http://dx.doi.org/10.5012/bkcs.2013.34.12.3919

Preparation and Photoluminescence of Green-Emitting Phosphors $SrGa_2S_4$:Eu

Sang-Hee Na, Young-Sik Cho, Young Rag Do,† and Young-Duk Huh*

Department of Chemistry, Center for Photofunctional Energy Materials, Dankook University, Gyeonggi-Do 448-701, Korea
**E-mail: ydhuh@dankook.ac.kr*
†Department of Chemistry, Kookmin University, Seoul 136-702, Korea
Received September 3, 2013, Accepted September 28, 2013

Key Words : Photoluminescence, $SrGa_2S_4$:Eu, Green-emitting phosphor, White LED

Europium ion doped strontium thiogallate ($SrGa_2S_4$:Eu) has been considered as an excellent green-emitting phosphor, due to the emission wavelength of 535 nm originated from the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ion in $SrGa_2S_4$:Eu.[1,2] $SrGa_2S_4$:Eu have been widely used as the green-emitting phosphor for low voltage (≤ 2 kV) and moderate voltage (2-10 kV) field emission displays (FEDs).[3,4] Recently, high luminescent blue light emitting diodes (LED) based on InGaN technology have been developed.[5-7] The phosphor-converted white LED using blue LED is considered as one of the most important lightning sources, due to its long lifetime, low energy consumption, and eco-friendly materials, without any mercury. The conventional white LED is fabricated by coating yellow-emitting $Y_3Al_5O_{12}$:Ce phosphor onto the blue InGaN LED chip.[8-10] White light is produced by the combination of unabsorbed blue emission of the blue InGaN LED chip, and yellow emission of the $Y_3Al_5O_{12}$:Ce phosphor. However, the color rendering index of this conventional white LED is very poor. To improve the color rendering index of white LED, a three-band white LED with red, green, and blue emissions must be developed. A three-band white LED can be fabricated by coating a mixture of red- and green-emitting phosphors onto a blue LED chip.[11,12] Since $SrGa_2S_4$:Eu has a strong absorption broadband in the 400-500 nm wavelength range, $SrGa_2S_4$:Eu is an appropriate green-emitting phosphor that is excited by the commercial blue InGaN LED chip. $SrGa_2S_4$:Eu has in recent years once again received great attention as a candidate for the green-emitting phosphor for the phosphor-converted three-band white LED.

$SrGa_2S_4$:Eu has generally been synthesized by a solid-state reaction of $SrCO_3$, Ga_2O_3, and Eu_2O_3 in a flowing toxic hydrogen sulfide (H_2S) gas.[13,14] To eliminate the harmful synthetic conditions, $SrGa_2S_4$:Eu was then prepared by a solid-state reaction of SrS, Ga_2S_3, and EuS in 5% H_2/95% N_2 gas, instead of H_2S.[15] $SrGa_2S_4$:Eu has also been prepared by a solid-state decomposition reaction from SrS, gallium complex [$Ga(Me_2dtc)_3$], and europium complex [$(Me_4N)Eu(Me_2dtc)_4$] with using inert Ar gas.[16] We have also synthesized $SrGa_2S_4$:Eu by using a similar solid-state decomposition reaction from SrS, $Ga(Me_2dtc)_3$, and $(Me_4N)Eu(Me_2dtc)_4$, without using any gases.[17] In this paper, we present an environmentally safe solid-state reaction for the preparation of $SrGa_2S_4$:Eu phosphor prepared from SrS, Ga_2S_3, and $(Me_4N)Eu(Me_2dtc)_4$, without using any gases. We investigated the optimal synthetic conditions of reaction temperature, reaction time, choice of flux, and amount of Eu^{2+} ion as activator, for the brighter green-emitting $SrGa_2S_4$:Eu phosphor. We also compared the photoluminescent properties of $SrGa_2S_4$:Eu phosphors prepared by two kinds of gallium precursors, $Ga(Me_2dtc)_3$ and Ga_2S_3.

