Effect of Nanoscaled SiO$_2$ Coating on Luminescent Properties of Blue Phosphors

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An investigation is reported on the growth of SiO$_2$ nano-film on BaMgAl$_{10}$O$_{17}$:Eu$^+$ blue phosphors using atomic layer deposition. Silicon oxide films were prepared at room temperature using Si(OC$_2$H$_5$)$_4$, C$_2$H$_5$N and H$_2$O as precursor, catalyst and reactant gas, respectively. XPS analysis showed the surface composition of coated phosphor powder was silicon oxide. In TEM and FESEM analysis, the growth rate was about 0.66 Å/cycle and the surface morphology became smoother than that of uncoated powder. The photoluminescence intensity for coated phosphors was 0.6~11.3% higher than that of uncoated.

Keywords: atomic layer deposition, BaMgAl$_{10}$O$_{17}$:Eu$^+$ phosphor, silicon oxide coating, photoluminescence, C$_2$H$_5$N catalysts

1. INTRODUCTION

BaMgAl$_{10}$O$_{17}$:Eu$^+$ (BAM) blue phosphors used in LCD and PDP display devices are one of the most attractive materials. This phosphor emits in the broad band of photo-luminescent peak around 450 nm due to the transition of divalent europium ions (Eu^{2+})4f^{6}5d^1 to 4f.$^{7[1]}$ However, BAM phosphors are found to be unstable and degraded because the luminance decrease due to oxidation.[2,3] The degradation process is caused by several paths, such as irradiation by ultraviolet photons, ion sputtering and the baking process during PDP manufacturing, etc. One solution to the problems is to passivate the surface of BAM phosphors with oxide. The coating of oxide on the ZnS phosphors was frequently applied to enhance the chemical stability of sulfide phosphors. Several coatings, such as SiO$_2$,[4] In$_2$O$_3$,[5] TiO$_2$,[6] and rare earth oxide,[7] have been investigated using sol-gel and CVD processes. In sol-gel and CVD processes, the optical intensity of the coated phosphor decreased more normally than that of uncoated phosphor due to oxide absorption, and the aggregation of phosphor powder was also a primary barrier for applications. However, ALD films are grown by a respective process of a single layer(or less than a layer) deposition sequence. Each sequence consists of several gas-surface interactions that are all self-limiting.[8-10]

In the present work, the thin silicon oxide coating on BAM phosphors by atomic layer deposition was investigated. Silicon oxide films grown by atomic layer deposition was prepared using Si(OC$_2$H$_5$)$_4$, C$_2$H$_5$N and H$_2$O as a precursor, catalyst, and reactant gas, respectively. The effect of silicon oxide films on the structural and optical properties of BAM phosphors was investigated as a function of the film thickness.

2. EXPERIMENTAL PROCEDURE

The growth process was carried out in a vertical flow-type ALD reactor.[11] Si(OC$_2$H$_5$)$_4$ was evaporated from a boat at 70°C and was transpired with Ar carrier gas. The heating line was maintained at 100°C to prevent recondensation of Si(OC$_2$H$_5$)$_4$. The chamber temperature was about 30°C. The working pressure in the reactor was about 1 torr. C$_2$H$_5$N was used as a catalyst, H$_2$O as a reactant gas, and Ar as a carrier and purge gas. The opening and closing sequences of the air valves were controlled using a personal computer. To improve the ability of BAM phosphors (Nichia, NP type) to adsorb the precursor and the reactant gas, the multi-pulsed sequence process was applied to the chamber. The exposure time per one cycle was 60s. Figure 1 shows the process sequence of the gas valve.

The composition of the films grown on phosphor powders was examined by X-ray Photoelectron Spectroscopy (XPS, ESCALAB 210). Field Emission Scanning Electron Microscopy (FESEM, JSM-6500F-Jeol) and Transmission Electron Microscopy (TEM, H-7600, Hitachi) were used to investigate the surface morphology and the thickness of the films, respectively. The photoluminescence was measured using a Spectroradiometer (PL, CS1000, Minolta) at room temperature. A mercury lamp was used for excitation of the phos-

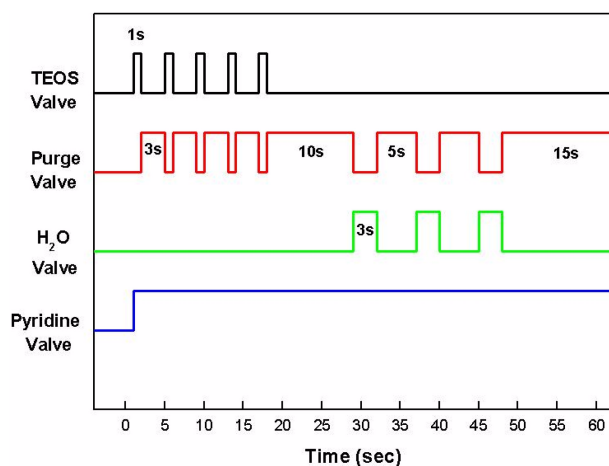*Corresponding author: choibh@kumoh.ac.kr

Fig. 1. The process sequence of the gas valve.

phor in the UV(254 nm) region.

