

# Thin SiO<sub>2</sub> coating on ZnS phosphors for improved low-voltage cathodoluminescence properties

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(Received 25 February 2000; accepted 10 August 2000)

A significant improvement (40–60%) was reported in the low voltage (100–1000V) cathodoluminescence efficiency of ZnS phosphors coated with SiO<sub>2</sub> by the sol-gel technique. The properties of the coatings were found to be critically dependent upon the precursor concentration, pH value and the temperature of the solution with optimum performance being obtained for a SiO<sub>2</sub> concentration of 1.0 wt%, pH values between 7–9, and a solution temperature of 83 °C. The efficiency curves exhibited a characteristic voltage dependence which was analyzed by a one-dimensional numerical model. Enhanced low voltage efficiency was attributed to a reduction of surface recombination and the actual shape of the efficiency curve was determined by the interplay between the reduction of surface recombination and energy losses in the SiO<sub>2</sub> coating.

The physical mechanism of phosphor excitation in the field emission display (FED) and conventional cathode ray tube (CRT) displays is the same. However, FEDs operate at much lower voltages, which makes it necessary to use higher current densities in order to maintain the same output luminance.<sup>1</sup> At low acceleration voltages, the electron penetration depth is small compared to the phosphor particle size, and therefore, phosphors exhibit low efficiency due to the loss processes associated with the surface. However, there are many advantages that can be achieved by very low voltage (<500 V) operation; more simple FED structures can be utilized because the need for focusing electrodes is eliminated, arcing is reduced, and switched anode operation becomes feasible. Low-voltage operation can also reduce electron beam stimulated chemical reactions which have been associated with phosphor and cathode degradation in FEDs.<sup>2</sup>

Because of the small penetration depth at low voltages, the loss processes are believed to be associated with surface recombination, and thus, the surface coating and encapsulation of phosphors is an important technique to improve low-voltage cathodoluminescence (CL) and chemical stability and to reduce outgassing. Coatings can

also reduce phosphor surface degradation (such as oxidation) associated with display fabrication processes thus reducing the surface dead-layer thickness and passivating surface recombination centers. Recently, Bechtel *et al.* reported a significant improvement in maintenance of ZnS:Ag by applying a thin calcium polyphosphate coating.<sup>3</sup> However, this work focused on the midvoltage region (approximately 4 kV) in which the surface effect is less critical. Also, no improvement in efficiency was reported. It is the aim of this paper to present a coating technique that can improve the CL efficiency at voltages less than 2 kV by reducing surface-related losses and at the same time protect the phosphors by completely encapsulating the phosphor particles. SiO<sub>2</sub> was used as the coating material because of its favorable band alignment when forming a heterojunction with ZnS.<sup>4</sup> Furthermore, SiO<sub>2</sub>, which consists of light elements and has low density, exhibits minimal losses in electron penetration and has a penetration depth nearly twice as large as ZnS. In the CRT manufacturing process, SiO<sub>2</sub> coating of ZnS phosphors is routinely performed to improve dispersion and adhesion properties.<sup>5</sup> However, this procedure results in noncontinuous particle-like coatings of SiO<sub>2</sub> microclusters<sup>6</sup> and any improvement in phosphor performance due to surface passivation is not expected. Therefore, this process is appropriate only for CRT displays operating at very high voltages (approximately 30 kV) where the phosphor performance is not sensitive to phosphor surfaces. For low-voltage phosphors, conductive

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coatings such as  $\text{In}_2\text{O}_3$  have mainly been investigated, which resulted in improved CL performance only at very low voltages ( $<400$  V).<sup>7</sup> In this paper, we present a technique for thin  $\text{SiO}_2$  coatings of ZnS which yielded a significant improvement in low-voltage CL efficiency. The experimental results were interpreted in terms of a 1-dimensional numerical model, which qualitatively reproduced the experimental CL efficiency curves, indicating that the observed enhancement was due to a reduction in surface recombination.

