

Effect of an Atmospheric Pressure Plasma Cleaning on the Outgassing Characteristics of MgO Layer for Plasma Display Panel

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In this study, the effects of atmospheric pressure plasma cleaning on the outgassing characteristics of MgO deposited on plasma display panel(PDP) glass have been investigated as a function of outgassing temperature. After the cleaning of the MgO deposited glass with He/O₂/Ar and He/O₂/Ar/N₂, the decrease of main outgassing species such H₂O, CO₂, CO, and H₂ and the increase of secondary electron emission from the MgO surface could be observed, possibly due to the removal of organic materials incorporated on the MgO layer. As the cleaning by He/O₂/Ar/N₂ showed, a lower outgassing vapor pressure, is possibly due to a higher cleaning rate. [DOI: 10.1143/JJAP.42.L74]

KEYWORDS: MgO, outgassing characteristics, atmospheric pressure plasma, cleaning, PDP, display

The plasma display panel (PDP) is one of the most promising candidates for large-area wall hanging displays because of the simple panel structure, easy and cheap processes appropriate for large area displays, good display quality, and high-speed addressing ability. MgO thin film is deposited to protect the dielectric layers of PDP from sputtering by ions and to emit relatively large secondary electrons when low-energy ions hit on the surface, and therefore, to reduce operation and sustaining voltage.¹⁻³⁾ However, MgO tends to adsorb H₂O on the surface and the impurities such as H₂, N₂, and CO₂ adsorbed during the processing may deteriorate the characteristics of PDP and reduce its operation time. Also, the impurities adsorbed on the surface increase the time required for the evacuation of the panel before the introduction of discharge gas, and therefore, decrease the throughput of the panel production.

In this experiment, MgO deposited by evaporation on PDP front glass, which is composed of an indium tin oxide(ITO) electrode, a bus electrode, and a PbO dielectric layer, was used as the sample. Each material including MgO was deposited on the glass using the same sequence used in the PDP production. The size of the MgO deposited glass sample was 14.5 cm × 11 cm. Using this sample, the effects of atmospheric plasma treatment on the characteristics of outgassing and secondary electron emission of the MgO layer were investigated.

For the surface treatment by plasma, modified dielectric barrier discharge (DBD) equipment with a number of capillary holes drilled in the dielectric material of the power electrode has been used. The capillary holes were drilled in the dielectric material to induce a more uniform distribution of feed gas and to achieve a higher plasma density. The gap between the electrodes (capillary dielectric covered power electrode and ground electrode) was 0.5 cm. 30 kHz and 4.5 kVrms AC voltage was applied to the power electrode to generate the plasma. The sample was located on the ground electrode. For the plasma treatment, a mixture of He(6 slm)/O₂(20 sccm)/Ar(20 sccm) and He(6 slm)/O₂(20 sccm)/Ar(20 sccm)/N₂(20 sccm) was fed through the power electrode under atmospheric pressure. The plasma treatment time was 5 min. More details of the atmospheric system used in the experiment can be found elsewhere.⁴⁾

The sample was loaded to the outgassing chamber using a

loadlock and the outgassing chamber was evacuated to 10⁻⁷ Torr before loading the sample. The sample was heated from room temperature to 350°C at 10°C/min using a halogen lamp and the outgassing species and their partial pressures were measured using a quadupole mass spectrometer (Hiden Analytical Inc. HAL-201: QMS). Due to the differences between the detected partial pressures of the species at the QMS and those outgassed from the chamber, each impurity gas detected at the QMS was calibrated using various calibration gases to obtain its quantitative partial pressure.^{5,6)}

