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Characteristics of He/O_2 atmospheric pressure glow discharge and its dry etching properties of organic materials

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Abstract

In this study, the characteristics of atmospheric low temperature plasmas generated by capillary electrodes with capillary dielectrics were investigated for the application of microelectronic cleaning processes. The characteristics of the plasmas were studied as a function of capillary aspect ratios, input power, electrode distance, He/O_2 gas flow rate, etc., using a high voltage probe, current probe, and optical emission spectroscopy (OES). The voltage between the electrodes increased with the increase of input power, the increase of electrode distance, the decrease of He flow rate, and the increase of O_2 flow rate. The increase of the voltage has led to unstable filamentary discharge from the stable capillary discharge. The use of electrodes with capillary dielectrics instead of a conventional dielectric barrier electrode (the electrode covered with non-capillary dielectric) not only decreased the electrode voltage, therefore, increased the stability of the plasma but also increased the discharge current and, therefore, the intensity of the plasma. Increased ionization and dissociation of the plasma species could be observed by OES with the increase of input power in He/O_2 mixtures. However, with the increase of O_2 flow rate in a constant He flow rate, the emission peaks from He decreased due to the increased electron consumption by oxygen while the emission peaks from O_2^+ and O increased due to the increased ionization and dissociation rates with the increase of oxygen concentration in the He/O_2 gas mixtures. Also, using a He/O_2 gas mixture, organic materials such as photoresist could be successfully removed with the average etch rates higher than 200 nm/min.

Keywords: Optical emission spectroscopy; Capillary dielectrics; He/O_2 gas mixtures

1. Introduction

In general, plasmas used for microelectronics such as for thin film deposition, dry etching, and surface treatment are operated at low pressures. However, to generate plasmas at low pressures, costly vacuum equipment and vacuum measurement tools are required, and the use of vacuum in the processing increases the fabrication cost and decreases throughput. If stable glow discharges can be realized under atmospheric conditions [1–3], the expensive vacuum equipment and the measurement tools can be eliminated and the throughput can be also increased. Recently, different kinds of atmospheric pressure plasmas such as dielectric barrier discharge, atmospheric microwave discharge, pulsed corona plasma, etc., have been studied for the application of surface treatment of organic materials [4,5], growth of organic thin films [6,7], dry etching [8–10], etc.

In this study, among the various atmospheric pressure plasmas, the dielectric barrier discharge with capillary electrode was studied. The basic concept of the discharge is the suppression of glow-to-arc transition instability by creating self-stabilizing cathode falls in the capillary hole and thereby preventing the formation of a cathode spot. Each hole acts as an active current limiting microchannel that prevents the overall current density from increasing above the threshold for the glow to arc transition. This dielectric barrier discharge with capillary dielectrics could give high-density plasmas with a reasonably good uniformity.

In this paper, the effects of the discharge parameters such as power, gas combinations of He/O_2, capillary aspect ratio, the distance between electrodes, etc., on the formation of stable plasmas were studied. Using

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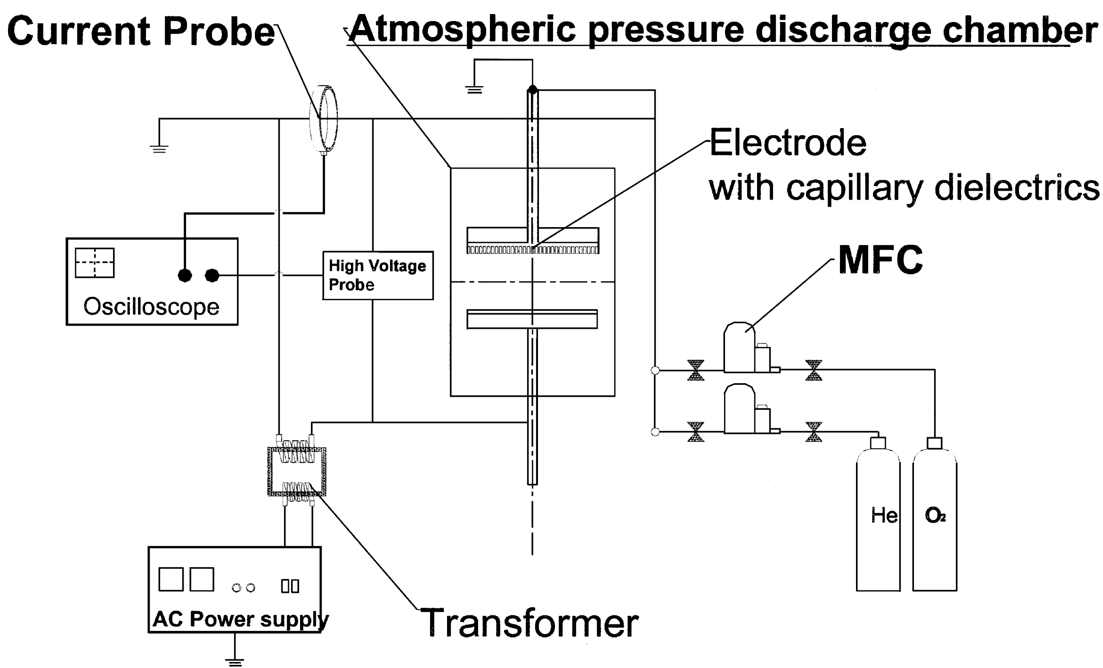

