

## 다결정 산화구리의 반도체성에 관한 연구

최 재 시 · 여 철 현  
연세대학교 이공대학 화학과  
(1971. 11. 10 접수)

## A Study of the Semiconductivity of Polycrystalline Cuprous Oxide

Jae Shi Choi and Chul Hyun Yo

Department of Chemistry, Yonsei University, Seoul, Korea

(Received Nov. 10, 1971)

**Abstract** The semiconductivity of polycrystalline  $\text{Cu}_2\text{O}$  has been studied between  $220^\circ\text{C}$  and  $680^\circ\text{C}$  under partial pressures of oxygen from  $4.06 \times 10^{-3}$  to  $10^{-5}$  mmHg. The plots of log conductivity vs  $1/T$  at constant oxygen pressure were found to be linear, and the activation energies obtained from the slopes of these plots above the first transition point showed that the energies were greater under high oxygen pressure than under low pressure. The transition points between the stable range and the unstable range of  $\text{Cu}_2\text{O}$  were found from the curves. The dependence of the semiconductivity on the  $\text{O}_2$  pressure, in the above temperature range, is shown hysteresis.

### Introduction

Cuprous oxide has been studied by several researchers and there are a number of published reports.<sup>1-5</sup> Despite the difficulty of securing large single crystals<sup>6</sup> of  $\text{Cu}_2\text{O}$ , these investigations involved the measurement of the conductivity of  $\text{Cu}_2\text{O}$  single crystals<sup>7-8</sup> in the temperature range from  $500$  to  $1100^\circ\text{C}$  under oxygen pressures from  $50$  mmHg to  $10^{-5}$  mmHg. This limited the research to the stable range of  $\text{Cu}_2\text{O}$ . The stability diagram shown in Fig. 1 was consulted to choose the range of temperatures and  $\text{O}_2$  pressures.

In this research polycrystalline  $\text{Cu}_2\text{O}$  was used, with measurements carried out in the temperature range from  $220^\circ\text{C}$  to  $680^\circ\text{C}$  under oxygen

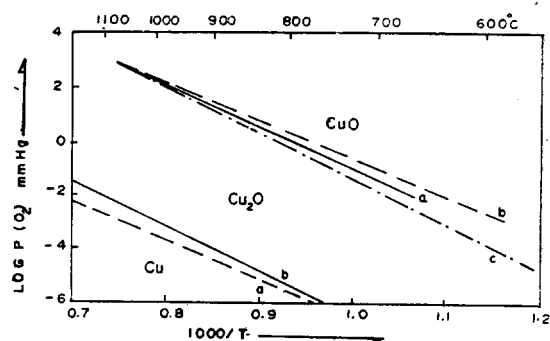


Fig. 1. Temperature dependence of the oxygen equilibrium pressure in the system  $\text{Cu}/\text{Cu}_2\text{O}/\text{CuO}$ ; (a) Gundermann, Hauffe, and Wagner (b) quoted by Engelhard and (c) after Hauffe, as quoted by Böttger.

pressures from  $4.06 \times 10^{-3}$  to  $10^{-5}$  mmHg, thus covering parts of both the stable and unstable ranges of  $\text{Cu}_2\text{O}$  near the transition points between

$\text{Cu}_2\text{O}$  and  $\text{CuO}$ . Semiconductors<sup>9-10</sup> are generally classified as *n*-type whose current carriers are electrons and *p*-type whose carriers are positive holes. In general, the conductivity of a *p*-type semiconductor increases with increasing  $\text{O}_2$  pressure. The samples used in this study were pure polycrystalline  $\text{Cu}_2\text{O}$  which is a *p*-type semiconductors due to the positive holes on the excess oxygen. However the conductivity of  $\text{Cu}_2\text{O}$  does not always increase with increasing  $\text{O}_2$  pressure because the  $\text{Cu}_2\text{O}$  may be in the unstable range under some  $\text{O}_2$  pressures. In this case, one of the main factors affecting the conductivity is the phase transition of the  $\text{Cu}_2\text{O}$  from the stable range to  $\text{CuO}$  in the  $\text{Cu}_2\text{O}$  unstable range. The transition points and the activation energies obtained from the slopes of

the plot of log conductivity vs  $1/T$  are discussed in this paper.

