Research Article

Atomic Layer Deposition of MgO Nanofilms on BaMgAl₁₀O₁₇:Eu²⁺ Blue Phosphors

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This paper reports the growth of MgO nanofilms on BaMgAl₁₀O₁₇:Eu²⁺ blue phosphors by using the atomic layer deposition method. MgO films were prepared at 120°C by using Mg(CpEt)₂ and H₂O as the precursor and reactant gas, respectively. X-ray photoelectron spectroscopy (XPS) analysis showed that the Mg peak of the coated powders was higher than that of the uncoated powders. This confirmed that the surface of the coated phosphor powder comprised MgO nanoscale film. Through TEM and FE-SEM analysis, it was observed that the growth rate was about 0.33 Å/cycle and that the surface morphology of the coated phosphors was smoother and clearer than that of uncoated phosphor. The photoluminescence (PL) intensity for the coated phosphors was 5%–19% higher than that of uncoated phosphor. This means that the reactive surface is uniformly grown with stable magnesium oxide to reduce the dead surface layer without change of bulk properties.

1. Introduction

The brightness of a plasma display panel (PDP) is mainly determined by the discharge efficiency of the Ne/Xe plasma, percentage of VUV photons absorbed by the phosphor layer, conversion efficiency within the phosphor layer, and efficiency of the out-of-visible light. The conversion efficiency of a luminescent material is determined by the amount of absorbed incident radiation and by its quantum efficiency. Both these parameters are strongly dependent on the excitation wavelength. The absorption of VUV photons by currently used PDP phosphors is very high because the bandgap absorption occurs in that wavelength range [1]. Moreover, the discharge efficiency itself is influenced by the PDP phosphor, since it is in close contact with the Ne/Xe plasma within the tiny discharge cells. The surrounding of a plasma has a strong impact on its efficiency since ions are accelerated towards the cathode and can generate new electrons (avalanche effect). The ratio of new electrons generated per incident ion is defined as the secondary electron emission coefficient γ , which

is material dependent. MgO has a one of the highest electron emission coefficients, hence MgO-coating is applied on the front plate of a PDP [2].

BaMgAl₁₀O₁₇:Eu²⁺ (BAM) blue phosphors are one of the most attractive materials for use in PDP devices. However, BAM phosphors are found to be unstable, and they undergo degradation because of a decrease in their luminance from oxidation [3, 4]. The degradation process is caused by several processes such as irradiation by ultraviolet photons, ion sputtering, and baking process during PDP manufacture. One of methods to solve these problems is to passivate the surface of BAM phosphors with oxides. The effectiveness of coating the surface of BAM phosphors with several oxides such as SiO₂ [5, 6] and MgO [7, 8] by using the sol-gel process has been investigated. However, the use of the sol-gel process resulted in certain problems such as nonuniform and highly defective coating of the phosphor, which, in turn, resulted in a decrease in the luminescence efficiency, despite excellent passivation. In our previous studies, surface treatment of BAM phosphors with SiO₂ [9, 10] using atomic

FIGURE 1: FE-SEM images of phosphor powder: (a) uncoated, (b) MgO-coated with 600 ALD cycles.

layer deposition (ALD) was proposed for increasing their luminance. ALD is used to fabricate ultrathin and thin film devices [11, 12].

In the present study, the effect of MgO films coating on the structural and optical properties of BAM phosphors was investigated as a function of the film thickness.

2. Experimental Procedure

The coating process was carried out in a vertical flow-type ALD reactor [9, 10]. $\text{Mg}(\text{CpEt})_2$ was evaporated from a boat at 80°C and was transpired with Ar carrier gas. The heating line was maintained at 100°C to prevent the recondensation of $\text{Mg}(\text{CpEt})_2$. The reactor temperature was about 120°C , and the working pressure in the reactor was about 1 torr. H_2O was used as the reactant gas, and Ar was used as the carrier and purge gas. The opening and closing sequences of the air valves were controlled by using a personal computer. The exposure time was 6 seconds for the $\text{Mg}(\text{CpEt})_2$, then 15 seconds for the purging, and a reactant gas was transpired for 10 seconds, followed by the purging for 20 seconds. The composition of the films coated on the phosphor powders was examined by X-ray photoelectron spectroscopy (XPS, ESCA-LAB-210). Field emission scanning electron microscopy (FE-SEM, JSM-6500F-Jeol) and transmission electron microscopy (TEM, H-7600, Hitachi) were used to investigate the surface morphology and thickness of the films. The photoluminescence of the phosphor powders was measured by using a spectrometer (PL, CS-1000A, Minolta), and a mercury lamp was used for the excitation of phosphor in the UV region (253 nm).

