Influences of ambient gases upon emission characteristics of Mo-FEAs during frit sealing cycle

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A 3.5-inch full-color field emission display (FED) has been developed for the applications of flat panel display. The Spindt tip array with a pixelated anode produces uniform and clean image. Changes of electron emission characteristics between before and after frit sealing cycle were measured on the same FEAs. And properties of thin Mo-films which frit-sealing cycle was being done in various gaseous ambient were estimated by AFM, AES, SIMS, XPS. Possibility of applying Ar as an ambient gas to frit-sealing cycle for vacuum packaging of field emission displays (FEDs) was reported. A set of uniquely printed spacers with the high aspect ratio is fabricated on ITO coated glass for high vacuum packaging. The low voltage phosphor is tested at anode voltage of 300V. Finally, full color images of 64 gray scale will be demonstrated.

Introduction

The advantages of field emission display (FED) over competing technologies are well known; the wide viewing angle, response time, low power, and wide temperature tolerance.[1)] In order to take advantages of these benefits, the experimental and developmental research of FEDs have been extensively carried out aiming at the positive mass production in near future.[2,3)]

Realization of image uniformity requires tight process control in cathode fabrication. Acceptable brightness also demands phosphors efficient, since their characteristics are not stabilized due to the low efficiency. The development of spacers is another important issue. The spacer should be designed according to pressure level and stress of glass.

In this paper, we will discuss the process for and demonstrate the 3.5-inch full-color FED. In addition, we compared electron emission characteristics of FEAs between before and after frit sealing cycle as a function of ambient gases, and surface analyses of thin Mo-films were reported, and FEDs which frit sealing cycle was processed with ambient gas was demonstrated.

Experiments

In the low voltage operation, the sulfide phosphors are commonly used, but the sulfide phosphor has some problem of decomposing and generating scattering sulfide gases with the electron excitation. Phosphors we use are (Zn,Cd)S:Ag, ZnS:Cu,Al, and ZnS:Ag phosphors for red, green, and blue colors, respectively. The spacers are formed by screen printing method on the anode plate. To maintain the best vacuum condition, the non-evaporable getter is used. We will make an overall report of the current status of our FED development.

The field emission in the display is achieved using arrays of Spindt tips on the cathode. A typical tip is shown in Fig. 1. We have achieved a repeatable tip radius below 30nm range from the cathode fabrication. Cathode design for FED requires careful consideration of many variables including metal-to-metal spacing and ballast topology. The use of redundancy in the design can decrease the susceptibility of the cathode to be processed including defects, and improve emission uniformity and reliability.

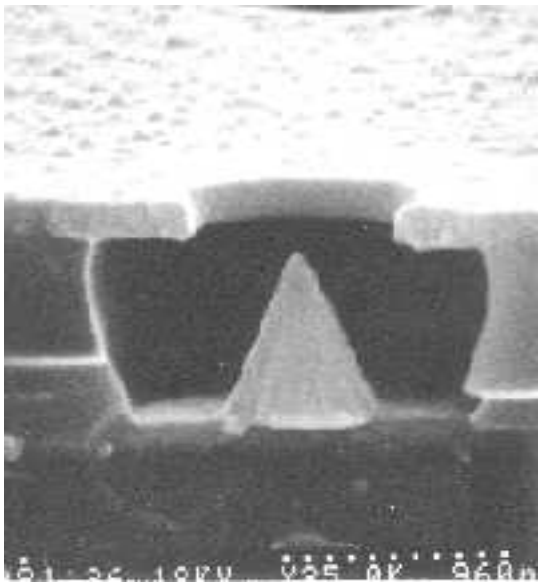

Fig. 1. Cross sectional view of Mo-tip.

Results and Discussions

We have developed the 3.5-inch FED consists of 160×3×120 lines for RGB colors with a pixel size of 450μm×450μm. Each pixel has 1,452 Mo tips. The a-Si:H thin film is used as a resistive layer for the improvement of emission stability. The 3.5-inch FED has been uniquely developed using low-voltage phosphors with black matrix and spacers. The sulfide phosphors are used for red, green, and blue color, respectively, with special activator. Figure 2

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shows the CIE diagram of chromaticity coordinates of each color. It is also coated by 3% of In_2O_3 conducting material in order to adjust phosphor's conductivity. If the phosphor layer is too thick, the image is not clear at transmissive mode of FED.[4] The thickness of screened phosphor layer is related to the crystal size and screening technology. The spacer is fabricated by thick film printing method, and aspect ratio of spacer is well controlled with the 1:0.6 (height:bottom) of 200μm:120μm on the anode plate. After spacer processing, cathode and anode plate is sealed with frit glass and the base pressure of the panel of 5×10^{-6} torr should be maintained to pump out the panel through evacuation in high temperature environment.

