X-ray effects on the oxidation of Cu nanoparticles

Chun-Hua Chen [a,*], Kenji Koga [b,**]

[a] Department of Materials Science and Engineering, National Chiao Tung University 1001 Ta-Hsueh Road, Hsin-Chu, 30010, Taiwan, ROC
[b] Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

ARTICLE INFO

ABSTRACT

X rays have been widely used for nondestructive analysis of nano-scaled materials for a long time; however, the effects of x-ray radiation have been less extensively discussed. In this work, by means of the in-situ x-ray diffraction and the ex-situ high-resolution electron microscopy, we have quantitatively investigated the x-ray effect on the oxidation behavior of Cu nanoparticles prepared by the vapor condensation method. Clear evidence shows that the x-ray irradiation increases the oxidation thickness as well as the oxidation rate. The results are of critical importance not only for the oxidation studies but also for the nanomaterial researches with x-ray related equipment.

1. Introduction

X rays have been widely used for nondestructive analysis of materials for a long time. However, the effects of x-ray radiation on materials have been less extensively discussed in comparison with those of the high energy photons or particles, e.g., γ-rays or neutrons, which can give great damages in solids [1]. The most well known x-ray effect is the generation of color centers in a series of simple ionic solids [2] and also oxides [3]. Recent detailed investigations have found that some specific physical and chemical phenomena in materials are rather sensitive to the x-ray radiation. For instance, even a short exposure to low energy x rays such as AlK_α or MgK_α (generally used in x-ray photoelectron spectroscopy) induces changes in the oxidation rate and the oxide amount as well as in the energy states of oxides [4–6]. In this report, we found that the x-ray sources often used in the x-ray diffraction (XRD) experiments have a strong effect on the oxidation of Cu nanoparticles. Our results are of critical importance not only for oxidation studies but also for the nanomaterial researches with XRD.

2. Experimental procedures

The Cu nanoparticles with a mean size of ~22 nm were prepared employing a vapor condensation method under which a vapor from a high purity Cu ingot (99.9999%) melted at 1583 K is cooled with purified helium at 4 kPa. They were carried with a helium stream through a stainless tube and deposited on an MgO(100) substrate that was placed inside a vacuum chamber on an x-ray diffractometer. X rays from a Cu rotating anode at 45 kV and 300 mA were utilized as the radiation source for this experiment. The white x-ray beam passes through a carbon window of the chamber to irradiate the substrate surface fixed at a 2° grazing-incidence angle. The diffracted beam from the particles was monochromatized to CuK_α by a HOPG crystal before detection by a scintillation counter. In our previous works [7,8], the instrumental performance has been quantitatively verified.

Just after the deposition, the initial condition of the Cu nanoparticles was checked by an XRD scan under 10^{-4} Pa for ~1 h, that has proved less detectable level of the surface oxide. The specimen chamber was then filled with dry air up to 93 kPa to initiate the oxidation. After 50 h exposure without x-rays, we started a continuous irradiation of the x-ray beam during which we repeated XRD scans (~1 h per scan) for 60 h. The foregoing measurements were accomplished while keeping the specimen temperature at 298 K. The same procedure was also performed at 323 K.

For the high-resolution electron microscopy (HREM) observation, the Cu nanoparticles were deposited on two amorphous-carbon microgrids. In the same manner as the XRD experiment, two specimens maintained at 298 K were first oxidized at 93 kPa for 50 h without x rays. One specimen was then transferred to the microscope for the observation and afterward exposed to x rays at 93 kPa for another 50 h. Meanwhile, another specimen was kept under dry air at atmospheric pressure (101 kPa) for another 50 h without x rays. Finally, these two specimens were observed together with HREM. We used a JEOL JEM-2010 (LaB_6 filament) with a 0.194 nm point-to-point resolution.
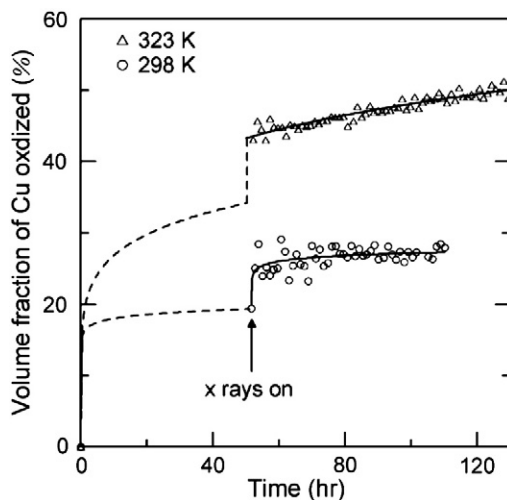
3. Results and discussion

