Oxide surface cleaning by an atmospheric pressure plasma

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Abstract

In this study, an atmospheric pressure plasma was generated using a dielectric barrier discharge (DBD) with a perforated dielectric covered electrode and its effect on the cleaning of organic materials on oxides such as indium tin oxide (ITO) and magnesium oxide (MgO) was investigated. He and O_2 were used as the ignition gas and cleaning gas, respectively. In addition to these gases, N_2 was added to improve the effect of surface cleaning. A small addition of O_2 to He increased the surface-cleaning rate due to the increase of oxygen radicals in the plasmas; however, further addition of oxygen decreased the surface-cleaning rate, possibly due to the decrease of plasma density by the formation of oxygen negative ions between oxygen molecules and electrons in the plasma. The additional mixture of N_2 to He/O_2 further increased the surface cleaning possibly due to the increased dissociation of O_2 in the plasma resulting in the increased chemical reaction and removal from the surface. Surface characteristics after the plasma treatment were investigated using X-ray photoelectron spectroscopy (XPS), and showed a decrease of carbon contaminants on the ITO and MgO by the atmospheric pressure plasma treatment. After plasma treatment of the surfaces, the decrease of contact angles of water was also measured.
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1. Introduction

To remove the organic contaminants from the surfaces of various materials such as mechanical and electrical components, printed circuit boards, substrates for flat panel display, etc., wet chemical cleaning is generally used. The wet cleaning can increase the wettability, increase the adhesion, or decrease the contact resistivity. However, the use of wet chemicals such as detergents, solvents, acids, etc., currently raises problems in disposing the waste chemicals as well as the health issues and additional cost of the chemicals.

Currently, various dry cleaning techniques such as UV/O_3 technique [1–3], plasma techniques [2–7], wet treatment [8,9], and dry CO_2 [10] are actively being studied to accommodate environmental and health concerns. In general, these dry cleaning techniques have a high cost of ownership, however, the operating cost is lower than wet chemical cleaning techniques. In the case of plasma techniques for surface cleaning, oxygen low-pressure plasmas, generated in a vacuum system,

have been studied. Recently, researchers are concentrating on plasma cleaning using atmospheric pressure plasmas due to possible advantages such as no need for an expensive vacuum system and components, increase of throughout applicability to in-line processing, and the scalability to larger area. Many different types of atmospheric pressure plasmas such as dielectric barrier discharges (DBD), pulsed corona discharges, microwave plasma discharge, and atmospheric pressure touch are currently under investigation, and are being applied to the cleaning of various materials and substrates [11–18].

In this study, $He/O_2/N_2$ DBDs with a perforated dielectric covered electrode were used to generate high density atmospheric pressure discharges, and the removal characteristics of organic materials were studied. Also, oxides used for the flat panel display such as ITO and MgO were cleaned using an optimized $He/O_2/N_2$ discharge, and their surface characteristics were investigated.

2. Experimental

The atmospheric pressure plasma system used in the experiment was similar to a typical planar DBD system

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except for the dielectric material covered on the powered electrode. The powered top electrode and the grounded bottom electrode were made of stainless steel. The top electrode was connected to an alternating current (AC) (3–15 kV, 20–30 kHz) power supply while the bottom electrode was grounded. The top electrode was covered with a 10-mm thick alumina plate with a number of parallel small holes (aspect ratio of the hole was 10:1). The distance between the two electrodes (air gap) was 4 mm. The details of the system used in the experiment can be found elsewhere [14,15].

He and additive gases such as O_2 and N_2 were introduced to the reaction chamber by a mass flow controller through the perforated dielectric on the top electrode. He gas flow rate was fixed at 4500 sccm and the flow rates of O_2 and N_2 were varied from 0 to 800 sccm at atmospheric pressure. The AC frequency and the voltage applied to the top electrode were maintained at 30 kHz and 6 kV, respectively. The glass sample coated with 1.2-μm (AZ 1512) thick photoresist was mounted on the bottom ground electrode, and was etched using the gas combinations such as He/O_2 and N_2/(He+O_2). Contact angle of water drop on the surface was measured by the contact angle measurement before and after the cleaning treatment of indium tin oxide (ITO) and magnesium oxide (MgO). The cleaning time was varied from 5 to 300 s before the contact angle measurement. The surface component ratios such as O/C and metal/O of the ITO and MgO after the cleaning were measured by X-ray photoelectron spectroscopy (XPS). In addition, a low-pressure oxygen plasma cleaning of the ITO and MgO surfaces was carried out using an inductively coupled plasma and the surface characteristics before/after the plasma treatments were compared. The low-pressure plasma was generated at 13 Pa of working pressure and 200 W of inductive power in O_2 gas.

