Effect of plasma cleanings on the characteristics of MgO layer for plasma display panel

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Abstract

In this study, the effects of plasma cleanings on the outgassing and surface characteristics of a MgO layer used for plasma display panel were investigated. As the plasma cleaning methods, an atmospheric pressure cleaning with $He/O_2/Ar/N_2$ and a low pressure inductively coupled plasma (ICP) cleaning with Ar/O_2 were used. When the outgassing characteristics of the MgO layer cleaned by the plasmas were measured in a vacuum from room temperature to 673 K by a quadrupole mass spectrometer, a decrease in vapor pressures from the outgassing species such as H_2O, CO_2, CO and H_2 could be observed due to the removal of the contamination such as H_2O and organic materials from the MgO surface by the plasma cleanings. The MgO layer after the atmospheric pressure plasma cleaning showed lower outgassing compared to that after the low pressure ICP cleaning, however, the surface roughness of the MgO after the cleanings was lower for the low pressure ICP cleaning. Secondary electron emission coefficient (SEEC) of the MgO layers was increased approximately 1.5–2.5 times after the plasma cleanings for both the atmospheric pressure plasma cleaning with $He/O_2/Ar/N_2$ and the low pressure plasma cleaning with Ar/O_2.
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1. Introduction

AC-plasma display panels (AC-PDPs) are currently obtaining intensive attention because of their potential application to a large-area high definition television with performances such as high brightness, fast response and wide viewing angle. Magnesium oxide (MgO) thin film is usually used as the dielectric layer in the PDPs to improve characteristics such as panel's lifetime, optical transmittance and secondary electron emission coefficient (SEEC) [1–3]. However, impurities such as H_2O, CO_2, CO, etc. easily adsorbed on the MgO layer are emitted during the operation of PDP and deteriorate the characteristics of PDP and reduce the operation lifetime. 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 output of the panel production [4].

To improve the surface characteristics of the MgO layer, plasma cleanings of the MgO surface before the evacuation of the panel could be used. For the plasma cleaning, low pressure plasmas operating under vacuum are generally used for various applications including cleanings of microelectronic devices. However, as the substrate size is increased, it is difficult to generate uniform plasmas over the large substrate size and the fabrication of the equipment is very costly. These days, various atmospheric pressure plasmas, which can generate glow discharges at atmospheric pressure are under investigation [5–8]. The use of atmospheric pressure plasma cleanings instead of the typical low pressure plasma cleanings can increase the handling capacity of extremely large-area substrates, can increase the throughput by in-line processing under the atmospheric environment and can decrease the equipment cost.

In this study, plasma treatments such as an atmospheric pressure plasma cleaning and a low pressure plasma cleaning were used to clean the MgO surface used for PDP and the effects of these cleanings on the

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characteristics of MgO thin film required for the PDP were compared.

2. Experimental

A MgO layer deposited by evaporation of MgO in an oxygen environment using an e-beam evaporator on the real 14.5×11 cm PDP front glass was used as the sample. Before the deposition of the MgO layer, the PDP front glass was composed of an indium tin oxide (ITO) electrode, a bus electrode and a PbO dielectric layer on the sodalime glass.

For the plasma treatment at the atmospheric pressure, a modified dielectric barrier discharge (DBD) equipment with a number of capillary holes drilled in the dielectric material of the power electrode was used. The MgO sample was located on the ground electrode. The air gap between the electrodes (between the capillary dielectric covering the power electrode and the ground electrode) was set at 0.5 cm. Thirty kilohertz and 4.5 kV rms AC voltage was applied to the power electrode to generate the plasma. A mixture of He (4.5 slm)/O_2 (40 sccm)/Ar (20 sccm)/N_2 (20 sccm) was fed through the powered electrode under atmospheric pressure. The plasma treatment time was 10 min, which removed approximately 2000-nm thick photoresist. More details of the atmospheric pressure plasma system used in the experiment can be found elsewhere [9,14]. For the plasma treatment at the low pressure, an inductively coupled plasma (ICP) system was used to clean the MgO surfaces. The processing conditions were set at 800 W of 13.56 MHz inductive power and -100 V of d.c. bias voltage. As the cleaning gas mixtures, 100 sccm of Ar, Ar (50 sccm)/O_2 (50 sccm) and 100 sccm of O_2 were used. The operating pressure was 2 Pa. The plasma cleaning time was 2 min, which removes approximately 400 nm and approximately 2000-nm thick photoresist for 100 sccm Ar and 100 sccm O_2, respectively. Details of the ICP system used in the experiment can be found elsewhere [10].

