Ozone Density Estimation and Stable Supply in the Thin Film Growth

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An ozone condensation system is evaluated from the viewpoint of an ozone supplier for Bi-superconductor thin film growth. An ozone condenser by a selective adsorption on the silica gel surface is constructed. Ozone density is evaluated by three methods; ultraviolet absorption, thermal decomposition and Q-mass analyzing methods. Thermal decomposition method is found to be available to the density evaluation from dilute to highly condensed ozone. The highest ozone density condensed by the adsorption method is evaluated to be 97 mol%.

Keywords : condensed ozone, absolute ozone density, thermal decomposition method, Q-mass analyzing method

1. INTRODUCTION

The very active oxidation source is required in the thin film fabrication under high vacuum condition. We adopted the O_3/O_2 mixed gas[1], 9.3 mol%(13.3 wt%) of which is easily produced using a commercial ozonizer, but a lot of impurity precipitates and different phases are formed in the thin film fabricated under this O_3 density owing to the deficiency of oxidizing power[2]. In order to suppress the appearance of the precipitates and obtain high quality thin film, the O_3 density must be increased.

There are two methods to condense the ozone; the one is the liquefaction method, and the other by the ozone gas adsorption 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], but only a few reports are presented. This adsorption method is advantageous to the liquefaction method in the point that the gaseous ozone can be handled safer than liquid ozone.

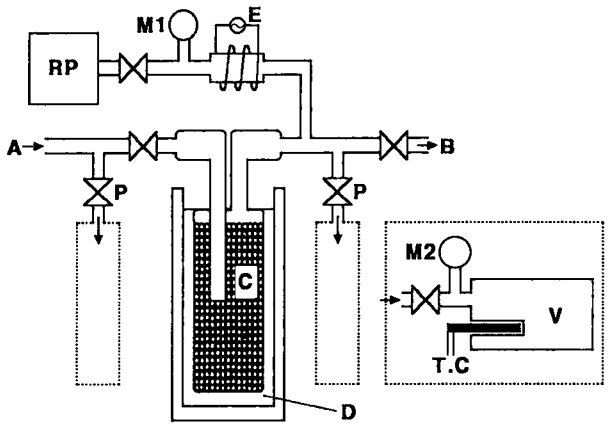
The evaluation for the density of the highly condensed ozone is important for the purpose of investigating ozone effect on the thin film fabrication systematically. As far as we know, there is only a report by Ichimura et al.[5], who evaluated the density of the ozone condensed by the liquefaction method using Q-mass analyzer[5]. Although T. Siegrist et al.[4] insist that the condensed ozone density by adsorption method is 100 %, the evaluation method is not made clear.

In this paper, we report about an apparatus condensing the ozone gas by the adsorption method and the evaluation of the ozone density. The density of ozone gas condensed from this apparatus is evaluated by two methods, that is, thermal decomposition(T. D.)[6] and Q-mass analyzing(Q-mass) methods[5]. Ultraviolet absorption method(UV method) is also carried out to ascertain the accuracy of two methods in the dilute ozone density region.

2. EXPERIMENTS

2.1. Ozone condenser system

An ozone condenser system is shown in Fig. 1 with a thermal decomposition vessel.



A: Ozonizer, B: Film Growth Chamber, C: Silica Gel Beads, D: Refrigerant(Dry Ice/Ethanol), E: Ozone Decomposition Tube, M1, M2: Capacitance Manometer, P: Gas Sampling Port, RP: Rotary Pump, TC: Thermocouple(CA), V: Aluminium Can

Fig. 1. Ozone condenser system with the thermal decomposition device.

The pyrex glass ozone condenser, in which silica gel beads of about 170 g was set, was cooled to around 200 K using the refrigerant of dry ice/ethanol. Then the ozone gas of 9.3 mol% generated by a commercial ozonizer(Sumitomo Precision Products Co. Ltd., OZONIZER SG-01A) was introduced into the cooled condenser. The temperature of 200 K is much higher than the boiling point of the oxygen(90.18 K) and a little higher than that of ozone(161.15 K), so that ozone molecule is selectively adsorbed on the surface of silica gel beads. When the ozone gas was fully adsorbed and condensed(about 3 hours), the supply from the ozonizer was stopped. After the condenser was evacuated by a rotary pump to exclude the remaining O_3/O_2 gas, the gas pressure in the condenser was set to a desired one, controlling by a gas flow bulb and the rotary pump. A capacitance manometer (Vacuum General: CML-1000) was used as a monitor of ozone gas pressure. The highly condensed ozone gas was introduced into the vacuum chamber with Q-mass analyzer and thermal decomposition vessel. Two ports are set for the gas sampling in front and behind of the ozone condenser, and the dilute and the highly condensed ozone gases were extracted.