3. Results and discussion

Fig. 1 shows the effect of gas combination such as He/O_2 and N_2/(He+O_2) on the photoresist etch rate. In the case of N_2/(He+O_2), N_2 was added to an optimized He+O_2 mixture. AC voltage to the top electrode with the perforated dielectric material and He flow rate were maintained at 6 kV and 4500 sccm, respectively. O_2 flow rate was varied from 9 to 63 sccm. As shown in the figure, the increase of oxygen flow rate to He increased the photoresist etch rate from 105 to 173 nm/min until 45 sccm (approx. 1%) of oxygen was added to He. However, the further increase of oxygen to He decreased the photoresist etch rate. When N_2 was added up to 200 sccm on the optimized gas mixture (4500 sccm He+45 sccm O_2), the photoresist etch rate was also increased to 216 nm/min. Further-
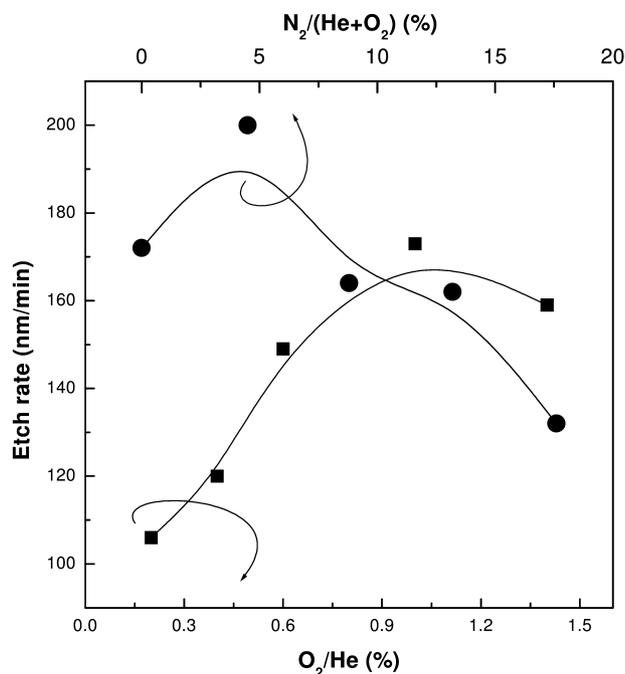

Fig. 1. Effect of various gas combinations such as He/O_2 and N_2/(He+O_2) on the photoresist etch rate. AC voltage was maintained at 6 kV and He at 4500 sccm. O_2 was varied from 9 to 63 sccm and N_2 from 0 to 800 sccm.

more, increase of N_2 also decreased the photoresist etch rate.