The MgO samples cleaned with the plasmas were transferred to an outgassing system by a loadlock system to measure the outgassing characteristics. The outgassing chamber was evacuated to less than 10^{-7} Torr before loading the samples. The samples were heated from room temperature to 673 K at 283 K/min using a halogen lamp. The outgassing species and their partial pressures were measured using a quadupole mass spectrometer (QMS, Hiden Analytical Inc.: HAL-201). In addition to the outgassing characteristics, the surface impurities of the MgO were investigated using Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The surface roughness was investigated by atomic force microscopy (AFM). The SEECs of the MgO layers before/after the cleanings were also measured by accelerating a PDP discharge gas ions such
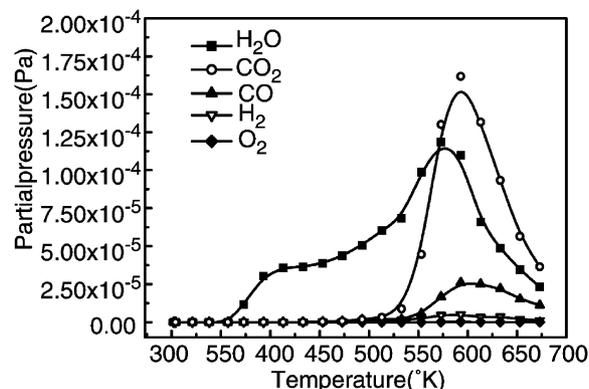
Fig. 1. Vapor pressures of outgassing species from the MgO layer deposited on ITO/bus electrode/PbO/glass by evaporation in an oxygen environment as a function of temperature measured before the plasma cleaning.

as Ne+ (incident ion current) to the MgO surface and by measuring the ratio of the emitted secondary electron current to the incident ion current. The details of the SEEC measurement technique can be found elsewhere [11].

3. Results and discussion

The outgassing characteristics of the as-received MgO layers on the ITO/bus electrode/PbO glass were measured using the outgassing system. The vapor pressures of outgassing species were measured from room temperature to 673 K. As shown in Fig. 1, major outgassing species were H_2O, CO_2, CO, H_2, etc. and, among these impurities, H_2O and CO_2 showed the highest partial pressures from room temperature to 573 K for H_2O and from 573 K to 673 K for CO_2, respectively. These outgassing species were originated mainly from the MgO layer, not from the under-layers such as ITO, bus electrode, and PbO and the glass substrate as investigated by a previous study [12].

