The enhancement of light-emitting efficiency using GaN-based multiple quantum well light-emitting diodes with nanopillar arrays*

Wan Tu-Tu(万图图), Ye Zhan-Qi(叶展圻), Tao Tao(陶 涛), Xie Zi-Li(谢自力)†,
Zhang Rong(张 荣), Liu Bin(刘 斌), Xiu Xiang-Qian(修向前), Li Yi(李 毅),
Han Ping(韩 平), Shi Yi(施 毅), and Zheng You-Dou(郑有炓)

Key Laboratory of Advanced Photonic and Electronic Materials, School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, *China*

(Received 24 October 2012; revised manuscript received 2 February 2013)

The quest for higher modulation speed and lower energy consumption has inevitably promoted the rapid development of semiconductor-based solid lighting devices in recent years. GaN-based light-emitting diodes (LEDs) have emerged as promising candidates for achieving high efficiency and high intensity, and have received increasing attention among many researchers in this field. In this paper, we use a self-assembled array-patterned mask to fabricate InGaN/GaN multi-quantum well (MQW) LEDs with the intention of enhancing the light-emitting efficiency. By utilizing inductively coupled plasma etching with a self-assembled Ni cluster as the mask, nanopillar arrays are formed on the surface of the InGaN/GaN MQWs. We then observe the structure of the nanopillars and find that the V-defects on the surface of the conventional structure and the negative effects of threading dislocation are effectively reduced. Simultaneously, we make a comparison of the photoluminescence (PL) spectrum between the conventional structure and the nanopillar arrays, achieved under an experimental set-up with an excitation wavelength of 325 mm. The analysis demonstrates that MQW-LEDs with nanopillar arrays achieve a PL intensity 2.7 times that of conventional LEDs. In response to the PL spectrum, some reasons are proposed for the enhancement in the light-emitting efficiency as follows: 1) the improvement in crystal quality, namely the reduction in V-defects; 2) the roughened surface effect on the expansion of the critical angle and the attenuated total reflection; and 3) the enhancement of the light-extraction efficiency due to forward scattering by surface plasmon polariton modes in Ni particles deposited above the p-type GaN layer at the top of the nanopillars.

Keywords: nanopillar arrays, InGaN/GaN, multiple quantum wells, quantum efficiency

PACS: 81.07.St, 78.67.Qa, 68.65.Fg **DOI:** 10.1088/1674-1056/22/8/088102

1. Introduction

Present-day theories suggest that one possible cause of the high efficiency of multi-quantum well (MQW) light-emitting diodes (LEDs) is the quantum confinement effect (QCE)[1] that appears in the active layers of the quantum wells. In some documents, researchers have proved that the strong confinement[2] of the electron–hole pairs in the nanostructures should increase the electron–hole wave function overlap and the radiative recombination rate. Inspired by this, compared with conventional thin-film LEDs, we consider whether it is possible to fabricate the nanopillars on the surface of the device using inductively coupled plasma (ICP) etching, with the purpose of introducing the QCE into LEDs, which will be conducive to the enhancement of the light-emitting efficiency. A number of research groups have conducted many experiments and studies on nanopillars. For example, GaN nanorods with a high aspect ratio and large surface area can dramatically reduce the dislocation density in the upper part of the nanorods.[3] Besides, small-sized nanorods help to relieve the strain induced by thermal expansion mismatch and avoid defect generation, which is a solution to the growth on large substrates or substrates with a large thermal expansion coefficient difference from GaN.[4] In addition, more basal-plane stacking faults can be observed using Ni as the catalyst.[5] The study of nanopillars based on GaN is a hotspot for the research field in GaN-based solid-state lighting devices. We also draw our inspiration from the work by other research teams.[6,7] In this paper, we conduct an experiment where the extraction efficiency of quantum wells is improved by introducing and further enhancing QCE and roughening the surface in order to reduce the total reflection loss. This is implemented by fabricating InGaN/GaN MQW-LEDs with a nanopillar structure using ICP etching technology and the self-assembled Ni nanodot-arrays as the mask.

