# Invariable optical properties of phosphor-free white light-emitting diode under electrical stress*

Long Hao(龙 浩), Fang Hao(方 浩), Qi Sheng-Li(齐胜利),
Sang Li-Wen(桑丽雯), Cao Wen-Yu(曹文彧), Yan Jian(颜 建),
Deng Jun-Jing(邓俊静), Yang Zhi-Jian(杨志坚)†, and Zhang Guo-Yi(张国义)

*State Key Laboratory for Artificial Microstructure and Mesoscopic Physics, School of Physics, Peking University, Beijing* 100871, *China*

(Received 4 March 2010; revised manuscript received 13 April 2010)

This paper reports that a dual-wavelength white light-emitting diode is fabricated by using a metal-organic chemical vapor deposition method. Through a 200-hours' current stress, the reverse leakage current of this light-emitting diode increases with the aging time, but the optical properties remained unchanged despite the enhanced reverse leakage current. Transmission electron microscopy and cathodeluminescence images show that indium atoms were assembled in and around V-shape pits with various compositions, which can be ascribed to the emitted white light. Evolution of cathodeluminescence intensities under electron irradiation is also performed. Combining cathodeluminescence intensities under electron irradiation and above results, the increase of leakage channels and crystalline quality degradation are realized. Although leakage channels increase with aging, potential fluctuation caused by indium aggregation can effectively avoid the impact of leakage channels. Indium aggregation can be attributed to the mechanism of preventing optical degradation in phosphor-free white light-emitting diode.

**Keywords:** light-emitting diode, gallium nitride, degradation, V-shape pits

**PACC:** 7360L, 7865K

## 1. Introduction

Since the first InGaN/GaN light-emitting diode (LED) was fabricated, GaN-based LED technology has been widely used in various areas.[1−5] Owing to its high luminous intensity and great performance, GaN-based LED is considered to be a next generation light source and a future replacement of the fluorescent lamp. However, the GaN-based LED still has plenty of unsolved problems, such as indium fluctuation, efficiency droop, degradation mechanism, and so on. According to the reported papers,[6−10] many phenomena of the LED's degradation have been reported, including electrical deterioration, $C$–$V$ evolution, optical weakening, and so on. The degradation properties of phosphor-packaged white LED included the aging of phosphor beside the phenomena mentioned above.[6−10]

Phosphor-free white LED, as an alternative for a complicated post-growth process, has become a hot research topic of gallium nitride material.[11−13] Many methods including prestrained layer,[10] wetting layer,[11] Si–Zn codoped,[8] and epitaxial lateral overgrowth (ELOG) microfacets,[13] have been successfully introduced into the fabrication of phosphor-free white LED. Taking application into account, optical stability of white LED is an important issue. However, the evolution of phosphor-free white LED's optical and electrical properties under electrical stress has never been reported. In this paper, the stability performance of white LED under electrical stress is reported. An enhanced "potential quantum confinement" mechanism for optical anti-degradation is discovered.

## 2. Experiment

Phosphor-free white LED was grown on $c$-plane sapphire substrate by metal-organic chemical vapour deposition (MOCVD). Ammonia, trimethylindium, and trimethylgallium were used as nitrogen, indium and gallium precursors, silane (SiH4) and bicyclopentadienyl magnesium (Cp2Mg) were the source of n-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 60990314, 60976009, 60577146, U0834001) and the National Key Basic Research and Development Project (973) of China (Grant No. 2007CB307004).

†Corresponding author. E-mail: zjyang@pku.edu.cn

© 2010 Chinese Physical Society and IOP Publishing Ltd

type and p-type dopant. The device included a 25-nm thick buffer layer and 1-$\mu$m unintentional doped GaN layer followed by a 2-$\mu$m n-type GaN. A 150-nm thick $In_xGa_{1-x}N$ layer with nominal $x = 0.15$ was deposited between the n-type and six multi-quantum wells (MQWs) to adjust the strain distribution of MQWs. Finally, a 15-nm p-$Al_{0.2}Ga_{0.8}N$ capping layer was deposited followed by a 200-nm p-type GaN. To fabricate LEDs with a size of 300×300 $\mu m^2$, the p-GaN and MQW layers were etched away by inductively coupled plasma (ICP) until the n-GaN layer was exposed for n-type Ohmic contact formation. Ti/Al and Ni/Au layers were used for the n- and p-type electrodes, respectively.

