# Evaluation of Ozone Condensation System by T.D. Method

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An ozone condensation system is evaluated from the viewpoint of an ozone supplier for oxide thin film growth. Ozone is condensed by the adsorption method and its concentration is analyzed using the thermal decomposition method. The concentration of ozone exceeds 90 mol% and ozone is supplied for a sufficiently long time to grow oxide thin films. Investigation of the ozone decomposition rate demonstrates that ozone can be transferred into the film growth chamber without marked decomposition. The ozone concentration is also evaluated using a quardrupole mass analyzer and the accuracy of this method is compared with the results of the thermal decomposition method.

*Keywords* : ozone condensation system, thermal decomposition method, ozone decomposition rate, ozone concentration, quardrupole mass analyzer

## 1. INTRODUCTION

Ozone is a strong oxidizing gas which is useful for the fabrication of oxide thin films under conditions of molecular beam epitaxy. Ozone is usually generated from oxygen gas using a silent discharge apparatus and its concentration is less than 10 mol%. This is so-called dilute ozone. Highly condensed ozone can be generated by both distillation[1],[2] and adsorption[1],[3] methods, which are widely used for the growth of oxide thin films such as high-$T_c$ superconductors[4],[5].

Measurement of ozone concentration is also an area of interest. Kucera et al.[6] used a method of oxidation of a silver-coated quartz oscillation rate monitor. Ichimura and Ilosokawa[2] analyzed ozone purity using a quadrupole mass(Q-mass) analyzer. Although both methods are available for the in-situ measurement of ozone concentration in the film growth chamber, these methods require some assumptions. That is, the detector response is assumed to be linear over the range of ozone flux[6], and the rates of oxygen generation by decomposition and fragmentation of ozone molecules are assumed to be low[2]. Therefore, the measurement of ozone concentration should be carried out using a direct method without any assumptions.

In this report, an ozone condensation system using the adsorption method is constructed and highly condensed ozone is generated. The performance of this system is evaluated from the viewpoint of an ozone supplier to a film growth chamber. Ozone concentration is measured using the thermal decomposition method. 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.

## 2. EXPERIMENTAL

An ozone condensation system using the adsorption method is illustrated in Fig. 1. The system is mainly composed of Pyrex glass and stainless steel. Commercial silica gels (Kishida Kagaku Co., Ltd.) of 170 g were employed as an ozone adsorbent and stored in a Pyrex glass cell(C). The inner surfaces of the stainless steel tubes were electrochemically polished in order to provide a stable surface against chemical reaction.

Ozone gas was condensed using the following process as shown in Fig. 1: the cell(C) was immersed into the refrigerant(dry ice and ethanol mixture(D)) and maintained at 195 K. Dilute ozone gas of 8.0 mol% on average(9.3 mol% at maximum) from the ozone generator(Sumitomo Precision Products Co., Ltd.; SG-

01A) was supplied into the cell(C) 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. The residual gas was exhausted out through valve 3.

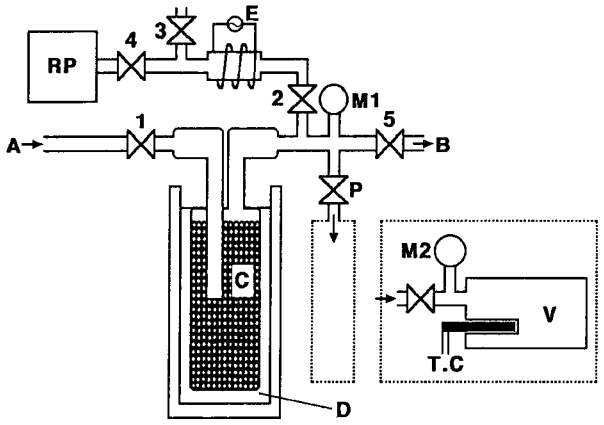


Fig. 1. Ozone condensation system with a thermal decomposition vessel. A: Ozone generator(8 mol% $O_3$), B: Film growth chamber, C: Pyrex glass cell containing silica gel beads, D: Refri- gerant(dry ice/ethanol), E: Ozone decomposi-tion tube, RP: Rotary pump, M1, M2: Capaci-tance manometer, P: Gas sampling port, TC: Thermocouple(CA), V: Aluminum can.

Ozone concentration in the residual gas was measured using an ultraviolet absorption method(UV method; Ebara Jitugyo Co., Ltd.; EG-2001). The UV method is based on the Lambert-Beer law and has already been shown to be accurate in the dilute ozone region. EG-2001 was temporarily connected to the outlet of the cell(C) in Fig. 1, and the ozone concentration in the residual gas was measured during the ozone condensation process. The result is shown in Fig. 2. At the beginning of the ozone condensation process, no ozone is detected in the residual gas. This means that ozone molecules are fully adsorbed on the silica gel. This situation continues for 50 min. After that, 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.

