Screening of spherical phosphors by electrophoretic deposition for full-color field emission display application

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Abstract — The photolithographic patterning on an indium-tin oxide (ITO) glass and the electrophoretic deposition were combined for preparing the screen of the full-color field emission display(FED). The patterns with a pixel of 400μm on the ITO-glass were made by etching the ITO with well-prepared etchant consisting of HCl, H_2O, and HNO_3. Electrophoretic method was carried out in order to deposit each spherical red(R), green(G), and blue(B) phosphor on the patterned ITO-glass. The process parameters such as bias voltage, salt concentration, and deposition time were optimized to achieve clear boundaries. It was found that the etching process of ITO combined with electrophoretic method was cost-effective, provided distinct pattern, and even reduced process steps compared with conventional processes. The application of reverse bias to the dormant electrodes while depositing the phosphors on the stripe pattern was found to be very critical for preventing the cross-contamination of each phosphor in a pixel.

Key words: photolithographic patterning, electrophoretic deposition, etching, etchant, reverse bias, high resistance.

I. Introduction

There has been much need for new technology to fabricate full-color screens consisting of phosphors with small particle size (1~2 μm) for use in FED [1]. The key issues in screening the phosphor powders for FED application are how to obtain a screen capable of high efficiency as well as high-resolution under the low voltage excitation. Phosphor screens typically used in display devices are composed of red, green, and blue phosphors. Their shapes and sizes have an influence on the display resolution. The high-resolution screens require a processing technique to produce a densely packed thin screen composed of small particles. It was reported that phosphor layers made of spherical phosphor could have good optical properties compared with conventional phosphors due to the high packing density and small scattering coefficient of phosphor [2]. Especially, the application of the spherical phosphor screen may become important in case of low voltage FED in which the transmission

of emitted light through screen should be maximized and the low scattering in screen be kept.

No contamination of phosphor surface during screening process is also very important to keep their efficiency. Electrophoretic deposition method in fabricating phosphor screens has drawn much attention for use in high-resolution flat panel display (FPD) applications because of simple process and no need to prepare the slurry for screening. It can dramatically reduce the possibility of phosphor contamination. This technique is currently used in manufacturing a thin layer of a luminescent material for advanced display applications [3]. It is known to have various advantages over the conventional screening process in terms of uniformity and adhesion issues of fine particles on the screen [4, 5].

In this work, the screening technologies have been investigated in order to address the aforementioned requirements of phosphor screens. Particular emphasis was given to the photolithographic patterning process combined with electrophoretic deposition for full-color phosphor screens. The

objective was to prevent the contamination of phosphors during the screening process. Here, new structure of anode was proposed for that purpose.

II. Experimental

The sequential steps for screening were followed. At first, the cleaning of ITO-glass was subsequently done with trichloroethylene (TCE), acetone, methanol, and deionized water in ultra-sonic bath to remove the organic contaminants that act as fatal impurities on the ITO-glass during the process of photolithographic patterning. The next step was the fabrication of patterned anode plate. First of all, the hexamethyldisilane (HMDS) and the positive commercial photoresist, AZ-1512, were spin-coated on the substrate to a thickness of about 1.2μm. After baked in a convection oven for 25 minutes at 95°C, it was placed on a mask aligner and exposed to ultraviolet (UV) light for 30 seconds under the beam intensity of 12 mW/cm². It was then developed in AZ-1512 developer for about 70 seconds, and baked for 35 minutes at 125°C. Subsequently, the samples were etched by etchant, which were prepared in the ratio of $HCl : HNO_3 : H_2O$ of 10 : 1 : 10, for about 5 minutes at bath temperature of 40~45°C. Sheet resistance of ITO was measured by four point probe and resistivity calculated.

The electrophoretic deposition was carried out on the patterned ITO-glass in a bath container with solvent consisting of phosphors, $Mg(NO_3)_2 \cdot 6H_2O$, and isopropyl alcohol (IPA). The $Mg(NO_3)_2 \cdot 6H_2O$ concentration ranged from approximately 10^{-5}M to 10^{-3} M was optimized in our previous work [6]. The phosphors used are the spherical shape made by aerosol pyrolysis method in our laboratory [7]. Mixed solution was stirred for about 24 hours to assure the complete dissolution of $Mg(NO_3)_2 \cdot 6H_2O$ and the dispersion of phosphor particles. The patterned ITO-glass and a stainless steel served as a cathode and an anode, respectively. Finally, the phosphor particles were deposited on the patterned ITO under an electrical potential of 400 V for a few minutes [8], while the reverse bias voltage in the range of 50V ~ 100V was applied to the area where the phosphors are not supposed to be deposited. The deposited screen was washed with IPA, and dried in a convection oven for 20 minutes at 200°C. The

other phosphors were also deposited on the rest of patterned ITO-glass. After R. G. B. phosphors were deposited, it was dried under an air environment at 450°C. The final patterned anode plates were observed with an optical microscope and a scanning electron microscope (SEM).