2. Experimental details

The MQWs based on InGaN/GaN experimental samples were produced using the Thomas Swan metal–organic chemical vapor deposition (MOCVD) growth system. The Ga source consists of trimethylgallium, the source of In is

*Project supported by the Special Funds for Major State Basic Research Project of China (Grant No. 2011CB301900), the High Technology Research Program of China (Grant No. 2009AA03A198), the National Natural Science Foundation of China (Grant Nos. 60990311, 60721063, 60906025, 60936004, 60731160628, and 60820106003), the Natural Science Foundation of Jiangsu Province, China (Grant Nos. BK2008019, BK2010385, BK2009255, and BK2010178), and the Research Funds from Nanjing University Yangzhou Institute of Opto-electronics, China.

†Corresponding author. E-mail: xzl@nju.edu.cn

© 2013 Chinese Physical Society and IOP Publishing Ltd

trimethylindium, and the N source is ammonia. First, a GaN buffer layer with a thickness of 2-μm adheres to the sapphire substrate with the *c* plane using the two-step method. On this layer there are five-period InGaN/GaN MQWs, and on the top there is a 200-nm thick p-GaN layer. At the end of these steps, a layer with a 4-nm thick Ni film is deposited through evaporation. Then, we treat the samples with rapid thermal annealing in a nitrogen atmosphere at 830 °C for 4 min, so that the coating self-assembles into a number of particulate Ni nanodots. These nanodots are used as masks for etching. After that, the sample is etched to form the InGaN/GaN nanopillars, utilizing the ICP instrument of Oxford Instrument Company, at a depth of 400 nm. During etching, the pressure of the cavity is kept at 1.33 Pa, the DC bias is set to be 300 V, the ICP power is stabilized at 300 W, and the flow rate of the chlorine gas is maintained at 48 sccm, while that of boron trichloride is 8 sccm. The PL spectra of the samples, both before and after etching, are excited by the 325 nm laser. To determine the morphology of the sample surface, the surface is scanned by the JSM-7000F thermal field of the field emission scanning electron microscope (SEM) of the JEOL Company.

3. Results and discussion

3.1. SEM image analyses of the etched and unetched InGaN/GaN MQW LEDs

Figure 1 shows the surface morphology SEM images of the different stages in the fabrication process of InGaN/GaN MQW-LEDs with nanopillar structures. As shown in Fig. 1(a), which is the 10^4-magnification image of the unetched conventional MQW surface, defects of various sizes, varying from 100 nm to 200 nm, are grown on the surface of the thin-film templates. This phenomenon was attributed in some documents[8] to the following factors: 1) lattice mismatch resulting from the difference in the lattice parameters between the substrate and the thin-film material; 2) the difference in the coefficient of thermal expansion (CTE) between the different materials; and 3) screw dislocation and mixed dislocation in the GaN material, which facilitates the formation and growth of defects. Therefore, it is normal to see defects in the MQW thin films. Meanwhile, figure 1(b) shows the SEM image of the material surface covered with the self-assembled Ni cluster after annealing treatment. From this image, nanodot arrays, formed in dispersive dot structures, can be clearly observed. Furthermore, these Ni dots, whose sizes are around 100 nm on average, assemble in the area with no defects. Accordingly, this suggests that in the self-assembling process of the Ni particles, we successfully avoid the defect zone and selectively deposit the particles in the nanodot array form, which thus contributes to the removal of these defects in the etching process. Figure 1(c) exhibits the nanopillar array structure of the InGaN/GaN MQW-LEDs etched by the ICP system. It is observed in Fig. 1(c) that the areas without self-assembled Ni clusters are etched into gaps between the pillars by the bombardment of chloride ions and boron trichloride ions, while the areas covered with these metal particles are not etched in that way, thus forming the pillars. In addition, we also find that the defects existing in Figs. 1(b) and 1(d) almost disappear. As demonstrated in some studies,[9] the defects are substantially non-radiative recombination centers, in which case the energy generated in the electronic transition to the valence band is largely converted into heat, thereby impeding the enhancement of the light-emitting efficiency. In this paper, we successfully reduce the defects, so this indicates that compared with conventional MQWs, InGaN/GaN nanopillar array LEDs can increase the light-emitting efficiency.

