Characteristics of Superposed Discharge type Ozonizer by Variation of Inner Dielectric Vacuum

Byung-Joon Chun*, Kwang-Sik Lee* and Hyun-Jig Song**

Abstract - In this paper, a superposed discharge type ozonizer with an internal dielectric that can be made into a vacuum tube has been designed and fabricated. Ozone generation and discharge characteristics have been investigated in accordance with output voltage of power supply, flow-rate, discharge power and vacuum of inside internal dielectric. Pure oxygen was used as the supply gas of the ozonizer. Ozone concentration and ozone generation are gradually increased when discharge power is increased at the same flow-rate and they are both proportional to the vacuum level. As such, the maximum ozone concentration of 8840 ppm was obtained at vacuum 0.1 Torr and flow-rate 0.5 ℓ /min.

Keywords: ozone, vacuum, superposed discharge, ozone concentration and ozone generation

1. Introduction

Many researchers have attempted to prove the bonding structure of ozone. In 1953, R. Trambarulo *et al.* proved that ozone has an isosceles triangle structure and that the bond angle of each oxygen atom is 116.5°, while bond distance between oxygen atoms is 0.1278 nm using the microwave spectrum method. According to this research, the structure of ozone was verified with triatomic as an allotrope of oxygen. We must consider ozone as a molecule of oxygen with an atom of O attached firmly. This atom, which is difficult to attach, is easily dissociated to the oxygen molecule, hence it has great oxidizing power and does not leave any hazardous residuum [1].

Therefore, ozone has been applied to various industrial fields such as water treatment, air cleaning, semiconductor fabrication, the medical field, surface processing of thin film, *etc.* It is essential that high concentration and high yield ozone should be generated to apply those industrial fields. So, to upgrade ozone concentration and ozone yield, we have suggested a superposed discharge type ozonizer that superposes two silent discharges within the same discharge gap [1, 2].

There are various methods for generating ozone; silent discharge method, photochemical method [2~4], electrolysis method, X-ray irradiation method, *etc.* [3]. Among these methods, the silent discharge method is commonly used to generate ozone because it is safe, easy to control and has high efficiency. In this study, a superposed discharge type ozonizer, having three electrodes and one discharge gap, was designed and fabricated. Furthermore the discharge and ozone generation characteristics of the superposed discharge type ozonizer were investigated by variation of vacuum degree of the inner dielectric.

In the superposed discharge type ozonizer, commonly, the vacuum dielectric tube or dielectric, in which a dilute electrolyte such as NaCl is filled, is employed to increase discharge current. In this paper, therefore, we controlled the vacuum of the internal dielectric to discover the effect of vacuum degree for ozone concentration.

2. Ozone Formation Process

In oxygen, at atmospheric temperature and pressure, typical microdischarges are preserved for a few nanoseconds with the charge usually being less than 1 nC. The most abundant charge carriers are electrons, positive oxygen ion O_2^+ and negative oxygen ions O^-, O_2^-, O_3^-. Their concentrations depend on the strength of the microdischarges [1, 2].

The most important reaction step of ozone formation is the dissociation of O_2 molecules by electrons in microdischarges with suitable energy (6~9 eV), a third body reaction among O, O_2, and a third collision partner M (O_2, O_3 or N_2 in air), which are as follows;

$$O_2 + e \rightarrow e + O\,(^3P) + O\,(^3P) \rightarrow e + 2O \qquad (1)$$

$$O_2 + e \rightarrow e + O\,(^1D) + O\,(^3P) \rightarrow e + 2O \qquad (2)$$

$$O + O_2 + M \rightarrow O_3^* + M \rightarrow O_3 + M \qquad (3)$$

* School of Electrical Engineering and Computer Science, Yeungnam University, Korea. (bjchun@yumail.ac.kr)
** Dept. of Electricity Applied Computer, Kumi College, Korea. (hjsong@kumi.ac.kr)
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where, M=O, O_2 or O_3 is a third collision partner, and O_3^* stands for an exited transient ozone species, which is the initial reaction product. Reaction (1) is extremely rapid and the timescale for O formation is given by the width of the current pulse (2 ns). Also, ozone formation takes just a few microseconds because charge carriers commonly disappear in periods shorter than 10 ns [4~6].

