The Effects of Surface Treatment for ZnS:Ag,Cl Using a Combination of Stirring and Ultrasonication in KOH Solutions

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A commercially available blue emitting ZnS:Ag,Cl phosphor was surface-treated with a combination of stirring and ultrasonication in KOH solutions. The stirring and ultrasonication (SUST) enhanced the cathodoluminescence efficiency by 58%. From surface analyses, it was confirmed that OH^- ions were physisorbed on the surface of the phosphor, and they formed an additional electrical field on the surface into the E-beam induced field present in cathodoluminescent mode of operation. We observed that the maximum increase of phosphor efficiency at low applied voltages was around 800 V, that the recombination rate of the nonequilibrium charge carriers increased over two times, and that the diffusion-drift length was reduced after SUST. This can be explained by the formation of the increased electrical fields induced by physisorbed OH^- ions on the phosphor surface.
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To enhance the cathodoluminescence (CL) intensity of many phosphors, various surface modifications of phosphors have been attempted, for example, electrically conducting materials are coated on or mixed with a phosphor surface.[1,2] It is known that surface modification is the most well known and easiest method for improving luminescent efficiency of phosphors. In this regard, ultrasonication is attractive because it leads to high luminescence property of phosphor powders.

When an ultrasonic wave passes through a liquid medium, a large number of microbubbles form, grow, and collapse in a very short time of about a few microseconds, and that is called ultrasonication. Ultrasonication can increase local temperatures as high as 5000 K and local pressures as high as 500 atmospheres with heating and cooling rates greater than 10^9 K/s, a very rigorous environment.[3] Therefore, it has been extensively applied to dispersion, emulsifying, crushing, and activation of particles.

In addition, it has been reported that ultrasonication leads to a coupling of the ultrasonic vibrations with extended crystal defects such as dislocations, grain boundaries, and precipitates. It interacts with point defects from both impurity and native origins, such as vacancies and self-interstitials. Being absorbed at extended defects, ultrasonic vibrations trigger defect reactions. Therefore, ultrasonication has been realized as a method of defect engineering in phosphors that increases luminescent efficiency.[4]

On the other hand, many researchers have used a surface treatment to obtain high luminescence of phosphor using chemicals. In particular, it is known that surface treatment using acid or hydroxide increases luminescence by cleaning the surface of phosphors.[5-7]

However, the above methods have limitations for improving the luminescence of phosphors and we would like to find a new method for improving the CL intensity of phosphors. In this study, we have attempted to obtain higher CL intensity of ZnS:Ag,Cl through surface modification by using a combination of ultrasonication and surface treatment with hydroxide solution, especially potassium hydroxide (KOH), and then verify the reasons for the enhancement of its luminescence if possible.

Experimental

Commercially available blue phosphors, ZnS:Ag,Cl (P22B), were used in this study. The ultrasonication on the phosphor was conducted as follows. KOH (0.2 g) was added to distilled water (250 mL) and mechanically stirred for 10 min. To fix the pH value of KOH solution, measurement of the pH value was conducted using a

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pH meter (Orion 720A). Subsequently, ZnS:Ag,Cl phosphor powders (3 g) were added to the KOH solution in a glass beaker and the ultrasonication on the phosphor was performed on an ultrasonicator (Branson 2210R-DTH). To prevent the powder from settling, a mechanical stirring (300-500 rpm) was conducted in addition to 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 h.

In order to analyze the surface of the phosphor, scanning electron microscopy (SEM), Auger electron spectroscopy (AES), and infrared (IR) transmittance spectroscopy were performed. AES measurements were done in an ultrahigh vacuum (UHV) system (PHI model 670) using electrons with a beam voltage of 1 keV and a continuous current of 0.0038 μA. For IR transmittance, samples in the form of pellets were prepared by mixing the phosphor with KBr powders to 5 wt % and drying at 100°C in a vacuum oven overnight. IR transmittance was obtained in dry air at room temperature using IR transmittance measurement system (Bruker IFS 66).