Figures 1(a) and 1(b) show the photoluminescence ex-

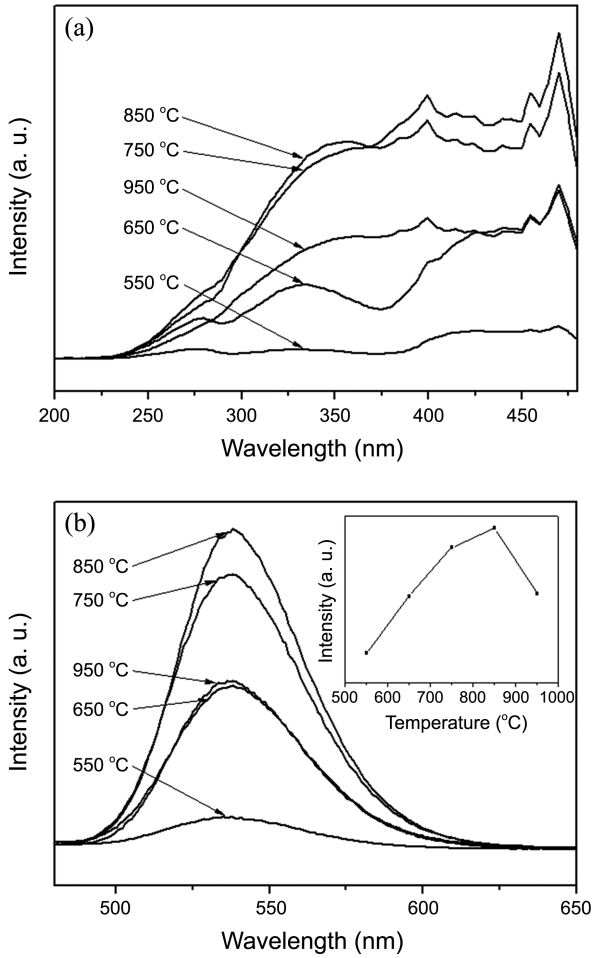

Figure 1. (a) Excitation and (b) emission spectra of $SrGa_2S_4$:Eu phosphors prepared at various reaction temperatures. The inset of (b) shows the relative intensity of the emission spectra of $SrGa_2S_4$:Eu phosphors at 535 nm as a function of reaction temperature.

citation and emission spectra of $SrGa_2S_4$:Eu phosphors prepared at various reaction temperatures between 550 °C and 950 °C, respectively. The excitation spectra have a large broad band located between 300 nm and 480 nm, due to the $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} ion in $SrGa_2S_4$:Eu. The characteristic multiple peaks between 400 nm and 480 nm are formed by spin-orbit coupling in the $4f^6$ configuration, leading to the splitting of the ^7F_J levels with J = 0-6.[1] Moreover, $SrGa_2S_4$:Eu has the strongest absorption of around 465 nm, which is equal to the emission wavelength of the commercial blue InGaN chip. The emission spectra show a single band around 535 nm originated from the lowest energy level of $4f^65d^1$ to the $4f^7$ energy level of Eu^{2+} ion in $SrGa_2S_4$:Eu.[1] This indicates that $SrGa_2S_4$:Eu can be used as a green-emitting phosphor excited by the blue InGaN chip for the phosphor-converted three-band white LED. The excitation and emission intensities increase gradually, with increases in temperature up to 850 °C, and then decrease at 950 °C.

