

The influences of film density on hydration of MgO protective layer in plasma display panel

Jung Heon Lee, Jae Hwan Eun, Sun Young Park, Soo Gil Kim^{a)} and Hyeong Joon Kim

School of Materials Science & Engineering, Seoul National Univ., Seoul, 151-742, Korea,

a) Department of Electronics Engineering, Kyungwon Univ., Seongnam, 461-701, Korea

82-2-880-7162,

hjkim@plaza.snu.ac.kr

Abstract

We report the effect of density of thin films on moisture adsorption and hydration of MgO thin film, usually used as a protective layer in AC-PDP. After hydration, lots of hemispherical shaped clusters, $\text{Mg}(\text{OH})_2$, formed on the surface of MgO thin films. However clusters formed on low-density thin films were bigger than those on high-density films. From ERD spectra, it seemed that the concentration of hydrogen was very high in the region 20 nm from the surface of MgO thin film. The low-density thin film had more hydrogen than high-density thin film. From simulation results of ERD and RBS it was found that hydration reaction also occurred in the inner part of the film. So diffusion of Mg atoms from the inner part of the film to the surface and H_2O molecules from the surface to the inner part of the film is important. And because low density thin film has many short paths for diffusion of Mg atoms and H_2O molecules, low-density thin film is more hydrated. So to suppress hydration of MgO thin films, high-density thin film is needed.

1. Introduction

MgO thin films are usually used as a protective layer of dielectrics in the AC-Plasma Display Panel (AC-PDP) to improve discharge characteristics and the panel's lifetime, because of its physical stability, high transmittance and secondary electron emission coefficient [1,2]. But MgO protective layer has a weak point such as chemical instability; MgO physically and chemically absorbs moisture, forming $\text{Mg}(\text{OH})_2$ easily [3,4]. These hydroxides cause the secondary electron emission coefficient to reduce, resulting in an increase of discharge voltage. And thus hydration should be suppressed to lower the discharge voltage, but there have been only a few reports about the hydration of MgO thin film [5,6] although there have been many reports about the hydration of MgO single crystal [7,8]. Many properties of thin film such as preferred

crystallographic orientation, grain size, roughness and density may influence hydration process. Although hydration is known as a reaction occurring in a few atomic layers, density can be one of important factors that can govern the hydration. The purpose of this study is to find the effect of density on hydration of MgO thin films.

2. Experimental

MgO thin films were deposited using RF magnetron sputtering method. 50 nm-thin thermal oxidized p-type Si wafer was used as a substrate. 3" sintered MgO with a purity of 99.99 % was used as a target. The base pressure was kept at 10^{-7} Torr. The distance between target and substrate was kept at 7 cm. The gas ratio was fixed as 10 % for stoichiometric composition and R.F. power and substrate temperature were fixed as 230 W and room temperature to gain thin film with similar grain size and same preferred orientation. In order to change the density of thin film the working pressure was varied from 2.5 mTorr to 30 mTorr.

The MgO thin films were hydrated by exposing to the humid ambient with 80 % relative humidity at room temperature during two to five days. Humidity in hydration chamber was controlled with N_2 bubbled water vapor. The hydration temperature was fixed at room temperature. In order to detect the extent of hydration, X-ray Photoelectron Spectroscopy (XPS), Elastic Recoil Diffraction (ERD) and Rutherford Backscattering Spectroscopy (RBS) were used. Scanning Electron Microscopy (SEM) was also used to observe surface morphology.

3. Results and discussion

Table 1 lists the properties of MgO thin films of high-density and low-density. The density of high-density film was 3.46 g/cm^3 , while that of low-density film was 3.11 g/cm^3 . The density of MgO thin film was indirectly measured from refractive index, which was acquired by ellipsometry. The density of single crystal MgO is 3.65 g/cm^3 . They had similar grain size and

(100) preferred crystallographic orientation although high-density film had better crystallinity.

Table 1. Properties of MgO thin films.