The  $\text{SiO}_2$  coatings on ZnS:Cu,Al were synthesized by the sol-gel method using tetraethyl orthosilicate (TEOS) as the precursor material. TEOS was first dissolved in an ethanol/water solution and refluxed at the boiling temperature ( $77^\circ\text{C}$ ) to ensure the completion of the hydrolysis reaction. At the completion of refluxing, ZnS phosphors were added to the solution and then dried in air. During this process, ZnS phosphors were immersed in the solution for 2–3 h. Then, the coated phosphors were fired at  $400^\circ\text{C}$  in air. The phosphors remained well powderized after firing, and no grinding was necessary. The sol-gel process has many variables, such as precursor concentration, solution pH, and temperature, that can affect the morphology of the coatings. Among these, the precursor concentration and the solution pH are the most important parameters controlling the hydrolysis reaction rate. First, the precursor concentration dependence was investigated for the  $\text{SiO}_2$  concentrations ranging from 0.5 to 5.0 wt%. The concentration represents the weight percentage of  $\text{SiO}_2$  compared to the ZnS phosphor. The scanning electron microscopy (SEM) micrographs showed smooth surfaces for all concentrations, except for the 5.0 wt% coating for which some agglomeration was observed. As shown in Figs. 1(a) and 1(b), the surfaces of uncoated and coated phosphors looked nearly the same although the coated phosphor had slightly smoother corners and edges. Figure 1(c) shows the transmission electron microscopy (TEM) image of the  $\text{SiO}_2$ -coated ZnS:Cu,Al phosphor. It is clearly seen that a thin and uniform  $\text{SiO}_2$  coating was formed on the ZnS particle.

The coating thickness was estimated to be 5 nm. The encapsulation of ZnS particles by  $\text{SiO}_2$  was also confirmed by etching the phosphors in a 50% HCl solution. The uncoated phosphors were etched rapidly, and the average particle size decreased from 7.0 to  $4.8\ \mu\text{m}$  in 10 min. However, the  $\text{SiO}_2$  (5.0 wt%) coated phosphors showed a much smaller decrease in particle size to  $6.2\ \mu\text{m}$ , showing that the coated phosphors were more resistant to the acid.

The intrinsic CL efficiency and spectral properties of the  $\text{SiO}_2$ -coated and uncoated phosphors were investigated between 100 V and 10 kV for a current density of  $1\ \mu\text{A}/\text{cm}^2$ . Figure 2 shows the relative CL efficiency of the  $\text{SiO}_2$ -coated phosphors as a function of voltage, in which the efficiency of the uncoated phosphor at a given voltage was set to be 100%. For all coated phosphors except for the 5.0 wt% coating, the CL efficiency was the same as the uncoated phosphors at high voltages but started to increase at voltages lower than 4 kV with the peak efficiency occurring between 500 V and 1 kV. Below 500 V, the efficiency decreased rapidly with decreasing voltage. The largest improvement of about 10% was observed at 1 kV for 1.0 wt% coating. The effect of adjusting solution pH values was then investigated by adding dilute acetic acid or ammonium hydroxide. Figure 3 shows the relative CL efficiency for various pH values while the  $\text{SiO}_2$  content was fixed at 1.0 wt%. The results clearly indicate that the best coating was formed for pH values between 7 and 9, which resulted in a very thin coating and consequently a 40% improvement at between 500 V and 1 kV. It should be noted that the spectral measurements showed the CIE chromaticity coordinates remained unchanged after coating, indicating that the observed enhancement was not due to the introduction of new luminescent centers. Finally, the effect of the reflux temperature was investigated. The coatings prepared with reflux temperatures lower than the boiling temperature of the solvent exhibited poorer performance showing a sharp decrease in efficiency at low voltages. Thus, the solvent was changed to 2-propanol, which boils

