Evaluation of Ozone for Metal Oxide Thin Film Fabrication

Jung-Kwan lim*, Yong-Pil Park*, Kyung-uk Jang**, Hee-Kab Lee***
Dongshin Univ.*, Kyungwon Coll.**, KCCI***

Abstract

Ozone is usually generated from oxygen gas using a silent discharge apparatus and its concentration is less then 10 mol%. An ozone condensation system is constructed for metal oxide thin film fabrication. Ozone is condensed by the adsorption method, which is widely used for the growth of oxidation thin films such as superconductor. Highly condensed ozone is analyzed by three methods; ultraviolet absorption, thermal decomposition and Q-mass analyzing methods. Thermal decomposition method is most effective in the highly condensed ozone region and its method is superior to Q-mass analyzer for determining ozone concentration because of the simplicity of the method.

Key Words : ozone condensation, absolute ozone concentration, thermal decomposition method, Q-mass analyzing method.

1. Introduction

Ozone is a strong oxidizing gas which is useful for the fabrication of oxide thin films under conditions of beam epitaxy. A high quality thin film fabrication is essential in using the superconductor thin film widely[1], and researching on the important parameter to the crystal structure of obtained thin film should be preceded in production of a high quality thin film. Accordingly researching on oxidizing gas is required. Hence it is expected that the effects of increasing gas pressure around the substrate and increasing oxidation on the substrate surface by radiating ozone on its surface. Ozone is usually generated from oxygen gas using a silent discharge apparatus and its concentration is about 8 mol%. This is so-called dilute ozone. In order to obtain high quality thin film, the O_3 concentration must be increased. There are two methods to condense the ozone; the one is the distillation method and the other by the ozone gas adsorption[2] onto silica gel beads.

The former is utilized by many researchers as an oxidizing source since the condensed ozone by this method was first applied to the thin film fabrication of Y-type superconductor by D. D. Berkley et al.[3]. On the other hand, the latter was first applied by T. Siegrist et al.[4], This adsorption method is advantageous to the distillation method in the point that the gaseous ozone can be handled safer than liquid ozone.

The evaluation for the concentration of the highly condensed ozone is important for the purpose of investigating ozone effect on the thin film fabrication systematically. On the study, an ozone condensation system using the adsorption method is constructed and highly condensed ozone is generated. The performance of this system is evaluated in the viewpoint of an ozone supplier to a thin film growth chamber. Ozone concentration is measured using the thermal decomposition method[5]. The rate of decomposition of ozone at room temperature is also calculated. A Q-mass analyzer is used for the in situ analysis of ozone concentration in the film growth chamber and the result is compared with the result obtained using the thermal decomposition method. In addition, Condensed ozone is evaluated by XRD patterns of the obtained Cu-films using condensed ozone.

2. Experimental

2.1 Ozone condensation system

An ozone condensation system using the adsorption method is illustrated in Figure 1. with a thermal decomposition vessel.

The pyrex glass ozone condenser, in which silica gel beads of about 170 g was set, was cooled to around 195 K using the refrigerant of dry ice/ethanol. Then the ozone gas of 8 mol% generated by the ozone generator (Sumitomo Precision Products Co. Ltd., OZONIZER SG-01A) was introduced into the cooled condenser at a rate of 2 liters/min. As ozone molecules were adsorbed onto the silica gel, the color of gel changed from opaque white to dark blue which is the color of ozone. Therefore, the ozone concentration in the residual gas slowly increases and reaches 8 mol% by 2.5 h since the beginning of the ozone condensation process, indicating the completion of condensation. The result is shown in Figure 2.

Then, the system was evacuated using the rotary pump. Ozone was continuously desorbed from the silica gel by the negative pressure. The pressure was kept at 10 Torr by regulating valve 2 which was monitored using a capacitance manometer. Ozone gas was introduced into the film growth chamber by regulating valve 5.

2.2 Evaluation of ozone concentration

The ozone concentration in the gas was determined using the thermal decomposition method, which measures the pressure variation caused by ozone decomposition in an isothermal closed vessel.

