Vol. 30, No. 8 Journal of Semiconductors August 2009

Room-temperature electroluminescence of p-Zn$_x$Mg$_{1-x}$O:Na/n-ZnO p–n junction light emitting diode*

Ye Zhizhen(叶志镇)†, Zhang Liqiang(张利强), Huang Jingyun(黄靖云), Zhang Yinzhu(张银珠),
Zhu Liping(朱丽萍), Lü Bin(吕斌), Lü Jianguo(吕建国), Wang Lei(汪雷),
Jin Yizheng(金一政), Jiang Jie(蒋杰), Xue Ya(薛雅), Zhang Jun(张俊),
Lin Shisheng(林时胜), and Yang Dan(杨丹)

(State Key Laboratory of Silicon Materials, Department of Materials, Zhejiang University, Hangzhou 310027, China)

Abstract: p-Zn$_x$Mg$_{1-x}$O:Na/n-ZnO p–n junction light emitting diode (LED) was produced on n-ZnO (0001) single-crystal substrate using pulsed laser deposition. The realization of band gap engineering was achieved by the incorporation of Mg in ZnO layers and was confirmed by photoluminescence spectrum. The p-type Zn$_x$Mg$_{1-x}$O:Na film with low resistance was obtained at 500 °C and in which, Na has taken effect evidenced by Hall and X-ray photoelectron spectroscopy measurements. The current–voltage curve of LED showed a rectifying behavior and obvious electroluminescence was realized by feeding a direct current up to 40 mA. Furthermore, its structural and electric characters are discussed as well.

Key words: ZnO; electroluminescence; Na doped; LED
DOI: 10.1088/1674-4926/30/8/081001 **PACC:** 7860F; 7340L

1. Introduction

ZnO, as a novel II–VI compound semiconductor material with a direct wide band gap (E_g = 3.37 eV), which enjoys outstanding optical and electric properties, has been considered a promising candidate for the next generation of ultraviolet (UV) light-emitting diodes (LEDs)[1, 2]. To facilitate the realization of UV LEDs, increasing demands are focusing on ZnMgO ternary alloys for extending the available band gap energy and combine them with ZnO to fabricate quantum well, double heterostructures, etc. The band gap engineering of ZnMgO can be achieved by alloying ZnO with different concentrations of MgO, modulating E_g from 3.37 to 4.3 eV[3, 4] without disturbing the wurtzite structure. However, as there exist native oxygen vacancies and zinc interstitials, the intrinsic ZnO is n type, and for the application of ZnO based optoelectronic devices, it is necessary to realize the conversion from n-type to p-type despite of difficulties due to the heavy compensation effect[5]. Thus, extensive efforts have been devoted to studying of acceptor doping in ZnO. As a result, some p-type ZnO films have been obtained using group-V elements (N, P, As)[6–8] as dopants. Compared with group-V elements, group-I elements (such as Li, Na) need lower energy for ionization and could be better acceptor dopants though less study has been done[9–11]. Recently, several groups reported on p-type ZnMgO films[12–16], which were focused on p-type doping with group-V elements. Few reports have taken group-I elements on substitutional Zn or Mg sites into account[11]. In our previous study, it is indicated that group-I element Na is a promising dopant for p-type ZnMgO[17, 18].

In this paper, we report on realization of obvious electroluminescence at room temperature (RT) from a p-Zn$_x$Mg$_{1-x}$O:Na/n-ZnO p–n junction LED. Na doped Zn$_x$Mg$_{1-x}$O film with good p-type electric properties was deposited on n-ZnO (0001) single-crystal substrate and formed a simple p–n junction LED. Our results shine new light on ZnO based LEDs solid-state lighting applications in future.

2. Experiment

A series of Na doped p-type Zn$_x$Mg$_{1-x}$O films were fabricated by pulsed laser deposition (PLD) on low-resistance, gallium doped n-ZnO (0001) single-crystal substrate. The ceramic target was prepared by the mixing of ZnO, MgO, and Na_2CO_3 powders. In the Na doped ZnMgO target, the Mg and Na content is 10% and 1% in Moore percent, respectively. Whereas, it is noted that in the as-grown Zn$_x$Mg$_{1-x}$O: Na film, Mg content is 11.85% and Na is 1.01% as identified from X-ray photoelectron spectroscopy (XPS) measurements within the instrument error. The electrical properties were investigated by using a four-point probe van der Pauw configuration (HL5500PC). The working pressure in the chamber was 40 Pa with O_2 as the ambient gas. A KrF excimer laser (Compex102, 248 nm, 25 ns) was used as the ablation source. The substrates were held at 500 °C during the film deposition. After deposition for 30 min, a film about 350 nm-thick was obtained.

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* Project supported by the State Key Development Program for Basic Research of China (No. 2006CB604906) and the National Natural Science Foundation of China (No. 50532060).

