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Investigation of the outgassing characteristics of the materials comprising a plasma display panel

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Long gas evacuation time before the introduction of the discharge gases into the panel is one of the major problems in the production of a plasma display panel (PDP). In this study, the outgassing characteristics during the panel evacuation stage were investigated using a quadrupole mass spectrometer. The origin of the impurity gas was studied by measuring the outgassed species from each layer comprising the PDP. Dominant species observed during the evacuation of the panel were H_2, H_2O, N_2, O_2, and CO_2 and water vapor was the most abundant species. When the outgassing characteristics of the panel were compared with the outgassing characteristics from each layer comprising the panel, the material most responsible for the water vapor turned out to be a MgO layer. The outgassing experiments of single panels have also shown that the long outgassing time of PDP is mostly related to the MgO layer and possibly also to red, green, and blue layers and white dielectric material coated on the each single panel. Therefore to reduce the gas evacuation time, controlled atmosphere appears to be required during the deposition of these materials and the storage of those deposited panels. © *2001 American Vacuum Society.* [DOI: 10.1116/1.1369788]

I. INTRODUCTION

A plasma display panel (PDP) is one of the most promising candidates for a large area displays because of its manufacturing processes appropriate for a large area, good display quality, and high speed addressing ability.[1] In the fabrication of a PDP, the evacuation of gas from the panel to achieve high vacuum state before the introduction of the discharge gas mixtures is required for display quality and long term reliability. Residual gas remaining inside the panel can degrade display performance and uniformity during the operation.[2,3] Currently, this gas evacuation process takes more than several hours to obtain a desirable vacuum state of around 10^{-7} Torr due to the outgassing from the materials inside of the panel. It is known that this gas evacuation process is one of the most time-consuming processes that reduces the production rate and increases the cost of PDPs. However, the factors or the materials causing the severe outgassing from the panel during the evacuation are not well-understood due to the variety of materials coated in the panel and complex processing. Accordingly, the basic research on the outgassing characteristics from the panel such as identification of outgassing species from the inside of the PDP, and materials responsible for the outgassing are required for the improvement of manufacturing process and development of the materials used in PDPs.

In this study, outgassing characteristics of the complete PDP itself and the layers of materials comprising the PDP were systematically studied using a quadrupole mass spectrometer to investigate the impurity species released from inside the PDP and to determine the material layers responsible for the outgassing of the PDP during the evacuation.

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II. EXPERIMENT

A. Sample preparation

Figure 1 shows the schematic diagram of a test panel structure of the color plasma display panel (7 in. diagonal) used in our experiment. The panel structure shown in Fig. 1 is known as the reflection type three-electrode surface discharge color plasma display.[4] Display electrodes on the front single panel are composed of a transparent indium tim oxide (ITO) to effectively emit a luminance and a narrow bus electrode of Ag to reduce the electrode resistance. These electrodes are covered by a dielectric layer, which is made of low melting glass material. A thin MgO also is deposited on the layer using electron beam evaporation. On the rear single panel, striped address electrodes are arranged. A white dielectric layer to reflect light covers these electrodes. On the white dielectric layer, striped barrier ribs are coated on both sides of the address electrodes line to separate the adjacent discharge cells and to eliminate the optical cross talk between them. Three primary color phosphor materials such as red, blue, and green are screen-printed in the neighboring channels of the ribs to cover both the sidewall of the barrier ribs and the white dielectric layer. The gas evacuation process is accomplished after the sealing of both front and rear single panels together using a frit material before filling with discharge gases (Xe+Ne, etc.) in the panel. The complete panels are evacuated through a small section of glass pipe (exhaust tip) attached to the corner of the rear panel.

The complete PDP panel has multilayer films consisting of various materials. In order to figure out the effect of each layer on the outgassing properties of the complete panel during the gas evacuation process, two different types of single panels were used in addition to the complete panel sealed with the frit material. The first type, was coated with each material only. The second type was coated sequentially with

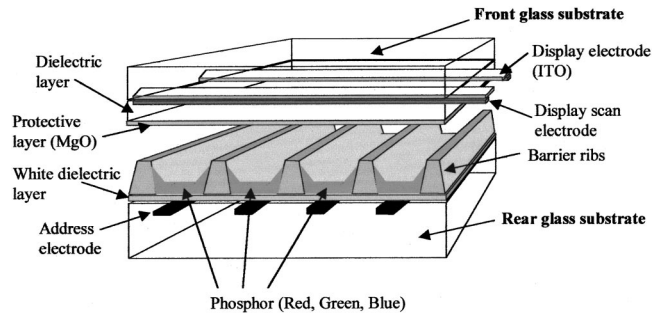

FIG. 1. Cross-sectional diagram of the plasma display panel structure used in the experiment.

multilayer thin films to a certain manufacturing step. The materials investigated were electrodes (metal, ITO), dielectric layers, barrier rib, phosphor layers (red, green, and blue), protective layer (MgO), and frit on the glass panel. The outgassing characteristics of the single panels coated with each material and sequentially coated multilayer materials were analyzed and compared with those of a complete panel.

