

Analysis of Enhancement in Phosphor Performance induced by Surface Treatments

Duk Young Jeon, Sergey A. Bukesov, Jin Young Kim, Zin-Min Park, and Dong Chin Lee
Dept. of Materials Sci. and Eng., Korea Advanced Institute of Sci. & Tech.
373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, Republic of Korea
TEL : +82-42-869-3337, FAX : +82-42-869-3310
e-mail : dyj@kaist.ac.kr

Abstract

A search for a new phosphor composition of excellent performance in systematic ways requires lots of research efforts, and often turns out to be very time-consuming and difficult. Thus, usually practical ways are taken to improve the performance of phosphors. A few examples of practical surface treatments on phosphors such as In_2O_3 coating on $\text{ZnGa}_2\text{O}_4:\text{Mn}$, phosphoric acid treatment on $\text{ZnS}:\text{Ag},\text{Cl}$, and base KOH treatment with ultrasonication on $\text{ZnS}:\text{Ag},\text{Cl}$ are presented. The reasons for the improvement of luminescence intensity or degradation properties after these treatments are discussed based upon careful analyses on the surface of the phosphors and a proposed model on charge carriers generated by electron beam excitation.

1. Introduction

High definition and large size screen displays have been attracting lots of attention. For the display devices larger than 40 inch, PDPs become dominant. CNT-based FED is also being developed, which possibly targets the market of large size displays. These two types of displays are believed to have a better color presentation than that of LCD. The better color presentation is provided by luminescence properties of phosphors, i.e. their intensities and color coordinates.

In principle one could design a high performance phosphor using a combination of modeling and experiment. However, such a development is usually time-consuming and very difficult. The example of such a development of phosphor is the combinatorial synthesis of phosphors [1]. Therefore, it is often the case that one improve the performance of phosphors

by relying on some practical methods, for example, modifying the surface of phosphors.

For both FED phosphors and PDP phosphors, the excitation sources penetrate only into the surface layer of phosphors. Thus, one can improve the performance of phosphors by either eliminating the surface layer which includes a lot of defects or passivating the surface of phosphors. Some surface treatment techniques are effective in improving the performance of phosphors, however, the detailed mechanisms of improvement are often not known.

In this study, some surface treatment techniques are revisited. The modified surfaces were analyzed by a few of analytical techniques. And it is attempted that the enhancement of cathodoluminescence after surface treatment is explained by a model that describe the possible behavior of the non-equilibrium carriers generated by electron beam under the surface layer.

2. Experimental setup

Cathodoluminescence (CL) measurement system - a vacuum chamber that employed a thermionic electron gun (Kimball Physics, FRA-2X1-2/EGPS-2X1) was used. For CL measurements, the electron accelerating voltage from 300 to 1000 V, the excitation current density from 60 to 100 $\mu\text{A}/\text{cm}^2$, and the vacuum level of 1×10^{-7} Torr were used.

Photoluminescence (PL) measurement system - For PL measurements, 500W Xe lamp was used. This system was designed for measuring the photoluminescence of powder. The sample holders consist of holder, fixing cap, and pure quartz plate for fixing powder.

3. Results and Discussion

3-1. Nanoscale Continuous In₂O₃ Coating

Low voltage phosphor, ZnGa₂O₄:Mn manufactured by Samsung SDI company was used in this study. The In₂O₃ coatings on the phosphor surface were processed by sol-gel method, which allowed the most comprehensive control over the surface morphology. A coating process was reported in our previous paper [2]. As was reported in the publication, the optimum performance was obtained for a In₂O₃ concentration of 2 wt % and a solution temperature of 80 °C. Then, the coated phosphors were heated at 450 °C in air. The phosphor powder was applied on ITO glass by a screen-printing method.

Figure 1 shows the luminance of the as-received and the In₂O₃ (2 wt %)-coated ZnGa₂O₄:Mn phosphors as a function of excitation voltage, together with that of the phosphor mixed with In₂O₃ powder of 15 wt %. As shown in this figure, the effect of both In₂O₃ coating and mixing on the CL of ZnGa₂O₄:Mn phosphors increased the luminance of low voltage CL markedly. The reason for this increase is known to be that the conducting material provides the charges charged up on the surface of the phosphor with some sort of conductive path, which lacks an exact description at the present time.