The LEDs were then stressed under a forward-current density of 26.5 A/cm$^2$ for 200 h. The tests were performed on packaged chip level at room temperature. During the 200-hours' 26.5-A/cm$^2$ current stress, current–voltage ($I$–$V$), luminescence output intensity-current ($L$–$I$), and electroluminescence (EL) properties of chips were performed. Evolution of wafer's cathodeluminescence (CL) intensity was also recorded during 30-min's 15-keV electron irradiation for exploring the degradation mechanism of electrical stress. In order to investigate the luminescence properties of phosphor-free white LED, the wafer was measured by transmission electron microscopy (TEM) and CL monochromatic experiments. The $I$–$V$ measurements were taken with the HP 4155C instrument. The TEM and CL experiments were performed on a system composed of Mono CL of Gatan and a JEOL JSM6700F instrument.

## 3. Results and discussion

Figure 1(a) shows logarithmic $I$–$V$ curves during the 200-hours' aging under 26.5-A/cm$^2$ current density condition. Figure 1(b) represents the forward part of the $I$–$V$ curves plotted in linear coordinates. With the longer aging time, the white LED's leakage current at −5 volt gradually increased three orders of magnitude from −8 to −5. However, represented by Figs. 1(a) and 1(b), our chip's forward $I$–$V$ characteristic (including forward leakage current in low voltage, ideal factor and parasitic resistance) did not change. Figure 2(a) represents luminescence output intensity of white LEDs as a function of current ($L$–$I$). Figure 2(b) shows the output intensity plot at 20 mA as a function of aging time.

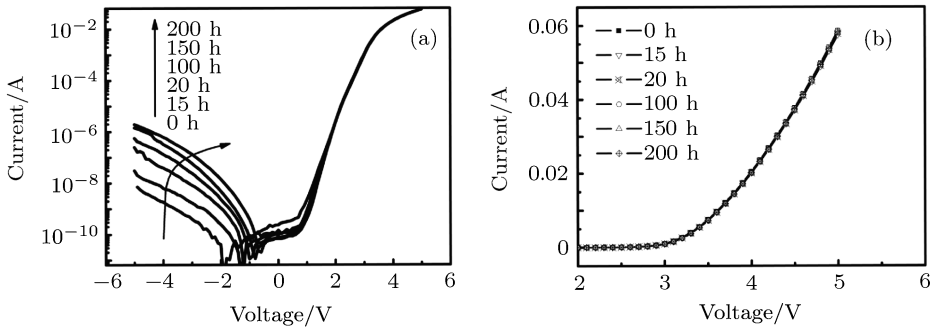



**Fig. 1.** (a) Evolution of logarithm $I$–$V$ curves during 200-hours' aging period under 26.5-A/cm$^2$ current density; (b) forward part of the $I$–$V$ curves plotted in linear coordinates during 200-hours' aging.

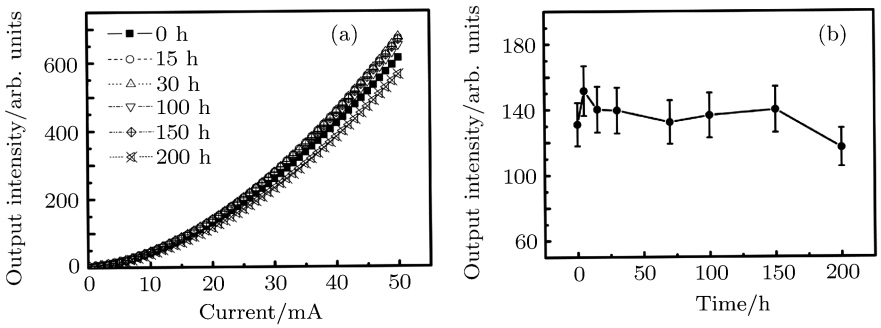



**Fig. 2.** (a) Light output intensity as a function of injection current during 200-hours' aging period; (b) light output intensity as a function of aging time at 20 mA during the stress.

