Effect of Al_2O_3 capping layer on properties of MgO protection layer for plasma display panel

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Abstract

Al_2O_3 capping layer and MgO protective layer were deposited by electron beam evaporation method using single crystal source. Thickness of the capping layer, Al_2O_3, was varied from 5 nm to 10 nm. Surface morphology was observed by SEM and AFM before and after hydration. And microstructure of deposited Al_2O_3 layer and chemical shift of electron binding energy were also observed by high resolution TEM and XPS, respectively, after hydration. From these results, it was found that Mg atoms diffused into Al_2O_3 layer, reacted with moisture and formed $Mg(OH)_2$ during hydration. As thickness of Al_2O_3 increased, extent of hydration increased. Al_2O_3 capped MgO thin films and uncapped MgO thin films were deposited on AC-PDP test panel to characterize discharge properties. Although Al_2O_3 has poor discharge properties rather than MgO, because of many hydrated species on the surface of MgO, similar discharge properties were observed.

1. Introduction

Recently MgO thin films have been used as a protective layer for dielectrics in the AC-Plasma Display Panel (AC-PDP) to improve discharge characteristics and the panel's life time [1,2]. But hydration is one of serious problems of MgO protective layer, since MgO is thermodynamically unstable compared with $Mg(OH)_2$. MgO reacts very easily with moisture in the air, especially at low coordination atomic site [3-6]. $Mg(OH)_2$ reduces panel's life time due to its low mechanical strength. And at some plasma condition, $Mg(OH)_2$ dissociates into MgO and H_2O, increases panel's pressure and eventually degrades panel's efficiency. Although these problems can be overcome by long time pre-aging before actual operation, new solution is needed due to its high cost. In this study, we introduce new layer (capping layer) on MgO thin film to suppress hydration during manufacturing process of AC-PDPs. Because Al_2O_3 is generally known as a thermodynamically stable material compared with $Al(OH)_3$, Al_2O_3 is a good candidate for a capping layer to protect MgO thin film against hydration [7]. From the results of hydration of Al_2O_3-capped MgO thin films, the applicability of Al_2O_3 capping layer was confirmed.

2. Experimentals

MgO and Al_2O_3 thin films were deposited using electron beam evaporation system (shown in Fig. 1). To stabilize deposition condition, single crystal source with a purity of 99.99% was used as source materials. Thermal oxidized p-type Si (100) wafers were used as substrates to characterize hydration properties and also AC-PDP test panels were used to characterize surface discharge properties. Base pressure of chamber was maintained at 10^{-7} Torr. Electron beam current was in the range of 10 60 mA. Thickness of deposited films and deposition rate were in-situ monitored by crystal thickness monitor. Thickness of MgO film was 300 nm for all samples. And the thickness of Al_2O_3 film was varied from 5 nm to 10 nm. Deposition rates for MgO and Al_2O_3 were 0.1 nm/sec and 0.01 0.1 nm/sec, respectively. Deposited samples were hydrated in the humid ambient with 80 % of relative humidity at room temperature. Humidity of hydration chamber was controlled by N_2 bubbled water vapor. The surface morphology of hydrated films was determined by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). In addition, High Resolution Transmission Electron Microscopy (HRTEM) was used to observe the microstructure of film. And X-ray Photoelectron Spectroscopy (XPS) was used to prove diffusion of Mg into Al_2O_3 layer and to observe chemical shift of electron binding energy during hydration reaction.

