Analysis of Ozone Concentration by TD and Q-mass Method

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In order to get oxidizing power enough for growth of a superconductive thin film with oxide gas, concentrated ozone was used. As a method for concentrating ozone, a method for concentrating ozone by adsorbing ozone selectively into silica-gel beads is adopted, and this concentration is analyzed by the ultraviolet absorption method, the thermal decomposition method and the Q-mass analyzing method. Thermal decomposition method is most effective for measurement of a high concentration of ozone. Ozone as concentrated by the adsorption method got to have a concentration of 97 mol % at the maximum, and it was identified that the concentration of the ozone gas was stable for the time while a thin film was formed

Keywords : Ozone condensation system, Quadrupole mass(Q-mass) analyzing method, Ultraviolet absorption method, Thermal decomposition method

1. INTRODUCTION

For using a superconductive thin film widely, it is essential to manufacture a superconductive thin film of good quality first of all, and a study on factors to play an important role in the crystal structure of the formed film when a thin film is manufactured should be conducted beforehand. For this reason, a study on oxide gas should be essentially conducted. Ozone in oxide gas can be synthesized from oxygen by using a silent discharging system, and dilute ozone gas of up to about 10 mol% can be easily obtained. As can be known from the report that a superconductive thin film is manufactured by using thin ozone, oxidizing power of ozone is very strong[1].

In this study, ozone was used as oxide gas, and concentrated ozone was used for the purpose of securing sufficient oxidizing power. As a method for concentrating ozone, a method for concentrating ozone by adsorbing ozone selectively into silica-gel is adopted[2]. This method has a characteristic that ozone molecules exist stably because ozone is physically adsorbed into respective pores of silica gel grains so that chained cracking reaction takes place and it is restrained by the force equivalent to the adsorption energy. Therefore, ozone was concentrated and extracted by using the method for concentrating ozone by adsorbing ozone selectively into silica-gel, and in order to use it as oxide gas when a superconductive thin film is manufactured, the concentration of ozone was measured and the characteristic thereof was evaluated by the thermal decomposition (TD) method and the Q-mass analyzing method.

2. EXPERIMENT

2.1 Generation and concentration of ozone

Thin ozone gas was generated by using an ozone generator (Sumitomo Precision Co., Ltd.: SG-01A), and the concentration of the generated thin ozone was measured against "Current I" by an ozone analyzer (Yimwon Industrial Co., Ltd.: EG-2001). An experiment for comparing the oxidizing power of this thin ozone with the oxidizing power of conventional oxygen gas was conducted. Therefore, the $SrTiO_3$substrate was fixed to a heater in a film forming device by having it held by an inconel holder and the substrate temperature was increased to 700 °C, and then, while Cu was sputter-deposited on it by the ion beam sputtering method, oxide gas was supplied. Oxide gas was emitted through a nozzle with a caliber of several millimeter toward the substrate surface, and the vacuum level of the film forming device was maintained at 5×10^{-5} Torr. The results of examining the structure of the formed film by X-ray diffraction were discussed. Then, a concentrating device for generating a high concentration of ozone by adsorbing ozone selectively into the cooled silica gel was built up.

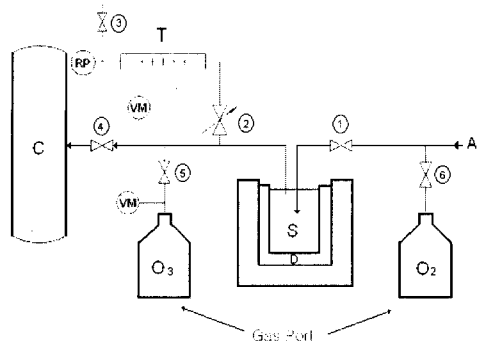

Fig. 1. Ozone condensation system by the adsorption method. (C: chamber, D: Refrigerant, S; Pyrex glass cell containing silica gel beads, T: Ozone decomposition tube, RP: Rotary pump, VM: Vacuum meter, ⋈: Valve, ⋈: Variable valve)

Figure 1 shows a schematic view of the ozone concentrating device. All pipes were made of stainless steel, and impurities existing inside the pipe were removed by jetting nitrogen gas through it before assembling it. Since silica gel in the form of powder is likely to be ejected in the process of vacuum exhausting, it was prepared in the granular form (Kisida Chemical Co., Ltd.) and put into a glass container (about 200 cc).
In the container, an inlet and outlet of gas are installed, and the inlet pipe leads from the upper part of the container to the lower part where silica gel is disposed. The outlet pipe is attached to the upper part of the container.

