Blue Thin film phosphors prepared by Pulsed Laser Deposition

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Abstract: *It is well known that $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) and $CaMgSi_2O_6$: Eu^{2+} (CMS) are a highly efficient blue phosphor. However, these phosphors in the form of thin films have not yet been realized due to technical difficulties. We prepared thin film type BAM and CMS phosphors on quartz glass using a pulsed laser deposition technique. The luminescent and structural properties of thin film phosphors were monitored as a function of key processing parameters such as oxygen partial pressure inside the deposition chamber, deposition time, laser energy density and the type of post-deposition treatments used. Even though we could not obtain homogenous phases, by optimizing these processing parameters, thin films with large homogenous areas and a high photoluminescence could be produced.*

Keywords: BAM; CMS; Phosphors; Thin film; PLD

Introduction

There have been a large number of thin film type blue phosphors developed, in the expectation of using them in thin film electroluminescent (TFEL) devices. The majority were based on non-oxide inorganic compounds, and, in fact, are mostly sulfides.[1-2] Recently oxide phosphors have gained much attention because of the variety of materials available and chemical stability as compared to sulfide phosphors.[3-5] A number of reports regarding oxide red, green, and blue emitting phosphors have appeared. Red thin film phosphors developed by pulsed laser deposition (PLD) are of particularly great interest. However, no reports have appeared on oxide blue thin film phosphors, the luminance of which is sufficiently high to replace powder phosphors, even though several practical but, unacceptable oxide blue thin film phosphors have been reported. In this paper, we attempt that $BaMgAl_{10}O_{23}:Eu^{2+}$ (BAM) and $CaMgSi_2O_6:Eu^{2+}$ (CMS) was prepared in the thin film form. The luminescent and structural properties of these phosphors were monitored as a function of key processing parameters such as oxygen partial pressure inside the deposition chamber, deposition time, laser energy density and the type of post-deposition treatments used

Experimental

The targets for laser ablation were prepared by means of a conventional ceramic sintering process. A commercially available CMS and BAM powder (Nemoto Co. Ltd. Japan) were cold-pressed into a pellet without a binder and then isostatically cold-pressed at a pressure of 170 MPa. The final targets were obtained by sintering the pellet at 1200^{o}C for 3 hours in a reducing atmosphere (25 % H_2 + 75 % N_2). The targets were ablated by means of a 248 nm KrF excimer laser with energy densities of 2.0 ~ 2.3 J/cm^2 at a 5 Hz repetition rate for 60 ~ 120 minutes and were deposited in quartz glass substrate which was maintained at 750 ^{o}C. The targets were rotated at a speed of 10 RPM during the laser ablation. The distance between the target and substrate was 3~ 3.5 cm. The chamber was initially evacuated to $4x10^{-6}$ Torr (hereafter referred to as vacuum), and oxygen was then introduced into the chamber in order to maintain an oxygen pressure of 15 ~ 200 mTorr. As-deposited films were heat-treated at 1100~1200 ^{o}C in a reducing atmosphere (5% H_2 + 95 % N_2). The crystallinity of the thin film phosphors was examined by XRD. The photoluminescence (PL) measurement at UV excitation (254 nm) was carried out on a large area (14 mm in dia.) in the transmission mode using a lab-made spectrometer

Results

1. CMS thin film phosphor

Figure 1 shows emission spectra of CMS thin films deposited at various partial pressures of oxygen and heat-treated at 1100 ^{o}C for 1h in a reducing atmosphere (95%N2+5%H2) and actual photographs of reduced films taken under UV exciation((λ=254nm).

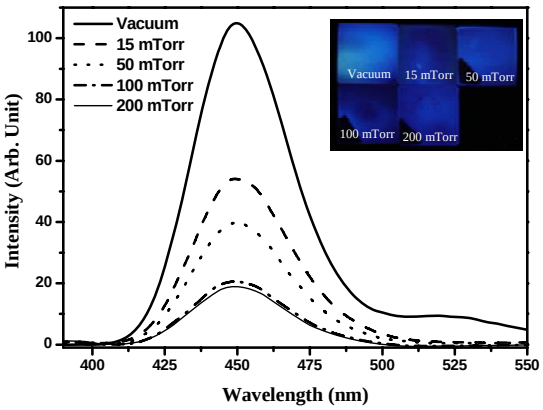

Figure 1. Emission spectra of CMS thin film phosphors deposited at various oxygen pressure and actual photographs of reduced thin films under UV excitation(λ=254nm)