B. Outgassing measurement system

The outgassing measurement system used in this study is shown in Fig. 2. The system consisted of two chambers. One chamber (that is, furnace) was used to measure outgassing characteristics of the complete panel and the other (that is, UHV chamber) was used to measure the characteristics of the single panels coated with single layers and multilayers. In order to investigate the outgassing species from the single panel during the evacuation, a quadrupole mass spectrometer (QMS: Hiden Analytical Inc., PSM 500) was connected on the sidewall of the UHV chamber. The temperature of the single panels was controlled using a halogen lamp installed inside of the chamber. In the case of the furnace chamber, the complete panel was located in the chamber at atmospheric pressure and the temperature of the panel was controlled using heating wires. The panel was pumped through the exhaust tip connected to the holding manifold and the QMS was installed near the holding manifold to measure the outgassing species. To measure the outgassing species continuously from atmospheric pressure to a high vacuum during the evacuation process, a sampling chamber with a bakeable variable leak valve was installed to control the conductance as shown in the figure. All of the vacuum lines were heated to prevent water vapor condensation and the QMS unit was differentially pumped. For both systems the panels were heated up to 350 °C at the rate of 10 °C/min and were maintained for several to 20 h at 350 °C to measure outgassing characteristics. The temperature profile used in this experiment was one of the typical temperature profiles of the panel evacuation process used in the fabrication of the PDP. The outgassing characteristics of the panels were investigated as a function of time and temperature.

In order to obtain quantitative results for the amounts of the outgassing species, mass currents measured by QMS have to be calibrated to the partial pressures of the various species observed in the experiment. The calibration of the mass spectrometer was conducted by introducing various calibration gas mixtures to the chamber shown in the figure using a method described by other researchers.[5–7]

III. RESULTS AND DISCUSSION

Outgassing was measured using the QMS while increasing the temperature from room temperature to 350 °C For the complete panels this was done through the exhaust pipe, and for the single panels through the UHV chamber. Mass peaks related to the adsorbed species such as H_2, H_2O, N_2, O_2, and CO_2 were observed. However, no other peaks related to thermal decomposition of the display material itself could be observed over the same range of temperature. When molecules are detected by QMS, dissociated molecular and

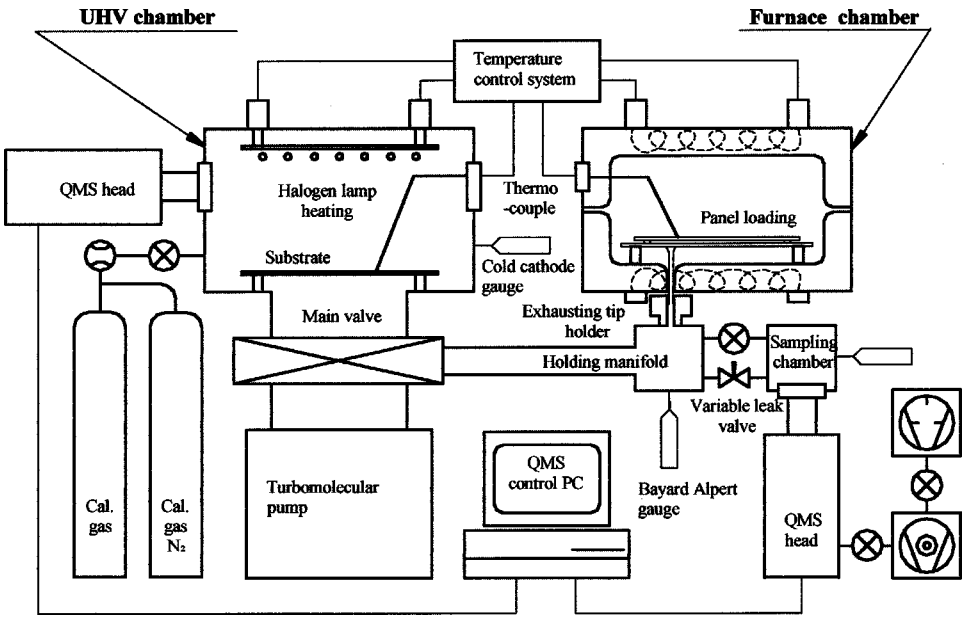

FIG. 2. Schematic of the apparatus for the measurements of outgassing species.