If the concentration of ozone gets to be 1.2 ppm, it is harmful to the human body, and further oxidizes and solidifies the rotary pump oil[3,4]. Therefore, a heater for cracking ozone was installed in the middle of the gas exhausting system and thereby, ozone gas was prevented from flowing out into the atmosphere and the rotary pump. In order to adsorbing ozone into silica gel, the container was cooled at 195 K by immersing it in a coolant. The coolant was manufactured by putting a mixture of dry ice/ethanol in a dewar. By opening "Valve 1, 2 and 3" as shown in Fig. 1, about 8 mol% of ozone gas was let to flow into it at 2 ℓ/min from "A", and ozone was concentrated.

2.2 Analysis of ozone concentration

The concentrated ozone was analyzed by the thermal decomposition method[5,6]. As a measuring instrument, an aluminium container (540 cc), where a thermocouple, a capacitance manometer and a stop valve were installed, was prepared. For analyzing the ozone concentration, in the first place, the container was vacuumized by the rotary pump, and then gas was collected. The pressure and the container temperature at this time were used as initial values. And, ozone in gas was cracked by heating the container. Such cracking reaction was completed by heating it at 150 °C for 20 minutes. If the mol ratio of ozone versus oxygen in gas is x : (1-x), the whole mol number is increased as ozone is cracked.

$$xO_3 + (1\text{-}x)O_2 \rightarrow (1+x/2)O_2 \ (0 \leqq x \leqq 1) \quad (1)$$

From this relation, "C", the concentration (mol%) of ozone in the collected gas can be obtained as follows[7]

$$C = 2 \cdot [(P_1\text{-}P_0) / P_0] \cdot 100 \quad (2)$$

Where in P_0 means the initial pressure value, and P_1 means the pressure value after cracking ozone. It can be known that in case a change in pressure is great in the domain of a high concentration of ozone, the analysis of the ozone concentration by the thermal decomposition method functions effectively. On the other hand, there is the in-situ method for measuring the ozone concentration in the film forming device. Ichimura et. al. of the Japan Federation of Electrical Organization reported the results of analyzing the ozone concentration by using the Q-mass analyzing method[8].

In this study, these two methods for measuring the ozone concentration were comparatively analyzed.

3. RESULTS AND DISCUSSION

3.1 Generation and oxidation characteristics of ozone

Thin ozone gas was generated by using the ozone generator (Sumitomo Precision Co., Ltd.: SG-01A). The ozone generator generates thin ozone of about 0 ~ 10 mol% by changing the flow rate of oxygen gas (1 ~ 2.5 ℓ/min) and the discharge current ("I") (1 ~ 3 mA).

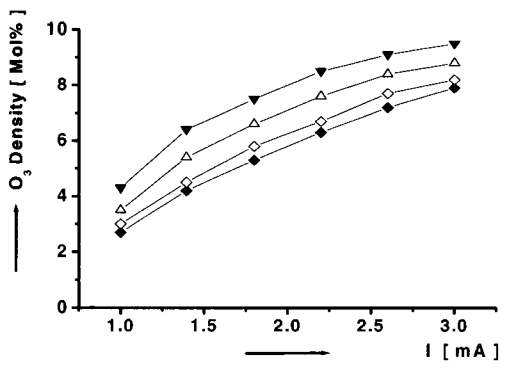

Fig. 2. Product of dilute ozone observed by ozone generator. (▼1.0 ℓ/min, △1.5 ℓ/min, ◇2.0 ℓ/min, ◆2.5 ℓ/min)

Figure 2 shows the results of measuring the concentration of thin ozone generated against "Current I" by using the ozone analyzer (Yimwon Industrial Co., Ltd.: EG-2001) using the ultraviolet absorption method. An experiment for comparing the oxidizing power of this thin ozone with the oxidizing power of conventional oxygen gas was conducted in the form of supplying oxide gas while sputter-depositing Cu on the substrate by the ion beam sputter method by increasing the substrate temperature to 700 °C.