### Experiment

A. Sample preparation and electrical contacts. Specpure Cu rod refined by the Johnson-Matthey Co. was used for the sample preparation. Before annealing, the Cu rod was cut to a rectangular shape, polished with abrasive paper (No. 1000), and then etched in dil.  $\text{HNO}_3$  solution. The Cu was preannealed at  $800^\circ\text{C}$  under air pressure for 350 hours. After the preannealing, the remaining Cu was removed and the  $\text{Cu}_2\text{O}$  reannealed at  $800^\circ\text{C}$  for 24 hours. Thus, the samples were pure polycrystalline  $\text{Cu}_2\text{O}$ . Pt leads were connected to the sample

Table 1. Conductivity (or  $\sigma$ ) at various temperatures. ( $1.2 \times 10^{-2}$  mmHg oxygen pressure)

Temp.	10000/T	Amp.	Volt	$\sigma(\text{ohm}^{-1} \text{Cm}^{-1})$
260	1.8762	$3.00 \times 10^{-5}$	0.32483	$4.61781 \times 10^{-4}$
280	1.8083	$6.00 \times 10^{-5}$	0.39800	$7.53769 \times 10^{-4}$
300	1.7452	$9.00 \times 10^{-5}$	0.49237	$9.13947 \times 10^{-4}$
320	1.6863	$1.15 \times 10^{-4}$	0.52800	$1.08902 \times 10^{-3}$
340	1.6313	$1.60 \times 10^{-4}$	0.52284	$1.53010 \times 10^{-3}$
360	1.5798	$2.00 \times 10^{-4}$	0.53376	$1.87350 \times 10^{-3}$
380	1.5314	$2.45 \times 10^{-4}$	0.52672	$2.32571 \times 10^{-3}$
400	1.4859	$3.00 \times 10^{-4}$	0.51292	$2.92443 \times 10^{-3}$
420	1.4430	$4.00 \times 10^{-4}$	0.45100	$4.43459 \times 10^{-3}$
440	1.4025	$4.70 \times 10^{-4}$	0.42280	$5.55818 \times 10^{-3}$
460	1.3643	$5.50 \times 10^{-4}$	0.39852	$6.90053 \times 10^{-3}$
480	1.3280	$7.00 \times 10^{-4}$	0.35216	$9.93866 \times 10^{-3}$
500	1.2937	$8.40 \times 10^{-4}$	0.32602	$1.28826 \times 10^{-2}$
520	1.2610	$1.15 \times 10^{-3}$	0.31765	$1.81017 \times 10^{-2}$
540	1.2300	$1.05 \times 10^{-3}$	0.17480	$3.00343 \times 10^{-2}$
560	1.2005	$1.05 \times 10^{-3}$	0.16335	$3.21396 \times 10^{-2}$
580	1.1723	$1.05 \times 10^{-3}$	0.12320	$4.26137 \times 10^{-2}$
600	1.1455	$1.06 \times 10^{-3}$	0.08530	$6.21335 \times 10^{-2}$
620	1.1198	$9.50 \times 10^{-4}$	0.05242	$8.89180 \times 10^{-2}$
640	1.0953	$1.00 \times 10^{-3}$	0.04405	$1.13507 \times 10^{-1}$
660	1.0718	$1.00 \times 10^{-3}$	0.02253	$1.53563 \times 10^{-1}$
680	1.0493	$1.00 \times 10^{-3}$	0.02320	$2.15517 \times 10^{-1}$

after it was polished, etched, washed and dried. The four leads winding method<sup>11-13</sup> was used in this measurement. The sample size and the distances between the leads were determined by reading microscope.

#### B. Furnace assembly and vacuum system.

The schematic drawing of the furnace assembly and vacuum system was reported in the earlier paper.<sup>(14)</sup> The vycore sample container was connected to the vacuum system by a glass joint to provide easy access to the sample and contacts. This connection also contained a stopcock

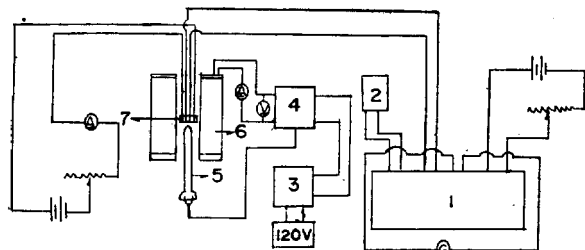


Fig. 2. Schematic drawing of the measurement circuit.