Figure 2 shows X-ray diffraction (XRD) patterns of the $SrGa_2S_4$:Eu phosphors prepared at various reaction temperatures between 550 °C and 950 °C. Since Eu^{2+} ions can occupy the Sr^{2+} sites in the host $SrGa_2S_4$, the crystal structure of the $SrGa_2S_4$:Eu is quite close to that of $SrGa_2S_4$. All XRD peaks of the $SrGa_2S_4$:Eu phosphors prepared at 750 °C and 850 °C match the orthorhombic crystal structure of $SrGa_2S_4$ (JCPDS 25-0895), with a = 2.084 nm, b = 2.050 nm, and c = 1.221 nm. When at 550 °C and 650 °C, the reaction temperature is too low to produce pure $SrGa_2S_4$ crystals, and XRD peaks due to the unreacted SrS and Ga_2S_3 were observed, as shown in Figures 2(a) and 2(b). SrS:Eu is a red-emitting phosphor with the emission wavelength of 600 nm.[18] In the emission spectra of Figure 1(b), the red emission peaks around 600 nm were not observed. It indicated that SrS:Eu phosphor was not formed. Moreover, Ga_2S_3 is not adequate for the Eu^{2+} ion doped host material. Therefore, the unreacted SrS and Ga_2S_3 do not affect the excitation and emission spectra of $SrGa_2S_4$:Eu phosphors. At 950 °C, two unidentified peaks marked by the asterisk were observed, as shown in Figure 2(e). Therefore, the reaction temperatures at 750 °C and 850 °C are adequate for the preparation of pure $SrGa_2S_4$:Eu phosphors. Figure 3 shows scanning electron microscopy (SEM) images of the $SrGa_2S_4$:Eu phosphors, prepared at various reaction temperatures between 550 °C and 950 °C. With increasing the reaction temperature, the sub-micron sized particles are aggregated to a few tens micron sized crystals with a rock-like shape. When the crystal size of inorganic phosphor is decreased, the ratio of surface area to the total volume is increased, and the emission intensity of inorganic phosphor is decreased, due to the non-luminescent

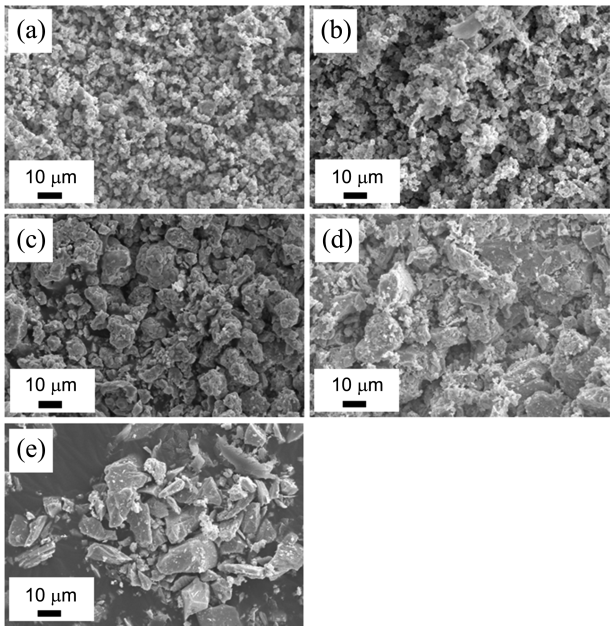

Figure 3. SEM images of $SrGa_2S_4$:Eu phosphors prepared at various reaction temperatures: (a) 550 °C, (b) 650 °C, (c) 750 °C, (d) 850 °C, and (e) 950 °C.

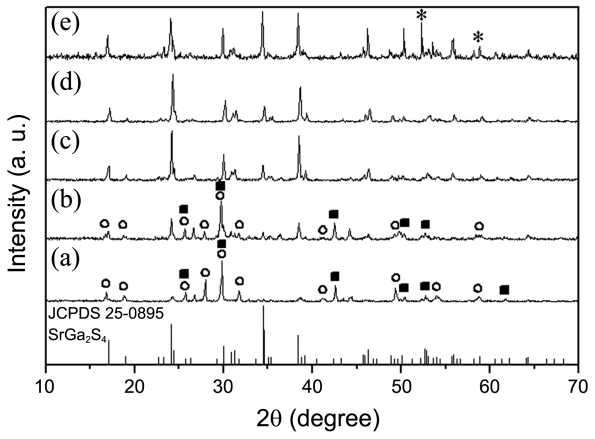

Figure 2. XRD patterns of $SrGa_2S_4$:Eu phosphors prepared at various reaction temperatures: (a) 550 °C, (b) 650 °C, (c) 750 °C, (d) 850 °C, and (e) 950 °C. ■, ○, and * represent the SrS, Ga_2S_3, and unidentified peaks, respectively.