To investigate optical properties, photoluminescence (PL) was measured using a photon counting spectrometer (ISS PC1) operated at 500 W. Cathodoluminescence (CL) was measured at a beam current density of 60 μA/cm^2 and an excitation energy of 500-1000 eV using a Kimball Physics FRA-2X1-2/EGPS-2X1 electron gun (E-gun) system. The E-gun system was installed in a demountable ultrahigh vacuum chamber equipped with an in-house assembled CL spectrophotometer. All luminescence measurements were conducted on powder samples.

Results and Discussion

The cathodoluminescent behavior of ZnS:Ag,Cl treated by stirring and ultrasonication (SUST) is illustrated in Fig. 1. It shows the results of nontreated and treated samples by SUST in distilled water and KOH solution, respectively. The CL intensity of the phosphor powder was increased when it was treated by SUST. It was observed that SUST in KOH solution showed an even higher increase ratio of CL intensity than one in distilled water. The maximum increase ratio was 58%, and this is the highest value among recent studies for ZnS:Ag,Cl.[7-11]

To analyze the detailed changes induced by SUST, PL and photoluminescence excitation (PLE) were attempted. From PLE measurements, the excitation wavelength was determined at 330 nm and PL spectra were obtained. Figure 2 shows the PL spectra of nontreated and SUST-treated samples, respectively. As shown in Fig. 2, it is observed that the PL property of ZnS:Ag,Cl was not changed at all after SUST. It is clearly different from the behavior of the CL spectra in which the change of intensity was detected, as shown in
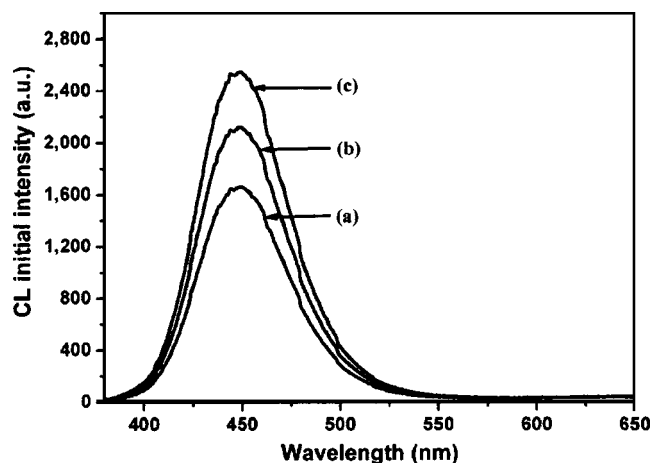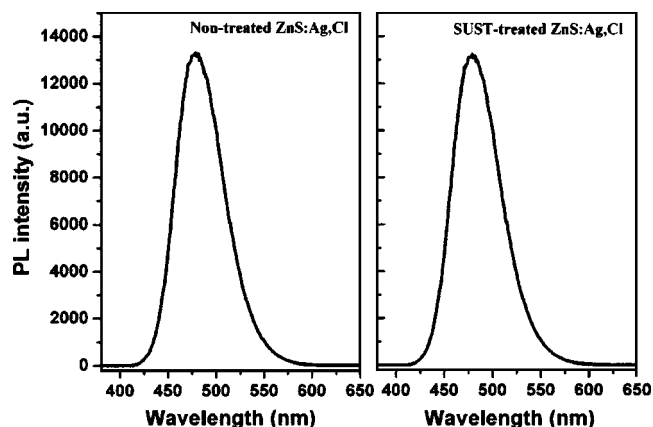
Figure 1. CL spectra of ZnS:Ag,Cl phosphor (a) nontreated sample, (b) SUST-treated sample in distilled water for 1 h, and (c) SUST-treated sample in KOH solutions for 1 h.

Fig. 1. From the previous studies on the effect of the coated layer on ZnS:Ag,Cl,[12] we can reasonably expect that if SUST forms a coated layer on the phosphor, a shift and intensity change of PL emission can be observed. However, in our results, these did not occur after SUST. From this, we expect that SUST in KOH solution did not give rise to a coated layer such as, for example, ZnO on the surface of phosphor.

To understand the origin of the luminescent property of the phosphor after SUST, several analyses for surface morphology, for example, SEM, TEM and particle size analysis, were performed on both nontreated and SUST-treated phosphors. However, we could not observe any change on the afore-mentioned analyses.

