PRODUCTION AND INVESTIGATION OF THIN FILMS OF Cu_2O

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The electron diffraction study of films of Cu_2O is of interest in two respects: in connection with the study of the oxidation processes of copper, which are important for technology, and also in connection with the determination of the values of the lattice potential. These data are utilized in contemporary semiconductor theory. Cuprous oxide is a prototype of the cubic structure C3: space group $Pn3m(O_h^4)$, Z = 2. With regard to the lattice period of Cu_2O, values from 4.235 to 4.290 A have been published. On the basis of a microscopic investigation of alloys (consisting of Cu_2O and Cu + Cu_2O), both cooled slowly and annealed at 300-350°C, it has been found that Cu_2O is unstable at a temperature below 375°C and decomposes according to

$$Cu_2O \rightarrow Cu + CuO.$$
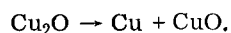
Electron diffraction studies of the oxidation processes of thin films of copper prepared by various methods and on various supports have been carried out by a number of authors [1-4]. It was found that in the heat treatment of copper films (pressure 760 mm Hg) in the range from 50° to 275°C, Cu_2O was formed, although this phase is unstable in macrospecimens at a temperature above 125°C. When the annealing temperature was increased to 300-500°C, the electron diffraction patterns of corresponding films, in addition to CuO rings, showed a CuO' ring, a previously unknown phase [1, 2]. The authors of [3, 4] suppose that CuO' crystallizes with a sphalerite structure. At a temperature above 600°C, it becomes CuO. The author of [1, 2] concludes from this that CuO' is a metastable phase, for which a monoclinic structure with the periods a = 4.653, b = 3.410, c = 5.108 and β = 99°29' has been found. In the investigation of thin copper layers heated to 410°C under a pressure of 0.5-0.75 mm Hg, the authors of [3, 4] also obtained layers of a different structure.

In our work, thin films of Cu_2O for electron diffraction studies were produced by two methods: 1) Vaporization of a copper wire in a vacuum (10^{-4} mm Hg) followed by condensation on freshly cleaved surfaces of rock salt, which were then placed in a thermostat and heated at different temperatures; 2) vaporization of a copper wire under the same conditions, but heating was at a pressure of the order of 0.5 mm Hg and temperature of 200°C for 2 h (these films were cooled in a high vacuum).

The electron diffraction patterns, obtained by the first method with an annealing temperature of 125°C for 10 min, corresponded to Cu_2O + Cu. When the annealing period was increased, pure cuprous oxide was formed (annealing for 25 min), the rings became sharper but were still rather diffuse.

Electron diffraction patterns were also obtained for films annealed at 160-170°C. Annealing for 20 min led to the formation of Cu_2O; when the duration of annealing was increased, the electron diffraction patterns from the corresponding films showed reflections from both Cu_2O and CuO. Under these conditions, the rings were also diffuse. Furthermore, distant reflections were absent, although it has been indicated [5] that the lattice period of Cu_2O varies (from 4.235 to 4.255 A), depending on the annealing conditions; we were unable to confirm this from the electron diffraction patterns we obtained. It is possible that broadening of the diffraction rings is due not only to the small size of the Cu_2O crystals, but also to scatter of the lattice period in them.

The electron diffraction patterns from films produced by annealing the latter at a pressure of 0.5 mm Hg and a temperature of 200°C for 2 h corresponded to polycrystalline specimens. The rings on these diffraction patterns were fairly sharp; the

Theoretical and Experimental Values of Φ (in Volts)