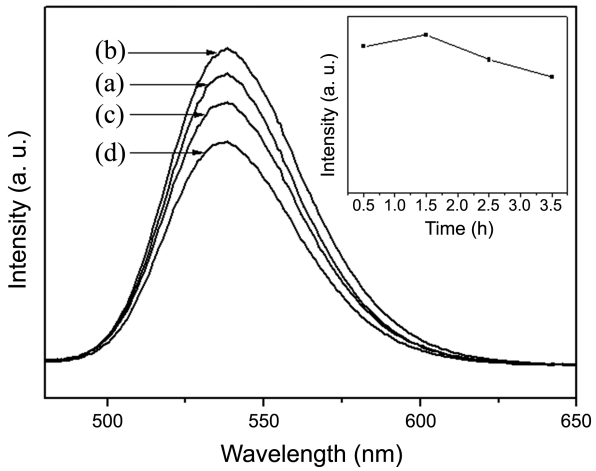

Figure 4. Emission spectra of $SrGa_2S_4$:Eu phosphors prepared at various reaction times at 850 °C: (a) 0.5 h, (b) 1.5 h, (c) 2.5 h, and (d) 3.5 h. The inset shows the relative intensity of the emission spectra of $SrGa_2S_4$:Eu phosphors at 535 nm as a function of reaction time.

characters of the defected surface area. Generally, inorganic phosphors show their brightest emission for crystal sizes of a few μm. By considering all XRD patterns, SEM images, and emission spectra of $SrGa_2S_4$:Eu phosphors prepared at various reaction temperatures between 550 °C and 950 °C, the $SrGa_2S_4$:Eu phosphor prepared at 850 °C was found to have the brightest emission, with pure crystal structures.

Figure 4 show the emission spectra of $SrGa_2S_4$:Eu phosphors prepared for various reaction times at 850 °C. The emission intensities of $SrGa_2S_4$:Eu phosphors slightly change with the reaction time. The brightest emission of $SrGa_2S_4$:Eu phosphor was obtained for a reaction time of 1.5 h. Figure 5 shows the emission spectra of the $SrGa_2S_4$:Eu phosphors prepared with five different kinds of fluxes at 850 °C for 1.5 h. This indicates that the emission intensities of $SrGa_2S_4$:Eu phosphors are changed with the kinds of flux. A brighter emission intensity of $SrGa_2S_4$:Eu phosphor was observed

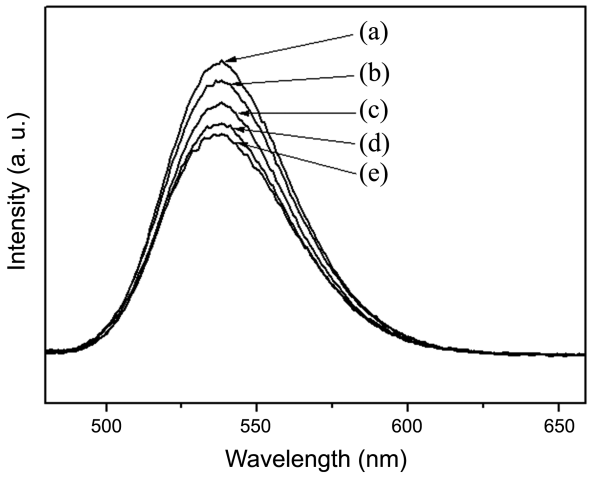

Figure 5. Emission spectra of $SrGa_2S_4$:Eu phosphors prepared with different kinds of flux at 850 °C for 1.5 h: (a) Li_2CO_3, (b) Na_2CO_3, (c) KBr, (d) KI, and (e) NaCl.