3. Results and Discussion

The sol-gel process involves a number of process variables such as concentration of precursors, pH, and temperature of solutions, which can affect the surface morphology [13, 14]. In ALD process, however, the film is deposited by a respective process of single layer (or less than a layer)

FIGURE 2: XPS spectra of BAM phosphors coated with MgO with 600 ALD cycles.

deposition sequences. Each sequence consists of several gas-surface interactions that are all self-limiting. Figure 1 shows that the surface of the coated phosphors is smoother and clearer than that of the uncoated phosphor. On the contrary, it has been reported that in the sol-gel process, the surface of the coated phosphors is rougher than that of the uncoated phosphor [13, 14]. Figure 2 shows the XPS spectra of the BAM phosphors coated with nanoscale MgO films with 600 ALD cycles; the spectra show characteristic peaks for both Mg and O_2 . The two peaks at $\sim 531.8\text{ eV}$ and $\sim 50.6\text{ eV}$ correspond to O (1s) and Mg (2p), respectively [15]. Therefore, nanoscaled films can be confirmed to be MgO. Figure 3 shows the TEM image of an MgO-coated BAM particle. The MgO film was grown with 600 ALD cycles. The TEM image reveals that the surface of the MgO film is extremely uniform, and its thickness is about $\sim 20\text{ nm}$. As a result, the growth rate is $\sim 0.33\text{ \AA}$ per cycle.

FIGURE 3: TEM images of BAM phosphors coated with MgO with 600 ALD cycles.

FIGURE 4: PL spectra of BAM phosphors coated with MgO thin films.

Figure 4 shows the PL spectra of the uncoated and MgO-coated BAM phosphors, excited by (UV) light of wavelength 254 nm. The PL spectra reveal that both phosphors show a broad blue emission with a peak near 450 nm.

This is due to the 5d-4f transition of Eu^{2+} [16]. The PL intensity of the coated phosphors was in the range of 51.86 to 56.94 cd/m^2 , depending on the number of ALD cycles, as shown in Table 1. These values are 5%–19% higher than those of uncoated phosphor. This means that the MgO-coating on the reactive surface is stable and also that its absorption is almost negligible, because the thickness of the films is extremely small: $\sim 12\text{ nm}$ up to 400 ALD cycles. The surface has a high free energy because of the abrupt discontinuation of the bulk. The excess free energy is reduced because of the rearrangement of the MgO thin film. This phenomenon may also be attributed to the high PL intensity

TABLE 1: Photoluminescence characteristics of uncoated and MgO-coated phosphors.

	Photoluminescence intensity (cd/m^2)
uncoated	49.04
100 cycles	51.86
200 cycles	55.50
300 cycles	57.62
400 cycles	58.54
500 cycles	57.18
600 cycles	56.94

of the coated phosphors [10]. The low reflectivity may also be attributed to the high PL intensity of the coated phosphors. However, when the number of ALD cycles was above 500, the PL intensity decreased because of the absorption of the thicker films. So far, it has been reported that the initial intensity of uncoated phosphor is higher than that of coated phosphor [16]. This inverse effect is probably due to the ALD growth mechanism. It was also proven that the films coated by ALD are more uniform, continuous, and free of surface defects when compared to those coated by using the sol-gel process. In our previous studies, it was observed that the PL intensities of the MgO-coated phosphors were about 5% higher than those of SiO_2 -coated phosphors. On the basis of these results, it may be inferred that the MgO film has a higher secondary electron emission coefficient, and that it contributes to an improvement in the luminescence properties of the phosphors.

4. Conclusions

The use of the ALD process for coating phosphors with oxide layers resulted in a remarkable improvement in the PL intensity of the coated phosphors. In the sol-gel process, the PL intensity of the coated phosphors was lower than that of the uncoated phosphor because of oxide absorption and the presence of aggregates of phosphor powder. In the ALD system, ultra-thin uniform-thickness films can be formed without resulting in the formation of aggregates of phosphor powder. Further detailed investigations will be carried out, including various powders such as the phosphors for plasma display panel, which have degradation problems.

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