Fig. 1. Schematic diagram of dielectric barrier discharge system with capillary dielectrics used in the experiment.

some of the stable capillary He/O_2 discharge conditions, photoresist covered wafers were etched and their etch characteristics were studied.

2. Experiment

The schematic diagram of the system used in our experiment is shown in Fig. 1. Dielectric barrier discharges with capillary dielectrics operated at the atmospheric pressure were generated in a pyrex reaction chamber which consisted of two parallel-plate electrodes. The powered electrode and the ground electrode were both 140 mm in diameter and were made of stainless steel coated with 50-μm thick polyimide. The bottom electrode was connected to an alternating current (AC) (20–100 kHz, 1 kW) input power supply. From 0 to 200 W of AC power was introduced to the bottom electrode while the top electrode was grounded. The top electrode was additionally covered with an 8-mm thick dielectric plate having different holes to induce glow discharges. The aspect ratios (L/d; d is the diameter of the capillary hole, L is the length of the capillary) of the dielectric plate were varied as 1.5/1, 5/1, and 10/1 and the distance between the capillary holes was 5 mm. An 8-mm thick dielectric plate without capillaries (holes) was also used on the top electrode to generate conventional dielectric barrier discharges and to compare them with the plasmas generated by the capillary dielectrics. The distance between the two electrodes (air gap) was varied from 5 to 15 mm. He or He/O_2 gas mixtures were introduced to the reaction chamber by a mass flow controller through the capillary holes on the top electrode. In the case of conventional dielectric barrier discharges, the gas was fed from the side of the chamber. The He gas flow rate was varied from 0.25 to 3 slm and the O_2 gas flow rate was varied from 0.1 to 0.4 slm at the atmospheric pressure.

The voltage (V peak-to-zero) and the current (mA peak-to-zero) between the electrodes were measured, respectively using a high voltage probe (Tektronix P6015A) and a current probe (Pearson Electronics 6600) connected to the electrode with an oscilloscope. Optical emission spectroscopy [(OES) SC Tech. PCM402] was used to detect plasma species such as He, O_2^+ and O and to characterize the plasma in the atmospheric pressure as a function of discharge parameters such as electrode gap, aspect ratio, power, and He/O_2 gas mixture.

The organic material such as photoresist was deposited using a spin coater on Si-wafers with 1.2 μm in thickness and was mounted on the bottom powered electrode, and was etched using some of the stable etch conditions with He/O_2 gas mixtures. The etched shapes of the photoresist were observed by an optical microscope as a function of O_2 flow rate to characterize the etch properties by the capillary plasmas generated using the electrodes with capillary dielectrics.