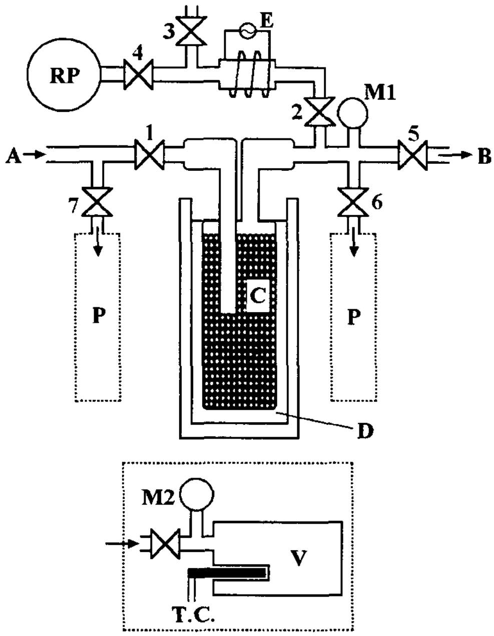

Fig. 1. Ozone condensation system using the adsorption method. A: Ozonizer Gas(8~10 mol%), B: Film Fabrication Chamber, C: Silica Gel Beads, D: Dry Ice/Ethanol Mixture(195 K), E: Ozone Decomposition Heater, M1, M2: Capacitance Manometer(100 Torr F.S.), P: Gas Sampling Port, RP: Rotary Pump, T.C.: Thermocouple(CA), V: Al. Vessel, 1~7: Valves.

Namely, when ozone molecules decompose to oxygen molecules, the total molar number varies via the reaction

$$xO_3 + (100 - x)O_2 \rightarrow (100 + x/2)O_2,$$

Accordingly, an initial ozone concentration x(mol%) is evaluated as,

$$x = 2[(P_1 - P_0)/P_0] \times 100(\text{mol\%}),$$

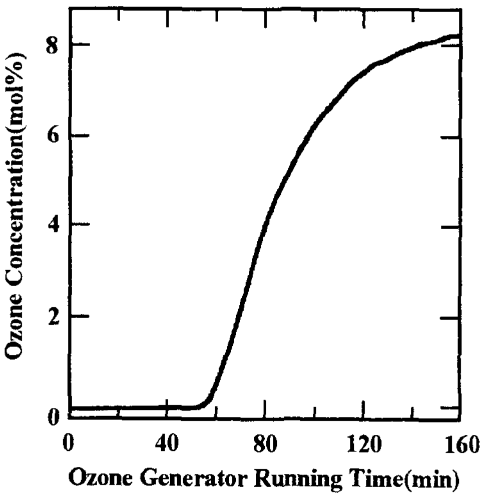

Fig. 2. Ozone concentration to the outlet of the silica gel cell during the ozone condensation process.

where P_0 and P_1 are the gas pressures before and after ozone is decomposed.

Thermal decomposition device which consists of the aluminium vessel(540 ml volume), a capacitance manometer, a chromel - alumel thermocouple and a stop valve, is shown in Figure 1.

In situ measurement of ozone concentration was also performed using an quadrupole mass analyzer(Q-mass: ANELVA Co. Ltd., AQA-100 MPX) equipped in the high vacuum chamber. Mass signals of m/e=16(O^+), 32(O_2^+) and 48(O_3^+) were detected and the ozone concentration was evaluated from the intensity ratio between m/e=32 and 48 according to the method proposed by Ichimura et al.. This result was compared with the result obtained using the thermal decomposition method. In addition, Condensed ozone is evaluated by XRD patterns of the obtained Cu-films using condensed ozone.

3. Results and discussion

An ozone condenser was constructed as a highly condensed ozone supplier for the film fabrication of superconductor.

The selective ozone adsorption method can evade the explosive ozone reaction on account of the adsorption in gas phase onto silica gel beads. Two methods were applied for the evaluation of the ozone concentration; thermal decomposition and Q-mass analyzing methods.

The ozone concentrations of dilute ozone gas were determined using the thermal decomposition method.

It can be seen that the ozone gas is condensed to 96 mol% at maximum and the supply of ozone gas 90 mol% is realized for longer than 5 hours.

A Q-mass analyzer was placed in the film growth chamber and the intensities of mass signals were determined for the gases of 90 mol% condensed ozone, 9 mol% dilute ozone, and pure oxygen. The results are shown in Figure 3. The characters of signals are similar to those in ref. 5 where it was reported that the signal intensity of O(atomic weight = 16) is identical for all kinds of gases and the signal intensity of O_2(32) is large even in the case of condensed ozone gas.