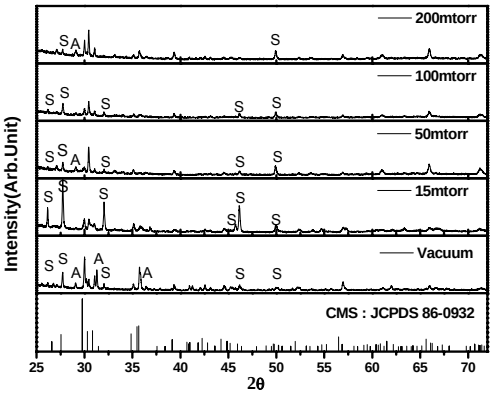

Figure 2. XRD patterns of CMS thin film phosphors deposited at various oxygen pressures

The film deposited in a vacuum was found to be the best in terms of the PL intensity of CMS emission, and thereafter the PL intensity decreased dramatically as the oxygen partial pressure increased. Fig 2 shows XRD patterns of thin film phosphors. The CMS thin films include two minor and undesired phases, $CaSiO_3$(A) and $CaSi_2O_6$(S), which had a negative influence on the PL behavior of CMS films since the Eu^{2+} doped phase A, emits a greenish light and Eu^{2+} doped phase S causes a purplish light. The XRD results, which are in good agreement with the PL data, showed that phase A was relatively dominant in the film deposited in a vacuum , so emission spectra is strong at around 525nm .

In spite of several more experimental implementations by varying at net processing parameters, we failed to develop a single phase CMS thin film at the, whereas we were able to rule out the inhomogeneity problem by optimizing the laser energy density (2.1 J/cm^2) and the distance(3.5 cm)between the target and substrate. Fig. 3 shows an XRD pattern of the optimized film, which is almost identical to the pattern of a film deposited in a vacuum, as shown in fig. 2.

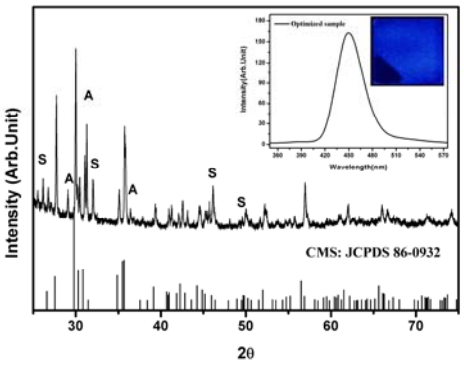

Figure 3. XRD patterns of the optimized CMS film. The inset shows the corresponding emission spectra and actual photograph.

The overall level of the XRD peak from the CMS phase was enhanced but phases A and S, which could not be avoided, were still observed. The Inset in fig. 3 shows a PL spectrum of the optimized film and photograph taken under UV excitation at 254 nm. The PL intensity of the optimized film was 160 % that of the best film shown in fig. 1. The presence of A and S phases was also obvious in the PL spectrum of the optimized film but it became relatively small, compared to the main emission from the CMS phase. The surface of the optimized film was quite homogeneous.

2. BAM thin film phosphor

Figure 4 shows XRD patterns of thin film phosphors deposited at various oxygen partial pressures and heat-treated at 1200^{o}C for 1h in a reducing atmosphere (95%N_2+5%H_2). The films deposited in a vacuum and at 50mTorr were well crystallized and according to increase the oxygen partial pressure, the BAM phase disappeared and a minor phase became conspicuous. This minor phase was found to be (Ba,Mg)$Al_2Si_2O_8$, and the element Si was considered to have originated from the quartz glass substrate. When this minor phase was doped with Eu^{2+}, it had only a slight influence on the PL behavior of BAM thin films by emitting soft ultra violet (purplish color) light peaking in the range from 370 to 390nm.