Properties	Thin films	High-density thin film	Low-density thin film
Preferred orientation		(100)	(100)
Crystallinity		bad	good
Grain size (nm)		67.4	71.3
Surface rms roughness (nm)		3.7	7.5
Density (g/cm ³)		3.46	3.15
(Refractive index)		(1.691)	(1.611)

Figure 1 shows SEM micrographs of hydrated surface of high-density and low-density MgO thin films. Many hemispherical-shaped clusters were formed on the surface of hydrated thin films. According to the previous work by Kim et al., these clusters must be Mg(OH)₂ [9]. From these observations, it could be concluded that hydration reaction occurs on the surface of MgO thin films. The clusters on low-density film, as shown in Fig. 1(b), were much larger than those on high-density film, as shown in Fig. 1(a), indicating that the extent of hydration of high density MgO thin film is larger than that of low-density thin film.

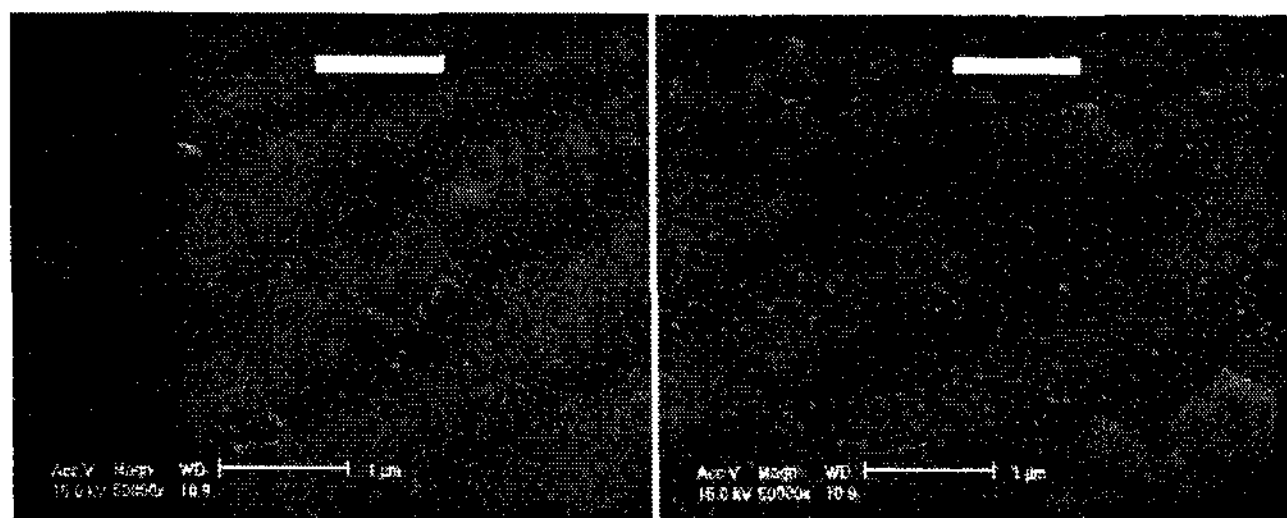


Fig.1. SEM micrographs of MgO thin films hydrated for 2 days in 80 % humidity; (a) high-density and (b) low-density MgO thin film.

XPS narrow scan spectra of O 1s electron of low-density film are shown in Fig. 2. The O 1s peak is composed of hydroxyl component (531.7eV) and O²⁻ component (529.7eV). The as-deposited film has both of these components, while the hydrated film has mainly hydroxyl component, indicating that Mg(OH)₂ was formed on the surface.

And it was found that the area of Mg(OH)₂ peak of low-density thin film is much larger than that of high-density thin film, indicating that the extent of hydration of low-density MgO thin film is larger than that of high-density thin film.