As a trivial matter, in SEM analysis, it appeared that many small size particles, formed by using flux during synthesis, were removed from the phosphor. This probably results from the cleaning effect of KOH solutions.[13]

To characterize the surface of the phosphor in detail, the compositional change in the surface layer was investigated using AES. Figure 3a and b show depth-profile results of AES for both the nontreated and the SUST-treated phosphors. In all samples, the elements, such as zinc, sulfur, and carbon were detected. On the other hand, potassium from the KOH solutions was not detected, even in the SUST-treated samples. This means that potassium was almost washed out due to washing with distilled water in the SUST process, and the concentration change in potassium does not affect the luminescent property of SUST-treated phosphor. Surprisingly, high con-

Figure 2. PL spectra of ZnS:Ag,Cl phosphor (left, nontreated sample; right, SUST-treated sample in KOH solutions for 1 h. Excitation source 330 nm).
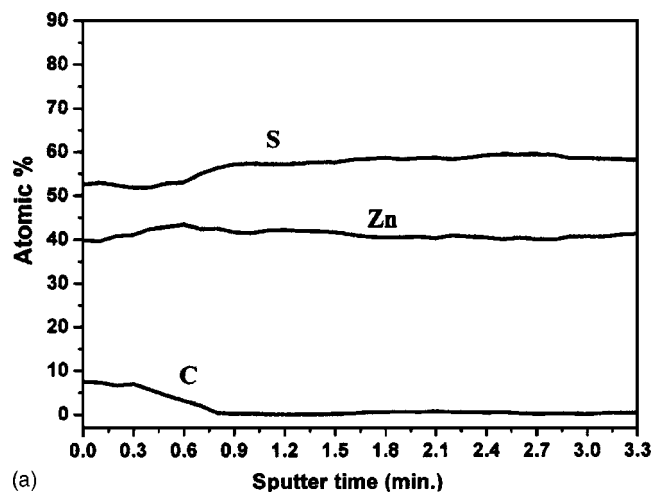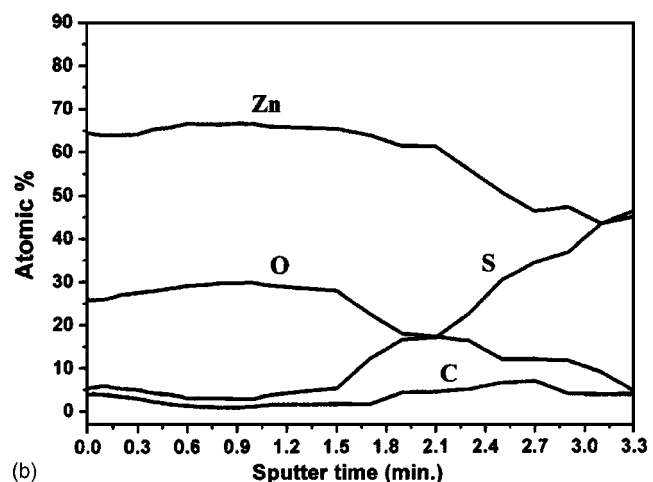

Figure 3. Auger depth profiles of elements in ZnS:Ag,Cl phosphor (a) the nontreated sample and (b) the treated sample with SUST in KOH solutions for 1 h.

tents of oxygen were detected in the SUST-treated phosphor as shown Fig. 3b. Although the change on concentration was observed, this information does not give us any information on the exact state of oxygen present on the surface of phosphor. Therefore, we attempted to analyze this definitely.

First of all, we can expect that the oxygen formed by SUST reacts with ZnS and new compounds such as ZnO can be formed, although the PL spectra implied that ZnO did not form on the surface of the phosphor. As a matter of fact, Swart *et al.* reported that a ZnO layer formed on the surface of ZnS:Ag,Cl.[8,9] Also, a previous study by Park *et al.*[14] showed that a coated layer led to a 60% enhancement in CL efficiency. In these studies, it was reported that the ZnO layer formed from electron bombardment on the phosphor surface deteriorated CL degradation property. According to these results, we arrived at this issue, if we measure CL degradation property of ZnS:Ag,Cl phosphor after SUST, we can learn whether ZnO was formed or not on the surface of the phosphor. To confirm this, the CL degradation property of the phosphor after SUST was measured.

