

Uniform and continuous Y_2O_3 coating on ZnS phosphors

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Abstract

An investigation is reported of the coating of ZnS by Y_2O_3 using a sol–gel process. Yttrium isopropoxide was used as the precursor material and was dissolved in a toluene/isopropanol solution. The solution was refluxed at an elevated temperature before the phosphors were added. The coated phosphors were then fired in air to convert the hydroxide to oxide. Scanning electron microscopy confirmed the formation of coatings on ZnS powders. The coating morphology was strongly dependent on the sol–gel processing parameters and the range of solution concentration and pH values necessary to form continuous coatings were determined. The cathodoluminescence properties of the coated phosphors were also investigated and an improvement in phosphor maintenance was observed. © 2000 Elsevier Science S.A. All rights reserved.

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By employing the same operating principles, the field emission display (FED) technology provides the potential of achieving a flat panel display with comparable or superior performance to the conventional cathode ray tube (CRT) displays. However, FEDs operate at a lower acceleration voltage and at a higher current density [1]. Thus, the penetration depth of the primary electrons is small and the phosphors exhibit more severe surface degradation. During operation, the phosphor decomposition products generated by electron stimulated processes can poison the emitter cathodes [2]. This lowers the efficiency of the phosphor and shortens the life of the device. The lack of efficient low voltage phosphors with high stability has been one of the most serious impediments limiting the commercialization of full color FED. Thus, it is important to develop new phosphor materials which show sufficient luminance when excited by low energy electrons and which also have high stability against electron bombardment and any interactions with the residual atmosphere in these vacuum devices.

Because the electron penetration depth is very small compared with the phosphor particle size, the surface plays a very important role. Consequently, the ideal phosphor for FEDs should consist of defect-free particles with large grains and perfect surfaces. Furthermore, phosphors undergo a baking process during the manufacture of FEDs during which the surface of the phosphors is to some extent oxidized. The oxidation causes deterioration of the crystallinity of the phosphor surface and consequently the oxidized surface decomposes more easily during operation. Therefore, the surface modification of phosphors is an important technique to improve low voltage cathodoluminescence (CL), since it can reduce the thickness of the surface dead-layer and even passivate surface recombination centers.

Sulfide phosphors, which have been used extensively in CRT displays, have also become very important for low voltage devices. For example, $\text{ZnS}:\text{Cu},\text{Al}$ and $(\text{Zn},\text{Cd})\text{S}:\text{Ag},\text{Cl}$ phosphors have been mixed with fine powders of In_2O_3 to provide adequate screen conductivity [3]. However, vacuum fluorescent displays (VFD) utilizing these mixes have a short life time compared to those using traditional high conductivity $\text{ZnO}:\text{Zn}$. One serious impediment which limits the use of conventional