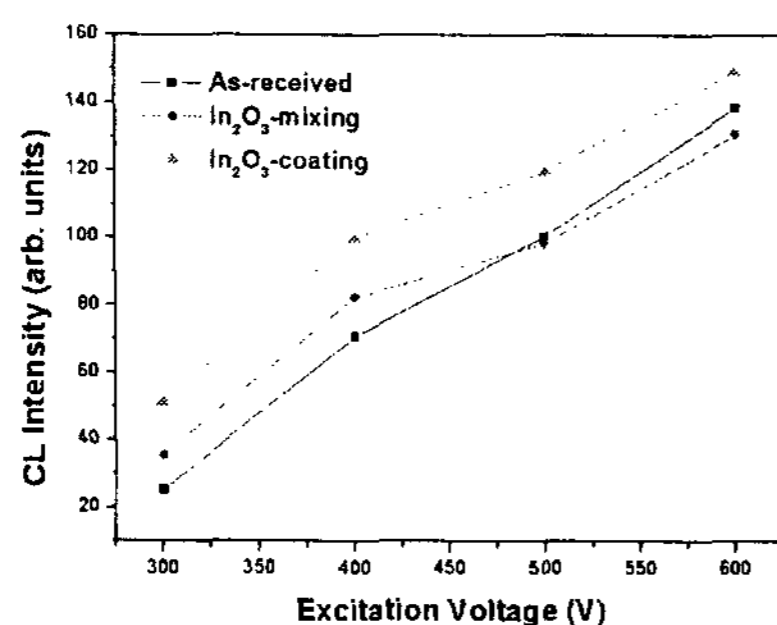


Figure 1. Luminance of ZnGa₂O₄:Mn phosphor before, after In₂O₃ coating, and with In₂O₃ mixing as a function of accelerating voltage. ($\lambda_{\text{emission}} = 440 \text{ nm}$)

Figure 2 shows the CL intensity as a function of time for 800 eV electron accelerating with an average current density of 100 $\mu\text{A}/\text{cm}^2$ for the In₂O₃-mixed and the In₂O₃-coated phosphor screens. As shown in this figure, at the completion of the accelerated aging experiments, the final relative CL intensities of the In₂O₃-coated phosphors were much higher than those of the In₂O₃-mixed counterpart. This result suggests that the coating on the phosphor surface by In₂O₃ layer suppresses the aging rate of the low voltage CL efficiency.

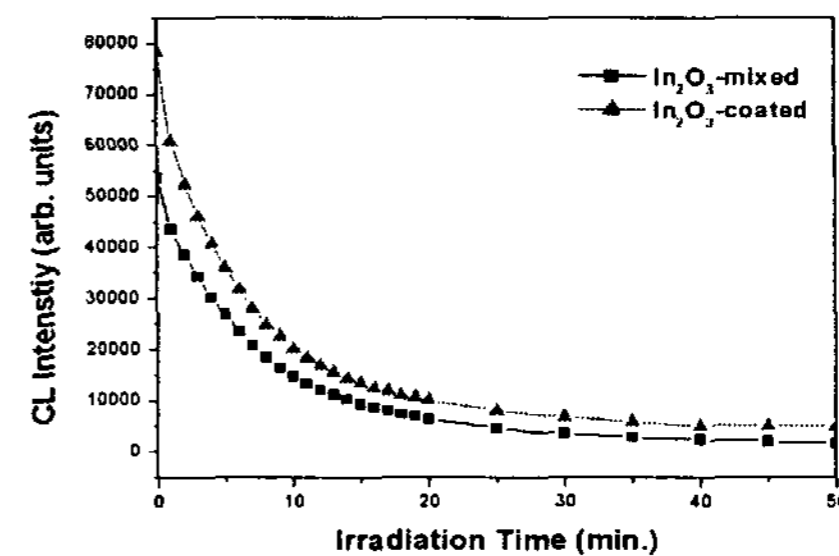


Figure 2. Comparison of CL degradation behavior of In₂O₃-mixed and In₂O₃-coated ZnGa₂O₄:Mn phosphor screens

In this study, a nanoscale continuous coating of In₂O₃ on phosphors for low voltage display applications, in which the electrical conductivity of phosphor screen plays a major role, was proposed. The effect of In₂O₃ coating by sol-gel method on the CL of ZnGa₂O₄:Mn phosphors improves the intensity of low voltage CL noticeably, compared with that of In₂O₃ mixing. It is understood that electrically conductive channels are formed by much smaller amount of In₂O₃ addition than that of In₂O₃ mixing. Especially, the formation of uniform nanoscale continuous In₂O₃ layers on the phosphor surface was confirmed. In result, the nanoscale encapsulation of In₂O₃ layers on phosphors served as protective layers retarding the CL degradation introduced by the low energy electron irradiation, which is critically important for the development of the low voltage display applications.

