Epitaxial Growth and Characteristics of Nonpolar *a*-Plane InGaN Films with Blue-Green-Red Emission and Entire In Content Range

Jianguo Zhao(赵见国)^{1,2*}, Kai Chen(陈凯)¹, Maogao Gong(宫毛高)¹, Wenxiao Hu(胡文晓)¹, Bin Liu(刘斌)^{1*}, Tao Tao(陶涛)¹, Yu Yan(严羽)¹, Zili Xie(谢自力)¹, Yuanyuan Li(李元元)², Jianhua Chang(常建华)², Xiaoxuan Wang(王潇璇)⁴, Qiannan Cui(崔乾楠)⁴, Chunxiang Xu(徐春祥)⁴,

Rong Zhang(张荣)^{1,3}, and Youdou Zheng(郑有炓)

¹Jiangsu Provincial Key Laboratory of Advanced Photonic and Electronic Materials,

School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, China

²School of Electronics and Information Engineering, Nanjing University of Information Science and Technology,

Nanjing 210044, China

³Xiamen University, Xiamen 361000, China

⁴State Key Laboratory of Bioelectronics, School of Biological Science and Medical Engineering,

Southeast University, Nanjing 210096, China

(Received 27 December 2021; accepted 19 February 2022; published online 15 March 2022)

Nonpolar (11 $\overline{2}0$) plane In_xGa_{1-x}N epilayers comprising the entire In content (x) range were successfully grown on nanoscale GaN islands by metal-organic chemical vapor deposition. The structural and optical properties were studied intensively. It was found that the surface morphology was gradually smoothed when x increased from 0.06 to 0.33, even though the crystalline quality was gradually declined, which was accompanied by the appearance of phase separation in the In_xGa_{1-x}N layer. Photoluminescence wavelengths of 478 and 674 nm for blue and red light were achieved for x varied from 0.06 to 0.33. Furthermore, the corresponding average lifetime ($\tau_{1/e}$) of carriers for the nonpolar InGaN film was decreased from 406 ps to 267 ps, indicating that a high-speed modulation bandwidth can be expected for nonpolar InGaN-based light-emitting diodes. Moreover, the bowing coefficient (b) of the (11 $\overline{2}0$) plane InGaN was determined to be 1.91 eV for the bandgap energy as a function of x.

DOI: 10.1088/0256-307X/39/4/048101

III-nitride InGaN-based light-emitting diodes (LEDs) have revealed promising performance in applications of lighting sources,^[1] micro-LED displays,^[2-4] and visible light communications.^[5-7] These prevalent applications require high-quality red, green, and blue light sources with high efficiencies and large switching rates. Efficiencies of green and red LEDs are much lower than those of blue LEDs due to the challenges in InGaN growth with relatively high x.^[8,9] Recently, the successful fabrication of yellow-to-red light LEDs was reported extensively. $^{[10-17]}$ However, conventional polar InGaN-based LEDs are inevitably restricted owing to the polarization-induced quantum confined Stark effect (QCSE).^[18,19] Meanwhile, switching rates of InGaN-based LEDs are limited because lifetimes of carriers were extended by separations of wavefunctions for holes and electrons caused by QCSE.^[20,21] It was found that a nonpolar InGaN-based structure can eliminate QCSE, resulting in improved efficiency and a fast decay lifetime of carriers.^[21,22] Nevertheless, epitaxial growth of nonpolar InGaN-based semiconductors is much more challenging than growth of polar counterparts.^[23] The achievement on semipolar InGaN-based structures, such as the $(11\overline{2}2)$ plane,^[24]

 $(10\bar{1}1)$ plane,^[25] and $(20\bar{2}1)$ plane,^[7,26] was reported recently due to the alleviation in growth inhibition rather than nonpolar counterpart and the weaker QCSE rather than the polar counterpart. Although the advancement on nonpolar AlGaN- and GaN-based structures was successively reported,^[27-29] the research progress on nonpolar InGaN-based structures is clearly behind. Furthermore, growth and research on nonpolar InGaN-based structures remain lacking, especially with high In content.