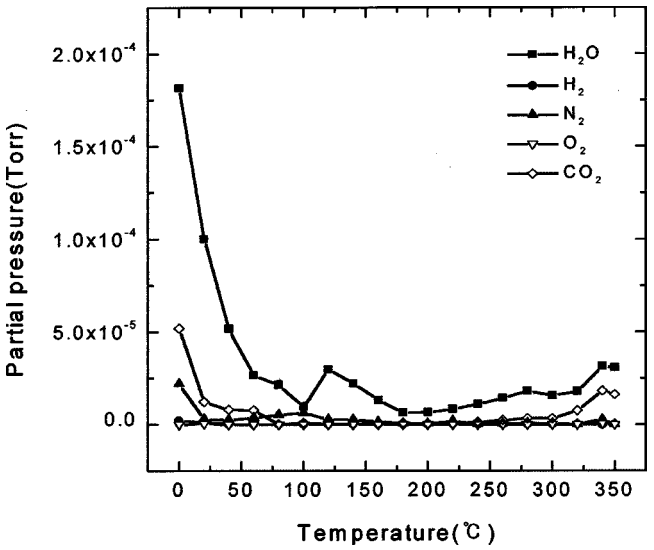

FIG. 3. Partial pressures of the outgassing species observed for the complete panel during the evacuation from atmospheric pressure while increasing the temperature to 350 °C (10 °C/min).

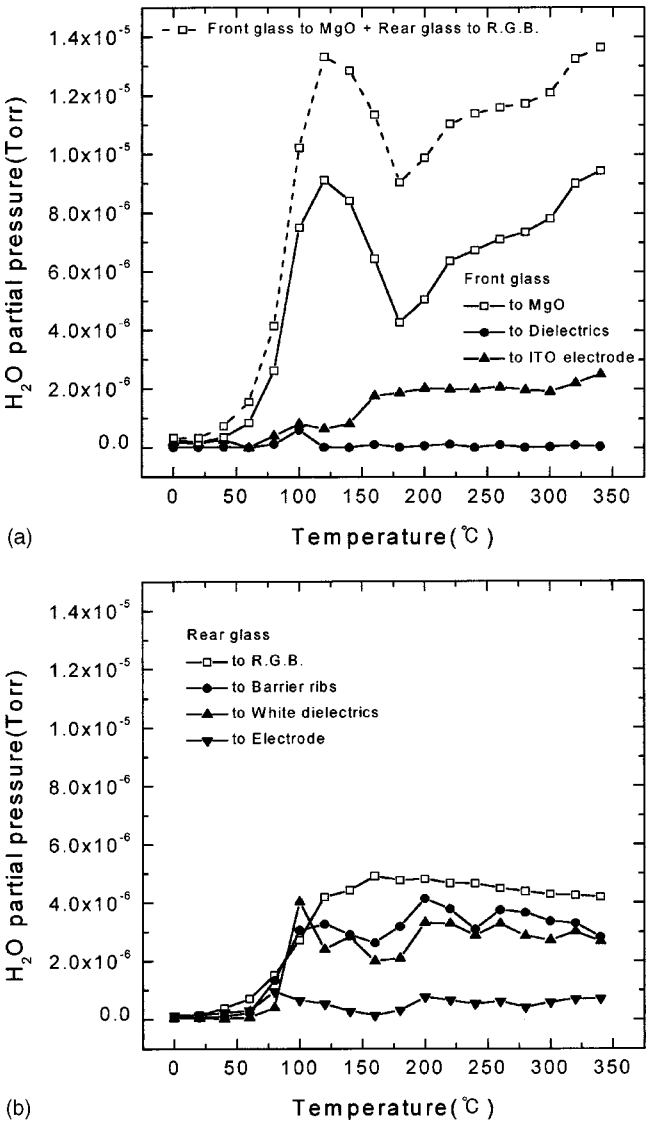

FIG. 4. H_2O partial pressures observed as a function of temperature for sequentially deposited layers of materials on the front glass (a) and on the rear glass (b). The sum of H_2O partial pressure measured from the single panel after the deposition of MgO on the front glass and that measured from the single panel after the deposition of the RGB layer on the rear glass is also shown in (a) as a dotted line.

