Characteristics of Doped MgO Layer Deposited under Hydrogen Atmosphere

Kyung-Hyun Park and Yong-Seog Kim
Dept. of Material Science Engineering, Hong-ik Univ., Mapo-gu, Seoul, Korea
Phone:+82-2-322-0644, E-mail: kidkid97@hotmail.com

Abstract

Characteristics of doped MgO layer deposited under hydrogen atmosphere were investigated. Hydrogen gas was introduced during e-beam evaporation of doped MgO and its effects on microstructure, cathodoluminescence, discharge voltages and effective yield of secondary electron emission were examined. The results indicated that the hydrogen influences and doped impurities the concentration and energy levels of defects in MgO layer and that affects the luminance efficiency and discharge delays of the panels significantly.

1. Introduction

MgO layer formed on transparent dielectric layer of ac-PDPs reduces discharge voltage and protects dielectric layer from ion sputtering. As the MgO has a rare combination of high coefficient of secondary electron emission and resistance for ion sputtering, it has been mainly used as electron emission/protective layer for PDPs. For further enhancement in luminance efficacy and reduction of firing voltages of PDPs, electron emission characterization such as secondary electron and exo-electron emission from MgO must be improved further.

There have been various attempts to increase the coefficient of secondary electron emission of MgO, which include doping of MgO material [1], patterning of the layer [2], and controlling of orientation of MgO layer [3], etc. These approaches, however, have resulted in a marginal improvement of such characteristics. Recently, Okada et. al. [4], has reported that addition of hydrogen in discharge gas to reduce the discharge voltages and aging time.

Our previous work [5] showed that the addition of hydrogen during e-beam process of MgO improves luminance efficiency and reduces statistical delay. These enhancements are believed to be related with creation of deep donor energy levels in band gap of MgO, which increases lifetime of electrons trapped in excited states. This should enhance the luminance efficiency and/or reduced discharge delays of PDP.

For further improvements of such characteristics, it is necessary to create defects levels within MgO band gap and increase the state density of defects that may trap electrons or holes. The defects include oxygen vacancies, magnesium vacancies, substitutional cation or anion impurities, interstitial cation or anion impurities. There are several sources of such defects in MgO. Firstly, intrinsic defects such as Frenkel and Schottky disorders are the intrinsic defects. Concentrations of these defects in bulk of MgO are estimated to be negligible since their formation energy is very large. On the surface of MgO, their concentrations were reported to be on the order of few percent due to the structural defects such as kinks and steps on MgO [6].

Secondly, thermo-chemical reduction of MgO under magnesium vapor atmosphere at elevated temperatures has been used to increase oxygen vacancy concentration [7]. When heated to 2200K under magnesium vapor of 6 atmospheric pressure, oxygen vacancy concentrations was increased to few hundred ppms [8]. This approach, however, has been mainly used for bulk MgO.

Finally, the defects can be created by doping with compounds. For example, Li_2O doping creates the vacancy at anion site(i.e., oxygen site vacancy) and Al_2O_3 doping the vacancy at cation site(i.e., magnesium site vacancy). Amount of doping with compound of different valency that can be made is generally limited by its poor solubility in MgO. Thus, the defect concentration with impurity doping is restricted by its solubility. This approach has been mainly used in modifying the defect concentrations in MgO film.

In this study, therefore, an attempt was made to prepare doped MgO film under hydrogen atmosphere. The doping should create more defect levels in MgO and the addition of hydrogen is expected to increase the population density of electrons trapped in the excited states. Test panels were prepared using the films prepared, the firing voltage, luminance efficiency, and discharge delays and ICCD image analysis were evaluated.

2. Experimental

For the doping, three different doping compounds were used, which includes Al₂O₃, SiO₂, and BeO. The doping compound was mixed with MgO powder and compacted into a form of pellet. Subsequently, the pellets were sintered at 1400°C for 8 hours and used as the source of e-beam evaporation process. MgO layer was formed using an e-beam evaporator under various hydrogen partial pressure, follow rate, 8.5 $x10^{-5}$ torr $\sim 1.5x10^{-3}$ torr. Base pressure was $8.5x10^{-7}$ $\sim 1.0 \times 10^{-6}$ torr and the substrate was heated to 300°C. Thickness of the film was $\sim 5000\,\text{Å} \pm 500\,\text{Å}$. The cathode luminescence of the films was measured using a SEM equipped with double mono-chrometer. In addition, the orientation and microstructure were analyzed using XRD, FE-SEM, and UV/VIS light Transmittance.