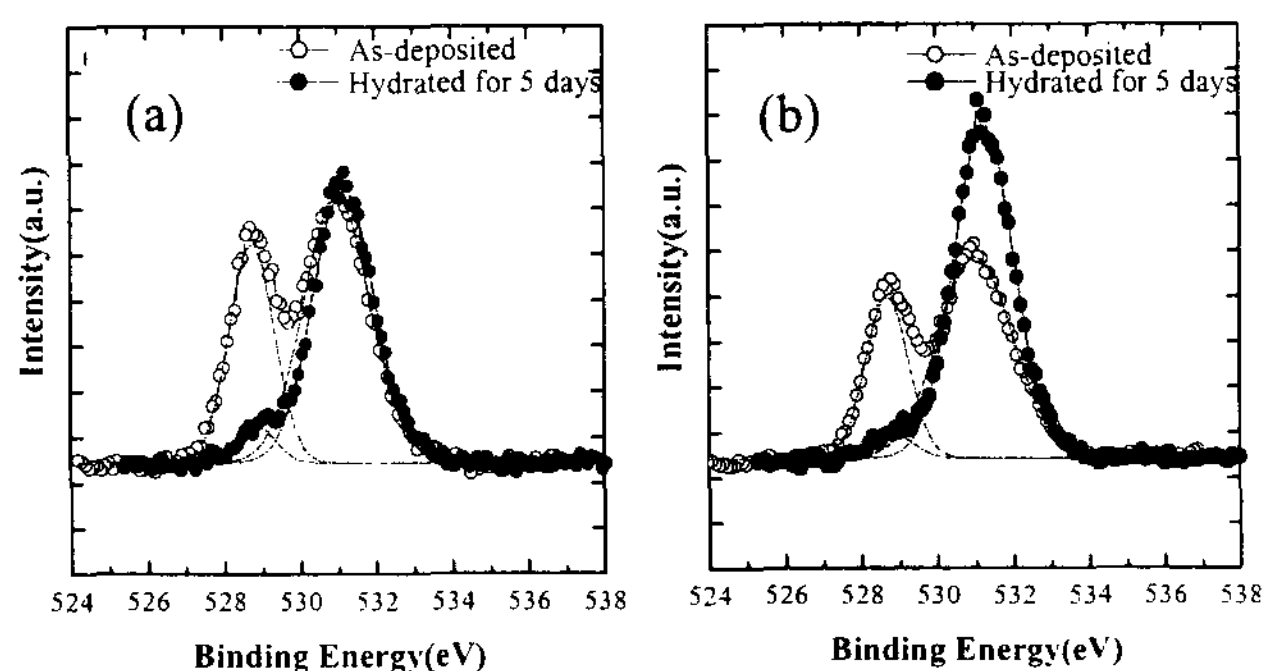


Fig.2. XPS narrow scan spectra of O 1s electron of the high and low-density film. The hydrated film was exposed to the humid ambient with 80% humidity for 5 days.

The ERD spectra of as-deposited and hydrated thin films are shown in Fig 3. From the spectra (b) and (c), it was found that more hydrogen occurred in low-density thin film than in high-density thin film.

