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Fabrication of Cu_2O nanoparticles in SiO_2 by ion implantation combined with low-oxygen-pressure oxidation and reduction in Ar-gas

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Cuprous-oxide (Cu_2O) nanoparticles (NPs) are fabricated in silica glasses (SiO_2) by two different methods, (1) low oxygen-pressure (LOP) oxidation of Cu NPs which were previously formed by Cu$^-$ ion implantation to SiO_2 and (2) LOP reduction of cupric oxide (CuO) NPs which were previously formed by Cu$^-$ ion implantation to SiO_2 combined with atmospheric oxidation. The LOP oxidation at 800°C converts a small portion of Cu NPs to Cu_2O phase, but most of Cu NPs survive in the metallic state. At 900°C, no Cu_2O phase but only Cu NPs are detected. On the other hand, the LOP reduction at 800°C converts some portion of CuO NPs to Cu_2O phase. With increasing temperature to 900°C, the portion of Cu_2O phase increases. After the LOP reduction at 900°C for 5 hours, most of CuO NPs convert to Cu_2O phase.

Key words: oxide nanoparticle, valence state control, ion implantation, Cu_2O, CuO

1. INTRODUCTION

Metal-oxide nanoparticles (NPs) in insulators draw much attention because of the highly efficient lasing at room temperature [1], optical switching with phase transition [2], peculiar magnetic properties [3], etc. Some successes were reported in fabrication of metal-oxide NPs in insulators using the sequential implantation of metal-ions and oxygen ions, e.g., VO_2-NPs in SiO_2 [2].

Up to now, we have proposed an alternative method for the fabrication of oxide-NPs, i.e., ion implantation combined with thermal oxidation (IICTO) method, and succeeded in fabrication of NiO- [4], ZnO- [5] and CuO-NPs [6] in SiO_2. However, some metal ions, e.g., Cu, Fe, V, etc. have multi-valence states: In case of Cu, the ions show Cu^+ and Cu^{2+} states, and form different oxides, i.e., cuprous oxide (Cu_2O) and cupric oxide (CuO). Control of the valence states is important in fabrication of the metal-oxide NPs. In this paper, the valence state control of the oxide NPs is examined in the Cu oxide system as a model case.

Fabrication of copper oxide NPs in SiO_2 using the sequential implantation of Cu and O ions in MeV energy region has been reported [7]. However, the implanted samples always included not only CuO NPs, but also Cu_2O and Cu NPs, although the partitioning ratio depended on the implantation conditions and post-implantation annealing conditions.

Contrary, the Cu-oxide NPs fabricated by the IICTO method were almost in the CuO phase [6]. Figure 1 shows x-ray diffraction pattern from a SiO_2 sample containing Cu-oxide NPs fabricated by IICTO method [6]. The diffraction pattern after oxidation is well explained by a powder diffraction spectrum of CuO [8]. The existence of Cu_2O phase was not detected. Lack of Cu_2O phase is reasonable, because the latter process of the IICTO method is thermal oxidation which is governed by thermodynamics. Figure 2 shows a phase-diagram of Copper-Oxygen system plotted in oxygen-pressure versus temperature [9], and indicates that only CuO-phase is stable under heat treatment at atmospheric oxygen pressure of ~760 Torr up to

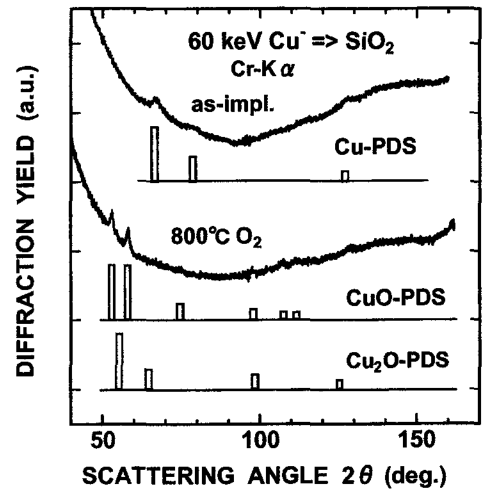

Fig. 1. Grazing incidence x-ray diffraction (GXRD) spectra of SiO_2 implanted with Cu$^-$ ions of 60 keV to 6.5×10^{16} ions/cm^2, in as-implanted state and after annealing in oxygen gas of the atmospheric pressure at 800°C for 1 hour. Powder diffraction patterns (PDS) of Cu, CuO and Cu_2O are shown as rectangles.

