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The study of atmospheric pressure plasma for surface cleaning

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Abstract

In this study, capillary dielectric-covered dielectric barrier discharge was used to generate atmospheric pressure plasmas. The effect of various gas combinations such as $He+O_2$, $(He+O_2)/Ar$, and $(He+O_2)/SF_6$ was studied with respect to the changes in contact angle, surface energy and photoresist etch rate (ER). By adding a small percentage of O_2 (40 sccm) to He (4 slm), we observed the increase in photoresist ER and the reduction of contact angle compared with the as-received sample. The effect of adding SF_6 to the optimized He/O_2 did not show any improvement in the contact angle. When SF_6 was added more than 40 sccm, deposition has occurred instead of etching. The contact angle of the glass surface was decreased from 30° to 9.5–11° after cleaning with He/O_2 based plasmas for 5–30 s. The lowest contact angle of 9° with the higher photoresist ER of 210 nm/min was obtained with (4 slm He+40 sccm O_2)/Ar (20 sccm) at 400 W of alternating current power. Using $He/O_2/Ar$ based plasma to treat indium tin oxide (ITO), Ag, and polycarbonate surface, the contact angle is decreased, while the surface energy is increased. The contact angle decreased 78% for ITO deposited on the glass, decreased 24% for Ag patterned on the ITO, and decreased 70% for polycarbonate as-received samples. And the surface energy increased 46% for ITO deposited on the glass, increased 7% for Ag patterned on the ITO, and increased 68% for polycarbonate.
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Keywords: Atmospheric pressure; Plasma; Surface; Cleaning

1. Introduction

Plasmas used in dry etching, thin film deposition and surface treatment for display or semiconductor industries are operating at low pressures in general. However, low pressure processing is very costly due to the use of vacuum equipment and vacuum components. Subsequent wet processing is environmentally undesirable due to the use of large amount of chemicals. Also, the usage of vacuum processing increases fabrication cost and decreases productivity. If stable atmospheric plasmas can be used, not only the decrease in processing costs but also the increase in productivity could be obtained. These days, many researchers are developing glow discharges generated at atmospheric pressure [1–4,13] for various thin films and surface processing. For example, dielectric barrier discharge (DBD), atmospheric microwave discharge, pulsed corona plasma, etc. have been studied for the applications of surface treatment of organic materials [5–7], growth of organic thin films [8,9], dry etching [10,11], etc.

Among the various atmospheric pressure plasmas, DBDs are studied mostly due to the easy formation of stable plasma and their scalability. However, the low plasma density of the DBD is one of the key problems in applying DBD to various applications. As a variation of DBDs, a capillary dielectric-covered DBD, where the blank dielectric DBD material is replaced by a perforated dielectric material with a number of small holes, has been investigated for generating higher plasma density compared with the conventional DBD [10].

In this study, using the capillary dielectric-covered DBD, the effects of various gas combination such as $He+O_2$, $(He+O_2)/Ar$, and $(He+O_2)/SF_6$ are studied for the organic material cleaning, for example, photoresist etching. The contact angle and surface energy of various surfaces were analyzed for the applications of surface cleaning and surface treatment in flat panel display processing.

2. Experiments

The discharge system with capillary dielectric-covered electrode used in this experiment is similar to a typical planar DBD system except for the dielectric-covered

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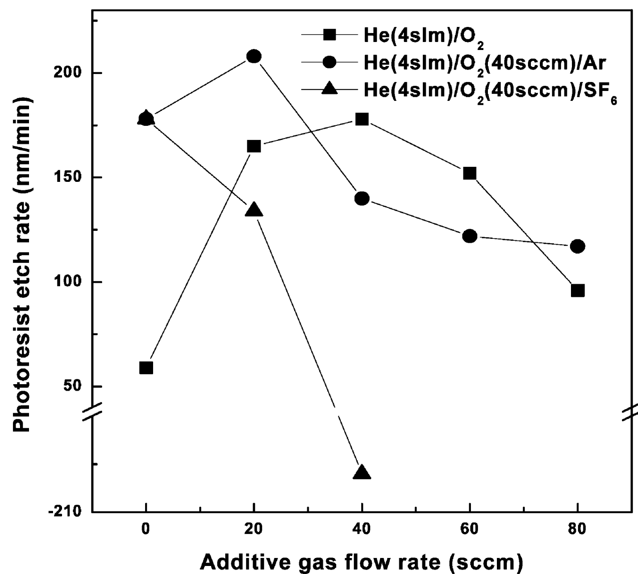

Fig. 1. Effect of various gas combinations such as He/O_2, $(He+O_2)/Ar$, and $(He+O_2)/SF_6$ on the ER of photoresist. AC power was maintained at 400 W and He at 4 slm. O_2, Ar, and SF_6 were varied from 0 to 80 sccm.

powered electrode. The powered electrode and the ground electrode were made of stainless steel. The top electrode was connected to an alternating current (AC) (20–100 kHz, 3 kW) power supply while the bottom electrode was grounded. The top electrode was covered with a 10-mm thick alumina plate with a number of small holes (aspect ratio of the hole was 10:1) in parallel. The distance between the two electrodes (air gap) was 4 mm. The details of this system used in the experiment can be found elsewhere [10].

