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Low-temperature plasma coating of electroluminescence particles with silicon nitride film

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A Si_3N_4 thin film was deposited on ZnS phosphor particles of 18 μm diameter in a silane–nitrogen radio-frequency (r.f.) plasma at 310–330 K. The particles were frequently shaken to maintain contact with plasma gas. The film deposited was characterized by X-ray photoelectron spectroscopy XPS, Fourier-transformed infrared spectroscopy and high-resolution scanning electron microscopy (SEM). The Si/N ratio of the film was about 1.25, and little change in the infrared spectrum was observed following the exposure in the ambient air for 10 days. The performance of the film as a diffusion barrier was evaluated by monitoring the lifetime of electroluminescence (EL). A film as thin as 50–60 nm could cover the EL powder without pinholes, and successfully protected the phosphor from water vapour.

1. Introduction

Various particles have been developed as starting materials for the preparation of advanced ceramics and other composite bodies. To improve the handling and functionality of these particles, they are sometimes coated with protective film. Coating of fine particles is usually performed by a wet method, which unavoidably includes a drying step that requires much energy.

The sequence of coating by a dry method, on the other hand, is much simpler than that by a wet process. As noted in an overview by Morooka *et al.* [1], nanometre-scale composite particles have been prepared by a dry process. Kobata *et al.* [2] coated submicrometre Al_2O_3 or Si_3N_4 particles with very fine titanium nitride particles by chemical vapour deposition (CVD) reaction carried out in a fluidized bed. Toda and Kato [3] introduced mixed tetraethyloxysilane–ethanol–water vapour with air or nitrogen into a fluidized bed of magnesia particles at 473–673 °C and achieved uniform coating of fine magnesia particles with non-crystalline silica film. The resistance of the coated particles against acid increased with increasing film thickness.

Si_3N_4 is an excellent diffusion barrier for vapour and ions and is obtained by CVD reaction, usually at 700–1000 °C [4]. Plasma-enhanced CVD (PECVD), on the other hand, has the advantage that the substrate can be held at a relatively low temperature of around 20–400 °C [5, 6]. Si_3N_4 film formed by PECVD is used in applications where a high processing temperature is not allowable. This can be said about the treatment of EL phosphors. The light output from an a.c. powder EL cell decreases with operation time, because of the introduction of foreign substances from the phosphor surface into the interior or by the escape of entity necessary to EL from the interior to the surface [7, 8]. Faria [9] suggested that the cell life could be improved by insulating EL particles with an inert protective film. Nakamura and Hirate [10] treated the surface of ZnS particles with Si_3N_4 film in an r.f. plasma and found that cell life was considerably improved. However, the film formed on the surface of particles was not characterized.

In the present work Si_3N_4 thin film was deposited on Cu-activated ZnS particles in an r.f. plasma of silane and nitrogen. Particles were fluidized by shaking the reactor frequently. The quality of the film formed was evaluated as the lifetime of coated EL particles. The film was also characterized with high-resolution SEM, Fourier-transformed infrared spectroscopy and XPS.

2. Experimental procedure

A diagram of the deposition equipment used for this work is shown in Fig. 1. The deposition reactor was a Pyrex tube 250 mm high and 28 mm in diameter. The

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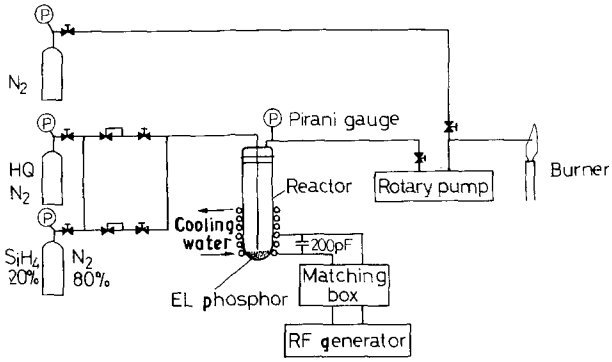

Figure 1 Schematic diagram of the plasma deposition apparatus.

feed nozzle for reactant gases, facing downwards, was positioned 25 mm above the bottom of the reactor. The particles used as the substrate were Cu-activated ZnS EL powder with an arithmetic mean diameter of 18 μm. SEM micrographs of the as-received particles are shown in Fig. 2a and b. Glass beads 140 μm in diameter were used as a reference. The particles were frequently shaken to increase contact with the gas phase. A 25 mm × 18 mm glass plate, used to test the quality of the deposited film, was set at the bottom of the reactor.