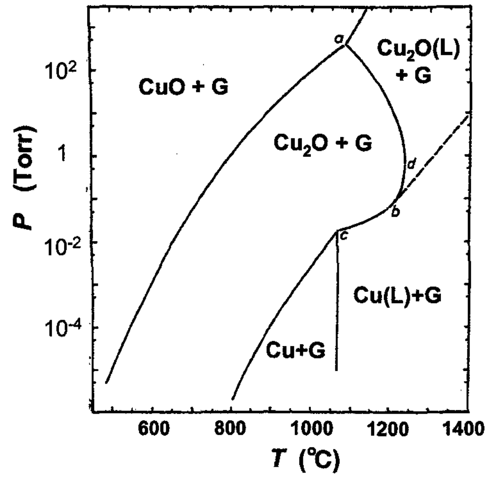

Fig. 2. Phase diagram of the copper-oxygen system plotted for oxygen partial pressure versus temperature, after Schmidt-Whitley et al. [9].

~1000°C, while Cu_2O-phase is stable at lower oxygen-pressure. This is an advantage of the IICTO method under the atmospheric pressure, because only CuO-NPs are formed, i.e., the formation of Cu_2O NPs is excluded. However, to extend the applicability, the fabrication of Cu_2O-NPs using the IICTO method or its modification is worthwhile challenging. It should be noted, for example, that VO_2-NPs which show an attractive optical switching response are also in a lower-pressure phase [10], i.e., the VO_2-phase is not formed by oxidation under atmospheric oxygen-pressure.

In this paper, the fabrication of Cu_2O-NPs in SiO_2 is examined using two different modifications of the IICTO method. We carried out annealing at low oxygen-pressure (LOP) of ~10^{-3} Torr using commercial-available high-purity Ar-gas which contains O_2 impurities of ~10^{-3} Torr in the partial pressure (LOP-Ar). To obtain Cu_2O NPs, we carried out both (1) oxidation in LOP-Ar gas of Cu NPs which were previously formed by ion implantation, and (2) reduction in the LOP-Ar gas of CuO NPs which were previously formed by the IICTO method.

2. EXPERIMENTALS

Optical grade KU-1 type silica glasses (OH^-: 820 ppm) of 15 mm in diameter and 0.5 mm in thickness were implanted with Cu negative-ions of 60 keV from a Cs-assisted plasma-sputter-type high-flux ion source [11]. According to SRIM2000 code [12], the projectile range and the straggling of Cu ions of 60 keV are 46 nm and 15 nm in SiO_2, respectively. The ion fluence was ~5×10^{16} ions/cm^2, which was confirmed by Rutherford backscattering spectrometry (RBS) using 2.06 MeV He^+ beam. Identification of NP species to Cu_2O-, CuO- or Cu-NPs was due to the grazing incidence x-ray diffraction (GXRD) with an incident angle of 3 degrees. A Cr tube was used for the x-ray source. The scattered x-ray was detected at once by a position-sensitive proportional counter.

Heat treatments were carried out in a tube-furnace at ~100 sccm flow of pure O_2 gas or high-purity LOP-Ar gas (purity: 99.999%) under a total pressure of 1.0 atm (atmospheric pressure). Two types of heating sequences were carried out: (1) SiO_2 samples containing Cu NPs which were previously fabricated by ion implantation were annealed at 700 – 900°C under the LOP-Ar gas flow, to oxidize softly the Cu NPs to Cu_2O phase under LOP of 10^{-3} Torr. (2) Another sets of SiO_2 samples containing Cu NPs were first annealed at 800°C for 1 hour under oxygen gas of 1.0 atm in pressure, to oxidize the Cu NPs to CuO NPs. Then the samples were again annealed in the LOP-Ar gas flow, to reduce softly the CuO NPs to Cu_2O NPs.