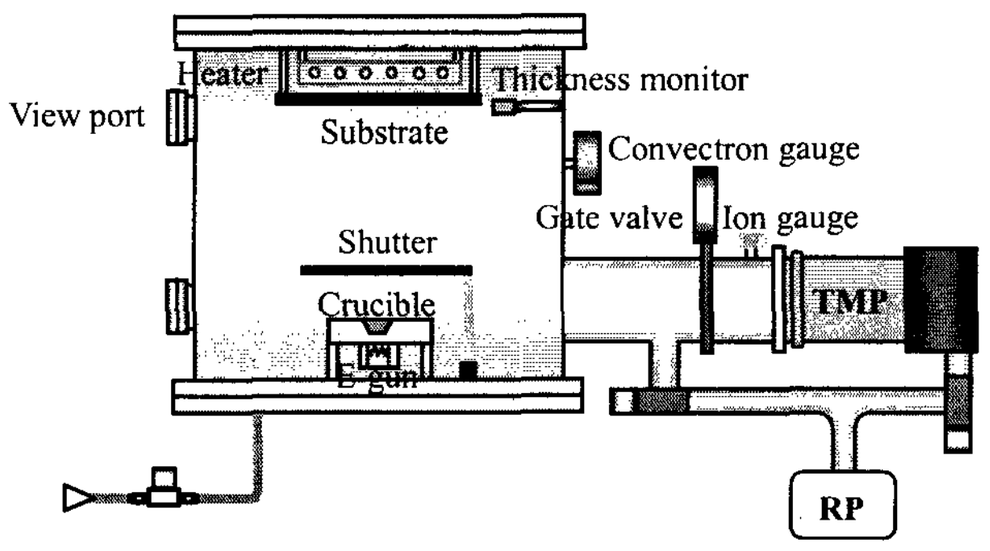

Fig. 1. Schematic diagram of electron beam evaporation system.

The surface discharge characteristics were also examined by using test panel. AC-PDP cell structure and detail experimental procedure were previously reported by Park et al [8].

3. Results and discussion

Surface morphology of as-deposited films was very clean for both Al_2O_3 capped MgO and uncapped MgO thin films. Surface roughness of MgO increases generally after hydration because of volume expansion due to lattice mismatch between MgO and $Mg(OH)_2$. After hydration, a lot of hemispherical-shaped clusters of $Mg(OH)_2$ were formed on the surface of MgO film, as shown in Fig. 2(a). According to the previous work by Kim et al., the large cluster was $Mg(OH)_2$ [9]. After applying Al_2O_3 capping layer over MgO film, many clusters were also produced, but both size and number of clusters decreased, as shown in Fig. 2(b), (c) and (d).

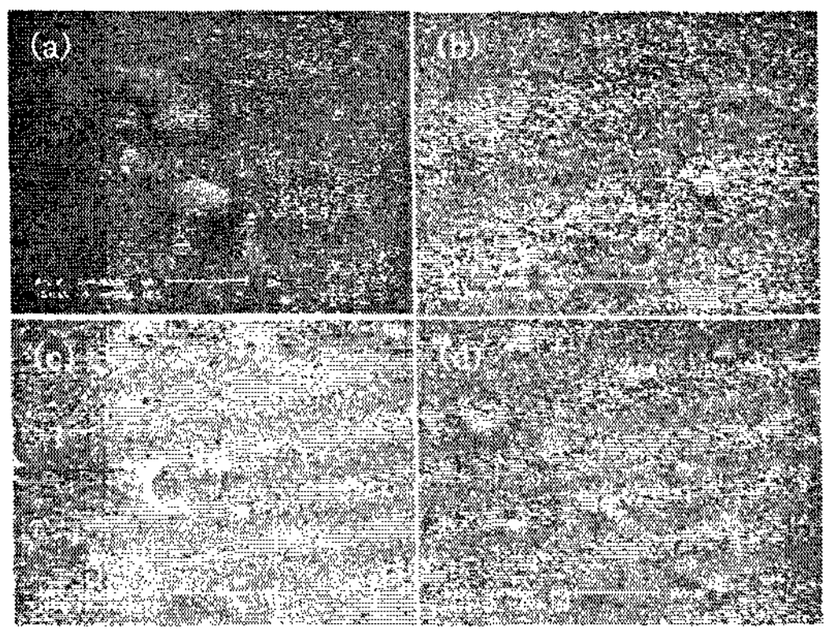

Fig. 2. SEM micrographs of hydrated MgO and Al_2O_3 capped MgO films; (a) uncapped MgO , (b) thickness of Al_2O_3 5 nm, deposition rate of Al_2O_3 0.05 nm/sec, (c) 10 nm, 0.05 nm/sec and (d) 10 nm, 0.1 nm/sec. For all samples thickness of MgO is 300 nm and deposition rate of MgO is 0.1 nm/sec.

From this result, it was found that Al_2O_3 layer can be effective to suppress hydration of MgO layer considerably. But considerable difference could not be found when we changed deposition rate of Al_2O_3, as shown in Fig. 2(c) and (d), even though slight difference was observed when we changed thickness of Al_2O_3, as shown in Fig. 2(b) and (c). As thickness of Al_2O_3 increased from 5 nm to 10 nm, more hydration occurred. This result was confirmed from the variation of surface rms roughness as a function of hydration reaction time, as shown in Fig. 3. Generally, because clusters of $Mg(OH)_2$ are formed during hydration, surface rms roughness increases during hydration. So from variation of surface rms roughness, we can expect extent of hydration. From Fig. 3, it can be easily shown that comparing with uncapped MgO thin films, Al_2O_3 capped MgO thin films had far better rms roughness, showing high protection capability of hydration of Al_2O_3 capping layer.

