Journal of The Electrochemical Society, **148** (10) G548-G551 (2001)
0013-4651/2001/148(10)/G548/4/$7.00 © The Electrochemical Society, Inc.

Uniform Nanoscale SiO_2 Encapsulation of ZnS Phosphors for Improved Aging Properties under Low Voltage Electron Beam Excitation

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A significant improvement (220%) is reported in the low voltage (2000 V) aging characteristics under cathodoluminescence (CL) excitation for ZnS phosphors coated with 1.0 wt % SiO_2 by the sol-gel technique. The formation of nanoscale uniform coating was confirmed by structural analysis. An improvement in chemical and thermal stability was also confirmed by chemical etching and heat-treatment of the SiO_2-coated phosphors. Also, the CL aging study showed a much improved CL efficiency curve for the SiO_2-coated ZnS phosphors. The Auger electron spectroscopy study showed that the SiO_2-coated phosphors were far more resistant to the loss of S species and to the formation of oxide dead layer. The structural, chemical, and CL characterizations demonstrated that the thin and uniform SiO_2 layers on ZnS phosphors served as protective layers retarding the surface-related degradation, which is critically important for the development of commercial field emission displays.
 [DOI: 10.1149/1.1397775]

Manuscript submitted January 24, 2001; revised manuscript received May 16, 2001. Available electronically August 21, 2001.

For the successful development of commercially viable field emission display (FED) devices, the critical problems of efficiency and maintenance characteristics of the phosphors should be overcome. Under low voltage E-beam excitation conditions used in FED, the electron penetration depth is very small compared to the phosphor particle size, and thus, the surface plays a crucial role in determining phosphor/display luminance, efficiency, and maintenance properties. A previous report indicated that Auger studies suggested the loss of sulfur from sulfur containing materials and the loss of oxygen from oxides and silicates.[1] The aging rate of both sulfide and oxide phosphors could be altered by coating. We have already reported a 60% enhancement in efficiency achieved by thin SiO_2 coating on ZnS phosphors.[2,3] The results were also found to be consistent with a theoretical modeling for coated phosphors. In this paper, we focused on how to improve the aging properties of phosphors under low voltage excitation. While the improved low voltage efficiency is expected to help relieve aging of phosphors, the surface coating, and encapsulation of phosphors will also improve thermal and chemical stability and 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.[4] However, this work focused on the midvoltage region (~4 kV) in which the surface effect is less critical. Also, no improvement in efficiency was reported. In this paper, we present physical and chemical analysis of nanoscale continuous coating of SiO_2 that increased the longevity of the phosphors by completely encapsulating the phosphor particles, in addition to the improved optical properties as shown in previous publications.[2,3]

Experimental

The SiO_2 coatings on ZnS:Cu were synthesized by the sol-gel method using tetraethyl orthosilicate (TEOS) (Arkos 99.9%) as the precursor material. The detailed coating process was reported in a previous paper.[2] As was reported in our previous publication, the optimum performance was obtained for a SiO_2 concentration of 1.0 wt %, pH values between 7 and 9, and a solution temperature of 83°C. Then, the coated phosphors were heated at 400°C in air. This sample exhibited a significant improvement (40-60%) in the low voltage (100-1000 V) cathodoluminescence efficiency. The same sample was used for the investigation of the aging properties reported in this paper.

The coated phosphors were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), particle size analyzer, cathodoluminescence (CL) efficiency, and aging measurements. The intrinsic cathodoluminescence efficiency measurements were described in the previous paper.[2] For the aging study, the cathodoluminescence efficiency was measured as a function of time at 2 kV using 400 μs current pulses with a repetition rate of 200 Hz and a peak current density of 30 mA/cm^2. Both coated and uncoated phosphors were tested at the same time and under the same conditions by deflecting the electron beam (at 400 Hz) from one sample to the other after each pulse. The luminance of each sample was measured using two photometers. For these conditions and duty cycle, charge was deposited at a rate of ~8.5 C/cm^2 per h.