3. Results and discussion

3.1. The characteristics of atmospheric pressure plasma

To investigate the atmospheric pressure plasmas using the electrode with capillary dielectrics, discharge para-

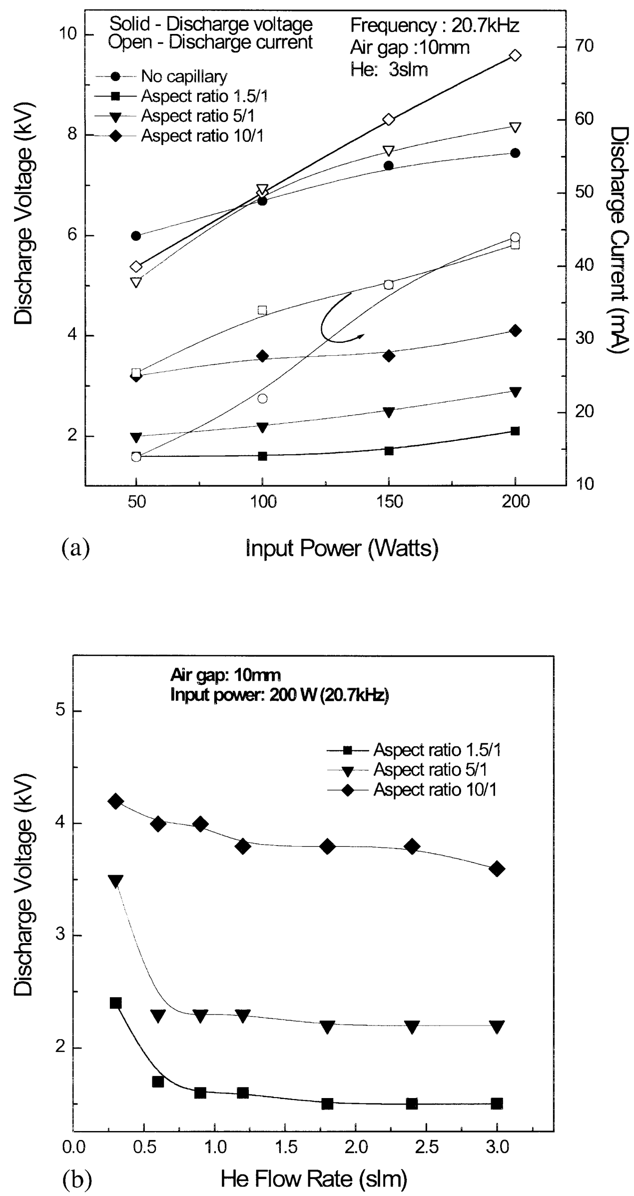

Fig. 2. The effects of input power (a) and He flow rate (b) on the discharge voltage and current for different hole aspect ratios of the electrodes with capillary dielectrics. Discharge voltage and current for the conventional dielectric barrier discharge was included in the figure to compare with the discharges with capillary dielectrics.

meters such as electrode gap, aspect ratio, power and He/O_2 gas mixture were varied and the effects of those parameters on the formation of the capillary plasmas were studied. Fig. 2a,b shows the effects of input power at 20.7 kHz and He flow rate on the discharge voltage and discharge current, respectively. The plasmas were generated with the top electrode installed with dielectric plates having different aspect ratios of the holes (for the dielectric barrier discharge with capillary dielectrics) or no hole (for conventional dielectric barrier discharge). The air gap between the electrodes was kept to 10 mm. When the plasma was generated with these configurations, the three distinct discharges were observed. One was arc type filamentary discharge, possibly from the current concentration at a few points of the electrode, and non-uniform plasmas are obtained between the electrodes. The second type of discharge was glow discharge where all area of the electrode is weakly glowing such as abnormal glow discharges, and in this case, the dielectric barrier discharge studied by other researchers [1,3,10] is obtained. The third type of plasma is the capillary discharge, where intense ion beam-like plasma was obtained at the holes (or capillaries) in the dielectrics. This ion beam-like discharge gives high-density plasma with a reasonably good uniformity, therefore, by varying the above parameters, we tried to obtain stable discharges.