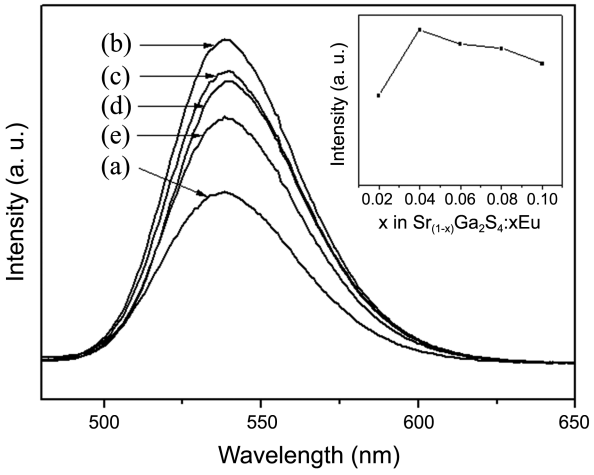

Figure 6. Emission spectra of $Sr_{(1-x)}Ga_2S_4$:xEu phosphors prepared at various amounts of Eu^{2+} ions (x) at 850 °C for 1.5 h with Li_2CO_3 flux: (a) x = 0.02, (b) x = 0.04, (c) x = 0.06, (d) x = 0.08, and (e) x = 0.10. The inset shows the relative intensity of the emission spectra of $Sr_{(1-x)}Ga_2S_4$:xEu phosphors at 535 nm as a function of the amount of Eu^{2+} ions (x).

with the choice of Li_2CO_3 as a flux.

In general, when the concentration of the activator is low, the emission intensity of inorganic phosphors increases with the concentration of the activator. However, the emission intensity of inorganic phosphors decreases with the concentration of the activators, due to the interaction within activators, when the concentration of the activators is high. This concentration quenching effect is a well-known behavior of inorganic phosphors. Therefore, it is important to find the optimal concentration of Eu^{2+} ions as an activator in $SrGa_2S_4$:Eu phosphors.

Figure 6 shows the emission spectra of $Sr_{(1-x)}Ga_2S_4$:xEu phosphors prepared at various amounts of Eu^{2+} ions at 850 °C for 1.5 h. The emission spectra of $Sr_{(1-x)}Ga_2S_4$:xEu phosphors increases with increasing Eu^{2+} concentration up to x = 0.04, but decreases with further increase in the Eu^{2+} concentration, due to the concentration quenching by Eu^{2+}-Eu^{2+} interaction. Therefore, the brightest green emission was obtained for the $Sr_{0.96}Ga_2S_4$:0.04Eu phosphor prepared at 850 °C for 1.5 h, by using Li_2CO_3 as a flux. Finally, we present the emission spectra of $SrGa_2S_4$:Eu phosphors with two kinds of gallium precursors, $Ga(Me_2dtc)_3$ and Ga_2S_3, while keeping the other synthetic conditions the same. The emission intensity of $SrGa_2S_4$:Eu prepared with the use of Ga_2S_3 as gallium precursor is increased by a factor of 1.53, compared to that of $Ga(Me_2dtc)_3$ as gallium precursor, as shown in Figure 7. The emission intensity of $SrGa_2S_4$:Eu prepared with the use of Ga_2S_3 as gallium precursor is 91.4 % of commercial $SrGa_2S_4$:Eu phosphor. The commercial $SrGa_2S_4$:Eu phosphor was prepared by using toxic H_2S gas. Therefore, we developed the excellent photoluminescent $SrGa_2S_4$:Eu phosphor without using toxic H_2S gas.

In conclusion, the photoluminescent properties of $SrGa_2S_4$:Eu phosphors were examined, for the green-emitting phosphor for a three-band white LED. The optimal synthetic conditions of reaction temperature, reaction time, choice of flux, and amount of Eu^{2+} ion for the brightest green-emitting

