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Phosphor-converted light-emitting diode based on ZnO-based heterojunction

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ABSTRACT

A phosphor-converted light-emitting diode (LED) was realized by coating $BaMg_2Al_{16}O_{27}$:$Eu^{2+}\cdot Mn^{2+}$ and $(SrCaPO_4)\cdot B_2O_3$:$Eu^{2+}\cdot Na^{+}$ phosphors onto an n-ZnO/i-MgO/p-GaN heterojunction diode. Two emission bands at around 450 and 520 nm were observed in the phosphor-converted LED under the injection of continuous current. By analyzing the optical properties of the heterojunction diode and phosphors, it is concluded that the emission at 450 nm comes from $(SrCaPO_4)\cdot B_2O_3$:$Eu^{2+}\cdot Na^{+}$ phosphor, while the one at 520 nm comes from $BaMg_2Al_{16}O_{27}$:$Eu^{2+}\cdot Mn^{2+}$ phosphor under the excitation of the light emitted from the n-ZnO/i-MgO/p-GaN heterojunction diode. The results reported in this paper may provide a route to ZnO-based phosphor-converted LEDs for future lighting or displaying purpose.

1. Introduction

White light-emitting diodes (LEDs) for the purpose of solid state lighting have attracted much attention in recent years [1,2]. Currently the most promising candidate for solid state lighting is phosphor-converted LEDs, in which white LEDs are fabricated by coating yellow and/or red phosphors onto blue or near-ultraviolet (UV) light-emitting chips [3–6]. Recently, gallium nitride (GaN) based quantum well structures have been widely employed as the chips of white LEDs [1]. However, the performance of GaN-based phosphor-converted white LEDs is still below expectation for their relatively low emission efficiency and high cost. Zinc oxide (ZnO) has a similar band gap with GaN, but the exciton binding energy of ZnO (60 meV) is much larger than that of GaN (25 meV), which implies that higher emission efficiency could be expected from ZnO [7–10]. Additionally ZnO is abundant and cheap, which is favorable to reduce the cost of LEDs made from it. The above factors make ZnO a strong candidate for white LEDs. Although some ZnO-based homojunction LEDs have been reported [11–13], the reproducible and stable p-type doping of ZnO is still a huge challenge. On this account, some efforts have been made on n-ZnO/p-GaN heterojunctions, from which white emission has been observed by mixing the blue emission from GaN and red emission from ZnO [14,15]. However, no ZnO-based phosphor-converted LED has been reported up to date to the best of our knowledge.

We have recently found that by modulating the carrier transportation process in n-ZnO/p-GaN heterojunction using a thin MgO dielectric layer, intense electroluminescence (EL) or even low-threshold lasing can be obtained [16,17]. In this paper, an n-ZnO/MgO/p-GaN heterojunction diode with MgO layer modulating the carrier transportation has been fabricated, and a phosphor blend was coated onto the heterojunction diode to form a phosphor-converted LED. Obvious EL emission has been observed from the LED.

2. Experimental details

The ZnO-based heterojunction diode was fabricated by depositing 30 nm MgO and 300 nm undoped n-ZnO film in sequence onto a commercial available p-GaN/sapphire template in a VG V80H plasma-assisted molecular beam epitaxy (MBE) system. For more details about the growth process please refer to our previous publication [17]. The thickness of the GaN layer is about 2 μm, and the hole concentration and mobility are $3.0\times10^{17}\,cm^{-3}$ and $10\,cm^2V^{-1}\,s^{-1}$, respectively. The ZnO layer exhibits n-type conduction with an electron concentration of $3.0\times10^{18}\,cm^{-3}$ and a mobility of about $24\,cm^2V^{-1}\,s^{-1}$. Bilayer Ni–Au and In–Au contacts were evaporated onto the p-GaN and n-ZnO layers acting as electrodes, respectively. The heterojunction diode was then coated with the blend of $BaMg_2Al_{16}O_{27}$: $Eu^{2+}\cdot Mn^{2+}$ and $(SrCaPO_4)\cdot B_2O_3$:$Eu^{2+}\cdot Na^{+}$ phosphors. The schematic diagram of the heterojunction diode and the photograph of the finished phosphor-converted LED are shown in Fig. 1.

