Stability of Coated Green Phosphors for Enhancing Picture Quality of PDP

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Abstract

The picture quality of a plasma display panel is very sensitive to the phosphor characteristics such as luminescence, decay time, surface properties, and even longevity of phosphor material in itself. In our previous work, the discharging characteristics in green cell of PDP were demonstrated to be enhanced by coating $Zn_2SiO_4:Mn^{2+}$ phosphors with positively charged metal oxide such as MgO. Here, $Zn_2SiO_4:Mn^{2+}$ phosphors were coated by various metal oxides for examining the coating effect on the picture quality. Specially, longevity while fabricating the panel was investigated for panel application in this work. Also the effects of ion and electron bombardment on the phosphor surface will be discussed in this work.

1. Introduction

PDP is the emissive display device which uses the visible rays from the phosphors excited by vacuum ultraviolet rays, which were generated by discharging He-Xe, Ne-Xe mixed gas in R, G, B, cells. Consequently, the R, G, B phosphors determine the image quality of PDP. Many options are available for PDP application, depending on the manufacturer. For typical application, $BaMgAl_{10}O_{17}$:Eu, Eu-doped yttrium borate, and $Zn_2SiO_4:Mn^{2+}$ are used as blue, red, green phosphors, respectively. But, critical problems of green phosphor are coming to the front among these. As for the $Zn_2SiO_4:Mn^{2+}$ phosphor, absorption of ultraviolet rays near 147nm and 173nm is good and color purity of green emission is known to be the most suitable among green phosphors for PDP application. On the other hands, it was reported that the $Zn_2SiO_4:Mn^{2+}$ has a negative surface charge which is from the non-stoichiometric matrix of the host lattice, while red and blue phosphors have positive surface charges.[1)] The negative charge of the green phosphor may reduce the wall charge accumulated on the dielectric surface in PDP cell. Because the wall charges help to sustain the discharge in the cells that were subjected to the previous discharge, the reduction of wall charges can lead to non-uniform discharge or even non-discharge phenomenon in the PDP cell.[2)] As a consequence of this unstable discharge characteristic in the green cell, the efficiency of PDP device can be seriously reduced and a higher discharge voltage is required for driving the PDP device for compensating the reduced wall charges. One of the solutions is the coating on the $Zn_2SiO_4:Mn^{2+}$ phosphor with metal oxide which has the positive charge at the surface. [3,4,5)]

However, negative effect of coating on the phosphor has to be considered for panel application. Here, we separated dominant effects such as intensity of electron beam and ion beam. Then, each independent variable was examined in terms of luminance. Also, we will present what happened to phosphors under VUV plasma condition.

2. Experimental

Zn_2SiO_4:Mn, metal oxide coated Zn_2SiO_4:Mn and nano sized metal oxide mixed Zn_2SiO_4:Mn were selected for the analysis. For paste, binder (Tokyo Kasei) and vehicle were mixed with phosphor at the ratio of 60:40. Complete mixing was carried out for more than 24 hours. Then, phosphor layer were made on the glass with the thickness of 120μm. The experimental were carried out under two conditions. Each powder samples and corresponding phosphor layer on the glass were aged under muffle furnace at atmosphere. Condition was in the temperature range of 400℃~700℃ for 1 hour.

Aging characteristics of phosphor powder as well as phosphor film were examined. Temperature and pressure while aging were the main independent variables in our case.

And, we experimented to observe the change of luminescence and surface state after exposed the electron and ion beam on phosphor layer. Each sample exposed the electron to the condition of 5.5×10^{-5} Torr, 400V, 12.5μA, 1hour. And also each sample exposed the ion beam to the condition of 2.4×10^{-4} Torr, accelerator voltage 600V, Beam voltage 600V, 1hour. PL was measured in each case. The optical properties of prepared phosphors were investigated by photoluminescence measurement with xenon lamp (ORC lighting products, LH1751300). The scanning electron microscopy (SEM, Philips co.515) micrographs were used for the change of surface state of phosphor layer. In order to look at the change of chemical composition and binding energy on phosphor layer, X-ray photoelectron spectroscopy (XPS, PHI 5800 ESCA System) measurements on phosphor layer were performed.

3. Results and discussion

Zn_2SiO_4:Mn^{2+} phosphors were coated by metal oxides such as Y_2O_3, La_2O_3, Al_2O_3 and ZnO which are all positively charged on the surface coated Zn_2SiO_4:Mn^{2+}. Also, nano-sized Y_2O_3 mixed Zn_2SiO_4:Mn^{2+} phosphors were considered. Here, we assumed that coated Zn_2SiO_4:Mn^{2+} phosphors are superior to bare phosphors in terms of discharging characteristics. Figure 1 shows how the luminescence of a phosphor film is influenced under vacuum annealing. In this experiment, phosphor film was exposed to 1 hour at 480℃.[6] Dramatic change in luminance was observed all samples that we dealt with. However, we did not observe any change in host lattice and Mn^{2+} of phosphors. They could be recovered simply by annealing, as shown in Fig. 2. The vehicle and binder are consists of organic compounds. To eliminate the organic compounds, we believe that the processing condition should be adjusted for vacuum annealing. We confirm all the samples regain the original luminescence when they re-heated by 1 hour at 500℃ atmospheric pressure.