Within the allowed range of error, figures 2(a) and 2(b) show that the output intensity did not change during the stress. Figure 3 shows the normalized EL spectrum at 20 mA.

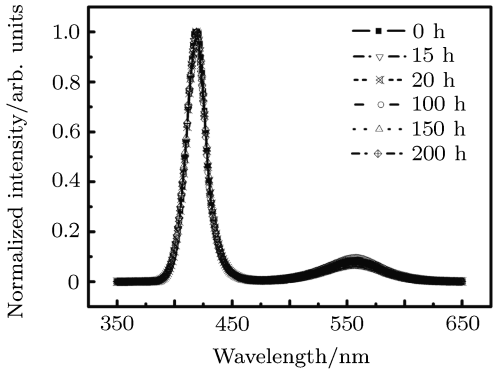



**Fig. 3.** Change of normalized intensity spectrum at 20 mA during the aging period.

Besides the intensity shown in Fig. 2(b), the spectrum of white LED did not change as well in Fig. 3. It means that the colour of this chip was stable during its operation.

The increase of reverse leakage current cannot be explained by deterioration of Ohmic contact or other effects (such as temperature), because such effects would also increase the forward leakage current. More convincing crystal quality's deterioration under electron injection will be shown in electron irradiation experiment later. Thus, crystalline quality degradation and increase of leakage channels were expected to interpret the enhanced reverse leakage current. The results of $L$–$I$ and EL curves exhibit significant differences from properties of conventional GaN-based blue LEDs. Results of conventional blue LEDs reportedly had nearly exponential decay of luminescence output power at the same aging period.[14−16] Their luminescence output intensity declined quickly when reverse leakage current increased.[7,10,14−17] The stable spectrum and unchanged light output intensity of the white LED distinguished it from blue LEDs.

For comparison, figure 6(a) represents the CL spectrum of the wafer under 15-keV electron injection. From Fig. 6(a), two emission peaks at 460 nm and 560 nm were detected. Figure 4 shows the CL intensity's evolution of both bands under 15-keV electron irradiation in 30 min. The intensity of both blue and green band decreased with irradiation time. The decreased intensity under electron irradiation indicated that the crystalline quality of white LED indeed deteriorated under electron injection. Considering the difference between EL and CL mechanism, explanation for the stable output power in EL experiments will be presented after the study of white light emission origin.

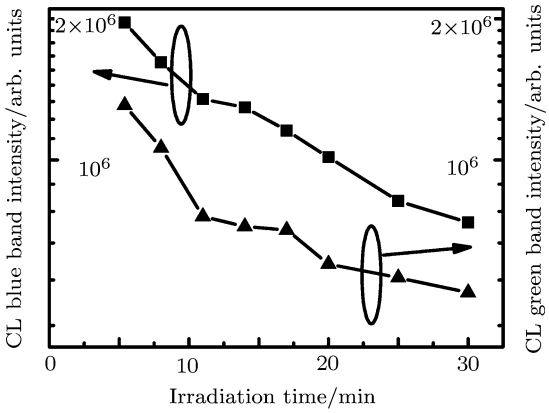



**Fig. 4.** CL intensity's evolution of both bands under 15-keV electron irradiation.

To further investigate the origin of degradation characteristic, the white light emitting mechanism was first realized by TEM and CL experiments. Figure 5(a) shows the image of the six quantum wells in phosphor-free LED. The regions with dark contrast in Fig. 5(a) constituted the wells' areas. In Fig. 5(b), the arrows mark a V-shape pit at the location of the six quantum wells. Around the bottom of this V-shape pit, dark spots indicate the aggregation of indium atoms. Similar results demonstrating indium aggregation around V-shape pits have also been reported by Lin *et al.*[14] and Yang *et al.*[18]

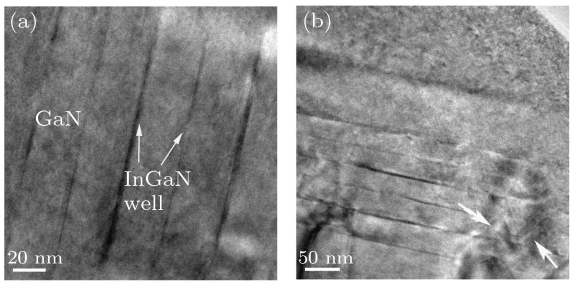



**Fig. 5.** Transmission electron microscopy (TEM) (a) on the region of multiple quantum wells (MQWs) and (b) on the region of V-shape pits.