Fig. 1 shows the volume fraction of the Cu oxide (Cu_2O) grown at 298 and 323 K as a function of the dry air exposure time at 93 kPa. The

* Corresponding author. Tel.: +886 35 131 287; fax: +886 35 724 727.
** Corresponding author. Tel.: +81 29 861 4875; fax: +81 29 861 6236.
E-mail addresses: ChunHuaChen@mail.nctu.edu.tw (C.-H. Chen), k.koga@aist.go.jp (K. Koga).

Fig. 1. The volume fractions of Cu_2O on the Cu nanoparticles at 298 and 323 K as a function of 93 kPa dry air exposure time. The x-ray diffraction measurements were started after the 50 h exposure. Note that it takes about 1 h to obtain a data point. The white x rays from a Cu rotating anode at 45 kV and 300 mA were employed as the radiation source.

Fig. 2(a) shows a partial HREM image of an icosahedral Cu nanoparticle that possesses only (111) surfaces. As clearly seen in this figure, the epitaxial growth [10] of Cu_2O(111) with a 0.25 nm lattice spacing on Cu(111) with a 0.209 nm spacing was also observed in our particles. We derived the oxide thickness distribution from HREM pictures of the particles oxidized at 93 kPa for 50 h without x rays, as shown in Fig. 2(b). The average oxide thickness obtained from Fig. 2(b) was 6.6 ML. We confirm no change in the thickness even after the additional 50 h exposure at 101 kPa, since the room-temperature oxidation of the Cu nanoparticles show the strong self-limiting behavior as revealed in our previous study [9].

Fig. 2(c) shows the thickness distribution of the particles in Fig. 2(b) after additional 50 h exposure at 93 kPa under x-ray irradiation. The average thickness was found to be 7.6 ML. It is clear that the presence of x rays leads to a 1 ML increase in the average thickness. Thus, we could confirm the x-ray irradiation effect also via the HREM observations. The estimated increase in the Cu_2O volume was ~20%, which is somewhat smaller than the observed value from XRD. Other researchers have also reported the great effects of photon irradiations on the oxidation of metals. For instance, Cabrera demonstrated an 80% increase (from ~2.5 nm to ~4.5 nm) in the oxide thickness of Al_2O_3 at room temperature after an exposure to UV for ~5 days [11]. X rays increase the dissolution rate of copper in KCN solution up to ~30% [12].

On the other hand, the oxidation of Cu nanoparticles at 323 K shows a non-self-limiting behavior described by a modified parabolic rate law [6]. However, as can be seen in Fig. 1, we could not find any drastic changes in this figure. Presumably, this change was too fast to be recorded by the present XRD scan. Here, we assumed the same rate of the irradiation effect at 298 K (i.e., a 40% increase) to draw a dashed line based on the modified parabolic rate law, as shown in Fig. 1. The oxidation of a spherical particle follows the following equation: $[1 + (z-1)x]^{2/3} + (z-1)(1-x)^{2/3} = z + 2(1-z)kt/r_0^2$ where z is the Cu_2O volume formed per unit Cu volume (1.64), x the fraction of oxidized