As shown in Fig. 2a, the increase of input power at a fixed He flow rate of 3 slm increased the discharge voltage and discharge current. Also, the increase of aspect ratio of the hole generally increased the discharge voltage and discharge current. When the electrode with conventional non-capillary dielectric (non-capillary electrode) was compared with electrodes with the capillary dielectric (capillary electrode), the non-capillary electrode showed higher electrode voltages with lower current as shown in the figure. Also, the use of the non-capillary electrode showed a weak dielectric barrier discharge while the use of the capillary electrode generally showed bright ion beam-like discharges with more stability. The increase of discharge current with the increase of aspect ratio at a given input power appears to indicate the increase of power consumption to the plasmas. The increase of discharge voltage at a given electrode configuration increased the possibility of filamentary discharges, however, the use of high aspect ratio capillary increased the stability of the discharge even though the discharge voltage was higher. Frequencies in the range of 20–30 kHz were required to generate the stable ion beam-like discharges (capillary discharges), and lower frequency appeared to be the better for the conditions used in our experiment (not shown). Therefore, the input power frequency of near 20 kHz was used for the rest of the experiment.

The effects of pure He flow rate on the discharge voltage and current between the electrodes were also investigated and the result is shown in Fig. 2b. The input power and frequency were fixed at 200 W and 20.7 kHz, respectively. As shown in the figure, the increase of the He flow rate from 0.25 to 1.5 slm generally decreased the discharge voltage and the further increase of He flow rate did not change the voltage significantly for all of the cases. The effect of the aspect ratio of the hole on the discharge voltage and discharge current was similar to the results shown in Fig. 2a, that is, the increase of the hole aspect ratio increased the discharge voltage and current at a given He flow rate in general. The decrease of discharge voltage with the increase of He flow rate appears to be from the increase of electrical conductance between the electrodes by transferring more charged particles generated on an electrode to the other electrode through the gas flow before the recombination. If the conductance of the discharge is increased, the discharge current has to be increased at a given input power. The lower discharge current with the increase of He flow shown in the experiment might be from the loss of input power to the He excitation rather than ionization even though it is not clear at this time. The effect of gas flow on the decrease of the discharge voltage appears to saturate at approximately 1.5 slm of He flow rate. In the condition shown in Fig. 2b, lower than 0.6 slm of He flow generally showed a transition from an ion beam-like capillary discharge to a filamentary discharge, and stable capillary discharges were obtained with more than 1.5 slm of He flow rate at 200 W of input power.

To investigate the degree of ionization and dissociation with the capillary discharges, OES was used and the intensities of the molecular, ionic, and atomic species observed in the plasmas were measured. The results are shown in Fig. 3a,b. Fig. 3a shows an optical emission spectrum measured from 200 to 800 nm for pure 3 slm of He at 150 W of input power, the hole aspect ratio of 10/1, and 10 mm of the electrode air gap. As shown in the figure, in the pure He discharge, the peaks such as N_2 (300–500 nm), O (777.5 nm), O_2^+ (686.3 nm) and OH (308.6 nm) in addition to He atomic peaks (707.6, 667.2 nm, etc.) were observed. These N_2, O, O_2^+ and OH peaks appeared to be from the air and H_2O leaked into the chamber during the operation at the atmospheric pressure. The intensities of O_2^+ (686.3 nm) and O (777.5 nm) in addition to the intensity of the He atomic peak at 707.7 nm were measured as a function of input power while other conditions were kept the same as the conditions in Fig. 3a and the results are shown in Fig. 3b. As shown in the figure, the intensities of He, O and O_2^+ increased with the increase of input power, and it appears to suggest the increased degree of excitation, ionization, and dissociation with the increase of input power in our atmospheric pressure discharges.

In the atmospheric pressure discharge, the air gap between the dielectric-covered electrodes can be an important parameter because it changes the operational conditions. In this experiment, the effects of air gap between the electrodes on the discharge voltage, discharge current, and optical emission intensities were measured for 150 W of input power, 3 slm of He flow, and 10/1 aspect ratio, and the results are shown in Fig. 4. As shown in Fig. 4, the discharge voltage between the electrodes increased linearly with the increase of the air gap while the discharge current decreased with the increase of the gap. The increase of discharge voltage and the decrease of discharge current with the increase of the gap appear to be from the increase of the resistive discharge volume. The increase of the gap also increased the emission intensities such as He, O_2^+ and O up to 10 mm of the gap possibly due to the increased power consumption to the discharge volume and the further increase of the gap decreased the emission intensities. When the gap was larger than 10 mm, a filamentary discharge was obtained possibly due to the high electric field generated on the electrode at a high electrode voltage. Therefore, the decrease of optical emission intensities longer than 10 mm distance appears to be from the change of the discharge type from capillary to filamentary.