3. RESULTS AND DISCUSSION

As shown in Fig. 2, Cu_2O-phase is stable only at less than a few hundred Torr and in limited temperature region. With decreasing the oxygen pressure, the stable region moves to the lower temperature side. However, there is another limitation for the Cu_2O NP formation, i.e., the adequate temperature range for oxygen migration in the implanted layer. From the diffusion constant of oxygen in SiO_2 [13], annealing at temperatures higher than ~700°C for 1 hour is required [14]. On the other hand, temperature higher than ~1000°C is not adequate because of dissolution of Cu NPs in SiO_2 [15,16]. Consequently, the adequate temperature window is between 700 and 900°C, which corresponds to the oxygen pressure window of 10^{-4} and 10^{-1} Torr with safety margins. Since highly-pure Ar-gas contains O_2 impurities of normaly ~10^{-3} Torr, i.e., LOP-Ar gas, this is a good candidate for annealing atmosphere. Using the LOP-Ar gas, we have carried out two sets of heat treatments to obtain Cu_2O NPs, i.e., (1) LOP oxidation of Cu NPs in SiO_2 and (2) LOP reduction of CuO NPs in SiO_2.

3.1 Low oxygen-pressure oxidation of Cu NPs

First, we intended to convert Cu NPs to Cu_2O NPs in SiO_2 by oxidation in LOP-Ar gas. Figure 3 shows GXRD spectra of Cu-implanted SiO_2 after three different

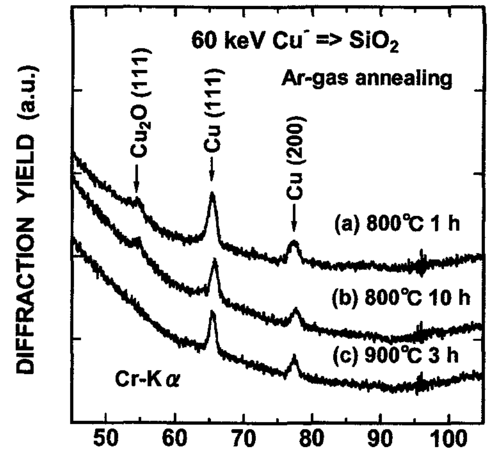

Fig. 3. GXRD spectra of SiO_2 samples implanted with Cu^- ions of 60 keV and annealed in LOP-Ar gas flow.

Table I. Intensity ratios of $Cu_2O(111)$ line to Cu(111) line after oxidation of Cu NPs to Cu_2O NPs in LOP-Ar gas.

Oxidation	Temp.	Time	$Cu_2O(111)$ / Cu(111)
LOP-Ar	800°C	1 h	0.26
LOP-Ar	800°C	10 h	0.43
LOP-Ar	900°C	1 h	~0

heat treatment conditions. After 800°C annealing for 1 hour (curve (a)), a weak peak of Cu_2O (111) diffraction appears at ~55 degrees in the scattering angle, in addition to more intense peaks of Cu (111) and Cu (200) diffraction at 66.5 and 78.6 degrees, respectively. This indicates that most of Cu NPs keep the metallic form, although a small portion of Cu NPs converts into Cu_2O phase. This result is very instructive, because some researchers have reported that they carried out annealing of Cu NPs in Ar-gas of atmospheric pressure to reduce radiation damage and to improve the optical properties. However, some portions of Cu NPs in their samples are possibly oxidized.

We increased the annealing time to 10 hours with keeping the temperature at 800°C. The $Cu_2O(111)$ peak increases to ~120% of the value after 1 hour annealing and the Cu(111) peak decreases to 70%. Intensity ratio between $Cu_2O(111)$ and Cu(111) is summarized in Table I. It should be noted that any peaks which were ascribed to CuO phase were not observed after Ar-gas annealing. Although the Cu_2O phase increases with increasing the annealing time, the efficiency is poor.