The MgO layers were cleaned by atmospheric pressure plasma using the He/O_2/Ar/N_2 gas mixture and by low pressure ICP plasma using 2 Pa of Ar and their outgassing characteristics were compared. Fig. 2a, b and c show the vapor pressures of main outgassing species such as H_2O (a), CO_2 (b) and CO (c) as a function of temperature from room temperature to 673 K for the as-received, the atmospheric pressure plasma cleaned and the low pressure ICP cleaned MgO layers. Fig. 2a shows the effect of the plasma cleanings on the H_2O partial pressure as a function of temperature. As shown in the figure, as the temperature is increased, H_2O desorbed from the MgO surface increased and showed two peaks near 403 and 573 K. The H_2O peak near 403 K appears from the outgassing of physisorbed H_2O and the peak near 573 K from the outgassing of chemisorbed H_2O.
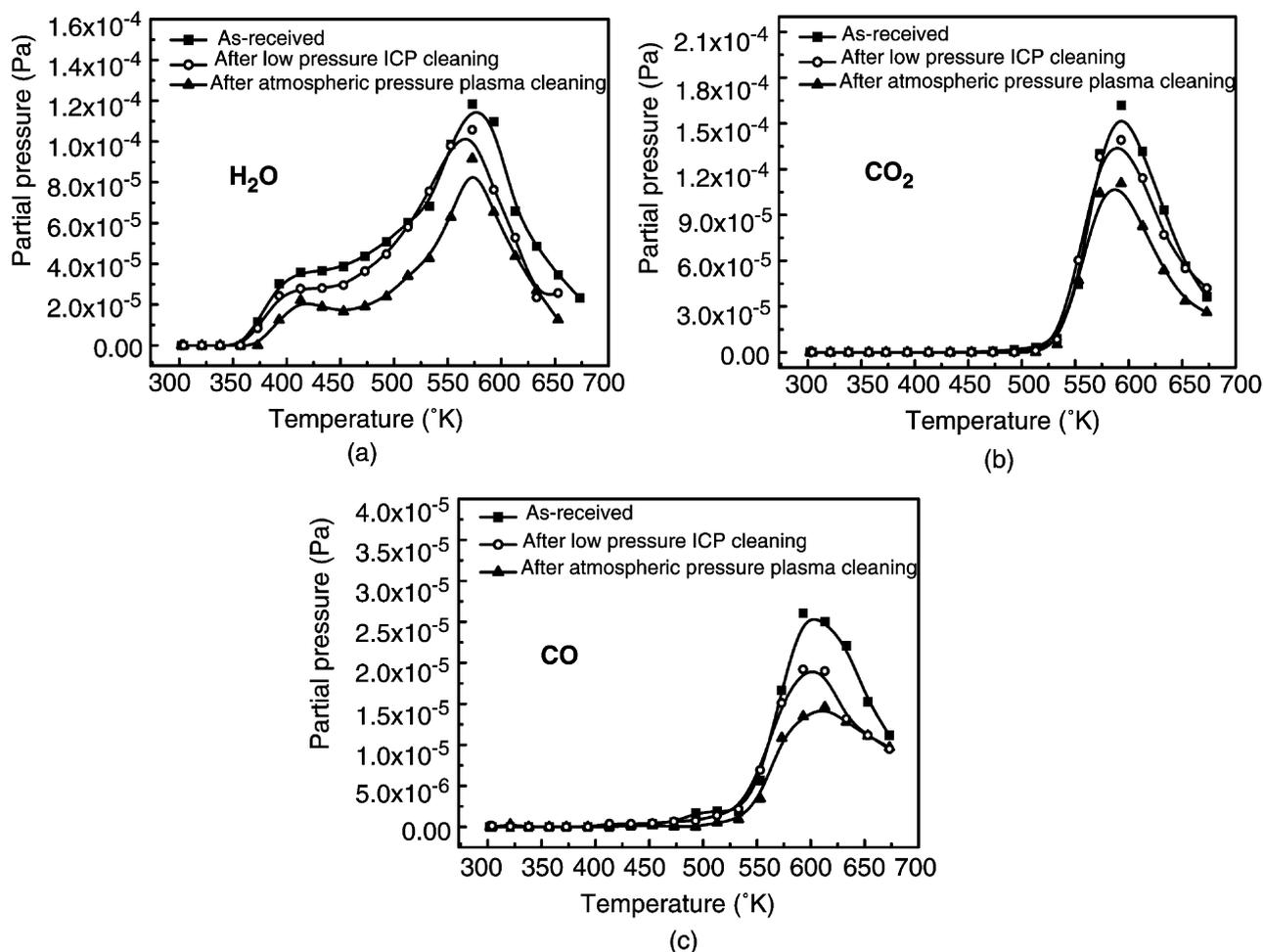
Fig. 2. Vapor pressures of outgassing species from the MgO layer as a function of temperature before and after the plasma cleanings such as the atmospheric pressure $He/O_2/Ar/N_2$ plasma cleaning and the low pressure Ar ICP cleaning. The atmospheric pressure plasma removed approximately 2000-nm thick photoresist and the low pressure Ar ICP cleaning removed approximately 400-nm thick photoresist. (a) H_2O, (b) CO_2 and (c) CO.

Also, as shown in the figure, the vapor pressure of these outgassing H_2O decreased after the plasma cleanings. Compared to the low pressure Ar ICP cleaning, the atmospheric pressure plasma cleaning used in the experiment showed the lower vapor pressure of H_2O.