3-2. Acid treatment

A phosphor screen is exposed to a thermal process during the sealing of a FED panel using frit, and the thermal process causes degradation of the phosphor screen in FED panel [3,4]. The surface reactions that occur during the thermal process result in the formation of non-luminescent ZnO layer which is responsible for CL degradation of phosphor screen [4,5]. So, it is desirable to suppress the formation of ZnO layers.

Commercially available blue-emitting ZnS:Ag,Cl phosphor were used and the phosphor particles were treated with aqueous solutions of phosphoric acid, controlled in a wide range of hydrogen ion concentration (pH). The phosphor screened samples (phosphor particles on ITO glass) were prepared by electrophoretic deposition after acid treatment and they were followed by a thermal process, which was

carried out at 420 °C taken in the actual panel sealing process.

The luminescence data of phosphor screen were obtained with CL and PL measurements before and after the thermal process.

One of the main origins of CL degradation of phosphor screen in panel sealing environment is the formation of ZnO layer on the surface of phosphor screen due to the processing temperature. In order to suppress the oxygen adsorption, a surface modification of phosphor particles was performed with aqueous solution of phosphoric acid. Figure 3 shows the PL spectra of ZnS:Ag,Cl powder before and after acid treatment with various pH conditions of acid solution. All acid-treated phosphors showed higher PL intensities than non-treated phosphor sample, and the largest of increased PL intensity was shown in the case of phosphor treated with acid solution of pH 3.0. However, it is of much importance that the CL intensity and color purity of phosphor screen is maintained or improved even after the heat treatment, considering the thermal process of FED panel packaging. So we measured the CL of the acid-treated phosphor screen samples before and after the heat treatment.

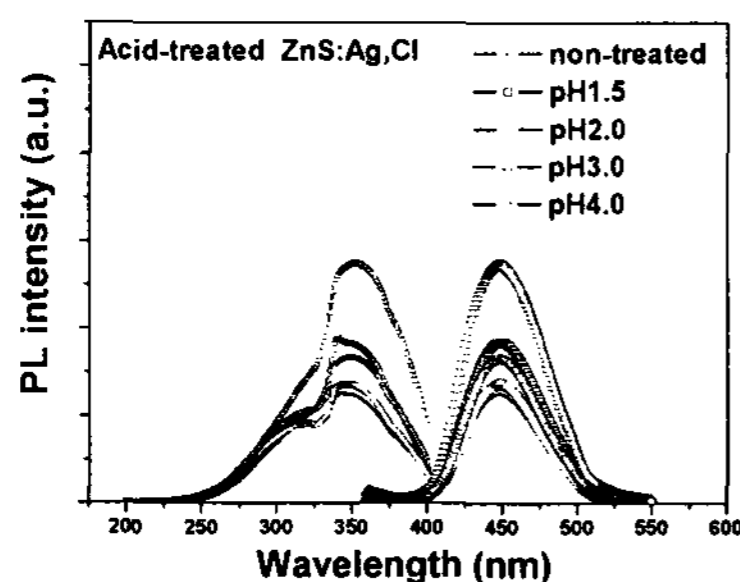


Figure 3. PL excitation and emission spectra of ZnS:Ag,Cl powders treated with phosphoric acid.

3-3. Base treatment using ultrasonication

The surface treatment on the phosphor was performed in glass beakers filled with KOH solutions (~pH 13) on an ultrasonicator (Branson 2210R-DTH). Unlike normal ultrasonication, mechanical stirring (300~500 rpm) was performed to homogenize a concentration of KOH in a glass beaker at the same time with ultrasonication. After that, the treated phosphor powders were filtered and washed with distilled water, and dried in a convection oven at 120 °C for 24 hours.

The cathodoluminescent behavior of ZnS:Ag,Cl treated by a combination of stirring and ultrasonication (SUST) in KOH solution is illustrated in Fig. 4. L. Spanhel et al. reported in his study that the fluorescent intensity of ZnS nano-sized powder was drastically increased by covering its surface with Cd(OH)₂, and this hydroxide layer introduced higher electrical conductivity on the surface of sulfide materials [6]. From their study, it can be expected that the increase in electrical conductivity due to adsorbed OH⁻ ions leads to enhancement of luminescent property of CL phosphors. It is supported in Figure 4.