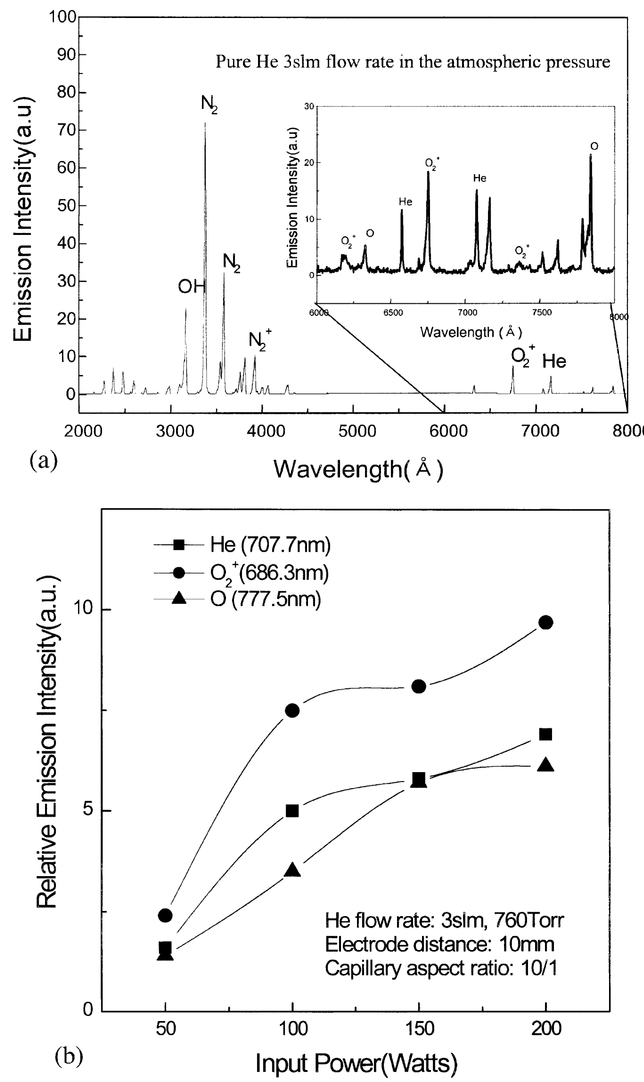

Fig. 3. Optical emission spectra of dielectric barrier discharges with capillary dielectrics using He gas; (a) optical emission spectrum of a discharge and (b) relative emission intensities of plasma species (H_2, O_2^+ and O) of the discharges as a function of input power. Emission peaks such as OH, N_2, O_2^+, etc., appear to be from the air leak during the atmospheric pressure operation.

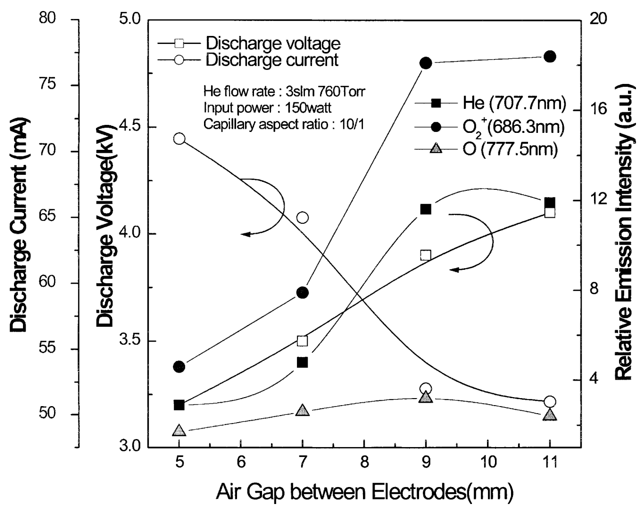

Fig. 4. The effects of air gap between the electrodes on the discharge voltage, discharge current, and relative emission intensities of the discharges with capillary dielectrics.