Fig. 2b,c shows the vapor pressures of CO_2 and CO measured as a function of temperature for the as-received, the atmospheric pressure plasma cleaned and the low pressure ICP cleaned MgO layers, respectively. As shown in the figures, the vapor pressure of CO_2 was higher than that of CO, however, those vapor pressures showed a peak at similar temperatures near 593 K for CO_2 and near 613 K for CO. The MgO layer after the plasma cleanings also showed the lower vapor pressures of CO_2 and CO. The atmospheric pressure plasma cleaning showed the lower vapor pressures of CO_2 and CO compared to the low pressure ICP cleaning. To investigate the origin of the CO_2 and CO desorbed from the MgO surface, the surface composition of the as-

received MgO was investigated using AES. Fig. 3 shows the atomic composition of the as-received MgO layer measured by AES as a function of the depth from the surface. As shown in the figure, the as-received MgO film was not a stoichiometric MgO compound. Also, as shown in the figure, 45 at.% of carbon was remaining on the surface of the as-received MgO possibly due to the adsorption of carbon during the exposure to air after the deposition of MgO layer. However, even inside of the MgO layer, approximately 2 at.% of carbon was remaining possibly due to the adsorption of carbon component during the MgO deposition by the residual gas in the vacuum chamber. Therefore, the desorption of the carbon component on the MgO surface appears to cause the outgassing peak during the heating shown in Fig. 2b,c and the decrease of the peak intensity by the plasma cleaning can be explained by the removal of the carbon from the MgO surface. The more significant decrease of H_2O, CO_2 and CO by the atmospheric
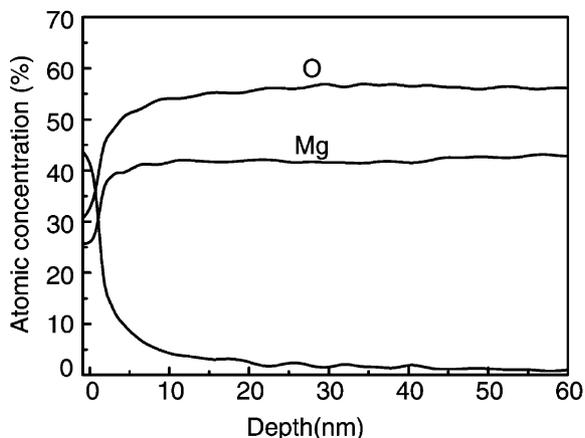
Fig. 3. Atomic composition of the as-received MgO layer measured by AES as a function of the depth from the surface.

pressure plasma cleaning by $He/O_2/Ar/N_2$ compared to those by the low pressure ICP cleaning by Ar shown in Fig. 2 might be from the more effective removal of carbon component on the MgO surface by the chemical reaction of the carbon on the MgO surface with oxygen in the plasma for the atomospheric pressure plasma cleaning. If oxygen is added to Ar or the cleaning time is increased to 10 min for Ar in the low pressure ICP cleaning, a similar effect as the atmospheric pressure plasma cleaning might be expected.

The surfaces of the as-received and the atmospheric pressure plasma cleaned MgO layers were also studied by XPS. Fig. 4a, b, c and d show the O1s peak of the as-received MgO surface (a), the O1s peak after the atmospheric pressure plasma cleaning (b), the C1s peaks of the as-received and the atmospheric pressure plasma cleaned MgO (c) and the Mg2p peaks of the as-received and the atmospheric pressure plasma cleaned MgO (d). As shown in Fig. 4a,b, O1s peak was divided into two peaks related to MgO itself and $Mg(OH)_2$ formed by H_2O adsorption to MgO. Before the cleaning, the $Mg(OH)_2$ peak was higher than the MgO peak, however, after the cleaning, the $Mg(OH)_2$ peak decreased approximately 6.2%. Also, as shown in Fig. 4c,d after the plasma cleaning, the C1s peak decreased approximately 18.5% and the Mg2p peak increased approximately 4.3%. Therefore, the decrease of vapor pressure shown after the atmospheric pressure plasma cleaning during the outgassing experiment in Fig. 2 is believed from the removal of surface contaminants such as H_2O and organic contaminants adsorbed on the MgO surface.