The increase of photoresist etch rate with O_2 in Fig. 1 is believed from the increase of dissociated oxygen atoms in the plasma. However, the decrease of photoresist etch rate with further increase of oxygen appears related to the decrease of plasma density by the formation of oxygen negative ions which consume electrons in the plasma [14]. Also, when the added oxygen was equal to or lower than 45 sccm, ion beam-like glow discharge was observed through the holes of the perforated dielectric on the top electrode forming a dense plasma. When the oxygen flow rate was higher than 45 sccm, the plasma changed to a filamentary discharge where the dense discharge is concentrated on local areas between the electrodes possibly due to the current concentration at few points of the electrodes. The increase of photoresist etch rate with N_2 gas up to 200 sccm in Fig. 1 might be related to increased oxygen atom concentration in the plasma by a nitrogen-induced increase in the oxygen atom generation (that is, increase in the electron density and/or average energy) as suggested by other researchers [19]. The decrease of photoresist etch rate with further increase of N_2 to the optimized He+O_2 gas mixtures is possibly related to the decreased residence time of active oxygen atoms or by the formation of filamentary discharge at the higher N_2 flow rate conditions similar to the case of He+O_2.
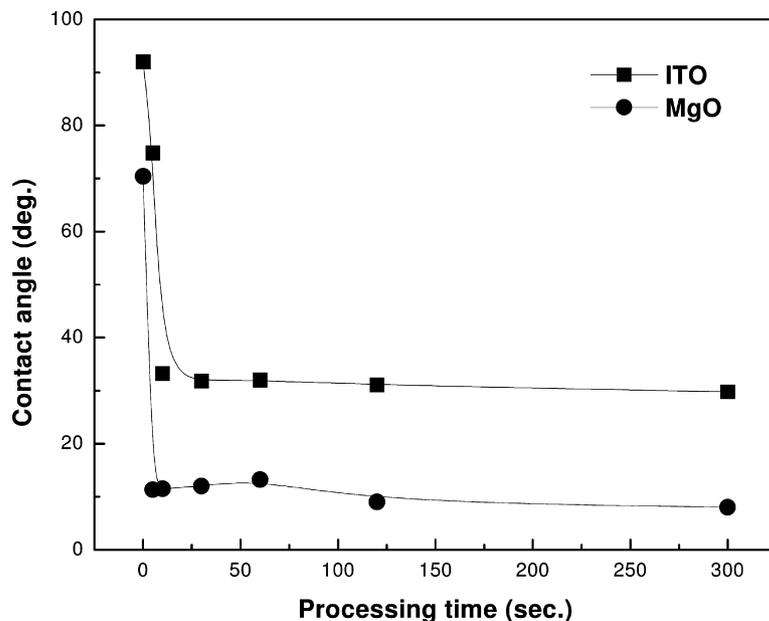
Fig. 2. Effect of plasma exposure time on the contact angles of ITO and MgO surfaces after the cleaning by a perforated dielectric covered DBD with N_2 (200 sccm)/(4500 sccm He + 45 sccm O_2) at 5 kV of AC voltage.

The formation of filamentary discharge could be observed by measuring the discharge current curve at the top electrode as investigated in our previous researches [14,15]. When a filamentary-type discharge occurred, the current curve showed noisy sharp peaks on the sine current curve. The formation of filamentary-type discharge is known to decrease plasma density compared to diffuse-type or glow-type discharge due to the formation of localized current flow [20].

Using a $N_2/(He + O_2)$ condition which showed the highest photoresist etch rate, the surfaces of the oxides such as ITO and MgO which are used for flat panel display devices were cleaned, and the contact angles of water after the cleaning were measured to observe the change of wettability after the cleaning. Fig. 2 shows the measured contact angles of the ITO and MgO surfaces as a function of plasma processing time. The applied AC voltage was 5 kV and the gas mixture was 200 sccm $N_2/(4500$ sccm He + 45 sccm O_2). As shown in the figure, as-received ITO and MgO showed the contact angles of 90° and 74°, respectively. However, after the plasma treatment for 10 s, the contact angles of ITO and MgO changed to 30° and 9°, respectively. However, the further increase of plasma treatment time up to 5 min did not change the contact angles significantly. The decrease of contact angles of ITO and MgO surfaces is believed to be from the removal of surface organic contaminants by the oxygen atoms in the plasma. No change of contact angles after the treatment for 10 s up to 5 min appears to show that short treatment time is enough in removing surface organic contaminants.