atomic peaks are also observed and some of these dissociated peaks are superimposed.[8] For example, 2 amu from H_2 are superimposed by the dissociated H_2 from H_2O and 28 amu of CO are superimposed by N_2. However, the dissociated H_2 from H_2O in the QMS is less than 5%, therefore the detected H_2 was close to H_2 from the original H_2. In the case of N_2, the estimated intensity of N_2 from the detected intensity of mass 14, which is from the N dissociated from N_2, was close to that of N_2 for all of the cases, therefore the possible detection of CO was also disregarded. The mass peaks such as H_2, H_2O, N_2, and O_2 are also observed when the chambers were heated from room temperature to 350 °C without installing the panels although the intensities are much smaller. To obtain intensities of the outgassing species from the panels, the reference signals measured without installing the panels (single panel or complete panel) upon heating from room temperature to 350 °C were subtracted from the observed signals. For accuracy, the reference signals were measured before and after the measurement of the outgassing from the panels and the consistency of the reference signals were monitored.[8]

Figure 3 shows the calculated partial pressures of the species outgassed from the complete panel when the temperature of the furnace was increased by 10 °C/min from room temperature to 350 °C while the panel was evacuating. As the outgassing species, H_2O, CO_2, N_2, H_2, and O_2 were observed as mentioned above and the most abundant species was H_2O. The initial decrease of the partial pressures was from the decrease of the residual gas pressure through the gas evacuation process and most of the gas pressures were decreased nearly continuously with the increase of temperature to 350 °C while pumping the panel. However, in the case of H_2O, additional peaks near 120 and 350 °C were shown.

To identify the material layer responsible for the H_2O outgassing, the outgassing characteristics of single panels were investigated for front glass and rear glass after the sequential deposition of each layer. To measure the outgassing species from the single panels, the chamber was evacuated for a few hours before the increase of the temperature. The reference outgassing peaks measured without the panels as a function of temperature were also measured before and after the measurement and subtracted for accuracy. Figure 4 shows H_2O partial pressures observed as a function of temperature for sequentially deposited layers of materials on the front glass (a) and on the rear glass (b). As shown in the figure, a huge increase of H_2O partial pressure was observed after the deposition of MgO for the front glass. Some increase of H_2O partial pressure was also observed after the deposition of the ITO layer. However, the ITO layer is completely covered by the following dielectric layer and the H_2O

partial pressure after the deposition of the dielectric layer was very low. Therefore H_2O partial pressure observed after the deposition of the ITO layer on the front glass may not contribute to the H_2O partial pressure observed after the deposition of the MgO layer on the dielectric layer. In the case of the rear glass, a certain increase of H_2O partial pressure is observed after the deposition of white dielectric on the address electrodes and also after the deposition of the red, green, and blue (RGB) layers on the barrier ribs. The white dielectric layer is partially covered by the barrier ribs and the RGB layers and some of the white dielectric layer remains exposed even after the deposition of the RGB layers. Therefore in addition to the RGB layers, the white dielectric layer may be partially responsible for the H_2O partial pressure observed after the deposition of the RGB layers.

In Fig. 4 (a), H_2O partial pressure calculated by the addition of H_2O partial pressure measured after the deposition of MgO for the front glass and H_2O partial pressure measured after the deposition of the RGB layers for the rear glass is also shown. The calculated H_2O partial pressure in the figure appears to be similar to the H_2O partial pressure obtained for the complete panel in Fig. 3 except for the low temperature regime. The difference in the low temperature regime is from the difference in the measurement method. In the case of the complete panel, the partial pressures were measured while pumping the panel from the atmosphere, however, in the case of the single panels, the partial pressures were measured after the chamber was evacuated for a few hours. Therefore the H_2O partial pressure for the complete panel can be correlated to the H_2O partial pressure measured from the single panels.

The material layer, which is the most responsible for high H_2O partial pressure, appears to be on MgO layer. To identify the source of the H_2O partial pressure, outgassing characteristics from a single layer of materials deposited on the glass were also investigated using the method used for the single panels coated with multilayers of the materials. Figure 5 shows H_2O partial pressures measured as a function of temperature for the single layer of the materials deposited on the front glass. As shown in the figure, the MgO layer itself showed the H_2O partial pressure curve similar to that of a single panel coated with the multilayers from the ITO to MgO layer. Other single layers of materials showed lower H_2O partial pressures. In the figure, H_2O partial pressure of the frit material used to seal the front glass and rear glass to form a complete panel was included. H_2O vapor pressure of the frit material from room temperature to 350 °C was relatively low compared to other materials. In fact, frit material has a low melting point around 450 °C to bond the front and rear glasses and could be decomposed during the heating. However, in our experiment, outgassing species decomposed from the frit material were not detected even when the frit material was heated to 400 °C.

