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Optical and adhesive properties of composite silica-impregnated Ca-α-SiAlON:Eu^{2+} phosphor films prepared on silica glass substrates

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Abstract

The compaction of a Eu-doped Ca-α-SiAlON phosphor powder was performed by electrophoretic deposition (EPD). The effect on the adhesion and optical properties of the silica precursor as both a binder of the powder and a filler of the air voids were evaluated. The adhesion of the silica impregnated composite film to the silica glass substrate was characterized by the tape test. The improvement of the external quantum efficiency was confirmed from the PL spectra measurement after the silica impregnation. The temperature dependence of the external quantum efficiency was also investigated in order to discuss the advantage of using the silica precursor as a binder for high-brightness LED applications.

Keywords: Optical properties; Suspensions; Sol–gel processes; SiO_2; SiAlON phosphor

1. Introduction

SiAlON phosphors have attracted attention as a new material for LEDs.[1–8] It is expected to be used for general lighting because of its high brightness, superior thermal stability and excellent color-rendering property.[9–15] The SiAlON phosphor is normally synthesized as a powder by a solid phase reaction method. Therefore, it is essential to establish the packaging technology which enables us to obtain uniform, thickness-controlled dense wide-area deposited films for their practical application to general lighting. Furthermore, thermal degradation of the resin, which is commonly used as a mounting agent, is another problem to be solved when using a high-brightness pump source.

Electrophoretic deposition (EPD) is a colloidal process wherein ceramic bodies with a high homogeneity and green density are directly shaped from a stable colloidal suspension by a dc electric field. The EPD process also has the advantage of being able to control the deposit thickness by altering the applied voltage and the deposition time. We have proposed that EPD is a promising technique to prepare a thickness-controlled SiAlON phosphor layer on a substrate and reported the PL properties of a pseudo-white light-emitting device consisting of the deposited film of the yellow-emitting Eu-doped Ca-α-SiAlON and blue LED.[16,17] The compaction of the SiAlON phosphor powder on a substrate by EPD has been performed using polyvinyl butyral (PVB) as the binder. However, PVB has no sufficient thermal stability that prevents peeling-off and slipping-off of the deposit layer under the influence of increasing temperature during irradiation with a high brightness LED as the pump source. Furthermore, the external quantum efficiency of the deposit was insufficient,[16] probably because the diffuse reflection of the light at the interfaces between the air voids, PVB layers and particles hinders the rectilinear propagation performance of the light. We have considered that the diffuse reflection could be reduced and the deposit adhesion to the substrate could be improved by removing the PVB and filling the voids with a transparent material as the mounting agent and filler. In this study, the surface modification of a Ca-α-SiAlON powder with a silica precursor was performed as a substitute for the PVB. Moreover, the voids in the deposit layers of the SiAlON phosphor particles were filled with SiO_2 to improve their adhesion to the substrates and increase the external quantum efficiency. The effect of the application of SiO_2 as the mounting agent on the adhesion and optical properties of the phosphor film was examined.

2. Experimental

The phosphor powder used in this study was Eu-doped Ca-α-SiAlON[4] synthesized by the gas-pressure-sintering method[10,11]

