The residual C concentration control for low temperature growth p-type GaN*

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In this work, the influence of C concentration to the performance of low temperature growth p-GaN is studied. Through analyses, we have confirmed that the C impurity has a compensation effect to p-GaN. At the same time we have found that several growth and annealing parameters have influences on the residual C concentration: (i) the C concentration decreases with the increase of growth pressure; (ii) we have found there exists a Ga memory effect when changing the Cp_2Mg flow which will lead the growth rate and C concentration increase along the increase of Cp_2Mg flow; (iii) annealing outside of metal–organic chemical vapor deposition (MOCVD) could decrease the C concentration while *in situ* annealing in MOCVD has an immobilization role to C concentration.

Keywords: nitride materials, p-GaN, C concentration

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1. Introduction

Gallium nitride (GaN) and its ternary alloys have attracted a great deal of attention for their material properties which are useful for applications in light emitters and detector devices.[1–5] However, up to now, the low hole concentration and high resistivity of p-GaN sometimes still act as bottle-necks limiting the performance of these devices.[6] Mg is a singly useful element to dope p-type GaN, and the Mg atoms doped in the GaN layer are often passivated by H (forming a neutral Mg–H complex) as the H is contained in the growth environment of MOCVD system.[7,8] This issue was first treated by Amano *et al.* through the low-energy electron beam irradiation.[9] Unfortunately, this way has a fatal defect that it only can activate several hundred nanometer-thick material. Subsequently, the thermal annealing reported by Nakamura *et al*. is well done to solve this Mg passivated problem,[7] and since that, the thermal annealing becomes an indispensable part of p-type GaN growth. However, though this Mg acceptor activation problem is dealt with well by thermal annealing, it is often still difficult to get high performance p-GaN, as there is normally a strong compensation of Mg acceptors. Obloh *et al.* has reported that there is Mg self-compensation for very heavily Mg-doped GaN.[10] At the same time, the residual carbon impurities, nitrogen vacancy (V_N), and complexes of V_{Ga}–O_N in p-GaN were having a compensation effect on Mg acceptors.[11–13] Thus, decreasing compensation to improve the performance of p-GaN is necessary. Recently, some research found that high growth temperature and high annealing temperature will lead to an In-segregation in InGaN quantum well active region for laser diodes (LD) or light emitting diodes (LED), so a comparatively low growth and annealing temperature is needed for p-GaN growth and thermal treatment.[14–16] However, it is proved by Chen *et al*. that the C concentration remarkably increases with the decrease of growth temperature.[17] So it is critical to decrease the C compensation in these low-temperature grown and treated samples to gain a high performance of p-type conductive GaN.

In this paper, we mainly analyze the C impurity influence to the performance of p-GaN, and try to find an effective way to reduce the concentration of C impurity in p-GaN layer based on studying the relationship between C concentration and growth condition. In particular, the growth pressure, Cp_2Mg flux, and annealing environment are investigated to have influence on the residual C concentration in p-GaN.

2. Experiment

In our study, a series of 1-μm thick Mg-doped GaN films were grown on a 2-μm thick unintentionally doped GaN layer

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in metal–organic chemical vapor deposition (MOCVD) system to investigate the influence of different growth conditions to residual C concentration in GaN films; at the same time, we have also studied the influence of *in situ* and *ex situ* annealing on C concentration. Trimethylgallium (TMG), ammonia (NH_3), and bis-cyclopentadienyl magnesium (Cp_2Mg) were used as precursors for Ga, N, and Mg, respectively. The detailed messages about p-GaN layer samples are shown in Table 1, where samples A, B, and D are grown on different pressures: 150 mbar, 260 mabr, and 400 mbar (1 bar = 10^5 Pa), respectively. They are designed to investigate the pressure influence on residual C concentration. Compared with samples A and B, the samples A1 and B1, which grow with different CP_2Mg fluxes, are used to study the Mg doping concentration influence on residual C concentration. At the same time, sample annealing in different environment conditions, either *in situ* or outside of the MOCVD reactor, is studied. The sample A1* is annealed *in situ* in the MOCVD system, closely after the p-GaN layer growth, while sample A1 was annealed in an annealing furnace outside of the MOCVD system. As a comparison, sample A1* and A1 have the same growth condition. Both annealing treatments are taken in a N_2 atmosphere. The growth temperature and annealing temperature are set as 930 °C and 680 °C respectively. The annealing time is fixed to 20 mins. After thermal annealing, the carrier concentration and resistivity were measured by van der Pauw (Hall) measurement, and the photoluminescence (PL) spectra were measured by a 325-nm line excitation of a He–Cd laser. The Mg and C concentrations of p-GaN films with different growth conditions were measured by secondary ion mass spectroscopy (SIMS).

