Reversible Transformation between Cu_2O and CuO by Ambient Gas Heat Treatment

Norimichi Tamura** and Junji Shirafuji*

Abstract

Cu_2O and CuO are typical p-type semiconducting oxides and thus promising for gas sensors. However, heat-treatment necessary for sintering Cu_2O powder into porous thick films in air changes Cu_2O to CuO. As a result, it is not possible to prepare Cu_2O sensors. To this connection the reversible transformation between Cu_2O and CuO is examined. It turns out that CuO can be brought back to Cu_2O by holding CuO in an ambient of ethanol-added air at 330 ℃ for 1 hr. However, the Cu_2O sample thus obtained is found to be rather insensitive to reductive gases. The CuO samples prepared by sintering Cu_2O in air are satisfactorily potential as p-type semiconducting oxide sensors.

1. Introduction

There exist two types of copper oxides, Cu_2O (cuprous oxide) and CuO (cupric oxide). Both are known as p-type semiconducting oxides in which acceptor states are originated from the presence of an excess of oxygen content over chemical stoichiometry. Particularly Cu_2O had been used to be a useful material for making rectifying devices. Because of their semiconducting nature Cu_2O and CuO are both to be potential materials for gas sensors.

However, CuO and Cu_2O show catalytic activity through oxidation reaction, during which the oxidation state of copper changes forward in a way Cu^{++} (CuO) → Cu^{+} (Cu_2O) → Cu^{0} (metallic Cu). This means that the charge states of copper can easily change irreversibly during the use of CuO or Cu_2O gas sensors for detecting reductive gases, introducing a difficulty of providing stable gas sensors of copper oxide materials.

In this article the changeable nature between Cu_2O and CuO is described in terms of the visual color, the temperature dependence of the electrical resistance and the valency change of copper by ESCA measurement.

---

* Department of Electrical and Electronic Engineering ** Graduate student

2. Samples and Experiments

Commercially available Cu_2O (red-colored) powder (the grain size was not specified) was mixed with a dilution agent (Tanaka Kikinzoku Kogyo Co. Ltd. TMC-10T) to obtain the Cu_2O paste. The Cu_2O paste was spread manually onto an aluminum substrate on which platinum/titanium interdigital electrodes were prepared by sputtering method, and then dried at 80 ℃ in the laboratory air. The dried Cu_2O layer was then fired at 700 ℃ for 1 hr in the laboratory air to form a porous sintered film. However, this sintering process in the atmospheric air rendered the color of the copper oxide from red into black, suggesting that the initial Cu_2O was changed to CuO in an excess oxygen partial pressure. Such change of Cu_2O into CuO during the sintering process at 700 ℃ in atmospheric air can be supported by the phase diagram shown in Fig. 1[1].

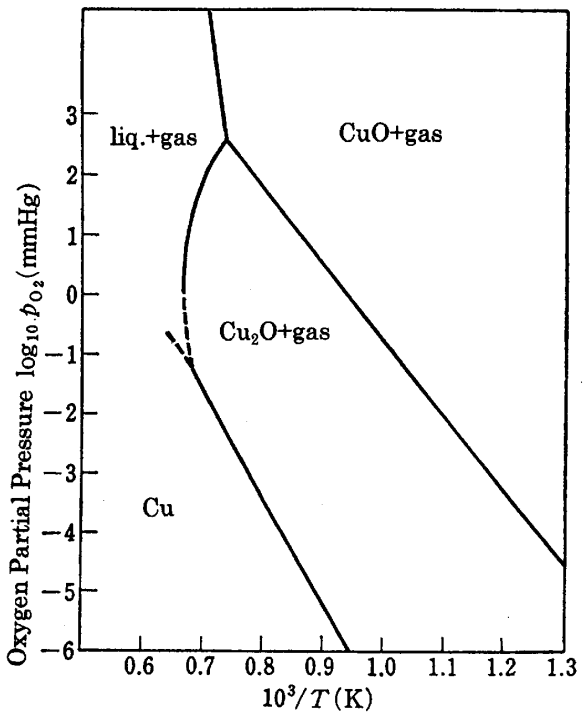

Fig. 1 Phase diagram between oxygen partial pressure and temperature.

The black-colored sample obtained after the sintering process on Cu_2O layer (called hereafter black-colored) was hold in a flowing nitrogen containing reductive gas (ethanol in this experiment) in order to check the possibility of returning CuO-like black-colored sample back to Cu_2O-like red-colored one. It was found that the color of the black-colored sample turned to red (called hereafter red-colored), suggesting the appearance of Cu_2O phase after the treatment in the flowing nitrogen with ethanol at 330 ℃.

In order to confirm the phase change from the CuO-like black-colored sample to the Cu_2O-like red-colored one, two samples (black- and red-colored) were prepared and their copper oxidation states (Cu^{++} or Cu^{+}) were examined in terms of chemical shift of Cu 2p spectra by ESCA method.