Curve (c) shows diffraction spectrum after the annealing at 900°C. No Cu_2O diffraction is observed. This behavior is explained from the thermodynamics. The Cu_2O phase formation via oxidation of Cu NPs is written as,

$$Cu_2O \rightarrow 2Cu + 1/2\ O_2. \qquad (1)$$

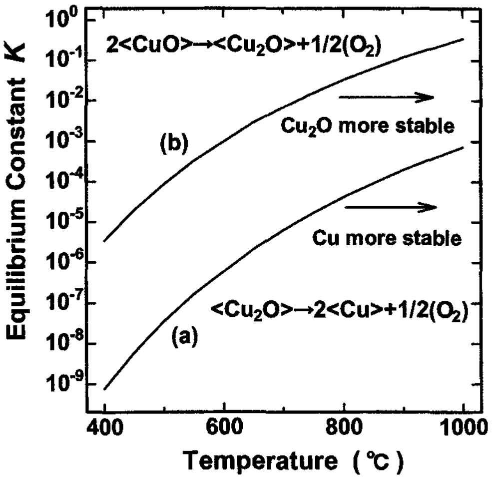

Fig. 4. Temperature dependences of equilibrium constants of the reaction $Cu_2O \rightarrow 2Cu + 1/2O_2$ and the reaction $2CuO \rightarrow Cu_2O + 1/2O_2$ are shown as curves (a) and (b), respectively. Thermodynamic data from Ref. [17] were used.

Table II. Intensity ratios of $Cu_2O(111)$ line to CuO(11-1) line after reduction of CuO NPs to Cu_2O NPs in LOP-Ar gas.

Reduction	Temp.	Time	$Cu_2O(111)$ / CuO(11-1)
LOP-Ar	800°C	1 h	1.13
LOP-Ar	800°C	20 h	1.09
LOP-Ar	900°C	1 h	1.34
LOP-Ar	900°C	5 h	2.29

The equilibrium constant K_1 of the reaction (1) is given by,

$$K_1 = \exp\left(-\frac{\Delta G_1^0}{RT}\right) \qquad (2)$$

where ΔG_1^0, R and T denote the standard Gibbs energy change of the reaction (1), the gas constant and temperature, respectively. The standard Gibbs energy change of the reaction (1) is given by

$$\Delta G_1^0 = A_1 + B_1\ T\log T + C_1 T \quad \text{(cal)} \qquad (3)$$

where A_1 = 40,500 cal, B_1 = 3.92 cal/K and C_1 = -29.5 K^{-1} at 298 K < T < 1356 K [17]. Temperature dependence of the equilibrium constant K_1 is shown as curve (a) in Fig. 4. With increasing temperature, the K_1, i.e., the right-hand side of the eq. (1), Cu and O_2, increases. This result qualitatively explains the reason why Cu_2O phase decreases with increasing temperature from 800°C to 900°C. If temperature decreases, e.g., to 700°C, Cu_2O phase may increase. However, this way is probably not practical, because it requires much longer time for the reaction.

3.2 Low oxygen-pressure reduction of CuO NPs

Next, following reaction, i.e., the LOP reduction of CuO NPs to Cu_2O NPs, is examined:

$$2CuO \rightarrow Cu_2O + 1/2\ O_2 \qquad (4)$$

The equilibrium constant K_2 of the reaction (4) is given by

$$K_2 = \exp\left(-\frac{\Delta G_2^0}{RT}\right) \qquad (5)$$

and

$$\Delta G_2^0 = A_2 + B_2\ T\log T + C_2 T \quad \text{(cal)} \qquad (6)$$

where A_2 = 34,950 cal, B_2 = 6.10 cal/K and C_2 = -44.3 K^{-1} at 298 K < T < 1300 K [17]. The calculated temperature dependence is shown as curve (b) in Fig. 4. With increasing temperature, the right-hand side of eq. (4), i.e., Cu_2O phase, increases.