2.2. Thermal decomposition method(T. D. method)

Ozone gas is dissociated to molecular oxygen by heat decomposition, so that before and after the heat decomposition, the pressure in the vessel changes with the molecular number change. The molar change in the ozone gas of the molar fraction x is written as follows;

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

Accordingly, an initial ozone density y(mol%) is evaluated as,

$$y = 100 \cdot x = 100 \cdot (2 \cdot \Delta P / P_0)$$

Here, P_0 is an initial total pressure of the gas and ΔP is a pressure variation before and after heat treatment. In this T. D. method, the accuracy of the absolute ozone density depends on both the accurate temperature control and precise detection of pressure variation ΔP.

Thermal decomposition device which consists of the aluminium vessel(539.2 ml volume), a capacitance manometer(ULVAC: CCM-100), a chromel-alumel thermocouple and a stop bulb, is shown in Fig. 1. The accuracy for the detection of the pressure variation is affected by the following points; (1) the reaction between the ozone gas and the vessel and (2) gas out-diffusion from the vessel. Thus, the vessel is made of aluminium metal to reduce these influences. Once the surface of aluminium is oxidized, it is covered with thin oxide layer made of alumina.

The experimental process for evaluating the ozone density is as follows; the vessel was first evacuated using a rotary pump. After the vessel was attached to the gas sampling port and the air remained in a connected port was pumped, the highly condensed ozone gas was introduced into the vessel. Then the vessel was detached and soaked in a water bath kept at a constant temperature within ±0.13 °C to determine the initial pressure. Taking the vessel out of the water bath, the ozone decomposition was carried out for more than 20 minutes at 150 °C. After the vessel was again soaked in the water bath and cooled to the initial temperature accurately, the pressure variation was measured using the capacitance manometer.

2.3. Q-mass analyzing method(Q-mass method)

We evaluated also the ozone density 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 density was evaluated from the intensity ratio between m/e=32 and 48 according to the

method proposed by Ichimura et al.[5]. This method has an advantage of evaluating the ozone density in situ.

3. RESULTS AND DISCUSSION

3.1. Dilute ozone density region

Dilute ozone gas of lower than 9.3 mol% generated from the ozonizer was evaluated using a well-established UV method(Ebara Jitsugyo Co. Ltd., EG-2001) based on Lambert-Beer's law. The ozone density evaluated by UV method may be superior to those by the T. D. and Q-mass methods in the dilute ozone density region. The experimental error in the lower region would be caused by small pressure change ΔP in the T. D. method, and by small mass signal of m/e=48 in the Q-mass method.

Figure 2 shows the comparison among the results estimated by three methods on the basis of UV method. The ozone densities estimated by two methods agree well with that by UV method. The experimental results and the evaluation in the respective densities show good reproducibility in these methods.

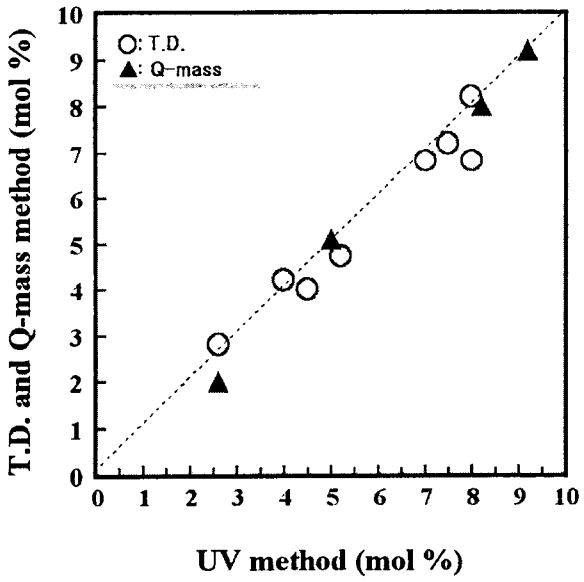


Fig. 2. The comparison of T. D. and Q-mass methods with UV one in the dilute ozone density region.

However, the following problem occurs in the evaluation by the Q-mass method. The absolute ozone density for the unknown gas is evaluation in comparison with a mass signal ratio of m/e=32 and 48 from a standard ozone density gas, so that a definite standard gas must be determined. When the 9.3 mol% ozone gas is adopted as a standard density, the density estimations of the arbitrary gases in the dilute region show good linear relation with that of UV method as shown in Fig. 2, whereas when 2.6 mol% ozone gas is adopted, these calculated results deviate gradually from a linear relationship with that by UV method as the density is denser. This will be discussed later in detail.

3.2. Highly condensed ozone region

Figure 3 shows the ozone density dependence on the gas pressure, which is estimated using both T. D. and Q-mass methods. In this region, it is impossible to evaluate by UV method because the absorption intensity at 253.7 nm is too large and nondetectable.