3. Results and Discussion

Figure 2 shows the ESCA spectra from Cu 2p state in black-colored and red-colored samples. It is suggested in Fig. 2 that the main peak of Cu 2p spectrum from the black-colored sample shows the chemical shift larger by about 0.5 eV than that of the red-colored sample; this means that Cu atoms in black-colored sample are doubly positively charged while those in red-colored sample are singly positively charged, in accordance with the phase of black-colored and red-colored samples to be CuO and Cu_2O, respectively.

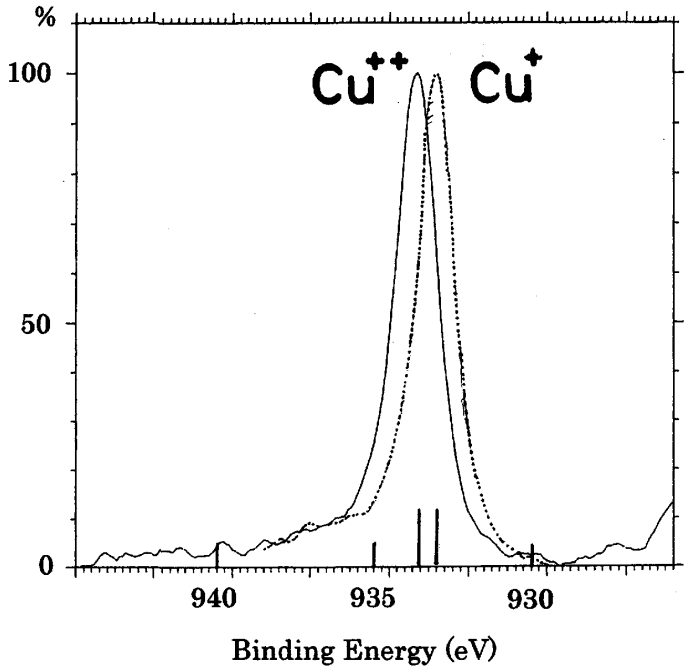

Fig. 2 ESCA spectra for red- colored (dotted line) and black-colored (solid line) samples.

For examining the semiconducting properties of the black- and red-colored samples, the temperature dependence of their electrical resistance was measured in flowing dry air for the black-colored sample and in flowing dry nitrogen for the red-colored one. The results are illustrated in Fig. 3 where the logarithmic resistance is plotted against the reciprocal temperature. The temperature dependence of the

resistance in the black-colored sample (open triangles) is an activation type typically in semiconducting oxide. The activation energy of about 0.3 eV can be estimated.

There are no data published on the activation energy of the resistivity and/or the resistance in CuO. However, it is supposed that the activation energy of 0.3 eV observed in the present experiment is related to the thermal excitation of holes from Cu vacancy-type (V_{Cu}) acceptors. In connection to this, it can be added that the activation energy of 0.3 eV of the resistivity in Cu_2O has been ascribed to the inonization energy of V_{Cu} acceptors[2].

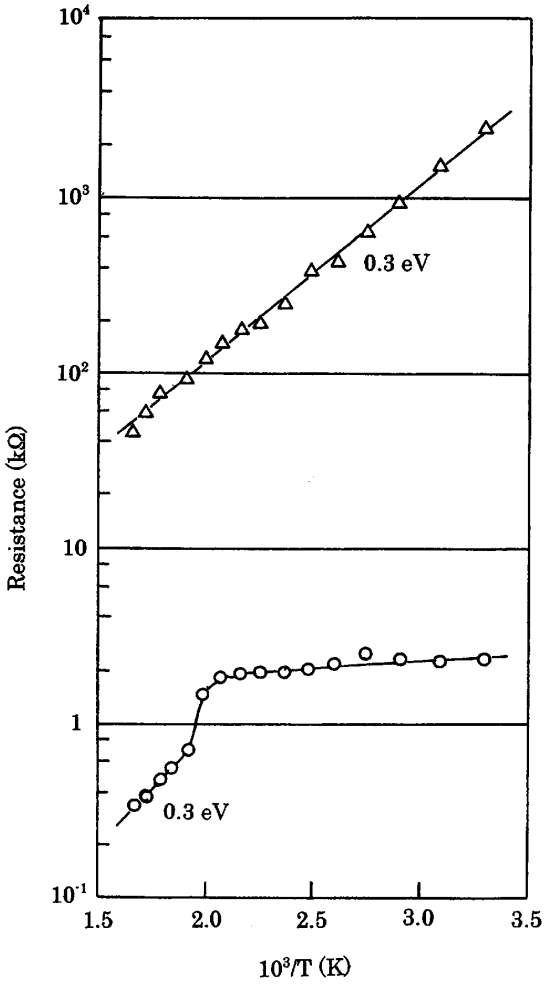

Fig. 3 Temperature dependence of sensor resistance in black-colored (triangles) and red-colored (circles) samples.

