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Formation of MgO Thick Film Layer for AC-PDP via Electrophoresis Deposition of Nano-sized MgO Powders

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Abstract

MgO thick film for ac-PDPs was formed via electrophoresis deposition process and its effect on luminance and luminance efficiency were evaluated. The electrophoresis deposition process of MgO thick film was optimized through parametric study and defects levels in MgO powders was evaluated using cathodoluminescence spectra measurements. The results demonstrate a possibility of using MgO thick film as electron emission layer for ac-PDPs.

Keywords : PDP, MgO, thick film, luminance efficiency, powder

1. Introduction

Magnesium oxide (MgO) thin film has been used as secondary electron emission layer for ac-PDPs. Electron emission characteristics of the MgO layer control significant parts of the luminance efficiency, firing voltage, wall voltage and discharge delay of the ac-PDPs. This electron emission behavior is identified to be affected by dopant type and concentration [1] and stoichiometry of MgO [2], and crystal emissive layer consisted of cubical MgO powders [3]. Although the doping is relatively effective in enhancing the electron emission characteristics, it is still difficult to control precisely the dopant concentration in the thin film deposited via e-beam evaporation and ion-plating routes because the evaporation and deposition rates of dopants are significantly different from that of MgO matrix. Thus, the concentration may vary considerably with deposition time and location of the panel, leading to a marked variations in performance of ac-PDP devices. In addition to such variations, the MgO film formed via the evaporation processes contains a substantial defect concentration as it is formed at low temperatures (~300°C) and under non-equilibrium oxygen partial pressure. These defects are generic to the thin film forming process itself and thus influences the electron emission characteristics of the film, adding another complexity to the control of the characteristics.

One possible way to deal with such comp-lexities is to form the layer via thick film forming processes using MgO powders. In the thick film layer, the dopant and defect concentration would be more homogeneous and be controlled rather precisely, since the MgO powders are synthesized at elevated temperatures (~1700°C). One of the additional merits of this thick film processing route is low processing cost as the film forming process is carried under atmospheric conditions. Kim et al [4] demonstrated that the panel with a MgO thick film using nano-sized powders can have similar luminance efficiency to that of the panel with thin film.

The thick film in general, however, has rather poor uniformity in packing density as well as thickness. The poor uniformity is mainly due to the use of the paste of low solid content for the thick film forming process. The paste contains more than 50 vol.% of organic vehicle which needs to be removed subsequently during drying and burnt-out steps. During those steps, the nano-sized MgO powders may undergo inhomogeneous compaction, making the film non-uniform in density and thickness. This non-uniformity mill render a small or near zero operation margin of the

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panel. A wider margin is necessary to operate ac-PDPs.

In order to improve such poor operation margin of the panels with nano-sized MgO thick film, an attempt was made to form the film via electrophoresis deposition (EPD) process in this study. For that purpose, the film was formed through electrophoresis of nano-sized MgO powders between two electrodes. The powders have been known to densely pack as a layer on the electrode surface when the EPD process is induced by applied electric field between the two electrodes. The thickness of the film is determined by the electric filed applied and time of the coating, and remains uniform as long as the electric field applied is uniform on the electrode surface [4]. Thus, the uniformity of the packing and thickness of the thick film is expected to be improved significantly compared with conventional thick film forming processes like spin coating, printing, and green tape lamination. In this study, the effects of processing parameters such as electric field, suspension composition and dispersant on packing density of MgO powder layer were investigated. In addition, the luminance and luminous efficacy of the test panels with the MgO powder thick film were measured.

2. Experimental procedure

Fig. 1 shows a schematic illustration of experi-mental setup for our EPD system used in this study. DC voltage was applied between two electrodes separated 1 cm apart. For the cathode, the front glass plate of ac-PDP module coated with 10nm thick aluminum thin film on the transparent dielectric layer was used. The aluminum thin film served as a transient electrode for the EPD process as it is transformed to aluminum oxide layer by subsequent heat treatment. The front glass substrate with thick film coating was heated to 530°C in air atmosphere to remove any solvents and organic components remaining in the film. During the heat treatment step, the aluminum film was converted to aluminum oxide layer via oxidation reaction with oxygen in the air. For the counter anodic electrode, graphite plate was used to contaminate the suspension. The voltage between the electrodes was varied between 30~120V and coating time between 60 to 120 seconds.