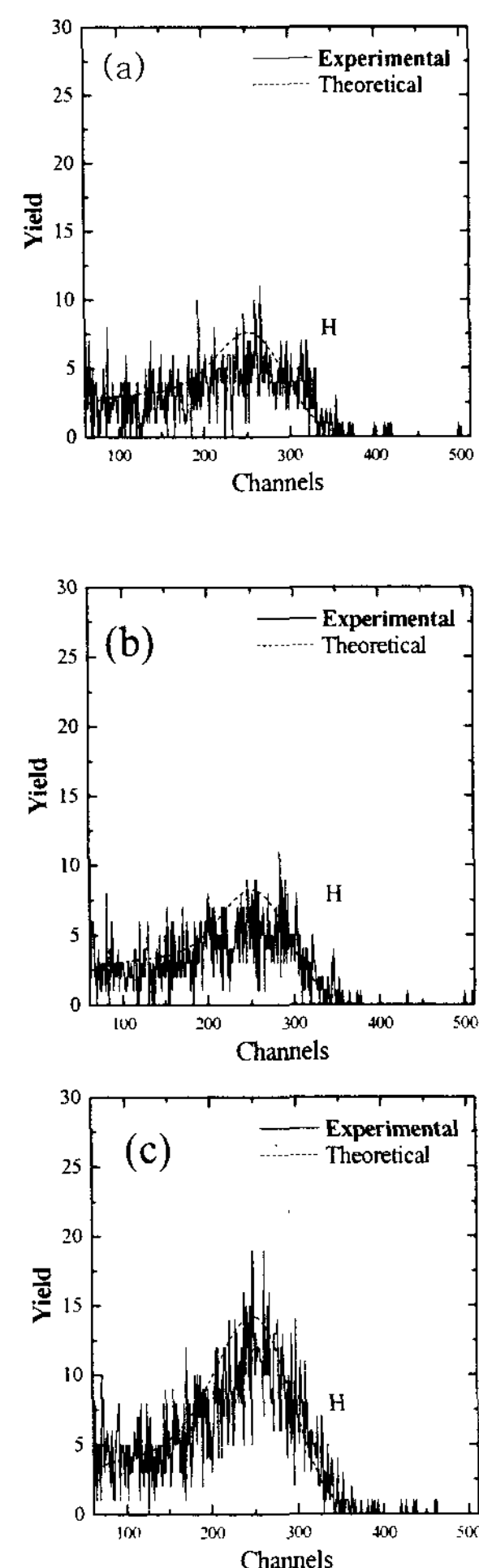


Fig.3. ERD spectra of (a) as-deposited, (b) hydrated high-density and (c) hydrated low-density MgO thin films. The hydrated MgO thin films are hydrated for 5 days.

And the intensity of peak was very high at the channel between 250 and 300, which was the region near the surface. From this observation it could be concluded that the concentration of hydrogen was very high in the region 20 nm from the surface of MgO thin films. From spectra (a) and (b), it could also be concluded that nearly no additional hydration occurred on high-density thin film. But it does not mean that high-density thin film was not hydrated at all. As shown in Fig. 2, hydration occurred on high-density film to some extent. The ERD spectra of as-deposited and hydrated high-density MgO thin films seemed to be similar because the as-deposited MgO thin films were already hydrated to some extent. Because ERD detects the amount of hydrogen of the entire film, if the extent of hydration is similar and concentrated on the surface, it could not detect them. But from the spectra (a) and (b), it was found that if the density of MgO film was high, the amount of hydration was similar to that of as-deposited thin film and hydration reaction saturated quickly.

Table 2 lists the results of simulation by using data from RBS and ERD spectra. Simulation was executed by Charls Evans & Associates' Hypra. From this result it was found that hydrogen penetrated through the MgO thin films during hydration reaction.

Table.2. The results of simulation of RBS and ERD analyses. The unit of thickness is nm. The hydrated film was exposed to the humid ambient with 80 % humidity for 5 days.

Sample Layer	As-dep.		Low-density film		High-density film	
	Thick	Comp.	Thick	Comp.	Thick	Comp.
Layer1 (MgO)	100	O-48.78 Mg-47.94 H-3.16 Imp.-0.12	50	O-48.48 Mg-43.85 H-7.43 Imp.-0.23	50	O-49.16 Mg-45.96 H-4.22 Imp.-0.66
Layer2 (MgO)			50	O-50.24 Mg-45.44 H-4.08 Imp.-0.23	50	O-50.13 Mg-46.86 H-2.34 Imp.-0.67
Layer3 (MgO)	482	O-49.49 Mg-49.38 H-1.01 Imp.-0.12	100	O-51.20 Mg-46.15 H-2.42 Imp.-0.23	428	O-50.46 Mg-47.83 H-1.05 Imp.-0.66
Layer4 (MgO)			343	O-51.21 Mg-47.21 H-1.35 Imp.-0.23		
Bulk Si	Bulk	Si(100)	Bulk	Si(100)	Bulk	Si(100)

As the amount of hydrogen increased, the amount of the magnesium decreased while that of oxygen remained constant. This means that the hydrogen, penetrated through the film, is the form of H⁺ or OH⁻. From this result it could be concluded that hydration occurred not only on the surface of MgO film but also in the inner

part of the films. And it could also be concluded that the hydrated depth of low-density thin film was larger than that of high-density thin film and the hydrated depth of high-density thin film was similar to that of as-deposited thin film, which was already hydrated to some extent.