The firing voltage and coefficient of secondary electron emission were measured for MgO layers formed under hydrogen atmospheres and compared with MgO formed under vacuum atmosphere. The measuring procedures of this set-up can be found in more detail elsewhere [9, 10]. In addition, test panels were prepared using MgO layers formed under different hydrogen partial pressures. With the panels, the luminance efficiency and address discharge delay were evaluated.

3. Results

3.1. Relationship of defect levels in MgO pellets with MgO film

Prior to MgO thin film formation process, the defect types and levels formed in MgO pellets were examined by cathodoluminescence(CL) measurement. As shown in Fig. 1, the CL spectrum varied significantly with the doping compound. With Al₂O₃ and BeO doping, peaks near 730nm were observed. The intensity of such peaks were relatively weak. With SiO₂ doping, very different peaks were observed near 250nm and 500nm in addition to 380nm. The addition of Al₂O₃ and BeO created acceptor levels and SiO₂ donor levels within the band gap. These results clearly show that doping with compounds of different valency can create various defect levels in MgO. Especially, the peak intensity from the pellet with SiO₂ doping was two orders of magnitude larger than commercially available pellets.

In order to examine the effect of doping on the defects levels in MgO thin film formed via e-beam evaporation process, CL measurements were

conducted both on film and pellets. Figure 2 shows CL peaks from a MgO pellet commercially available and from a MgO pellet doped with BeO. Those pellets showed distinctive peaks, indicating different energy levels.

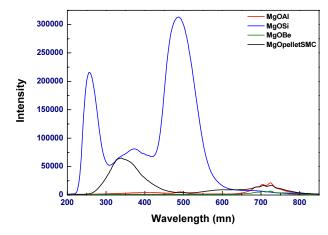


Figure 1. CL spectra of MgO pellets with dopants.

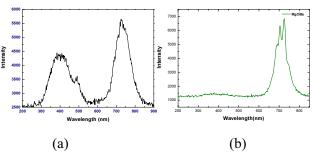


Figure 2. CL spectra from (a) commercially pure MgO pellet and (b) MgO pellet doped with BeO.

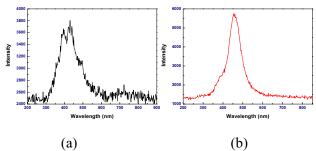


Figure 3. CL spectra from e-beam evaporated MgO film using (a) commercially pure MgO pellet and (b) MgO pellet doped with BeO.

The CL spectra from the MgO thin films formed using such pellets are shown in Fig. 3. As noted from the figure, the CL spectra from both the films are

rather similar each other even though very different pellets were used. These results indicate that the defect levles and their concentration in MgO film are mainly determined by the e-beam processing conditions rather than by source materials.

There are several parameters that may have contributed to such behavior. One is the solubility of dopants in MgO pellets and in MgO film. Solubility of dopants may be different each other since the processing temperature are quite different. Sintering temperature of commercially available MgO pellets is 1700°C and the substrate temperature during e-beam evaporation process is 300°C. Thus, the solubility of dopants in MgO film should be rather low. Secondly, since the e-beam process occurs at low temperature, the film formation process may be controlled by kinetics rather than thermodynamics. In other words, the defects concentration may not be determined by thermodynamic properties.

3.2. Effects of hydrogen partial pressure and doping elements on luminance efficiency

Figure 4 shows morphology of MgO layer formed under various hydrogen partial pressures. As noted from the figure, morphology, grain size and orientation were affected by the partial pressure. In general, grain size increased with the partial pressure.

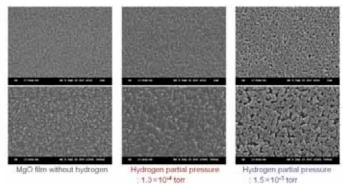
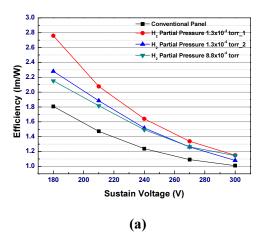
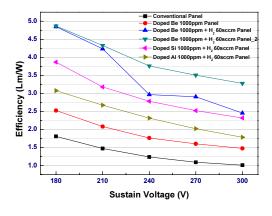


Figure 4. Effect of hydrogen partial pressure on morphology of MgO film formed.