For the nano-sized MgO powders, four different types of powders were used. The chemical compositions and average sizes of the powders provided by materials

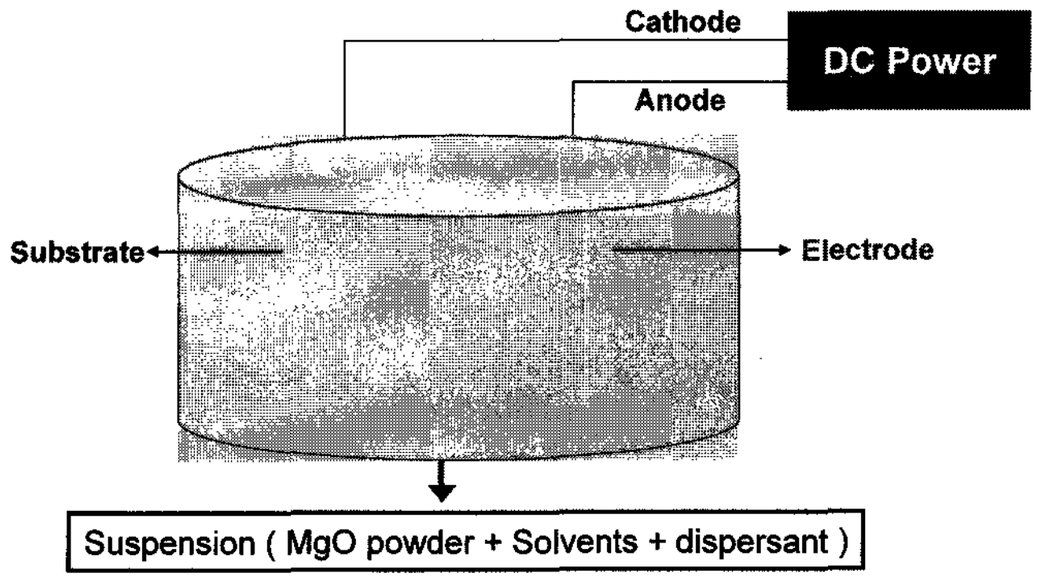

Fig. 1. Schematic illustration of Electrophoresis Deposition System

suppliers are shown in Table 1. To form densely packed MgO powder thick film, it is essential to have well-dispersed MgO suspension. The dispersion of powders in a suspension is determined based on various parameters such as the type of solvent and dispersant used, and milling conditions in the preparation of suspension. For the organic solvent, a composition of solvent mixture was selected (Table 2) because it has better dispersion of the MgO powder and appropriate evaporation speed during drying of the film. For the dispersant, four different types of dispersants were used. For the milling condition, the planetary milling time was 2 hours after experimental optimization process.

After the thick film forming by the EPD process, the front plate was heated to 530°C in air for drying and burning-out of any organic components remaining in the film. After cooling, the front plate prepared was sealed with a rear plate coated with $ZnSiO_4$:Mn green phosphor to evaluate operation margin and luminous efficacy of the test panel. The resolution of the pixel was VGA grade of 42 inch panel.

3. Experimental results and discussion

3.1. Effects of EPD processing parameters on packing density of MgO thick film

Fig. 2 shows the effect of dispersant on the mor-phology of MgO thick film formed via EPD process.

For this experiment, the MgO powder was fixed to powder 'C' in Table 1. The thick film was formed using the suspension without dispersant and pores up to 5 μm in

Table 1. Chemical compositions and size of powders used in this study.

Powder	Al	Ca	Na	Cu	Fe	Li	Mn	K	Si	Ni	Cr	Zn	Size (nm)
A	-	<0.005	<0.003	-	-	-	-	<0.02	-	-	-	-	36
B	-	0.01	0.09	0.003	0.002	0.002	0.001	-	-	-	-	-	100 ~200
C	-	0.001	-	-	0.001	-	0.001	-	0.003	-	-	0.002	100
D	0.001	0.003	0.01	-	0.003	-	0.01	0.005	0.022	0.003	0.001	-	50

Table 2. Chemical compositions of the solvent system and dispersants used in this study.

	Chemical composition	Supplier
Solvent system	IPA-Reagent plus 2-Methyl-1-Propanol (IBA) Methyl Alcohol-anhydrous	SK chemical KANTO chemical Sigma-Aldrich
Dispersant A	BYK 181	BYK chemie
Dispersant B	BYK 111	BYK chemie
Dispersant C	BYK 116	BYK chemie
Dispersant D	BYK 180	BYK chemie

diameter were observed from the surface of the film as shown in Fig. 2(a). This indicates that large agglomerates of MgO powders remain in the suspension prepared without suspension and that are causing the pores in the film. As the dispersants were added to the suspension, the pores size in the film decreased significantly as shown in Figs. 2(b)~(e). The packing density of the film was affected by the type of the dispersant used in the suspension. With the dispersant D, the film was formed essentially by packing of primary MgO powders as shown in Fig. 2(e). Thus, in this study, dispersant 'D' was used to prepare the suspension.

