Materials Research Express

PAPER

The influence of excessive H$_2$ during barrier growth on InGaN light-emitting diodes

Yangfeng Li$^{1,2}$, Shen Yan$^{1,2}$, Die Junhui$^{1,2}$, Xiaotao Hu$^{1,2}$, Yimeng Song$^{1}$, Zhen Deng$^{1,2,5}$, Chunhua Du$^{1,2,5}$, Wenqi Wang$^{1,2}$, Ziguang Ma$^{1,2}$, Lu Wang$^{1,2}$, Haiqiang Jia$^{1,2,6}$, Wenzhong Wang$^{1,2,6}$, Junming Zhou$^{1,2}$, Yang Jiang$^{1,2}$, and Hong Chen$^{1,2,*}$

1 Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
2 Center of Materials and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China
3 Fine Optical Engineering Research Center, Chengdu, 610041, People’s Republic of China
4 School of Mathematics and Physics, Beijing Key Laboratory for Magneto-Photoelectrical Composite and Interface Science, University of Science and Technology Beijing, Beijing 100083, People’s Republic of China
5 The Yangtze River Delta Physics Research Center, Liyang 213000, People’s Republic of China
6 Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, People’s Republic of China
7 Authors to whom any correspondence should be addressed.

E-mail: jiangyang@iphy.ac.cn and hchen@iphy.ac.cn

Keywords: hydrogen, InGaN, TDPL, EQE, leakage current

Abstract

The influence of excessive H$_2$ flow during barrier growth on optical and electrical properties of InGaN light-emitting diodes (LEDs) is investigated in this study. The room temperature photoluminescence of LEDs decays with excessive H$_2$ treatment. Temperature-dependent photoluminescence (TDPL) reveals an increase of the density and a decrease of the activation energy of deep non-radiative recombination centers in the H$_2$ treated LEDs. The external quantum efficiency (EQE) of the LEDs suffers from excessive H$_2$ treatment. The leakage current on the reverse and forward sides of the LEDs are reduced significantly when treated with H$_2$, which may be due to the suppressed Poole–Frenkel effect.

Introduction

Due to the high radiative efficiency and widely adjustable bandgap width, InGaN plays an important role in light-emitting diodes (LEDs) [1, 2], laser diodes [3, 4], display [5, 6] and communication [7]. Traditionally, the InGaN/GaN multiple quantum wells (MQWs) are grown under pure nitrogen ambient as the indium incorporation is rather poor when exposed to hydrogen flow [8–13]. However, the crystalline quality of GaN grown under nitrogen ambient is inferior to that grown under hydrogen ambient, where the hydrogen benefits the GaN with reduced defects and enhanced atomic mobility [14]. Some researchers investigated the effect of H$_2$ during the quantum barrier growth and the results are different in some aspects. Czernecki et al found the barrier surface became smoother with 25% H$_2$ showing eradicated V-pits [15]. Zhou et al reported the smoother MQWs interface when introducing an appropriate amount of H$_2$ into the barrier growth process [16]. The photoluminescence (PL) of InGaN MQWs will be greatly augmented by N$_2$/H$_2$ mixture gas as reported by some researchers [17]. The electroluminescence (EL) and external quantum efficiency (EQE) will also be improved by H$_2$ treatment [18, 19]. However, the other researchers suggested that mixing H$_2$ into the carrier gas during barrier growth will deteriorate the EQE performance and reduce the leakage current [20]. In our previous work, we found the interface of MQWs will be roughened by the H$_2$ while an appropriate amount of H$_2$ (2.7%) will be beneficial to the EQE and reduce the leakage both in forward and reverse sides [21]. In this study, we systematically investigated the optical performance of LEDs treated with excessive H$_2$ flow by temperature-dependent photoluminescence (TDPL). The density and activation energy of non-radiative recombination centers were obtained from the TDPL measurement results. It is found the density of deep non-radiative...
recombination centers increases significantly and the activation energy decreases with H₂ flow. Such must be the main reason responsible for the decaying optical performance. According to the EL results, the reverse and forward leakage currents are reduced by introducing H₂ into barrier growth process which may be attributed to the suppressed Poole–Frenkel effect.