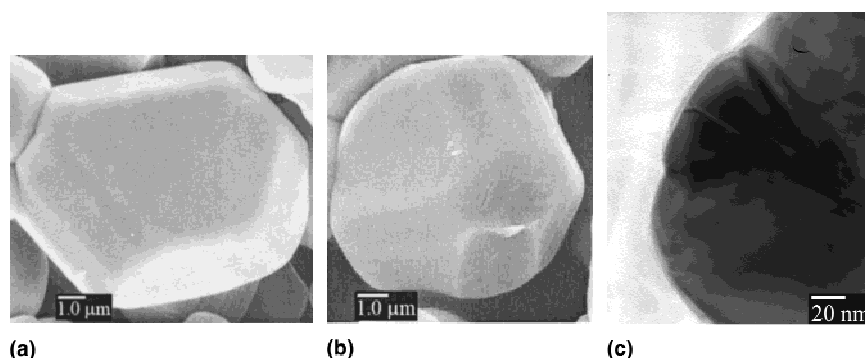


FIG. 1. SEM micrographs of (a) uncoated, (b)  $\text{SiO}_2$  (1.0 wt%) coated ZnS:Cu,Al phosphors and (c) TEM micrograph of  $\text{SiO}_2$  (1.0 wt%) coated ZnS:Cu,Al phosphor.

at 83 °C. Because the change of solvent is known to affect mainly the gelation process<sup>8</sup> and our system always remains as a clear solution due to the low concentration of TEOS, we believe that the biggest influence of changing solvents comes from the temperature in our case. Figure 4 shows the relative CL efficiency curves for the coatings prepared with  $T_{\text{reflux}} = 83$  °C. In contrast to the coatings prepared with ethanol, the relative efficiency continued to increase with decreasing voltages. As discussed later, this indicates that the effect of reduced sur-

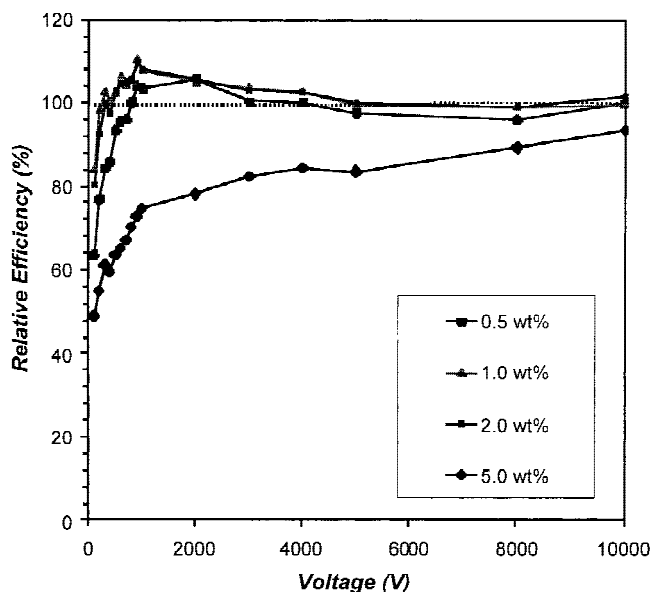


FIG. 2. Relative enhancement in CL efficiency as a function of voltage for  $\text{SiO}_2$ -coated  $\text{ZnS:Cu,Al}$  for coating concentrations ranging from 0.5 to 5.0 wt%.

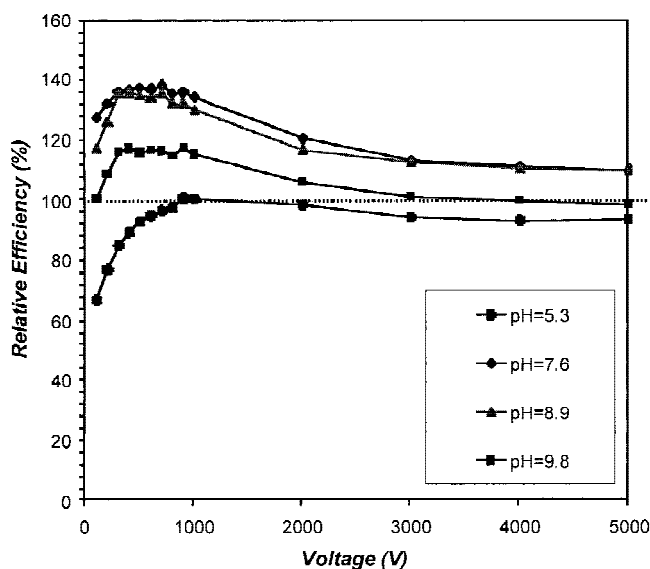


FIG. 3. Relative enhancement in CL efficiency as a function of voltage for  $\text{SiO}_2$ -coated  $\text{ZnS:Cu,Al}$  prepared for solution pH values ranging from 5.3 to 9.8 at a constant reflux temperature of 77 °C.