oxidation of Cu nanoparticles at 298 K shows a self-limiting behavior ruled by the direct-logarithmic law [9]. As can be seen in Fig. 1, the volume fraction of oxidized Cu at 298 K drastically increased from ~19% up to ~25% just after the ~1.5 h x-ray irradiation and then slowly increased to a saturated value of ~27% during the 60 h irradiation. The Cu_2O volume increase caused by the x-ray irradiation was estimated to be about 40%. The dashed line to connect the first and the second data points is drawn with the logarithmic rate equation found in our previous study [9].
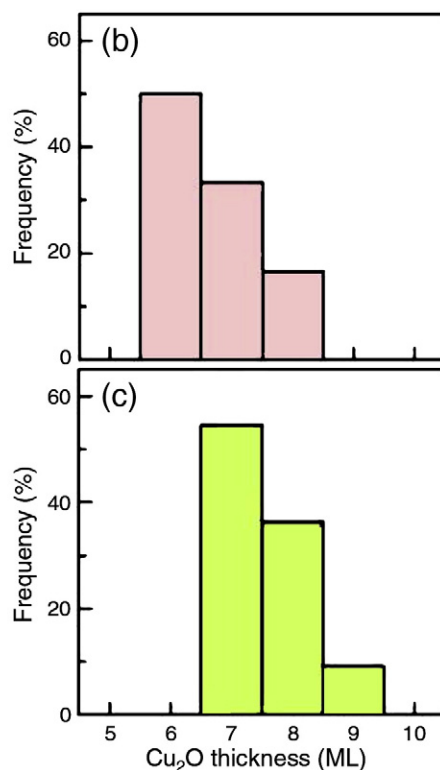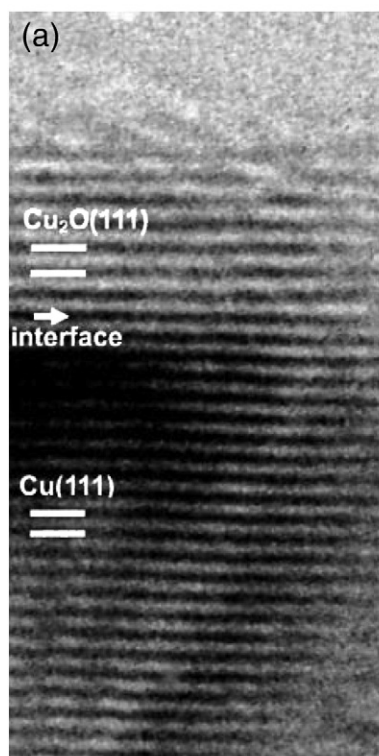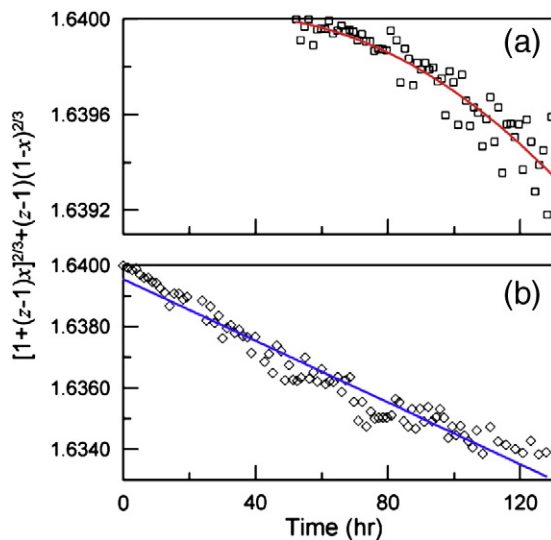

Fig. 2. (a) A partially enlarged HREM image of an icosahedral Cu nanoparticle (~17 nm) with Cu_2O(111) surface oxide layers (7 ML). (b) The Cu_2O thickness distribution obtained from the particles oxidized at 298 K with 93 kPa dry air exposure for 50 h without the x-ray irradiation, and (c) the thickness distribution after the additional exposure for 50 h under the x-ray irradiation. The average thicknesses were found to be (b) 6.6 ML and (c) 7.6 ML.