1. Leeds and Northrup K-2 potentiometer
2. Standard cell
3. Powerstat
4. Temp. controller
5. Thermocouple
6. Electrical Furnace
7. Sample

so that the desired pressure could be maintained. Temperature control of the sample was possible by moving the furnace up or down with a jack. The temperature at the sample position was determined from a calibration curve between the sample position temperature and the temperature shown on temperature controller data for which was initially obtained using a Pt-Rh thermocouple. The low oxygen pressure down to  $10^{-5}$  mmHg was obtained with a Cenco Hyvac fore pump and CEC GF-20A oil diffusion pump.

**C. Measurement circuit** As shown in Fig. 2 the two inner leads from the sample were connected to a Leeds and Northrup K-2 Potentiometer to measure the voltage and the outer two leads to an ammeter to check the D.C. current. The sensitivity of the galvanometer

was  $0.005 \mu\text{a/mm}$ .

**D. Experimental procedure** Under controlled conditions of temperature and pressure, the sample was annealed for 2 hours. Then, as the temperature was gradually raised or lowered, current-voltage measurements were made at intervals of  $20^\circ\text{C}$ ; with these data, the conductivity of the sample was calculated using the known distances between contacts and the cross sectional area of the sample. Measurements were made on a total of 5 samples, and a typical set of results at constant oxygen pressure of  $1.2 \times 10^{-2}$  mmHg is shown in Table 1. The results of measurements for a given condition were similar for all samples.

#### Results and discussion

Readings on the samples were taken over a complete cycle of the temperature range for a given  $\text{O}_2$  pressure starting from the high tem-

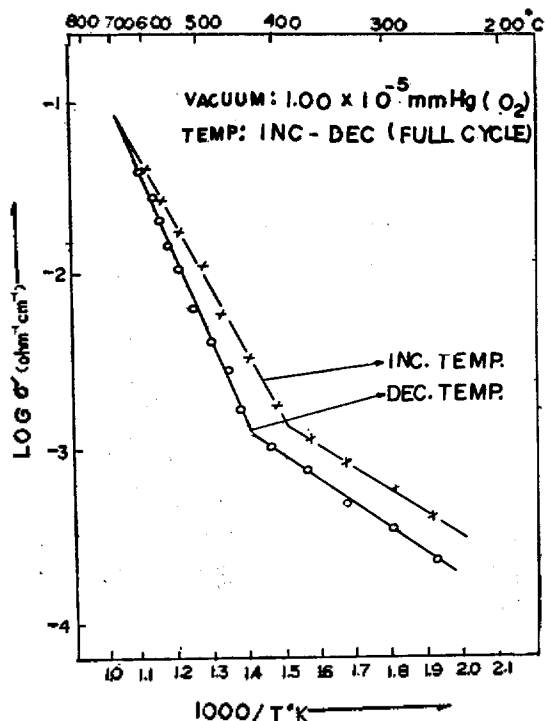
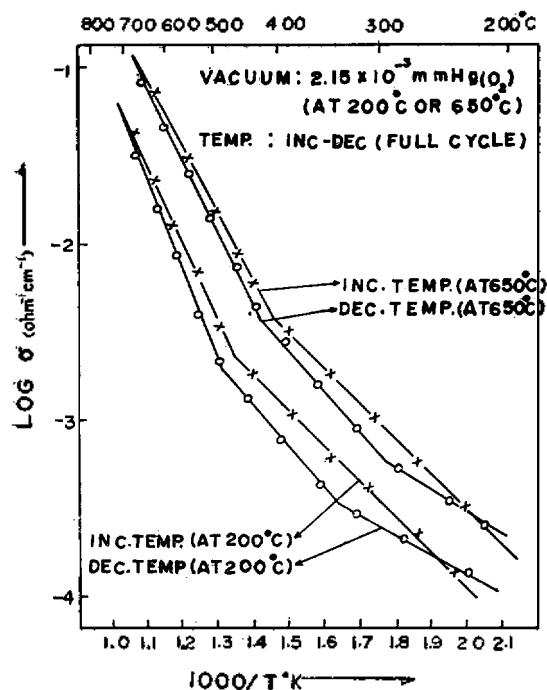
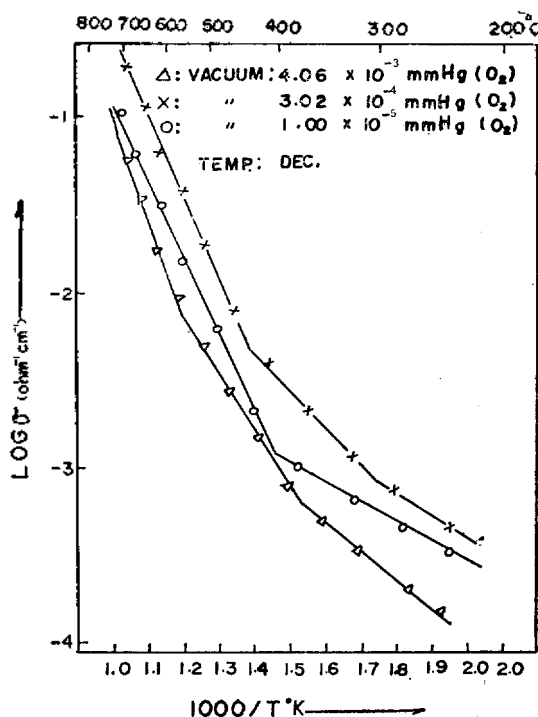