3. RESULTS AND DISCUSSION

In the sol-gel process, there are many process variables, such as concentration of precursors, pH, and temperature of solutions, which can affect the surface morphology. In the ALD process, however, the rough surface of uncoated phosphor became smoother and clearer as the number of ALD cycle increased from 300 to 600 cycles, as shown in Fig. 2. On the contrary, it was reported that in the sol-gel process, the surface of coated phosphor became rougher than that of uncoated.[4]

Figure 3 shows XPS peak intensity of BAM phosphors grown with nanoscaled films by a 600 ALD cycle. The two peaks at ~100.2eV and ~103eV correspond to SiOx and SiO_2, respectively. Therefore, nanoscaled films can be confirmed to be the silicon oxide.

Figure 4 shows a TEM image of a silicon oxide-coated BAM particle. The film was deposited by 300 cycles. The TEM image reveals that the surface of the silicon oxide film is extremely uniform and the thickness is about ~20 nm. As a result, the growth rate is ~0.66 Å per cycle.

Figure 5 shows the photoluminescence spectra of uncoated and silicon oxide-coated BAM phosphors under 254 nm excitation. The PL intensity of coated phosphor was 78.31~86.59 cd/m^2 as a function of ALD cycles, as shown in Table 1. These values were 0.6~11.3% higher than that of uncoated phosphor, but the color coordinate was invariant. This means that the reactive surface is coated with stable silicon oxide and also the oxide absorption is almost negligible due to ultra thin films of~20 nm up to 300 ALD cycles. The surface has high free energy due to the abrupt discontinuation of the bulk. The excess free energy is reduced by rearrangement of the silicon oxide. This phenomenon may attribute to higher PL intensity.[12] Considering the reflectiv-
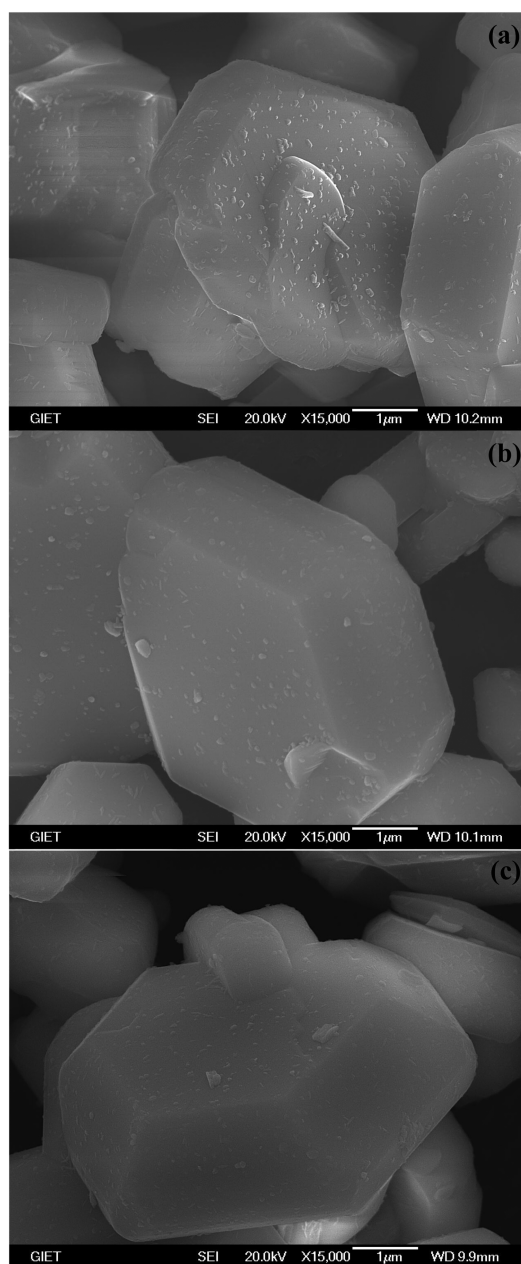

Fig. 2. FE-SEM photographs of phosphor powder: (a) uncoated, (b) SiO₂ coated by 300 cycles, and (c) 600 cycles.