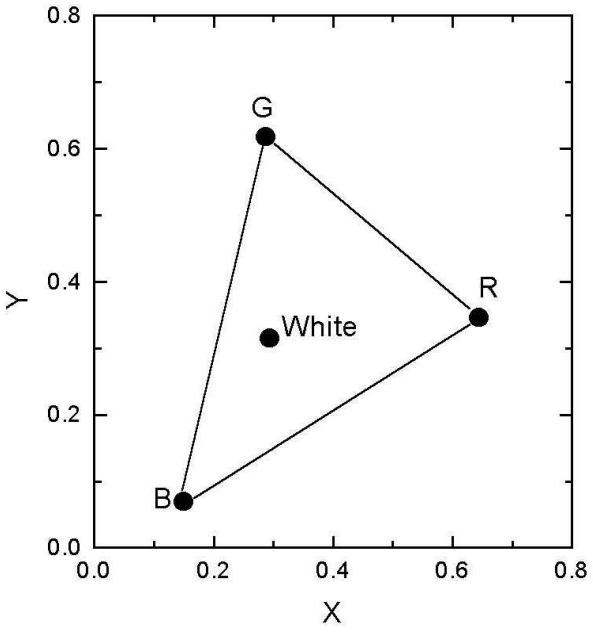

Fig. 2. CIE chart for color phosphor.

The real image on the 3.5-inch panel is demonstrated through the video controller of composite NTSC. The frequency of row line is 15.75kHz, and the row driver is a very simple part providing only the rows select signals. On the other hand, the column driver presents the gray scale image information to the pixel. Our 6-bit column driver differs from the row driver both in complexity and bandwidth performance.

Figure 3 shows the I-V characteristics with variable gate voltage on 15kHz-pulse mode of 3.5-inch FEA. The turn-on voltage is 40V and typical emission current is around 3mA at fixed anode and gate voltages of 300V and 90V, respectively. The emission current in DC mode is around 100μA/pixel and the ratio of gate current to emission current is less than 0.1%. However, the device has an unstable effect on the brightness and anode current. Special aging for 3 hours stabilizes the fluctuation in brightness and anode current.

To achieve 200μm height of spacer, it is necessary to print 6 times, and the cross sectional view of the spacer is shown in Fig. 4. If the spacer is porous and brittle, the field emitter array may be contaminated after packaging process and the anode may be easily electrically shortened with the leakage path between gate and anode, finally resulting in the phosphor burning or degradation.[5]

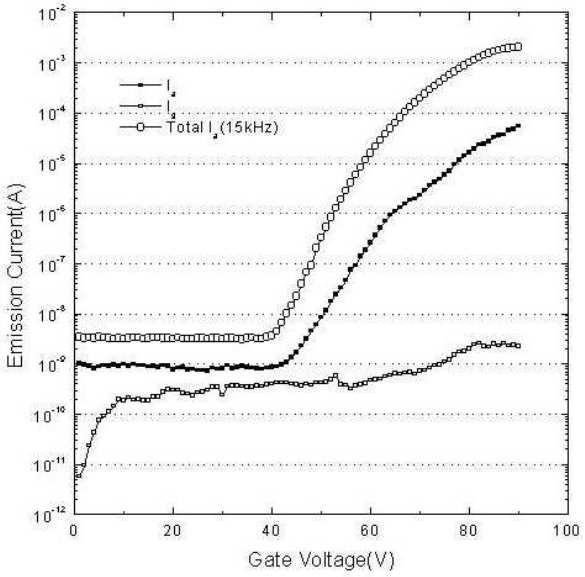

Fig. 3. I-V characteristics with variable gate voltage in DC and pulse mode.

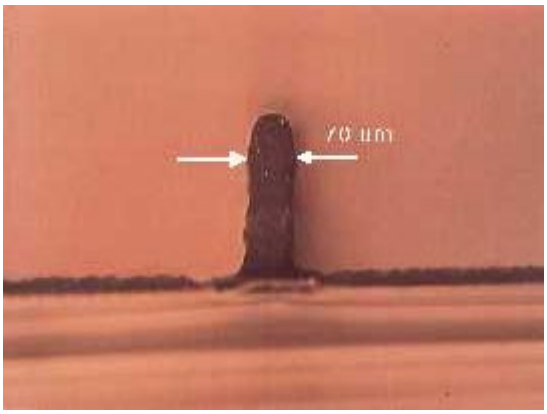

Fig. 4. Cross sectional view of the spacer.