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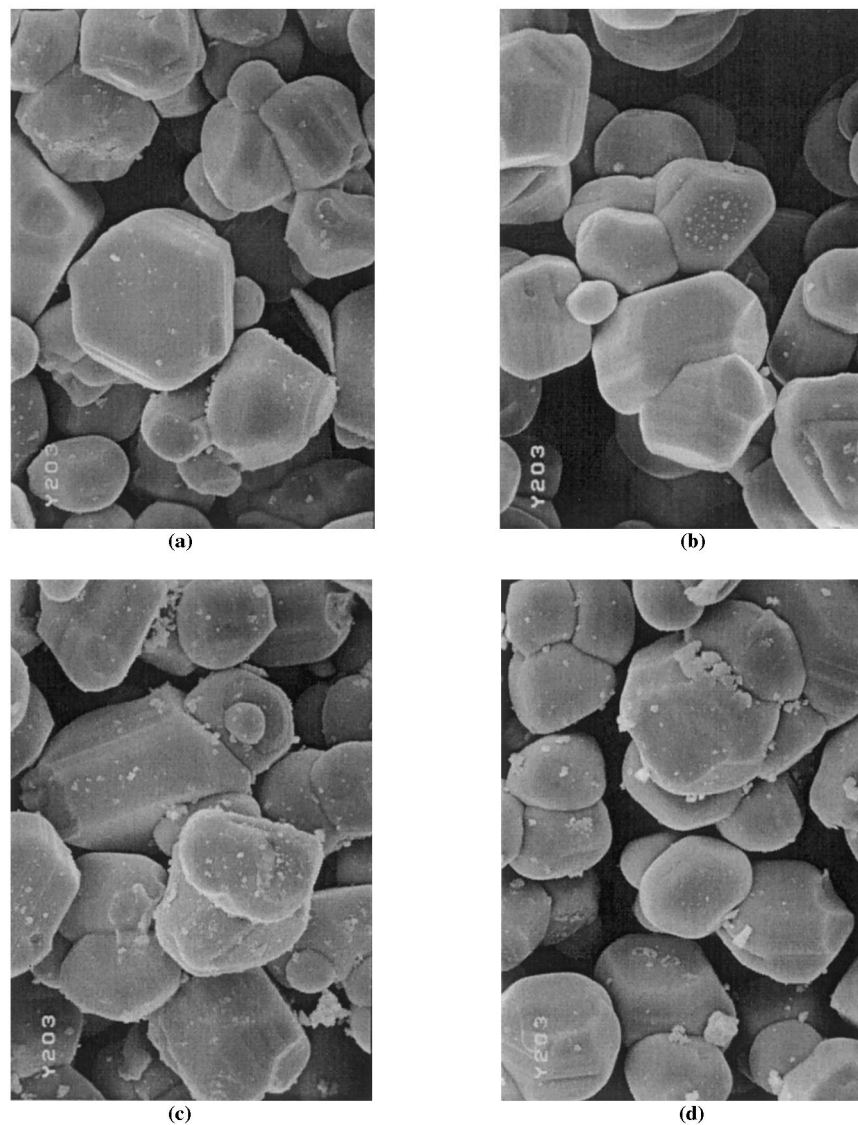


Fig. 1. SEM micrographs of ZnS:Cu phosphors coated with (a) 0.1 wt.%, (b) 0.5 wt.%, (c) 1.0 wt.%, and (d) 2.0 wt.% Y_2O_3 .

sulfide phosphors is the electron stimulated decomposition which generates harmful gases such as S, SO and SO_2 [2]. The sulfur related gases coming from the phosphor can dramatically reduce the electron emission efficiency of the cathodes and the degradation of the phosphor surface also leads to deteriorated phosphor performance. Thus, the development of thin, stable and continuous oxide coatings is essential to improving the low voltage performance of sulfide phosphors. 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 mid-voltage region (~ 4 kV) in which the surface effect is less critical. In this paper, a novel process for obtaining thin uniform Y_2O_3 coatings on ZnS-based phosphors is presented. Y_2O_3 has been shown to be one of the most stable phosphors under FED operating conditions [5]. Also, its electron penetration depth,

estimated to be 37 nm for a 2-kV electron beam compared with 48 nm for ZnS, is not too small to form a useful coating¹. Thus, it is expected that Y_2O_3 coating of sulfide phosphors will protect the surface and prevent surface degradation without causing severe losses in the incident electron beam.

Among various coating technologies, the sol–gel process allows the most comprehensive control over the surface morphology. For this Y_2O_3 coating study, yttrium isopropoxide ($\text{Y}(\text{OC}_3\text{H}_7)_3$) was used as the yttrium precursor material. Although there are other commercially available metal alkoxides, the alkyl groups of the other alkoxide precursors are much longer than the isopropoxides. Thus, the rate at which these precursors hydrolyze will generally be slower than for the isopropoxide precursors, which would make the

¹ The penetration depth was calculated by Monte Carlo electron trajectory simulation.

coating process less efficient and more time consuming. Also, the reaction byproducts of the isopropoxide precursors can be more easily removed from the system. Yttrium isopropoxide was first dissolved in a 50:50 toluene/isopropanol solution. Water was then added to the solution and the molar ratio between water and yttrium isopropoxide was set at 200:1. The solution was then refluxed at 65°C for 20 h in order to ensure completion of the hydrolysis reaction. At the completion of refluxing, the ZnS phosphors were added to the solution and dried in air. The coated phosphor was then fired in air at an elevated temperature for 1 h.