Helium and additive gases such as O_2, Ar and SF_6 were introduced to the reaction chamber by a mass flow controller through the capillary holes on the top electrode. He gas flow rate was fixed at 4 slm. The flow-rates of O_2, Ar and SF_6 were varied from 0 to 80 sccm at the atmospheric pressure. The AC frequency and the power applied to the top electrode were maintained at 20–22 kHz and 400 W, respectively. The glass sample coated with 1.2 μm thick photoresist was mounted on the bottom ground electrode and etched using the gas combinations such as He/O_2, $(He+O_2)/Ar$ and $(He+O_2)/SF_6$. Contact angle of water drop on the glass surface and its surface energy were measured by the contact angle measurement system before and after the glass cleaning treatment. Cleaning time was varied from 5 to 30 s and the exposure time to air before the contact angle measurement after the cleaning was varied from 30 to 120 min. In addition to the glass, other samples such as indium tin oxide (ITO) coated on the glass, Ag patterned on the ITO, and polycarbonate surface were

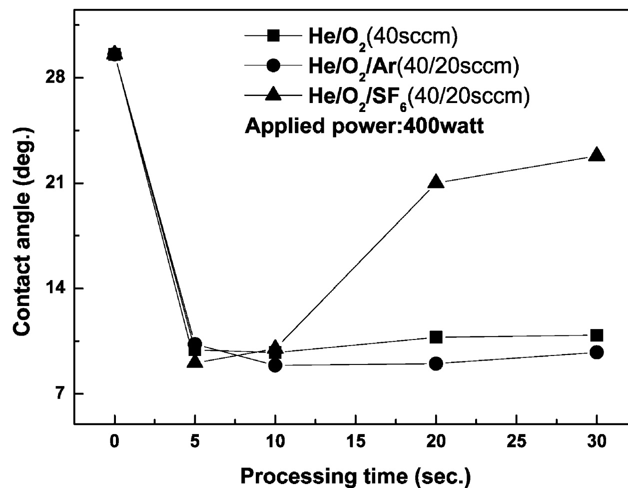

Fig. 2. Effect of processing time on the contact angle measured on the glass cleaned by capillary dielectric covered DBD with He (4 slm)/O_2 (40 sccm), (4 slm He+40 sccm O_2)/Ar (20 sccm), and (4 slm He+40 sccm O_2)/SF_6 (20 sccm) at 400 W of AC power.

also measured for the changes of contact angle and surface energy after the cleaning for the.

3. Results and discussion

Photoresist was etched using the capillary dielectric covered DBD system using He and additive gases such as O_2, Ar and SF_6. Fig. 1 shows the effect of additive gases to He on the photoresist etch rate (ER). He flow rate was maintained at 4 slm. AC power and its frequency were kept at 400 W and 22–23 kHz, respectively. As shown in the figure, when small O_2 was added to 4 slm of He, the photoresist ER was increased with the increase of oxygen flow, however, when O_2 flow rate was higher than 40 sccm, which decreased the photoresist ER. The maximum ER of photoresist was obtained 170 nm/min at He (4 slm)/O_2 (40 sccm). Other gases such as Ar and SF_6 were added to this optimized He/O_2 gas combination. The effect of the other additive gases on the photoresist ER was also investigated and is shown in the Fig. 1. As shown in Fig. 1, the addition of Ar to 20 sccm increased the photoresist ER to 210 nm/min, however, the further increase of Ar decreased the ER. In the case of SF_6, the addition of SF_6 to the optimized He/O_2 decreased the photoresist ER monotonically and the addition of SF_6 more than 40 sccm deposited a material instead of etching. The maximum photoresist ER obtained in our experimental conditions for He/O_2 and $(He+O_2)/Ar$ appear to be related to the oxygen atoms generated in the plasma.