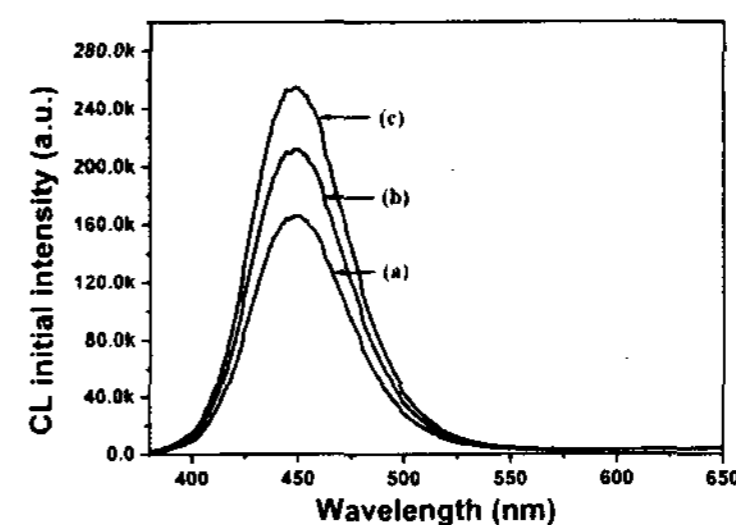


Figure 4. CL results of ZnS:Ag,Cl phosphor (a) non-treated sample, (b) treated sample with SUST in only distilled water for 1 hour, and (c) treated sample with SUST in KOH solutions for 1 hour.

The CL efficiency of the treated ZnS:Ag,Cl sample dramatically increases by 58% higher than that of the non-treated sample. Also, this amount of increase is higher than that obtained by only using ultrasonication in distilled water [7]. These spectra demonstrate that SUST has higher effects than normal ultrasonication does on CL efficiency.

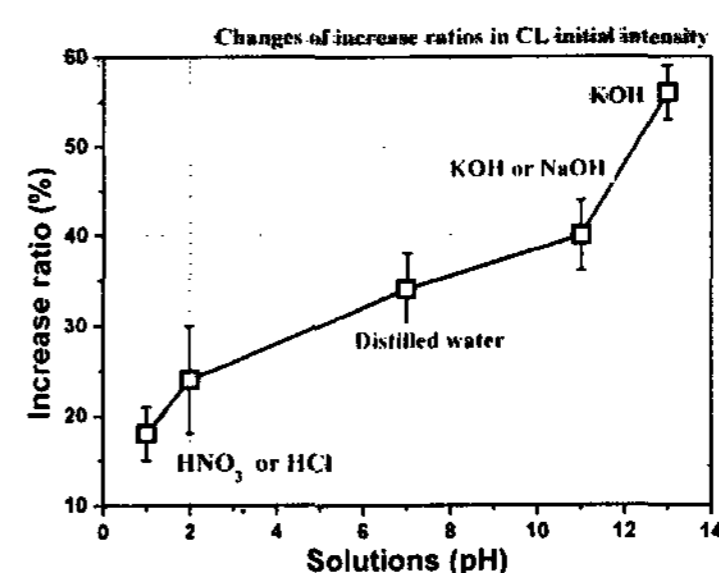


Figure 5. Changes in CL efficiency depending upon pH variation of various solutions.

Figure 5 shows a tendency about increase of CL efficiency increased by SUST. Various solutions from acids to base solutions were used in SUST. The sample treated in KOH solutions, which has higher pH

than other solutions do, showed a maximum CL increase ratio.

From aforementioned data, we confirmed that $\text{Zn}(\text{OH})_2$ layer was formed after SUST in KOH solutions and would like to discuss the mechanism about enhancement of CL efficiency due to SUST.

The recombination processes in a real phosphor surface are non-radiative because this region is saturated by various defects and contaminations. The thickness of this “dead” layer is several tens of nanometers [8]. Treatment of phosphor surface by weak solutions of some acids or bases is an effective method for their improvement [8,9] It usually removes the defective (dead) layer from the phosphor surface. But our results show that chemical composition of the phosphor were not improved after SUST treatment.

3-4. Model for Enhancement of CL

As the main reason of the CL efficiency improvement observed after SUST done for $\text{ZnS}:\text{Ag},\text{Cl}$, we propose an improvement of migration conditions of nonequilibrium charge carriers to the bulk region of the phosphor particles [10].

Primary bombarding electrons convert their energy to the luminescent light through three stages [11].

- 1) The energy of electron excitation is absorbed by phosphor matrix with the birth of the nonequilibrium charge carriers
- 2) The nonequilibrium charge carriers migrate to the bulk luminescent centers
- 3) They recombine radiatively, with emission of luminescent light.