The H_2O partial pressure curve shown as a function of temperature for the MgO layer appears to be related to the H_2O absorption mechanism. When the MgO surface is exposed to the atmosphere, H_2O can be physisorbed on the surface. This physisorbed H_2O tends to be desorbed as the temperature is increased from 25 to 105 °C. Also, some H_2O is chemisorbed on the surface of the MgO layer from 105 to 180 °C by the hydrogen bonding with MgO and this chemisorbed H_2O is known to be desorbed by increasing the temperature to 400 °C.[9–12] In fact, some gas including H_2O and other gas species can be trapped inside of the film and can be outgassed with the increase of time and temperature. In the case of rear glass, H_2O partial pressure was increased as the temperature was raised to 100 °C, but decreased very slowly with further increase of temperature. The increase of H_2O partial pressure to 100 °C appears to be related to the desorption of physisorbed H_2O from the surface of the materials. However, the slow decrease of H_2O with further increase of temperature appears to be related to outgassing of trapped gases because of the relatively high porosity of the white dielectric material and RGB materials.

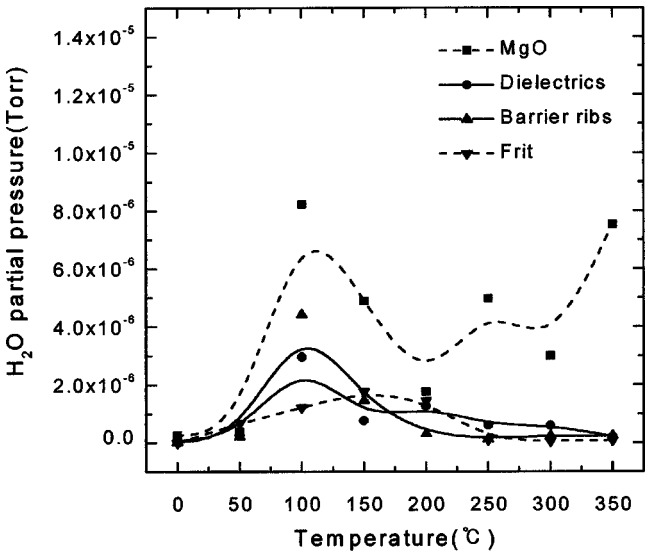

FIG. 5. H_2O partial pressures measured as a function of temperature for the single layers of the materials deposited on the front glass. H_2O partial pressure of the frit material used to seal the front glass and rear glass to form a complete panel was also included.

In PDP fabrication, after the complete panel temperature reaches 350 °C during the gas evacuation process, the panel temperature is kept at that temperature until the evacuation line pressure decreases to 10^{-7} Torr. The outgassing properties of the complete panel as a function of time were measured during the evacuation while keeping the panel at 350 °C and are shown in Fig. 6. After the temperature reached 350 °C (time=0), H_2O partial pressure decreased slowly with the increase of time. For other gas species, a relatively rapid decrease of partial pressure was seen with the increase in time. Therefore the control of H_2O partial pressure appears to be important in decreasing the gas evacuation time during the gas evacuation process. Outgassing characteristics of the single panels composed of the sequentially deposited materials and the single layers of materials were also investigated and some of the results on the H_2O partial pressures are shown in Fig. 7(a) for the front glass and 7(b)

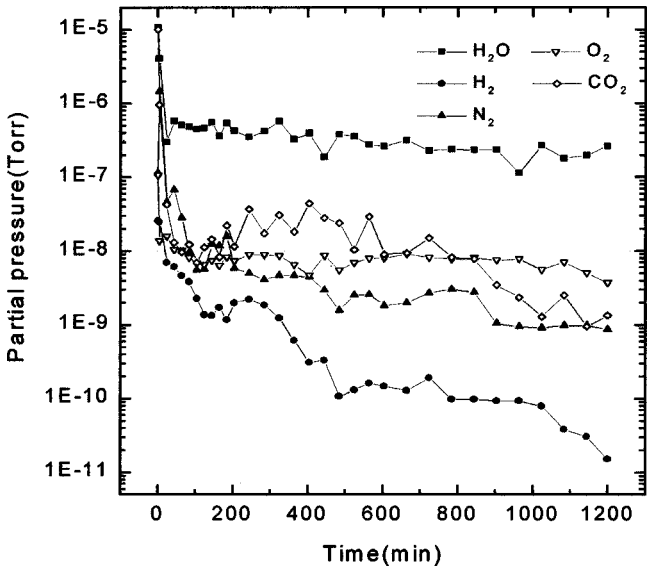

FIG. 6. Outgassing properties of the complete panel as a function of time up to 20 h measured during the evacuation while keeping the panel at 350 °C.