For studying the relationship between V-shape pits and white light luminescence further, we performed CL measurement for this wafer under 15-keV electron radiation. Figure 6(a) represents the CL spectrum of a 5×5 $\mu$m$^2$ region. Two emission peaks at 460 nm and 560 nm were detected. Monochromatic CL images were collected at the corresponding peaks'

wavelength, shown in Figs. 6(b) and 6(c), respectively. Comparing the arrow-marked regions in Figs. 6(b) and 6(c), the regions emitting green light were always surrounded by the areas emitting blue light. Related to indium aggregation in the V-shape pits emerged in TEM image, conclusions on V-shape pits regions emitting white light could be made. With the introduction of prestrained layer and the emergence of V-shape pits, strain distribution was modulated. This modulation resulted in more indium atoms aggregating into the bottom and less indium atoms assembling around the bottom. In the bottom of the V-shape pits, green light at 560 nm was emitted since more indium atoms aggregating. Surrounding the bottom, regions with less indium emitted blue light at 460 nm. The emission of white light induced by indium aggregations has been reported by Fang *et al.*[12] We make it more convincing here by addition of V-shape pits in TEM image.

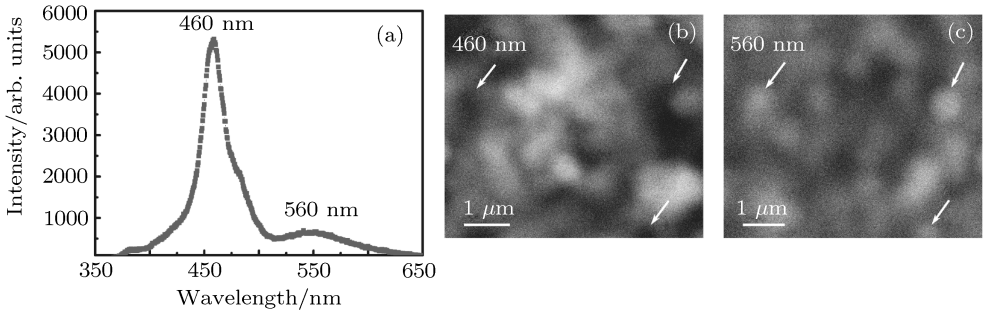



**Fig. 6.** (a) The CL spectrum in visible wavelength; monochromatic CL images of 460 nm (b) and 560 nm (c).

Considering the white luminescence from V-shape pits, the results could be explained by this model: in our phosphor-free white LED, the white light emitting mechanism was attributed to indium aggregations with different composition in and around the V-shape pits. During the current stress, as expected, the crystalline quality of white LED became worse, which has been verified by electron irradiation performance. From the view of electrical properties, reverse leakage current significantly increased. However, as a result of potential fluctuation enhanced by V-shape pits, carriers had more possibility for taking the radiative recombination path in the indium assembled regions under forward injection condition.[19−21] Thus, electrons and holes did not take leakage paths to form the forward leakage current as reported before in blue LEDs.[6−9] Instead, carriers took their special way through the "concave" of the energy band, and still recombined in the V-shape pits as the way before degradation. Indium aggregation in the V-shape pits, behaved as passages for the radiative recombination centre. Although leakage channels increased, it would not impact the carriers' path in the forward current. Therefore, the optical and forward electrical properties kept stable during the current stress. Carriers' quantum confinement seems not only to enhance the overlap of function waves, but also has the function of optical anti-degradation. However, CL spectrum was performed by scanning electron injected onto the whole region of corresponding SEM image. The carriers in CL were generated and recombined homogeneously in the whole active region including the leakage channels. This is the reason for CL intensity suffering the degradation while EL intensity retaining stable.