The r.f. plasma was generated with a crystal-controlled power unit (Pearl Kogyo Co. RF-500, 13.5 MHz). The discharge coil was a 4 mm outside diameter Cu tube, wound six turns around the outside of the reactor. The r.f. power was fixed at 150 W. The flow rates of the reactants, silane diluted in nitrogen (silane 20 vol %) and ultrapure nitrogen (99.9999 %) were regulated with thermal mass-flow controllers and both were fed at 5 $cm^3 min^{-1}$ at 25 °C and 0.1 MPa. The pressure in the reactor was kept at 300 Pa, and no heating devices were used. The temperature in the reactor was 310–330 K. The silane-containing effluent was burnt in a flame. Before and after the experiments the system was purged with ultrapure nitrogen to prevent explosion of silane.

XPS analysis was performed with a Shimadzu ESCA-850 spectrometer with MgK_α radiation. Fourier-transformed infrared absorption spectra were obtained with a Jasco FT-IR/3 spectrometer. Visible–ultraviolet spectra were determined with a Hitachi U-3400 spectrophotometer. To observe the film thickness, the EL particles covered with Si_3N_4 film were soaked in a nitric acid solution of about 30 wt %. The particles were lightly pressed with a glass bar, thus introducing cracks in the film. Then the mixture was stirred gently at 80 °C until the inner EL particles were dissolved. Hitachi S-2300 and S-900 SEM microscopes were used to observe particles as well as plates.

A schematic diagram of the EL measuring set-up is shown in Fig. 3. The EL cell was a parallel-plate condenser consisting of two transparent conducting glass plates. A 90 μm thick spacer was laid between the plates to ensure constant distance between the plates, as illustrated in Fig. 4. Castor oil with a dielectric constant of about 4.7 (reagent grade; Wako Pure Chemical Ind.) was used as the liquid phase. The water content in the castor oil was changed and was measured with a digital Karl Fischer analyser (Mitsubishi