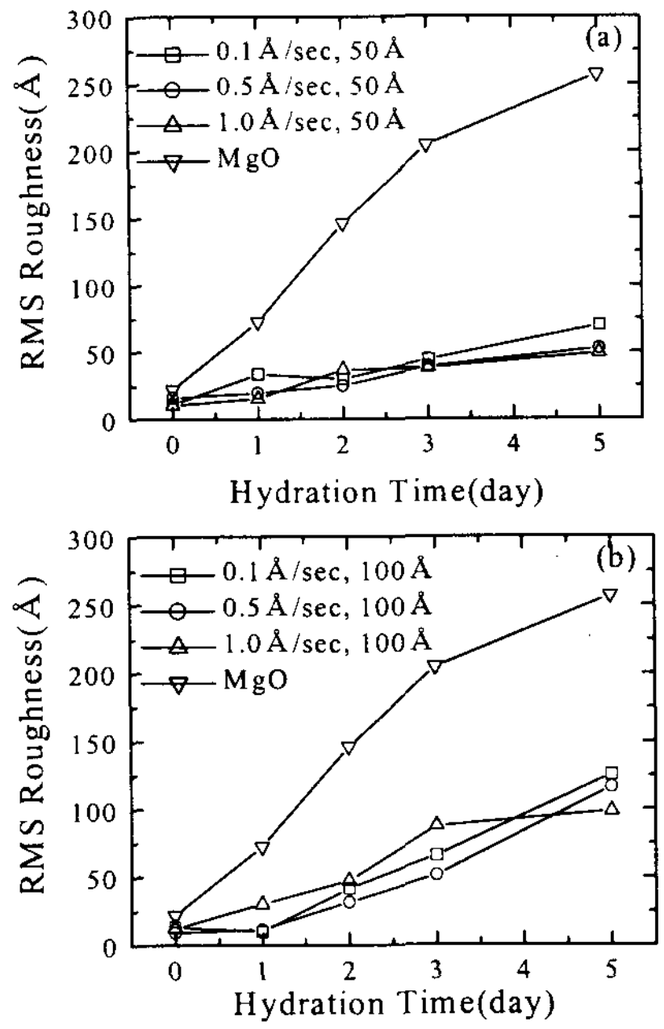

Fig. 3. Variation of surface rms roughness of Al_2O_3 capped MgO thin films as a function of hydration time. Thickness of Al_2O_3 is (a) 5 nm and (b) 10 nm.

Generally it is known that very thin oxide film deposited by electron beam evaporation method has amorphous structure. Thus 5 nm-thick Al_2O_3 would be amorphous, but 10 nm-thick might be partially crystallized. The results were confirmed by cross-sectional HRTEM shown in Fig. 4. Amorphous layer would be more effective for protecting from hydration due to its dense structure.

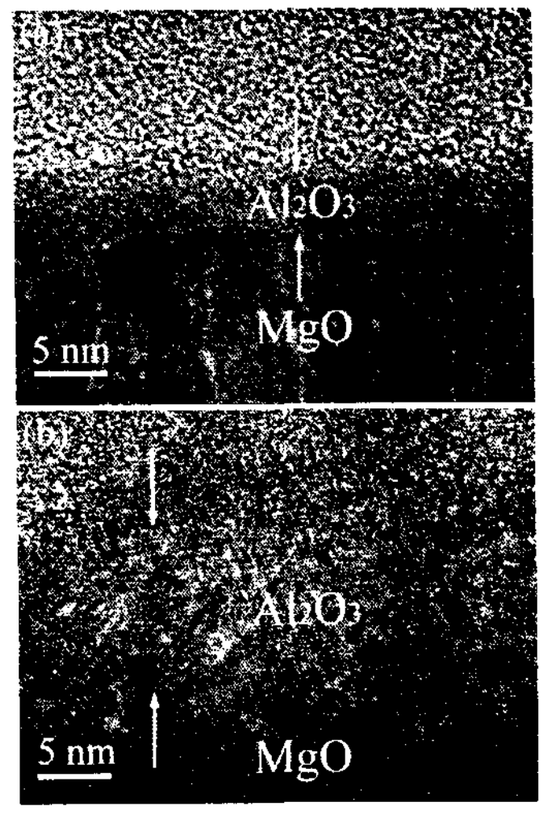

Fig. 4. Cross-sectional HRTEM micrographs of Al_2O_3 capped MgO thin films. Thickness of Al_2O_3 is (a) 5 nm and (b) 10 nm.