The sol–gel process has many variables that can affect the surface morphology of the coatings. Among them, the concentration of the precursor material and pH of the solution are the most important parameters

on which the hydrolysis reaction rate critically depends. First, the precursor concentration dependence was investigated. For this study, the yttrium concentrations ranged from 0.5 to 2.0 wt.% with respect to ZnS. Fig. 1 shows the SEM micrographs of the coated phosphors. The coatings were particle-like for all concentrations. The surface coverage was generally proportional to the coating concentration but, for the 2.0 wt.% coating, large agglomerates of Y_2O_3 were formed. From these results, it was concluded that 1.0 wt.% was the ideal concentration for the formation of a uniformly distributed Y_2O_3 coating.

This study showed that sol–gel Y_2O_3 coatings on ZnS phosphors have a tendency to form particle-like coatings unless very carefully controlled. A possible reason can be found from the fact that the toluene used

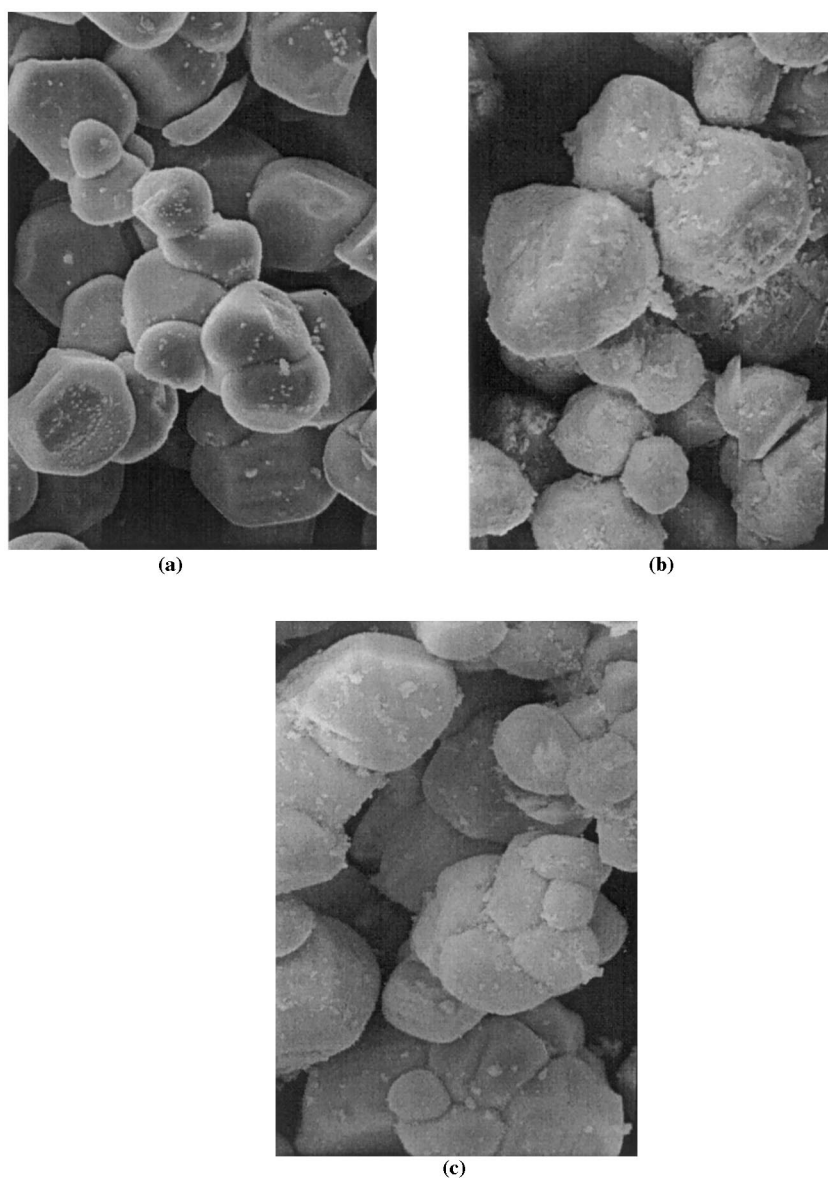


Fig. 2. SEM micrographs of Y_2O_3 coated ZnS:Cu phosphors with solution pH values of (a) 4.5, (b) 7.5, and (c) 10.5.