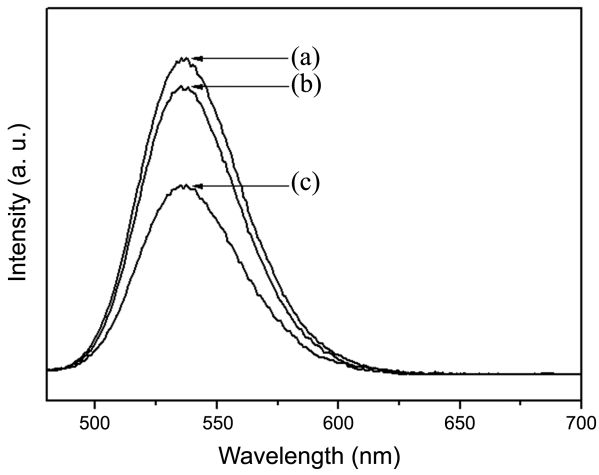

Figure 7. Emission spectra of (a) commercial $SrGa_2S_4$:Eu phosphor and $Sr_{0.96}Ga_2S_4$:0.04Eu phosphors prepared with two kinds of gallium precursors at 850 °C for 1.5 h with Li_2CO_3 flux: (b) Ga_2S_3 and (c) $Ga(Me_2dtc)_3$.

$SrGa_2S_4$:Eu phosphor were investigated. The brightest emission was obtained for the $Sr_{0.96}Ga_2S_4$:0.04Eu phosphor prepared at 850 °C for 1.5 h, by using Li_2CO_3 as a flux. We found that the use of Ga_2S_3 as gallium precursor was superior to the use of $Ga(Me_2dtc)_3$, for the brighter emission of $SrGa_2S_4$:Eu phosphor.

Experimental Section

SrS (99.9%, Strem Chemicals), Ga_2S_3 (99.99%, Alfa Aesar), S (99.98%, Aldrich), $Eu(NO_3)_3{\cdot}5H_2O$ (99.9%, Aldrich), $Ga(NO_3)_3{\cdot}xH_2O$ (99.9%, Aldrich), tetramethyl ammonium chloride (Me_4NCl, 98%, Aldrich), and dimethyldithiocarbamic acid sodium salt dihydrate ($NaMe_2dtc{\cdot}2H_2O$, 98%, TCI) were used as received, without any further purification. A europium complex, $(Me_4N)Eu(Me_2dtc)_4$, was precipitated by mixing of 10 mL of 0.25 M Me_4NCl, 10 mL of 0.25 M $Eu(NO_3)_3{\cdot}6H_2O$, and 10 mL of 1.0 M $NaMe_2dtc{\cdot}2H_2O$ aqueous solutions at room temperature. A gallium complex, $Ga(Me_2dtc)_3$, was precipitated by mixing 10 mL of 0.25 M $Ga(NO_3)_3{\cdot}xH_2O$ and 10 mL of 0.75 M $NaMe_2dtc{\cdot}2H_2O$ aqueous solutions at room temperature. The $(Me_4N)Eu(Me_2dtc)_4$ and $Ga(Me_2dtc)_3$ products were filtered, and dried under vacuum at room temperature.

$SrGa_2S_4$:Eu phosphors were prepared by a solid-state reaction, with a double crucible configuration system. One crucible was nestled in the other, with activated carbon as a reduction atmosphere in between. The starting materials were SrS, Ga_2S_3, $(Me_4N)Eu(Me_2dtc)_4$, S, and a flux. One of Li_2CO_3, Na_2CO_3, KBr, KI, or NaCl was used as the flux. The 0.20 mmol of flux and 50 mol of S were used, respectively. For the typical preparation of $Sr_{0.96}Ga_2S_4$:0.04Eu phosphor, the mixture of 3.84 mmol of SrS, 4.0 mmol of Ga_2S_3, 0.16 mmol of $(Me_4N)Eu(Me_2dtc)_4$, 50 mol S, and 0.20 mmol Li_2CO_3 was fired at 850 °C for 1.5 h in a box furnace. In this $SrGa_2S_4$:Eu phosphor, the atomic molar ratio of Sr:Ga:Eu was 0.96:2:0.04. Thus, the phosphor of $Sr_{0.96}Ga_2S_4$:0.04Eu formula was formed. To investigate the emission spectra dependence on the reaction temperature as one of the synthetic conditions, we used various reaction temperatures (550 °C, 650 °C, 750 °C, 850 °C, and 950 °C), with the other synthetic conditions kept the same. Similarly, we also examined the various synthetic conditions (reaction time, choice of flux, and amount of activator), with the other synthetic conditions kept the same. The commercial $SrGa_2S_4$:Eu phosphor was obtained from Phosphor Tech. Ltd.