Using some of the optimized conditions such as He (4 slm)/O_2 (40 sccm), (4 slm He+40 sccm O_2)/Ar (20 sccm), and (4 slm He+40 sccm O_2)/SF_6 (20

sccm), glass surface was cleaned and the effect of cleaning on the change of contact angle of water drop was investigated. Fig. 2 shows the effect of cleaning time from 5 to 30 s and cleaning gas combinations such as He (4 slm)/O_2 (40 sccm), (4 slm He+40 sccm O_2)/Ar (20 sccm), and (4 slm He+40 sccm O_2)/SF_6 (20 sccm) on the change of contact angle of water drop. Applied AC power and the frequency were also 400 W and 22–23 kHz, respectively. The measured rms voltage was approximately 9.3 kV for all conditions. As shown in the Fig. 2, when the cleaning time was 5 s, the contact angle decreased from 30° to 9.5–11° and the increase of cleaning time up to 30 s did not change the contact angle significantly for the gas combinations such as He/O_2 and (He+O_2)/Ar. In the case of (4 slm He+40 sccm O_2)/SF_6 (20 sccm), the cleaning time up to 10 s decreased the contact angle, however, the further increase of cleaning time increased the contact angle. The initial decrease of contact angle with (4 slm He+40 sccm O_2)/SF_6 (20 sccm) appears to be related to the removal of organic material on the glass surface and the increase of contact angle with further increase of cleaning time might be related to the formation of a material on the cleaned glass surface which has no organic material. In the figure, the use of (4 slm He+40 sccm O_2)/Ar (20 sccm) showed a little lower contact angle (9°) compared to that of He (4 slm)/O_2 (40 sccm) possibly due to the effect of the surface bombardment by Ar ion. The insignificant change of contact angle after 5 s of cleaning time for both He/O_2 and (He+O_2)/Ar appears to suggest that the cleaning time less than 5 s could be used for the glass surface cleaning for these conditions.

After the cleaning, the characteristics of the glass surface have to remain similar until the next process is conducted. Fig. 3 shows the effect of exposure time in the air after the cleaning on the contact angle for He (4 slm)/O_2 (40 sccm) and (4 slm He+40 sccm O_2)/Ar (20 sccm). Other process conditions are the same in Fig. 2. As shown in Fig. 3, the contact angles measured after the exposure to the air from 30 to 120 min were remained similar, therefore, the exposure to the air up to 120 min shows a little change in the characteristics of cleaned glass surfaces. Therefore, it is believed that the atmospheric pressure dry cleaning with He/O_2 or (He+O_2)/Ar used in this experiment could replace a wet processing used to remove organic materials or to improve hydrophilic properties of the glass surface.

In addition to removing organic materials on the surface, the oxidation and ion bombardment of the surface by reactive species in the plasma are known to decrease the contact angle [12]. The use of He/O_2 based atmospheric pressure plasma not only removes organic material on the glass surface but also oxidizes the surface by the oxygen atoms generated, and it decreases contact angle and increases surface energy. In addition

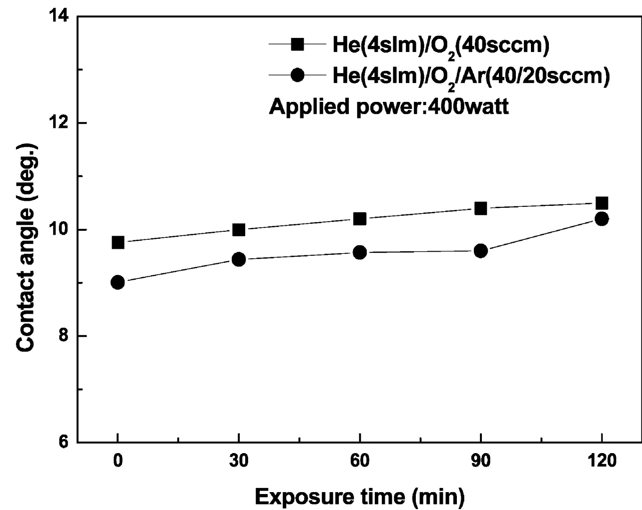

Fig. 3. Effect of exposure time after the cleaning using capillary dielectric covered DBD with He (4 slm)/O_2 (40 sccm) and (4 slm He+40 sccm O_2)/Ar (20 sccm) at 400 W AC power.

