Effects of Aging Treatment of doped-MgO Layer on Discharge Characteristics of ac-PDP

Kyung-Hyun Park, Min-Soo Ko, Sang-Hoon Yoon, and Yong-Seog Kim Department of Materials Science and Engineering, Hongik University, 72-1, Seoul, Korea

Abstract

Effects of aging treatment of doped-MgO electron emission layer on luminance efficiency of ac-PDP were investigated in this study. Morphological and luminance efficiency with aging treatment were examined, especially with emphasis on the effects of doping elements. The results indicate that the luminance efficiency of test panels depends on the type of doping elements used for MgO and that may be due to the redeposition of MgO during glow discharge.

1. Introduction

MgO thin film coated on transparent dielectric layer of front glass plate of ac-PDPs acts as a secondary electron emission source during glow discharge of the device. The ejection of secondary electrons from the MgO layer occurs as the electrons in valence band are excited to vacuum energy levels by external energy sources.

Among various external energy sources for the secondary electron ejection, energy released from Auger neutralization reaction of positive ions at the MgO surface has been noted to play a dominant role. In this electron ejection mechanism, the larger the ionization energy of the discharge gas, the higher the yield of secondary electron emission. For example, the yield of He⁺ is close to 0.3, but the yield of Xe⁺ was measured to be close to zero. The neutralization energy of Xe⁺ ion is not enough to eject the electrons from MgO.

In recent years, however, Xe content in glow discharge gas of ac-PDP is increasing since luminance efficiency of ac-PDPs, in general, becomes higher as the content of Xe is increased [1]. The increase of the Xe content in the discharge gas, however, raises the firing voltage of ac-PDPs [2] since the Xe⁺ ions can not eject the secondary electrons.

Thus, in order to induce secondary electron emission from MgO with Xe⁺ ions of low neutralization reaction energy, stoichiometry [3] and doping of MgO with aliovalent elements [4] have been attempted. Basic idea of these approaches is to create defect levels within the band gap such that electrons in those defect levels may be ejected with less amount of external energy. For example, by increasing F-type centers (anion vacancy with one or two electrons trapped) concentration via modification of stoichiometry of MgO film, discharge voltage of the film under Xe discharge gas was decreased significantly [5]. For the doping elements, aliovalent cations such as Al³⁺ and Si⁴⁺ have been found to be effective in reducing the firing voltage. These dopants create donor levels below the conduction band and that may provide a shallow source for emission of secondary electrons with low neutralization energy.

Hydrogen doping to single crystal MgO has been studied extensively for some time and its effects on electronic and/or hole trap levels are well-known [6]. When a proton is doped substitutionally to anion (oxygen) site with two electrons, H^- -center is created. This center has a net positive charge for the lattice site and therefore provides virtual traps for an electron. The trap level is located below 0.5~0.6 eV of conduction band bottom [7]. On the other hand, when a proton is placed substitutionally to cation (magnesium) site, it react with neighboring oxygen ion to form hole traps as in the following equation:

$$[OH^{-}]_{O}^{\bullet} - V_{Mg}^{"} - O_{O}^{\bullet} : V_{OH}$$

Energy level of the hole trap has not been identified precisely, but are believed to be located within less than 1eV above the top of the valence band.

These previous studies suggest that doping of hydrogen (hydrogenation) into MgO may generate shallow electron donor and/or hole acceptor levels by creating H^- and/or V_{OH} centers. In essence, the hydrogenation converts the deep levels such as F- and V-type defects to shallows level defects like the H^- and/or V_{OH} centers. This conversion should increase the possibility of ejecting secondary electrons during glow discharge of AC-PDP and that lead to reduced firing voltage. In addition, there is a possibility of enhancing the emission of delayed secondary electron emission from those shallow defect levels. The delayed emission is sometimes termed as exo-electron emission and provides seed electrons for initiation of glow discharge [8].

Aging of test panels has been used to homogenize the electron emission characteristics of MgO layer, such that discharge margin can be obtained uniformly throughout the panel. Previous studies claimed that the treatment leads to planarization of the MgO nodule and removes any contaminations on its surface via sputtering process [9]. The doping of MgO film either with gaseous elements like hydrogen or with metallic elements like Be²⁺, on the other hand, may cause different aging behavior of ac-PDPs since the MgO film is sputtered and redeposited actively during glow discharging.

