pattern. The signs of this reversal of crystal structure are seen in specimens annealed for 36 hours. They show the 4 arc pattern and also some prominent rings of normal Cu_2O viz $\sqrt{4}$, $\sqrt{8}$ and $\sqrt{19}$ $\sqrt{20}$.

The rate of formation of this undergrowth will depend on the velocity of migration of Cu ions (which in its turn depends on the temperature of the copper block) and the velocity of diffusion of oxygen ions (which for a given surface and air pressure will remain constant). At comparatively low temperatures, because of the low velocity of migration of the Cu ions, they may be able to penetrate through a thin layer of undergrowth and approach the oxygen layer but they may not be able to penetrate through a thicker layer. At this stage the Cu ions do not migrate any further, but the oxygen atoms continue to diffuse through the surface whose thickness has not changed. This results in an accumulation of oxygen below the surface film and make it unstable and peel off. This is what we observe at 410° C (Tab. 6). At ** 750° C the velocity of migration of Cu ions becomes appreciable, they are practically able to penetrate through all thicknesses of undergrowth normally observed and the surface does not peel off.

Temperature of formation °C	Wt. in mg	Thickness in microns
410	1.6	2,6
500	2.3	3.9
550	3.6	6.0
600	5.0	8.3
650	6.8	11.3
700	45.0	75.0
750	86.0 (does not peel off)	143.3

Table 6. Weight and thickness of the oxide film (formed at 0.5 mm of Hg air pressure) which peels off.

One of us (V. V. A.) thanks the National Institute of Sciences of India, for the award of a fellowship, during the course of which this work was done.

** It is interesting to note that this is approximately the temperature at which rectification becomes appreciable. Details of this work on peeling off will be published separately.