Figure 4 shows the normalized CL intensity as a function of time under 700 V electron excitation with an average current density of 60 μA/cm^2 for the nontreated and the SUST-treated ZnS:Ag,Cl. Figure 4a shows the normalized CL intensity of the nontreated phosphor, and b is the SUST-treated for 1 h. At the completion of the accelerated aging experiments, the final relative CL intensities for (a) and (b) were 19 and 21% of their initial values, respectively. It is
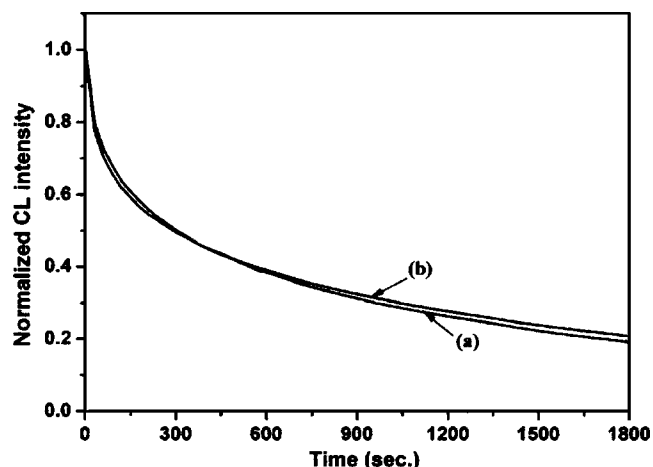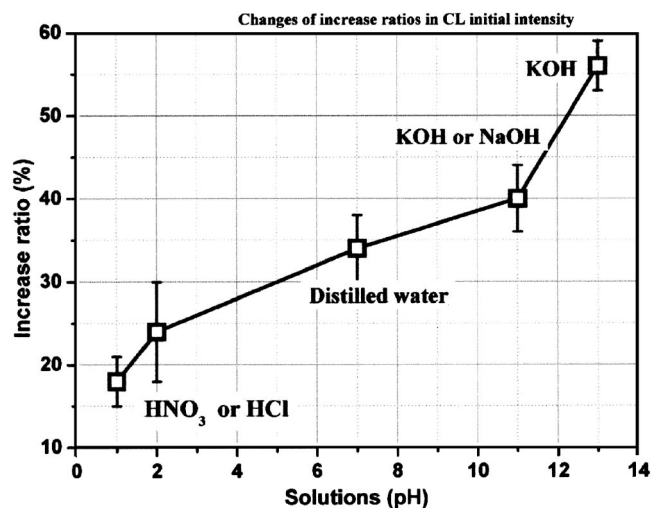
Figure 4. Normalized CL intensity at 700 V, 60 $\mu A/cm^2$ of ZnS:Ag,Cl phosphors as a function of time: (a) the nontreated solution (b) the SUST-treated solution in KOH solution for 1 h.

Figure 6. Infrared spectra of ZnS:Ag,Cl phosphor (a) nontreated sample, (b) treated sample with SUST in KOH solutions for 1 h, and (c) treated sample with SUST in KOH solutions for 6 h.
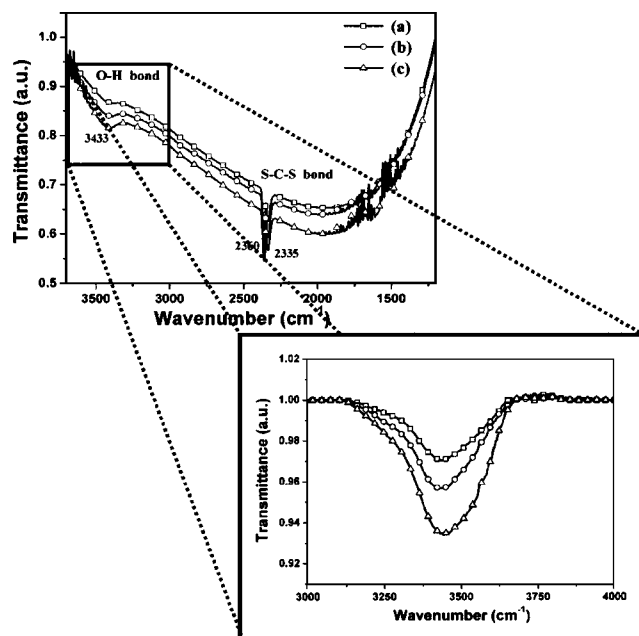
apparent that there is no difference in CL degradation property between the nontreated and the SUST-treated ZnS:Ag,Cl and the SUST does not change the CL degradation property of ZnS:Ag,Cl. From this result, we know that ZnO was not formed on the surface of phosphor.