Powder morphology of resultant phosphors was characterized using a JEOL model JSM-5300 scanning electron microscope. The SEM micrographs were used for the qualitative assessment of particle shapes of SiO_2 coating material. The size distribution of phosphor powder was analyzed by using a Leed and Northrup model microtra X100 particle size analyzer. In order to look at the presence of Si atom on the surface of ZnS:Cu, XPS measurements on SiO_2-coated ZnS phosphors were performed by using a Surface Science Instruments model SSX-100. It was operated with monochromator using Al-Kα line as an X-ray source. The beam spot size was 0.6 mm. The cross-sectional morphology of coated and uncoated phosphors were characterized using a JEOL model 2000-FX transmission electron microscope. The CL degradation of ZnS:Cu powder also was studied using AES. AES measurements on SiO_2-coated ZnS phosphors were performed by a Charles Evans & Associates model AESLAB 310-F.

Results and Discussion

The properties of the coatings were found to be critically dependent upon the precursor concentration, pH value, and the temperature of the solution. As reported in the previous paper,[2] with optimum coating conditions, the surfaces of uncoated and SiO_2-coated ZnS:Cu phosphors looked nearly the same although the coated phos-

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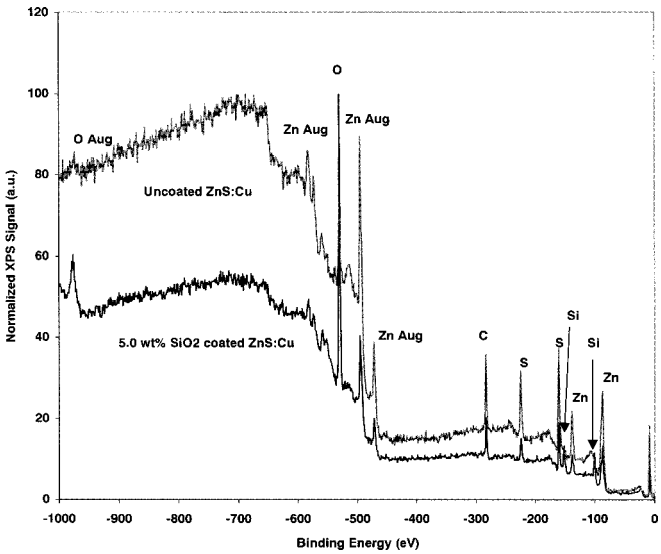

Figure 1. XPS spectra comparing uncoated and 5.0 wt % SiO_2-coated ZnS:Cu phosphors.

phor had slightly smoother corners and edges. It clearly indicated that uniform and continuous SiO_2 coating was formed on the surface of ZnS particle.

XPS measurements were performed to confirm the existence of the 5.0 wt % SiO_2 coating on the phosphor surface. As shown in Fig. 1, the XPS spectrum of the coated phosphor clearly shows the Zn, S, O, and Si peaks at their normal binding energies, indicating that the coating was in the form of SiO_2. In clear contrast, the Si peak of the coating was missing in the spectrum of the uncoated phosphor.

To further characterize the nature of the coatings, TEM analysis was performed on several coated and uncoated samples. Figure 2 shows TEM cross-sectional micrographs of 1.0 wt % SiO_2 coated ZnS:Cu phosphors. It can be seen clearly that thin and uniform coatings of SiO_2 have been obtained on ZnS phosphors. The coating thickness was estimated to be 5 nm. Therefore, based on the results of SEM, XPS, and TEM, we confirmed the complete encapsulation of ZnS particles by uniform nanoscale SiO_2 layers.

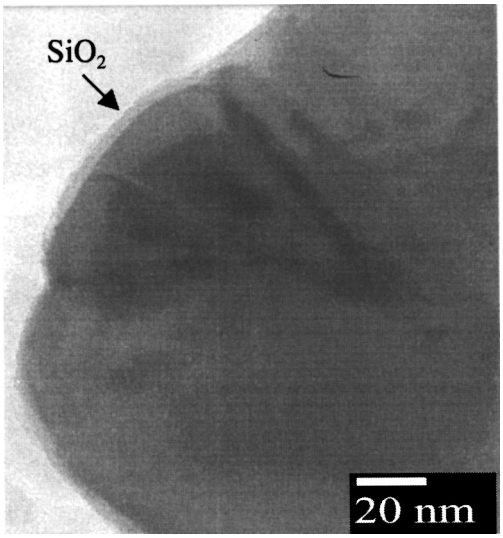

Figure 2. TEM cross-sectional micrographs of 1.0 wt % SiO_2-coated ZnS:Cu phosphors.