Table 1. The growth condition for p-GaN samples.

Sample	Growth temperature/°C	Growth pressure/mbar	CP_2Mg flow /sccm	Concentration /10^{17} cm^{-3}	Annealing environment	Annealing temperature/°C
A	930	150	135	2.58	outside	680
B	930	260	135	7.75	outside	680
D	930	400	135	2.24	outside	680
A1	930	150	672	4.05	outside	680
B1	930	260	1344	1.13	outside	680
A1*	930	150	672	2.34	*in situ*	680

3. Result and discussion

Figure 1 shows the C concentration and Mg concentration for samples A, B, and D which were grown in different pressure conditions. It is obvious that both C concentration and Mg concentration decrease with the increase of growth pressure. In general, for p-type GaN with the same annealing treatment and ignoring other impurity compensation effect, the conductivity of p-GaN:Mg contact layer should get better along with the increase of Mg doping concentration when it is not over 3×10^{19} cm^{-3} and a strong Mg self-compensation does not start to take effect.[10] However, the Hall measurement result for these samples, as shown in Fig. 2, indicates that sample B has the best performance among these three samples instead of sample A which has the highest Mg doping concentration, and even sample D with the lowest Mg concentration (2.84×10^{18} cm^{-3}) shows a better performance than sample A. Such a result means that there must be some compensation mechanism leading to lowering the carrier concentration of sample A. To examine what this compensation mechanism is, we have measured the PL spectra for these three samples, as shown in Fig. 3. It is found that the PL spectrum of sample A is different from those of the other two samples as its strongest peak is located at around 420 nm which is known to belong to the donor–acceptor-pair (DAP) transition originated from deep donor to Mg acceptor one,[18,19] while for samples B and D the highest intensity sharp peak is located at 360 nm, which is attributed to be the GaN intrinsic band-to-band transition, and an additional peak located at 380 nm which is attributed to the transitions from free electron to Mg acceptor or shallow donor to Mg acceptor transitions in these two samples.[20–22] A dominant DAP peak means that there is a strong compensation by the energy level of donors in sample A. However, the compensation is nearly negligible in samples B and D. As the Mg concentration for all of these three samples is lower than 3×10^{19} cm^{-3}, this compensation cannot be mainly from Mg's self-compensation. As shown in Fig. 1 the C concentration for these samples also has a great difference, so this compensation may be caused by the complexes formed by the residual C impurities. We also obtained the depth profiles of the O concentration for these three samples as shown in Fig. 4, It is obvious that the O concentration for these samples are the same, so the C impurity-related complexes are the most possible candidate to form the deep donors to compensate Mg acceptors for sample A. With this point, the Hall measurement result shown in Fig. 2 can be explained easily. For sample A, though it has the highest Mg concentration among these three samples, it has also the highest C concentration too. The net carrier concentration of sample A is low. Its p-type conductiv-

ity performance is reduced by the C compensation; for sample B, its C concentration is only one half in comparison to sample A, and its Mg concentration is only a little smaller than sample A. So its carrier concentration is much higher than sample A, and we gain a better performance of the p-type conduction. However, for sample D, its Mg concentration becomes so low that the C concentration's drop cannot make the p-type conductivity performance better. But it is worth noting that as the compensation is negligible in this sample, its p-type conductivity is still better than sample A. This suitable explanation means that the residual C concentration indeed has an important impact on the performance of p-type GaN.