So from these HRTEM results, it can be concluded that better protection of hydration of 5 nm-thick Al_2O_3 is due to its microstructure.

Figure 5 and Fig. 6 shows XPS narrow scan spectra of Mg 1s, Al 2p and O 1s electrons. In two cases, Al 2p and O 1s spectra were chemically shifted to higher energy side after hydration. Binding energy of Al 2p and O 1s electron in 5 nm-thick Al_2O_3 film was almost identical to $MgAl_2O_4$ (75.6 eV and 531.8 eV) while that of 10 nm-thick Al_2O_3 film was almost identical to Al_2O_3 (73.6 eV and 530.2 eV). Despite of this difference, chemical shift of 5 nm and 10 nm-thick Al_2O_3 films means diffusion of Mg atom into surface region [10]. This was confirmed by atomic ratio of Mg and Al measured by XPS and increase of intensity of Mg 1s spectrum. For 5 nm-thick Al_2O_3 film, Mg/Al ratio was 0.28 in as-deposited film and was 0.40 in 5 days hydrated film. For 10 nm-thick Al_2O_3 film, each value was 0.13 and 0.21. And from these results, it could be also found that mixing layer like $MgAl_2O_4$ was formed in interfacial region. It may be thought that during deposition, evaporated Al_2O_3 molecules had high energy to diffuse and mix with MgO. In Fig. 5(c) and Fig. 6(c) peak at 1308 eV is not exactly corresponding to Mg and $Mg(OH)_2$ peaks, but it seems to be $Mg(OH)_2$.

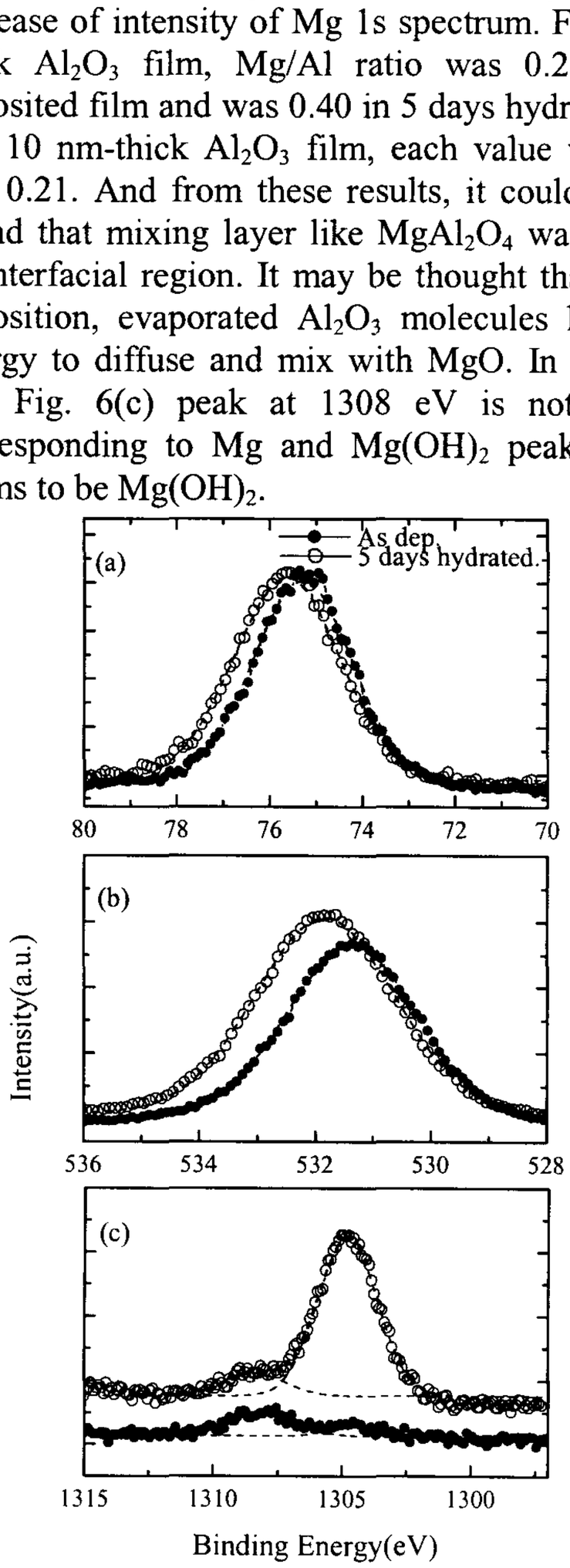

Fig. 5. XPS narrow scan spectra of 5 nm-thick Al_2O_3 capped MgO films before and after hydration. (a) Al 2p, (b) O 1s and (c) Mg 1s.