All these stages are separated in space as well as in time. The first one proceeds in a thin layer of phosphor surface. The thickness of this layer is determined by penetration depth of primary electrons, the value comparable with the “dead” layer depth, at low voltage range. The second stage (migration of the nonequilibrium charge carriers) allows the nonequilibrium carriers to reach the bulk, less-defective regions of phosphor particle, where a probability of radiative recombination is higher. The migration processes are less important for PL and high voltage CL, because the penetration depths of these types of excitations are much deeper than that of low voltage CL. The influence of surface layer on recombination processes of nonequilibrium charge carriers is negligible in this case. Therefore, the

effective way of improvement of CL characteristics of phosphor at low voltages is accelerating the nonequilibrium charge carriers to the bulk of a phosphor particle.

Now, we explain the influence of SUST on the CL characteristics of $\text{ZnS}:\text{Ag},\text{Cl}$ phosphor based on the effect of electrical fields formed on the phosphor surface.

The electrical fields on the phosphor surface are induced by the static charge of OH^- ions. The latter (OH^- ions) formed in the thin layer of the phosphor surface after SUST. The investigated $\text{ZnS}:\text{Ag},\text{Cl}$ phosphor is an n-type semiconductor. The surface region of this material is schematically presented in Figure 6.

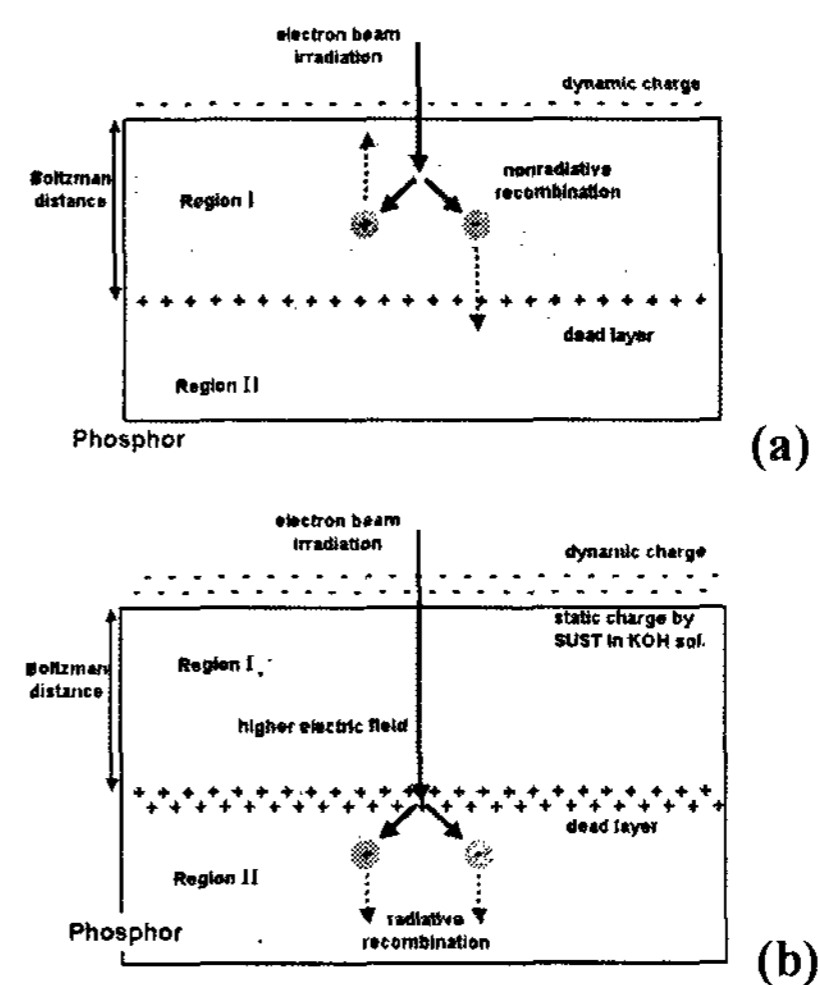


Figure 6. Phosphor surface for n-type semiconductor, ZnS [12]. (a) electrical field accelerates holes to the phosphor surface and (b) electric field accelerates holes to the phosphor bulk by formed static charges

The electrical field in the region I (Figure 6 (a)) accelerates nonequilibrium holes to the phosphor surface that reduces the probability of radiative recombinations. In the region II, the electrical field accelerates holes, which diffuse to the phosphor bulk and the efficiency of low voltage CL is increased (Figure 6 (b)).

Table. 1 shows calculated values of recombination parameters for non-treated and SUST treated $\text{ZnS}:\text{Ag},\text{Cl}$ phosphor. The obtained parameters are determined from experimental data based on the method described in literature of S. A. Bukesov [10]. The diffusion-drift length of the non-equilibrium charge carriers move to the phosphor surface is