Therefore, The T. D. method was most effective in the highly condensed ozone region. It is found by this method that the ozone is condensed to 96 mol% at maximum. This ozone condenser system is very effective to fabricate the thin film, because the ozone concentration can be easily controlled by the gas pressure. Therefore, the thermal decomposition method is superior to Q-mass analyzer for determining ozone concentration because of the simplicity and accuracy of the method.

The result of CuO thin film growth using condensed ozone is illustrated in Figure 4. It is outcome of thin film growth on the MgO(100) substrate for One hour. Then, thickness is 140 nm, temperature of substrate is set 825℃. CuO peak appears by XRD patterns.

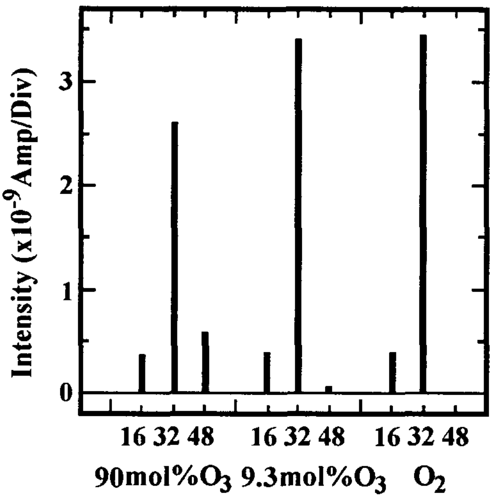

Fig. 3. The intensities of mass signals determined using a Q-mass analyzer for the gases of (a) 90 mol% condensed ozone, (b) 9 mol% dilute ozone, and (c) pure oxygen.

4. Concluding remarks

Ozone is a strong oxidizing gas which is useful for the fabrication of oxide thin films. It is usually generated from oxygen gas using a silent discharge apparatus and its concentration is less than 10 mol%. An ozone condenser was constructed as a highly condensed ozone supplier for the film fabrication of superconductor. The selective ozone adsorption method can evade the explosive ozone reaction on account of the adsorption in gas phase onto silica gel beads.

Two methods were applied for the evaluation of the ozone concentration; T. D. and Q-mass analyzing methods. The result of comparative analysis of this gas with thermal decomposition method and Q-mass analysis method proves that thermal decomposition method is suitable for the analysis of dilute ozone area and dense ozone gas. Therefore, the thermal decomposition method is superior to Q-mass analyzer for determining ozone concentration because of the simplicity and accuracy of the method. The result of CuO thin film fabrication using condensed ozone, CuO peak appears by XRD patterns.

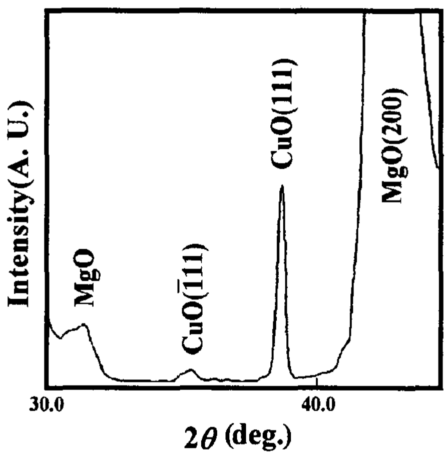

Fig. 4. XRD patterns of CuO film using condensed ozone.

References

[1] J. Y. Kim, M. S. Kim, S. Y. Lee, S. I. Lee, and D. H. Ha, Curr. Appl. Phys, 1, p. 157, 2001

[2] E. Coleman, T. Siegrist, D. A. Mixon, P. L. Trevor and D. J. Trevor, J. Vac. Sci. & Technol., 9 , p. 2408, 1991.

[3] D. D. Berkley, B. R. Johnson, N. Anand, K. M. Beauchamp, L. E. Conroy, A. M. Goldman, K. Mauersberger, M. L. Mecartney, J. Morton, M. Tuaminen and Y. J. Zhang, Phys. Lett., 53, p. 1973, 1988.

[4] T. Siegrist, D. A. Mixon, E. Coleman and T. H. Tiefel, Phys. Lett., 60, p. 2489, 1992.

[5] J. Ghaieb, R. S. Bes and G. Dartigues, Ozone Sci. & Engin., 14, p. 91, 1992.