The changes of MgO surface roughness after the atmospheric pressure plasma cleaning and the ICP cleaning were investigated using AFM. As shown in Fig. 5, the as-received MgO surface showed the rms roughness of approximately 28.3 nm, however, the rms roughness decreased to 25.7 nm after the atmospheric pressure plasma cleaning and to 16.3 nm after the ICP cleaning.
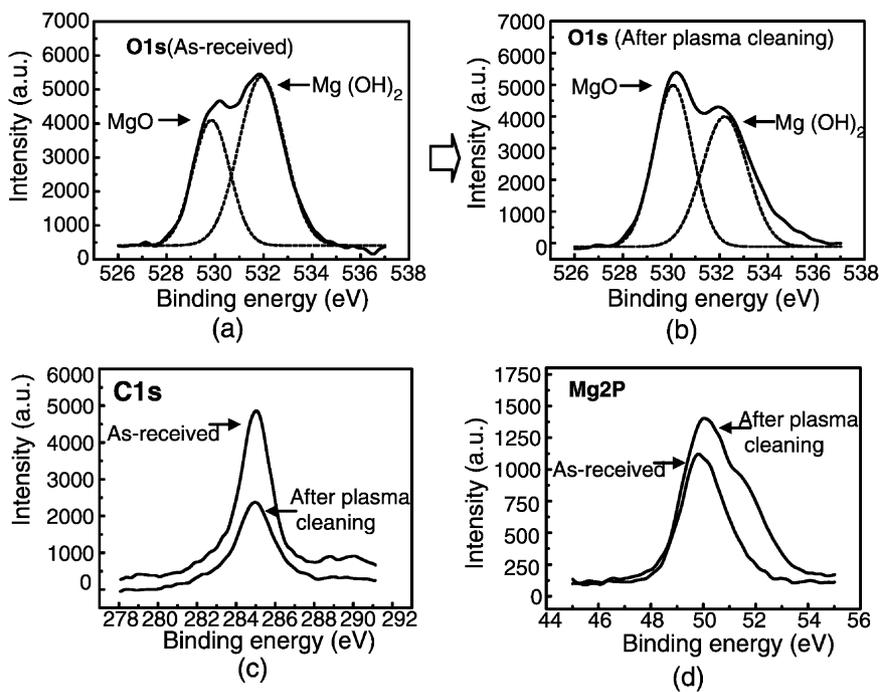
Fig. 4. XPS narrow scan data before and after the atmospheric pressure plasma cleaning. (a) O1s peak (as-received), (b) O1s peak (after the plasma cleaning), (c) C1s peaks and (d) Mg2p peaks.
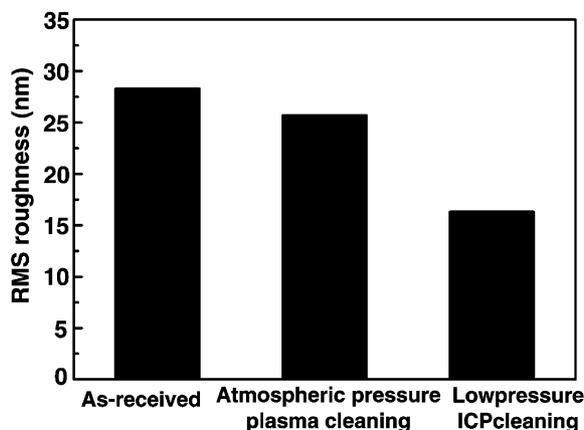
Fig. 5. RMS surface roughness of the MgO measured by AFM before and after the plasma cleanings using the atmospheric pressure plasma and the low pressure Ar ICP plasma.

The decrease of rms roughness of MgO after the ICP cleaning appears from the sputter etching (planarization) of the MgO surface by Ar ions during the cleaning. In the case of the atmospheric pressure plasma cleaning, due to the short distance between the atoms at atmospheric pressure, it is difficult to accelerate the ions to the surface for sputtering. The small decrease of surface roughness might be related to the removal of surface contaminants on the MgO surface.