Fig. 3 shows a comparison of surface morphologies of MgO thick film layer formed via spin coating of MgO paste and the EPD process of MgO suspension. As noted from the images, the thick film prepared by the EPD process appeared to be more dense and uniform in packing density. The enhanced packing density of the thick film from the EPD process was obtained as the nano-sized primary MgO particles became well-dispersed by the dispersing agent (dispersant 'D' in this case) in the suspension and deposited

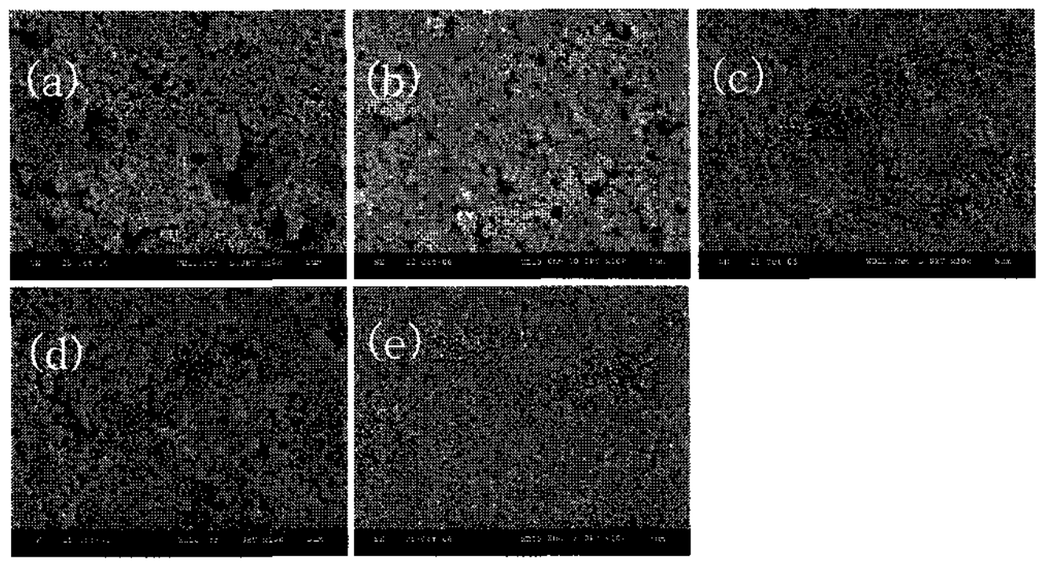

Fig. 2. Surface images of MgO thick film prepared with suspension (a) without dispersant and with dispersant 'A'(b), 'B' (c), 'C' (d), and 'D'(e).

as particles (not agglomerates) by the electric field applied. Cross-sectional images of the thick film also revealed that the packing density is uniform throughout the thickness without any large pores (not shown in this article).

Fig. 4 shows thickness of MgO thick film layer formed via EPD as a function of coating time. The thickness of the film increased linearly with coating time as shown in the

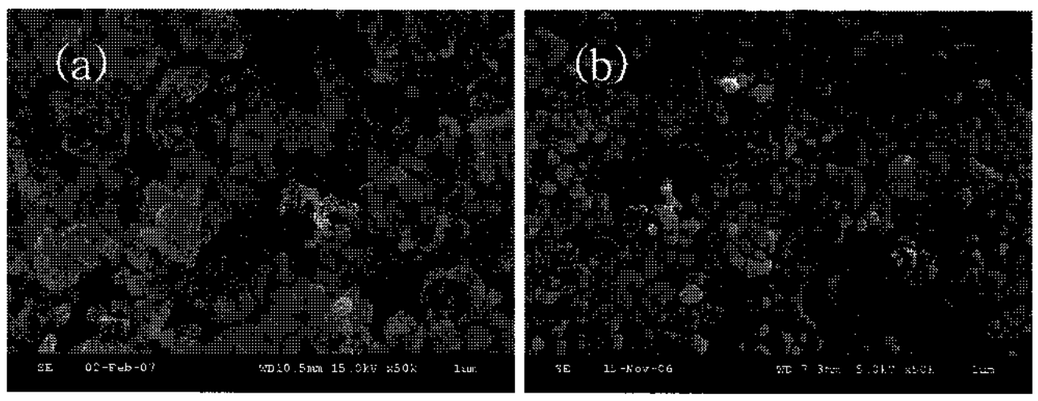

Fig. 3. Surface images of MgO thick film prepared by (a) spin coating of MgO paste and (b) electrophoresis deposition of MgO suspension.