In this study, therefore, an attempt was made to examine the sputtering behavior of doped-MgO film. For the doping elements, hydrogen and Be were selected. Using test panels prepared with those MgO films, microstructure of aged MgO film, and luminance efficiency change as a function of aging treatment were examined.

2. Experimental

Hydrogen doping to MgO layer was conducted by ebeam evaporation deposition of the layer under hydrogen atmosphere. Partial pressure of hydrogen was varied between 1.3×10^{-6} and 1.3×10^{-4} torr. The glass plate was heated to 300° C prior to coating. The film was deposited approximately at a rate of 0.5 nm/sec and its thickness was ~ $5000 \text{ Å} \pm 500 \text{ Å}$. For the Be-doping, pellets containing 1,000 ppm of Be were used for the e-beam evaporation deposition process. Using those front glass plates, test panels were produced by sealing with rear plates. The rear plate was formed with rectangular type barrier ribs of VGA grade of 42 inch diagonal size. Zn₂SiO₄:Mn green phosphor was coated on the rear plate. The discharge gas used was Ne-4%Xe and the pressure was 400 torr.

In order to evaluate defect levels and its concentration in the film, photoluminescence (PL) spectra of the films were measured. Excitation source for the PL spectra measurement was He-Cd laser (325nm) and the measurement was conducted at 5K \sim 300K. In addition, orientation and microstructure of the films were analyzed using XRD and FE-SEM.

The firing voltage of doped MgO layers was measured using voltage transfer close (VTC) curve and the measuring procedures of this set-up can be found in more detail elsewhere [10]. In addition, luminance efficiency and address discharge delay were evaluated. Surface morphology of the film after aging treatment was using FE-SEM.

3. Results and Discussion

3.1. PL spectra of MgO films e-beam deposited under hydrogen atmosphere

Photoluminescence (PL) spectra were measured on MgO thin film deposited under inert atmosphere and the film deposited under several hydrogen partial pressures (Fig. 1). Fig. 1(a) shows the PL spectrum from MgO thin film deposited under inert atmosphere. The PL spectrum of MgO film deposited under inert atmosphere was deconvoluted to several radiation of lights centered at 380nm(3.2eV), 420nm(2.95eV), 480nm(2.6eV), and 550nm(2.3eV). The luminescence of 380nm and 550nm has been known to be the radiation from the transition of excited electrons to ground states of F^+ - and F-type centers, respectively. In addition to those F-type radiations, luminescence centered at 420nm was detected as the predominant one. This blue radiation is due to hole-electron recombination reaction at V_{OH} defect center.











(c)

Fig. 1. Photoluminescence spectra from (a) MgO thin film without hydrogen gas, (b) MgO thin film formed under hydrogen partial pressure of 1.3×10^{-5} torr and (c) 1.3×10^{-4} torr.

The PL spectra from MgO film deposited under hydrogen atmosphere differed significantly from the one deposited under inert atmosphere. As shown in Fig. 2(b) and (c), luminescence intensities of the typical 380nm and 550nm from F-type centers were reduced with the introduction of hydrogen and almost disappeared as the hydrogen partial pressure was increased to 1.3x10⁻⁴ torr. The increase in hydrogen partial pressure must have augmented the concentration of H^- -centers and reduced the concentration of F-type centers. In other words, the introduction of hydrogen into MgO film has converted the F-type centers to H^- -centers to reduce the luminescence intensity from F^+ - and F-type centers. This H^- -center was noted to emit 520 nm radiation and its concentration increase with increase in hydrogen partial pressure [11]. Our PL spectra of hydrogenated MgO film indicated that the luminescence of 490nm shifted in wavelength to 520nm with the increase in partial pressure and its intensity to increase with the partial pressure.

These PL analyses of MgO thin films suggest that the addition of hydrogen gas into the atmosphere of e-beam evaporation process converts the F^+ - and F-type defects into H -centers, promoting the emission of 520nm radiations. In addition, the luminescence from proton trapped in cation vacancy site (V_{OH^-} center), 420nm, also is increased with the introduction of hydrogen gas into the processing chamber of e-beam evaporation process. In summary, the hydrogenation of MgO thin film passivated the disorders at anion and cation site vacancies with the protons and converts to shallow level donors and/or acceptors.

Figure 2 shows the PL spectrum from Be-doped MgO film. As noted from the spectrum, radiations centered at 380nm, 420nm, 490nm, 550nm were detected as with the MgO film formed under inert atmosphere. Those radiations are associated with F^+ -, V_{OH} , H^- , and F-type centers. In addition, radiations centered at 635nm, 730nm, and 780nm were observed, which may be associated with holes generated by the doped Be²⁺ ion.