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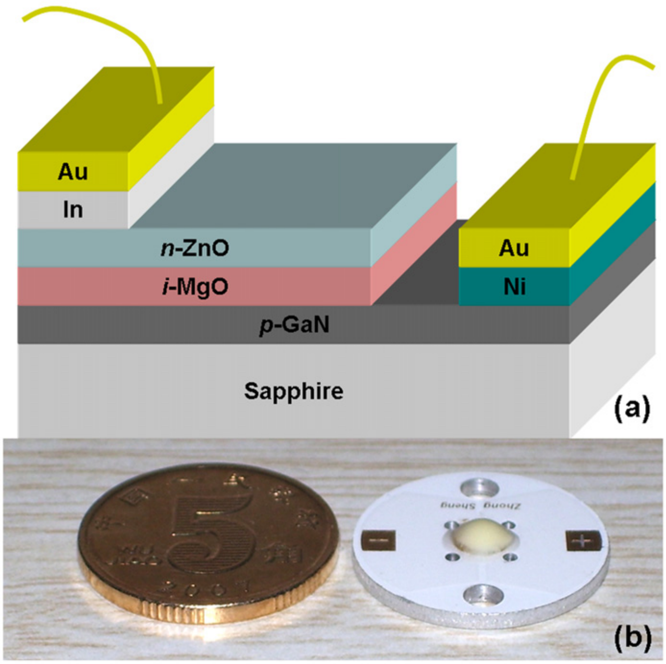

Fig. 1. Schematic diagram of the heterojunction diode (a) and a photograph of the phosphor-converted LED (b); note that a five chiao coin was used to show the size of the device.

The electrical characteristics of the component layers were measured in a Hall measurement system (LakeShore 7707). The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the phosphors, and the electroluminescence (EL) spectra of the device were recorded in a Hitachi F4500 spectrometer at room temperature. Note that a continuous current power source was used to excite the diodes for the EL measurements.

3. Results and discussion

The EL spectra of the phosphor-converted LED are displayed in Fig. 2. As shown in the figure, two emission bands can be observed from the LED under the injection of continuous current: one locates at around 450 nm, and the other at around 520 nm. Note that with increase in the injection current, the shape of the spectra remains, but their intensity varies. As indicated by the dependence of the emission intensity of the LED on the injection current shown in the inset of Fig. 2, the emission intensity of the LED increases greatly when the forward injection current is enhanced from 3.55 to 8.60 mA, but it almost saturates when the injection current is increased further. The above variation trend has been frequently observed in LEDs, and can be attributed to the decrease in luminescence efficiency and the enhancement in joule-heating of the n-ZnO/i-MgO/p-GaN chip at elevated injection current [18].

In order to explore the origin of the EL from the ZnO-based phosphor-converted LED, the EL spectra of the n-ZnO/i-MgO/p-GaN heterojunction diode have been measured, and the results are shown in Fig. 3. As the injection current increases from 3.05 to 8.80 mA, all the spectra exhibit a strong emission at about 395 nm. Similar emission has been observed in our previous publication [17], and it has been attributed to the emission from ZnO with the MgO layer modulating the carrier transportation in the heterojunction [16,17]. The MgO layer will block the drift of electrons in the n-ZnO to the p-GaN for the large conduction band offset between ZnO and MgO (3.55 eV), while because the valence band offset between GaN and MgO is much smaller (0.9 eV), and the conduction and valence bands of MgO will bend significantly under forward bias, the effective thickness of the barrier that blocks the injection of holes from p-GaN to n-ZnO will be greatly reduced. As a result, holes in the p-GaN layer can tunnel through the MgO layer and enter into the ZnO layer, and recombine radiatively with the electrons accumulated in the ZnO layer. Consequently, intense emission coming from the ZnO layer is observed [17]. In the EL spectra of the phosphor-converted LED shown in Fig. 2, the emission at 395 nm is totally invisible, which indicates that this emission from the n-ZnO/i-MgO/p-GaN heterojunction diode has been fully absorbed by the phosphors.