If the surface of the phosphor does not contain ZnO, what is the exact state of the oxygen observed on the surface after SUST? To answer this question, the CL intensity was observed as a function of the pH of the treating solutions. Figure 5 shows changes of increase ratios in CL intensity. As shown, in all pH solutions that we used, all SUST-treated phosphors showed increases of CL intensity. Especially, a tendency was observed-the higher the pH of solution is, the higher the CL ratio increase is. This means that the CL improvement of ZnS:Ag,Cl after SUST depends on the pH of the treating solution, in other words, H^+ or OH^- ions in the solutions. To verify this, infrared (IR) transmittance spectroscopy was done to find out the change of amounts of H^+ or OH^- ions on the surface of the phosphors because IR transmittance spectroscopy is well known as a useful analysis for H^+ or OH^-.[15]

Surprisingly, from IR transmittance spectroscopy for the SUST-treated phosphor, a physisorbed absorption peak of OH^- was observed ($\sim$3433 cm^{-1}). This is only for the physical bond of OH^-

and approximately in accordance with the absorption band for OH^- stretching vibration (3405-3419 cm^{-1}) that Gärd *et al.* reported in their study.[16] It was also observed that absorbance for the OH^- physisorption peak increased with SUST time as shown in the magnified inset in Fig. 6.

From IR transmittance spectroscopy, it was definitely shown that the amount of physisorbed OH^- ions was increased with SUST time. From these facts, it is reasonable to suppose that after SUST, OH^- ions physisorb on the surface of the ZnS:Ag,Cl phosphor and increase the CL efficiency of the phosphor. Because the ZnS:Ag,Cl phosphor is always Zn-deficient, it is conceivable that physisorbed OH^- ions form Zn^{2+}-2 OH^- double layers on the surface, similar to the protective oxidation of Si wafers,[17,18] and the CL intensity is increased by the formed Zn^{2+}-2 OH^- double layers with SUST time.