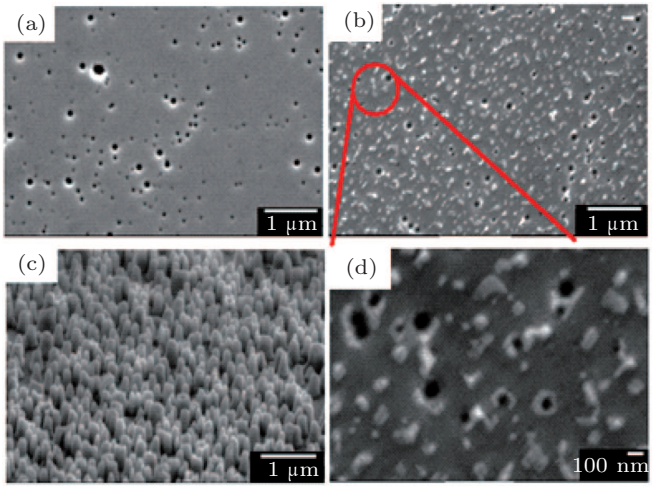


Fig. 1. (color online) Surface morphology SEM images of the different stages in the fabrication process of InGaN/GaN MQW-LEDs with a nanopillar structure: (a) the unetched conventional LED surface, (b) the SEM image of the material surface covered with the self-assembled Ni cluster after annealing treatment, (c) the SEM image of the nanopillar array structure of the InGaN/GaN MQW-LEDs etched in the ICP system, and (d) the partial enlargement SEM image of panel (b).

3.2. Analyses of the photoluminescence spectrum of conventional MQWs and nanopillar array MQWs

The two curves in Fig. 2 show the PL spectra of the InGaN/GaN LEDs with different structures. Specifically, the etched curve represents the PL spectrum of MQW-LEDs with nanopillar arrays, while the unetched curve denotes the PL spectrum of the conventional thin-film MQW.

We find that the two curves reach their peak intensity, respectively, at wavelengths of 453 nm and 455 nm. This shift can be attributed to the following factors: 1) the change in crystal lattice constant, caused by the release of stress[10] existing in the structure of quantum wells after ICP etching; and 2) the surface plasmon polaritons (SPPs) are guided along the Ni/GaN interfaces, which can be shorter in wavelength[11] than the incident light (photons). When the incident photon energy is close to the SPP energy, the coupling is stronger, i.e., higher SPP wave vectors appear at shorter wavelengths.[12]

Also, as shown in Fig. 2, the unetched curve features multiple peaks and vales, which are ascribed to the interference created in the MQWs. In contrast, the etched curve shows a single peak, indicating that the nanopillar array structure may dramatically attenuate the effect of interference.

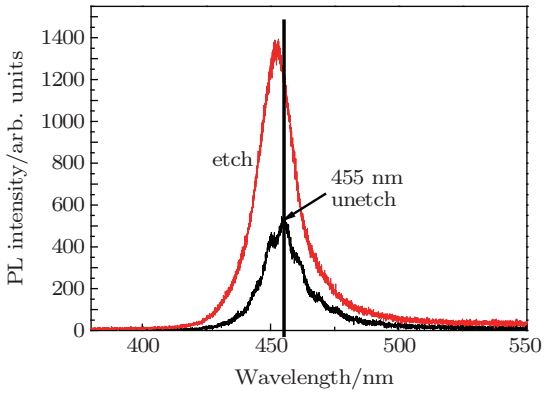


Fig. 2. (color online) The photoluminescence spectra of the conventional MQW (unetched) and nanopillar array MQW (etched).