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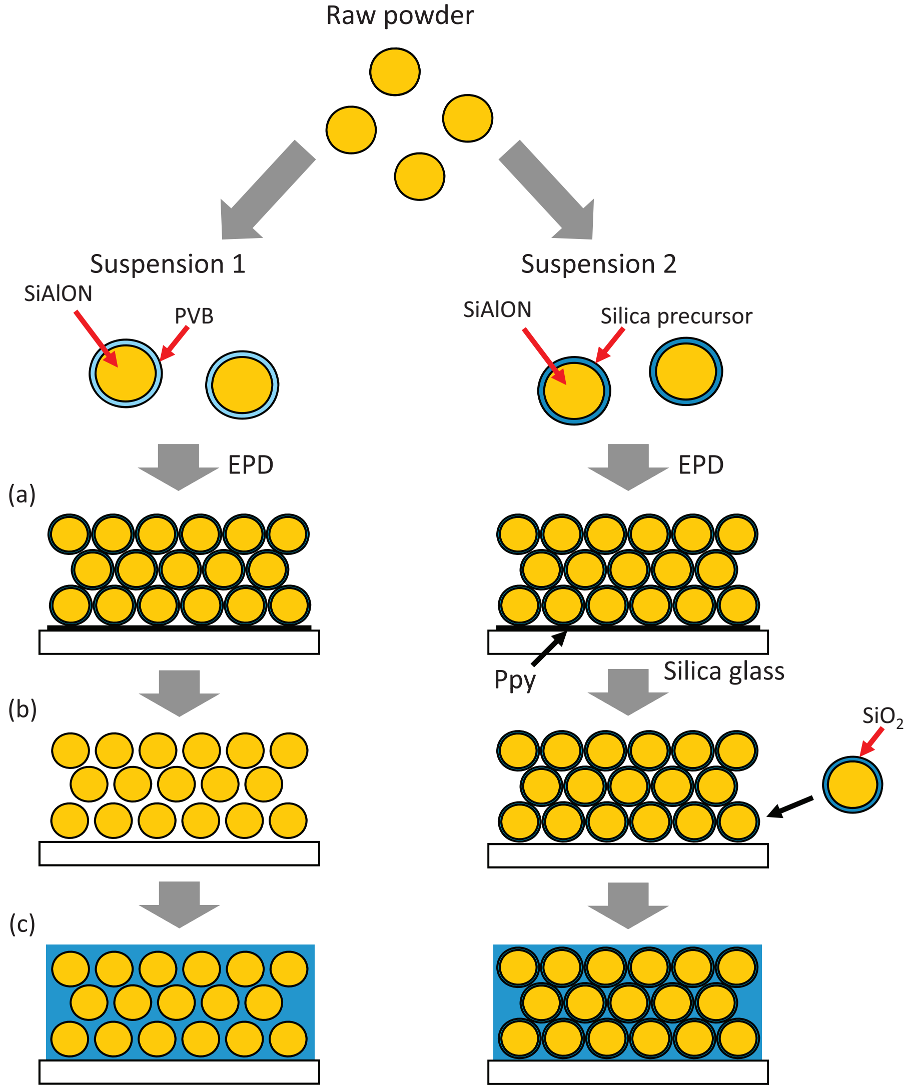

Fig. 1. Schematic diagram of the preparation procedure of the SiAlON–SiO_2 composite film; (a) as-deposited film prepared by EPD, (b) after the calcination to remove the Ppy and PVB or to convert the silica precursor to SiO_2, (c) after the thermal treatment to convert the impregnated silica precursor to the SiO_2 filler.

and supplied by the Denka Corporation, which shows a yellow light emission of $\lambda = 585$ nm. The deposition of the SiAlON phosphor was performed by EPD using two kinds of suspensions. Suspension 1:1 g of the powder was dispersed in 100 ml of ethanol with the phosphate ester (PE), polyethylenimine (PEI) and PVB, the formulation of which was the same as in previous reports.[16,17] Suspension 2:1 g of the powder was dispersed in a 100 ml solution of 5 mM tetraethoxysilane (TEOS)/ethanol, then hydrolyzed by water to form the silica precursor coatings.[18,19] Polypyrrole (Ppy), a conducting polymer, -coated silica glass slides were used as the cathodic substrate and a stainless steel sheet was used as the anodic counter electrode.[20–22] The applied electric field strength between the electrodes was 50 V/cm and the deposition time was 60 s. Fig. 1 shows a schematic diagram of the preparation procedure of the SiAlON phosphor–SiO_2 composite films. After the deposition of the phosphor powder, the as-deposited films were calcined at 773 K to burn out both the PVB and Ppy or to convert the silica precursor to SiO_2. The separately-prepared silica precursor sol consisting of 6 ml of TEOS mixed with 3 ml of distilled water, 4 ml of ethanol and 1 ml of 35N HCl solution was then impregnated into the open pores of the calcined deposit layers, followed by a thermal treatment at 773 K to convert the silica precursor to SiO_2. The zeta potential of the powders in suspensions 1 and 2 was measured by the phase analysis light scattering method (PALS) (Malvern, Zetasizer Nano Z). The particle size distribution was measured by a dynamic light-scattering method (NIKKISO, Nanotrack UPA). The adhesion of the deposit was evaluated by the tape test according the Japanese Industrial Standard (JIS) H8504[23] using NICHIBAN tape (width: 18 mm, adhesion: 9.7 N/25 mm). The surfaces and cross-sections of the prepared SiAlON phosphor–SiO_2 composite films were observed using a scanning electron microscope (SEM) (HITACHI S4100). The photo luminescence (PL) property of the composite films was characterized by a multi-channel photo-detector (Otsuka Electronics, MCPD-7000) using the 450 nm wavelength blue light as the pump source. The irradiation of the blue light was conducted from the particle-undeposited side of the substrate. The