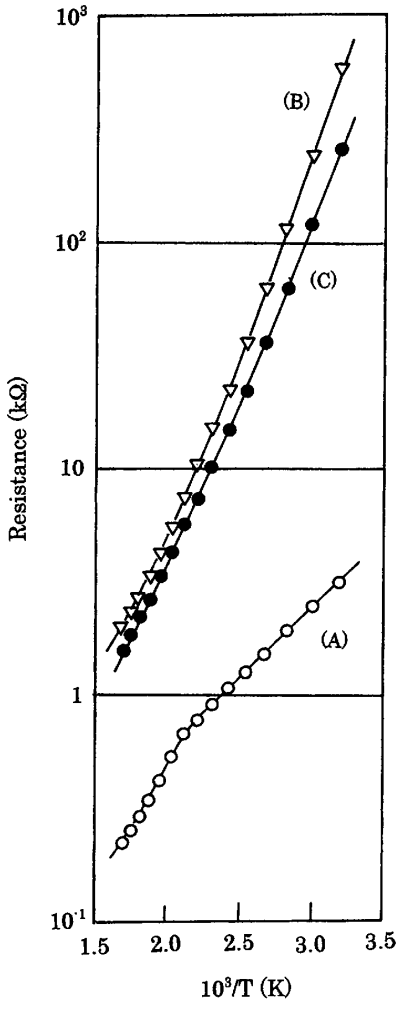

Fig. 4 Temperature dependence of sensor resistance for black-colored sample in dry air (A), in ethanol-added air (B) and in dry nitrogen (C).

On the other hand, the resistance of the red-colored sample (open circles) shown in Fig. 3 is relatively low in contrast to the expected value in semiconducting Cu_2O. At temperatures below 230 ℃ the resistance is nearly independent of temperature, while in the higher temperature range the resistance decreases with increasing temperature with an activation energy of about 0.3 eV. The rough estimation of the resistivity with reasonable assumption of the film thickness (100 μm) and the electrode length (10 mm) gives about $7x10^3$ Ωm at room temperature. This value can be compared with that reported so far[3]; the resistivity at room temperature in Cu_2O has been reported to be ranged from 10^7 to 10^3 Ωm depending on composition and/or surface condition[3]. The activation energy of 0.3 eV in the high temperature region as seen in Fig. 3 is associated with the ionization of holes from acceptor-type Cu^+ vacancies, which has been reported in crystalline Cu_2O[2].

The temperature dependence of the electrical resistance in a black-colored sample is shown in Fig. 4. These characteristics were measured for examining the stability and reproducibility of black-colored samples as odor sensors. The curve A was taken in flowing air, while the curve B was obtained when the black-colored sample was exposed to flowing air containing ethanol. The significant increase in the resistance in ethanol-added air (Curve B) over that in dry air (Curve A) suggests definitely the black-colored sample to be p-type. When the ambient gas was switched from ethanol-added air to dry nitrogen, the curve C very close to the curve B was measured. The parallel behavior between the curves B and C indicates that the black-colored samples are satisfactorily sensitive and stable as odor sensors.

On the contrary, the red-colored sample prepared by holding in ethanol environment showed no or faint sensitivity to ethanol suggesting poor potential for odor sensors. This may relate to the fact that the charge state of copper can easily proceeds in the series of CuO (Cu^{++}) → Cu_2O (Cu^+) → Cu^0 (metallic copper). The small fraction of metallic copper can be present in red-colored samples, which can cause such an insensitive nature to odor gases.

4. SUMMARY

The phase transformation between Cu_2O and CuO has been studied in terms of visual color, electrical resistance and ESCA spectrum. It turns out that :

(i) When Cu_2O-loaded substrate is sintered in dry air at 700 ℃ for 1 hr, the color of Cu_2O is changed into black suggesting that Cu_2O turns to CuO which is the stable phase in the sintering atmosphere.

(ii) ESCA study confirms that the charge state of copper in the black-colored

sample after the sintering is Cu^{++} while that in the red-colored sample after holding in ethanol environment corresponds to Cu^{+}.

(iii) The temperature dependence of the electrical resistance in the black-colored sample shows the activation energy of about 0.3 eV which is associated with V_{Cu} type acceptors.

(iv) The black-colored sample has sufficiently high sensitivity to ethanol. This suggests a potentiality of the black-colored samples to odor sensors.

(v) In contrast to the above, the red-colored sample which is obtained after holding in ethanol ambient at 330 ℃ does not show any significant response to ethanol.

References

1) M.O'Keefe and W.J.Moore, J. Chem. Phys. 36 (1962) 3009.
2) M.O'Keefe and W.J.Moore, J. Chem. Phys. 35 (1961) 1324.
3) K.Tabe, T.Seiyama and K.Fueki ed. "Metal Oxides and Complex Oxides" (Kodansha Scientific, 1978) p. 9 (in Japanese).

(Received December 11, 2003)