The PL and PLE spectra of the $BaMg_2Al_{16}O_{27}:Eu^{2+}\cdot Mn^{2+}$ and $(SrCaPO_4)\cdot B_2O_3:Eu^{2+}\cdot Na^{+}$ phosphors used in the phosphor-converted LED are shown in Fig. 4. The $(SrCaPO_4)\cdot B_2O_3:Eu^{2+}\cdot Na^{+}$ phosphor exhibits a PLE peak at 395 nm, as shown in Fig. 4a. Note that the position of the PLE peak of the phosphor is in sharp accordance with the emission of the heterojunction diode (395 nm) employed as the chip of the phosphor-converted LED. Under the excitation of the 395 nm light of a xenon lamp, a strong

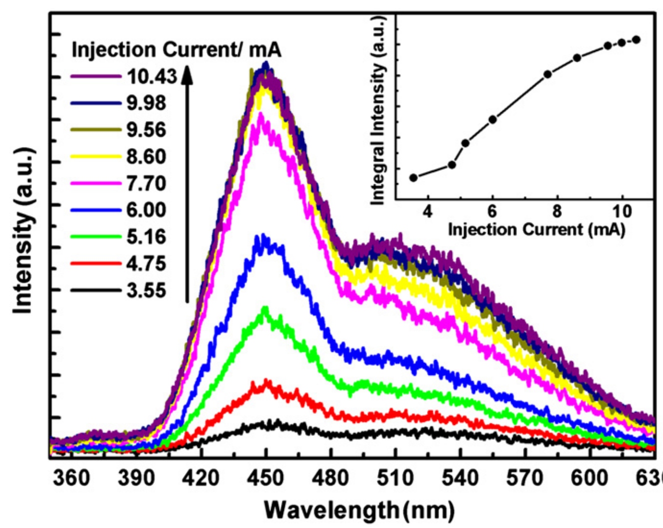

Fig. 2. EL spectra of the phosphor-converted LED under various injection currents; the inset shows the dependence of the emission intensity on the injection current.

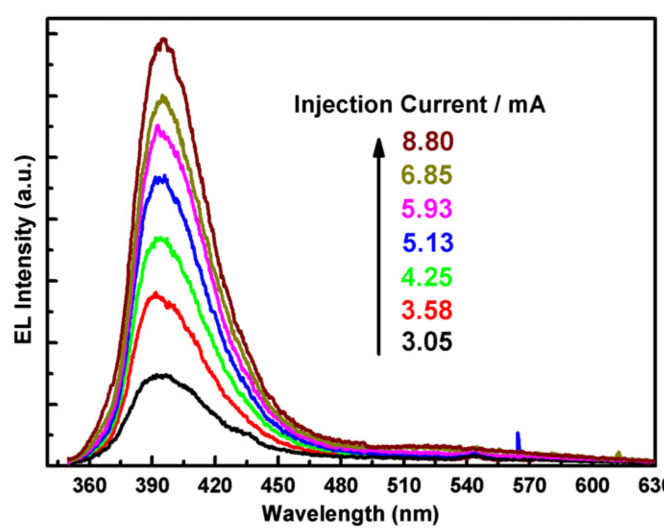

Fig. 3. EL spectra of the n-ZnO/i-MgO/p-GaN heterojunction diode under various injection currents.

