Enhanced emission from BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ by localized surface plasmon resonance of silver particles

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Abstract: The visible emission of BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ used for White LED and ACPDPs was enhanced by coupling electric transition with the localized surface plasmon oscillation of nanoscaled Ag particles. Phosphor films including Ag particles were prepared by the spin-coating method. Up to a 36% enhancement of the peak intensity, which was dependent on the morphology and concentration of Ag particles, was obtained. It was verified that the spectral overlap between the LSP energy of metal particle and the emission spectra of phosphor materials decided between the enhancement and quenching of the emission. It was indicated that localized field enhancement due to the LSPR of metal nanoparticles could improve the emission intensity of phosphor doped rare earth ions.

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OCIS codes: (240.6680) Surface plasmons; (160.5690) Rare-earth-doped materials.

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1. Introduction

High luminous efficacy in display devices has been studied extensively over the past two decades. Recently, enhanced emission from light emitters utilizing localized surface plasmon (LSP) has attracted the attention of many display engineers. For example, studies on the enhancement of light emission from ZnO film coated with Ag nanoparticles have become increasingly common [1,2]. Localized surface plasmon is defined as the electromagnetic oscillation of surface electrons in nanoscaled metal structures. Localized surface plasmon is decided by the material, size, and shape of metal nano-structure. Contrary to propagating surface plasmon (SP), the LSP of metal nanostructure has the advantage of easily controlling the plasmon resonance wavelength and obtaining the localized field enhancement without matching the KSP vector (propagation constant). A number of studies have successfully obtained higher performance by employing LSP resonance in applications including high harmonic lasers, display devices, bio sensors, and solar cells [3].

In the aforementioned display device, some studies on LSP resonance have been biased towards light emitting diodes (LEDs), organic light emitting diodes (OLEDs), zinc oxide, and quantum dots [4–9]. However, there has been little research regarding display devices using the photoluminescence (PL) phosphor such as White LEDs (WLEDs) and ACPDPs. In this paper, by employing the LSP resonance of metal nanoparticles, we attempt to obtain the enhanced emission of PL phosphor. The effect of Ag particles on the emission intensity of PL phosphor is investigated under the condition of some morphologies and Ag concentrations. The Ag particle inside phosphor film absorbs and scatters the emitted light from the phosphor, resulting in the electron clouds on the surface of Ag particle being collectively oscillated. Localized field enhancement by surface electron oscillation leads to the enhanced emission intensity of phosphor materials. It is reported that the emission intensity of phosphor in the proximity of metal particles can be enhanced owing to the LSP resonance of metal particles. The maximum emission intensity of LSP mediated phosphor is increased by about 36% compared to the non-treated phosphor.

2. Experiments: sample preparation

Figure 1 shows the graphical representation on the phosphor structure employing Ag nanoparticles. To prepare the phosphor sample, we mixed Ag nanoparticles with phosphor paste to place Ag nanoparticles on the surface of phosphors. We did this because, in the case of phosphor for ACPDPs, the penetration depth for vacuum-UV (VUV) light is very small, about 0.1–1 µm, and the visible light emission mainly occur at the surface of the phosphor [10]. Therefore, it was desirable that the Ag particles were attached to the surface of the phosphor or located nearby the phosphor. It was well-known that an emitter has to be located within a short distance because local field enhancement due to LSP resonance of Ag nanoparticles has an influence within a few of ten nanometers [11].
To implement the phosphor-Ag particle structure, two types of Ag nanoparticles were employed to induce localized surface plasmon coupling between phosphor and metallic structure. Ag sample 1 was synthesized from an AgNO$_3$ precursor by a wet-reduction method. The synthesis of Ag nanoparticles was carried out by mixing butanediol (99%, Sigma-Aldrich) solution containing 0.125 M AgNO$_3$ (99.9999%, Sigma-Aldrich) and 0.1875 M Polyvinyl-pyrolidone (PVP) as a surfactant for capping Ag nanoparticles. The reaction process for the reduction and growth of nanoparticles took place for more than three hours under stirring conditions. To eliminate any products such as NO$_3^-$ and butanediol, washing was carried out six times through centrifugation of the Ag solution with ethanol. We finally obtained Ag nanoparticles of 40 ~70 nm in diameter. Ag sample 2 was purchased from the ANAPRO Corp. (Republic of Korea). The BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$, which was PL phosphor for an ac plasma display device, was used as an emitter that had emission spectra in the blue wavelength, around 450 nm. The BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ paste mixed with Ag nanoparticles was spin-coated on the glass substrate and baked at 480°C for 30 min. The morphology of the phosphor film and Ag particle was confirmed using scanning electron microscopy (SEM) with an FEI (Netherlands) Sirion microscope and a Hitachi scanning transmission electron microscope (STEM, HD-2300A). The emission spectrum was measured using PSI spectrometers (PS-VUVPT-E1200, PS-PLU-X1420). This system holds the experimental conditions constant. For example, the wavelength of the excitation source is kept constant by filtering through a monochrometer. Additionally, the slit and excitation power are kept constant during the measurement. Emission spectra were measured sequentially under these constant experimental conditions. To measure the emission intensity, phosphor films were excited by a 147 nm Kr lamp and 254 nm Xe lamp with an incident angle of 90°, and the emission spectra in the range of visible light were collected through the Charge Coupled Device (CCD). The localized surface plasmon resonance can be confirmed by obtaining the extinction spectra that is composed of scattering and absorption coefficients. The extinction peak is located at the particular position corresponding to the size and shape of the metal nanoparticles. The extinction spectrum of Ag particles was detected using a Shimadzu spectrophotometer (UV-2550).