† Corresponding author. Email: yezz@zju.edu.cn

Received 16 July 2009

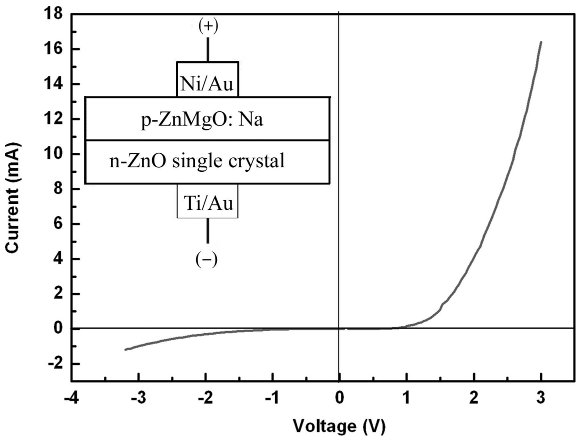

Fig. 1. Current–voltage characteristics of ZnO based p–n junction LED. The inset is the schematic cross-sectional view of a p-$Zn_xMg_{1-x}O$:Na/n-ZnO LED, in which Ni/Au electrode was deposited on the Na-doped p-type $Zn_xMg_{1-x}O$ layer, and Ti/Au electrode was deposited on the n-type ZnO layer.

The typical electrode Ni and Au were deposited on the Na-doped p-type $Zn_xMg_{1-x}O$ film by magnetron sputtering. Similarly, Ti and Au were deposited on the back side of the n-ZnO (0001) single-crystal substrate. Good ohmic contacts on both p-type $Zn_xMg_{1-x}O$:Na and n-ZnO were made by rapid thermal annealing at 600 °C for 1 min in N_2 atmosphere. A gelient E5270B parameter analyzer was used to analyze the current–voltage (I–V) characteristics. The EL spectra of the ZnO-LED were measured with a series of injecting current from 0 to 40 mA using a UV-vis spectrometer. Photoluminescence (PL) measurements were performed on a FLSP920 (Edinburgh Instruments) fluorescence spectrometer.

3. Results and discussion

The I–V characteristics of ZnO LED were measured at room temperature as shown in Fig. 1. The structure of p-$Zn_xMg_{1-x}O$:Na/n-ZnO p–n junction LED is shown in the inset of Fig. 1. A 350 nm-thick Na-doped p-type $Zn_xMg_{1-x}O$ layer was first deposited on the n-ZnO (0001) single-crystal substrate. The hole concentration of the Na doped p-type $Zn_xMg_{1-x}O$ film could reach 10^{17}–10^{18} cm^{-3} which was measured by Center of Material Characterization (CMA, Tianjin). Details of the p-type properties of Na doped $Zn_xMg_{1-x}O$ film will be discussed elsewhere. Subsequently, the electrodes were fabricated by magnetron sputtering of Ni/Au and Ti/Au bilayers on p-type $Zn_xMg_{1-x}O$:Na and n-ZnO, respectively. Good ohmic contacts on both p-type $Zn_xMg_{1-x}O$:Na and n-ZnO were made by rapid thermal annealing at 600 °C for 1 min in N_2 atmosphere and were confirmed by the good linear I–V dependences (not shown). As the n-ZnO (0001) single-crystal substrate is with a low resistance and the $Zn_xMg_{1-x}O$:Na layer shows good p-type properties, the fabricated p-$Zn_xMg_{1-x}O$:Na/n-ZnO LED has a good rectifying characteristic and its leakage current is low.

Figure 2 shows the EL spectra of the p-$Zn_xMg_{1-x}O$:Na/n-ZnO LED at RT. Upon increasing injecting current from 10 to 40 mA, the emitting light intensity enhanced obviously as well. There exist emission bands located at the UV and visible regions. The near-band-edge UV emission can be assigned to the donor-acceptor pair luminescence. As the carrier concentration in n-type substrate is one or two orders higher than that in the p-type Na doped $Zn_xMg_{1-x}O$ film, moreover, the electrons move faster than the holes, most of the radiative recombination should take place in the p-type Na doped $Zn_xMg_{1-x}O$ film layer. Mg and Na co-doping may inevitably induce impurity levels, which could play as the self-absorption traps limiting the UV emission. The reason why the emission has expanded to visible region could be explained as follows: the various impurity levels induced by Mg and Na co-doping could be new radiative recombination levels, yielding EL emission emerged in both UV and visible regions.