The threshold energies of reactions (1) and (2) are 6 and 8.4 eV respectively by the Franck-Condon region for excitation from the ground state. The combined action of reactions (1) and (2) allows using about 80 % of the electron energy for the dissociation process over the range of reduced field (100 Td $\leq$ *E/n* $\leq$ 300 Td). Here, *E/n* is reduced field (*E*: electric field intensity) and 1 Td = 10^{-17} V· cm². These two processes are engaged in the dissociation process of ozone because of its high dissociation ability by oxygen molecules [5, 6].

Ozone is mainly formed by dissociation of O_2 by means of electron impact that is shown in reaction (1). Moreover, ionic reactions contribute little to ozone formation.

In conclusion, large ozone concentration can be obtained by building a great number of microdischarges while maintaining optimum microdischarge strength.

3. Experimental Apparatus and Method

3.1 Experimental Apparatus

Fig. 1 shows the schematic diagram of discharge tubes of the superposed discharge type ozone generator (SDO), which has two dielectrics and three electrodes.

In Fig. 1, the internal dielectric is made of quartz glass with a thickness of 1.1 mm and, an outer diameter of 12.9 mm, as well as a central electrode, which is made of tungsten (W) with a thickness of 1.0 mm and, a total length of 250 mm, which is inserted into the center of the internal dielectric. The internal electrode, which is also made of tungsten with a thickness of 0.5 mm and, a pitch of 5 mm, is wound between the internal and external dielectrics. Furthermore, the external electrode is attached to the exterior of the external dielectrics, and it is comprised of copper tape. Lastly, Pyrex glass is the material of the external dielectric, which has an outer diameter of 18.0 mm and a thickness of 1.85 mm.

Microdischarge is generated between internal and external dielectrics, then gap spacing is setup to be 0.7 mm. AC high voltage generated from the neon transformer is applied to the central and internal electrodes and the external electrode plays the role of ground. Therefore, silent discharge occurs between the central and external electrodes, and between the internal and external electrodes during 1 cycle. Two silent discharges are superposed in the discharge gap, resulting in increments of ozone concentration.

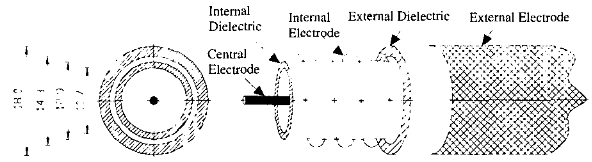

Fig. 1 Schematic diagram of discharge tube

The designed and manufactured ozone generator shown in Fig. 1 can evacuate air inside the internal dielectric using a rotary vacuum pump to study the ozone generation characteristics in accordance with the vacuum level of internal dielectric.

Furthermore, to study the discharge and ozone generation characteristics of the ozone generator according to vacuum level, the internal dielectric produced a vacuum using a rotary vacuum pump (Ultimate pressure: ~10^{-4} Torr, Free air displacement: 150 ℓ /min, Shimadzu Seidakusho Ltd., Japan). And then, a Pirani type vacuum gauge (PT-3P, Range: 1.3 × 10^{-1} Pa ~ 1 atm, Divac Ltd., Japan) was employed between the rotary vacuum pump and internal dielectric to measure the vacuum level of the internal dielectric. In this paper, the vacuum level was controlled in three steps; 0.1 Torr (13.3 Pa), 1 Torr (133 Pa) and 760 Torr (101,300 Pa = 1 atm) to conduct the experiments.

3.2 Experimental Method

Fig. 2 displays the schematic diagram of the arrangement of the ozone generation system for this experiment. The system consists of the ozone generator, process gas supply unit, power supply, measurement apparatus and vacuum pump unit. In Fig. 2, the solid line indicates the power line between power supply and measurement apparatus, and the dotted line indicates the gas flow line from oxygen bombe to ozone monitor.

The process gas used in the system was pure oxygen, controlled by flowmeter (0~10 ℓ /min, Chiyoda Seiki Co., Japan). Flow-rate was varied with 0.5, 1, 2, 4 and 8 ℓ /min.