Figure 1 shows the major outgassing species and their partial pressures measured as a function of temperature for the as-deposited MgO sample. As shown in the figure, the major outgassing species were H₂O, CO₂, CO, and H₂. Among these, H₂O showed the highest partial pressure. These impurity partial pressures could be from other layers in the glass such as the glass itself, ITO, bus electrode, and PbO. However, previous experiments on the measurement of outgassing from these layers showed that impurity vapor pressures of the MgO layer itself on the glass were similar to those from the MgO deposited on the glass with ITO, bus electrode, and PbO.⁷⁾ The glass itself did not show significant impurity vapor pressures. Therefore, the outgassing species observed in Fig. 1 are believed to be mainly from MgO itself. As shown in the figure, two outgassing

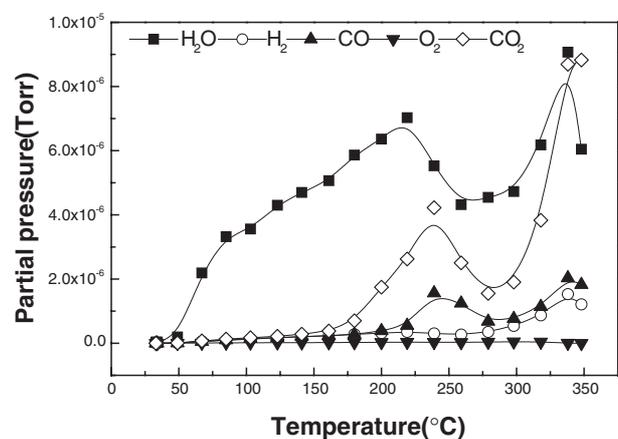


Fig. 1. Vapor pressures of outgassing species of the PDP front panel as a function of temperature measured before the atmospheric plasma cleaning (MgO/PbO/Ag/ITO on glass).

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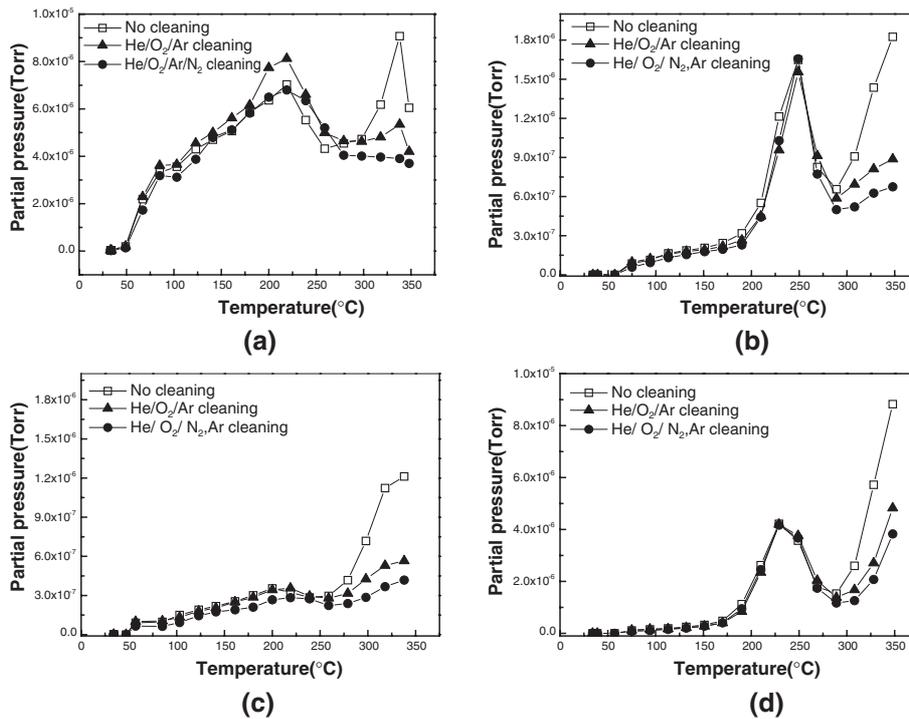