ity for uncoated and SiO₂ coated BAM, the calculated reflectivity of the coated BAM surface is about 0.044 while that of the uncoated BAM is 0.067. The lower reflectivity may also attribute to higher PL intensity. Above 400 cycles, however, PL intensity decreases due to the absorption of thicker films. Until now, it was generally reported that the initial intensity of uncoated phosphor was higher than that of coated phosphor.[4,7] This inverse effect is probably due to the ALD growth mechanism. It was also clear that the films grown with ALD were more uniform, continuous, and free of surface defects than those of sol-gel and CVD.
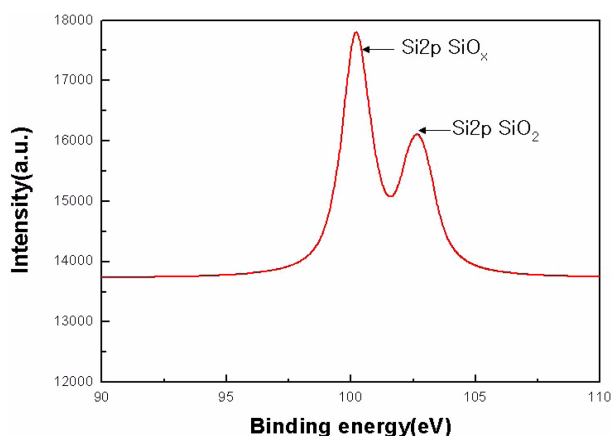
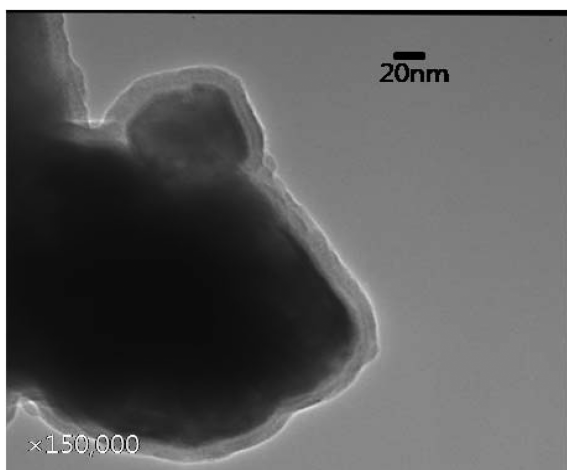**Fig. 3.** XPS spectrum of BAM phosphor coated by SiO₂ at ALD 600cycles.

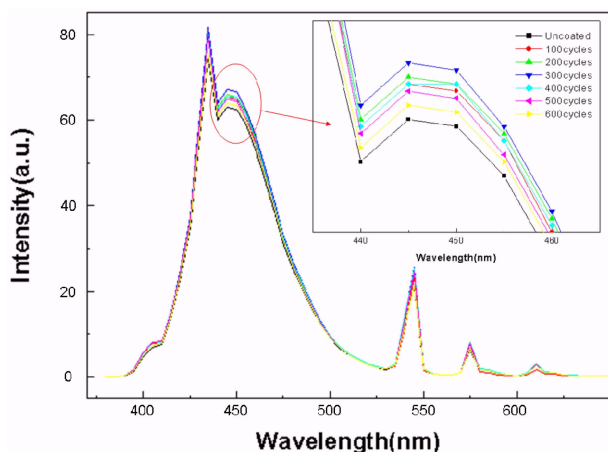**Fig. 4.** TEM photograph of BAM phosphor coated by the SiO₂ film at ALD 300cycles.

Fig. 5. PL spectra of BAM phosphors with various ALD cycles.

4. CONCLUSIONS

The ALD process for oxide coating phosphors showed a remarkable improvement in PL intensity. In the sol-gel and

Table 1. Photoluminescent characteristics of uncoated and SiO₂ coated phosphors

	Photoluminescence Intensity (cd/m²)	Color coordinate	
		X	Y
uncoated	77.83	0.157	0.081
100 cycles	79.29	0.157	0.081
200 cycles	84.07	0.157	0.080
300 cycles	86.59	0.157	0.081
400 cycles	85.99	0.157	0.078
500 cycles	82.80	0.157	0.081
600 cycles	78.31	0.157	0.081

CVD processes, the PL intensity of coated phosphor decreased more normally than that of uncoated due to the oxide absorption, and the aggregate of phosphor powders was also a primary barrier for application. In the ALD system, however, the ultra thin and uniform film can be controlled without the aggregate of phosphor powders. Further detailed investigations will be carried out on topics including various powders, such as the phosphors for plasma display panels, which have degradation problems.

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