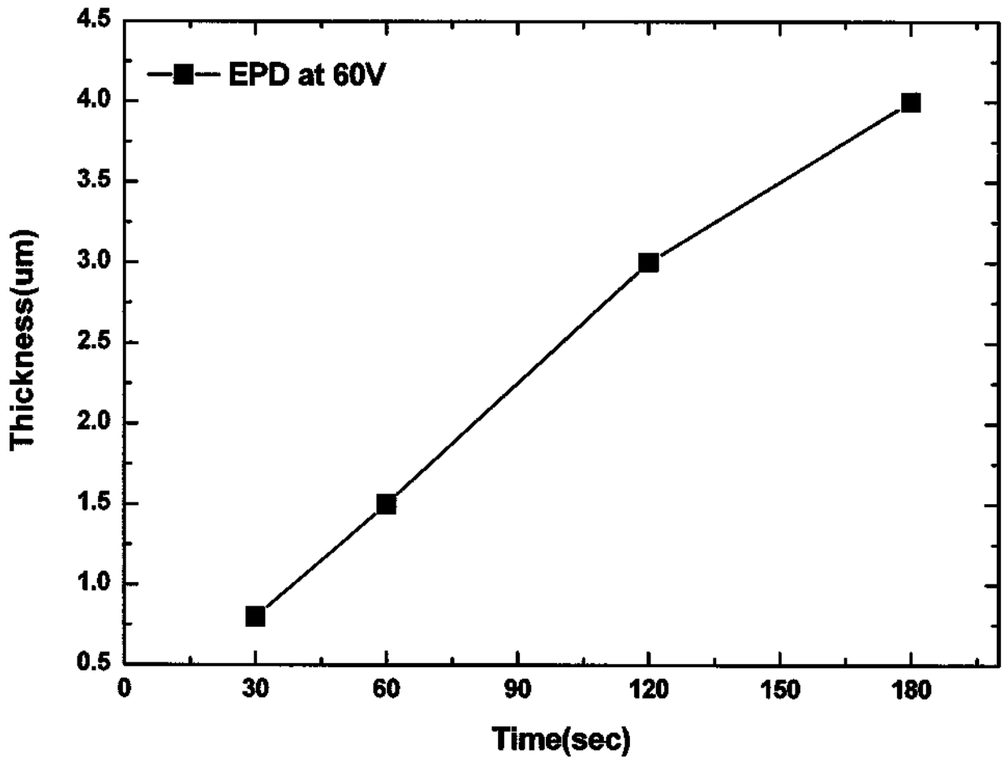

Fig. 4. Effect of coating time on the thickness of thick film formed via EPD process. The applied voltage was 60 V and the distance between the electrodes was 1 cm.

figure. This result suggests that the voltage drop across the deposited layer during the EPD process is negligible and the electric field remains almost constant throughout the coating process. In addition to the time of coating, the growth rate of the film was also affected by the applied voltages. The increase in the applied voltages increases the growth rate and density of the packing of the film. Although the increase in the applied voltage leads to such beneficial effects on the film, the thickness uniformity worsenes as the coating process becomes more sensitive to the processing conditions at high applied electric field. Thus, the applied voltage was fixed to 60 volts in this study.

3.2. Cathodoluminescence (CL) spectra of MgO thick film

In order to determine the type of major defects in the nano-sized MgO powders, cathodoluminescence (CL) spectra were measured using a SEM equipped with a vacuum spectrometer of UV-VIS range. Fig. 5 shows CL spectra from the MgO powders used in this study. The CL intensities from the powders were several orders of magnitude larger than those of MgO thin film formed by e-beam evaporation process. This indicates that the defect concentration in the MgO powders is higher than those in the thin film. In order to find out reasonable energy levels of such defects, the CL spectra were deconvoluted as shown in the figures. The dotted line is the original CL spectra and the solid lines with different colors are deconvoluted lines.