Fig. 2. PL spectrum from Be-doped MgO film Figure 3 shows the effect of aging treatment on the

luminance efficiency of test panel with hydrogenated MgO film. The aging was conducted at 270V, 100kHz continuous sustaining conditions. As noted from the figure, the luminance efficiency of the test panel with hydrogenated MgO was improved almost 30% compared with that with MgO film deposited under inert atmosphere. The aging of the test panel, however, degraded the efficiency and the hydrogenation effect almost disappeared when the test panel became aged for 48 hours.



Fig. 3, Effect of aging on luminance efficiency of test panel with hydrogenated MgO film.





Figure 4 shows the effect of aging treatment on the test panel with Be-doped MgO film. The Be-doping improved the luminance efficiency almost 50%. The aging treatment of the test panels degraded the efficiency like the test panels with hydrogenated MgO film, but the degradation was significantly less than the panel.

Figure 5 shows a SEM micrograph of MgO surface









Fig. 5. Morphology of MgO surface after aging treatments for 240 hours The sustaining frequency was 100 kHz.

after aging for 240 hours at sustaining voltage of 270V. The sustaining frequency was 100kHz. As noted from the micrograph, there are three distinctive areas with different morphologies, i.e., near the BUS electrode (a), center of ITO (b), and near discharge gap (c). MgO surface morphology near the BUS electrode appeared to have cylindrical columns with irregular surfaces(Fig. 5(b)). The density and the height of the column decrease as the location moves away from the BUS electrode toward to the center of the ITO electrode. Near the discharge gap, the morphology of MgO surface layer was similar to 'maple leaf'(Fig. 5(c)).

These results indicate that MgO layer surface became sputtered severely during the aging treatment. In addition,

the sputtered species should redeposited on the layer surface to form such layers of vastly different morphology from that of the e-beam evaporation deposited film. In the course of this redeposition, gaseous elements like hydrogen may not be reincorporated into the film due to its high vapor pressure. Thus, it is believed that the degradation of luminance efficiency of test panels with hydrogenated MgO films is caused by the lack of reincorporation of hydrogen during redeposition. On the other hand, with the Be-doped MgO film, most of the sputtered Be may be redeposited on the MgO film surface since the vapor pressure of the element is almost zero. Thus, the degradation of the efficiency with solid elements like Be is minimal as noted in Fig. 4.

4. Conclusion

In this study, effects of aging treatment on luminance efficiency of test panels with doped MgO film were investigated. The results indicated that the aging treatment degrades the efficiency significantly when the doping element is a gaseous element like hydrogen. The aging treatment of the test panels with solid element like Be did not degrade the efficiency significantly. This phenomenon may be attributed to the sputtering and redeposition occurring actively during glow discharging of ac-PDPs.

5. Acknowledgements

Authors would like to thank NRL research program and 21C Frontier Research Program of Korean government for financial assistance for this study. In addition, authors would like thanks CeNChem for supplying the doped MgO pellets.

6. References

- [1][2] G.Oversluize, S.de Zwart, S.Van Heusden, T.Dekker, J.of SID,197(2000)
- [3] M. Ishimoto, S.Hikada, K.Betsui, K Shinoda, SID'99 Digest 25(1999)
- [4] Rak-hwan Kim, Youn-hyun Kim, Jong-Wan Park, Thin Solid Films, 376, 183(2000)
- [5] Y. Motoyama, Y. Hirano, K. Ishii, Y. Murakami, and F. Sato, J. of Appl. Phys., 95(12), p8419-8424(2004).
- [6] R.I.Eglitis and A.I.Popov, Mat.Sci., Vol.5, 298 (1996)
- [7] Y. Chen, R. Gonzalez, 0 . E.Schow, and P. Summers, Phys. Rev. B, 27, 1276(1983)
- [8] M. Amatsuchi, Amatsuchi, A. Hirota, H. Lin, T. Naoi, E. Otani, H. Taniguchi, K. Amemiya, IDW'05, 435(2005)
- [9] B.T.Jeffries, R.Gonzalez, Y.Chen, and G.P.summers, Phys.Rev.B 25, 2077(1982)
- [10] K.Sakita, K.Takayama, K.Awamoto, and Y.hashimto, SID01 Digest 1022(2001)
- [11] Y.Chen, V.M.Orera, and R.Gonzalez, et al. Phys. Rev. B. 45. 1410 (1990)