Fig. 2. Vapor pressures of outgassing species of MgO deposited PDP glass (MgO/PbO/Ag/ITO on glass) as a function of temperature before and after the atmospheric pressure plasma cleanings, (a) H₂O, (b) CO, (c) H₂, and (d) CO₂. (Process condition: He(6 slm)/O₂(20 sccm)/Ar(20 sccm) and He(6 slm)/O₂(20 sccm)/Ar(20 sccm)/N₂(20 sccm) at 4.5 kV and 30 kHz AC voltage for 5 min.)

peaks are observed near 200–250°C and 300–350°C. The peak partial pressure near 200–250°C appears to be from the desorption of the physisorbed species and the further increase near 300–350°C appears to be from the desorption from the chemisorbed species. In fact, these outgassing peaks shown near 200–250°C and 300–350°C are known to occur not only for MgO but also for all of the solids during the heat treatment, however, as evident in the figure, MgO showed the most significant intensities among the materials investigated.

The outgassing species observed during the heating of the MgO glass are believed to be from the impurities adsorbed during the deposition and from the exposure to air after the deposition.^{8,9)} Therefore, surface cleaning of the MgO surface was carried out using atmospheric pressure plasma cleaning equipment, the use of which enables us to clean the contaminated surface at lower cost by eliminating the need for costly vacuum generation and measurement tools. Also, if a reasonably high cleaning rate could be obtained, a high processing throughput would also be obtained because no time delay in vacuuming the chamber is required. The MgO glass was cleaned with these plasmas for 5 min and the change of outgassing vapor pressures between observations before and after cleaning with the atmospheric pressure plasmas with He(6 slm)/O₂(20 sccm)/Ar(20 sccm) (photoresist etch rate : 150 nm/min) and He(6 slm)/O₂(20 sccm)/Ar(20 sccm)/N₂(20 sccm) (photoresist etch rate : 200 nm/min) was measured. The results are shown in Fig. 2(a) for H₂O, (b) for CO, (c) for H₂, and (d) for CO₂. As shown in the figures, no noticeable change of vapor pressure was observed for the temperature range from 200 to 250°C, however, there was a significant decrease in the vapor pressures of H₂O, CO, H₂, and CO₂ for the temperature

range from 300 to 350°C. The effect was more significant for the treatment with He/O₂/Ar/N₂, possibly due to the higher cleaning rate. There appears to be no significant change of vapor pressure for the temperature range from 200 to 250°C because of the air exposure of the treated MgO samples before the measurement, in other words, due to the re-adsorption of impurities from the air. However, the decrease of vapor pressures from the outgassing species such as CO, CO₂, and H₂ appears to be from the removal of organic materials chemisorbed on the MgO surface by the reaction with oxygen in the plasma.

The MgO sample surfaces were analyzed by X-ray photoelectron spectroscopy(XPS) to investigate the change of surface composition with plasma cleaning. Figure 3 shows the XPS narrow scan data of the MgO surfaces for (a) the C1 peak and (b) the Mg2p peak measured before and after the atmospheric pressure plasma cleaning with the He/O₂/Ar/N₂ gas mixture for 5 min. As shown in the figure, after the cleaning, the atomic percent of Mg was increased from 33.7% to 48.7% (close to the stoichiometric percent of Mg in MgO) and that of carbon was decreased from 33.7% to 23.2%. The decrease of carbon by the atmospheric plasma cleaning appears to be due to the removal of chemisorbed organic contaminants from the MgO surface, however, the remaining carbon after the plasma cleaning appears to be from the carbon physisorbed during the air exposure after the plasma treatment, and before the XPS measurement. The decrease of carbon contaminants on the MgO surface by the plasma cleaning is related to the decrease of vapor pressures of CO, CO₂, and H₂ during the heating from 300 to 350°C after the plasma cleaning, as observed in Fig. 3.