At a constant 2.4 slm of He flow rate, oxygen was intentionally added and the effects of oxygen flow rate on the discharge voltage, discharge current, and optical emission intensities were investigated. The hole aspect ratio was 10/1 and the input power was maintained at 150 W. The results are shown in Fig. 5. As shown in the figure, the increase of the oxygen flow rate generally increased the discharge voltage and decreased the discharge current. The oxygen is easily charged negatively, therefore, the addition and increase of oxygen consumes more electrons which are required to sustain plasmas, therefore, the increase of the voltage with the increase of oxygen appears to be related to the decrease of charged particle density and discharge current in the plasma. Also, the increase of oxygen flow more than a certain amount (larger than 0.35 slm) changed the discharge type from ion beam-like capillary to filamentary possibly due to the increase of the discharge voltage gradient in the plasma.

Optical emission intensities with the addition of oxygen were also investigated for the same condition and the results are also shown in Fig. 5, for the emission peaks related to He, O_2^+ and O. As shown in the figure, with the increase of oxygen flow rate, the emission peaks related to O_2^+ and O was increased slowly, however, the peak related to He decreased rapidly. The increase of O_2^+ and O emission peaks with the increase of oxygen flow rate is possibly related to the increase of oxygen concentration in the gas mixture, therefore, the increase of dissociation and ionization rates of oxygen. The rapid decrease of the emission peak related to He with the increase of oxygen flow rate at a constant He flow rate appears to be related to the increased electron loss to oxygen by the increase of oxygen concentration in the gas mixture with the increase of oxygen flow rate as discussed previously. The constant low He emission intensity region above 0.35 slm of oxygen was also related to the formation of filamentary discharge.

3.2. The application of atmospheric pressure plasma — dry cleaning of organics material such as photoresist

From the above experiments on the discharge characteristics, we were able to find a range of stable ion beam-like capillary discharge operation conditions and, with some of the conditions, 1.2-μm thick photoresist on Si-wafer was etched. The etch condition used was He (2.5 slm)/O_2 (0.2 slm), 20.7 kHz 200 W of input power, and 10 mm of electrode gap. The capillary ratio was varied from 1.5/1 to 10/1. The result showed the increase of photoresist etch rate with the increase of aspect ratio and, with the aspect ratio of 10/1, higher than 200 nm/min of photoresist etch rate could be obtained on the average. In fact, much higher etch rate (> 3000 nm/min) could be obtained on the wafer areas facing holes compared to the other areas, and circular shape of photoresist clearing pattern was obtained as shown in Fig. 6. Therefore, to improve the etch uniformity and the average etch rate, the denser capillary configuration or rotation of the substrate appears to be required.

4. Conclusions

In this experiment, the basic characteristics of dielectric barrier discharges with capillary dielectrics (capillary discharges) operated at the atmospheric pressure were investigated using a high voltage probe, current

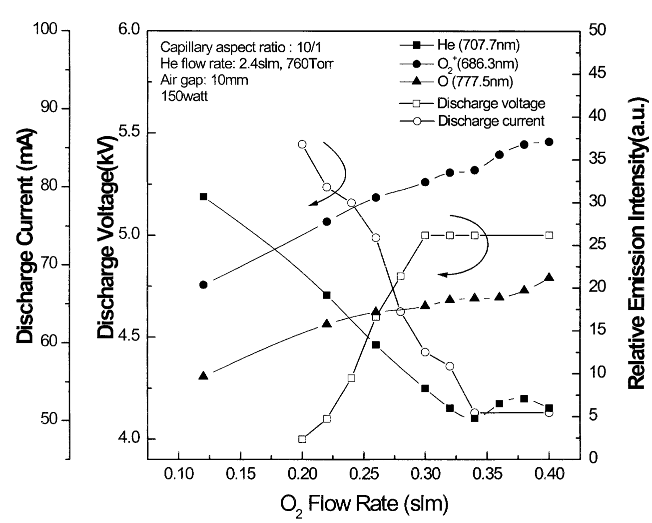

Fig. 5. The effect of O_2 flow rate at 2.4 slm He flow rate on the discharge voltage, discharge current, and relative emission intensities of the discharges with capillary dielectrics.