## 4. Conclusion

In summary, the phosphor-free white light-emitting diode was fabricated by MOVCD method. During the aging test, as illustrated by the enhanced reverse leakage current and decrease of CL intensity under electron irradiation, the chip's quality was indeed degraded. However, a stable optical property of the chip was obtained during the degradation. Through the TEM and CL methods, the white light luminescence mechanism was attributed to the indium aggregations related with V-shape pits. Thus, during the aging process, luminescence degradation induced by the leakage channels can be effectively avoided. Indium aggregation seems to be a new mechanism for optical anti-degradation and good for the application of white light-emitting diodes.

# References


[1] Nakamura S, Senoh M, Iwasa N, Nagahama S, Yamada T and Mukai T 1995 *Jpn. J. Appl. Phys.* **34** L1332

[2] Nakamura S, Mukai T, Senoh M, Nagahama S and Iwasa N 1993 *Jpn. J. Appl. Phys.* **32** L8

[3] Lu G J, Zhu J J, Jiang D S, Wang Y T, Zhao D G, Liu Z S, Zhang S M and Yang H 2010 *Chin. Phys.* B **19** 026804

[4] Li X H, Zhong F, Qiu K, Yin Z J and Ji C J 2008 *Chin. Phys.* B **17** 1360

[5] Xu H Y, Jian A Q, Xue C Y, Chen Y, Zhang B Z, Zhang W D, Zhang Z G and Feng Z 2008 *Chin. Phys.* B **17** 2245

[6] Trevisanello L, Meneghini M, Mura G, Vanzi M, Paversi M, Meneghesso G and Zanoni E 2008 *IEEE. Trans. Dev. Mater. Rel.* **8** 304

[7] Yu T J, Shang S P, Chen Z Z, Qin Z X, Lin L, Yang Z J and Zhang G Y 2007 *J. Luminescence* **122** 696

[8] Sheu J K, Pan C J, Chi G C, Kuo C H, Wu L W, Chen C H, Chang S J and Su Y K 2002 *IEEE Photonics Technol. Lett.* **14** 450

[9] Li D S, Chen H, Yu H B, Jia H Q, Huang Q and Zhou J M 2004 *J. Appl. Phys.* **96** 1111

[10] Rossi F, Pavesi M, Meneghini M, Salviati G, Manfredi M, Meneghesso G, Castaldini A, Rigutti L, Strass U, Zehnder U and Zanoni E 2006 *J. Appl. Phys.* **99** 053104

[11] Soh C B, Liu W, Teng J H, Chow S Y, Ang S S and Chua S J 2008 *Appl. Phys. Lett.* **92** 261909

[12] Fang H, Sang L W, Zhao L B, Qi S L, Zhang Y Z, Yang X L, Yang Z J and Zhang G Y 2008 *Appl. Phys. Lett.* **93** 261117

[13] Cho C Y, Park I K, Kown M K, Kim J Y, Park S J, Jung S R and Kwon S W 2008 *Appl. Phys. Lett.* **93** 241109

[14] Daniel L B, Osinski M, Perlin P, Eliseev P G and Lee J Y 1999 *Microelectronics Reliability* **39** 1219

[15] Zhao L X, Thrush E J and Humphreys C J 2008 *J. Appl. Phys.* **103** 024501

[16] Nakamura S and Chichibu F 2000 *Introduction to Nitride Semiconductor Blue Lasers and Light Emitting Diodes* (London and New York: Taylor & Francis) p. 271

[17] Lin Y S, Ma K J, Hsu C, Feng S W, Cheng Y C, Liao C C, Yang C C, Chou C C, Lee C M and Chyi J I 2006 *Appl. Phys. Lett.* **77** 19

[18] Yang Z J, Tong Y Z, Zhang G Y, Du X L, Fujii N, Jia A W and Yoshikawa A 2000 *Phys. Stat. Sol.* (a) **180** 81

[19] Chichibu S, Azuhata T, Sota T and Nakamura S 1996 *Appl. Phys. Lett.* **69** 4188

[20] Narukawa Y, Kawakami Y, Fujita S, Fujita S and Nakamura S 1997 *Phys. Rev.* B **55** R1938

[21] Nakamura S and Fasol G 1997 *The Blue Laser Diode* (New York: Springer) p. 215