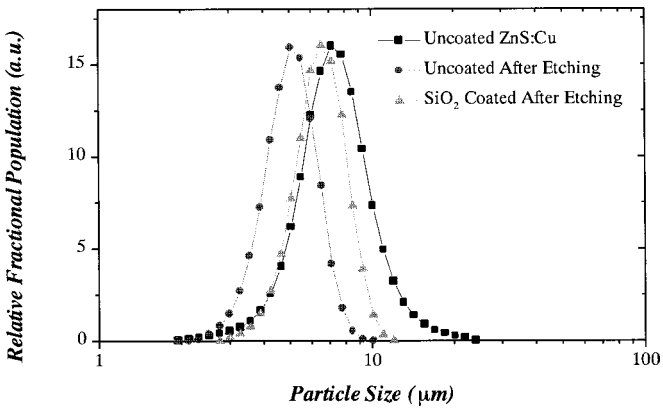

Figure 3. Particle size distribution of uncoated and 5.0 wt % SiO_2-coated ZnS:Cu phosphors before and after etching in HCl solution.

Previous papers reported the origin of aging process could be attributed to the electron beam stimulated chemical reactions (ESCR) occurring at phosphor surfaces.[5,6] Therefore, a surface coating that could prohibit such surface chemical reaction would improve the phosphor longevity and chemical stability.[7,8]

We first investigated the chemical stability of the coated phosphor. Since a well-densified continuous and uniform coating are expected to encapsulate and hermetically seal the phosphor, 5.0 wt % SiO_2 coated and uncoated phosphors were immersed in a strong HCl solution to determine whether any protection is provided by the coating. Figure 3 shows the particle size distribution of uncoated and coated ZnS:Cu phosphors before and after etching in HCl solution. The uncoated ZnS phosphors were dissolved in the acid very rapidly with the average particle size being reduced to half of the original value. In contrast, the 5.0 wt % SiO_2-coated phosphors largely maintained their sizes under the same etching condition. As shown in Fig. 4, SEM micrographs of uncoated and 5.0 wt % SiO_2 coated ZnS:Cu phosphors after etching in HCl solution looked different in shape and size. This morphological analysis after etching coated and uncoated sample clearly indicated that the SiO_2 layer serves as a protective layer making the coated phosphor more resistant to acid. Therefore, we could conclude that SiO_2-coated ZnS phosphors are more chemically stable than the uncoated sample.

Another important factor of low voltage phosphor for the application in the FEDs is the thermal degradation because a series of heating processes were performed to fabricate the FED panels.[9] As mentioned previously, SiO_2 coatings is expected to reduce phosphor surface degradation (such as oxidation) associated with display fabrication processes. In order to investigate the thermal stability after SiO_2 coating, 1.0 wt % SiO_2 coated and uncoated phosphors were heated simultaneously to 500, 550, 600, 650, and 700°C for 1 h in air. Then, CL measurements were performed to evaluate the degree of thermal degradation of SiO_2 coated and uncoated phosphors. Figure 5 shows the normalized CL intensity as a function of firing temperature under 1 kV electron excitation. As shown, the 1.0 wt % SiO_2-coated samples maintained the original efficiency up to 650°C before suffering a moderate decrease at 700°C. The uncoated sample, on the other hand, showed a continuous gradual decrease. After heat-treatment at 700°C for 1 h in air, the CL intensities were 82% of their original values for the 1.0 wt % SiO_2-coated sample and 11% for the uncoated sample, respectively. Therefore, it can be concluded that the SiO_2 coatings protect the phosphor surface by prohibiting further oxidation during the firing process, enhancing the thermal stability of phosphors, which is critically important for FED panel manufacturing.

The most direct evidence of the protective nature of SiO_2 coatings could be found by the CL aging measurements. Accelerated aging tests were carried out at 2 kV on phosphor screens deposited