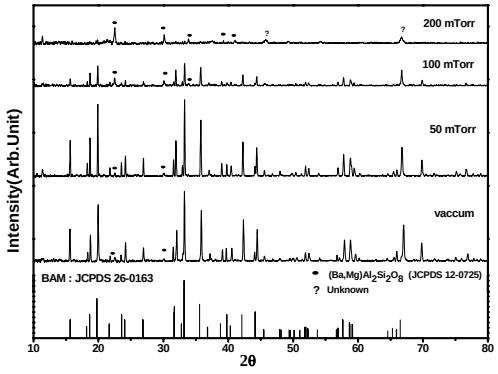

Figure 4. XRD patterns of BAM thin film phosphors deposited at various oxygen pressures

Figure 5 shows emission spectra and actual photographs of the thin film phosphors under 254nm. The film thickness was determined to be 1.2, 1.0, 0.6, and 0.3 μm for films deposited at a vacuum, 50, 100, and 200mTorr, respectively. Typical PL behavior of BAM was detected for all films, irrespective of oxygen partial pressure, that is, a broadband type emission spectrum peaking at around 450 nm originating from the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions was observed. The height of this band increased with decreasing partial pressure of oxygen, which was coincident with the thickness trend and also consistent with XRD data shown in fig 3. A slight emission band from the minor phase (Ba,Mg)$Al_2Si_2O_8$:Eu^{2+} was also detected in the soft UV range for all films and the height of this minor band did not vary dramatically. The film deposited in a vacuum was found to be the best in terms of the PL intensity of

BAM emission at 450 nm, and thereafter the PL intensity decreased significantly as the oxygen partial pressure increased. The thickness and crystallinity of film plays a decisive role in judging whether or not the luminescence is active. It was found that a thicker film with better crystallinity could be produced when oxygen is excluded during both the deposition and the post-deposition heat treatment. We also optimized the post-deposition heat treatment process, in an attempt to enhance the PL intensity. As a result, we concluded that pre-annealing in an oxidizing atmosphere before reduction was not helpful for enhancing PL intensity

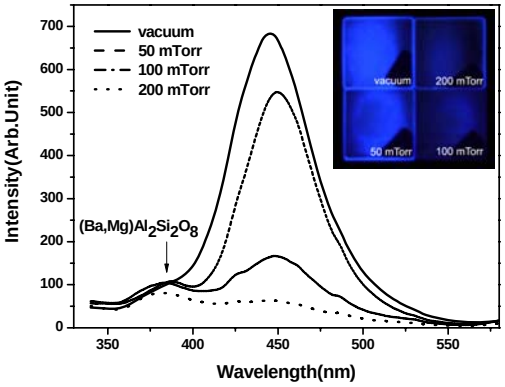

Figure 5. Emission spectra of CMS thin film phosphors deposited at various oxygen pressure and actual photographs of reduced thin films under UV excitation(λ=254nm)

Conclusion

The thin film type BAM and CMS phosphor was deposited on quartz glass using a PLD technique. The luminescent and structural properties of BAM thin film phosphors were investigated in terms of processing parameters such as the partial pressure of oxygen inside the deposition chamber, the deposition time, the laser energy density, and the type of post-deposition treatment used. Even though the undesired phases, which included $CaSiO_3$ and $CaSi_2O_6$ in CMS thin film and $(Ba,Mg)Al_2Si_2O_8$ in BAM thin film, gave rise to undesirable emission , we were able to obtain a well-developed thin films of large homogenous area with the minor phases, minimized by optimizing the processing parameters

References

1. S. J. Yun, Y. S. Kim and S. H. K. Park, "Fabrication of CaS:Pb blue phosphor by incorporating dimeric Pb^{2+} luminescent centers", *Appl. Phys. Lett*., **78**[6] 721-723(2001)
2. N. Miura, M. Kawanishi, H. Matsumoto and R. Nakano, " High-Luminance Blue-Emitting $BaAl_2S_4$:Eu Thin-Film Electroluminescent Devices", *Jpn. J. Appl. Phys*., **38** L1291- L1294
3. T. Minami, T. Miyata, Y. Suzuki and Y. Mochizuki, "Luminescent properties of rare earth-activated $Y_{1-x}Gd_xVO_4$ phosphor thin films", *Thin Solid Films*, **469** 65-69(2004)
4. N. Perea and G. A. Hirata, "Luminescent and crystalline properties of blue-white-emitting nanocrystalline Sr_2CeO_4 thin films produced by laser ablation", *Optical Materials*, **27**[7] 1212-1216(2005)
5. T. Miyata, Y. Mochizuki and T. Minami, " Blue - violet phosphate phosphor thin films for EL", *Thin Solid Films*, **496**[1] 174-178(2006)