It seems that hydration occurs both on the surface and inner part of MgO thin films. In the case of hydration reaction occurring on the surface, diffusion of Mg atoms from the inner part of the film to the surface is important because Mg atoms react with absorbed H₂O molecules on the surface. In the case of hydration reaction occurring in the inner part of the film, diffusion of H₂O molecules from the surface to the inner part of the film is important. From this fact it can be concluded that diffusion of Mg atoms and H₂O molecules is very important process in hydration. So density may be very important property of MgO thin films in hydration reaction because if the density of MgO thin films is low, films have many paths for diffusion of the Mg atoms and H₂O molecules.

The effects of preferred orientation and surface roughness were not referred in this study because the influences of these properties on hydration seemed to be less than that of density. According to the previous work by Refson et al., (111) surface of MgO single crystal is easily hydrated rather than other surfaces because the atomic arrangement of MgO (111) surface is similar to that of Mg(OH)₂ (0001) surface [3]. But it is widely reported that hydration occurs preferably on defect sites [8]. So the influence of preferred orientation may be neglected unless the grain size of MgO thin films is very large, because thin films have many preferable nucleation sites such as grain boundaries. According to the previous work by Uchiike et al., surface roughness of MgO thin films affects hydration reaction [6]. He reported that as the roughness of MgO thin films increased hydration reaction occurred more. But in this research the roughness of MgO thin films was very high compared with our case because rough surface was made by grinding the glass substrate with abrasive papers of various numbers from 1000 to 60. So the influence of roughness may be neglected.

4. Conclusion

From this study it was found that after hydration clusters of Mg(OH)₂ are formed on the surface of MgO thin film. This means that hydration reaction occurs on the surface of MgO thin films. From ERD spectra, hydrogen was detected in inner part of the film, which means that hydration reaction also occurs in the inner

part of the films. Because hydration reaction occurs both on the surface and inner part of MgO thin films, it can be concluded that diffusion of Mg atoms from the inner part of the film to the surface and H₂O molecules from the surface to the inner part of the film is important. Because low-density thin film has many paths for diffusion of Mg atoms and H₂O molecules, low-density thin films were more hydrated. So to suppress hydration of MgO thin films, high-density thin film is needed.

Through this study, we have tried to figure out the fundamentals, which are governing the hydration of MgO thin films. And thus we found that density of the films is one of the important factors and concluded that high-density MgO protective layer should be achieved to reduce hydration and improve the efficiency of the panel.

5. Acknowledgements

The authors would like to acknowledge the financial assistance of Ministry of Information and Communication of Korea supported by IMT 2000 project.

6. References

- [1] T. Urade, T. Iemori, M. Osawa, N. Nakayama, IEEE Trans. Electron Dev., 23, 313 (1976)
- [2] H. Uchiike, K. Miura, N. Nakayama, T. Shinoda, Y. Fukushima, IEEE Trans. Electron Dev., ED-23, 1211 (1976)
- [3] K. Refson, R. Wogeliue, D. G. Eraser, Phys. Rev. B, 52, 10823 (1995)
- [4] Kuroda, E. Yasugi, H. Aoi, K. Miura, T. Morimoto, J. Chem.Soc.Faraday Trans. 1, 84, 2421 (1988)
- [5] M.O. Aboelfotoh, K. C. Park, W. A. Pliskin, J. Appl. Phys 48.7, 2910, (1977)
- [6] H. Uchiike, S. Harada SID 91 Digest (1991) 444
- [7] Scamehorn N. M. Harrison, M. I. McCarthy, J. Chem. Phys. 102 (2), 1547 (1994)
- [8] J. A. Mejias, A. J. Berry, K. Refson, D. G. Fraster, Chem. Phys. Letters, 314, 558 (1999)
- [9] B. I. Kim, J. W. Hong, G. T. Jeong, and S. H. Moon, J. Vac. Sci. Technol. B. 12(3), 1631 (1994)