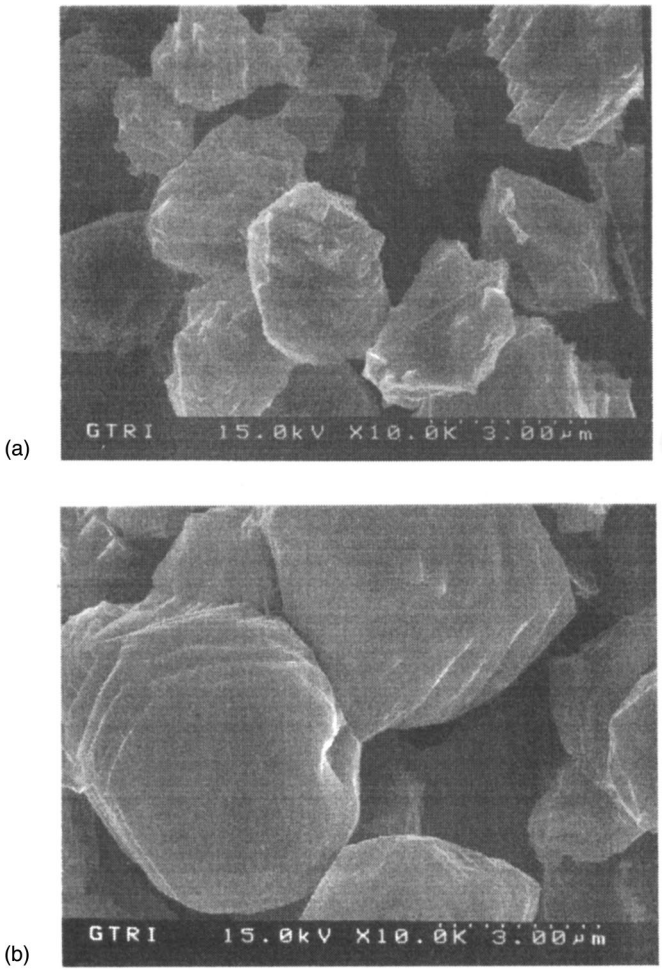

Figure 4. SEM micrographs of (a, top) uncoated and (b, bottom) 5.0 wt % SiO_2-coated ZnS:Cu phosphors after etching in HCl solution.

on indium tin oxide/glass substrates at a density of 3 mg/cm^2. These samples were aged simultaneously with uncoated phosphors as a reference. Figure 6 shows the normalized CL intensity as a function of time under 2 kV electron excitation with an average current density of at 3.88 mA/cm^2 for uncoated and 1.0 wt % SiO_2 coated ZnS:Cu (optimum coating sample for the enhancement of brightness) screens. The time for these curves correspond to an electron dose of approximately 207 C/cm^2. It is apparent that the SiO_2 coating reduces the aging rate, resulting in the final CL intensity of the coated phosphor more than twice as that of the uncoated sample. At the completion of the accelerated aging experiments, the final relative CL intensities for the 1.0 wt % SiO_2 coated and uncoated phosphors were 22 and 10% of their original values, respectively.

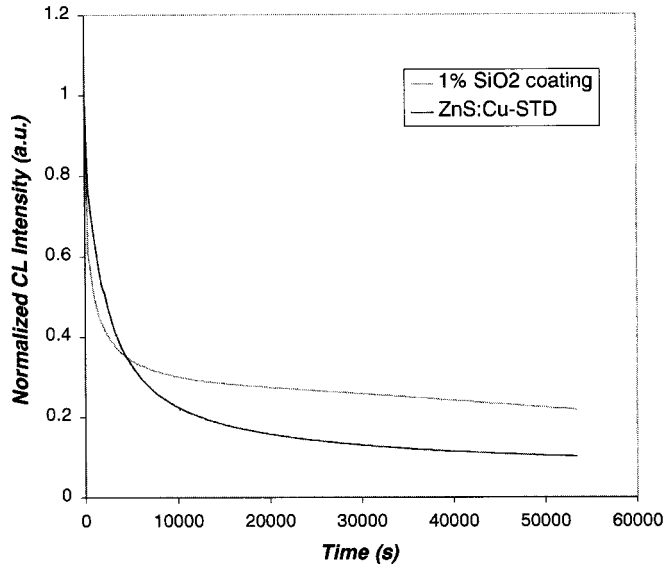

Figure 6. Normalized CL intensity at 2 kV of 1.0 wt % SiO_2-coated and uncoated ZnS:Cu phosphors as a function of time. The total aging time corresponds to ~207 C/cm^2.