In this Letter, nonpolar (1120) plane InGaN epilayers with the entire In content range were first grown on nanoscale GaN islands by metal-organic chemical vapor deposition. The structural and optical properties were examined using x-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), photoluminescence (PL), timeresolved PL (TRPL), and spectrophotometers. PL wavelengths of 478 and 674 nm for blue and red light were achieved for x varied from 0.06 to 0.33. The bowing coefficient of the bandgap energy as a function of x was explored. This study lays the foundation for development of nonpolar InGaN-based LEDs.

In this work, five Ga-rich (A1-A5) and In-rich

^{*}Corresponding authors. Email: bliu@nju.edu.cn; zhaojg@nuist.edu.cn

^{© 2022} Chinese Physical Society and IOP Publishing Ltd

(B1-B5) nonpolar $(11\overline{2}0)$ plane InGaN samples were grown on semipolar $(1\overline{1}02)$ plane sapphire substrates with a metal-organic chemical vapor deposition sys-Trimethylindium (TMIn), trimethylgallium tem. (TMGa), ammonia (NH_3) , and silane (SiH_4) were used as the precursors for In, Ga, N, and Si, respectively. Moreover, H_2 was used as the carrier gas for all the growth processes except for the growth of the InGaN layer, whose carrier gas was N₂. Before growth, high-temperature baking and a nitridation process were conducted at 990 °C as the sapphire substrate pretreatment. A 20-nm-thick low-temperature GaN nucleation layer was deposited at 550 °C followed by a high-temperature GaN buffer layer grown at $1030 \,^{\circ}$ C. The thickness of the high-temperature GaN buffer layer was $1 \,\mu m$ for samples A1–A5 and 50 nm for samples B1–B5. Subsequently, the self-organized nanoscale GaN islands were triggered by introducing a SiN_x interlayer, which was deposited with a supply of NH₃ and SiH₄. The detailed growth parameters were described in our previous report.^[30] Then, the nonpolar (11 $\overline{2}0$) plane $In_x Ga_{1-x}N$ films were grown on the prepared nanoscale GaN islands. For samples A1–A5, the $In_x Ga_{1-x}N$ film was grown with a fixed growth time of 45 min, a fixed V/III ratio of 1000, the varied growth temperature decreased from 720 °C to 660 °C, the varied vapor phase value of x increased from 0.13 to 0.61, and the thickness of the $In_x Ga_{1-x}N$ film was decreased from 850 nm to 600 nm. For samples B1-B5, $In_x Ga_{1-x}N$ film was grown with an increased vapor phase where x varied from 0.72 to 1, and the corresponding growth time, V/III ratio, growth temperature, and thickness were 2h, 12000, 550 °C, and $\sim 300 \,\mathrm{nm}$, respectively.

The XRD curves were detected using a PANalytical X'Pert Pro MRD system with the "double-axis" mode, and the surface morphology was measured utilizing the ZEISS Gemini500 SEM and NT-MDT NTE-GRA Spectra II AFM. Additionally, the relative transmission spectra were performed with the PERSEE TU-1900 spectrophotometer for samples A1–A5 and the HITACHI U-4100 spectrophotometer for samples B1–B5. The PL and TRPL spectra were measured at room temperature with a 375 nm laser as the excitation source, respectively.

The peaks located at $2\theta = 52.56^{\circ}$ and $2\theta = 57.73^{\circ}$ in Fig.1 were assigned to be the diffraction peaks from the (2204) plane sapphire and (1120) plane GaN buffer layer. The rest peaks monotonously moved from $2\theta = 57.32^{\circ}$ to $2\theta = 51.52^{\circ}$ due to the diffraction from the (1120) plane $\ln_x \operatorname{Ga}_{1-x} N$ epilayer with varied x. Thus, the apparent XRD peaks signified the successful growth of nonpolar (1120) plane $\ln_x \operatorname{Ga}_{1-x} N$ layers. Here the x was estimated based on Vegard's law by ignoring the effect of strains:

$$d\left(\mathrm{In}_{x}\mathrm{Ga}_{1-x}\mathrm{N}_{(11\bar{2}0)}\right) = xd\left(\mathrm{In}_{(11\bar{2}0)}\right) + (1-x)d\left(\mathrm{GaN}_{(11\bar{2}0)}\right). (1)$$