Figure 2 shows the SEM and STEM images of the Ag samples used in this work. As shown in Fig. 2(a), it was confirmed that Ag sample 1 had nearly a spherical shape of 40 ~70 nm in diameter. Figure 2(b) shows that Ag sample 2 was also the same size as sample 1 and
nearly had a spherical shape, though rod and triangular shaped particles were slightly included. The uniformity of Ag sample 1 was verified to be better than Ag sample 2 from STEM images. Figure 3 depicts the extinction spectra of two Ag samples dispersed in ethanol. The extinction spectra of Ag samples 1 and 2 showed peaks at 415 nm and 450 nm in an ethanol medium, respectively. It was remarkable that the extinction spectrum of Ag sample 2 had the broad characteristics due to the morphology of particles. It was clearly observed that the extinction spectra overlapped the emission spectra of blue phosphor.

![Fig. 2. STEM images of two Ag samples: (a) Ag sample 1 synthesized using a wet-reduction method and (b) commercial Ag sample 2. The inset figures show SEM images of Ag sample 1 and 2, respectively.](image)

![Fig. 3. Extinction spectra of (a) Ag sample 1 synthesized using a wet-reduction method and (b) commercial Ag sample 2 dispersed in an ethanol medium.](image)

**3. Results: emission spectra of Eu$^{2+}$ doped phosphors and numerical analysis**

Figure 4 depicts the emission spectra of phosphor films as a function of Ag concentration. Figure 4(a) shows the concentration dependence of Ag sample 1 on the emission intensity of phosphor. In this case, phosphor films were excited by a 147 nm vacuum-UV source, which was the same as the excitation source in plasma discharge. The concentration of Ag nanoparticles in the present of solution was selected as 15 ~60 g/L, and the emission intensity represents the average of four samples in each case. As shown in Fig. 4(a), the emission
intensity was increased as Ag concentration increased. The concentration dependence of Ag sample 2 on the emission spectra was illustrated in Fig. 4(b). Figure 4(b) shows the emission intensity under a 254 nm excitation. Similarly to Fig. 4(a), the emission intensity of phosphor films were increased as the Ag concentration increased. According to increase in the Ag concentration, numerous phosphors were influenced by field enhancement due to the LSP resonance of the Ag particles. Also, because this enhancement effect is described by the distance and the coupling direction between the emitter and localized surface plasmon oscillation, the enhancement factors have all of the characteristics of a random process [12]. In Figs. 4(a) and (b), the inset figures show the standard errors at the peak intensity. It was remarkable that emission intensity when using Ag sample 2 had a wide variation, as shown in the inset figures. It was considered that the non-uniformity of Ag sample 2 affected the emission intensity and thus broadened it. The Ag particles of the rod and triangular types have a weak resonance or do not have any resonance in blue emission according to their specification. When an Ag particle has a weak resonance, the plasmon effect on the light enhancement is small. In the case of an Ag particle out of resonance, these can absorb the light and dissipate it [8,13,14].
Figure 4. Emission spectra of phosphor films as a function of the Ag concentration: (a) Ag sample 1 (b) Ag sample 2. The inset figure shows the standard error of the integrated emission intensity.

Figure 5 shows the LSP wavelength dependency on the emission spectrum. To examine the coupling effect between the LSP resonance and emission spectrum, two inorganic phosphors were additionally used: (Y,Gd)BO\textsubscript{3}:Eu\textsuperscript{3+} for 618 nm emission and Zn\textsubscript{2}SiO\textsubscript{4}:Mn\textsuperscript{2+} for 530 nm emission. The distinct phosphors used in this work were employed as phosphors for an ACPDP. The distinct phosphor samples were fabricated via the same method. Each film sample was made by mixing the phosphor with Ag sample 2 and spin-coating on the glass. Consequently, the conditions of the size/morphology of the Ag particles and their distance were all equal to each other. Moreover, Ag particles are randomly distributed in all of the samples [13]. Blue (450 nm) emission intensity was increased as the concentration of the Ag sample increased. However, green (530 nm) emission intensity decreased as Ag concentration increased. In red (618 nm) emission, intensity increased at low concentrations and decreased at high concentrations. From this result, Ag nanoparticles can enhance or quench the emission intensity of phosphor by matching the emission spectra and LSP
resonance position. It was thought that Ag nanoparticles having a plasmon resonance peak in the range of 400 ~450 nm enabled the enhancement of the blue emission intensity. On the contrary, a decrease of green and red emissions was attributed to the quenching effect due to the absorption of Ag nanoparticles.