Fig. 3. Plots of $[1+(z-1)x]^{2/3}+(z-1)(1-x)^{2/3}$ versus the 93 kPa dry air exposure time at 323 K in case of (a) 22 nm particles and (b) 11 nm particles. The x-ray irradiation, i.e. the x-ray diffraction measurement, was started from the exposure time of (a) 50 h and (b) 0 h.

Cu, k the rate constant, t the oxidation time, and r_0 the initial particle radius [13]. From the plot of $[1+(z-1)x]^{2/3}+(z-1)(1-x)^{2/3}$ versus t, the rate constant k can be obtained from its slope. Fig. 3(a) shows this plot in the present sample. For comparison, we showed the case of Cu nanoparticles (11 nm) oxidized at 323 K under the x-ray irradiation through the whole oxidation process in Fig. 3(b). In contrast to the straight line fitted to derive a rate constant of 2.9×10^{-7} nm^2 s^{-1} [9] in Fig. 3(b), we clearly find a gradual change in the rate constant from 9.1×10^{-8} to 2.5×10^{-7} nm^2 s^{-1} in Fig. 3(a). The final rate constant is very close to the value from Fig. 3(b). This result clearly indicates that the x-ray irradiation enhances the oxidation rate.

Since the parabolic law is based on the ion diffusion mechanism, the x-ray effect at 323 K might directly be related to an increase in the concentration of copper vacancies or their diffusion coefficient.

Recently, it has been reported that x rays [8] or electrons [14] induce the dissociation of adsorbed oxygen. In our case also, the dissociative adsorption of O_2 might play an important role in increasing the Cu vacancies to accelerate the oxidation. Let us assume the linear gradient in the vacancy concentration in the oxide from n_0 to n_L towards the surface, that leads to the parabolic oxidation with a rate constant of k_L as described in classic oxidation theory. As the specimen is exposed to x rays to induce the oxygen dissociation, the surface vacancy concentration immediately rises up to a new steady value $(n_{L'})$ whereas the vacancy concentration in the oxide is remained unchanged. It will then take a time to establish a new linear concentration gradient between n_0 and $n_{L'}$ due to the diffusion process of defects. In connection with that, the rate constant will thus increase from k_L to higher final value of $k_{L'}$. The model may explain the present observations in Figs. 1 and 3(a).

4. Conclusions

In this work, we have clearly observed the x-ray effect on the oxidation of nano-scaled materials which has less been discussed before. The data presented here will benefit material science researchers using x rays and provide a deeper understanding of the oxidation phenomena.

References

[1] Harwood JJ, Hausner HH, Morse JG, Rauch WG. The effects of radiation on materials. New York: Reinhold Press; 1958.
[2] Eley DD, Selwood PW, Weisz PB. Advances in catalysis and related subjects. New York: Academic Press; 1962.
[3] Kotomin EA, Popov AI. Nucl Instr Meth B 1998;141:1–15.
[4] Seo JM, Li YZ, Anderson SG, Aastuen DJW, Ayyala US, Kroll GH, et al. Phys Rev B 1990;42:9080–7.
[5] Joyner RW, Robert MW, Singh-Boparai SP. Surf Sci 1981;104:L199–203.
[6] Vayer-Besançon M, Rousseau B, Estrade-Szwarckopf H. Surf Sci 1995;336:L741–5.
[7] Koga K, Takeo H. Rev Sci Instrum 1996;67:4092–7.
[8] Koga K, Takeo H, Ikeda T, Ohshima K. Phys Rev B 1998;57:4053–62.
[9] Chen CH, Yamaguchi T, Sugawara K, Koga K. J Chem Phys B 2005;109:20669–72.
[10] Rönnquist A, Fischmeister H. J Inst Met 1960–1961;89:65–76.
[11] Cabrera N. Phil Mag 1949;40:175–88.
[12] Pestrecov A. Collection Czech Chem Comm 1930;2:198–200.
[13] Carter RE. J Chem Phys 1961;34:2010–5.
[14] Stirniman MJ, Li W, Sibener SJ. J Chem Phys 1995;103:451–60.