Furthermore, x was calculated to be 0.06, 0.10, 0.21, 0.26, and 0.33 for samples A1–A5, and 0.47, 0.62, 0.71, 0.93 and 1 for samples B1–B5, respectively, as labeled in Fig. 1. Meanwhile, the x-ray rocking curves (XRCs) of corresponding $\ln_x \operatorname{Ga}_{1-x}$ N-related diffraction peaks were scanned at $\phi = 0^\circ$ and $\phi = 90^\circ$ for all samples, and the full widths at half maximum (FWHM) of these XRCs are summarized in Table 1.



Fig. 1. XRD $2\theta - \omega$ curves for all the nonpolar InGaN samples.

Table 1. FWHMs of XRCs measured at $\phi = 0^{\circ}$ and $\phi = 90^{\circ}$ and rms roughness within a detection area of $5 \times 5 \,\mu\text{m}^2$ for samples A1–A5 and B1–B5.

Sample		A1	A2	A3	A4	A5	B1	B2	B3	B4	B5
$\operatorname{FWHM}\left(\operatorname{deg}\right)$	$\phi = 0^{\circ}$	0.413	0.463	0.571	0.597	0.592	0.944	0.882	0.836	0.825	1.056
	$\phi=90^\circ$	0.446	0.521	0.728	0.795	0.704	1.080	1.343	1.273	0.958	1.245
rms roughness (nm)		9.80	8.68	8.17	7.89	6.39	9.72	10.60	12.40	14.82	20.03

By carefully observing the XRD $2\theta-\omega$ curves, it can be found that the InGaN diffraction peak of samples A3–A5 evidently broadened. In other words, another diffraction peak seemed to have emerged to the left of the original peak, which is usually considered to be the result of phase separation of the InGaN epilayer. Furthermore, the linewidth of the In_xGa_{1-x}N- related XRCs and $2\theta-\omega$ diffraction peak was broadened simultaneously from sample A1 to A5. Specifically, the FWHM values of the XRCs measured at $\phi = 0^{\circ}$ and $\phi = 90^{\circ}$ were increased from 0.413° and 0.446° for sample A1 as well as 0.592° and 0.795° for sample A5, respectively. The increased FWHM values demonstrated that the crystalline quality of the In_xGa_{1-x}N films degenerated as x increased from 0.06 to 0.33 for samples A1–A5. On the other hand, excellent symmetry was observed on the $2\theta-\omega$ curves of samples B1–B5, meaning the absence of phase separation in samples B1–B5 grown on a thin GaN buffer layer. The much larger FWHM values for samples B1–B5 than those for samples A1–A5 were due to the much lower growth temperature and thinner thickness.



Fig. 2. The top-view surface SEM images for the nanoscale GaN islands (a), samples A1-A5 (b)–(f), and samples B1-B5 (g)–(k) with a same scale bar.

As shown in Fig. 2(a), the dominant scale of the GaN islands was controlled to be submicron by carefully optimizing the growth parameters of the SiN_x interlayer and GaN islands layer. The directional pits distributed on all the nonpolar $In_x Ga_{1-x}N$ films are the typical surface morphology of $(11\overline{2}0)$ plane GaNbased materials.^[27,30] It can be seen clearly that the density and depth of the directional pits decreased from sample A1 with x = 0.06 to sample A5 with x = 0.33. This phenomenon is confused as the quality of InGaN film with high x was generally relatively poor owing to the low growth temperature and the large strains occurring in the InGaN film.^[31] To quantitatively evaluate the surface morphology of all the nonpolar (11 $\overline{2}0$) plane $In_x Ga_{1-x}N$ samples, an area of $5 \times 5 \,\mu m^2$ was detected by AFM, and the rms roughness was summarized in Table 1. It was determined that the rms roughness was gradually decreased from 9.80 to $6.39 \,\mathrm{nm}$ when x decreased from 0.06 to 0.33. This fact represented that the surface morphology of the grown nonpolar (11 $\overline{2}0$) plane $\ln_x \operatorname{Ga}_{1-x} N$ films became smoother with increasing x. Considering the apparent phase separation of the InGaN epilayer for samples A3–A5 as discussed above, the reduction in the density and depth of directional pits was inferred due to the strains in the InGaN layer, which were partially relaxed by the phase separation.^[32,33] Thus, proper phase separation in InGaN may be beneficial to smooth surface morphology. Conversely, both the