To conduct the measurement of ozone concentration, a UV absorption type gaseous ozone monitor (0~100,000 ppm, Okitronics Ltd., Japan) was employed. The ozone monitor inhaled 0.3 ℓ /min of ozone gas at each sampling time. Ozone generation and ozone yield were both calculated. The experiments were carried out 5 times and the mean value was hired. The ozone generator was cleaned for about 5 minutes using process oxygen gas to obtain a uniform discharge state.

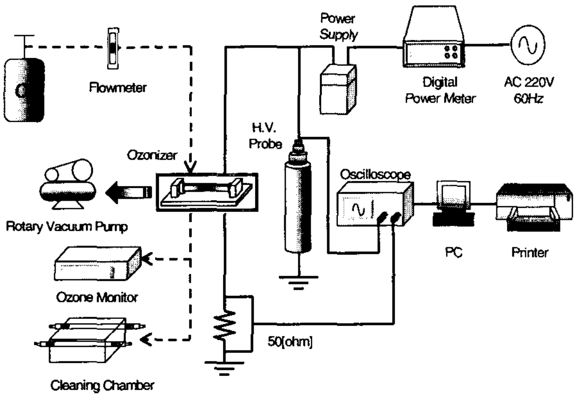

Fig. 2 Schematic diagram of arrangement of ozone generation system

A commercial neon transformer (NT, Input voltage: AC 220 V, Input power: AC 150 VA, Maximum output voltage: 15 kV, Output current: 20 mA) was used as a high voltage source. Discharge voltage, discharge current and waveforms varying according to vacuum level were measured through a high voltage divider (EP-50K, Divide rate = 2000:1, Pulse Electronics Ltd., Japan) and an oscilloscope (TDS 3014, 100 MHz, 1.25 Gs/s, Tektronics), and then waveforms were printed out.

At this point, discharge voltage equaled the voltage between the central and external electrodes plus the voltage between the internal and external electrodes; these are CH1 and CH2 oscilloscope voltages.

Consumed discharge power was measured by a digital power meter (GPM-8212, 5 ~ 640 V, 0.64 ~ 20.48 A, 0 ~ 9999 W, accuracy: ±0.2 %, Instek Ltd., Taiwan). The measured discharge power includes the loss of neon transformer and line loss.

4. Experimental Results

4.1 Discharge Characteristics

Fig.s 3 ~ 5 show waveforms of discharge voltages and discharge currents at a flow-rate of 0.5 ℓ /min and a vacuum level of 0.1, 1, 760 Torr respectively. Here, Ch1 is the voltage applied to the central electrode, Ch2 is the voltage applied into the internal electrode and Ch3 is the current of external electrode used as ground.

At each Fig., Ch1 voltage is higher than Ch2 voltage because the gap between the central electrode and the external electrode is relatively wider than the gap between internal electrode and external electrode. Therefore, the insulation strength of Ch1 voltage is stronger than Ch2 voltage; resulting in the magnitude of voltage. In Fig. 5, positive and negative currents are superposed as pulse shape, and silent discharge is generated while pulse currents turn on. This obviously confirms that discharge pause period is shorter than single silent discharge. Discharge current is leading current; this should be the effect of capacitance of the discharge gap.

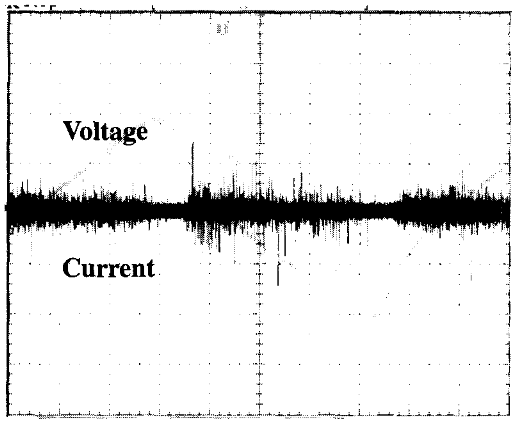

Fig. 3 Waveforms of discharge voltage (13.15 kV) and discharge current (0.39 mA)at vacuum 0.1 Torr