![Graph showing selectivity of localized surface plasmon resonance as a function of the integrated emission wavelength of various phosphors: blue, red, green corresponding to emissions of 450 nm, 618 nm, 530 nm, respectively.]

The emission intensity of UV-excited phosphors is changeable as a function of thickness in case of the film. Therefore, it was important to confirm the thicknesses of both the reference and sample for clarity of the enhancement effect due to LSPR. The thicknesses of phosphor films were physically measured from cross-sectional SEM images. All of the phosphor films were spun onto glass substrates at 3500 rpm for 30 s. Phosphor films used for Ag samples 1 and 2 showed 4 µm and 5 µm thickness, respectively. Green and red phosphor films just showed 4.8 µm and 3.9 µm thicknesses, respectively. All the films had the same thickness independent of Ag contents in each experimental group. Therefore, the enhanced emission of phosphor films is not attributed to the variation of thickness, but local field enhancement due to the LSPR of Ag nanoparticles.

In the present work, FDTD calculation was additionally investigated for insight into the enhancement of electromagnetic near-field distribution around Ag nanoparticles. Figure 6(a) shows a schematic diagram for numerical analysis using FDTD. Blue emitting phosphor was modeled as a 450 nm emitting point dipole at the origin point [15]. Ag particles with a radius of 30 nm based on SEM images was placed 2 nm from the dipole oscillator. For simple calculation, Ag particles were assumed to have a spherical shape. The point dipole source was perpendicularly oriented to the metal surface. The electric field intensity distribution in the absence of Ag particles was shown in Fig. 6(b). The electric field intensity distribution in the present of Ag particles was shown in Fig. 6(c). Figure 6(d) shows the enhanced or quenched electric field intensity ratios in the X-Y plane around the 30 nm radius Ag particle. The field intensity enhancement factors were obtained by dividing the field intensity around the Ag particle by the field intensity of an isolated phosphor. All the figures were represented in a logarithmic scale (base 10) for clarity. As shown in Fig. 6(d), the near-field distribution of the emitting dipole in presence of Ag particles was increased drastically, which means that the Ag nanoparticle has a resonance with blue phosphor emission centered at 450 nm and induces the enhancement of the local field around the emitting dipole. It was noteworthy that the near field intensity was quenched at the region between the dipole source and the Ag nanoparticle. From these results, it is understood that surface of phosphors responsible for light emission can be placed under the enhanced local field due to the Ag nanoparticles [16].

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4. Discussion

It is generally well-known that transitions $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ of the rare earth ion Eu$^{3+}$ are of magnetic and electric dipole transitions, respectively. Therefore, resonant coupling between localized surface plasmon and 4f electrons can influence the electric dipole transition of Eu$^{3+}$ and enhance emission intensity of $^5D_0 \rightarrow ^7F_2$ [17,18]. We believe that the coupled interaction between localized surface plasmon due to Ag nanoparticles and 4f electrons of Eu$^{2+}$ occurred similarly to the case of $^5D_0 \rightarrow ^7F_2$ of the rare earth ion Eu$^{3+}$. The reason for this is that the 4f→5d transition on the blue emission of the Eu$^{3+}$ ion is electric-dipole allowable, and the energy transfer between two Eu$^{2+}$ ions is described to electric dipole-electric dipole interaction [19,20]. Furthermore, the electric dipole transition of rare earth ions such as europium (Eu) is sensitive to the distribution of charges around the rare earth ion [21,22]. Therefore, the origin of the increase of phosphor emission investigated in this work might be the coupling between the localized surface plasmon and 4f electrons, and localized field enhancement. To conclude, the local field enhancement due to Ag particles enables the electric dipole transition of the Eu$^{2+}$ ion to be more sensitive by inducing asymmetric charge distribution around the Eu$^{2+}$ ions.

5. Conclusion

In summary, the present paper shows that the visible emission of BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphor can be enhanced by coupling electric dipole transition with localized surface plasmon.
oscillation of nanoscaled Ag particles. It was found that the localized field enhancement of Ag particles leads to the improvement of the emission intensity of BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) in thin film samples made by using the phosphor paste embedding Ag nanoparticles. The localized surface plasmon resonance of Ag particles enhances the emission intensity of phosphor when the LSP energy of Ag matches the emission wavelength of phosphor materials. Also, the increase of Ag concentration leads to major enhancement of the emission intensity. Of course, the present work was limited to thin film phosphor, and further studies on Ag concentration are needed for deciding the optimum Ag content [13]. Additionally, the conditions of the size/morphology of the Ag particles and their distance to emitting materials are interesting topics in the plasmon enhanced emission. Such research must be extended to display devices. These results can yield a promising method to increase the luminous efficacy of display devices through the localized surface plasmon resonance of metal particles.

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