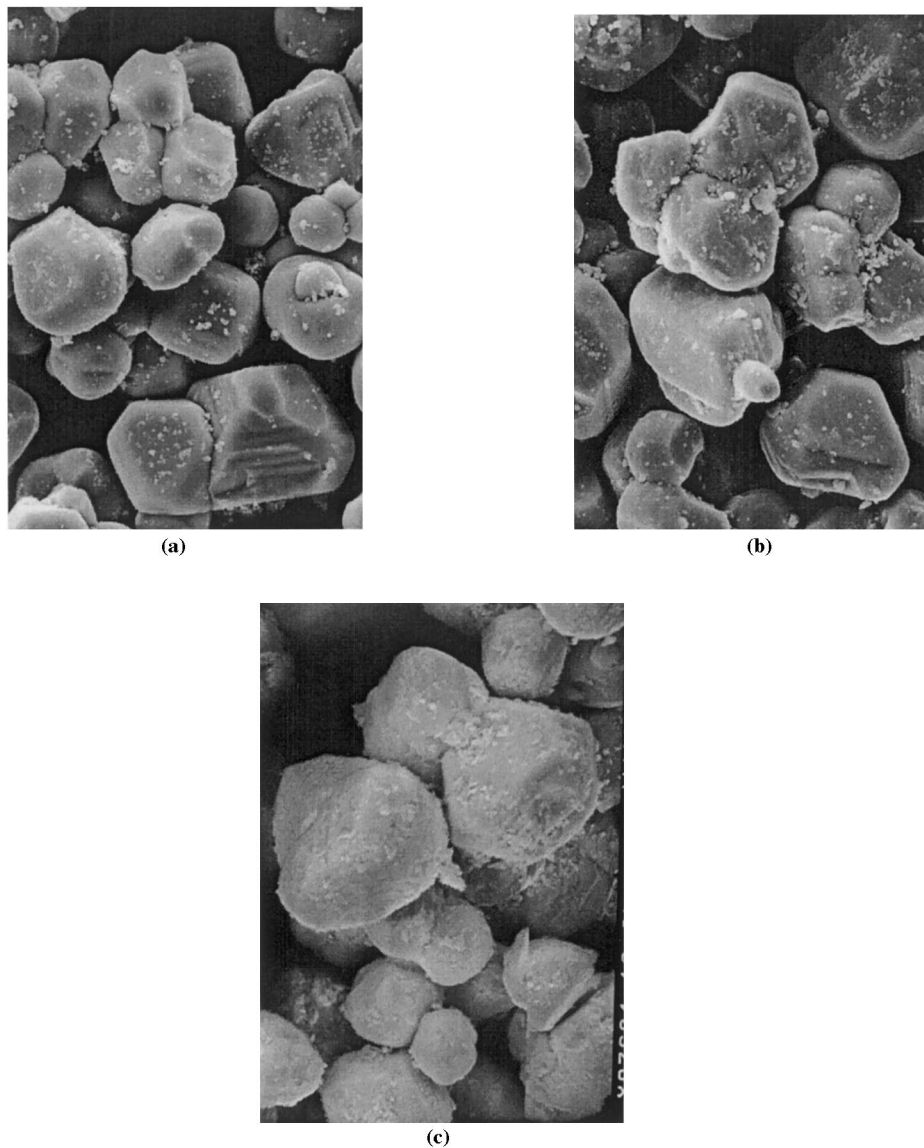


Fig. 3. SEM micrographs of 1 wt.% Y_2O_3 coated ZnS:Cu phosphors refluxed at 65°C and fired at (a) 130°C , (b) 200°C and (c) 400°C . The pH of the solution was fixed at 7.5.

as the solvent for yttrium isopropoxide has a very low solubility for water and thus the water tended to form droplets when added to the solution, thus contributing to the formation of particle-like coatings. In order to increase the water solubility of the solution, isopropanol was replaced with acetone, which has an extremely high solubility for water. It was clearly observed during the sol–gel process that water was more easily dissolved in this solution than in toluene/isopropanol solution. Keeping all of the other parameters the same, Y_2O_3 coatings on ZnS phosphors were performed with a 50:50 toluene/acetone solution. Unfortunately, however, the SEM results showed little difference between the two different solvents and thus it was concluded that the surface morphology was deter-

mined mainly by the coating concentration and the pH values.