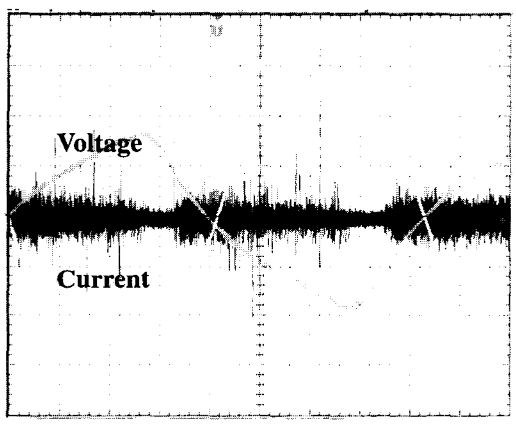

Fig. 4 Waveforms of discharge voltage (13.01 kV) and discharge current (0.39 mA)at vacuum 1 Torr

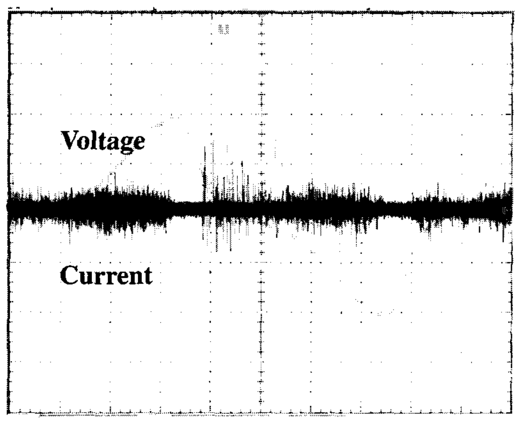

Fig. 5 Waveforms of discharge voltage (12.06 kV) and discharge current (0.32 mA)at vacuum 760 Torr

In Fig. 5, Ch1 voltage at vacuum 760 Torr is higher than the voltages of 0.1 Torr and 1 Torr. This could be explained by the fact that discharge firing voltage, between central electrode and external electrode, is increased because the mean free path of the free electron, generated within the internal dielectric, is becoming shorter with a decrease in vacuum level. Hereby, higher voltage is applied to Ch1.

4.2 Ozone Concentration and Generation Characteristics

Fig.s 6, 7 and 8 exhibit ozone concentration and ozone generation characteristics with variation of discharge power at vacuum 0.1 Torr, 1 Torr and 760 Torr respectively. In Fig. 6 ~ Fig. 8, ozone concentration and ozone generation are gradually increased with increasing discharge power because the numbers of microdischarges, generated in the discharge gap, are increased by increasing input energy applied to the ozone generator. This results in activating the dissociation process of oxygen molecules.

Therefore, maximum ozone concentrations of 8840 ppm, 7770 ppm and 6595 ppm were obtained at a flow-rate of 0.5 ℓ /min, with discharge powers at 22.9 W, 21.0 W, 26.2 W and at each vacuum of 0.1 Torr, 1 Torr and 760 Torr, respectively. Maximum ozone generations of 593 ㎎/h, 506 ㎎/h and 388 ㎎/h were obtained at flow-rates of 1 ℓ /min, 1 ℓ /min, and 0.5 ℓ /min, with discharge powers at 23.4 W, 21.3 W, and 26.2 W and at each vacuum of 0.1 Torr, 1 Torr and 760 Torr, respectively.

The vacuum in the internal dielectric is lower, and the mean free path of the electrons is shorter because there are many gaseous molecules in the internal dielectric. Thereby, ionization probability of the oxygen molecule is decreased; this results in a decrease of ozone concentration [7, 8].

Moreover, at the same vacuum level such as in equation (4), the velocity of process gas is decreased with decreasing flow-rate of process gas, so that the crossing time of oxygen molecules becomes longer. Therefore, collision probability between the electrons, generated by microdischarges in the gap, and oxygen molecules becomes higher. Hereby, probability of ozone concentration was increased. According to these results, ozone concentration and ozone generation, given by multiplying ozone concentration and flow-rate, are increased with decreasing flow-rate [9].

$$Q = A \times U, \tag{4}$$

where, Q is flow-rate of process gas m³/s, U is velocity of process gas m/s and A is sectional area of discharge tube.