for the rear glass. H_2O partial pressures for the frit material on the glass are also included in Fig. 7(a). As shown in Fig. 7(a), in the case of the front glass, the panel deposited to MgO showed the longest evacuation time of about 3 h 40 min to reach to 10^{-7} Torr and the panel deposited to the ITO layer showed the next longest time of about 2 h to reach 10^{-7} Torr. The single layer of MgO material also showed the longest evacuation time (not shown). In the case of the rear glass, the panel deposited to RGB layers showed the longest time of about 3 h to reach 10^{-7} Torr and the panel deposited to the white dielectric layer and the barrier rib

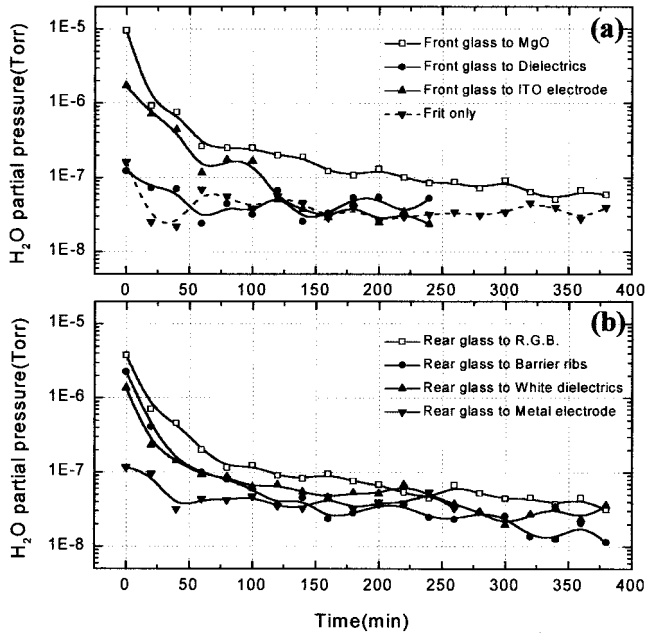

FIG. 7. H_2O outgassing characteristics of the single panels composed of the sequentially deposited materials and the single layers of materials (a) for the front glass and for frit material only and (b) for the rear glass.

showed a time near 2 h. The frit material showed also about 2 h to reach 10^{-7} Torr. The outgassing characteristics from the single panel were similar to those from the complete panel. Therefore to decrease the gas evacuation time, the MgO layer from the front glass and the RGB layers and white dielectric materials from the rear glass should be deposited and stored in a controlled environment to reduce H_2O adsorption to the layers.

IV. SUMMARY

In this study, outgassing characteristics of the plasma display panel during the gas evacuation process were observed using a quadrupole mass spectrometer, and the outgassing species and their source were investigated using either various single panels made of multilayers of materials deposited sequentially or single panels with only single layers of materials.

H_2, H_2O, N_2, O_2, and CO_2 were observed as the main outgassing species and thermal decomposition of display materials was not observed when temperature was increased to 350 °C by 10 °C/min and kept at the temperature. H_2O showed the highest partial pressure for the experimental conditions and the materials most responsible for the high H_2O vapor pressure were MgO deposited on the front glass and possibly the RGB layers and the white dielectric material deposited on the rear glass. H_2O partial pressure of the complete panel as a function of temperature showed two peaks near 120 and 350 °C that appeared to be related to desorption of physisorbed H_2O and chemisorbed H_2O to MgO surface, respectively.

Partial pressures of the complete panels and single panels were decreased continuously when the panel temperature was kept at 350 °C during the pumping. The longest H_2O evacuation time was observed for the panel deposited up to MgO, and this possibly originated from H_2O outgassing from the MgO layer itself. The panel deposited to the RGB layers showed the next longest H_2O evacuation time and again the outgassing appears to be related to the outgassing of the trapped gases in the RGB layers and partially exposed white dielectric materials.

ACKNOWLEDGMENT

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