Figure 5 shows the morphology of Mo films as a function of ambient gas after frit sealing process. And table 1 depicts a RMS value, average roughness and sheet resistance of Mo films after frit sealing process in various gaseous ambient (air, N_2, Ar). Roughness of sealing processed Mo film in air was greater than that of one processed with N_2 or Ar. And frit sealing processed Mo film with Ar has most smooth surface. Thus, we can infer that electric field distribution can be changed by roughness of Mo film and this electric field variation can lead to fluctuation of emission current. In this figure, roughed Mo surface can lead to changes in the field enhancement factor of the emitters. But, in this study, we think that the main factor of degradation on field emission is formation of Mo oxide. And we suppose that increment of potential barrier

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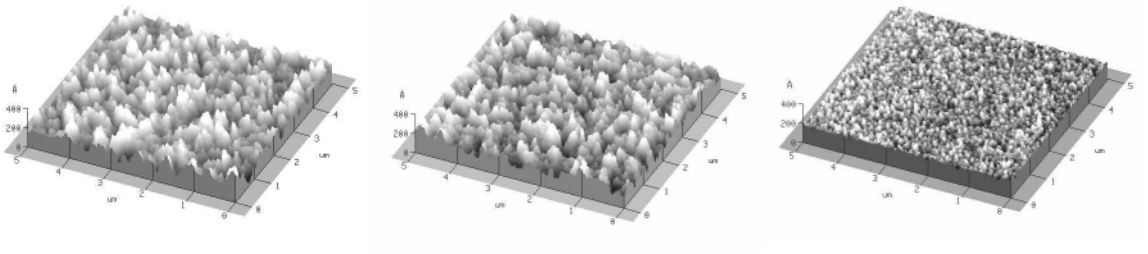

Fig 5. Surface morphology of Mo surface that used (a) air (b) N_2 and (c) Ar as an ambient gas.

by Mo oxide on field emitter has more influence on destructive degradation than effect of changes in the field enhancement factor of field emitter. It is because that change in the field enhancement factor is caused by increment of the angle in tip apex, roughed surface of tip. But, radical degradation like this study has some difficulty in explanation by these effects. Thus, the origin of degradation is formation of Mo oxide on field emission tip caused by frit sealing process in various gaseous ambient. Thus, we think that work function of field emitter increased by formation of Mo oxide during frit sealing process, also degradation of filed emitter caused by increment of work function.

Table 1. RMS values, average roughness and average sheet resistance of Mo films after frit sealing cycle as a function of various ambient gas (air, N_2, Ar)

	RMS(Å)	Average Roughness(Å)	Average R_s(Ω/)
Air	49.5	39.3	1.854
N_2	45.4	36.1	1.739
Ar	12.4	9.7	1.600

Figure 6 shows SIMS spectra indicating relative quantity and composition of Mo films after frit sealing process in various gaseous ambient. In this figure, we can see that Mo films has MoO_3 compound and as sputtered time increased, quantity of oxygen was decreased and Mo film processed with Ar has a lowest quantity of MoO_3 as a function of depth.

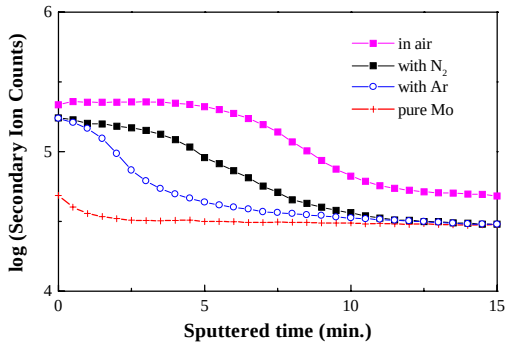

Fig. 6. SIMS spectra of Mo films after frit sealing cycle in various gaseous ambient.

Figure 7 shows by AES that relative quantity of Mo films after frit sealing process in various gaseous ambient. Mo film after frit sealing process with Ar has minimum oxygen depth profile among the processed Mo film with other gases. This means that Mo film after frit sealing process with Ar has the lowest oxygen contents than that of processed films with other gases. Thus Ar gas effectively kept away the combination with oxygen at the Mo film surface during frit sealing cycle. But MoO_x also existed in frit sealing processed Mo film with Ar. Thus the origin of the Mo oxide formation during the exposure to N_2 and Ar is remaining Oxygen during the exposure to gases. Remaining possibility of Oxygen can exist during the frit sealing process in various gaseous ambient because our experiment was done in the atmosphere without vacuum instrument. Thus, if the flow rate of Ar as an ambient gas has the same as that of N_2, Ar is more suitable ambient gas than N_2 in frit sealing process.