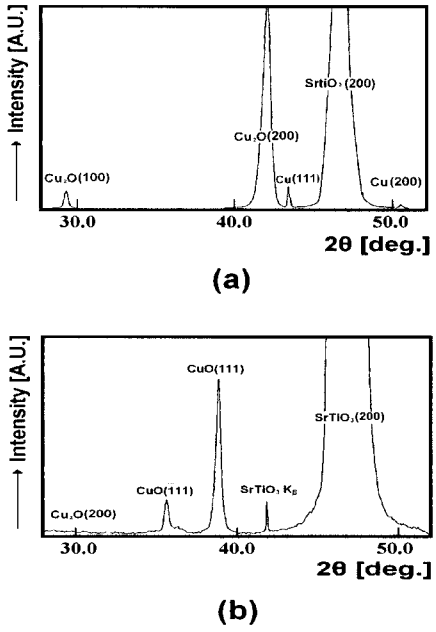

Fig. 3. XRD patterns of the observed Cu-thin films.
(a) pure oxygen (b) dilute ozone

Figure 3 shows the results of examining the structure of the formed film by X-ray diffraction, maintaining the vacuum level of the film forming device at 5×10^{-5} Torr. In case convention oxygen is used, a monovalent copper peak appears greatly, and particularly, a small peak of non-oxidized metal copper is observed. Meanwhile, it can be known that in case thin ozone of 10 mol% is used, bivalent copper oxide (CuO) is generated. It is shown that as thin ozone is used, the oxidation state of copper is greatly improved under the same conditions.

When a thin film is formed, it is necessary to change the substrate temperature in the range of 700 ~ 800 °C in correspondence to the superconductive state as manufactured. In order to secure sufficient oxidizing power in this temperature range, concentrated ozone was used.

3.2 Measurement of the ozone concentration by the thermal decomposition method

Figure 4 showed the results of comparing the values of concentration of thin ozone measured by the ultraviolet absorption method[9] with those measured by the thermal decomposition method. It can be thought that causes of measurement errors are a change in volume resulting from deformation of the container and a hysteresis of the value as indicated (read) by the manometer.

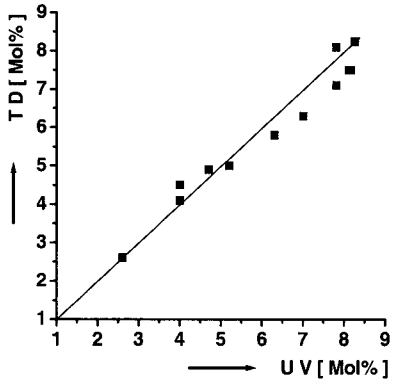

Fig. 4. Comparison between UV and TD methods.

Thus, oxygen gas was imported into the container and it was analyzed several times. Thereby, it could be identified that an error resulting from such causes was so tiny enough to be ignorable. It can be known from this result and the above Expression (2) that the thermal decomposition method is effective for analysis of the ozone concentration in the thin ozone domain, and further it functions effectively in the ozone domain of a high concentration in case a change in pressure is great.

Meanwhile, since the time required to manufacturing a thin film with a high concentration of ozone is more than 4 hours including the time for the substrate temperature to fall, stability of the ozone concentration is required for this time. So, the ozone gas of a high concentration was analyzed several times for the time while a thin film was actually formed. As an experimental condition, the ozone gas pressure in the film forming device was maintained at 5×10^{-5} Torr. In calculation, this value is equivalent to the maximum ozone pressure when a thin film is manufactured, and ozone molecules are supplied from the nozzle to the substrate at a rate of 2×10^{19} molecules/min.

Figure 5 shows the result of plotting the ozone concentration measured in several times of experiments for manufacturing a thin film against the gas supply time. When gas starts to be supplied, the ozone concentration of 97 mol% at the maximum was obtained, and the ozone concentration of 90 mol% was maintained even when gas was supplied for more than 5 hours. Thereby, it was identified that the concentration of ozone gas was stable for the time while a thin film was formed. The current ozone concentrating system realizes the semi-permanent supply of ozone of a high concentration by

the system for concentrating ozone and supplying ozone to the film forming device alternately by installing two silica gel containers in parallel.

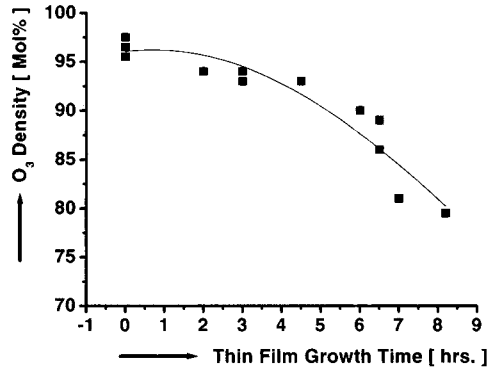

Fig. 5. Thin film growth time versus the ozone concentration.