From Fig. 7, we also confirmed this suggestion. It shows normal-

Figure 5. Changes in CL efficiency depending upon pH variation of various solutions.
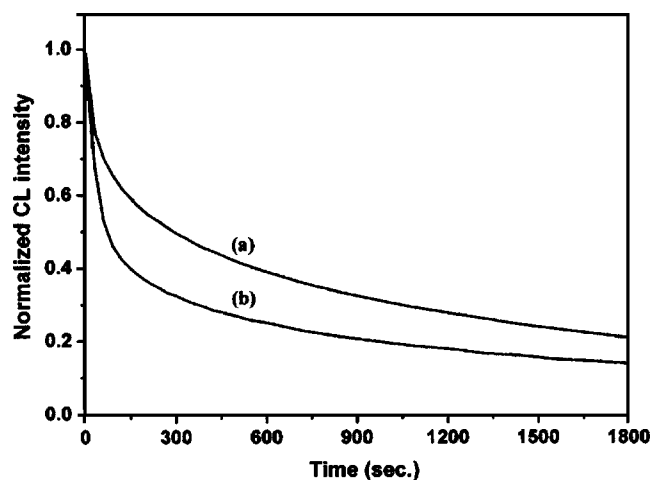
Figure 7. Normalized CL intensity at 700 V, 60 $\mu A/cm^2$ of ZnS:Ag,Cl phosphors as a function of time: (a) the SUST-treated in KOH solution for 1 h, and (b) heat-treated in (a) at 450°C for 1 h.
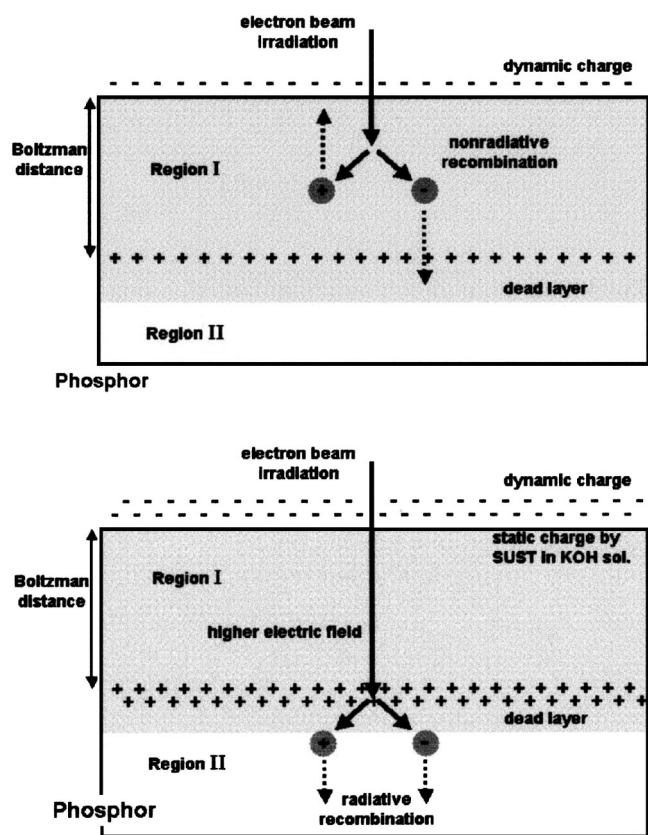
Figure 8. Phosphor surface for n-type semiconductor, ZnS,[21] where, p is the penetration depth of primary electrons, and d is the depth of the dead layer. (a) Electrical field accelerates holes in the phosphor surface and (b) electric field accelerates holes in the phosphor bulk by formed static charge.

ized CL intensity as a function of time under 700 V and 60 μA/cm^2 for the nontreated and the SUST-treated ZnS:Ag,Cl. In Fig. 7a is shown the normalized CL intensity of the SUST-treated ZnS:Ag,Cl in KOH solution for 1 h, and in Fig. 7b is the one with heat-treatment for 1 h at 450°C after SUST in KOH solution for 1 h in air. In Fig. 4, after SUST, ZnS:Ag,Cl phosphor showed no difference in CL degradation compared with the nontreated sample. However, with heat-treatment, serious degradation of CL intensity was observed. As Swart mentioned in his study,[9] this is related to the formation of ZnO on the surface of the ZnS:Ag,Cl phosphor. It is expected that Zn^{2+}-2 OH^- double layers were formed on the surface after SUST and with heat-treatment, ZnO was more easily formed. Figure 7, CL degradation property after heat-treatment, also clearly shows that SUST does not form ZnO compounds on the surface.

From several results as mentioned before, we realize that the SUST is powerful for improving CL efficiency of ZnS:Ag,Cl phosphor, and this results from the physisorbed OH^- ions on the surface. Already, many researchers have reported an effect of physisorbed double layers on the phosphor surface and also the mechanism for improving CL efficiency has been proposed.[19-21] Especially, Swart reported that if the electron beam was off for a period of time during the degradation process of ZnS:Ag,Cl, then as soon as the electron bombardment was resumed, the measured CL intensity was initially about 20% higher then before the beam was shut off.[9] This was from the charge built up on the surface of the phosphor and, in our findings it also resulted from the same phenomenon as his result which occurs by formed Zn^{2+}-2 OH^- physisorbed double layers.