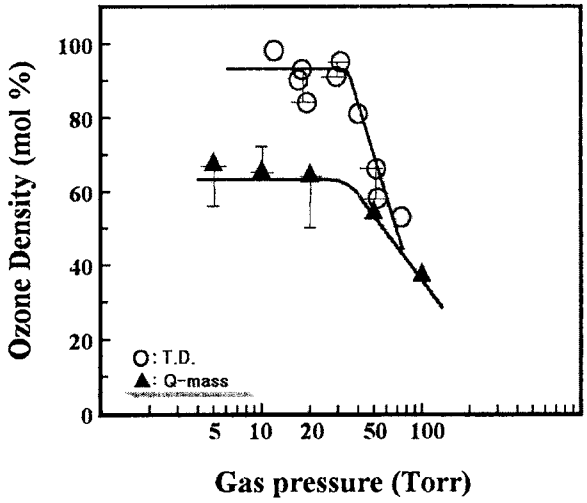


Fig. 3. Ozone density evaluated by T. D. and Q-mass methods in the highly condensed ozone region.

When the gas pressure in the ozone condenser is 12 Torr, the ozone density reached 97 mol% by the T. D. method, and the ozone densities in the lower region than 30 Torr seem to stay within (93±4) mol% from several repeated measurements. On the other hand, when the gas pressure is set over 30 Torr, the ozone densities change in proportional to logarithm of the pressure. Accordingly, this ozone condenser can easily yield the ozone gas of the arbitrary density by controlling the gas pressure and enables me to investigate systematically the effect on the oxidizing power using the different ozone densities in the process of thin film fabrication.

Here, we discuss about the difference of the evaluation between two methods in highly condensed ozone region. The estimation by the T. D. method is more precise as ozone density is higher because pressure variation ΔP is increased in accordance with

the decomposed amount. It is considered that about 10 mol%- degree scattering of these data at maximum is mainly attributed to the ozone gas sampling into the aluminium vessel, because a small variance of the gas pressure P0 was observed when the sample gas was introduced into the measured vessel. Whereas, the ozone density was evaluated to (64±7) mol% using the Q-mass method in the same region. It is crucial to make clear the cause of this large difference between the evaluations of the ozone density by the T. D. and the Q-mass methods. The experimental error in case of the T. D. method is described above, while in case of Q-mass method it comes from the following factors; (1) Ozone or oxygen gas is compelled to decompose via the ionization process in the Q-mass analyzer. Even in the pure oxygen gas, the mass signal of the atomic oxygen is observed about 1/9 as large as that of the molecular oxygen. (2) The mass signal ratio between m/e=32 and 48 is changed with time according to the exhaustion of a filament in the Q-mass analyzer by the oxidizing gas. We guess that the former factor gives the strongest influence to the evaluation by the Q-mass method. The dissociation reaction from $O_2(32)$ or $O_3(48)$ to O(16) cannot be negligible in the highly condensed ozone region, in contrast to Ichimura's proposed estimation, because the mass signal ratio of $O(16)/O_2(32)$ increases from 1/9 to 1/5.5 as the ozone density increases.

In the evaluation using the Q-mass method, the ozone gas by the adsorption method, (64±7) mol%, corresponds to Ichimura's result by liquefaction method, 70 mol%[5] within the experimental error. It is considered that the ozone gas is approximately condensed by the adsorption method as same density as by the liquefaction one. Taking the explosive danger into consideration, the adsorption method is a very distinguished one to condense the ozone gas. Accordingly, we guess that the apparent maximal value, 70 mol%, evaluated by Q-mass method must be corrected to about (93±4) mol%.

It seems that the ozone density evaluated by Q-mass method approaches gradually to that by T. D. method in the lower than 60 mol% region. It implies that the experimental error decreases because the dissociation reaction toward O(16) atom becomes gradually negligible in this region, that is, these data supports my speculation. Judging from the fact described above, it will be difficult to evaluate the ozone at present, in spite of a prominent merit to be able to evaluate directly the ozone density in high vacuum. Thus, we now take consideration of the correction including the dissociation reaction to O(16).

4. CONCLUSIONS

An ozone condenser was constructed as a highly condensed ozone supplier for the film fabrication of Bi-superconductor. The selective ozone adsorption method can evade the explosive ozone reaction on account of the adsorption in gas phase onto silica gel beads. Three methods were applied for the evaluation of the ozone density; ultraviolet absorption, thermal decomposition and Q-mass analyzing methods. In the dilute ozone region, the oxygen density evaluated by these three methods showed good agreement with each other, while it was found that the evaluation by T. D. method was most effective in the highly condensed ozone region. It is found by this method that the ozone is condensed to 97 mol% at maximum. This ozone condenser system is very effective to fabricate the thin film, because the ozone density can be easily controlled by the gas pressure.

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