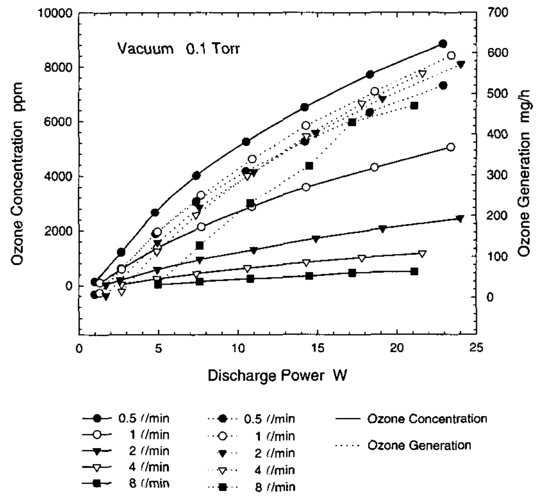

Fig. 6 Characteristics of ozone concentration and generation at vacuum 0.1 Torr

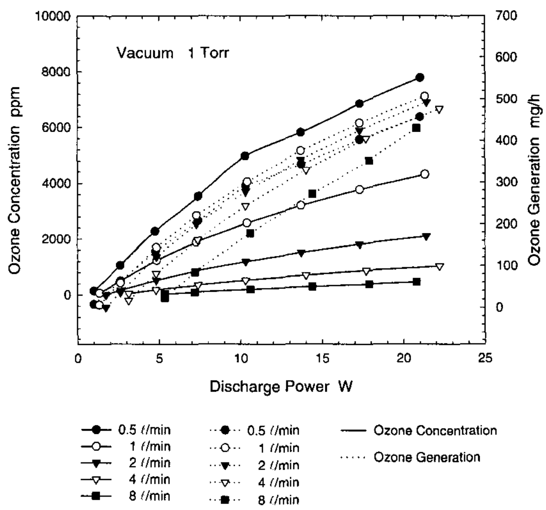

Fig. 7 Characteristics of ozone concentration and generation at vacuum 1 Torr

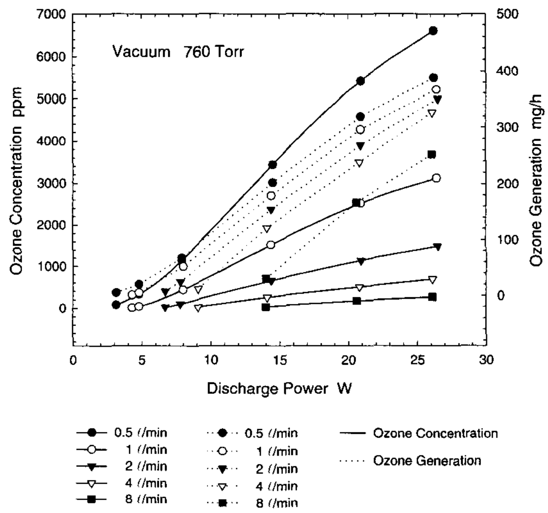

Fig. 8 Characteristics of ozone concentration and generation at vacuum 760 Torr

4.3 Ozone Yield Characteristics

Figs 9~11 display the characteristics of ozone yield with variation of flow-rate at 0.1 Torr, 1 Torr and 760 Torr. Throughout these Fig.s, ozone yield is increased with increasing discharge power at relatively lower flow-rate, and it has a maximum value at about a discharge power of 5 W, at which point it slightly decreases because of the dissociation processes of ozone. Incidentally, ozone yield has a slow increase tendency with increasing discharge power at a relatively higher flow-rate.

Therefore, maximum ozone yields 32.69 g/kW h, 30.27 g/kW h and 15.25 g/kW h were obtained at flow-rates of 1 ℓ /min, 1 ℓ /min, and 0.5 ℓ /min and discharge powers of 4.94 W, 7.30 W, and 20.9 W and at each vacuum of 0.1 Torr, 1 Torr, 760 Torr, respectively.