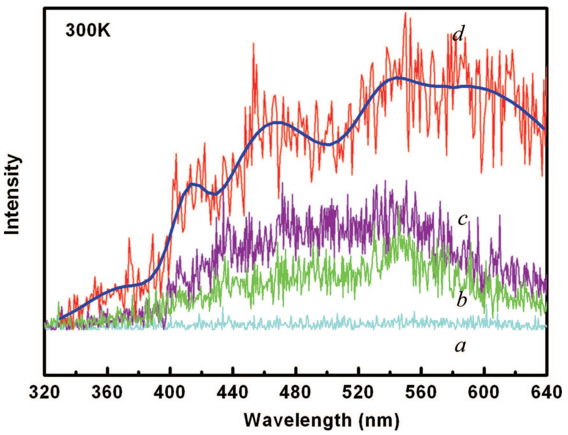

Fig. 2. Electroluminescence (EL) spectra from a p-$Zn_xMg_{1-x}O$:Na/n-ZnO LED by feeding in a series of direct current of 0, 10, 20 and 40 mA (*a*: 0 mA; *b*: 10 mA; *c*: 20 mA; *d*: 40 mA). A fitted smooth line with I = 40 mA is marked as well.

Fig. 3. EL photograph of the p-$Zn_xMg_{1-x}O$:Na/n-ZnO LED. An obvious light was observed in a direct current of 40 mA.

The EL photograph of the fabricated p-$Zn_xMg_{1-x}O$:Na/n-ZnO LED is shown in Fig. 3. In a direct current of 40 mA, distinct EL in the white region could be clearly seen by naked eye in the dark. The EL in this study could last more than 20 min. As there exists light in ultraviolet, violet, blue, green, and red regions, thus a mixed light was emitted from our fabricated p-$Zn_xMg_{1-x}O$:Na/n-ZnO LED.

In order to investigate the quality of the p-type Zn_x-$Mg_{1-x}O$:Na layer, a study of the PL of the Na doped

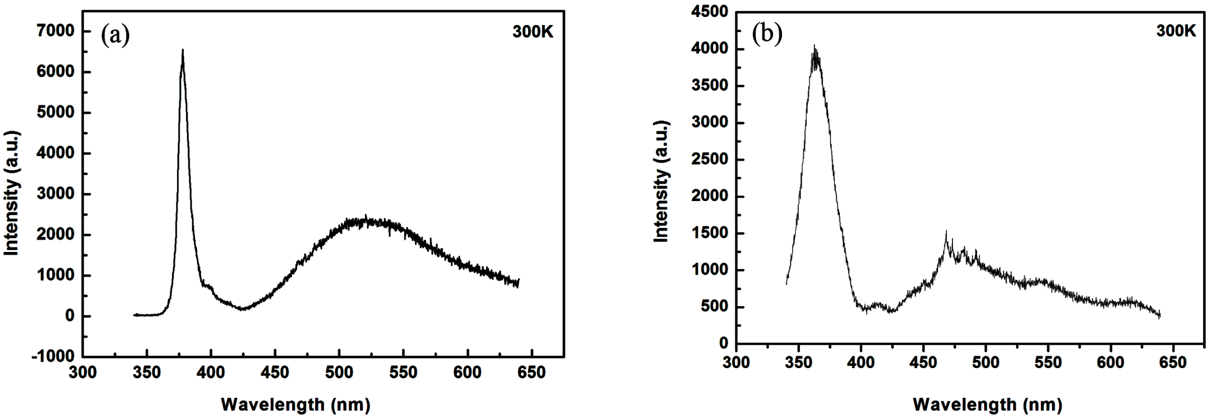

Fig. 4. PL spectra of (a) n-ZnO single-crystal substrate and (b) Na doped $Zn_xMg_{1-x}O$ film.

$Zn_xMg_{1-x}O$ film and the n-ZnO single-crystal substrate was done. The PL spectra of the n-ZnO single-crystal substrate and the Na doped $Zn_xMg_{1-x}O$ film are shown in Figs. 4(a) and 4(b), respectively. In Fig. 4(a), a clear band edge emission peak at 378 nm related to ZnO was revealed. The strong intensity of the wide peak at 540 nm is related to oxygen vacancies and/or zinc interstitials[19]. Since there existed intrinsic defects in the n-ZnO single-crystal substrate, the film epitaxially grown on it has defects as well, as indicated in Fig. 4(b). The additionally induced radiative recombination levels by the defects could also be taken into account to explain why our fabricated p-$Zn_xMg_{1-x}O$:Na/n-ZnO LED emitted a mixed light other than the pure UV light.

4. Conclusion

In conclusion, we fabricated a p-$Zn_xMg_{1-x}O$:Na/n-ZnO LED device by PLD technique and realized obvious light emission at RT. This ZnO-based LED shows good rectifying behavior with a threshold voltage of about 1.5 V and a low leakage current. By feeding a direct current of 40 mA, distinct electroluminescence could be clearly seen by naked eye. The reason why the EL emission has expanded to visible region besides UV emission was assigned mainly to the existence of impurity levels in the Na-doped p-type $Zn_xMg_{1-x}O$ film.

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