AFM and SEM results indicated that the surface morphology of samples B1–B5 became gradually rough as x increased from 0.47 to 1. The rms roughness increased from 9.72 nm for sample B1 to 20.03 nm for sample B5 due to the relatively low growth temperature and the remarkably high V/III ratio.



Fig. 3. (a) Normalized PL spectra for Ga-rich samples A1–A5 measured at room temperature. (b) TRPL decay spectra collected with a single photon counting system for samples A1–A5 at their peak wavelength measured at room temperature.

It can be seen from Fig. 3(a) that the PL peak wavelengths were 478, 503, 550, 602, and 674 nm for samples A1–A5, respectively. The PL peak lineshape was significantly broadened from sample A3, which was identical to the XRD $2\theta - \omega$ curves. Furthermore, a "shoulder" peak appeared on the left of the main PL peak for samples A4 and A5, as shown in Fig. 3(a). This was very similar to the reported spectra of the InGaN/GaN MQWs.^[34] In fact, the low energy emission peak was attributed to phase separation-induced localized energy states in the In-rich cluster region as studied previously.^[34,35] Alternatively, it was found that $\tau_{1/e}$ was 406, 384, 343, 300, and 267 ps for samples A1–A5, as shown in Fig. 3(b). This result was similar to the previously reported results of the nonpolar (11 $\overline{2}0$) plane GaN and In_{0.1}Ga_{0.9}N films.^[35,36] For comparison, the value of $\tau_{1/e}$ of carriers of the conventional c-plane polar counterparts was reported to be several nanoseconds or more.^[21,35] In contrast, the carrier lifetime of the nonpolar InGaN film was an order of magnitude lower than that of the conventional polar counterpart, meaning that a high-speed modulation bandwidth can be expected for the nonpolar InGaN-based LED.

In order to further determine the bandgap energy of the nonpolar (11 $\overline{2}0$) plane $In_x Ga_{1-x}N$ epilayers, the absorption edges were estimated based on the transmission spectra as illustrated in Fig. 4. Here, the relative transmittance was defined as the ratio of the light intensity transmitted through the samples to that transmitted through the substrate. Then, the bandgap energy obtained from the PL spectra and relative transmission spectra versus x is plotted in Fig. 5. It was clear that the bandgap energy from the PL spectra was remarkably lower compared to the relative transmission spectra. The bandgap energy of the nonpolar (11 $\overline{2}0$) plane $In_x Ga_{1-x}N$ epilayers as a function of x was fitted based on the equation as follows:

$$E_{g}(\operatorname{In}_{x}\operatorname{Ga}_{1-x}\operatorname{N}) = xE_{g}(\operatorname{In}\operatorname{N}) + (1-x)E_{g}(\operatorname{Ga}\operatorname{N}) - bx(1-x).$$
(2)



Fig. 4. Relative transmission spectra for Ga-rich samples A1–A5 (a) and In-rich samples B1–B5 (b).



Fig. 5. Bandgap energy for $\ln_x \operatorname{Ga}_{1-x} N$ obtained from PL and absorption results. The black line is the fitted bandgap energy curve as a function of In content x.

Moreover, b was fitted to be 1.91 eV when the bandgap energy of GaN and InN were regarded as 3.42 and 0.77 eV, respectively. This result was basically consistent with the equation expressed as $E_{\rm g} =$ $3.42 - 2.65x - 2.4x(1 - x) [\rm eV].^{[37]}$ Meanwhile, the absorption edge results of the nonpolar InGaN films on the In-rich side were identical to the report of Liu *et al.*,^[38] as shown in Fig. 5.