The CL degradation process of ZnS:Cu powder was further studied using AES. The surfaces were exposed up to a ~100 C/cm^2 of electrons at 2 kV, normally at dc current density below 1 mA/cm^2. As has been reported previously, ESCR results in the removal of S and growth of a nonluminescenct ZnO on the surface of ZnS powders.[5] We used AES to investigate the growth of the surface dead layer. Figure 7 shows the normalized Auger peak-to-peak height of S and O of 1.0 wt % SiO_2-coated and uncoated ZnS:Cu during electron bombardment. When exposed to electron beam, the S signal of the uncoated sample immediately started to decrease, indicating the loss of S species from the phosphor surface. At the same time, the O signal showed a gradual increase with exposure time, which was attributed to the formation of the oxide phase dead layer. In contrast, the SiO_2-coated sample exhibited an exactly op-

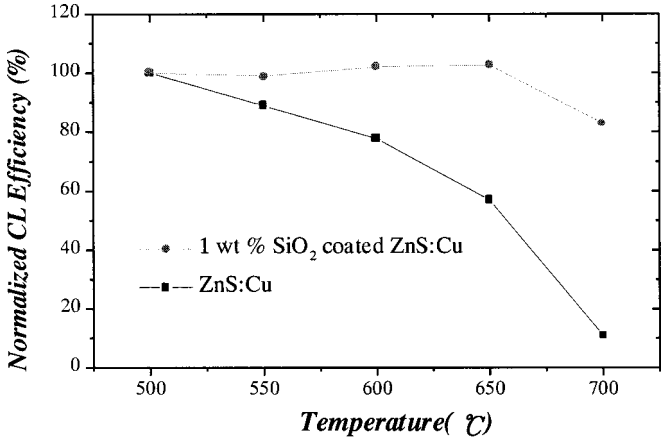

Figure 5. Normalized CL intensity at 1000 V of 1.0 wt % SiO_2-coated and uncoated ZnS:Cu phosphors as a function of firing temperature.

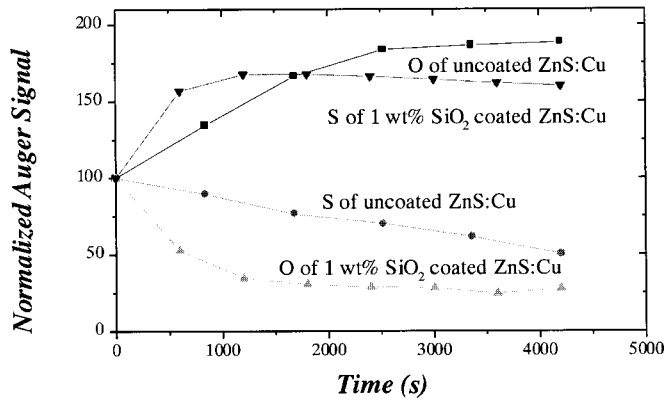

Figure 7. Normalized AES peak-to-peak height of S and O of 1.0 wt % SiO_2-coated and uncoated ZnS:Cu phosphors as a function of electron dose at 2 kV.

posite behavior. The O signal of the SiO_2-coated sample decreased and S signal increased with increasing coulombic dose. This behavior was attributed to the partial removal of O from the SiO_2 coatings and the subsequent exposure of ZnS surface. Note that with increasing coulombic loading, the S signal decreased very slowly after reaching the maximum, indicating that the SiO_2-coated samples are much more resistant to the loss of S from the phosphor surface. The results of the AES study clearly indicate that the thin and uniform encapsulation of SiO_2 provides much more stable phosphor surface and retards the formation of dead layer on the surface of ZnS.

Conclusion

A significant improvement (220%) is reported in the low voltage (2000 V) aging characteristics under CL excitation ($\sim$207 C/cm^2 of total electron dose) for ZnS phosphors coated with 1.0 wt % SiO_2 by the sol-gel technique. SEM, XPS, and TEM confirmed the formation of thin and uniform coatings on ZnS powders with a thickness of $\sim$5 nm. Much improved chemical and thermal stability of the SiO_2-coated ZnS:Cu was confirmed by etching and firing test. Also, the CL aging study showed much improved CL efficiency curves for the coated phosphors, confirming that the encapsulation of thin and uniform SiO_2 coatings on ZnS helped protect the phosphor surface under electron beam irradiation. The AES study showed that the SiO_2-coated phosphors were far more resistant to the loss of S species and the formation of oxide dead layer. The structural, chemical, and CL characterizations presented in this paper clearly demonstrated that the uniform nanoscale SiO_2 layers on ZnS phosphors served as protective layers retarding the surface-related degradation, which is critically important for the development of commercial FEDs.

Acknowledgments

This project has been supported by the CRD center of Samsung SDI Company, Limited. The authors would like to thank the members of the luminescent material group for their great help.

Samsung SDI Co., Ltd., assisted in meeting the publication costs of this article.

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