Increase of ozone yield somewhat depends on ozone generation. The numbers of microdischarges are increased with increasing input power, while it affects to activate the ozone dissociation process by heat. So, ozone yield is saturated after the peak point because of an over supply of input power. Another reason is that when low flow-rate of oxygen is supplied, the travel time of oxygen molecules is longer; hereby the cooling effect of process gas drops rapidly. These contribute to the saturation of ozone yield.

In the case of Fig. 11, the exterior of the internal dielectric is weakly charged compared with high vacuum because the inside of the internal dielectric is under atmospheric pressure. Silent discharge in the gap is weakly generated; in other words, the numbers of microdischarges outside of the internal dielectric are smaller than those under high vacuum conditions. According to this reason, the flow-rate dependency of ozone yield is high. Silent discharge in the gap is weakly generated under infirm ionization process as compared with higher vacuum conditions.

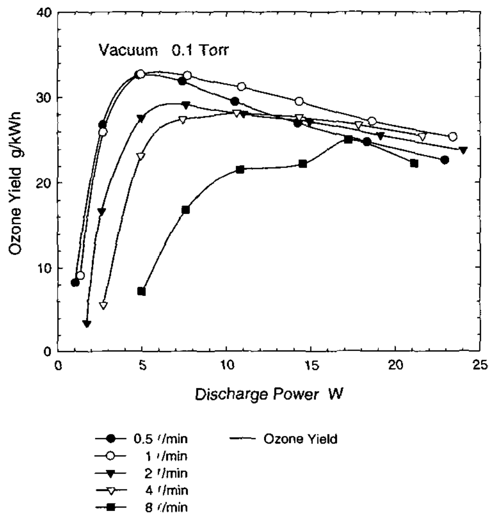

Fig. 9 Characteristics of ozone yield at vacuum 0.1 Torr

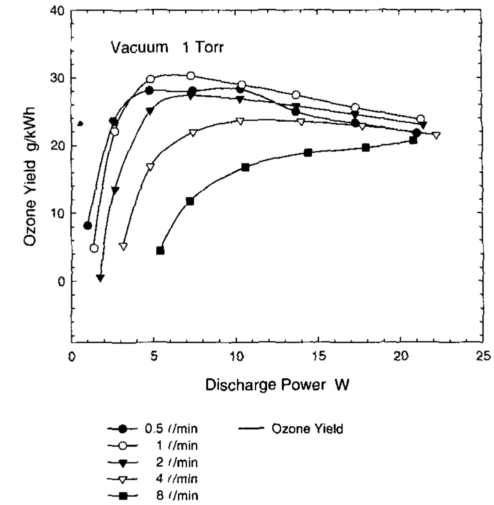

Fig. 10 Characteristics of ozone yield at vacuum 1 Torr

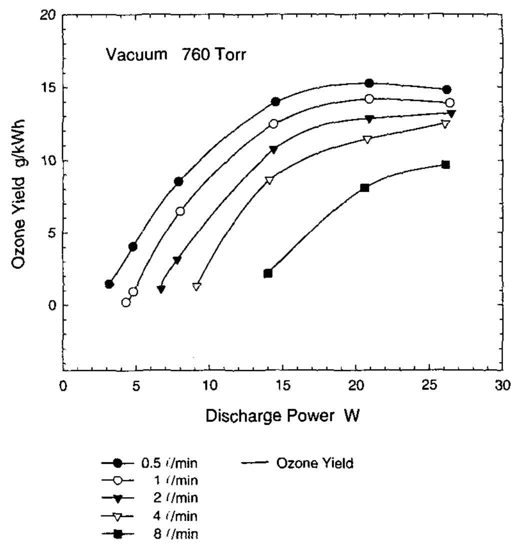

Fig. 11 Characteristics of ozone yield at vacuum 760 Torr

Moreover, if flow-rate is increased, velocity of the gas is proportionally faster, so that the collision probability of oxygen molecules with microdischarges is lower. Consequently, flow-rate dependency on ozone yield characteristics at low vacuum is much higher than that at high vacuum.