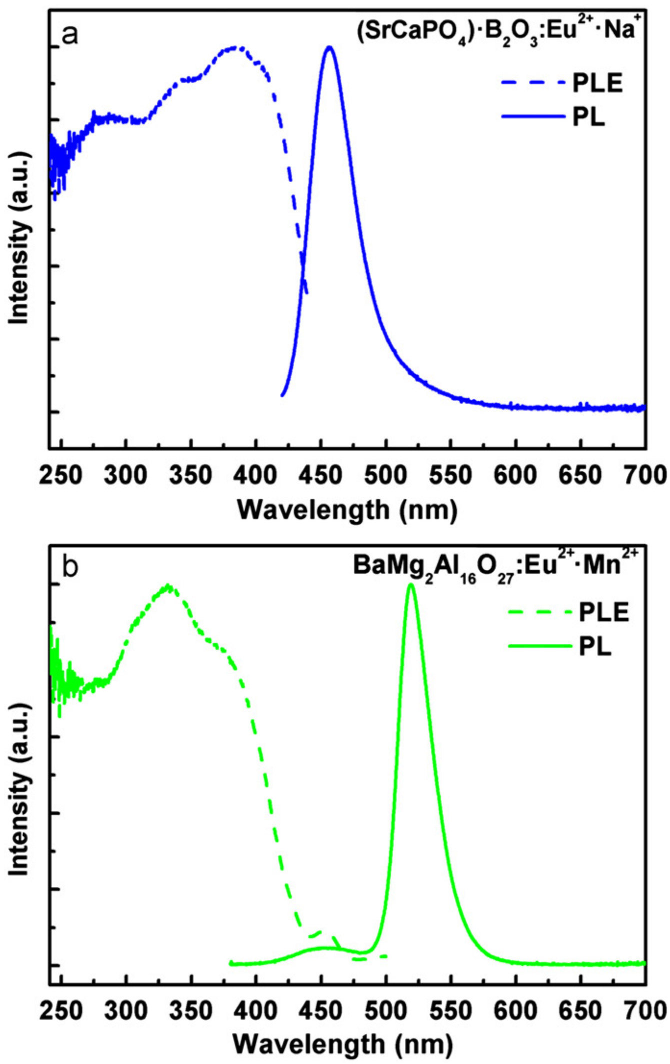

Fig. 4. PL and PLE spectra of the $(SrCaPO_4)\cdot B_2O_3:Eu^{2+}\cdot Na^{+}$ (a) and $BaMg_2Al_{16}O_{27}:Eu^{2+}\cdot Mn^{2+}$ (b) phosphors.

blue emission centered at 456 nm is observed from the phosphor, which is close to the emission band at around 450 nm of the phosphor-converted LED. The above phenomenon indicates that the emission at around 450 nm of the phosphor-converted LED observed in Fig. 2 comes from the $(SrCaPO_4)\cdot B_2O_3:Eu^{2+}\cdot Na^{+}$ phosphor under the excitation of the 395 nm light emitted from the n-ZnO/i-MgO/p-GaN heterojunction diode. The PL and PLE spectra of $BaMg_2Al_{16}O_{27}:Eu^{2+}\cdot Mn^{2+}$ phosphor are shown in Fig. 4b. The PLE spectrum shows a broad curve spanning from 250 to 450 nm, which means that the $BaMg_2Al_{16}O_{27}:Eu^{2+}\cdot Mn^{2+}$ phosphor can also be excited by the 395 nm light emitted from the heterojunction diode. Under the excitation of the 395 nm line of a xenon lamp, the PL spectrum of $BaMg_2Al_{16}O_{27}:Eu^{2+}\cdot Mn^{2+}$ phosphor shows an intense emission at 525 nm, the position of which matches well with the 520 nm emission observed from the phosphor-converted LED shown in Fig. 2. Therefore, the emission at around 520 nm of the phosphors-converted LED should come from the $BaMg_2Al_{16}O_{27}:Eu^{2+}\cdot Mn^{2+}$ phosphor. Summarily, an emission at around 395 nm will be emitted from the n-ZnO/i-MgO/p-GaN heterojunction diode under the injection of continuous current, and the emission is almost totally absorbed by the phosphors coated onto the diode. Under the excitation of the 395 nm light emitted from the heterojunction diode, an emission at around 450 nm coming from $(SrCaPO_4)\cdot B_2O_3:Eu^{2+}\cdot Na^{+}$ phosphor and another emission at around 520 nm from $BaMg_2Al_{16}O_{27}:Eu^{2+}\cdot Mn^{2+}$ are observed from the phosphor-converted LED. This is the reason why two emission bands at around 450 and 520 nm are observed in the n-ZnO/i-MgO/p-GaN heterojunction diode based phosphor-converted LED under the injection of continuous current.