III. Results and Discussion

Various negative photoresists have been tried in fabricating the full color screens in our work. But, there remains unclear in patterning process due to the inappropriate properties of these photoresists. This complexity forced us to design a new type of anode plate. The characteristics of pattern proposed in this work allow us to deposit color phosphors without any interaction between the phosphor powder and photoresists, once the patterned electrodes on the ITO-glass are given. Thus, the chance of contaminating phosphor powders can be dramatically decreased. Figure 1 shows the schematic diagram of designed pattern. The patterns, which we adopted, have merits of easy fabrication as well as anode switching. But the possibility that the high resistance for one specific color line may cause problem for driving in a large panel may not be eliminated. Actually this problem was revealed through our experiment. More than three electrodes should be made in order to solve this problem as shown in Figure 1-(a). Designed pattern consists of 76 pixels on the 3 cm×3 cm size on the substrate of 5 cm×5 cm. Each pixel with 400 μm is composed of 100μm, 50 μm, 100 μm, and 50 μm, and the etched line was 33 μm, as well shown in Figure 1-(b). However, the reduction of resistance was considered as an essential factor in designing the anode plate. However, it was observed that etching process of ITO provided distinct patterns, as shown in Figure 2 and reduced many process steps in comparison with a conventional method. Another issue in our anode plate is to isolate the three electrodes on which each R. G. B. phosphor would be deposited. Due to the inhomogeneous etch rate on the patterned ITO-glass, the breakage of electrode by over-etching was commonly observed. Especially, etchant was considered as an important factor influencing on etching process. Proper etching temperature was determined through the repetitive
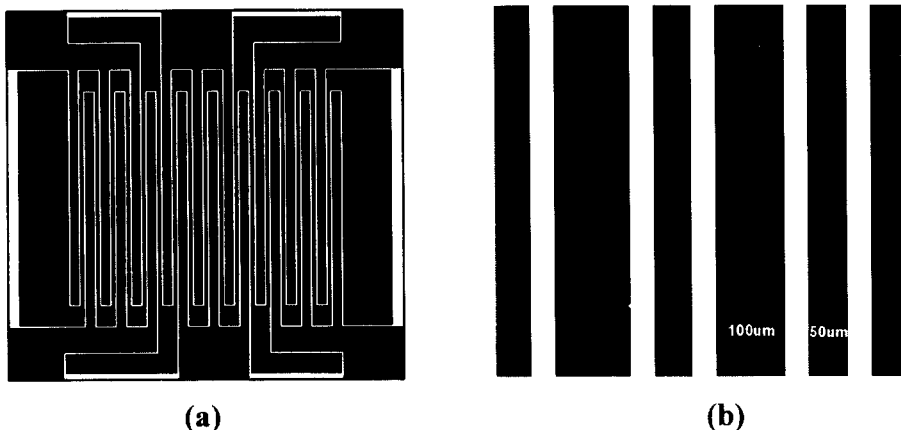
(a)   **(b)**

Fig. 1. Anode plate for low voltage field emission display application. (a) Schematic diagram of mask design, (b) Optical microscope image of real mask.
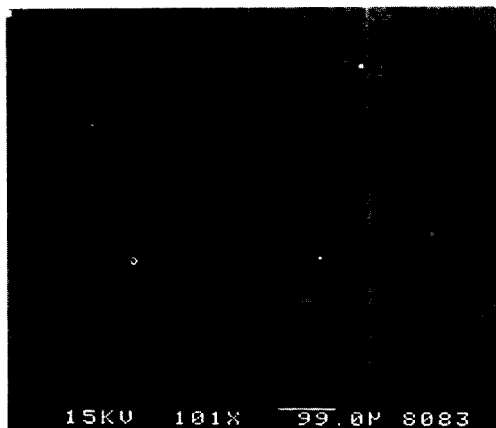
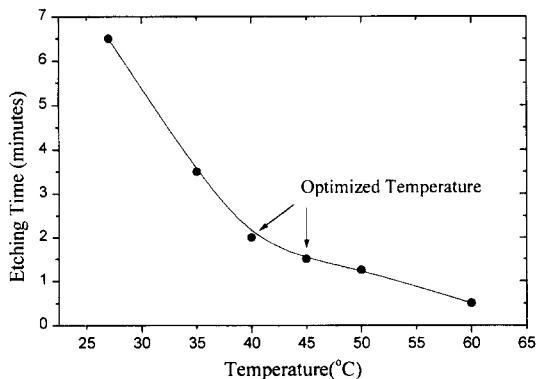

Fig. 2. SEM image of etched pattern.