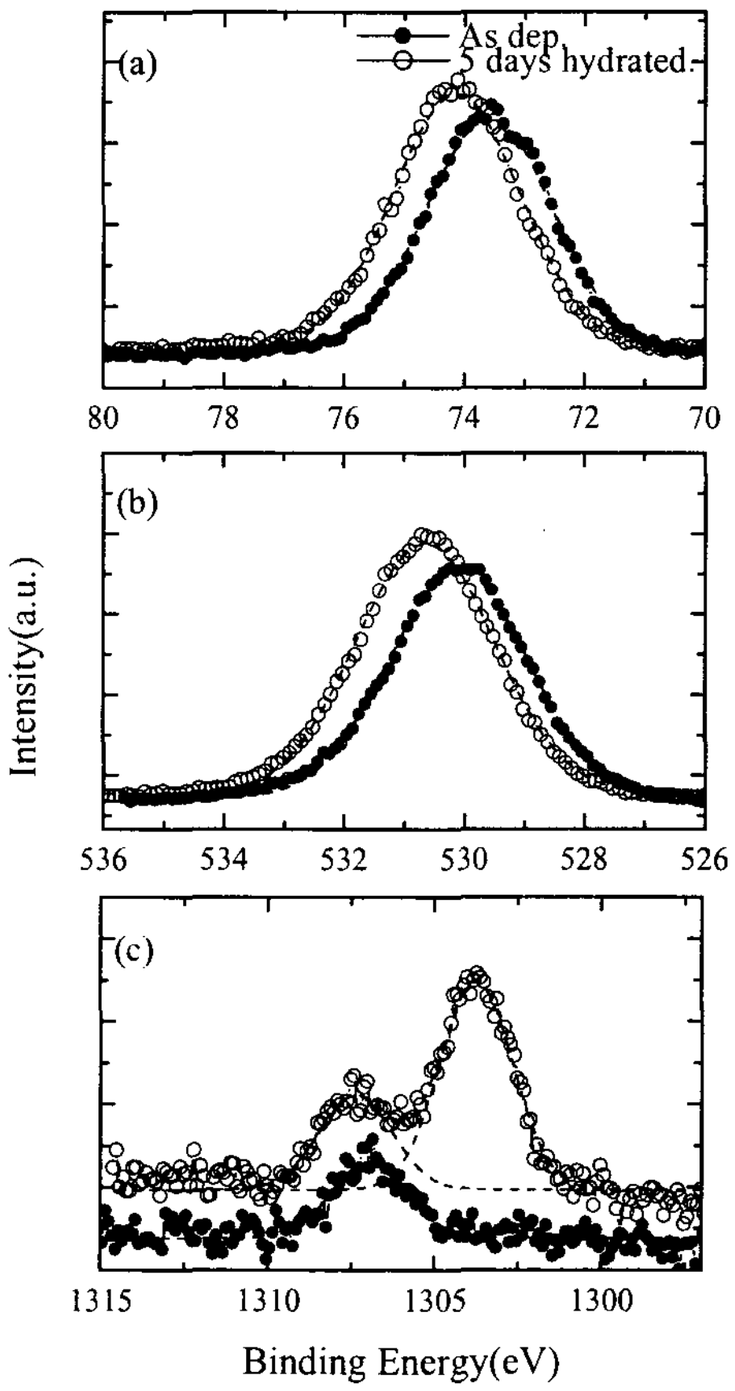

Fig. 6. XPS narrow scan spectra of 10 nm-thick Al_2O_3 capped MgO films before and after hydration. (a) Al 2p, (b) O 1s and (c) Mg 1s.

Surface discharge characteristics of Al_2O_3 capped MgO protective layer were characterized by test panel experiment.