Experiment

Three LED samples labelled A, B, and C were epitaxially grown on n-GaN templates by an AIXTRON metal organic chemical vapor deposition (MOCVD) system. The n-GaN templates were grown on 2-inch c-plane sapphire substrates by the same MOCVD. Trimethyl-gallium (TMGa), triethyl-gallium (TEGa), trimethyl-indium (TMIn), and ammonia (NH₃) were used as the precursors. The dopants for the n-type and p-type GaN were silane (SiH₄) and dicyclopentadienyl magnesium (Cp²Mg), respectively. Prior to the growth of 5 pairs of InGaN (3 nm, 728 °C)/GaN (14 nm, 858 °C) MQWs, 3 pairs of shallow well (SW) [InGaN(1.5 nm)/GaN (11 nm)] were deposited on the n-GaN templates. The V/III ratio was 28 240 with the TEGa flow of 8.64 μmol min⁻¹ and the TMIn flow of 11.12 μmol min⁻¹ during the MQWs growth process. Sample A was grown under pure N₂ ambient while B and C were grown with 5% and 10% H₂ mixed in the total gas flow respectively during the quantum barrier growth process. The total flow was preserved at 28 slm during the MQWs growth time of all the samples. A 25-nm thick p-AlGaN layer was deposited right atop the MQWs followed by a 300 nm p-GaN layer. The as-grown wafers were annealed in situ at 780 °C to activate the magnesium dopant. The schematic diagram of the LED structure is illustrated in figure 1(a) and the in situ monitored growth temperature curves are shown in figure 1(b). The inset in figure 1(b) was the magnified picture of the red dotted rectangular region where the growth of quantum well occurs. Seen from figure 1(b), the growth temperature in quantum well regime was almost identical of the three samples. The indium composition and the periods of MQWs were characterized by the Panalytical high resolution x-ray diffraction (HRXRD) system with a CuKα1 line of 1.5406 Å. The TDPL spectra were acquired in a closed-loop helium cryostat from 15 K to 300 K with a 325 nm He-Cd continuous wavelength laser in conjunction with an optical fiber to collect the PL signal. Part of the wafers of the three samples were fabricated to 300 μm × 300 μm LED chips with Ni/Au as the current spreading layer. The detailed parameters of the chip technique could be reached in our previous studies [10]. The EL performance of the LED chips was carried out by a standard industrial LED testing machine (WEIN MING LED Tester 630), while the current-voltage (I-V) curves were given by a Keithley 4200 semiconductor characterization system.

Results and discussion

The omega-2 theta scan XRD curves are shown in figure 2. Up to ‘−4th’ satellite peak could be clearly distinguished in both samples indicating the abrupt interface of the MQWs. The indium component, thickness of well and barrier layers deduced from the XRD curves are listed in table 1. The experimental results are coincident well with the designed structural parameters in figure 1(a). The barrier thickness of B and C decreases compared to that of A, which should be due to the etching effect caused by the H₂ [14]. As three pairs of SW were
added under the MQWs, the full-width at half maximum (FWHM) of the satellite peaks will be adjusted by the SW, thus it is difficult to obtain the roughening tendency by using the broadening relationship \[22\].

The PL spectra measured at 300 K of A–C are presented in figure 3 (a). It is found that B and C present inferior PL performance to that of A indicating the deterioration of the optical performance with excessive H\(_2\) treatment. The curves of peak energy changing with temperature were extracted from the TDPL spectra. The S-shaped (decrease–increase–decrease) curves reveal the existence of localization states \[23\]. The integral PL intensity changing with temperature of A–C was depicted in figure 3 (c) where the cyan dotted lines are the fitted curves by using the Arrhenius formula \[17, 23\]:

\[
I(T) = \left[1 + C_1 \exp\left(-\frac{E_{A1}}{k_B T}\right) + C_2 \exp\left(-\frac{E_{A2}}{k_B T}\right)\right]^{-1},
\]

where \(I(T)\) is the normalized integrated PL intensity, \(C_1\) and \(C_2\) are two constants related to the density of non-radiative recombination centers, \(E_{A1}\) and \(E_{A2}\) are the activation energies of the non-radiative recombination process and \(k_B\) is Boltzmann’s constant. The fitted values and the ratio of \(I_{300K}/I_{15K}\) are listed in table 2. The values of \(I_{300K}/I_{15K}\) decreases monotonically as the \(H_2\) flow increases, indicating exacerbation of the optical performance by excessive \(H_2\). It is found that the activation energy \((E_{A2})\) of the deep non-radiative recombination centers decreases with increasing \(H_2\) flow, while the density of deep non-radiative recombination center \((C_2)\) increases. The decrease of the activation energy and the enhanced density contaminate the radiative recombination process resulting in a concomitant luminescence decay. The lowest activation energy of shallow non-radiative recombination centers in sample C further exacerbates the optical performance thus leading to the lowest \(I_{300K}/I_{15K}\) value of C. While in sample B, the increase of \(E_{A1}\) alleviates part of the negative effect caused by the deep non-radiative recombination centers, therefore, the optical performance of B is better than C.