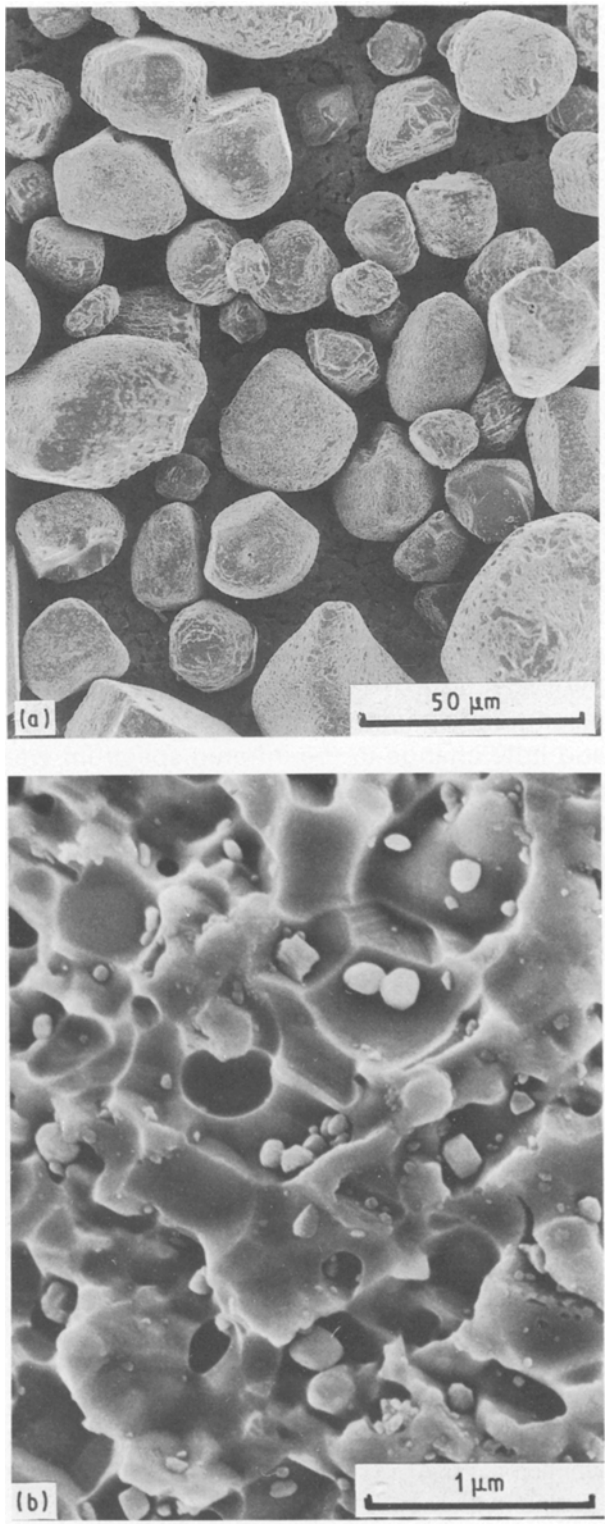

Figure 2 EL particles used.

CA-1 MCI). The weight ratio of the phosphor to castor oil was kept at 4:1. The EL emitted by the cell was detected with a photomultiplier placed at the outlet of a monochromator (Jasco CT-400). The phosphor was excited by a sinusoidal wave of 6 kHz and 180 V. The cell was kept in a water bath at 35 °C. The phosphor emitted a narrow spectrum of 420–570 nm.

3. Results and discussion

Fig. 5 is an SEM micrograph of the film deposited on the glass plate. A similar smooth film was formed on

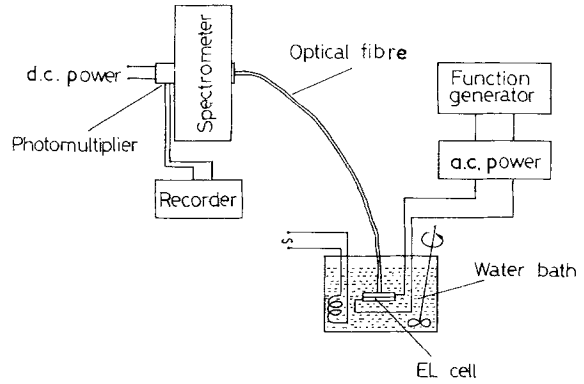

Figure 3 Set-up for measuring EL intensity.

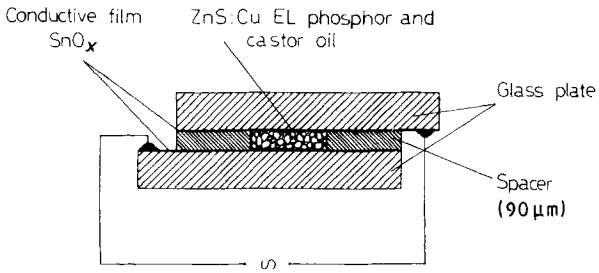

Figure 4 Details of EL cell.

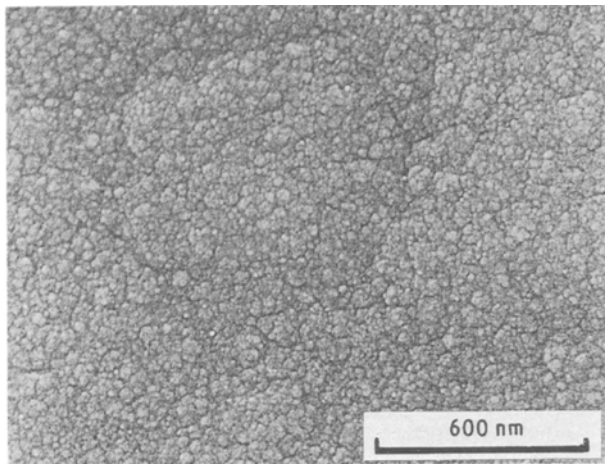

Figure 5 Si_3N_4 film deposited on glass plate.

the surface of the glass particles. Fig. 6 shows typical Fourier-transformed infrared spectra of the film measured immediately and 10 days after formation. Major absorption peaks are due to the Si–N stretching mode at 850 cm^{-1}, Si–O stretching at 1200 cm^{-1} and N–H stretching at 3350 cm^{-1} [4, 11]. Little change was observed in the infrared absorption spectrum following exposure in the ambient atmosphere.