Fig. 3.  $\text{LOG } \sigma$  vs  $1/T$

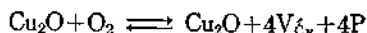
Fig. 4.  $\text{Log } \sigma$  vs  $1/T$ 

perature and, proceeding toward the low end, and then back to the high temperature. As shown in Fig. 3, the conductivity with increasing temperature was higher than those with decreasing temperature for a given temperature. This tendency is obvious in the lower temperature region, and negligible above 650°C. This could be explained on the basis that temperature or oxygen pressure equilibrium of the sample was established more easily in the higher temperature regions. There is some additional concern over the validity of the curves at  $\text{O}_2$  pressures lower than  $10^{-4}$  mmHg due to the Knudsen effect. Since the sample is at a high temperature while the ionization gauge reading the pressure is at room temperature, a correction for the  $\text{O}_2$  pressure should be made for each experimental point. However, the points shown were plotted without applying the Knudsen correction since it was felt that the variation in the conductivity due to the changing temperature

far outweighed any change due to the changing  $\text{O}_2$  pressure caused by the changing temperature. Measurements made with an oxygen pressure of  $2.15 \times 10^{-3}$  mmHg and sample temperature of 200°C and 650°C respectively are shown in Fig. 4. From these data it can be concluded that with conversion to the same temperature the former would be at a higher oxygen pressure. From a theoretical view, the conductivity of p-type semiconductors such as  $\text{Cu}_2\text{O}$  should be larger at higher oxygen pressures, but in this temperature range, the data does not obey the theory. It can be seen that Knudsen effect are negligible and one of the main factor affecting the conductivity of the  $\text{Cu}_2\text{O}$  is not the oxygen pressure but whether the sample is in the stable range or not. In the case of Fig. 5, the conductivity change due to oxygen pressures does not follow Wagner and Hammen's theory<sup>(15)</sup>. Wagner and Hammen were the first to

Fig. 5.  $\text{Log } \sigma$  vs  $1/T$

postulate an equilibrium between the  $O_2$  and solid  $Cu_2O$  of the form



where  $V_{Cu}$  represents a Cu ion vacancy and  $p$  represents a positive hole. They obtained the relation  $P^3 = k_{ox}P(O_2)$ . They then assumed that the conductivity was due primarily to hole conduction and arrived at the relation

$$\sigma = k_{ox}[P(O_2)]^{1/3}$$

However, the experimental work by Wagner and coworker<sup>16</sup> showed that  $\sigma$  varied with  $P(O_2)$  to the  $1/7$  power. Our data obtained on the polycrystalline  $Cu_2O$  under the special condition does not support the work of Wagner. It shows that the conductivity changes depend

largely on the condition in which the sample is in the stable range or not rather than  $O_2$  pressure. At  $10^{-5}$  mmHg  $O_2$  pressure only one transition point appears in the log conductivity vs  $1/T$  plot, while at pressures above  $10^{-4}$  mmHg, two points appear. Comparison of the  $Cu_2O$  stable range diagram with the above results shows that at oxygen pressures above  $10^{-4}$  mmHg a  $Cu_2O$ - $CuO$  equilibrium is established between the two transition points but that at oxygen pressures below  $10^{-4}$  mmHg only the transition from  $Cu_2O$  to  $CuO$  due to oxygen deficiency appears. The transition points are lined up with the phase diagram (Fig. 1) and therefore, we can extend the stability curve with conductivity data below  $600^\circ C$ .