In PDP, the MgO layer is required to have a higher SEEC (γ) for the lower voltage operation of the devices [13].The SEEC of the as-received, the atmospheric pressure plasma cleaned and the low pressure ICP cleaned MgO were measured using a γ-focused ion beam (γ-FIB) system and the ratios of γ (plasma cleaned) to γ (as-received) are shown in Fig. 6. For the low pressure ICP cleaning, instead of 100 sccm Ar, Ar (50 sccm)/O_2 (50 sccm) and O_2 (100 sccm) at 2 Pa of operating pressure were used to increase the surface cleaning. In the case of 2 Pa O_2 cleaning, approximately 2000-nm thick photoresist was removed. As shown in the figure, the SEEC ratios of the atmospheric pressure plasma cleaned MgO and that of the low pressure Ar/O_2 ICP cleaned MgO to the as-received MgO were similar and were in the range from 1.5–2.5, therefore, the SEECs were increased by the plasma cleanings. However, in the case of the low pressure O_2 ICP cleaning, the ratio of SEEC was remained close to one, therefore, the O_2 ICP cleaning of MgO surface did not show any improvement in SEEC even though the removal rate of organic material is similar to that of the atmospheric pressure plasma cleaning. Insignificant effect on SEEC by the O_2 ICP cleaning is possibly due to the oxygen implanted on MgO surface, however, more investigation of the oxygen effect on the MgO surface is required.

4. Conclusions

In this study, the effects of plasma cleanings such as an atmospheric pressure cleaning with He/O_2/Ar/N_2 and a low pressure ICP cleaning with Ar/O_2 on the characteristics of a MgO layer used for PDP were investigated.

When the outgassing characteristics of the MgO deposited by evaporation in an oxygen environment were measured from room temperature to 673 nm, outgassing species such as H_2O, CO_2, CO and H_2 were observed as major species. Among these, H_2O showed the highest vapor pressure from room temperature to 573 K and CO_2 showed the highest vapor pressure from 573 to 673 K. These vapor pressures could be decreased by the removal of surface contaminants adsorbed on the MgO by the cleanings as observed by the XPS results. The MgO cleaned by atmospheric pressure plasma using He/O_2/Ar/N_2 showed lower vapor pressures compared to that cleaned by the low pressure Ar ICP possibly due to more removal of MgO surface contaminants used in the experimental condition. However, the low pressure Ar ICP cleaning showed a lower surface roughness compared to the atmospheric pressure plasma cleaning possibly due to the sputter etching (planarization) of MgO surface by Ar for the low pressure Ar ICP cleaning. When SEEC was measured, the MgO surfaces cleaned by the low pressure Ar/O_2 ICP and the atmospheric pressure plasma increased the SEEC similarly approximately 1.5–2.5 times, therefore, the decrease of
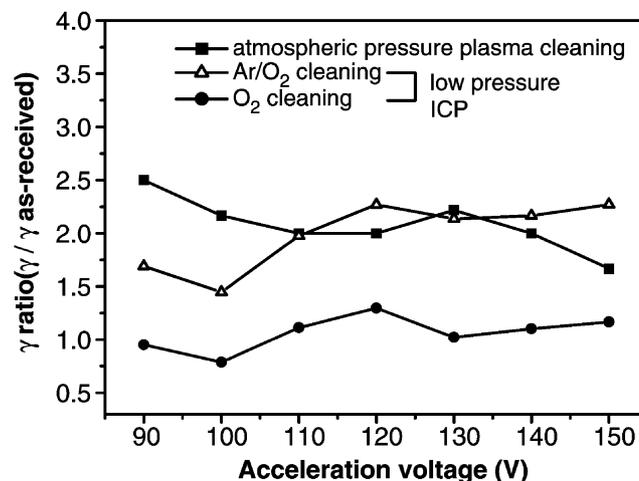
Fig. 6. The ratios of SEECs of MgO surface, that is, the ratios of γ (the plasma cleaned)/ to γ(as-received) measured as a function of acceleration voltage of Ne before and after the plasma cleanings such as the atmospheric pressure plasma cleaning and the low pressure ICP Ar/O_2 and O_2 cleanings. For the ICP cleanings, gas mixtures of Ar (50 sccm)/O_2 (50 sccm) and O_2 (100 sccm) at 2 Pa of operating pressure were used.

driving voltage of PDP could be expected by the plasma cleaning.

Acknowledgments

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