Fig. 7 indicates the hollow shells of particles obtained after the 3 h deposition and the dissolution of initial EL particles. The Si_3N_4 film insoluble to nitric acid was deposited homogeneously with a good step coverage. Large holes were intentionally formed by the light crushing procedure, without which only a few pinholes were observed. Fig. 8 shows a particle surface after 3 h deposition. The sharp unevenness on the initial substrate surface shown in Fig. 2a was rounded by the 3 h deposition, but the difference between the

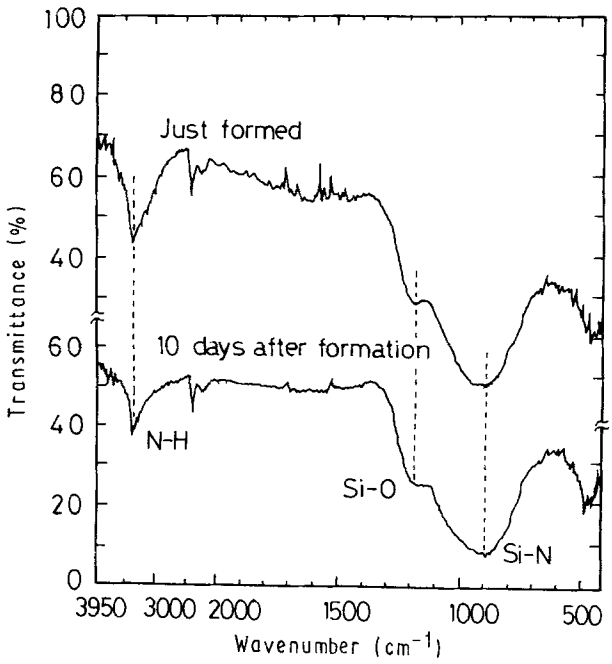

Figure 6 Fourier-transformed infrared spectra of Si_3N_4 film deposited.

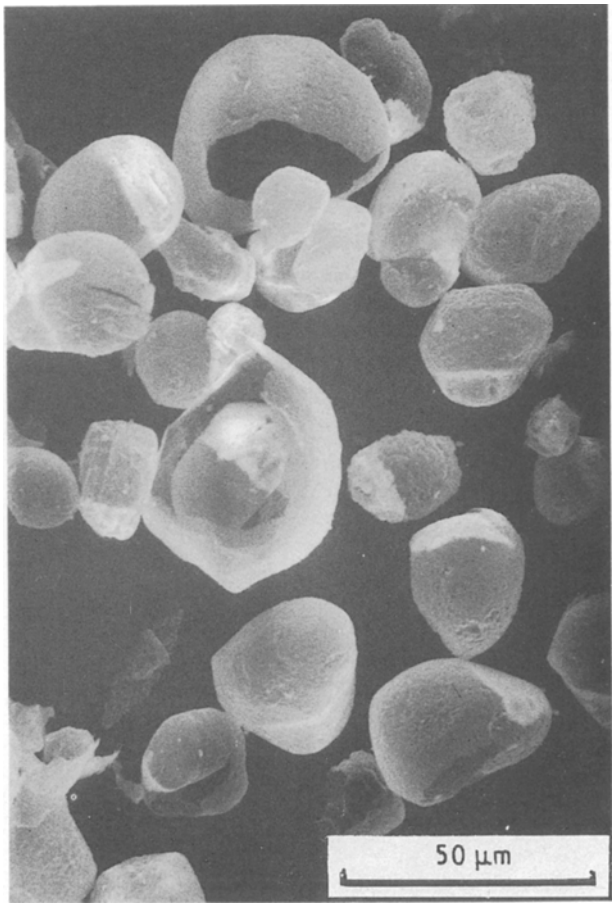

Figure 7 Si_3N_4 shells on particles treated for 3 h.

1 and 3 h depositions was not clear. Fig. 9 shows the cracked section of the film. The irregular solid seen below the film is the residue of partially dissolved ZnS. The average film thickness is plotted against time in Fig. 10, indicating that the film grows linearly with the deposition time.