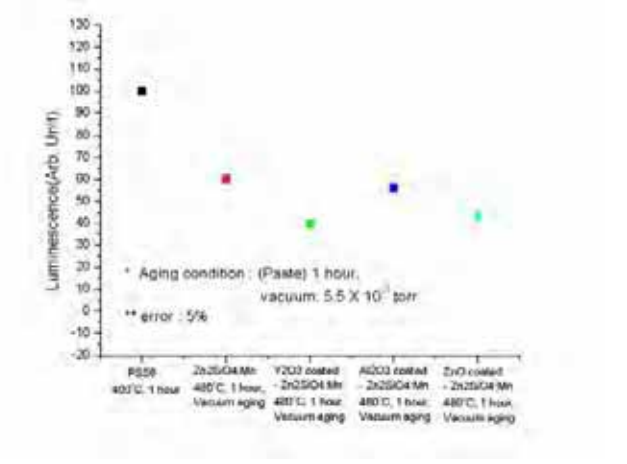

Figure 1. The change of the luminescence for the vacuum annealing

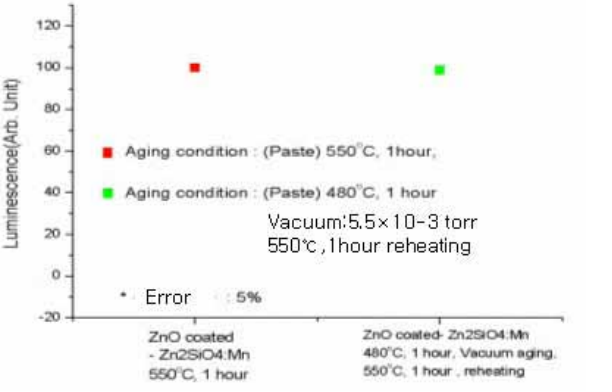

Figure 2. The change of the luminescence for re-heated after vacuum annealing.

Figure 3 shows changing of luminescence of phosphors after exposing to electron beam (400 anode voltages with 12.5 uA). Damage to phosphor was observed and smaller particle and rougher surface was more influenced by electron.

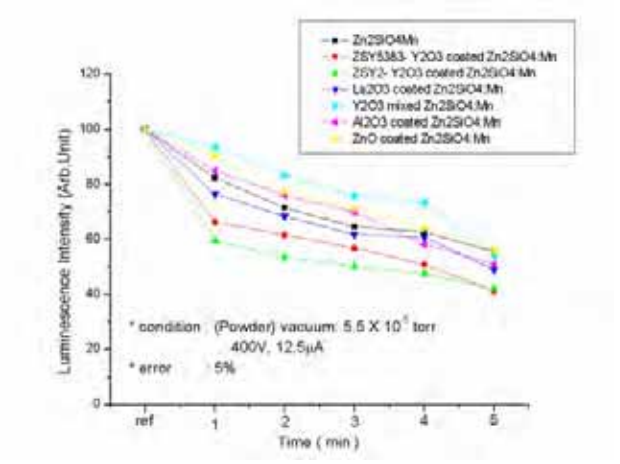

Figure 3. The change of the luminescence after exposed the electron.

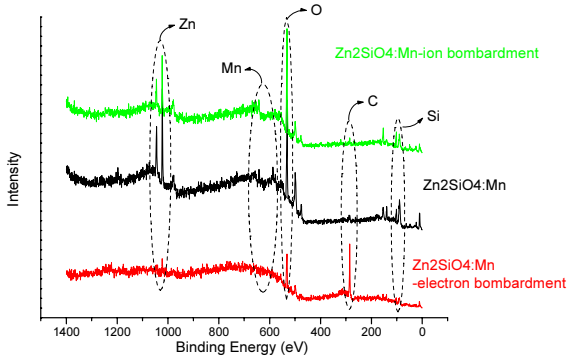

Figure4. The change of the chemical composition and binding energy after exposed to the ion beam

Figure 4 shows variation of binding energy of each component after exposing to electron and ion beam on phosphor layer. Here, note that source of ions was Ar ions from RF-ion gun (Density~ 3 x 10^{13} Ar ions/S. cm^2). In case of ion bombardment, Zn-O bonding was observed to be destroyed. Obviously, the active ions and electron bombardment can give damage to the phosphor and such damages have the influence to the luminescence of the phosphor.. SEM analysis also showed the change of the surface state of the phosphor after exposing to electron and ion beam.