The activation energies, calculated from the

Table 2. activation energy at various conditions

Condition	$O_2$ pressure	$E_{act.1}$	T. P. — I	$E_{act.2}$	T. P. — II	$E_{act.3}$
Increasing Temperature	$4.06 \times 10^{-3}$	25.17Kcal/mole (1.09ev)	553.45° C	10.40Kcal/mole (0.45ev)	613.50° C	8.32Kcal/mole (0.36ev)
	$1.21 \times 10^{-3}$	24.23 (1.05 " )	546.67° C	16.02 (0.70 " )	389.25° C	8.08 (0.35 " )
	$1.00 \times 10^{-5}$	14.67 (0.64 " )	402.68° C	5.95 (0.26 " )	—	—
Decreasing Temperature	$4.06 \times 10^{-4}$	22.31 (0.97 " )	550.05° C	14.68 (0.64 " )	372.16° C	7.32 (0.31 " )
	$3.02 \times 10^{-4}$	21.05 (0.91 " )	446.42° C	10.04 (0.44 " )	305.03° C	6.20 (0.22 " )
	$1.00 \times 10^{-5}$	19.83 (0.86 " )	411.93° C	5.16 (0.22 " )	—	—

slopes of the log conductivity vs  $1/T$  curves are listed in Table 2. The activation<sup>17-18</sup> energy is the summation of the vacancy formation energy and the counter-migration energy of the electron. The activation energies increase with increasing oxygen pressures at temperatures above the first transition point, though in other temperature ranges there are some irregularities. As the sensitivity of the Galvanometer used was not adequate for measurements below  $220^\circ C$ ,

it was impossible to check the conductivity at low temperatures.

#### Acknowledgment.

This work was supported by the Graduate School of Yonsei University.

## References

1. H. K. Henisch: "Rectifying Semiconductor Contact" pp. 88-94. Oxford University Press, London, (1957).
2. G. F. J. Garlick: "Handbuch der Physik", Vol., XIX, pp. 377-80 Springer-Verlag, Berlin, (1956).
3. J. S. Anderson and N. N. Greenwood: *Proc. Roy. Soc., (London)*, pp. 215, 353, (1952).
4. Z. Haskin and S. Shtrikman: *The Physical Review*, 130, 129 (1963).
5. John Wiley and Sons: "Semiconductor Abstracts Battelle Memorial Institute", New York (1954-1959).
6. R. S. Toth, R. Kilkson, and D. Tribich: *The Physical Review*, 122, 482 (1961).
7. R. S. Toth, R. Kilkson, and D. Tribich: *J. Appl. Phys.*, 31, 117 (1960).
8. Tomoyasu Nakano: Japan, *J. Appl. Phys.*, 3, 124 (1964).
9. N. B. Hannay: "Semiconductors", p. 1, Reinhold Publishing Corporation, New York (1958).
10. W. E. Garner: "Chemistry of the Solid State", p. 123, (1955) Academic Press Inc., New York.
11. L. B. Valdes: "Proceeding of the IRE", 42, 420 (1954).
12. P. Nagels, J. Devreese, and M. Denayer: *J. Appl. Phys.*, 35, 1175 (1964).
13. L. J. Vander Pauw: *Philips Res. Rept.*, 13, 1 (1958).
14. Jae Shi Choi and Chul Hyun Yo: *JKCS* 12, Number 2, pp. 39 (1967).
15. C. Wagner and H. Hammen: *Z. Physik, Chem.*, 40, 197 (1938).
16. J. Gundermann, K. Kauffe, and C. Wagner: *Z. Physik. Chem.*, 37, 148 (1937).
17. K. Stecker: *Ann. Physik*, 3, 55 (1959).
18. C. Boettger: *Ann. Physik*, 10, 232 (1952).