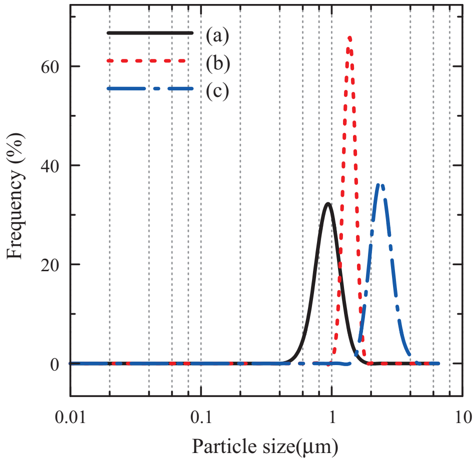

Fig. 2. Particle size distribution of the (a) suspension 1, (b) suspension 2 (single-coated), (c) suspension 2 (double-coated).

temperature dependence of the PL intensity was also measured from room temperature to 573 K. The external quantum efficiency was calculated from the ratio of the total photon number of the actual measured light to the total photon number of the incident light.[16]

3. Results and discussion

For suspension 2, the second coating of the sample was also performed by adding the same amount of the TEOS solution to the single-coated suspension to compare the effect of the double coating. The zeta potentials of the as-prepared suspensions 1 and 2 (single-coated and double-coated) were +25.0, +29.0 and +29.2 mV, respectively. This indicated that the silica precursor-coated SiAlON phosphor particles have a positive charge potential without using PEI, a cationic dispersant, probably because of the strong acidic pH due to the HCl and seemed to be well-dispersed. Therefore, the EPD process using the TEOS-added suspension was performed without adding any dispersants and binder. Fig. 2 shows the particle size distribution of the suspensions. The average particle sizes of the powders in suspension 1, suspension 2 (single-coated) and suspension 2 (double-coated) were 0.8, 1.2 and 2.1 μm, respectively. The average particle size increased after the coating with the silica precursor. The narrowest particle size distribution of the single-coated powder was probably due to the increase in the zeta-potential causing the improvement of the dispersion. However, the second-coating might have caused re-agglomeration due to the formation of the excessive amount of silica precursor. Fig. 3 shows the cross-sectional SEM images of the as-deposited films from suspension 1 (a), suspension 2 (b) and the silica-impregnated film from suspension 1 (c). There are many open pores in the PVB-used deposit as shown in Fig. 3(a). On the other hand, the voids decreased in the silica precursor-coated deposit (Fig. 3(b)) compared to the PVB-used one. This is attributed to the fact that the silica precursor on the surface of the powder worked as a binder. The voids in the prepared composite film were further decreased by the silica precursor impregnation followed by the thermal treatment. Fig. 3(c) shows that most of the voids in the composite film are filled with SiO_2. The interfacial adhesion of the composite film to the silica glass substrate seems to be fairly good. Fig. 4 shows the results of the tape test of the calcined films from suspension 1 (a) and suspension 2 (b) and the silica-impregnated films (c and d). After the calcination, the adhesion of the films to the substrate became very weak; especially, the silica precursor-coated one (Fig. 4(b)) mostly peeled-off without breaking probably because the silica precursor on the particles promoted the interparticle binding rather than the particle-substrate bindings thus causing the easy separation of the deposit layer from the substrate. On the other hand, the silica-impregnated composite films, Fig. 4(c) and (d), did not come off the silica glass substrate. This composite film maintained its bonding to the substrate even against a high impact by dropping it on the floor from a 1-m height. Fig. 5 shows the PL spectra measured for a silica-impregnated composite film prepared from suspension 1. The PL intensity of the composite film increased compared to that of the previ-