With powder 'A', a strong peak around 248nm in addition with peaks around 472nm and 534nm were observed. The peak around 248nm is believed to have originated from recombination reaction between trapped electrons and holes. This peak has similar peak position like the MgO cube-shaped powders used in crystal emissive layer (CEL) layer [3]. The peaks around 472nm and 534nm should be from mid-level defects like F-type centers. The formation of F-type centers are generally promoted with oxygen vacancy forming impurities such as K_2O and Na_2O.

With powder 'B', a major peak was observed around 750nm along with minor peaks at 400 nm and 620nm were observed. The 750nm peak is believed to be due to electron trap levels shallower than F-type centers and deeper than trivalent donors like Al_2O_3. Al^{3+} ions in MgO form defect level at 0.5 eV below the condition band edge [5]. Other possibility is hole traps above the balance band. Hole traps are usually formed 0.5~1.5 eV above the valence band and that may promote the emission of visible light in red range like 750nm wavelength. It is not clear which dopants were responsible for this emission, but the major impurity, CaO, has been noted to form hole traps in MgO and that may have been responsible for the emission. With powder 'C', peaks around 348nm, 388nm, and 442nm were observed and those peaks are believed due to the F-type defects. With powder 'D', which is smoke cubic powder produced by oxidation reaction of metallic magnesium in air atmosphere, revealed various peaks as shown in the figure. This indicates that various types of defect levels were formed by the higher level of extrinsic impurities as shown in Table 1.

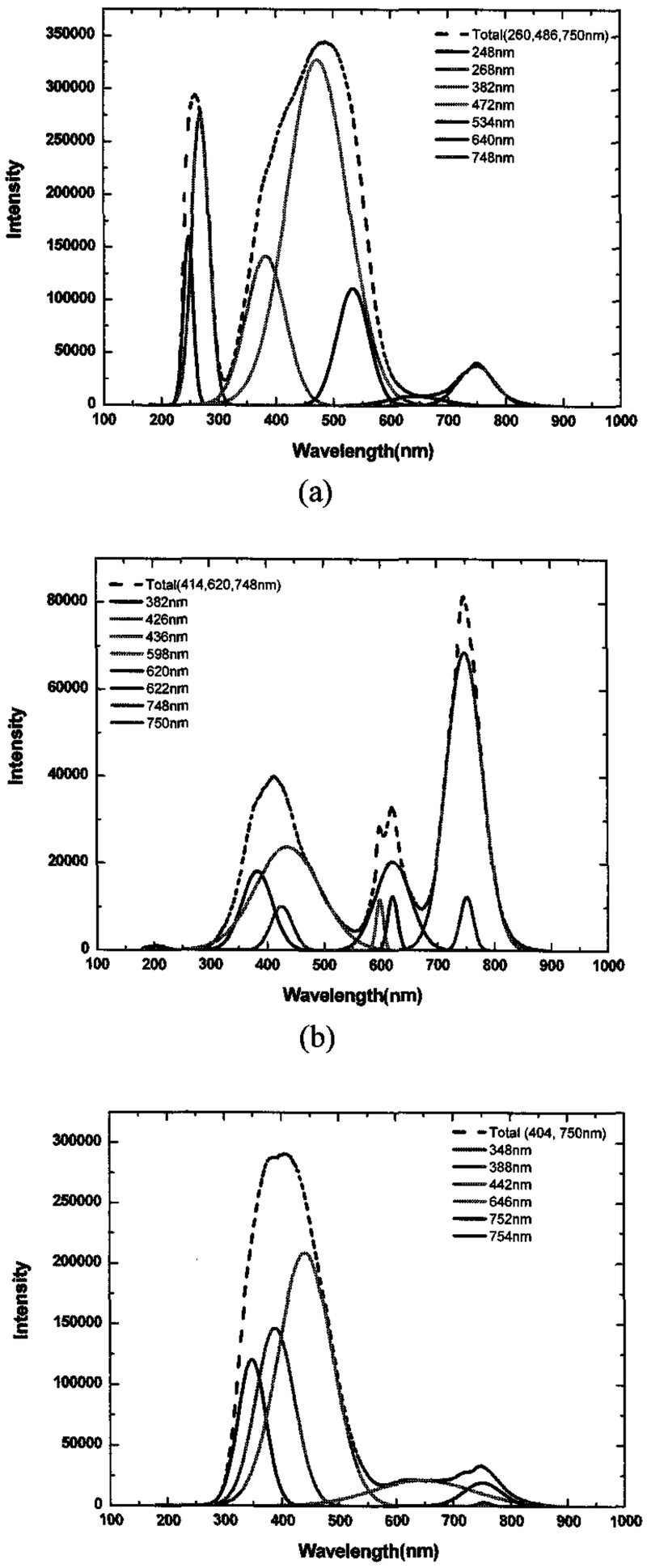

Fig. 5. CL spectra from nano-sized MgO powders: (a) powder A, (b) powder B, (c) powder C, and powder D.

