Electrophoretic deposition of Eu^{2+} doped $\text{Ca-}\alpha\text{-SiAlON}$ phosphor particles for packaging of flat pseudo-white light emitting devices

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The preparation of Eu^{2+} doped $\text{Ca-}\alpha\text{-SiAlON}$ phosphor films were conducted on ITO glasses by electrophoretic deposition (EPD). The thickness of the SiAlON phosphor films was controlled by altering the deposition time. The photoluminescent (PL) properties of the SiAlON phosphor films were characterized by blue-light ($\lambda = 450 \text{ nm}$) irradiation through the ITO glass substrates. The light emission from the deposit surfaces was characterized by comparing the intensities of the excited yellow light and the transmitted blue light. The chromaticity coordinates were calculated from the PL spectra and compared with actual colors perceived by human eyes.

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1. Introduction

Recently, the luminescent materials based on rare-earth-doped nitrides/oxy-nitrides have attracted attention because of their non-toxicity, thermal stability and interesting luminescence properties.^{1)–5)} Among the nitride/oxy-nitride luminescent materials, yellow light emission phosphor of Eu^{2+} doped $\text{Ca-}\alpha\text{-SiAlON}$ has advantages for the application of pseudo-white light-emitting diodes (LEDs). Hirotsaki et al.^{6)–10)} have demonstrated the warm-white LED lamps using the Eu^{2+} doped $\text{Ca-}\alpha\text{-SiAlON}$ and blue LED. In the near future, the SiAlON phosphor may be applied to general illuminations and liquid crystal displays (LCDs).

The SiAlON phosphor is generally synthesized by solid phase reaction in the form of powders, therefore it is essential to establish the packaging technologies for the diversity of applications. Electrophoretic deposition (EPD) is a colloidal process wherein ceramic bodies with high homogeneity and green density are directly shaped from a stable colloidal suspension by a dc electric field.^{11)–14)} The EPD process also has the advantage of the controllability of deposit thickness by altering the applied voltage and the deposition time. Therefore EPD is a possible technique for the packaging of phosphor powder. In this study, the fabrication of flat, uniform films of the Eu^{2+} doped $\text{Ca-}\alpha\text{-SiAlON}$ phosphor powder was performed by EPD. The light emission properties of the SiAlON phosphor films excited by blue light were also characterized by measuring the photo luminescence (PL) spectra.

2. Experimental

The Eu^{2+} doped $\text{Ca-}\alpha\text{-SiAlON}$ powder was prepared by gas-pressure sintering (GPS).^{2),3)} The scanning electron microscope (SEM) image of the $\text{Ca-}\alpha\text{-SiAlON}$ phosphor powder is shown in

Fig. 1. The primary particle size is about $1 \mu\text{m}$ but the powder contains relatively large aggregates of $\sim 20 \mu\text{m}$. 2 g of powder was dispersed in 100 ml of ethanol with small amounts of phosphate ester (PE) and polyethylenimine (PEI) as dispersants, polyvinyl butyral (PVB) as a binder, and a colloidal suspension of the SiAlON phosphor was prepared. An ultrasonic homogenizer was used to improve the particle dispersion but further mechanical grindings was not conducted since they might affect the PL property of the SiAlON phosphor. An ITO glass was used as a cathodic substrate and a stainless steel sheet was used as an anodic counter electrode. The EPD was conducted at a constant voltage mode and the applied voltage was optimized in the range of 5–100 V depending on the samples. The deposition area was $20 \times 20 \text{ mm}^2$. As the SiAlON phosphor powder contains large secondary aggregates of 1–20 μm as shown in Fig. 1, it is con-

Fig. 1. SEM image of the Eu^{2+} doped $\text{Ca-}\alpha\text{-SiAlON}$ phosphor powder.

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sidered that the quality of deposited films such as its density and optical properties differs depending on the particle sizes. Therefore, the EPD process was conducted at two different conditions: Condition 1: EPD was started just when the stirring of the suspension was stopped.

Condition 2: EPD was started when 1 min passed after stirring stopped.

Figure 2 shows the particle size distribution measured for the suspensions at conditions 1 and 2 by the dynamic light scattering (DLS) analysis method (Otsuka Electronics, LASER PARTICLE ANALYZER PAR-III). In the case of condition 1, the powder with a variety of particle sizes can deposit on a substrate. In the case of condition 2, large aggregates of the powder sediment in the suspension and relatively small particles can deposit on a substrate. The thickness of the SiAlON phosphor films was controlled by altering the deposition time from 0 to 300 s. The adhesion of the deposit on an ITO glass substrate was evaluated by a tape test of JIS H8504¹⁵⁾ using a NICHIBAN tape (Width: 18 mm, Adhesion: 9.7 N/25 mm). The microstructures of the deposited films were observed by a field emission scanning electron microscope (FE-SEM) (Hitachi S-4100).

The PL properties of the SiAlON phosphor films were characterized by using blue light of the wavelength of 450 nm as a pump source. The blue-light irradiation was conducted through the ITO glass substrates as shown in **Fig. 3**. The light emission from the deposit surfaces was characterized by comparing the

intensities of the excited yellow light and the transmitted blue light through the deposit using a multi channel photo detector (Otsuka Electronics, MCPD-3700). In addition, chromaticity coordinates were calculated from the PL spectra and compared with actual colors perceived by human eyes.