MgO is deposited on PDP glass not only to protect the cell from sputtering but also to increase the secondary electron

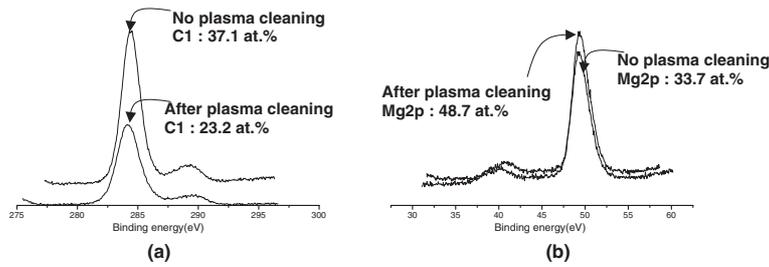


Fig. 3. MgO surface analysis using XPS before and after the plasma cleaning, (a) C1 peak, and (b) Mg2p peak. (Process condition: He(6 slm)/O₂(20 sccm)/Ar(20 sccm)/N₂(20 sccm) at 4.5 kV and 30 kHz AC voltage for 5 min.)

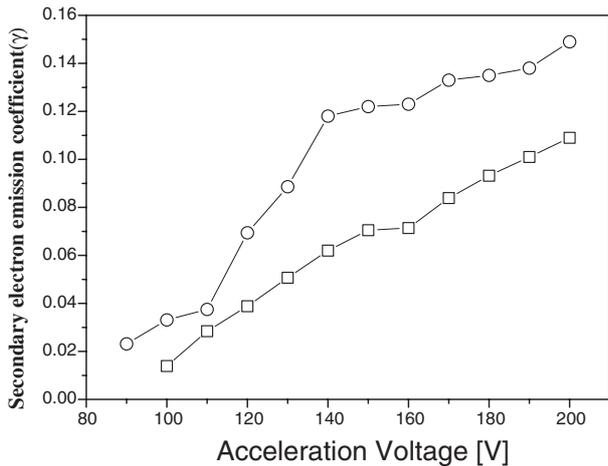


Fig. 4. Secondary electron emission coefficient of MgO surface measured as a function of acceleration voltage before and after the plasma cleaning. (Process condition: He(6 slm)/O₂(20 sccm)/Ar(20 sccm) at 4.5 kV and 30 kHz AC voltage for 5 min.)

emission coefficient(SEEC). To investigate the effect of the plasma cleaning of MgO on the SEEC, the SEEC was measured for the MgO deposited samples before and after the atmospheric pressure plasma cleaning with He/O₂/Ar and the result is shown in Fig. 4. SEEC was measured by accelerating the PDP discharge gases such as He⁺, Ne⁺, Ar⁺, and Xe⁺ to the MgO surface and by measuring the ratio of total current (ion current + secondary electron emission current) to ion current as a function of ion acceleration voltage. The details of the SEEC measurement system can be found elsewhere.¹⁰⁾ As shown in the figure, the SEEC was increased after the plasma cleaning, possibly due to the decrease of impurity species chemisorbed on the MgO surface during the deposition and air exposure after the deposition. Therefore, the atmospheric pressure plasma cleaning of MgO deposited PDP glass appears to not only decrease the outgassing species but also to improve the discharge characteristics by decreasing the firing voltage and the sustaining voltage of PDP.¹¹⁾

In summary, the MgO deposited PDP glass showed outgassing species such as H₂O, CO₂, CO, H₂, and O₂ when the glass was heated to 350°C, and outgassing peaks were observed from 200 to 250°C and also from 300 to 350°C, possibly due to the release of physisorbed species and chemisorbed species from the MgO surface, respectively. By an atmospheric pressure plasma cleaning of the MgO deposited PDP glass using He/O₂/Ar and He/O₂/Ar/N₂ for 5 min, the decrease of outgassing peaks from 300 to 350°C could be observed, possibly due to the removal of organic materials incorporated on the MgO layer during the deposition. The outgassing peaks from 200 to 250°C did not show any significant change after the plasma cleaning, possibly due to the re-adsorption of impurity species during the air exposure after the cleaning. The plasma cleaning increased the SEEC of the MgO layer by removing the organic material from the MgO surface and by improving the surface stoichiometry of MgO layer.

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