3.3. Discharge characteristics of test panels with MgO thick film

Fig. 6 shows luminance and luminance efficiency of test panels with MgO thick film formed via EPD process. As noted from the figure, the luminance of the test panels with MgO thick film was lower than that of the test panel with MgO thin film. The efficiency of the test panels with the thick films was estimated to be lower than that of the thin film (Fig. 6(b)), except the panel with powder 'C' thick film. This lower luminance efficiency of the test panels with MgO thick film is mainly due to lower luminance of the panels.

There might be several parameters that may be responsible for such low luminance efficiency of the test panels with MgO thick film, including lower luminance efficacy and poor transmittance of visible light through the thick film. Thus, we measured total transmittance of visible lights through the thick film layer. The total transmittance

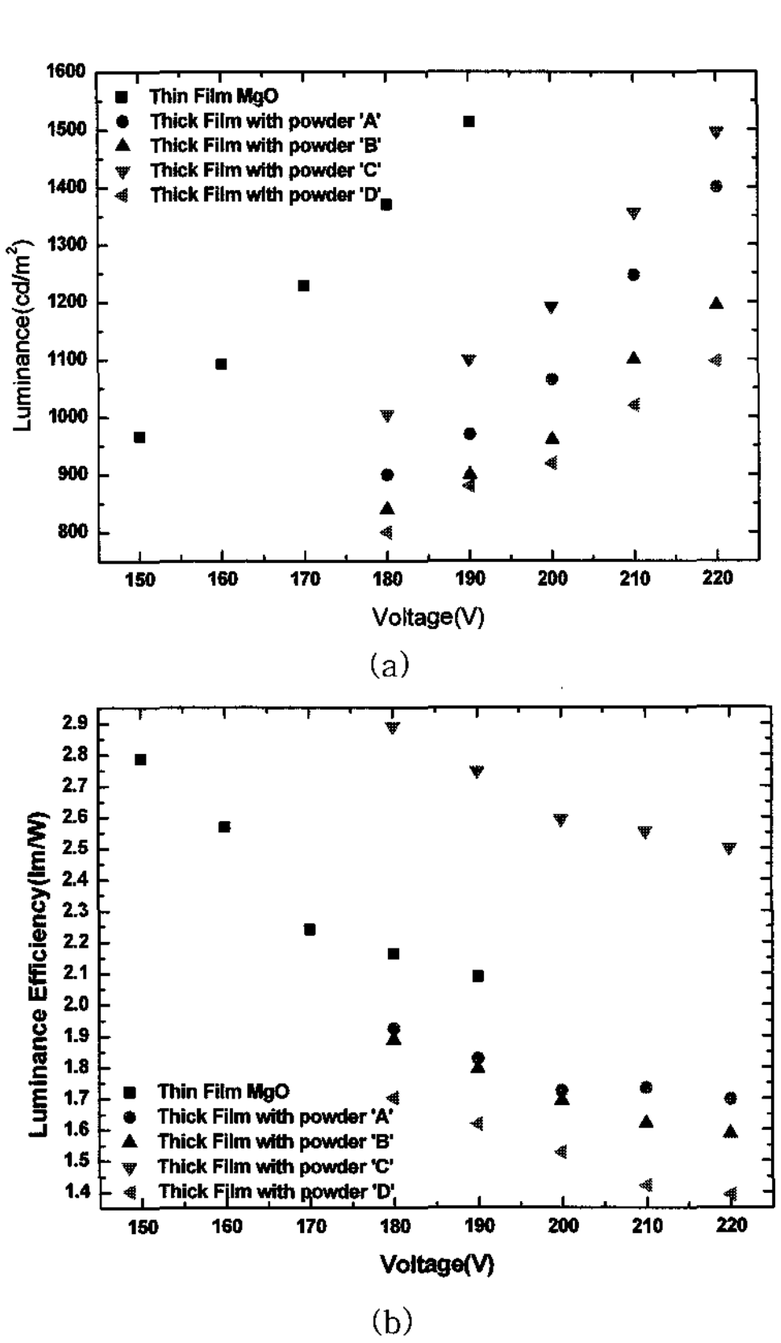

Fig. 6. Luminance (a) and luminance efficacy (b) of test panels with MgO powder thick film layers with different powder source. For comparison, the luminance of the test panel with MgO thin film was shown in the figure.