When the adsorption process was completed, the gas supply was shut off and all valves were closed. 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(ULVAC Co., Ltd.; CCM-100)(M1). Ozone gas was introduced into the film growth chamber by regulating valve 5.

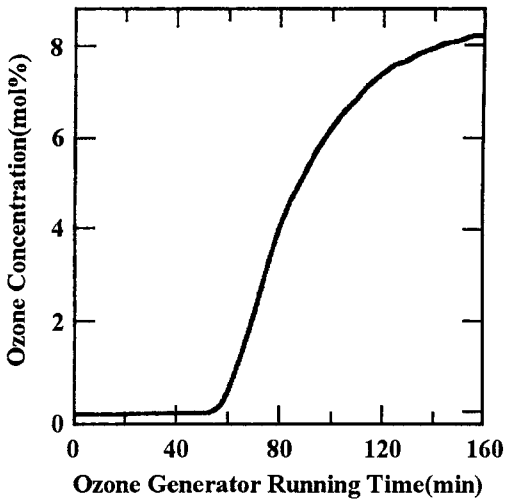


Fig. 2. Detection of ozone in the residual gas during the ozone condensation process. The detector was temporarily connected to the outlet of the silica gel cell in Fig. 1.

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

$$xO_3 + (100 - x)O_2 \rightarrow (100 + x/2)O_2, \quad (1)$$

where x(mol%) is the molar percentage of ozone in the gas mixture. In an isothermal closed vessel, the molar variation brings about pressure change. Accordingly, the initial ozone concentration x can be estimated from the expression

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

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

The vessel used for the thermal decomposition is illustrated at the bottom of Fig. 1. The vessel consists of an aluminum can with a volume of 540 ml, a Chromel/Almel thermocouple, a capacitance manometer(ULVAC Co., Ltd.; CCM-100), and a stop valve. Several cycles of the ozone decomposition process were repeatedly carried out to form an inactive alumina layer on the inner surface of the vessel. The procedure was as follows. The pre-evacuated vessel was connected to the port P(Fig. 1) which was prepared on the way to the film growth chamber and the condensed ozone gas was supplied into it. The initial gas pressure $P_0$ and the temperature $T_0$ of the vessel were measured.

The pressure was about 10 Torr, equivalent to the pressure of the ozone condensation system. The vessel was at room temperature. Then the vessel was heated to 150 °C and kept at this temperature for 20 min. Ozone was completely decomposed to oxygen using this process. Then the vessel was cooled down to the initial temperature $T_0$ and the total gas pressure $P_1$ was measured. For example, when the ozone concentration of supplied gas is 100 mol%, the pressure of the vessel changes from 10 Torr to 15 Torr using this process.

The rate of decomposition of ozone was determined in order to ensure that condensed ozone was supplied into the film growth chamber. The time dependence of ozone concentration was checked at room temperature. Two materials were used as vessels in this experiment, aluminum and stainless steel. The aluminum vessel was the one described above and the stainless steel vessel was a commercial gas sampler with a volume of 300 ml(WIIITEY Co., Ltd.). Condensed ozone was supplied in these vessels and the pressure variations were monitored at room temperature using the capacitance manometer.

In situ measurement of ozone concentration was also performed using a Q-mass analyzer(ANELVA Co., Ltd.; AQA-100). It was placed in the film growth chamber in the same manner as described in ref. 2. Ozone concentration was determined using the formula proposed by Ichimura and Ilosokawa[2]. This result was compared with the result obtained using the thermal decomposition method.

## 3. RESULTS AND DISCUSSION

### 3-1. Evaluation of ozone concentration

The ozone concentrations of dilute ozone gas were determined using the thermal decomposition method. The result is compared with the result using the UV method. The comparison between these methods is plotted in Fig. 3 and a good linear correlation is found. This indicates that the thermal decomposition method is useful even for the evaluation of ozone concentration in dilute ozone gas.

Next, highly condensed ozone was analyzed by sampling the gas from the port P(Fig. 1) on the way to the film growth chamber. The flow rate of ozone molecules through valve 5 was set at $2 \times 10^{19}$ molecules/min. This flow rate is sufficient for the growth system. The relationship between the ozone concentration and the supplying period of condensed ozone to the film growth chamber is shown in Fig. 4. It can be seen that the ozone gas is condensed to 97 mol% at maximum and the supply of ozone gas 90 mol% is realized for longer than 5 hours. The duration of condensed ozone supply can be controlled by the amount of silica gel in the cell.