5. Conclusion

In this study, a superposed discharge type ozonizer was designed and fabricated, and vacuum degree of the internal dielectric was varied to conduct discharge and ozone generation characteristics. Therefore, we obtained the following results.

Maximum ozone concentrations of 8840 ppm, 7770 ppm and 6595 ppm were obtained at a flow-rate of 0.5 ℓ /min, with discharge powers of 22.9 W, 21.0 W, and 26.2 W and at each vacuum of 0.1 Torr, 1 Torr and 760 Torr, respectively.

Furthermore, maximum ozone generations of 593 mg/h, 506 mg/h and 388 mg/h were obtained at flow-rates of 1 ℓ /min, 1 ℓ /min, and 0.5 ℓ /min, with discharge powers of 23.4 W, 21.3 W, and 26.2 W and each vacuum of 0.1 Torr, 1 Torr and 760 Torr, respectively.

Ozone concentrations and ozone generations are gradually increased with increasing discharge power at the same flow-rate, and they are proportional to vacuum level. So, the maximum ozone concentration of 8840 ppm was obtained at vacuum 0.1 Torr, flow-rate 0.5 ℓ /min and discharge power 22.9 W. Also, the maximum ozone generation was 593 mg/h at vacuum 0.1 Torr, flow-rate 1 ℓ /min and discharge power 23.4 W.

Maximum ozone yields 32.69 g/kW h, 30.27 g/kW h and 15.25 g/kW h were obtained at flow-rates of 1 ℓ /min, 1 ℓ /min, and 0.5 ℓ /min, with discharge powers of 4.94 W, 7.30 W, and 20.9 W and at each vacuum of 0.1 Torr, 1 Torr, 760 Torr, respectively.

Based on the above results, ozone concentration, ozone generation and ozone yield are increased with a decrease in the degree of vacuum of the internal dielectric. Ozone concentration of the fabricated ozonizer can be controlled at the same flow-rate and input power by varying the degree of vacuum in the internal dielectric.

Therefore, this ozonizer can be applied to not only industrial facilities, where high ozone concentration is needed, but also small size ozonizers, in which low ozone concentration is required at the same input power.

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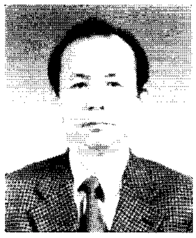
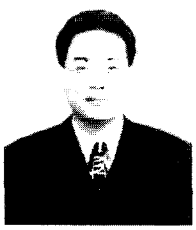
Byung-Joon Chun
He was born in 1970 in Daegu, Korea. He received his B.E., M.E. and Ph. D. degrees from the Department of Electrical Engineering at Yeungnam University in 1996, 1999 and 2003, respectively. Currently, he is a senior research engineer of the FA R&D Lab. at SFA Engineering Corp., and his interests are DBD, plasma cleaning of semiconductors and ozonizers. He is a member of the Korean Institute of Electrical Engineers (KIEE) and the Korean Institute of Illuminating and Electrical Installation Engineers (KIIEE).



Kwang-Sik Lee
He received his B.E., M.E. and Ph.D. degrees in Electrical Engineering from Yeungnam University in 1971, 1973 and 1987 respectively. During the period from 1988-1989 he was engaged as a Visiting Research Professor at Nagoya Institute of Technology in Japan. Currently, he is a Professor in the School of Electrical Engineering at Yeungnam University in Korea. His research interests include electrical discharge, and high voltage engineering and its applications. He is a member of the Korean Institute of Electrical Engineers (KIEE) and the Korean Institute of Illuminating and Electrical Installation Engineers (KIIEE), and IEEE.



Hyun-Jig Song
Hyun-Jig Song was born in 1968 in Daegu, Korea. He received his B.E., M.E. and Ph.D. degrees from the Department of Electrical Engineering at Yeungnam University in 1991, 1993 and 1997, respectively. Currently, he is a full time Lecturer of electricity applied computers at Kumi College. He is a member of the Korean Institute of Electrical Engineers (KIEE) and the Korean Institute of Illuminating and Electrical Installation Engineers (KIIEE).