Low-pressure oxygen plasmas can also be used in cleaning oxide surfaces such as ITO and MgO. To investigate the effectiveness of our atmospheric pressure plasma treatment, low-pressure oxygen plasma treatment which is more conventionally used in surface cleaning as a dry cleaning method was used to clean ITO and MgO, and compared with those cleaned by the atmospheric pressure plasma. Fig. 3 shows the contact angles of ITO and MgO surfaces after the cleaning by a low-pressure oxygen plasma. The low-pressure plasma was generated by an inductively coupled plasma equipment with 200 W of inductive power at 13 Pa O_2. The cleaning was carried out for 2 min without applying a bias voltage. Photoresist cleaning rate with the ICP equipment was approximately 170 nm/min similar to that of the atmospheric plasma used in the experiment. In the figure, the contact angles of as-received ITO and MgO, and those after the cleaning by the atmospheric pressure plasma for 2 min shown in Fig. 2 are also shown for comparison. As shown in the figure, after the low-pressure oxygen plasma cleaning, the contact angles of ITO and MgO surfaces decreased to 24° and 9°, respectively, and these contact angles were similar to those surfaces after the atmospheric pressure plasma cleaning for 10 s. The decrease of contact angle of water by the plasma treatment not only increases the wettability but also increases the adhesion and decreases electrical contact resistivity [21,22]. The improvement of surface characteristics by the atmospheric pressure plasma treatment similar to those by the low-pressure oxygen plasma treatment will give not only economical advantage but also technical advantage in the cleaning
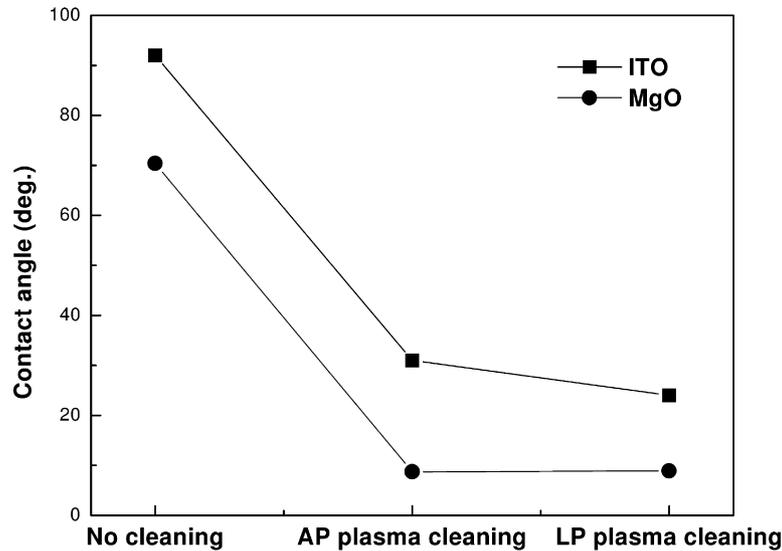
Fig. 3. Contact angles of ITO and MgO surfaces after the cleaning for 2 min by a low-pressure oxygen plasma using an inductively coupled plasma equipment with 200 W of inductive power at 13 Pa. As references, the contact angles of as-received, and atmospheric pressure plasma cleaned ITO and MgO surfaces (for 2 min) shown in Fig. 2 are also shown.

of various flat panel display substrates. That is, the use of atmospheric pressure cleaning tools enables us to process the large substrates in-line without using vacuum.

Fig. 4 shows the ratios of O/C and metal/O on the ITO and MgO surfaces measured by XPS after the cleanings by the atmospheric pressure plasma and by the low-pressure oxygen plasma shown in Fig. 3. As a reference, the ratios of O/C and metal/O of as-received ITO and MgO surfaces were included in the figure. As shown in the figure, the ratio of O/C for ITO surface