Fig. 3. The relationship between the bath temperature and etching time.

experiments. It was observed that the higher temperature was, the faster etch rate was, as shown in Figure 3. But it was found that the etching of ITO over 45°C was not stable. The proper etching temperature was determined as 40~45°C. The ITO films were 1500 Å thick and had a resistivity of 1.12×10^{-3} Ωcm. Etch rate could be controlled by the concentration of acids and the addition of oxidizing agent. Patterned substrate images made by photolithographic patterning process were shown in Figure 4. The developed pattern image before etching ITO and the etched patterned image before removing photoresist were shown in Figure 4-(a), (b), respectively. The anode plate, on which photoresist was stripped completely, was shown in Figure 4-(c).

Figure 5 shows the image of phosphor deposition on the patterned substrate. Basically, the charged particles are moving by electric filed near ITO-electrode in electrophoretic process. So, it is not easy to control the selective deposition if the electric field is not precisely manipulated. Applying the reverse bias to dormant electrodes, on which the other color phosphor would be successively deposited, was introduced in order to reduce this cross-contamination. A dramatic reduction in bridging deposition was observed, comparing to the deposition without reverse bias, as shown in Fig. 5.

Spherical green phosphor $ZnGa_2O_4$:Mn was deposited on the etched pattern in order to optimize a clear boundary, as shown in Fig. 6-(a). Deposition process was carried out by mainly controlling the
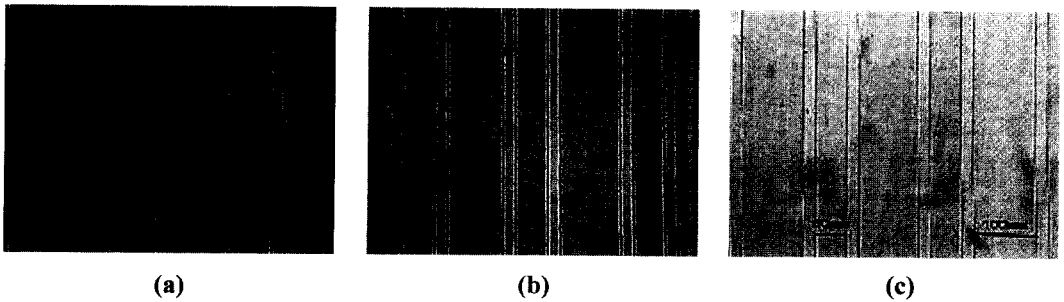
(a)   **(b)**   **(c)**

Fig. 4. Patterned substrate by photolithographic patterning process. (a) Developed pattern image before etching, (b) Etched pattern image before removing PR, (c) Etched pattern image after removing PR.
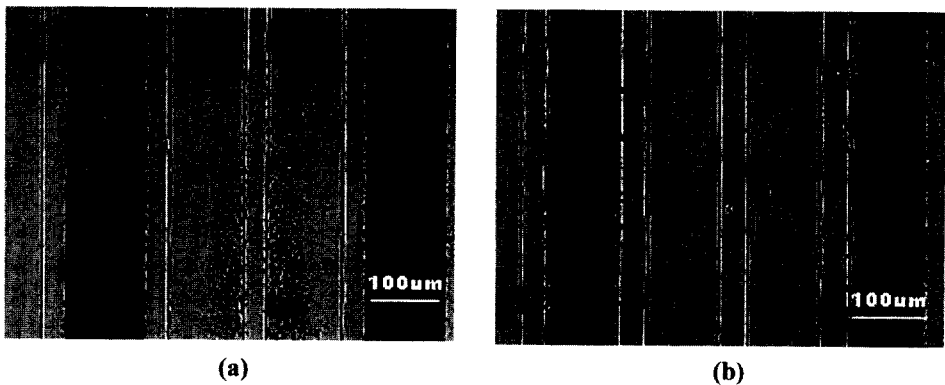