hkl	$\dfrac{\sin \vartheta}{\lambda}$	a) 100% of the oxygen		b) 70% of the oxygen	
		$\Phi_{calc.}$	$\Phi_{exp.}$	$\Phi_{calc.}$	$\Phi_{exp.}$
110	0.1667	—1.89	—1.24	—1.27	—1.26
111	0.2036	9.46	9.80	9.50	10.25
200	0.2352	6.75	6.20	7.26	7.00
211	0.2880	1.16	0.86	0.84	0.84
220	0.3320	6.20	6.55	5.96	5.85
310	0.3720	0.86	0.61	0.60	0.60
311	0.3900	4.11	4.11	4.07	4.05
222	0.4075	3.07	3.07	3.28	3.12
321	0.4400	—0.51	—0.43	—0.52	—0.44
400	0.4700	3.48	2.60	3.40	2.71
330	0.4990	—0.45	—0.34	—0.34	—0.35
411	0.4990	—0.45	—0.34	—0.34	—0.35
331	0.5130	2.46	2.46	2.46	2.54
420	0.5265	1.92	1.83	2.02	1.87
332	0.5510	0.38	0.25	0.26	0.25
422	0.5750	2.26	2.00	2.17	1.97
431	0.5960	0.31	0.21	0.22	0.21
510	0.5960	—0.31	—0.21	—0.22	—0.21
511	0.6100	1.66	1.65	1.64	1.60
333	0.6100	1.66	1.65	1.64	1.60
521	0.6420	0.25	0.16	0.19	0.16
440	0.6650	1.52	1.59	1.50	1.48
530	0.6850	0.21	0.25	0.15	0.14
433	0.6850	—0.21	—0.25	—0.15	—0.14
531	0.6975	1.18	1.28	1.19	1.31
600	0.7050	0.94	1.11	0.99	1.09
442	0.7050	0.94	1.11	0.99	1.09
620	0.7424	1.14	1.00	1.12	1.00
533	0.7750	0.84	0.89	0.85	0.90
622	0.7790	0.70	0.76	0.73	0.78
444	0.8100	0.85	0.84	0.80	0.86
640	0.8500	0.53	0.72	0.57	0.71
642	0.8800	0.65	0.52	0.62	0.52
731	0.9010	0.42	0.52	0.51	0.43
553	0.9010	0.42	0.52	0.51	0.43

interplanar distance of the last visible ring was d_{731} = 0.552 A. The lattice period as measured on these diffraction patterns was a = 4.250 ± 0.005 A. Short-exposure electron diffraction patterns were obtained for measuring the intensity of the rings. Microphotometer MF-4 was used for measuring the intensities, a photographic density curve being constructed. In many cases a qualitative estimate of uniform density of the ring was insufficient, and therefore the diffraction patterns were measured with the microphotometer also at an angle to the original. Comparison of the intensity of the rings measured on the photomicrographs for different directions showed good agreement.

Transition from intensities to structure amplitudes was effected in accordance with the formula $\Phi_{hkl}^{exp} = \sqrt{I_{hkl}/p d_{hkl}^2}$. The calculated values of Φ_{hkl} were multiplied by a temperature factor B = 1.3 A^2, obtained from the relationship B $= -1/2 (\sin \vartheta/\lambda)^{-2} \ln I_{hkl}^{exp}/_{hkl}^{calc}$. As the result of the comparison of Φ_{hkl}^{calc} and Φ_{hkl}^{exp}, the character

of the scattering was found to be partly dynamic. The divergence factor after introduction of the dynamic correction was R = 9.4% (table a). The values of Φ_{hkl}^{exp} obtained were used for constructing a Fourier synthesis in the [111] direction for calculating the character of the distribution of potential in the Cu$_2$O lattice. The maxima on the potential cross section had the following values: φ_{Cu}^{exp} = 795 V; φ_{O}^{exp} = 185 V. From this φ_{mean}, the potential of the lattice, was also obtained, being calculated according to [6].

In addition to calculating the Fourier series from the experimental amplitudes, the values of the potentials at the maximum points were also calculated according to the exact formula of [6]. In doing this, the same value of B was used, and the integration limits corresponded to the termination of the potential series in the experimental investigation. These calculations gave the following results: φ_{Cu}^{calc} = 790 V; φ_{O}^{calc} = 270 V. Comparison of φ^{calc} with φ^{exp} clearly shows that while the agreement for copper is good, for oxygen φ^{exp} is 70% of φ^{calc}. This difference cannot be due to ionization of the oxygen atoms, since scattering of electrons by the O^{2-} ion scarcely differs from scattering by neutral oxygen atoms.

Thus, the difference between φ_{O}^{calc} and φ_{O}^{exp} is evidently due to the partial displacement of the oxygen atoms from their positions.

Taking 70% of the oxygen atoms, we found 8.3% for R (table, b). We thus came to the conclusion that the compound Cu$_2$O is a defect phase.

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