3.3 Measurement by Q-mass analyzer

The ozone concentration is obtained on the basis of the strength ratio ($m=I_{32}/I_{48}$) of oxygen peak versus ozone peak as indicated in the Q-mass analyzer. By using the peak ratio (m_1) of oxygen molecule versus ozone molecule as obtained from thin ozone (Co mol%) of which the concentration is known, the peak ratio (m_2) of oxygen versus ozone in the ozone gas of a high concentration is interpreted. Thereby, the ozone concentration (C mol%) is obtained. This is expressed in the following expression :

$$C = [1+(1-C_0) / (C_0 \cdot m_1/m_2)]^{-1} \quad (3)$$

The ozone gas generated by the silica gel adsorption method was analyzed in the same manner. The Q-mass analyzer (AQA-100MPX) of ANELVA was used in this experiment.

Figure 6 showed peaks of the Q-mass analyzer when oxygen gas of 9.3 mol% and ozone gas of 90 mol% were respectively imported to the film forming device. When this result was analyzed, the peak (M=16) of oxygen atom had the same strength in any gas. In the domain of ozone of 9.3 mol%, good responsive characteristic appeared, but in the domain of ozone of 90 mol%, responsive characteristic got deteriorated in comparison with measurement by the thermal decomposition method. This is because the ozone cracking effect by thermal electron of the filament of the Q-mass analyzer is ignored, and because the ozone cracking effect by measurement of the Q-mass analyzer gets to be greater when the ozone concentration is high.

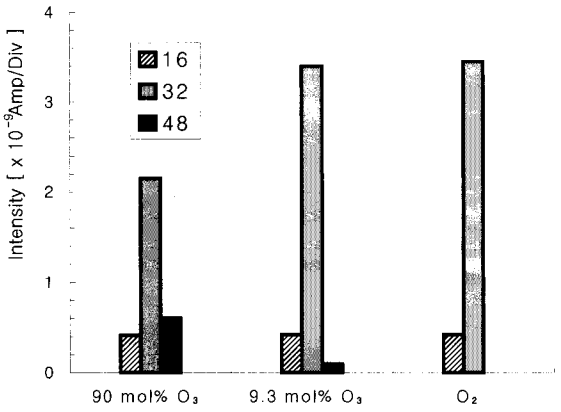

Fig. 6. Mass signals peaks obtained by Q-mass analyzer. (ⓐ 90 mol% O_3 ⓑ 9.3 mol% O_3 ⓒ pure oxygen O_2)

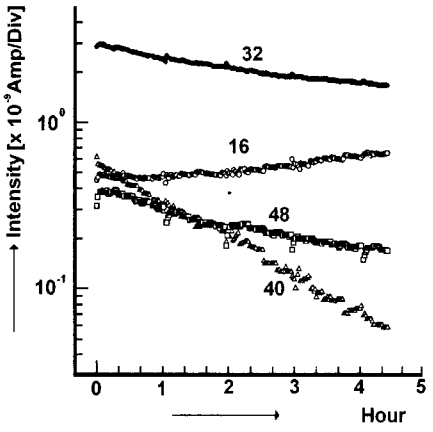

Fig. 7. Degradation of Q-MASS filament.

Figure 7 showed the results of analyzing components of gas in the device by using the Q-mass analyzer for more than 4 hours while the film was formed. It can be observed that because it is exposed to strong oxidation atmosphere, the filament gets to be deteriorated so that the balance between respective peaks is lost. For this reason, for the present, in-situ measurement of the ozone concentration by the Q-mass analyzer remains subject to qualitative evaluation.

4. CONCLUSION

Ozone gas for growth of a superconductive thin film was generated by an ozone generator, and then, it was analyzed by comparing it with conventional oxygen. As a result, it was identified that in the case of using ozone gas, sputter-deposition of Cu was greatly improved. Further, in order to secure sufficient oxidizing power, an

experiment for concentrating ozone was conducted. Ozone was condensed by the selective adsorption method using silica gel, and it was extracted by the vacuum exhaustion method. In order to analyze the ozone concentration of gas, the and the Q-mass analyzing method were used. As a result of analyzing a high concentration of ozone gas by the thermal decomposition, a high concentration of ozone gas of 97 mol% at the maximum was generated, and the ozone concentration was maintained at 90 mol% even for more than 5 hours. On the other hand, in-situ analysis was attempted in the film forming device by using the Q-mass analyzer, but it was impossible to conduct quantitative evaluation due to deterioration of the filament in the device.

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