Figure 5 shows the surface morphology of $Zn_2SiO_4:Mn^{2+}$ phosphor after exposing to electron and ion beam. The case of the sample which exposed ion beam, surface of phosphor was sputtered heavily. Once the phosphor was damaged, color purity as well as luminance of each cell was changed.

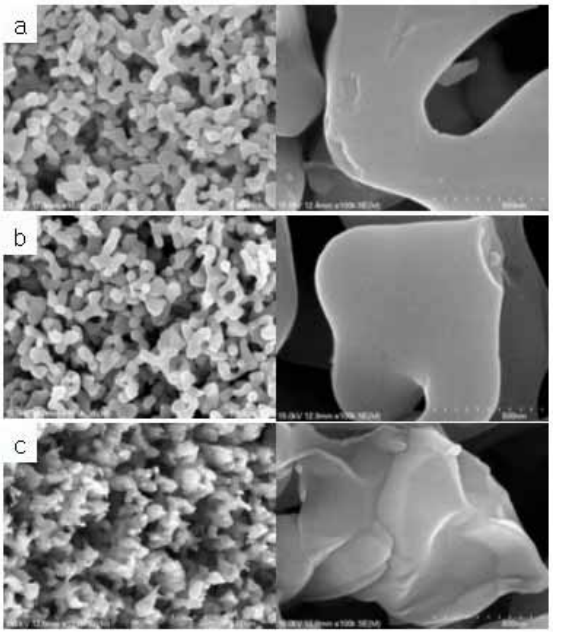

Figure 5. The change of the SEM micrographs after exposed to the electron and ion beam.

(a) The surface state of raw $Zn_2SiO_4:Mn^{2+}$ phosphor

(b) The change of the surface state after exposed to the electron beam on $Zn_2SiO_4:Mn^{2+}$ phosphor

(c) The change of the surface state after exposed to the ion beam on $Zn_2SiO_4:Mn^{2+}$ phosphor

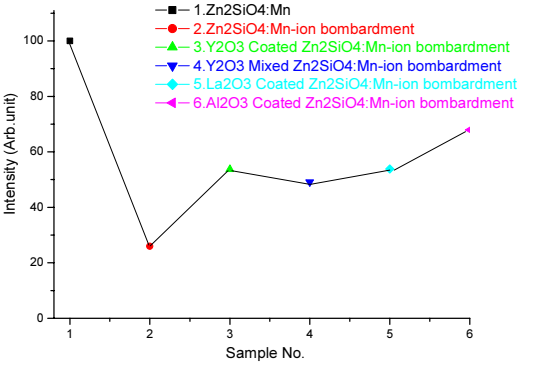

Figure 6. The change of the luminance of the phosphors which were exposed to the ion beams

Figure 6 shows the change of luminance of green phosphors which were exposed to the ion beam. The case of Al_2O_3 coated $Zn_2SiO_4:Mn^{2+}$ phosphor was the best from the longevity point of view.

4. Conclusion

For coated $Zn_2SiO_4:Mn^{2+}$, aging characteristics were examined under the electron and ion bombardment in order to identify the key attribute that has the influence on the picture quality in PDP cell. More works had put on the checking the stability of coated-phosphors under our previous work that coated $Zn_2SiO_4:Mn^{2+}$ phosphor with the positively charged metal oxide can be very helpful for uniform discharging in green cell. The factors that influence the damage of phosphors are divided by ion bombardment, electron collision and VUV excitation. The damaged samples are investigated by XPS and Auger analysis. As of now, Al_2O_3 coated $Zn_2SiO_4:Mn^{2+}$ was found to be very stable. After checking out these stability issues, we believe that the coated- phosphors could be applied to the panel. More quantitative analysis needs to simulate the Green cell. Also the influences of vacuum UV are under study.

5. Reference

[1] M. Tamatani, *J. Lumin*., 100, 317 (2002)

[2] S. J. Yoon, Y. K. Jung, J. W. Seo, B. H. Lee, Y. H. Kim and K.W. Whang, *Displays*, 23, 183 (2002)

[3] G. Y. Hong, B. Y. Jeoung, B. S. Jeon and J. S .Yoo, *J. Electrochem. Soc*, 151, (10) H205-H209 (2004)

[4] B. W. Jeoung, G. Y. Hong, B. Y. Han and J. S. Yoo, *Jpn. J. Appl. Phys*., 43, No 12, 7997-8001 (2004)

[5] B. Y. Han, B. W. Jeoung, G. Y. Hong and J. S. Yoo: *IMID'04* (2004) p. 575-578

[6] B. Y. Han, J. S. Yoo: *IMID'05* (2005) p. 1262-1265