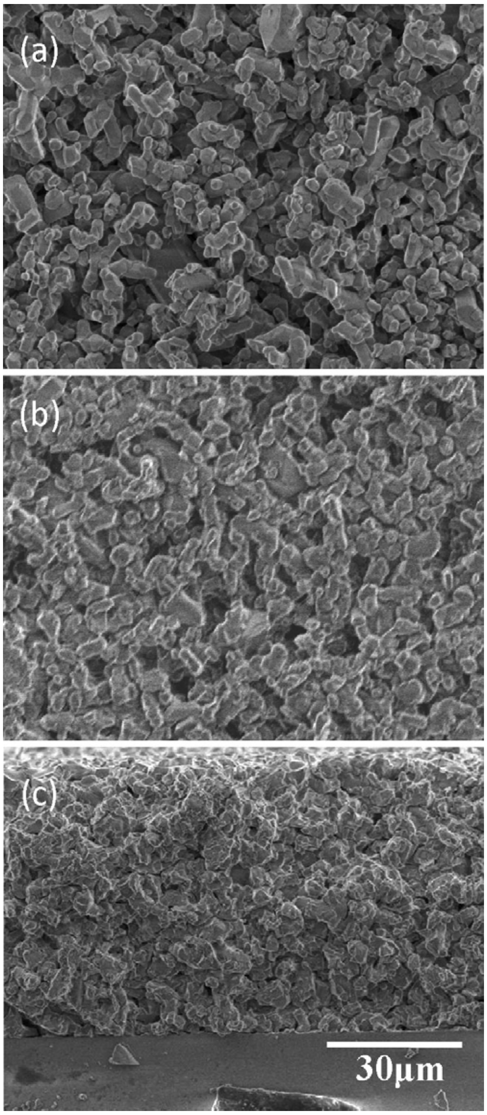

Fig. 3. Cross sectional SEM images of the deposited films; (a) PVB-used film, (b) silica precursor-coated film, (c) composite film.

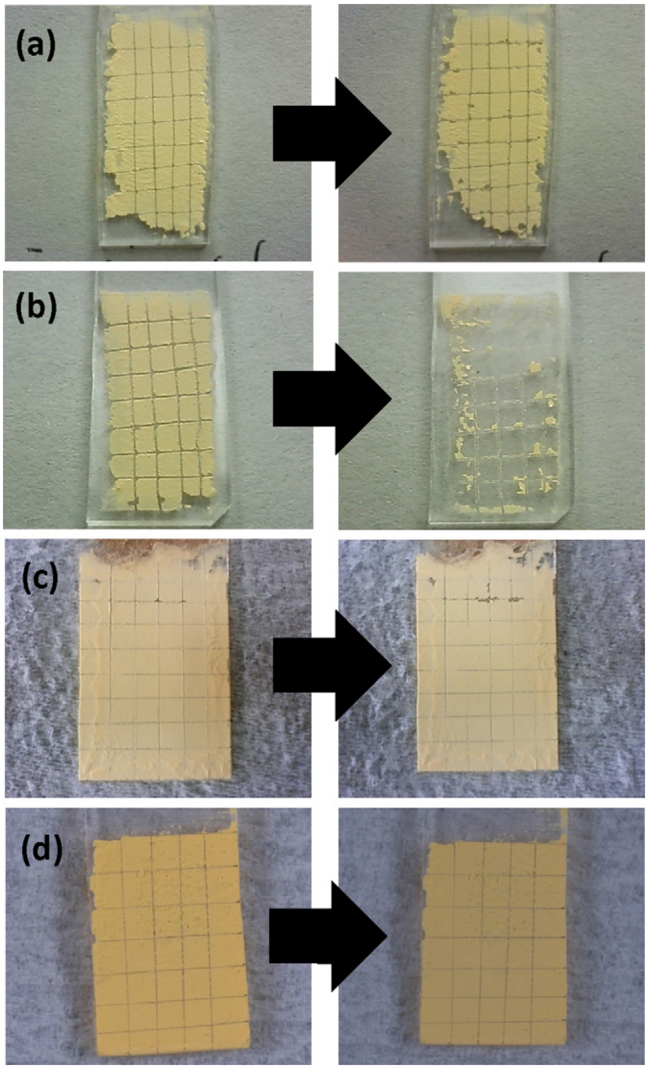

Fig. 4. Surface appearance of the films before and after the tape test. The cross-cut lines are made using a cutting knife; (a) PVB-used film, (b) silica precursor-coated film, (c) the composite film (single-coated) and (d) double-coated. The right photo is the result of the tape test.