Excitation and emission spectra of the $SrGa_2S_4$:Eu phosphors were obtained by using a spectrum analyzer (DARSA, PSI). The excitation spectra were obtained by fixing the emission wavelength (λ_{em}) of 535 nm. Similarly, the emission spectra were obtained by fixing the excitation wavelength (λ_{ex}) of 465 nm, which was the wavelength of the commercial blue InGaN LED chip. The crystal structures of the $SrGa_2S_4$:Eu phosphors were analyzed by using powder X-ray diffraction (XRD, Rigaku DMAX-3A) with Cu Kα radiation. The morphologies of the $SrGa_2S_4$:Eu phosphors were examined with scanning electron microscopy (SEM, Hitachi S-4300).

Acknowledgments. This work was supported by the GRRC program of Gyeonggi province (GRRC-Dankook-2011-B02).

References

1. Chartier, C.; Barthou, C.; Benalloul, P.; Frigerio, J. M. *J. Lumin.* **2005**, *111*, 147.
2. Dorenbos, P. *J. Lumin.* **2003**, *104*, 239.
3. Yang, S.; Stoffers, C.; Zhang, F.; Jacobsen, S. M.; Wagner, B. K.; Summers, C. J. *Appl. Phys. Lett.* **1998**, *72*, 158.
4. Na, S. H.; Sung, H. J.; You, Y. C.; Ko, K. Y.; Do, Y. R.; Huh, Y. D. *Bull. Korean Chem. Soc.* **2006**, *27*, 1708.
5. Mukai, T.; Yamada, M.; Nakamura, S. *Jpn. J. Appl. Phys.* **1998**, *37*, L1358.
6. Schlotter, P.; Baur, J.; Hielscher, Ch.; Kunzer, M.; Obloh, H.; Schmidt, R.; Schneider, J. *Mater. Sci. Eng. B* **1999**, *59*, 390.
7. Yam, F. K.; Hassan, Z. *Microelectron. J.* **2005**, *36*, 129.
8. Mueller-Mach, R.; Mueller, G. O.; Krames, M. R.; Trottier, T. *IEEE J. Selected Topics Quantum Electron.* **2002**, *8*, 339.
9. Schlotter, P.; Schmidt, R.; Schneider, J. *Appl. Phys. A* **1997**, *64*, 417.
10. Huh, Y. D.; Cho, Y. S.; Do, Y. R. *Bull. Korean Chem. Soc.* **2002**, *23*, 1435.
11. Huh, Y. D.; Shim, J. H.; Kim, Y. H.; Do, Y. R. *J. Electrochem. Soc.* **2003**, *150*, H57.
12. Yang, C. C.; Lin, C. M.; Chen, Y. J.; Wu, Y. T.; Chuang, S. R.; Liu, R. S.; Hu, S. F. *Appl. Phys. Lett.* **2007**, *90*, 123503.
13. Ko, K. Y.; Huh, Y. D.; Do, Y. R. *Bull. Korean Chem. Soc.* **2008**, *29*, 822.
14. Do, Y. R.; Bae, J. W.; Kim, Y.; Yang, H. G. *Bull. Korean Chem. Soc.* **2000**, *21*, 295.
15. Kim, J. M.; Kim, K. N.; Park, J. K.; Kim, C. H.; Jang, H. G. *J. Korean Chem. Soc.* **2004**, *48*, 371.
16. Jiang, Y. D.; Villalobos, G.; Souriau, J. C.; Paris, H.; Summers, C. J.; Wang, Z. L. *Solid State Commun.* **2000**, *113*, 475.
17. Huh, Y. D.; Shim, J. H.; Do, Y. R. *J. Korean Chem. Soc.* **2002**, *46*, 164.
18. Kim, J. M.; Kim, K. N.; Park, J. K.; Kim, C. H.; Jang, H. G. *J. Korean Chem. Soc.* **2005**, *49*, 138.