By comparison with what we discussed above, the increased light-emitting efficiency draws much attention. The data obtained from Fig. 2 show that the PL intensity in the MQWs with nanopillar arrays increases 2.7 times as compared with that in the conventional MQW, which is similar to the result of other studies.[7] We conclude that the nanopillar array structure is conducive to enhancing the light-emitting efficiency. Certainly, more than one factor often contributes to the enhancement. Many researchers have performed studies on this subject.[13] On the basis of their studies, we suggest that the enhancement of light-emitting intensity can be attributed to the following factors: a) the improved crystal quality; b) the surface roughness effect that expands the critical angle and thus largely diminishes the total reflection; and c) the incident photons from the p-type GaN layer, which couple with the surface plasmons in Ni particles to create self-sustaining, propagating electromagnetic waves known as SPPs[14] and are trapped at the metal–dielectric interfaces.[11] These SPP couplings then lead to a collective oscillation[15] at the interface, namely, surface plasmon resonance (SPR), which accounts for the enhancement of the light-extraction efficiency (LEE).[16,17] This point is demonstrated in Refs. [12] and [18]. As figure 1(c) indicates, few defects can be observed on the nanopillar array structured LEDs. Some documents[19,20] have reported on the same result as those mentioned previously, i.e., the defects are substantially non-radiative recombination centers, contributing little to light emission and causing energy to be released in the form of heat in turn. In this paper, the nanopillar array structure effectively reduces the number of visible defects, thereby obtaining a much higher PL intensity.

In addition, based on the theory of surface roughness,[21] the irregular nanopillars in this experiment can be considered as a kind of roughened film surface. Consequently, this changes the direction of incident light, enlarges the angle of total reflection and allows more photons to escape from the interiors of the quantum wells, thereby increasing the external quantum efficiency (EQE).

Another explanation we proposed in this paper is based on the theory of the optical waveguide.[22] On the one hand, due to the fact that the refractive index of InGaN is lower than that of GaN, two sidewalls composed of the interfaces of InGaNGaN constrain the photons to enter into the InGaN layer, thus reducing the non-radiative recombination center absorptivity of the photons. On the other hand, the nanopillars act as a surface waveguide or metallic waveguide, and photon activity is confined to the surface of the sidewalls of the pillars, which also reduces the absorptivity of the photons, thus enhancing the LEE.[23] Due to the influence of the optical waveguide, photons traveling in QWs undergo multiple reflections between the lower end and the top of the QWs, thus generating a stimulating process that is similar to lasing with the simultaneous action of divided quantum states induced by QCE.[24] As a result, the PL intensity of the light emission is increased.

4. Conclusions

In this paper, we use the self-assembled Ni cluster as an array-patterned mask to etch the surface of InGaN/GaN MQWs grown on the sapphire substrate by MOCVD and successfully fabricate the InGaN/GaN MQW-LEDs with a nanopillar array structure. Subsequently, from the observation of the SEM images of the MQW-LEDs with a nanopillar array surface, it is found that the defects existing in the conventional MQW are almost totally removed in the nanopillar array MQW. We also make a comparison of the PL spectrum between InGaN/GaN LEDs with different surface structures, indicating that the PL intensity of the MQWs with nanopillar arrays reaches 2.7 times that of the conventional one. Finally, we conclude that the reasons for the enhancement of the light-emitting efficiency are summarized as follows. The first is the improvement of the crystal quality, namely the reduction in V-defects; the second is the roughened surface effect on the expansion of the critical angle and attenuating total reflection; and the third is the excited SPPs propagating at the Ni/GaN interfaces on the top of the pillars that do not stray from this narrow path, thus increasing the extraction efficiency of the photons from the p-type GaN layer.[11,12,25,26]