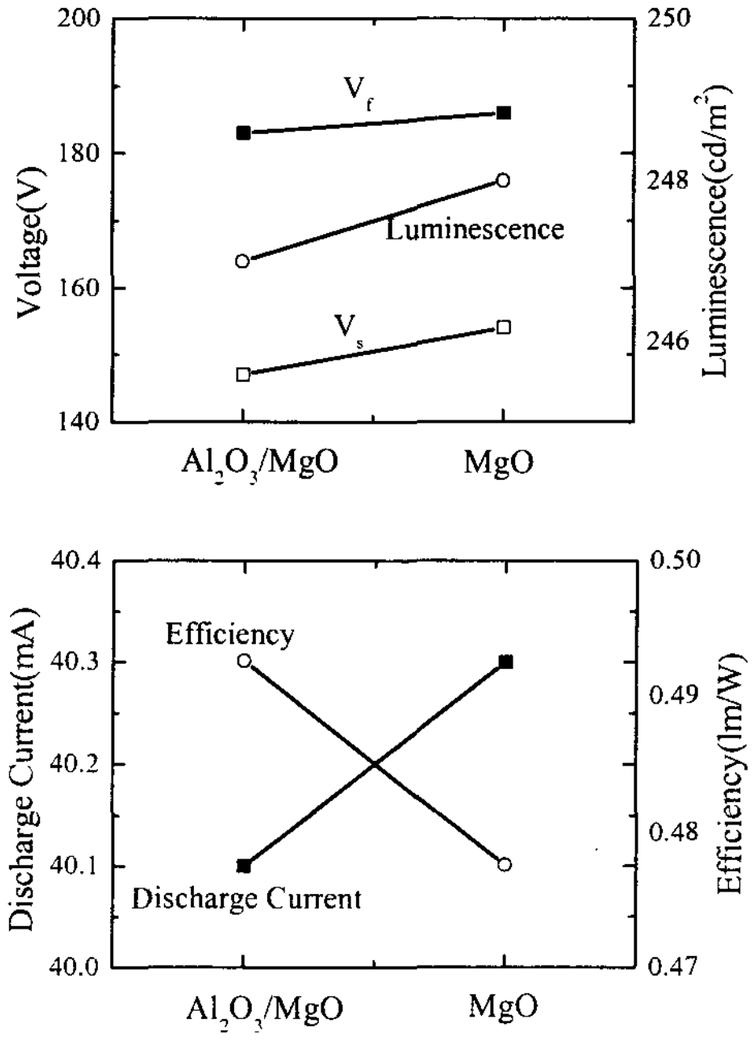

Fig. 7. Discharge characteristics of Al_2O_3 capped MgO and uncapped MgO protective layers

Figure 7 shows discharge characteristics of Al_2O_3 capped MgO and uncapped MgO protective layer. Because Al_2O_3 has poor electrical properties rather than MgO, Al_2O_3 capped MgO protective layer was expected to show poor discharge characteristics. But discharge characteristics of two cases were similar. This is because uncapped MgO thin film adsorbs moisture in the air and forms $Mg(OH)_2$ on the surface. The formation of $Mg(OH)_2$ degraded discharge characteristics of MgO. So uncapped MgO thin film and Al_2O_3 capped MgO thin film show similar discharge characteristics.

4. Conclusion

Hydration of MgO is an important problem in AC-PDP. Because MgO is thermodynamically unstable compared with $Mg(OH)_2$, new layer is needed to protect hydration. We deposited Al_2O_3 thin film on the MgO film. Although Al_2O_3 capped MgO thin films were hydrated to some extent, we could reduce hydration of MgO significantly by using Al_2O_3 capping layer. By using several analyses we could conclude that hydration of Al_2O_3 capped MgO thin films is due to reaction of diffused Mg atoms with moisture in surface region. The diffusion of Mg atoms was proved by XPS analysis. And formation of $Mg(OH)_2$ clusters on the surface of Al_2O_3 was proved by SEM, AFM. Comparing 5 nm-thick Al_2O_3 with 10 nm-thick Al_2O_3, it was found that the protection of 5 nm-thick Al_2O_3 is more effective than 10 nm-thick Al_2O_3. It is thought that 5 nm-thick Al_2O_3 would be amorphous while 10 nm-thick might be partially crystallized. It was confirmed by HRTEM observation. And from AC-PDP test panel experiment, we could confirm a possibility of capping layer for protecting hydration. In AC-PDP process long time pre-aging is needed to stabilize discharge characteristics because of hydration of MgO films. But it is suggested from the results in this experiment that adoption of Al_2O_3 capping layer is one of the possible methods to solve the hydration problem. As a result, the manufacturing cost of AC-PDPs would be reduced through shortening the pre-aging time by adoption of Al_2O_3 capping layer on MgO protective layer.

5. Acknowledgements

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6. References

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