includes parallel and scattered lights through the film. Thickness of the film was fixed at 3 μm. As shown in Fig. 7, the total transmittance was close to 77% at 550nm with powder 'D'. The transmittance was lower with other types of powders: 50% for powder 'A', 68% for powder 'B', and 72% for powder 'C', respectively. If we consider such transmittance through the thick films, luminance efficacy of the test panels with thick film should be equal to or better than that of the panel with thin film. The efficiency of the panel with powder 'C' was estimated to be almost twice that of the thin film. These results suggest that the luminance efficacy is affected significantly by the type of the defects in MgO powders and the powder with F-type defect centers (powder C) resulted in the highest luminance efficiency. Although thin films produced by the e-beam evaporation has mainly F-type defects, its concentration is at least two-orders of magnitude lower than that of the MgO powder and that may have led to lower luminance efficiency as shown in Fig. 6(b).

Fig. 8 shows a voltage transfer curve of test panel with MgO (powder 'C') thick film. The measurement was conducted through the procedure proposed by Slotow et al [6]. The sustain voltage margin was approximately 12V. This value is smaller than that of the test panel with MgO thin film, which is close to 20V. The margin obtain with the panel of MgO thick film formed via EPD process, however, was a significant improvement compared with near-zero margin with the test panels prepared via spin coating of MgO thick film. This suggests that modest operational margin can be secured with the MgO thick film when prepared by EPD process. Preliminary study by authors indicated that the operational margin can be improved significantly when a mixture of MgO powders is used as thick film and the results will be published in the near future.

After aging treatment of the test panel for 92 hours at 270 V at 100 kHz, microstructure of MgO thick film layer was examined. Fig. 9 shows SEM images of MgO thick film surface after such aging treatment. In the outside discharge area (region 'A' in Fig. 9(a)), nano-sized MgO powder morphology was maintained as shown in Fig. 9(b). On the other hand, at the area where active glow discharge occurred, the powder morphology disappeared completely and 'maple-leaf' like morphology appeared on the surface. This type of microstructure is generally observed when the test panel with MgO thin film has undergone aging treatment [7]. This morphology forms when active sputtering and redeposition reaction occur on the surface of the thick film. These reactions make the thick film morphology similar to that of thin film and that may have contributed to the modest operational margin of the test panels.

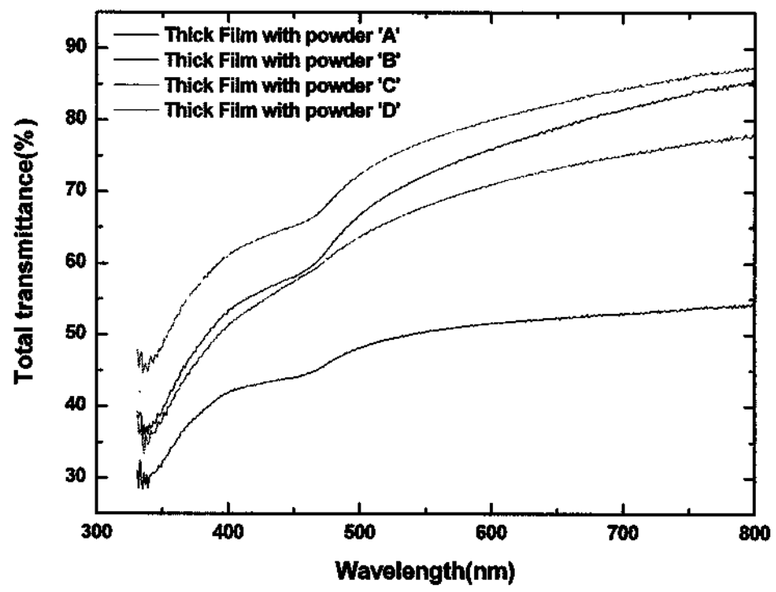

Fig. 7. Total transmittance of test panels with MgO powder thick film layers with different powder source.