4. Conclusion

A phosphor-converted LED was realized by coating phosphors onto an n-ZnO/i-MgO/p-GaN heterojunction diode, and two broad emission bands at around 450 and 520 nm were observed from the LED. By analyzing the emission of the heterojunction diode, together with the PL and PLE spectra of $BaMg_2Al_{16}O_{27}:Eu^{2+}\cdot Mn^{2+}$ and $(SrCaPO_4)\cdot B_2O_3:Eu^{2+}\cdot Na^{+}$ phosphors employed, the origin of the emissions has been attributed to the emission from the two phosphors under the excitation of the 395 nm light emitted from the heterojunction diode. Although the performance of the LED reported here needs improvement, the results reported in this paper may suggest a route to ZnO-based phosphor-converted LEDs for possible applications in lighting or displaying in the future.

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References

[1] S. Nakamura, G. Fasol, in: The Blue Laser Diodes, Springer, Berlin, 1997.
[2] M.G. Craford, in: Commercial Light Emitting Diode Technology, Kluwer, Dordrecht, 1996.
[3] S. Neeraj, N. Kijima, A.K. Cheetham, Chem. Phys. Lett. 387 (2004) 2.
[4] Z.D. Hao, J.H. Zhang, X. Zhang, X.Y. Sun, Y.S. Luo, S.Z. Lu, X.J. Wang, Appl. Phys. Lett. 90 (2007) 261113.
[5] T. Tamura, T. Setomoto, T. Taguchi, J. Lumin. 87–89 (2000) 1180.
[6] P. Thiyagarajan, M. Kottaisamy, M.S. Ramachandra Rao, J. Lumin. 129 (2009) 991.
[7] M. Kawasaki, A. Ohtomo, I. Ohkubo, H. Koinuma, Z.K. Tang, P. Yu, G.K.L. Wong, B.P. Zhang, Y. Segawa, Mater. Sci. Eng. B 56 (1998) 239.
[8] D.C. Look, D.C. Reynolds, C.W. Litton, R.L. Jones, D.B. Eason, G. Cantwell, Appl. Phys. Lett. 81 (2002) 1830.
[9] D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, Appl. Phys. Lett. 70 (1997) 2230.
[10] Ü. Özgür, Ya.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.J. Cho, H. Morkoç, J. Appl. Phys. 98 (2005) 041301.
[11] S.J. Jiao, Z.Z. Zhang, Y.M. Lu, D.Z. Shen, B. Yao, J.Y. Zhang, B.H. Li, D.X. Zhao, X.W. Fan, Z.K. Tang, Appl. Phys. Lett. 88 (2006) 031911.
[12] A. Tsukazaki, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S.F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, M. Kawasaki, Nat. Mater. 4 (2005) 42.
[13] W. Liu, S.L. Gu, J.D. Ye, S.M. Zhu, S.M. Liu, X. Zhou, R. Zhang, Y. Shi, Y.D. Zheng, Y. Hang, C.L. Zhang, Appl. Phys. Lett. 88 (2006) 092101.
[14] S. Kishwar, K. ul Hasan, G. Tzamalis, O. Nur, M. Willander, H.S. Kwack, D. Le Si Dang, Phys. Status Solidi A 207 (2010) 67.
[15] L. Zhao, C.S. Xu, Y.X. Liu, C.L. Shao, X.H. Li, Y.C. Liu, Appl. Phys. B 92 (2008) 185.
[16] H. Zhu, C.X. Shan, B.H. Li, J.Y. Zhang, B. Yao, Z.Z. Zhang, D.X. Zhao, D.Z. Shen, X.W. Fan, J. Phys. Chem. C 113 (2009) 2980.
[17] H. Zhu, C.X. Shan, B. Yao, B.H. Li, J.Y. Zhang, Z.Z. Zhang, D.X. Zhao, D.Z. Shen, X.W. Fan, Y.M. Lu, Z.K. Tang, Adv. Mater. 21 (2009) 1613.
[18] A.A. Efremov, N.I. Bochkareva, R.I. Gorbunov, D.A. Lavrinovich, Yu.T. Rebane, D.V. Tarkhin, Yu.G. Shreter, Semiconductors 40 (2006) 605.