(a)   **(b)**

Fig. 5. The effects of reverse bias on the bridge deposition during process. (a) Deposited pattern image of one line phosphor(No reverse bias), (b) Deposited pattern image under reverse bias, 100 V.
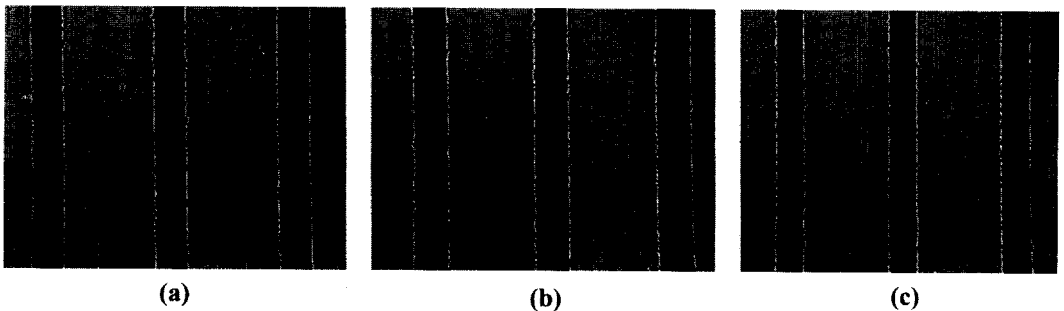

(a)   **(b)**   **(c)**

Fig. 6. Optimized screen weight on the patterned substrate for R. G. B. phosphors. (a) Deposition image of one line of $ZnGa_2O_4$:Mn, (b) Deposition image of one line of Y_2O_3:Eu, (c) Deposition image of one line of Y_2SiO_5:Ce.

deposition time with aforementioned conditions. Generally, it was proved in previous work that as the deposition time is increased, more phosphors are deposited on the substrate [9]. So in order to obtain clear boundary and thin layer of phosphor powders with high packing, it is essential to reduce the deposition time and to increase the deposition rate. To obtain the proper screen weight for a given time, the suspension consisting of IPA (300 ml), phosphor (0.6 g), and $Mg(NO_3)_2 \cdot 6H_2O$ added to 1% H_2O (3 ml), so that deposition rate increased remarkably. $ZnGa_2O_4$:Mn phosphor was optimized at deposition time, 20 seconds. Figure 6-(b), (c) shows optimized deposition image of Y_2O_3:Eu and Y_2SiO_5:Ce,

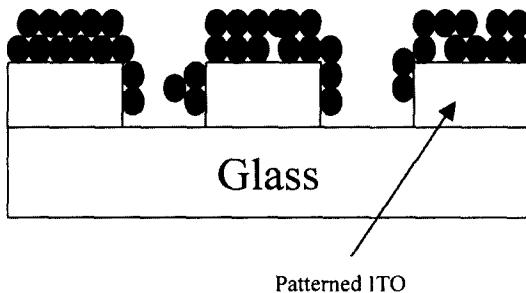**Fig. 7.** SEM image of deposited Y_2O_3:Eu.

Patterned ITO

Fig. 8. Schematic diagram of deposited phosphors.

respectively. Red phosphor Y_2O_3:Eu and blue phosphor Y_2SiO_5:Ce were optimized at the deposition time 25 seconds and 30 seconds, respectively. As shown in Fig. 6, clear boundary of line was not obtained yet. It could not be obtained in spite of reducing the deposition time. It means that clear boundaries can not be controlled only by changing the process parameters in electrophoretic deposi-

tion. One of the reasons is believed to be due to the deposition on etched cross section and edge of ITO. The other is due to inhomogeneous particle size and agglomerated particles, as shown in Fig. 7 and schematically in Fig. 8. This tolerance may be within a specification if the black matrix is introduced between the lines. However, it is very important to understand this observation fully and improve the patterning from the practical point of view.