increased from 0.72 to 2.52 after the cleaning by the atmospheric pressure plasma and to 2.62 by the low-pressure oxygen plasma. In the case of MgO surface, the ratio increased from 0.77 to 1.26 for the cleaning by the atmospheric pressure plasma and to 1.21 for the cleaning by the low-pressure oxygen plasma. The carbon percentage on the surfaces of ITO and MgO decreased from 45.79 and 43.58% to 19.36 and 29.39% for the atmospheric pressure plasma cleaning and to 18.53 and 29.05% for the low-pressure oxygen plasma cleaning, respectively (not shown). Also, as shown in the figure,
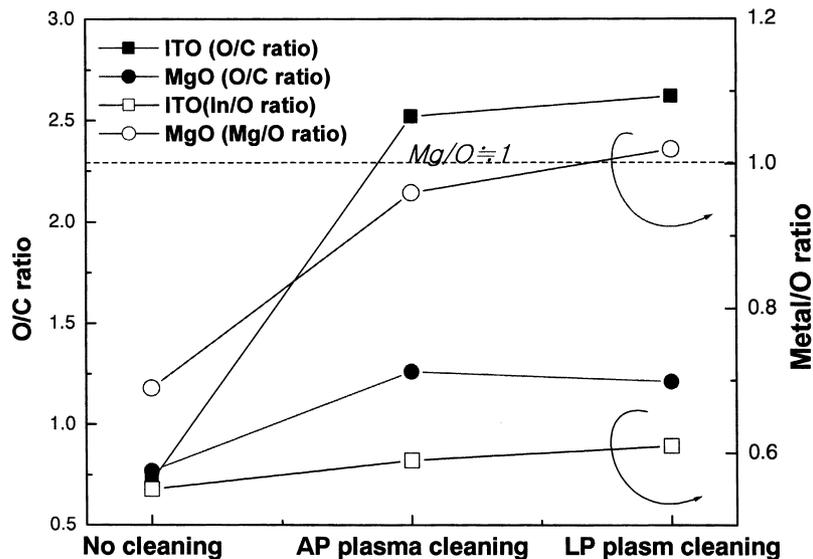

Fig. 4. The ratios of O/C and metal/O on the ITO and MgO surfaces measured by XPS after the cleanings by the atmospheric pressure plasma and by the low-pressure ICP shown in Fig. 3. As a reference, the ratios of O/C of as-received ITO and MgO surfaces were included in the figure.

the ratio of metal to oxygen of the ITO and MgO surfaces changed close to those of stoichiometric composition of ITO and MgO by the atmospheric pressure plasma cleaning and also by the low-pressure oxygen plasma cleaning even though the surface composition cleaned by the low-pressure oxygen plasma appears closer to the stoichiometry. Therefore, cleanings both by the atmospheric pressure plasma and by the low-pressure oxygen plasma decreased carbon percentage on the surface and improved the stoichiometry of the surface by increasing oxygen percentage. As a result, the decrease of contact angles after the plasma cleanings shown in Figs. 2 and 3 is believed to be from the removal of organic contaminants from the surface and the improvement of stoichiometry of the surfaces. The increase of oxygen on the surface is reported to decrease the contact angle [4–7,9]. Also, the decrease of carbon and the improvement of stoichiometry of ITO surface can also increase the work function, which is beneficial in electroluminescence devices by decreasing driving voltage of the devices [5].

4. Conclusions

In this study, a perforated dielectric covered DBD was used to generate atmospheric pressure plasmas, and the effect of gas combination such as He/O_2 and $N_2/(He+O_2)$ on the photoresist etching was investigated. Also, oxide surfaces such as ITO and MgO used for the flat panel display devices were cleaned using the atmospheric pressure, and the effects of the cleaning on the surface properties were investigated.

The small addition of oxygen to He up to 45 sccm and the addition of N_2 to an optimized $(He+O_2)$ up to 200 sccm increased the photoresist etch rate, and the further increase of O_2 or N_2 decreased the photoresist etch rate possibly due to the decrease of plasma density and by the change of plasma from glow-type to filamentary-type. The highest photoresist rate obtained was 216 nm/min with 200 sccm $N_2/(4500$ sccm $He+45$ sccm $O_2)$ at 6 kV of AC voltage. With the optimized $N_2/(He+O_2)$ gas mixture, ITO and MgO surfaces were cleaned, and significant decreases of contact angles from 90 to 30° for ITO surface and from 76 to 9° for MgO surface could be obtained after the cleaning for more than 10 s. The cleaning of the surfaces using a low-pressure oxygen plasma showed similar results. When the O/C ratios and metal/O ratios of ITO and MgO surfaces were measured after the cleanings with the atmospheric pressure plasma and the low-pressure oxygen plasma, the ratios increased similarly and signifi-

cantly after the cleanings. It indicates the removal of organic contaminants and the improvement of stoichiometry of the surfaces. The improvement of surface characteristics using the atmospheric pressure plasma similar to those by low-pressure oxygen plasma is believed to give not only economical advantage but also technical advantage in the cleaning of various flat panel display substrates.

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