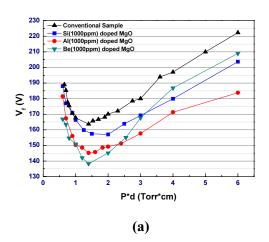
Figure 5(a) shows the effect of hydrogen partial pressure on luminance efficiency. As shown in the figure, the efficiency was enhanced approximately 30% when hydrogen partial pressure was increased to 1.3x10⁻⁴ torr. When the sample was doped with BeO, the improvement in luminance efficiency became more pronounced. The MgO film formed without hydrogen addition resulted in approximately 20% improvement in luminance efficiency. The addition of

hydrogen in combination with BeO doping resulted in 150% improvement in efficiency. This suggests that it is required to control not only the defect concentration but also the population density of electrons in excited levels in order to improve luminance efficiency.





(b)
Figure 5. Effect of (a) hydrogen partial pressure and (b) doping elements on luminance efficiency



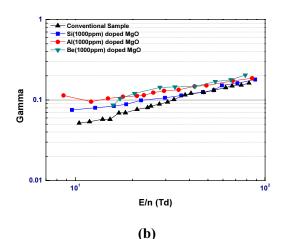


Figure 6. Effect of doping elements on (a) Paschen Curve and (b) effective secondary electron emission coefficient

Figure 6(a) shows Paschen curves of MgO doped with various elements. As noted from the figure, the firing voltage was measured to be lowest with the sample doped with BeO. The effective yield of secondary electron emission estimated from the Paschen curves(Figure 6(a)) had the similar trend. These results show that BeO doping increases the yield of secondary electron emission.

Figure 7 shows the Laue plot of discharge delays. The discharge delay was significantly reduced with the MgO prepared under hydrogen atmosphere. Especially, the statistical delay was reduced by 80% with the sample.

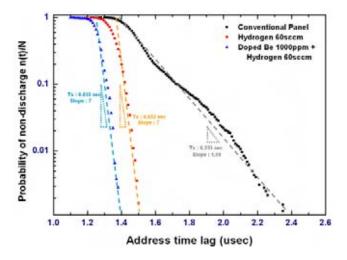


Figure 7. Effect of hydrogen and doping elements on discharge delay.

4. Conclusion

In this study, a combined effect of doping and hydrogen atmosphere was investigated. The results indicate that the luminance efficiency and discharge delay are significantly improved when MgO film is formed with doping elements under hydrogen. These results can be of value in developing MgO film processing technology with controlled defect levels at low cost.

5. Acknowledgements

Authors would like to thank NRL research program and 21C Frontier Research Program of Korean government for financial assistance for this study.

6. References

- [1] Rak-hwan Kim, Younghyun Kim, Jong-Wan Park, Thin Solid Films 376, 183-187. (2000)
- [2] J.S. Oh, J.Y. Lim, H.S. Jeong., J.W. Cho, Kang and E.H. Choi, IDW'02 digest, 785-788 (2002).
- [3] M. Ishimoto, S. Hikada, K. Betsui, K Shinoda, SID'99 Digest P-25. (1999).
- [4] T. Okada and T. Komaki, SID Digest of Technical Papers, v.36 no.2, , pp.1245-1247. (2005)
- [5] K.H. Park and Y.S. Kim SID'06 Digest 36-4 (2006)
- [6] R.I. Eglitis, A.I. Popov, Computational Materials Science 5 (1996) 298-306
- [7] B. T. Jeffries, R. Gonzalez, Y. Chen, and G. P. Summers, Phys. Rev. B 25 2077 (1982)
- [8] G. H. Rosenblatt, M. W. Rowe, G. P. Williams, Jr., R. T. Williams, and Y. Chen, Phys. Rev. B 39 10309 (1989)
- [9] V. v. Elsbergen, P. K. Bachmann, and T. Juestel, SID Tech. Digest, pp. 220-223 (2000).
- [10] M.-S. Lee, Y. Matulevich, J.-S. Choi, S.-K. Kim, J.-H. Kim, S.-S. Suh, D.-S. Zang, and K.-D. Kim, SID Tech. Digest, pp1232-1235(2005).