To verify the influence of excessive \(H_2\) on EL properties, the EL spectra at 20 mA injection condition, the EQE and the current–voltage (I–V) characteristics of A–C are depicted in figures 4 (a)–(c), respectively. The emission peak of A–C is around 440 nm indicating the precisely control of the growth parameters. The efficiency droop is suppressed \[21\]. The leakage currents both in the reverse and forward sides are reduced more than one magnitude lower than the sample grown under pure N\(_2\) ambient. It is to be noted that the sidewall isolation technique was omitted in our chip process, the absolute value of leakage current is somewhat high. However, the tendency of reduced leakage current with increasing \(H_2\) flow is clear to be found in figure 4 (c). It is reported that at the room temperature regime, the reverse leakage current is dominated by the Poole–Frenkel effect, following the

![Figure 2. The omega-2 theta scan XRD curves of samples A–C.](image-url)
equation $I \propto \exp(F^{1/2})$, where $F$ is the average internal electric field strength which is proportional to $(V_{bi} - V)$ with $V_{bi}$ as the built-in voltage of the GaN LED [24–26]. The relationship of reverse current changing with the square root of reverse voltage is elucidated in figure 4(d). The curves are fitted well by the exponential equation with the R-square values larger than 0.994. The slope of the fitted curve is recognized as an evidence of the activation energy of the defect density. The larger the slope is, the more difficult the hopping conduction becomes, resulting in lower reverse leakage current. The LEDs treated by H$_2$ during barrier growth present lower
reverse current and the concomitant higher activation energy for nearest-neighbor hopping (NNH) conduction [25]. It is acknowledged that H₂ reduces defects such as carbon, oxygen, V-defects and other defects [17]. Such defects may play the role of localization states which assist the carriers in transiting across the space charge region [25]. As the defects are partly eliminated by the H₂, the reverse leakage current is reduced significantly.

Conclusion

The optical and electric properties of LEDs underwent excessive H₂ treatment during the barrier growth process have been systematically investigated in this study. The PL intensity decays when the LEDs are treated with excessive H₂ flow. TDPL results reveal the increase of density and the decrease of the activation energy of deep non-radiative recombination centers with increasing H₂ flow, resulting in the deterioration of the photo- and electro-luminescence efficiency. The leakage currents in both the reverse and forward sides are reduced more than one magnitude when introducing H₂ into the barrier growth process. By using a nearest-neighbor hopping (NNH) conduction model to analyze the reverse leakage current, we conclude that the H₂ reduces the density of defects thus making the hopping conduction process more difficult to happen.

Acknowledgments

This work was supported by National Natural Science Foundation of China (Grant No. 11574362, 61210014, 11374340, 11474205, 62004218, and 61804176), Innovative clean-energy research and application program of Beijing Municipal Science and Technology Commission (Grant No. Z151100003515001), National Key Technology R&D Program of China (2016YFB0400302) and the Strategic Priority Research Program of Chinese Academy of Sciences (Grant No. XDB33000000).
Conflicts of interest

There are no conflicts to declare.

ORCID iDs

Yangfeng Li https://orcid.org/0000-0001-9896-9116
Lu Wang https://orcid.org/0000-0001-9930-9435