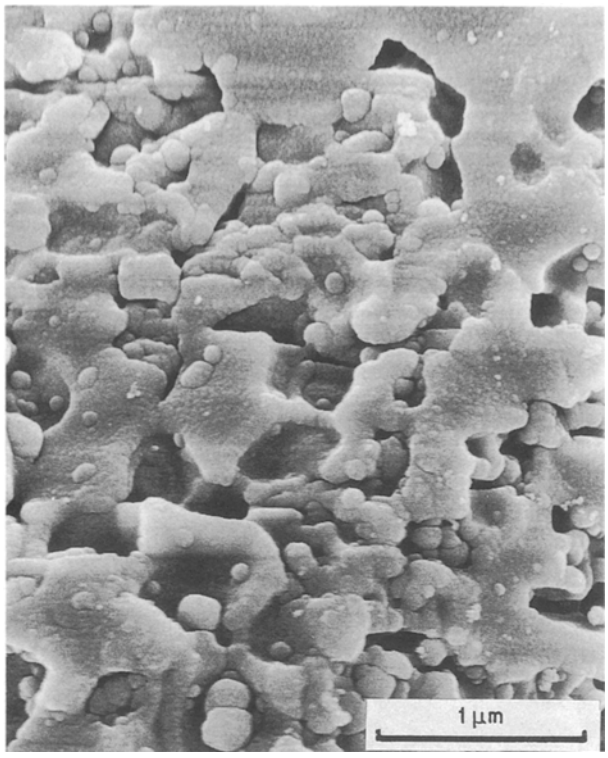

Figure 8 Surface of a particle treated for 3 h.

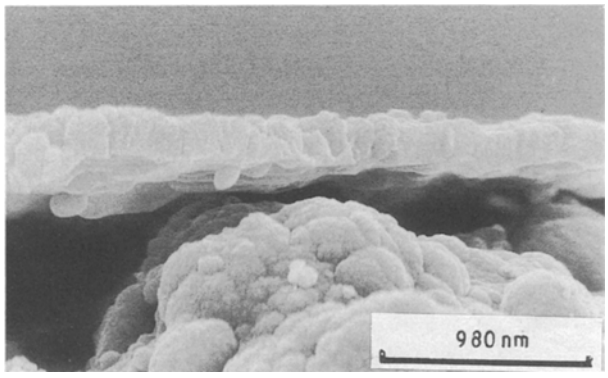

Figure 9 Cracked section of a particle treated for 3 h.

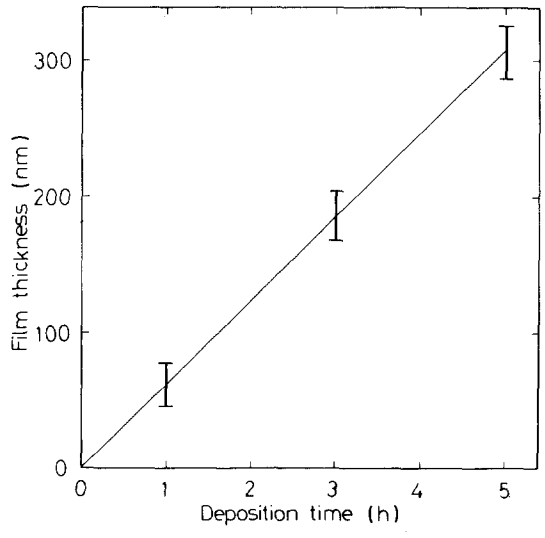

Figure 10 Time evolution of film thickness coated on EL particles.

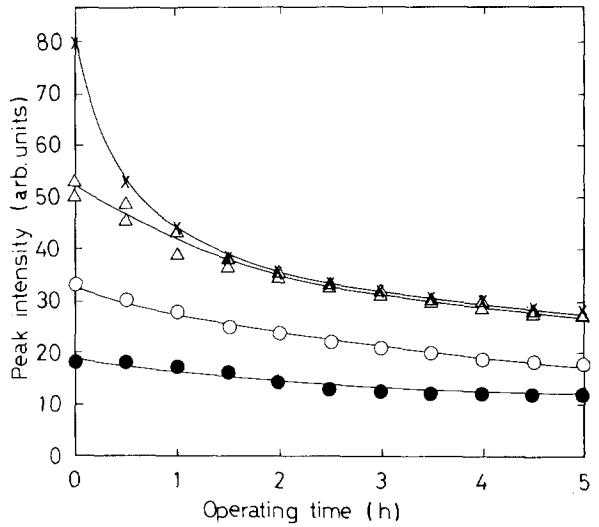

Figure 11 Effect of film deposition on time evolution of EL intensity. 0.05% water in castor oil: (×) as-received, (△) 1 h deposition, (○) 3 h deposition and (●) 5 h deposition.