In order to obtain a more uniform and continuous coating, the effect of the solution pH was investigated. It was found that the toluene/isopropanol/water solution became highly alkaline when yttrium isopropoxide was added. This gave unstable results and thus the pH value was reduced by adding diluted acetic or nitric acid. Fig. 2 shows the SEM micrographs for 1.0 wt.% Y_2O_3 coated ZnS:Cu,Al phosphors prepared with pH values of 10.5, 7.5 and 4.5. As can be seen clearly from the micrographs, the pH value of 10.5 resulted in a particle-like coating whereas the pH value of 7.5 yielded a continuous coating. For the coating formed from a solution with a pH value of 4.5, it was evident

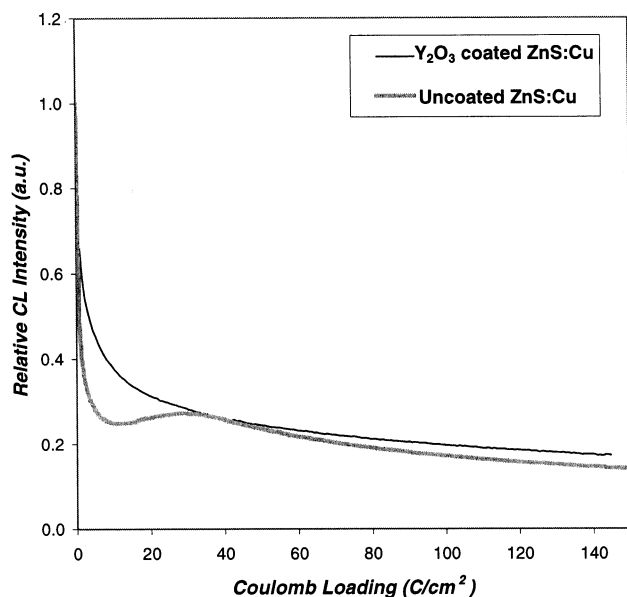


Fig. 4. CL aging curves for Y_2O_3 coated and uncoated ZnS:Cu phosphor screens.

that only a small amount of Y_2O_3 was deposited to form the coating. This study indicated that the ideal pH value for a continuous coating was ~ 7.5 and that a higher pH value is necessary for particle-like coatings.

The effect of the firing temperature was also studied. For this study, the coating concentration was fixed at 1.0 wt.% and the reflux temperature was 65°C . Fig. 3 shows the surface morphologies of the coated phosphors fired at 130, 200 and 400°C . The firing temperature was not increased above 400°C because ZnS phosphors are known to be oxidized at higher temperatures. The coating obtained at 400°C exhibited the most complete surface coverage and the amount of coating material formed on phosphor surface decreased with decreasing firing temperature.

The CL properties of the coated phosphors were also investigated. For this investigation, both the coated and

uncoated phosphor screens were made with a screen weight of 2 mg/cm^2 . The electron excitation beam energy was set to be 2 kV with a peak current density of 30 mA/cm^2 . To simulate the FED operating conditions, the measurements were performed under a pulsed excitation with a pulse width of $400 \mu\text{s}$ at 200 Hz. As shown in Fig. 4, the Y_2O_3 coated phosphor exhibited an improved aging behavior compared to the uncoated phosphor. After a Coulomb loading of 140 C/cm^2 , the coated phosphor screen exhibited $\sim 10\%$ higher relative efficiency than the uncoated phosphor screen as well as a lower rate of degradation.

In summary, a range of processing conditions has been defined for obtaining continuous Y_2O_3 coatings on ZnS-based phosphors. Yttrium isopropoxide was used as the yttrium precursor and was dissolved in toluene/isopropanol/water solution. After refluxing the solution, the phosphor powders were added, dried in air, and then fired. The optimum coating concentration was found to be 1.0 wt.% and the optimum pH of the solution was 7.5. Also, the best reflux and firing temperatures were determined to be 65 and 400°C , respectively. The coated phosphor exhibited an improved aging behavior under cathodoluminescence excitation.

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