In conclusion, the nonpolar $(11\overline{2}0)$ plane $\ln_x \operatorname{Ga}_{1-x} N$ epilayers with x varied from 0.06 to 1 were successfully grown with the assistance of nanoscale GaN islands. It was found that the surface morphology was gradually smoothed when x increased from 0.06 to 0.33, even though the crystalline quality was gradually declined, which was accompanied by the appearance of phase separation in the InGaN layer.

The smoothed surface morphology is beneficial to the growth of the quantum well structure. Moreover, a PL peak wavelength of 478 to 674 nm was achieved for x varied from 0.06 to 0.33, and their $\tau_{1/e}$ of carriers was reduced from 406 to 267 ps. On the other hand, b was obtained to be 1.91 eV for the bandgap energy as a function of x.

Acknowledgements. This work was supported by the National Natural Science Foundation of China (Grant Nos. 62074077, 61921005, 61974062, and 61904082), the China Postdoctoral Science Foundation (Grant No. 2020M671441), the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (Grant Nos. 19KJB510006 and 19KJB510039), and the Natural Science Foundation of Jiangsu Province (Grant No. BK20190765).

References

- Liu B, Chen D, Lu H, Tao T, Zhuang Z, Shao Z, Xu W, Ge H, Zhi T, Ren F, Ye J, Xie Z and Zhang R 2020 Adv. Mater. 32 1904354
- [2] Zhou X, Tian P, Sher C W, Wu J, Liu H, Liu R and Kuo H C 2020 Prog. Quantum Electron. 71 100263
- [3] Lu S, Li J, Huang K, Liu G, Zhou Y, Cai D, Zhang R and Kang J 2021 Nanoscale Res. Lett. 16 99
- [4] Meng W, Xu F, Yu Z, Tao T, Shao L, Liu L, Li T, Wen K, Wang J, He L, Sun L, Li W, Ning H, Dai N, Qin F, Tu X, Pan D, He S, Li D, Zheng Y, Lu Y, Liu B, Zhang R, Shi Y and Wang X 2021 Nat. Nanotechnol. 16 1231
- [5] Chen S W H, Huang Y M, Chang Y H, Lin Y, Liou F J, Hsu Y C, Song J, Choi J, Chow C W, Lin C C, Horng R H, Chen Z, Han J, Wu T and Kuo H C 2020 ACS Photon. 7 2228
- [6] Zhou Y, Wei Y, Hu F, Hu J, Zhao Y, Zhang J, Jiang F and Chi N 2020 Opt. Express 28 2302
- [7] Khoury M, Li H, Li P, Chow Y C, Bonef B, Zhang H, Wong M S, Pinna S, Song J, Choi J, Speck J S, Nakamura S and DenBaars S P 2020 Nano Energy 67 104236
- [8] Maur M A D, Pecchia A, Penazzi G, Rodrigues W and Di Carlo A 2016 Phys. Rev. Lett. 116 027401
- [9] Zhuang Z, Iida D, Velazquez-Rizo M and Ohkawa K 2021 IEEE Electron Device Lett. 42 1029
- [10] Zhang S, Zhang J, Gao J, Wang X, Zheng C, Zhang M, Wu X, Xu L, Ding J, Quan Z and Jiang F 2020 Photon. Res. 8 1671
- [11] Bi Z, Lenrick F, Colvin J, Gustafsson A, Hultin O, Nowzari A, Lu T, Wallenberg R, Timm R, Mikkelsen A, Ohlsson B J, Storm K, Monemar B and Samuelson L 2019 Nano Lett. 19 2832
- [12] Iida D, Zhuang Z, Kirilenko P, Velazquez-Rizo M, Najmi M A and Ohkawa K 2020 Appl. Phys. Lett. 116 162101
- [13] Zhuang Z, Iida D and Ohkawa K 2020 Appl. Phys. Lett. 116 173501
- [14] Zhuang Z, Iida D, Kirilenko P, Velazquez-Rizo M and Ohkawa K 2020 Opt. Express 28 12311
- [15] Pasayat S S, Gupta C, Wong M S, Ley R, Gordon M J, DenBaars S P, Nakamura S, Keller S and Mishra U K 2020 *Appl. Phys. Express* 14 011004
- [16] Huang D M, Zhang J Y, Wang J H, Wei W Q, Wang Z H, Wang T and Zhang J J 2021 Chin. Phys. Lett. 38 068101
- [17] Zheng C, Zhao D, Cai X, Huang W, Meng F, Zhang Q, Tang L, Hu X, Gu L, Ji S H and Chen X 2020 Chin. Phys. Lett. 37 087401
- [18] Bernardini F, Fiorentini V and Vanderbilt D 1997 Phys.