ously reported as-deposited film. These PL spectra have almost the same chromaticity coordinates ($x = 0.50$, $y = 0.42$) showing almost the same color. The external quantum efficiency was further improved by replacing the binder for the EPD from PVB with the silica precursor. The external quantum efficiency calculated from the PL spectra is shown in Table 1. The external quantum efficiency ratios of the composite films are shown relative to that of the as-deposited PVB-used film defined as 100%. The efficiencies of all the composite films were improved compared to the as-deposited PVB-used film.[16] This is because the voids are filled or reduced in size by the condensation polymerization of the silica precursor. These results suggest that the rectilinear propagation performance of the light is improved by controlling the diffuse reflection by filling the voids in the film with SiO_2. Fig. 6 shows the temperature dependence of the PL intensity of the silica-impregnated composite film and the as-deposited PVB-used film. The PVB-used film in this experiment was prepared under the same conditions as the previously-reported one,[16,17] using PE, PEI and PVB, with the applied electric field strength of 50 V/cm and the deposition time of 60 s. The PL intensity decreased as the temperature increased. The temperature dependence of the composite film would be

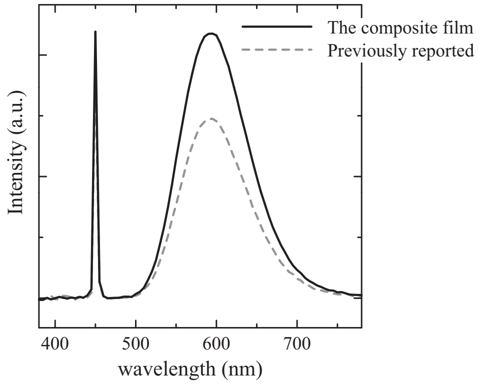

Fig. 5. PL spectra of the silica-impregnated composite film and the previously-reported as-deposited film prepared using PVB as the binder.

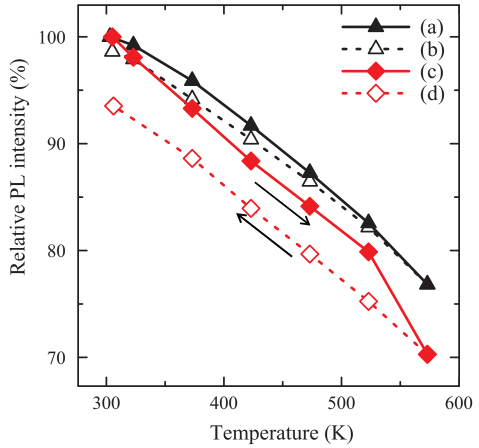

Fig. 6. Temperature dependence of the PL intensity. The measurement was performed during heating and then cooling; (a) the SiAlON–SiO_2 composite film (heating), (b) cooling, (c) the PVB-used previously reported film (heating), (d) cooling.

Table 1
External quantum efficiency ratio of the silica-impregnated composite films to the as-deposited PVB film.

Binder for the EPD	Chromaticity coordinate		External quantum efficiency ratio (%)
	x	*y*	
PVB	0.45	0.36	105–119
Silica precursor (Single coated)	0.50	0.42	124–127
Silica precursor (Double coated)	0.50	0.42	135–140

due to the intrinsic property of the SiAlON phosphor. For the composite film, the PL intensity at each temperature was similar during the heating and cooling, showing the reproducibility of the temperature dependence of the PL intensity. On the other hand, the PL intensity of the PVB-used film deteriorated after the heating to 573 K. The reason for this deterioration is attributed to the inferior thermal stability of PVB. PVB starts to burn out at over about 623 K; however, SiO_2 is stable up to a much higher temperature and works as a binder in the composite film. These results indicate that using SiO_2 as a binder and a filler is effective for high-brightness LED applications.

4. Conclusions

TEOS addition to a Eu-doped Ca-α-SiAlON phosphor suspension allowed the preparation of the deposits by EPD without adding any dispersants and binder. The silica-impregnated composite films had an excellent adhesion to the silica glass substrate. The external quantum efficiency of the composite films was improved compared to the PVB-used films. The Eu-doped Ca-α-SiAlON phosphor–SiO_2 composite films are superior to the PVB-used films based on both their adhesive and optical properties.

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