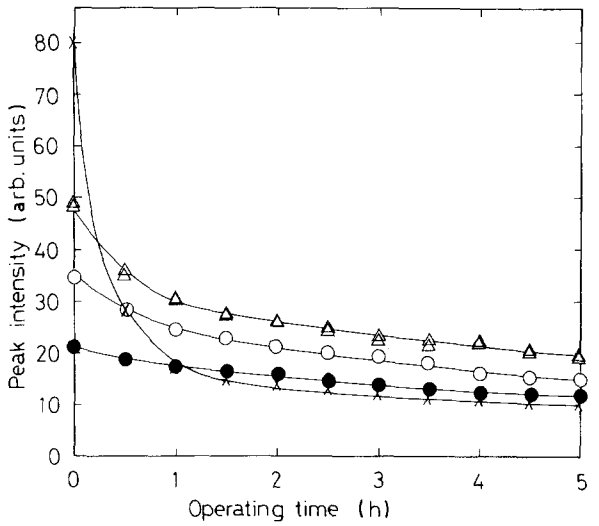

Figure 12 Effect of film deposition on time evolution of EL intensity. 1.6% water in castor oil: (×) as-received, (△) 1 h deposition, (○) 3 h deposition and (●) 5 h deposition.

Figs 11 and 12 show the time evolution of the emission intensity of the EL particles. When the water content in castor oil was 0.05 %, the emission intensity of the as-received particles soon approached that of the particles coated by the 1 h deposition. With a water content of 1.6% the deterioration of the as-received particles was very rapid. However, deactivation is prevented by the Si_3N_4 film. Fig. 13 shows the transmittance spectrum of the film deposited on the glass plate. The Si_3N_4 film adsorbs the light emitted from the phosphor. Therefore, optimum film thickness should be decided as a balance between the opposing facts that a thick film is more effective in preventing deterioration and that a thin film is more transparent. In the present experiment the optimum deposition time was 1 h and the film thickness was 50–60 nm, as indicated in Figs 11 and 12. From XPS analysis of the coated EL particles, the Si : N atomic ratio was determined as 1 : 0.8 from N 1s and Si 2p peaks. This is in

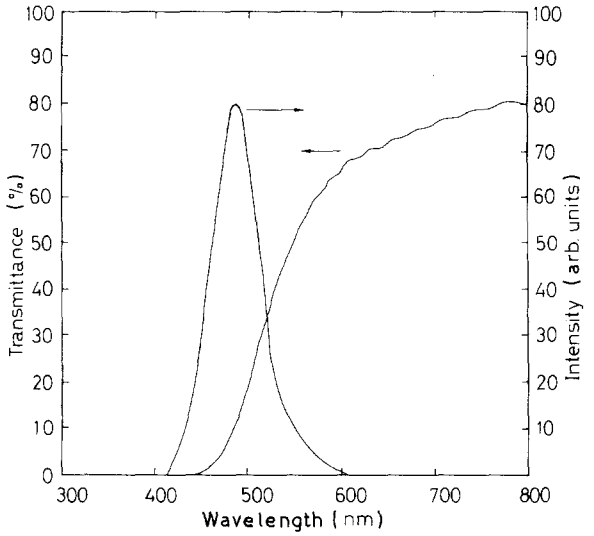

Figure 13 Transmittance spectrum of 5 μm-thick Si_3N_4 film formed on glass plate.

agreement with the literature [12, 13], showing that PECVD Si_3N_4 film is in the range $0.7 < Si/N < 1.5$.

4. Conclusions

Si_3N_4 thin film was deposited on EL phosphor particles of average diameter 18 μm at 310–330 K in a silane–nitrogen r.f. plasma. The film deposited showed an Si/N ratio of 1 : 0.8 and covered the surface of the particles well. The optimum thickness of the film was about 50–60 nm for the film obtained in this experiment. The thickness chosen must be such as to increase the lifetime of the EL particles without much decrease in the fluorescence intensity. The process developed in this study can be applied to the coating of particles which are weak against high temperature.

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