References

[1] Kuniharu T, Fang H, Kumar S B, Kapadia R, Gao Q, Madsen M, Kim H S, Liu C H, Chueh Y L, Plis E, Krishna S, Bechtel H A, Guo J and Javey A 2011 *Nano Lett.* **11** 5008
[2] Okamoto K and Kawakami Y 2009 *IEEE Journal of Selected Topics in Quantum Electronics* **15** 1199
[3] Zubia D and Hersee S D 1999 *J. Appl. Phys.* **85** 6492
[4] Hiroto Sekiguchi, Katsumi Kishino and Akihiko Kikuchi 2010 *Appl. Phys. Lett.* **96** 231104

[5] Cheze C, Geelhaar L, Brandt O, Weber W M, Riechert H, Munch S, Rothemund R, Reitzenstein S, Forchel A, Kehagias T, Komninou P, Dimitrakopulos G P and Karakostas T 2010 *Nano Res.* **3** 528
[6] Li S F and Waag A 2012 *J. Appl. Phys.* **111** 071101
[7] Tang L J, Zheng X H, Zhang D Y, Dong J R, Wang H and Yang H 2011 *Chin. Sci. Bull.* **56** 174 (in Chinese)
[8] Liang C G and Zhang J 1999 *Chin. J. Semicond.* **20** 89
[9] Li J W, Wang Y and Ye Z Z 2001 *Semicond. Inf.* **38** 13
[10] Zhang D Y, Zheng X H, Li X F, Wu Y Y, Wang H, Wang J F and Yang H 2012 *Chin. Phys. B* **21** 087802
[11] Zhang J X, Zhang L D and Xu W 2012 *J. Phys. D: Appl. Phys.* **45** 113001
[12] Gao N, Huang K, Li J C, Li S P, Yang X and Kang J Y 2012 *Sci. Rep.* **2** 816
[13] Sugawara H, Ishikawa M and Hatakoshi G 1991 *Appl. Phys. Lett.* **58** 1010
[14] Kock A, Beinstingl W, Berthold K and Gornik E 1988 *Appl. Phys. Lett.* **52** 1164
[15] Wang G P 2006 *Physics* **35** 502 (in Chinese)
[16] Oh Y J and Jeong K H 2012 *Adv. Mater.* **24** 2234
[17] Lin Y Z 2011 "The Research on the Improvement of Lighting Efficiency of LED by Surface Plasmon Technique", Ph. D. dissertation, Shandong University (in Chinese)
[18] Derkacs D, Lim S H, Matheu P, Mar W and Yu E T 2006 *Appl. Phys. Lett.* **89** 093103
[19] Zong X F, Weng Y M, Gao J R and Shao L 1985 *Chin. J. Infr. Res. A* **4** 379
[20] Liu Y Z and Ma R X 1982 *Acta Electronica Sinica* **5** 104
[21] Liu S N, Zou D S, Zhang J M, Gu X L and Shen G D 2008 *Research & Progress of SSE* **28** 245
[22] Wu C Q 2000 *Optical Waveguide Theory* (Beijing: Tsinghua University Press) p. 176 (in Chinese)
[23] Zhu J H, Wang L J, Zhang S M, Wang H, Zhao D G, Zhu J J, Liu Z S, Jiang D S and Yang H 2011 *Chin. Phys. B* **20** 077804
[24] Liu F Q, Zhang Y Z, Zhang Q S and Wang Z G 2000 *Chin. J. Semicond.* **21** 1038
[25] Qiu D J, Fan W Z, Weng S, Wu H Z and Wang J 2011 *Acta Phys. Sin.* **60** 087301 (in Chinese)
[26] Dang S H, Li C X, Wei J, Zhang Z X, Li T B, Han P D and Xu B S 2012 *Opt. Express* **20** 23290