face recombination is more pronounced than the effect of penetration loss. The largest improvement of 60% over the uncoated phosphor was obtained at 100 V. The reflux temperature was further increased to 100 °C by using isobutanol as the solvent. At this temperature, however, the CL efficiency was either decreased or exhibited only a small improvement compared to the uncoated phosphor.

The results of these CL efficiency measurements were interpreted by considering two competing mechanisms. First, the observed improvement in CL efficiency at low voltages was attributed to the reduction in the surface recombination due to the  $\text{SiO}_2$  coating. Dielectric coatings such as  $\text{SiO}_2$  typically have energy band gaps larger than the semiconductor-like ZnS. Ban *et al.* showed that  $\text{SiO}_2$  forms a heterojunction with ZnS with nearly equal conduction band and valence band offsets of 2.4 and 2.8 eV, respectively.<sup>4</sup> The wide band gap  $\text{SiO}_2$  layer with a positive conduction band offset relative to ZnS is then expected to reflect the electrons generated by the incident electron beam from the defective high surface recombination velocity region back into the phosphor. It is also possible that the  $\text{SiO}_2$  could passivate surface recombination centers. In both cases, the surface recombination velocity will be reduced, resulting in an enhancement in the low-voltage CL efficiency. However, as can be seen from Figs. 2 and 3, all samples exhibited a decrease in the CL efficiency below 1 kV. This was attributed to the penetration loss of the electron beam in the nonluminescent  $\text{SiO}_2$  coatings. As the coating becomes thicker, the low-voltage CL efficiency will be progressively reduced until the effect of the penetration loss finally dominates. Thus, as shown in Fig. 2, the improvement achieved by

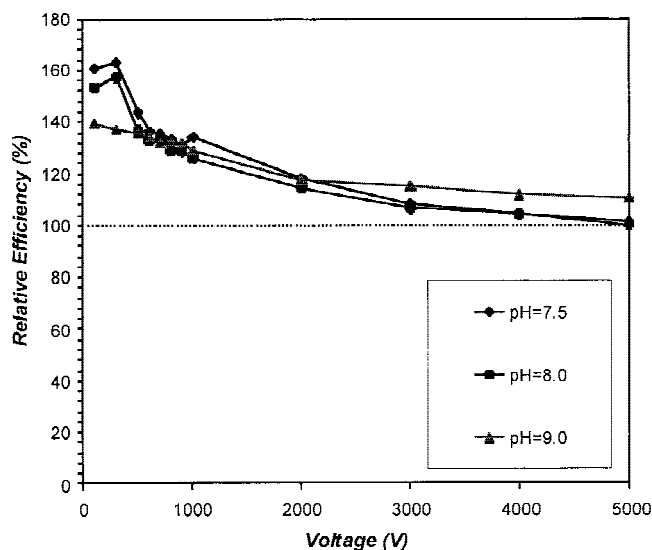


FIG. 4. Relative enhancement in CL efficiency as a function of voltage for  $\text{SiO}_2$ -coated  $\text{ZnS:Cu,Al}$  prepared at a reflux temperature of 83 °C.

reducing the surface recombination is completely offset and the CL efficiency exhibited a large decrease for the 5.0 wt% coating. The opposite extreme is shown in Fig. 4 for very thin coatings where the relative CL efficiency exhibited a monotonic increase with decreasing voltage. This is an indication that the coating thickness is so thin that the effect of reducing the surface recombination dominates over the penetration losses. On the other hand, the 0.5 wt% coating showed less of an improvement than the 1.0 wt% coating. This was attributed to incomplete surface coverage. From these results, it was concluded that the relative magnitude of the two competing mechanisms determines the shape of the actual CL efficiency curve and that a 1.0 wt% coating processed at pH values between 7 and 9 for  $T_{\text{reflux}} = 83^\circ\text{C}$  yielded a large improvement in the low-voltage CL efficiency.