Rev. B **56** R10024

- [19] Fiorentini V, Bernardini F, Sala F D, Di Carlo A and Lugli P 1999 Phys. Rev. B 60 8849
- [20] Liu X, Lin R, Chen H, Zhang S, Qian Z, Zhou G, Chen X, Zhou X, Zheng L, Liu R and Tian P 2019 ACS Photon. 6 3186
- [21] Waltereit P, Brandt O, Trampert A, Grahn H, Menniger J, Ramsteiner M, Reiche M and Ploog K 2000 Nature 406 865
- [22] Zhao J, Pan J, Liu B, Tao T, Chen D, Long X, Feng Z C and Chang J 2021 IEEE Photonics J. 13 2300107
- [23] Sun Q, Yerino C D, Ko T S, Cho Y S, Lee I H, Han J and Coltrin M E 2008 J. Appl. Phys. **104** 093523
- [24] Li H, Khoury M, Bonef B, Alhassan A I, Mughal A J, Azimah E, Samsudin M E A, De Mierry P, Nakamura S, Speck J S and DenBaars S P 2017 ACS Appl. Mater Interfaces 9 36417
- [25] Wang Q, Yuan G, Liu W, Zhao S, Liu Z, Chen Y, Wang J and Li J 2019 J. Mater. Sci. 54 7780
- [26] Gong M G, Xing K, Zhang Y, Liu B, Tao T, Xie Z L, Zhang R and Zheng Y D 2020 Appl. Phys. Express 13 091002
- [27] Zhao J, Zhang X, Dai Q, Wang N, Wu Z, Wang S and Cui Y 2017 Appl. Phys. Express 10 011002
- [28] Zhao J, Zhang X, He J, Chen S, Wu Z, Fan A, Dai Q, Feng Z C and Cui Y 2018 ACS Photon. 5 1903
- [29] Ketzer F A, Horenburg P, Henning P, Korn E R, Bremers

H, Rossow U and Hangleiter A 2019 Appl. Phys. Lett. 114
[30] Zhao J, Zhang X, Wu Z, Dai Q, Wang N, He J, Chen S, Feng Z C and Cui Y 2017 J. Alloys Compd. 729 992

- [31] Jiang F, Zhang J, Xu L, Ding J, Wang G, Wu X, Wang X, Mo C, Quan Z, Guo X, Zheng C, Pan S and Liu J 2019 *Photon. Res.* 7 144
- [32] Krost A, Bläsing J, Lünenbürger M, Protzmann H and Heuken M 1999 Appl. Phys. Lett. 75 689
- [33] Niu X, Stringfellow G B and Liu F 2011 Appl. Phys. Lett. 99 213102
- [34] Meng Y, Wang L, Zhao G, Li F, Li H, Yang S and Wang Z 2018 Phys. Status Solidi A 215 1800455
- [35] Chichibu S F, Uedono A, Onuma T, Haskell B A, Chakraborty A, Koyama T, Fini P T, Keller S, Denbaars S P, Speck J S, Mishra U K, Nakamura S, Yamaguchi S, Kamiyama S, Amano H, Akasaki I, Han J and Sota T 2006 *Nat. Mater.* 5 810
- [36] Zhao J, Zhang X, Fan A, Chen S, He J, Pan J, Chen D, Tian M, Feng Z C, Chang J, Liu Q and Ge J 2020 Jpn. J. Appl. Phys. 59 010909
- [37] Schubert E F 2006 Light Emitting Diodes 2nd edn (Cambridge: Cambridge University Press)
- [38] Liu B, Luo W, Zhang R, Zou Z, Xie Z, Li Z, Chen D, Xiu X, Han P and Zheng Y 2010 Phys. Status Solidi C 7 1817