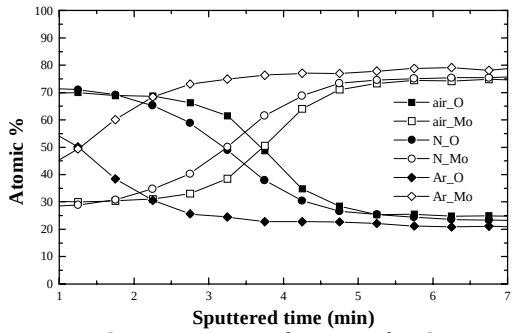

Fig. 7. Relative quantity of oxygen for the Mo samples annealed in Air, N_2 and Ar

Figure 8 shows narrow-scanned XPS spectra for the samples with various ambient gases: as-fabricated samples and those after frit sealing process with Ar, N_2, and air. In order to investigate the chemical binding between the Mo surface and the adsorbed oxygen, we measured the binding energies of the Mo$3d_{5/2}$ and Mo$3d_{3/2}$ levels by narrow-scanned XPS. In comparison with each sample, we can see that Mo$3d_{5/2}$ (228eV) and Mo$3d_{3/2}$ (231eV) are chemically shifted toward higher energy by sequential order of as fabricated, after frit-process with Ar, N_2, and air. Thus, Mo$3d_{5/2}$ (228eV) and Mo$3d_{3/2}$ (231eV) peaks of as-fabricated sample was chemically shifted after frit sealing process in air, and we confirmed that these peaks of one processed in air included the MoO_3 (233eV) peak by analyzing each peak height ratio. And in the case of the oxygen absorption on a clean Mo surface, MoO_3 usually

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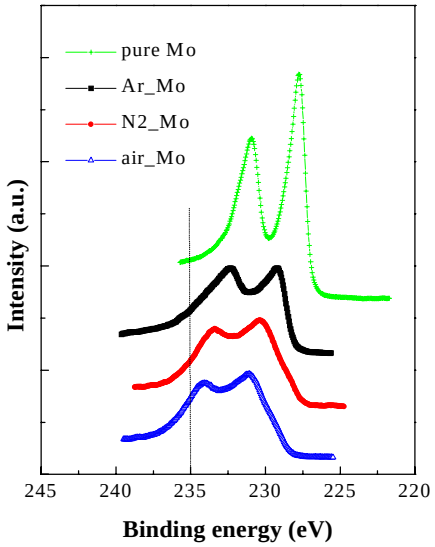

Fig. 8. XPS spectra as a function of ambient gases.

coexists with lower oxides such as MoO_2, MoO [6,7]. In this measurement, it is difficult to say the absolute quantity of these oxides. But when Mo film was processed in air, we can infer that oxygen was more adsorbed, it was because that the peaks are chemically shifted toward high level. Thus the XPS spectra show that the Mo surface after frit-process in air contains the MoO_3 and lower oxide such as MoO_2, and note that the peaks of Mo surface after frit-process with Ar has a small MoO_3 distribution.

Fig. 9. Moving images of 3.5-inch full-color FED.

Figure 9 shows the snapshot of moving images of3.5-inch full-color FED. With this system, the white luminance of 80cd/m^2 was achieved at 300V of anode bias.

The improvement of electron emission characteristics in Mo-tip FEAs after frit sealing cycle at atmosphere was achieved by using Ar as an ambient gas. This remarkable improvement in electron emission characteristics after frit sealing cycle at atmosphere is attributed to the properties of Ar as an ambient gas. The limitation of increment in work-function by using Ar causes lower turn-on voltage and more stable emission characteristics than using other ambient gases. Also, we think that using Ar as an ambient gas has not adverse effect on the phosphor layer during frit sealing cycle. Thus, using Ar as an ambient gas during frit sealing cycle was most suitable for the vacuum packaging with frit paste.

Conclusion

3.5-inch full-color FED with clear and stable color images has been successfully developed. This paper describes experimental results on the fabrication of 3.5-inch FED on soda-lime glass substrates for practical use in manufacturing displays. By fabrication of the panel with field emitters, the tip sharpening technology, which is closely related to these emitter arrays, are stable and repeatable. The low voltage phosphors with special activator are being used. These results will be the basis for color panel development and large panel application. For the practical use of the low-voltage full-color FED, further improvement is needed required for the structure and drive system. In addition, the spacer with high aspect ratio will be developed for large panel and high resolution display application. We will continue our effort towards the realization of the practical use and mass production for full-color FED.

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