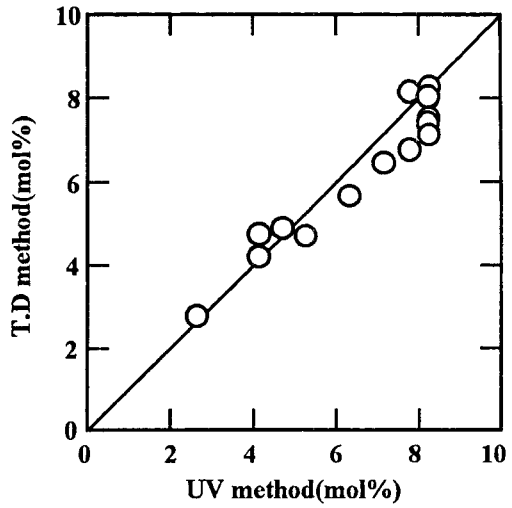


Fig. 3. Ozone concentration in the dilute ozone region determined by both the thermal decomposition (T.D.) and ultraviolet light absorption(UV) methods.

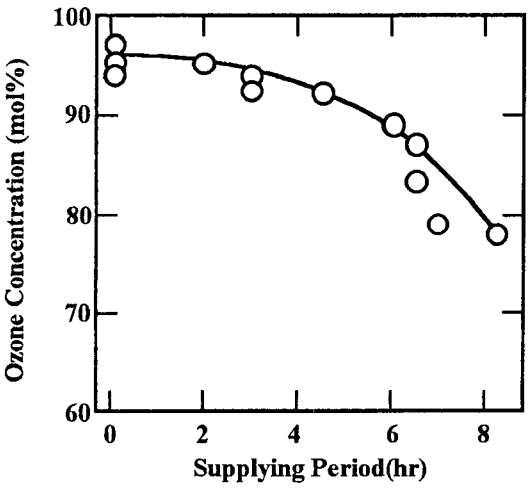


Fig. 4. The relationship between the ozone concentration and the supplying period of condensed ozone to the film growth chamber. The pressure in the silica gel cell(Fig. 1) is maintained at 10 Torr and ozone is extracted and transferred to the film growth chamber at a rate of $2 \times 10^{19}$ molecules/min.

### 3-2. Rate of decomposition of ozone gas in a closed vessel

The time dependence of the ozone concentration in a closed vessel was examined at room temperature. Both the aluminum and stainless steel vessels were used as closed vessels, and the temperatures of the gas supplied into them were maintained at 30 °C and 24 °C, respectively. The results are shown in Fig. 5. In both

cases, ozone concentration within a few minutes of supply, the decomposition of ozone is negligible. Therefore, ozone gas must be transferred to the film growth chamber over a short period of time. This is not so difficult in a conventional setup. For example, we supplied the condensed ozone gas from valve 5(Fig. 1) to the film growth chamber using a stainless steel tube 2 m in length with an inside diameter of 2 mm.

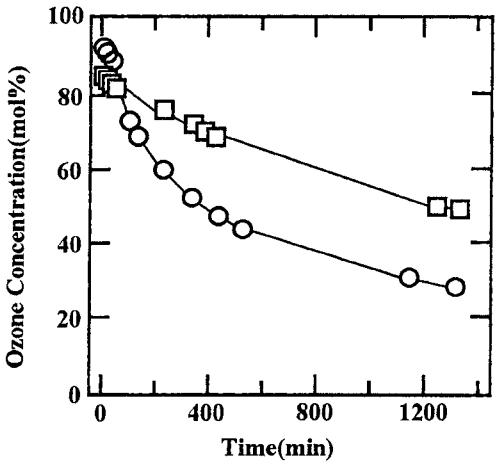


Fig. 5. Time dependencies of ozone concentration in the closed vessels. The initial pressure of the condensed ozone gas was 10 Torr and the vessel was maintained at room temperature. Circles represent ozone gas at 30 °C in the aluminum vessel and squares represent ozone gas at 24 °C in the stainless steel vessel.

The equations of the ozone decomposition reaction are given under two typical conditions[1]: for the condensed ozone region,

$$-d[O_3]/dt = k1[O_3]^2 \quad (3a)$$

and for the dilute ozone region,

$$-d[O_3]/dt = k_2[O_3]^2/[O_2]. \quad (3b)$$

Here, $k_1$ and $k_2$ are the rate constants of the ozone decomposition, and $[O_3]$ and $[O_2]$ are the respective molar concentrations. Considering the case of condensed ozone, eq. (3.a) is integrated as

$$1/[O_3] = k_1t + A, \quad (4)$$

where A is an integral constant.