Consulting their model, we propose our model, which is explained below and in Fig. 8. As the main reason of the CL efficiency improvement after SUST, we propose an improvement of migration

conditions of nonequilibrium charge carriers to the bulk region of the phosphor particles, based on the previous reports.[9,19-21]

Figure 8 shows the surface of the ZnS phosphor, which is known as an n-type semiconductor.[19] At low voltage CL, the generation of nonequilibrium charge carriers by the deacceleration of primary electrons proceeds in a thin surface layer, called a dead layer, which has a thickness of less than several tens of nanometers. Under this condition, the majority of recombinations are nonradiative, and diffusion and drift processes of electrons and holes become very important because the recombination rates are saturated by various defects and contaminations.[21]

Briefly, we can assume that primary bombarding electrons convert their energy to the luminescent light in three stages,[11,19] (*i*) the energy of electron excitation is absorbed by phosphor matrix with the birth of nonequilibrium charge carriers, (*ii*) the nonequilibrium charge carriers migrate to the bulk luminescent centers, and (*iii*) they recombine on these centers radiatively, with the emission of luminescent light.

All these stages are separated in space as well as in time. The first one proceeds in the dead layer of phosphor surface. The thickness of this layer is determined by the penetration depth of primary electrons, 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 recombinations is higher. The migration processes are not so important for PL and the high voltage CL because the penetration depths of these types in excitation are comparable with the phosphor grain size. The influence of the surface layer on recombination processes of nonequilibrium charge carriers is negligible in this case. Therefore, the effective way for improving CL characteristics of a phosphor at low voltages is accelerating the nonequilibrium charge carriers to the bulk of a phosphor particle.[19,21]

In our study, we confirmed that physisorbed OH^- ions, formed by SUST, increase the internal electrical field on the surface of ZnS:Ag,Cl phosphor. This shows the limitation of the CL increased ratio because the surface recombination rate has a saturation point in constant depth of surface due to the dead layer. In fact, Fig. 9b shows this result. In this figure, we observed the maximum increase of phosphor efficiency at low applied voltages. It shows that the best improvement of CL efficiency was achieved at 800 V rather than at a lower voltage range, and this means a critical depth related to OH^- adsorbed region.[20-22] It is clearly different from the result in the case of the coated layer with ZnO as reported in the previous studies.[11,14,15] On the other hand, it is consistent with the results by Gergely and Bukesov.[19,21] Therefore, we can propose this model as one of the main reasons of the CL efficiency improvement observed after SUST treatment for ZnS:Ag,Cl. Based on this model, we can explain the influence of SUST on the CL characteristics of the ZnS:Ag,Cl phosphor using the additional static electrical field formed by physisorbed OH^- ions.

Therefore, we can briefly explain the improvemed CL model based schematically on Fig. 8. Because the investigated ZnS:Ag,Cl phosphor is an n-type semiconductor, the electrical field in the surface region I (Fig. 8a) accelerates nonequilibrium holes to the phosphor surface that reduces the probability of radiative recombinations, in the case of the nontreated phosphor. On the other hand, in the case of the SUST-treated phosphor, SUST forms physisorbed OH^- ion layer on the surface of the phosphor and the formed OH^- layer gives a role of the additional static charged layer. The additional electrical field by static charged layer accelerates holes deeply inside, which diffuse to the phosphor bulk and increases the recombination rate. Finally, it leads to higher efficiency of low voltage CL in the region II (Fig. 8b).