As already written in Introduction, CuO NPs are easily formed in SiO_2 using Cu-ion implantation and following oxidation at 800°C for 1 hour under oxygen gas of 1.0 atm in pressure. Using the CuO NPs as a starting material, the reduction of CuO NPs to Cu_2O in LOP-Ar gas flow was carried out. Figure 5 shows GXRD spectra of CuO NPs, in as-formed and after the reduction in LOP-Ar gas at 800°C and 900°C. The ratio of $Cu_2O(111)$ peak to CuO(11-1) peak is summarized in

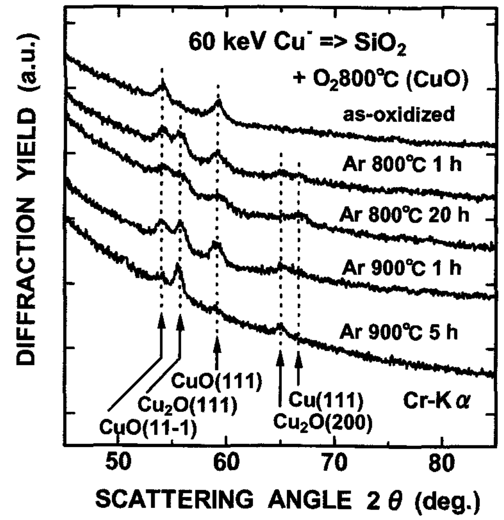

Fig. 5. GXRD spectra of SiO_2 samples including CuO NPs which were formed by Cu-ion implantation and atmospheric pressure oxidation at 800°C for 1 hour, in as-formed state and after reduction in LOP-Ar gas flow at 800°C and 900°C.

Table II. After heat treatment (reduction) at 800°C for 1 hour in LOP-Ar gas, the $Cu_2O(111)$ diffraction appears at 55.3 degrees, in addition to strong peaks of CuO (11-1) at 53.9 degrees and CuO (111) at 59.0 degrees. Even increasing the annealing time up to 20 hours at 800°C, the peak ratio $Cu_2O(111)/CuO(11\text{-}1)$ did not significantly change. When the annealing temperature increases to 900°C, a drastic improvement is observed. The diffraction peak ratio increases to 1.34 after 1 hour annealing at 900°C, and to 2.29 after 5 hours annealing. As shown in Fig. 5, the dominant product after the 5 hours annealing at 900°C is Cu_2O phase, although the diffraction from CuO phase still remains. It should be noted that Cu metal phase is less than the detection limit. The conversion efficiency of CuO NPs to Cu_2O phase at 900°C is higher than that at 800°C. This behavior is qualitatively consistent with the dependence shown as the curve (b) in Fig. 4.

For comparison, CuO NPs were also reduced at 800°C for 1 hour in vacuum (less than 1×10^{-5} Torr). Cu_2O phase was not observed. This result confirms the important role of the low-pressure oxygen.

4. CONCLUSIONS

Oxidation at atmospheric oxygen-pressure converts Cu NPs in SiO_2 not to Cu_2O phase but only to CuO phase. To obtain Cu_2O NPs, two different methods were applied, i.e., (1) LOP oxidation of Cu NPs which were previously formed by Cu^- ion implantation to SiO_2 and (2) LOP reduction of CuO NPs which were previously formed by Cu^- ion implantation to SiO_2 combined with atmospheric-pressure oxidation. The LOP oxidation at 800°C converts a small portion of Cu NPs to Cu_2O phase, but most of Cu NPs survive in the metallic state. Even increasing temperature to 900°C, no Cu_2O phase but only Cu NPs is observed. On the other hand, the LOP reduction at 800°C converts some portion of CuO NPs to Cu_2O phase. With increasing the temperature to 900°C, the portion of Cu_2O phase increases. After the reduction at 900°C for 5 hours, most of CuO NPs transform to Cu_2O phase.

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