The molar ozone concentration shown in Fig. 5 are re-plotted in Fig. 6 with the lines fitted by eq. (4). The rate constant $k_1$ in eq. (3a) is calculated as 2.835 liters/(mol min) for the aluminum vessel and 0.708 liters/(mol min) for the stainless steel one. The difference of the rate constants between the experiments is large. This means that the ozone decomposition reaction on the inner surface of the vessels.

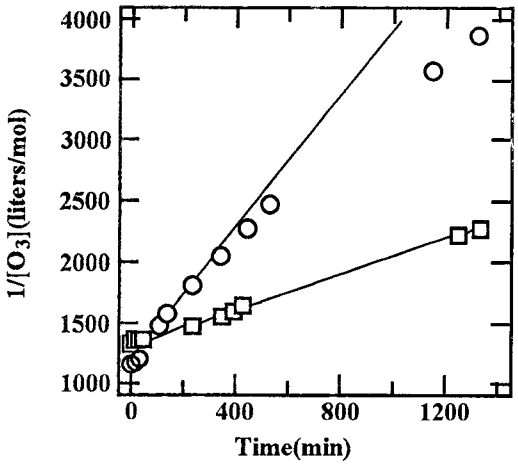


Fig. 6. Re-plots of ozone concentrations in Fig. 5 using the equation $1/[O_3] = k_1*t + A$. Circles and squares are the results for the aluminum and stainless steel vessels, respectively.

### 3-3. Estimation of ozone concentration using a Q-mass analyzer

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, 9.3 mol% dilute ozone, and pure oxygen. The results are shown in Fig. 7. The characters of signals are similar to those in ref. 2 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.

Ozone concentration is calculated using the peak intensity ratio I48/I32 between $O_3(48)$ and $O_2(32)$. The concentration of the condensed ozone is calculated to be about 70 mol% which is smaller than the value of 90 mol% calculated using the thermal decomposition method.

For the estimation of ozone concentration using Q-mass analyzer, the following should be noted. ( i ) $O_2$ and O are inevitably generated as decomposition components of $O_3$ gas by the irradiation of thermo-electrons. Moreover, because the ionization probabilities by the electron impact are different for $O_3$, $O_2$, and O, the intensity ratios between their mass signals do not correspond simply to the nominal composition. ( ii ) The filament of the Q-mass analyzer, a wolfram thread, exhibits rapid reduction in performance with time due to the strong oxidizing species, ozone. Thus this equipment can be used only for short periods.

We conclude that the Q-mass analyzer is useful to check the quality of ozone gas in the growth chamber. However, the accuracy of the determination of ozone concentration using this method remains uncertain until the sensitivity of the Q-mass analyzer is investigated in detail.

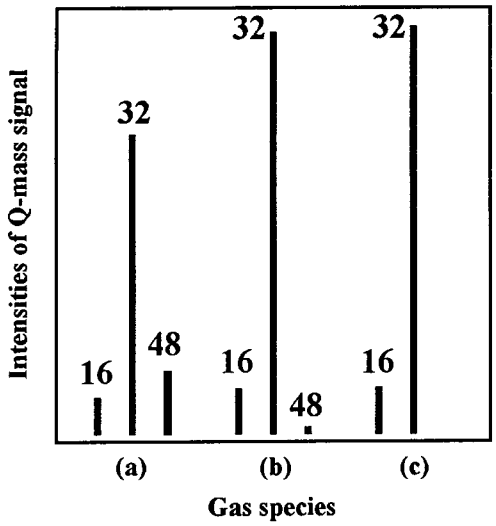


Fig. 7. The intensities of mass signals determined using a Q-mass analyzer for the gases of (a) 90 mol% condensed ozone, (b) 9.3 mol% dilute ozone, and (c) pure oxygen.

## 4. CONCLUSION

An ozone condensation system using an adsorption method is shown to be applicable to the growth of oxide thin films. Ozone concentration is analyzed using the thermal decomposition method and following results were obtained.

( i ) Ozone is condensed to more than 90 mol%.

(ii) This concentrated ozone can be supplied to the film growth chamber for different periods of time, depending on the amount of the silica gel adsorbent used.

(iii) The decomposition of condensed ozone takes place mainly on the inner surface of the vessel. However, the decrease in the ozone concentration is negligible if the condensed ozone is transferred between the ozone condensation system and the film growth chamber within a few minutes.

(iv) At the present time, the thermal decomposition method is superior to Q-mass analyzer for determining ozone concentration because of the simplicity of the method.

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