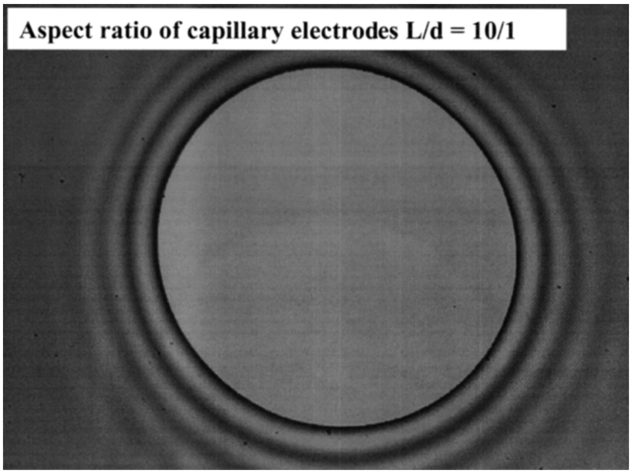

Fig. 6. Optical micrograph of photoresist clearing pattern in He (2.5 slm)/O_2 (0.2 slm), 20.7 kHz 200 W of input power, 10 mm of electrode gap, and the capillary aspect ratio of 10/1.

meter, and optical emission spectroscopy. Also, using some of the stable He/O_2 capillary discharges, the photoresist etch characteristics were investigated.

The discharge voltage of He capillary discharges increased with the increase of input power, electrode distance, and the aspect ratio of the hole while the increase of He flow rate decreased the voltage. Also, the discharge current of He plasma increased with the increase of input power and aspect ratio while the increase of He flow and air gap decreased the discharge current. The addition of oxygen flow to a constant He flow rate also increased the discharge voltage, however, decreased the discharge current. The increase of discharge voltage due to the higher input power, larger electrode gap (>10 mm), lower He flow rate (<1.5 slm), and higher oxygen flow rate (>0.35 slm) caused the transition of the discharge type from the stable ion beam-like capillary discharge to unstable filamentary discharge for the condition used in this experiment. The electrodes with capillary dielectrics showed the lower voltage and higher current compared with conventional non-capillary dielectric covered electrode possibly due to the increased ionization effect in the holes in the dielectrics and also brighter ion beam-like discharge was obtained with these electrodes. All of the optical emission intensities of He, O_2^+ and O, therefore, the degree of ionization and dissociation appear to increase with the increase of input power possibly due to the increased power deposition to the plasma. However, the increase of oxygen flow rate in a constant He gas flow rate decreased the He emission peaks. It appears to be from the increased electron consumption by the oxygen even though the emission peaks related to the O_2^+ and O increased with the increase of the oxygen flow rate by the increase of the oxygen ionization and dissociation in the He/O_2 gas mixture.

Using some of the stable He/O_2 discharge conditions, photoresist on Si-wafers was etched and higher than 200 nm/min was obtained on the average. Circular photoresist clearing pattern was observed due to the increased etch rate at the holes. To improve the etch rate and overall uniformity, electrodes containing denser holes in the dielectrics or rotation of the substrate need to be used.

Acknowledgements

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References

[1] T. Yokotama, M. Kogoma, T. Moriwaki, S. Okazaki, J. Phys. D: Appl. Phys. 23 (1990) 1125.
[2] T. Yokoyama, M. Kogoma, S. Kanawaza, T. Moriwaki, S. Okazaki, J. Phys. D: Appl. Phys. 23 (1990) 374.
[3] S. Okazaki, M. Kogoma, M. Uehara, Y. Kimura, J. Phys. D: Appl. Phys. 26 (1993) 889.
[4] F. Massines, G. Gouda, J. Phys. D: Appl. Phys. 31 (1998) 3411.
[5] K. Kiyokawa, A. Itou, H. Matsuoka, M. Tomimatsu, K. Sugiyama, Thin Solid Films 345 (1999) 119.
[6] S.P. Bugaev, A.D. Korotaev, K.V. Oskomov, N.S. Sochugov, Surf. Coat. Technol. 96 (1997) 123.
[7] Y. Sawada, M. Kogoma, Powder Technol. 90 (1997) 245.
[8] J.Y. Jeong, S.E. Babayan, A. Schuitze, V.J. Tu, J. Vac. Sci. Technol. A 17 (2581) 2581.
[9] Z. Falkenstein, J. Appl. Phys. 85 (1999) 525.
[10] Z. Falkenstein, J. Appl. Phys. 83 (1998) 5095.