To evaluate the effect of these heterojunction coatings upon CL efficiency, a 1-dimensional computer model based upon semiconductor diffusion equations and electron beam generation function was employed to solve for the generated steady-state electron-hole density distributions as a function of coating thickness.<sup>9-11</sup> To understand the interplay between surface recombination velocity and coating thickness, the CL efficiency was calculated for various coating layer thicknesses (currently, the model assumes a coating of nonluminescent phosphor) from 1 to 20 nm while the surface recombination velocity was kept constant. Figure 5 shows the effect of coatings on the CL efficiency, compared to the uncoated phosphor whose surface recombination velocity was assumed to be approximately three times greater than the coated samples. As seen, the effect of coating is most prominent at voltages below 2 kV. When the coating layer is thin enough, the positive effect caused by reducing surface recombination is dominant. Therefore, the relative CL efficiency shows a monotonic increase with decreasing voltages, which was observed for the coatings formed at a reflux temperature of  $83^\circ\text{C}$ . However, as the coating thickness increases, the CL efficiency at low voltages decreases progressively and finally the losses in the coating become dominant. The intermediate regime was observed for coatings formed with a reflux temperature of  $77^\circ\text{C}$ , and the extreme case in which penetration losses dominate was observed for the thicker 5.0 wt% coating. Though a more quantitative analysis is necessary to accurately determine the interplay between the two competing mechanisms, it is clear that this model qualitatively reproduced the experimental CL efficiency curves, indicating that the observed enhancement was due to a reduction in surface recombination. Also, this modeling study suggests the need for a thin and uniform coating to achieve the best low-voltage CL performance.

In summary, we have presented a study on the effect of coatings on the low-voltage CL properties of ZnS phosphors. The sol-gel method was used to coat ZnS phosphors

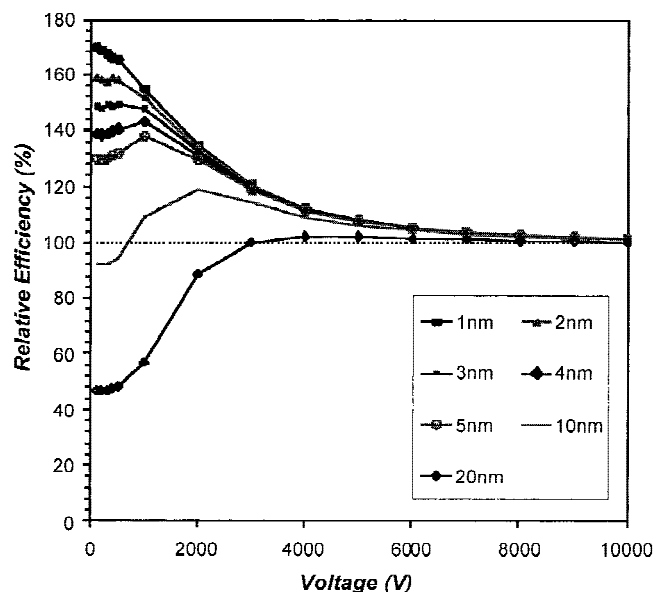


FIG. 5. Calculated CL efficiency relative to uncoated phosphor for a reduced surface recombination velocity and several coating thicknesses.

with a thin layer of  $\text{SiO}_2$ . The best result was a 60% enhancement in CL efficiency at voltages below 500 V. A model was presented which attributed the improvement in CL efficiency to a reduction in surface recombination while the decrease in CL efficiency for thicker coatings was ascribed to electron beam penetration losses in the coating. The improved low-voltage CL efficiency reported in this work has a significant impact on FED performance because it gives higher luminance but also because it will enable operation at lower current densities which will improve the phosphor maintenance and thus the reliability of the display.

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