3. Results and discussion

3.1 Optimization of colloidal suspension

It is essential for the EPD process that the colloidal particles in a solvent should be electrostatically stabilized for the electrophoresis. As the SiAlON is oxynitride and its surface is easily oxidized in an aqueous suspension, ethanol was selected as a dispersing medium. Phosphate ester (PE) was an effective electrostatic stabilizer, which made the SiAlON phosphor surface positively charged in ethanol by donating protons to the surface hydroxyls of the powder. The amount of PE was determined by measuring the pH and conductivity of the colloidal suspension.^{16),17)} The additional amounts of PVB and PEI were optimized from the density measurement of the deposited films and the external homogeneity check with eyes. As the result of the adhesive tape test, one-third of the deposited films were peeled off from the substrates. However, the deposited film stuck well to the substrate even by the centrifugalization at 5000 rpm for 5 min. We think that the adhesion of the deposited film is strong enough against the vibration and impact. It must be important for the packaging of the SiAlON phosphor. The optimal data of the component of the suspension, the appropriate applied voltage and the green density of the obtained deposits are shown in **Table 1**.

Table 1. Optimized Suspension Component and Applied Voltage

Et-OH	100 ml
Eu ²⁺ doped Ca- α -SiAlON	2 g
PE	0.001 g
PVB	0.25 g
PEI	0.001 g
Applied voltage	30 V
Relative density	55–60%

3.2 Characterization of deposited films

Figure 4 shows the deposit yield and the thickness of the SiAlON phosphor film as a function of time during EPD. The deposit yield increased proportionally with time, and then saturated at the amount of 0.01 g/cm² for both conditions 1 and 2. The deposition rate of condition 2 was higher than condition 1. The surface microstructure of the two films observed by SEM is shown in **Fig. 5**. The deposit film prepared at condition 1 consisted of larger particles than condition 2 though the surface appearances of both the films were similar. The visible luminescent color of the two deposit films was compared by irradiating blue LED lights behind the substrates. These films show the colors from blue-white to yellow-white. Though the film thickness and deposited yield are similar, the visible color was different between conditions 1 and 2; the deposit film of condition 2 showed a more yellowish color. This is probably due to the difference of the absorption and scattering of the light between the two films with different particles sizes. When the blue incident light strikes a SiAlON phosphor particle, a part of the light refracts at the surface and then enters the crystal; the rest of the

Fig. 2. Particle size distribution of the suspension at conditions 1 and 2.

Fig. 3. Schematic illustration of a flat pseudo-white light emitting device.

Fig. 4. Deposit yield and the thickness of the SiAlON phosphor film as a function of time: $\diamond$ condition 1, $\blacktriangle$ condition 2.

Fig. 5. SEM micrographs of the SiAlON phosphor films prepared in conditions 1 and 2. A photograph of a typical SiAlON phosphor film is also shown here.

blue light is reflected and goes towards another particle. The total absorption of the blue light in the lattice should be proportional to the frequency of the light hit on the particles, which must be higher for small powders having a large specific surface area. Therefore, the deposit layer of condition 2 could emit yellow light more effectively.

Figure 6 shows the PL spectra of the deposited films of conditions 1 and 2. The intensity of the transmitted blue light at 450 nm decreased with an increase of the film thickness. The intensity of the excited yellow light at 585 nm decreased with an increase of the film thickness by the same token. The intensity of the excited yellow light of the condition 1 film was lower than that of the condition 2 film.

Figure 7 shows the CIE (Commission Internationale de l'Eclairage) chromaticity diagrams calculated from the PL spectra of the films prepared at conditions 1 and 2. The color on the chromaticity diagram agreed well with the actual color perceived by human eyes. These figures also indicated that the color coordination is possible by controlling the thickness of the deposit

Fig. 6. PL spectra of the deposited films of conditions 1 and 2.

Fig. 7. Chromaticity diagram of the films prepared at conditions 1 and 2. Ref. was reported by Hirosaki et al.⁸⁾

films. From the comparison of conditions 1 and 2, it is suggested that the particle size and the deposit density greatly affect the color tone. Therefore, the thickness, density and quantum efficiency were compared between the two samples deposited for 120 s at condition 1 and deposited for 20 s at condition 2, which are considered to be almost the same in color on the chromaticity diagrams. The quantum efficiency was calculated from the total photon number of floodlight and the measured photon number. The results are shown in **Table 2**. The quantum efficiency of the films of conditions 1 and 2 are 0.39% and 1.2%, respectively. The quantum efficiency of the condition 2 film is three times higher than the condition 1 film. It is probable that the light attenuation of the condition 1 film is high due to the large thickness of the film. The light absorption is an important factor, which affects the quantum efficiency. The use of smaller particles with a narrow particle size distribution would increase the efficiency of the SiAlON phosphor film. It was demonstrated that the EPD is a quite useful technique for the fabrication of a flat pseudo-white light emitting device.

Table 2. Quantum Efficiency of the Films of the Conditions 1 and 2

	chromaticity coordinate		film thickness (μm)	relative density	quantum efficiency
	x	y			
Condition 1 120 s	0.353	0.254	3.83	55%	0.39%
Condition 2 20 s	0.374	0.269	2.09	52%	1.2%

4. Conclusions

Homogeneous Eu^{2+} doped $\text{Ca-}\alpha\text{-SiAlON}$ phosphors films were prepared on ITO glasses by EPD. Adhesions of prepared films were high and they were not peeled off from the ITO glass substrates even by centrifugalization at 5000 rpm for 5 min. The color coordination of the deposit films is controllable from blue-white to yellow-white by optimizing the relative intensities of the transmitted blue light and the excited yellow light. The excitation of yellow light was dependent on the particle size of the phosphor powder. The color on the chromaticity diagram calculated from the PL spectra agreed well with the actual color perceived by human eyes.

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