To calibrate recombination parameters of phosphors, we used the reported equations to obtain recombination parameters from Fig. 9a in this study, as already reported.[19,21] They show changes of CL initial intensity of the nontreated and the SUST-treated phosphor at
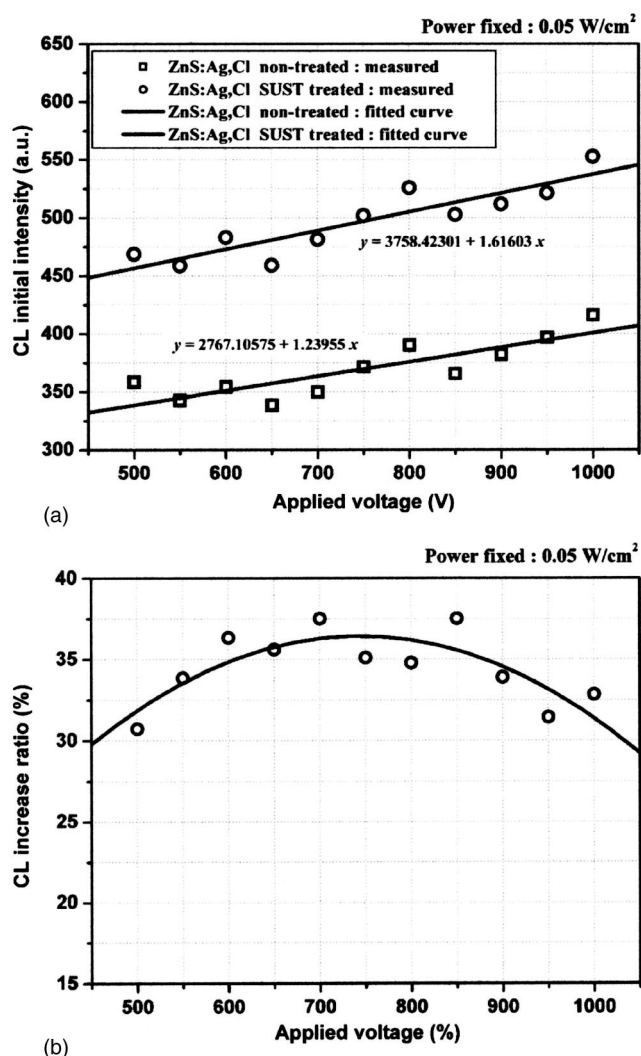
(a)

(b)

Figure 9. (a) Changes of CL initial intensity and (b) changes of increase ratio of CL of nontreated *vs.* treated samples at constant power of E gun (0.05 W/cm^2).

constant power of the E-gun. Both nontreated and SUST-treated phosphors showed almost a linear relationship with applied voltage. It is exactly consistent with results of the previous studies.

According to these observations, the proposed mechanism explains well the experimentally recorded characteristics of phosphors, as shown in Fig. 9b, after the SUST at different accelerating voltages of electrons. It is conceivable that the electrical field, which accelerates holes to the phosphor bulk, is formed at the distance comparable to the penetration depth of electrons with energy 800 V. This can explain the maximum increase of relative CL efficiency observed at 800 V.

Table I shows calculated values of recombination parameters for nontreated and SUST-treated ZnS:Ag,Cl phosphor, and the obtained parameters were determined from experimental data based on the method described in the works of Gergely[19] and Bukesov.[21] It was calculated that the recombination rate of the nonequilibrium charge carriers, which migrate toward the phosphor surface, increased over two times and the diffusion-drift length was reduced after SUST.

Table I. Recombination parameters calculated for nontreated and SUST-treated samples.

Phosphor	Recombination rate (cm^{-1})	Diffusion drift length (cm)
Nontreated	5.39×10^5	15.6×10^{-7}
SUST-treated	12.3×10^5	8.14×10^{-7}

This can be explained by the formation of the increased electrical fields induced by OH$^-$ ions on the phosphor surface.

Conclusions

The effects of the surface treatment by SUST in KOH solution, were investigated. It was found that the SUST did not change the surface morphology of ZnS:Ag,Cl phosphor, unlike normal ultrasonication, but it enhanced the CL efficiency by 58%. It was observed that OH$^-$ ions from the SUST process physisorbed on the surface layer, confirmed by AES and IR spectroscopy. After OH$^-$ ions physisorbed on the surface of the phosphor, they introduced an additional electrical field on the surface into the E-beam induced field, and it was clearly shown by a schematic diagram for the static charged surface of the phosphor.

We propose a model that can explain the enhanced CL efficiency. This model is based on the static charged layer from physisorbed OH$^-$ ions on the surface of the phosphor. When the E-beam bombards the surface, this static charge plays a role by increasing an internal electrical field and generated e$^-$-h$^+$ pair can recombine deeper inside the surface. We confirmed that this model is compatible with observing our results, such as the maximum increase of phosphor efficiency at low applied voltages around 800 V, the increased recombination rate of the nonequilibrium charge carriers over two times, and the reduced diffusion-drift length after SUST. Therefore, CL property improvement can be explained by using this model.

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