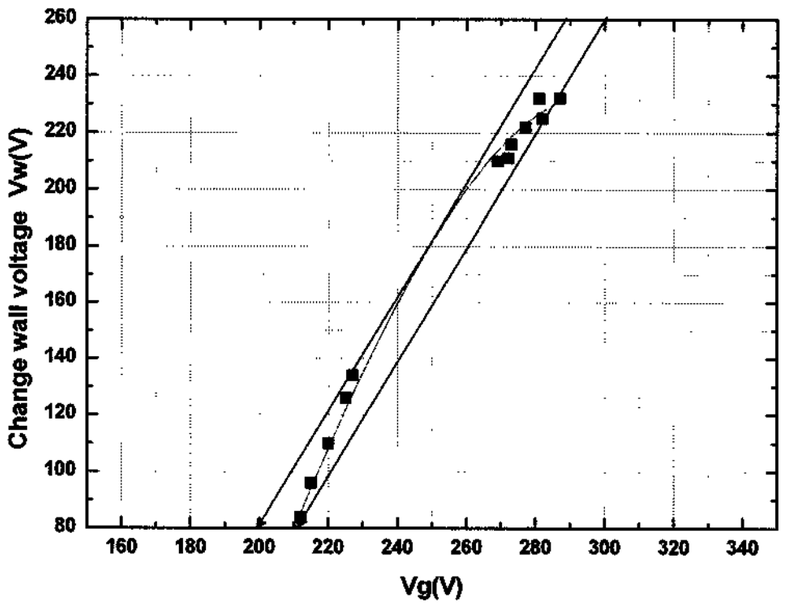

Fig. 8. Operation margin of test panel with MgO thick film.

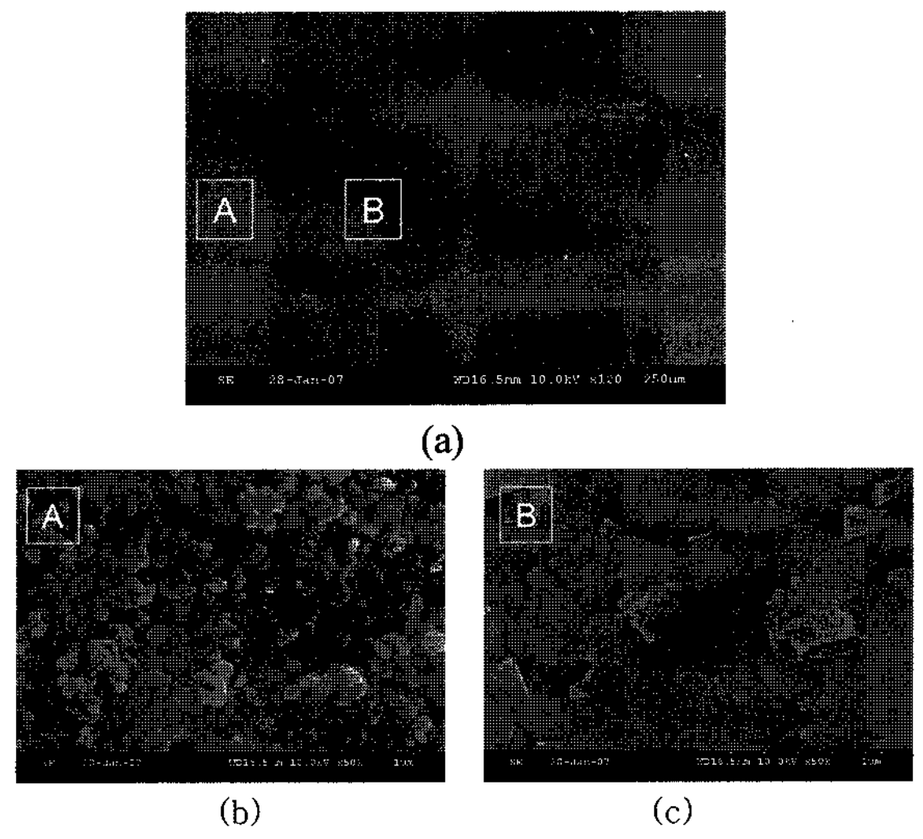

Fig. 9. SEM images of surface 'A' is none discharge region and 'B' is discharge region

4. Conclusion

Possibility of forming MgO thick film for ac-PDP using electrophoresis deposition process was explored. Was explored The packing density of the film was affected by the dispersant type and applied voltage between the electrodes. The luminance and luminance efficiency of the test panels with MgO thick film was measured to be affected by the type of defects formed within the MgO powders. The results indicated that luminance and lumiunance efficiency of test panels with MgO thick film formed via electrophoresis process may be similar or superior to that of test panels with MgO thin film formed via e-beam evaporation process. This process should provide ways to reduce processing cost and improve luminance efficiency of ac-PDPs.

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