To realize full color anode plate, green phosphor was deposited on the first electrode with optimized deposition condition, as shown in Fig. 9(a). Subsequently, red phosphor was deposited on the second electrode as the same way, and then blue phosphor on the third electrode finally as shown in Fig. 9(b) and (c). As shown in Fig. 9(b), red phosphor, Y_2O_3:Eu, deposited on the second electrode was deposited less than it deposited on one specific line as shown in Fig. 6(b), which was optimized at deposition time, 20 seconds. It is observed that although the electrophoretic process was carried out at the same condition, deposited weight on the patterned substrate was different from that of independent experiment for mono color screen, as expected. It is mainly ascribed to the change of electric field near electrode. Also blue phosphor, Y_2SiO_5:Ce, deposited on the third electrode occurred to the same result. In this work, the designed pattern with R.G.B. phosphors were proposed to meet the requirements of low voltage FED application and demonstrated to check the validity. High resistance of the long electrode could be effectively resolved by dividing the extra electrodes in this design. Clear boundaries and optimized thickness of phosphors deposited on the substrate should be controlled with
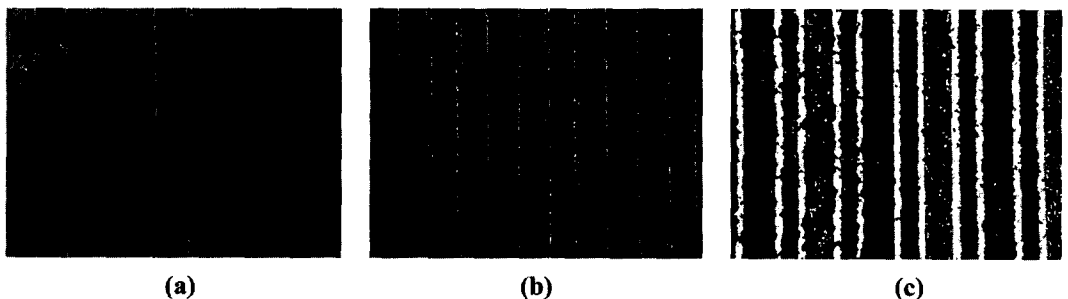

(a)   (b)   (c)

Fig. 9. Full-color phosphor deposition image. (a) Deposition image of first line of $ZnGa_2O_4$:Mn., (b) Deposition image of second line of Y_2O_3:Eu, (c) Deposition image of third line of Y_2SiO_5:Ce.

black matrix as well as deposition condition. Black matrix was not introduced to this work yet. However, the full understanding on the electric filed and their exact control near pattern was found to be necessary for more refined fabrication of anode plate.

IV. Conclusion

New type of anode plate for low voltage FED application was presented and the applicability of photolithographic process combined with electrophoretic deposition (EPD) to full-color screen was demonstrated.

The pattern obtained by etching ITO has important merits such as anode switching and easy fabrication in comparison with conventional process. The conventional EPD process should undergo three times of spin coating and ashing process, which causes phosphor contamination by photoresist residue and the change of surface state. CL intensities and efficiency of phosphors are known to be very sensitive to the surface state of phosphor in case of low voltage excitation of phosphor. The process that we adopted could get over this problem by eliminating the use of photoresist with phosphors. In electrophoretic process, bridging deposition of phosphors on the patterned substrate could be decreased by applying the reverse bias on the dormant electrode while depositing. Also, clear boundaries and optimized thickness of phosphors deposited on the substrate were expected to be effectively controlled by changing the process parameters as well as black matrix. However, it is necessary to develop proper

black matrix materials and control the electric field near electrode in order to obtain the realistic anode plate applicable to FED.

Acknowledgement

Reference

[1] D. C. Chang, R. P. Rao, and J. B. Talbot, in proceedings of *1ˢᵗ International conference on Science and Technology of Display Phosphors*, p. 221 (1995).

[2] A. K. Albessard, M. Tamatany, M. Okumura, H. Natsude, H. Hattori, S. Motoki, *Proceedings of the 15ᵗʰ International Display Research Conference*, p. 643 (October 16~18, 1995).

[3] M. J. Shane, J. B. Talbot, B. G. Kinney, E. Sluzki, and K. R. Hesse, *J. Colloid Interface Sci.* **164**, 334 (1994).

[4] J. A. Siracuse, J. B. Talbot, E. Sluzky, T. Avalos, and K. R. Hesse, *This Journal* **137**, 2336 (1990).

[5] M. J. Shane, J. B. Talbot, E. Sluzky, and K. R. Hesse, *Mater. Res. Soc. Symp. Proc.* **345**, 294 (1994).

[6] B. S. Jeon, J. S. Yoo, and J. D. Lee, *J. Electrochem. Soc.* **143**, 3923 (1996).

[7] S. H. Cho, J. S. Yoo, and J. D. Lee, *J. Electrochem. Soc.* **145**, 1017 (1998).

[8] S. W. Kang, B. S. Jeon, J. S. Yoo, and J. D. Lee, *Technical of 10ᵗʰ IVMC*, p. 682 (1997).

[9] S. W. Kang, J. S. Yoo, J. D. Lee, *J. Vac. Sci. Technol.* B **16**, 2891 (1998).