to the glass surface, various material surfaces were cleaned with (4 slm He+40 sccm O_2)/Ar (20 sccm) and the changes of the contact angle and surface energy were measured. Fig. 4 shows (a) contact angle and (b) surface energy measured on the various materials such as ITO on glass, polycarbonate, and Ag on ITO/glass before and after the cleaning with (4 slm He+40 sccm O_2)/Ar (20 sccm). In order to prevent possible arcing on the metal surface, the cleaning condition used was 100 W of AC power (4 kV of rms voltage), 22–23 kHz of frequency, and 5 min of cleaning time. As shown in Fig. 4, the contact angle of ITO on glass decreased from 92 to 20°, that of polycarbonate decreased from 72 to 21°, and that of Ag on ITO/glass from 65 to 48°. The decrease of contact angles increased the surface energy of ITO on glass from 55 to 101 mJ/m^2, that of polycarbonate from 21.6 to 72.2 mJ/m^2, and that of Ag on ITO/glass from 56 to 59 mJ/m^2. Therefore, the application of the (He+O_2)/Ar atmospheric pressure plasma improved the hydrophilic properties of various materials possibly due to the removal of organic materials on the surface and the oxidation of the surface.

4. Conclusions

In this study, the effects of capillary dielectric-covered DBD on photoresist etching and surface cleaning have been investigated using He/O_2, (He+O_2)/Ar, and (He+O_2)/SF_6 gas mixtures. Small addition of O_2 (40 sccm) to He (4 slm) showed a maximum photoresist ER of 170 nm/min and the addition of small Ar (20 sccm) to the optimized He (4 slm)/O_2 (40 sccm) showed the highest photoresist ER of 210 nm/min at 400 W of 22–23 kHz AC power. The addition of SF_6

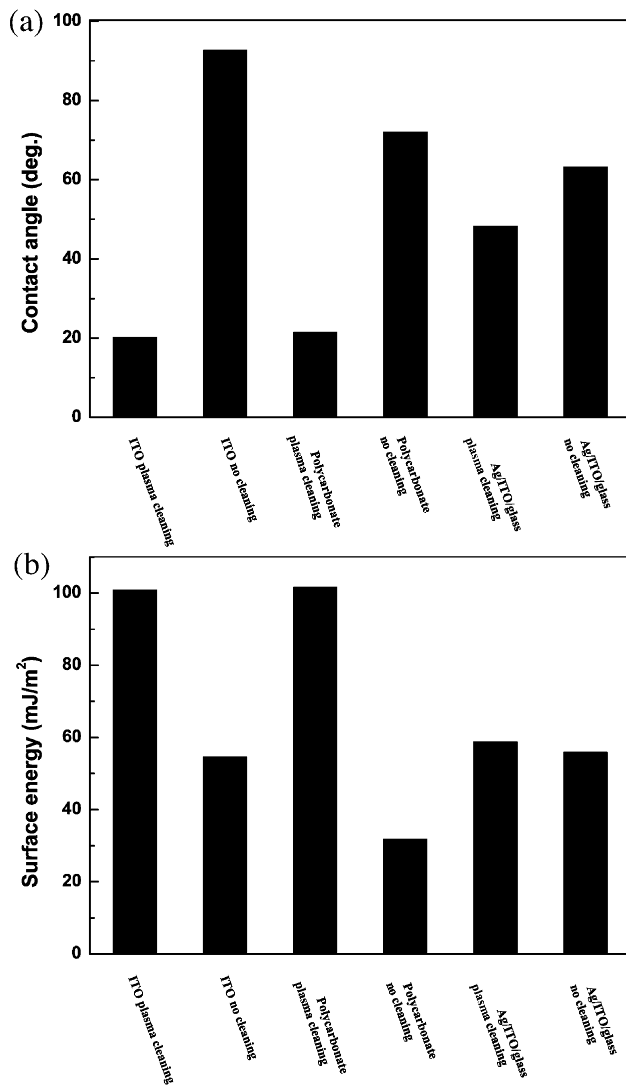

Fig. 4. Effect of surface cleaning with capillary dielectric-covered DBD using (4 slm He+40 sccm O_2)/Ar (20 sccm) at 100 W AC power for 5 min on (a) contact angle and (b) surface energy for various materials such as polycarbonate, ITO, and Ag.

to the optimized He/O_2 did not show any improvement in photoresist ER, instead, when SF_6 was added more than 40 sccm, deposition instead of etching has occurred. When glass was cleaned with various gas combinations, the contact angle of the glass surface was decreased from 30° to 9.5–11° after the cleaning with He (4 slm)/O_2 (40 sccm) and to the lowest contact angle of 9° after the cleaning with (4 slm He+40 sccm O_2)/Ar (20 sccm). Cleaning time from 5 to 30 s and the exposure to air up to 120 min after the cleaning did not show any significant change in the contact angle. The exposure of $He/O_2/Ar$ based plasma to ITO, Ag, and polycarbonate surface also decreased the contact angle from 92 to 20° for ITO, from 72 to 21° for polycarbonate, and from 65 to 48° for Ag.

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