References

[1] Wang L et al 2019 Abnormal stranski-krastanov mode growth of green ingan quantum dots: morphology, optical properties, and applications in light-emitting devices ACS Appl. Mater. Interfaces 11 1228–36
[2] Jiang F et al 2019 Efficient InGaN-based yellow-light-emitting diodes Photon. Res. 7 144
[3] Zhang H, Li H, Li P, Song J, Speck J S, Nakamura S and DenBaars S P 2020 Room-temperature continuous-wave electrically driven semipolar (2021) blue laser diodes heteroepitaxially grown on a sapphire substrate ACS Photonics 7 1662–6
[4] Yang J, Zhao D G, Jiang D S, Chen P, Zhu J J, Liu Z S, Liang F, Liu S T and Xing Y 2020 Suppression the formation of V-pits in InGaN/ GaN multi–quantum well growth and its effect on the performance of GaN-based laser diodes J. Alloys Compd. 822 153571
[5] Zhang X, Li P, Zou X, Jia J, Yuen S H, Tang C W, Liu K M 2019 Active matrix monolithic LED micro-display using GaN-on-Si epi-layers IEEE Photon. Technol. Lett. 31 165
[6] Bai J, Cai Y, Feng P, Fletcher P, Zhao X, Zhu C and Wang T 2020 A direct epitaxial approach to achieving ultrasmall and ultrabright InGaN micro light-emitting diodes (µLEDs), ACS Photonics 7 411–5
[7] Holguin-Lerma J A, Kong M, Alkhazragi O, Sun X, Khee T and Ooi N B 2020 480-nm distributed-feedback InGaN laser diode for 10.5-Gbit/s visible-light communication Opt. Lett. 45 742–5
[8] Czernecki R et al 2014 Influence of hydrogen and TMIn on indium incorporation in MOVPE growth of InGaN layers J. Cryst. Growth 402 330–6
[9] Li Y, Deng Z, Ma Z, Wang L, Jia H, Wang W, Jiayang Y and Chen H 2019 Visualizing carrier transitions between localization states in a InGaN yellow–green light-emitting-diode structure J. Appl. Phys. 126 095705
[10] Jiang Y et al 2015 Realization of high-luminous-efficiency InGaN light-emitting diodes in the ‘green gap’ range Sci. Rep. 5 10883
[11] Li Y et al 2017 Improvement of green InGaN-based LEDs efficiency using a novel quantum well structure Chin. Phys. B 26 087311
[12] Li Y, Jin Z, Han Y, Zhao C, Huang J, Tang C W, Wang J and Lau K M 2019 Surface morphology and optical properties of InGaN quantum dots with varying growth interruption time Mater. Res. Express 7 015903
[13] Li Y, Tang C W and Lau K M 2020 Comparison of the AlN and GaN crystalline quality on 2-inch silicon substrate via two growth methods J. Cryst. Growth 535 12545
[14] Koleske D, Wickenden A, Henry R, Culbertson J and Twigg M 2001 GaN decomposition in H2 and N2 at MOVPE temperatures and pressures J. Cryst. Growth 223 466–83
[15] Czernecki R et al 2015 Effect of hydrogen during growth of quantum barriers on the properties of InGaN quantum wells J. Cryst. Growth 414 38–41
[16] Zhou X, Lu T, Zhu Y, Zhao G, Dong H, Jia Z, Yang Y, Chen Y and Xu B 2017 Surface morphology evolution mechanisms of InGaN/GaN multiple quantum wells with mixture N2/H2-grown GaN barrier Nanoscale Res. Lett. 12 354
[17] Zhu Y, Lu T, Zhou X, Zhao G, Dong H, Jia Z, Liu X and Xu B 2017 Origin of huge photoluminescence efficiency improvement in InGaN/GaN multiple quantum wells with low-temperature GaN cap layer grown in N2/H2 mixture gas APEX 10 061004
[18] Lv W, Wang L, Wang J, Hao Z and Luo Y 2012 InGaN/GaN multilayer quantum dots yellow-green light-emitting diode with optimized GaN barriers Nanoscale Res. Lett. 7 617
[19] Lai W-C and Yang Y-Y 2013 Effects of H2 in GaN barrier spacer layer of InGaN/GaN multiple quantum-well light-emitting diodes J. Disp. Technol. 9 234
[20] Wu Q et al 2018 Effects of hydrogen treatment in barrier on the photoluminescence of green InGaN/GaN single-quantum-well light-emitting diodes with V-shaped pits grown on Si substrates Chin. Phys. Lett. 35 050850
[21] Li Y et al 2020 Effect of H2 treatment in barrier on interface, optical and electrical properties of InGaN light emitting diodes Superlattice. Microst. 145 106606
[22] Li Y et al 2019 Characterization of periodicity fluctuations in InGaN/GaN MQWs by the kinematical simulation of x-ray diffraction APEX 12 015502
[23] Lu T et al 2014 Temperature-dependent photoluminescence in light-emitting diodes Sci. Rep. 4 6131
[24] Zhi T, Tao T, Liu B, Xie Z, Chen P and Zhang R 2016 Reverse leakage current characteristics of GaN/InGaN multiple quantum-wells blue and green light-emitting diodes IEEE Photonics J. 8 16011606
[25] Zhou S, Lv J, Wu Y, Zhang Y, Zheng C and Liu S 2018 Reverse leakage current characteristics of InGaN/GaN multiple quantum well ultraviolet/blue/green light-emitting diodes Opt. J. Appl. Phys. 57 051003
[26] Lee M, Lee H I, Song K M and Kim J 2019 Significant improvement of reverse leakage current characteristics of Si-based homoepitaxial InGaN/GaN blue light emitting diodes Sci. Rep. 9 9707