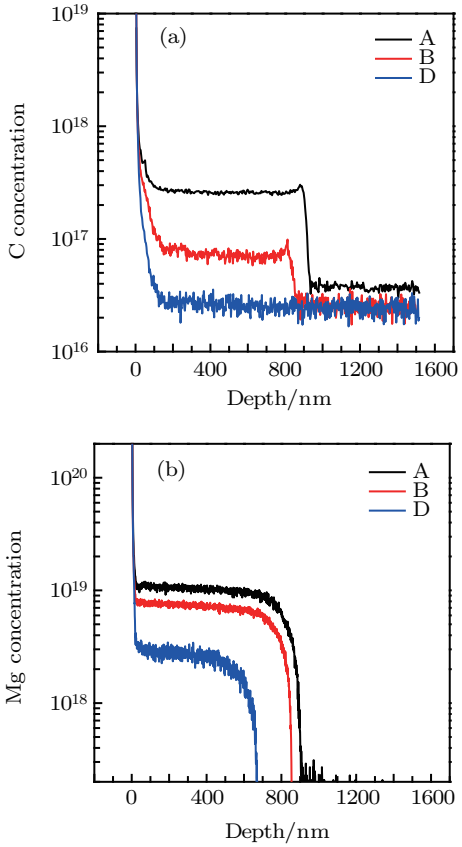


Fig. 1. (color online) The depth profiles of C concentration (a) and Mg concentration (b) for samples A, B, and D grown under different pressures.

As the growth time was set to be a fixed value of 3000 s for all these samples, from the different distribution profiles of Mg in Fig. 1 we can deduce that along the pressure increasing the growth rate of GaN layer decreases, and the growth rate is 0.3 nm/s, 0.27 nm/s, and 0.22 nm/s, respectively, for samples A, B, and D. The influence of the growth rate on the carbon incorporation can be explained by the model proposed by Parish *et al.*[23] that during the growth the carbon removal from GaN surface is facilitated by the conversion of methyl (CH_3) groups coming from TMGa into methane (CH_4) with adsorbed hydrogen. Along with the growth rate decrease the probability of CH_4 formation and carbon release from the sample will increase, so the residual C concentration decreases with the increasing pressure. Through the above analyses, to improve the performance of p-GaN a relatively high growth pressure is needed in order to decrease the C concentration in p-GaN layer. However, at the same time a high Cp_2Mg flow is indispensable to keep a high enough Mg doping concentration because otherwise it will decrease with the increasing growth pressure.

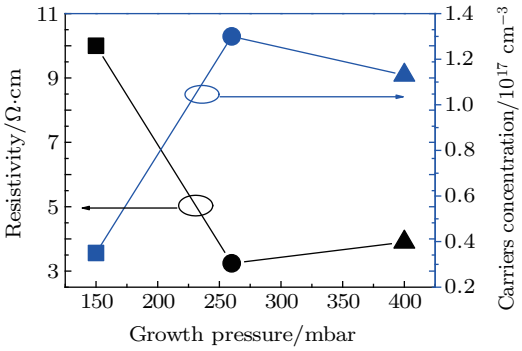


Fig. 2. (color online) The Hall measurement result for samples A, B, and D. Square, circle, and triangle respectively represent samples A, B, and D.

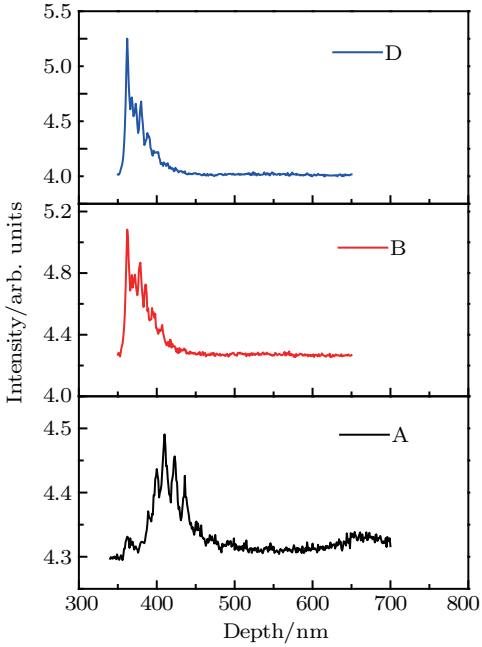


Fig. 3. (color online) The room temperature PL spectra for samples A, B, and D excited by a 325-nm He–Cd laser.

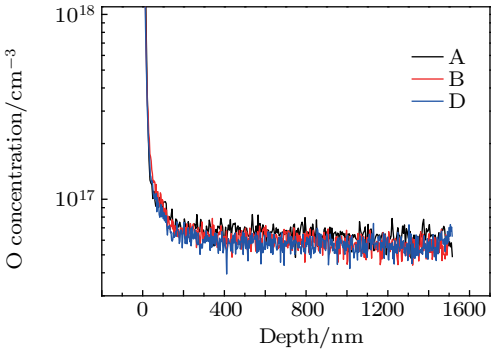


Fig. 4. (color online) The depth profiles of O concentration for samples A, B, and D.

It is interesting to note that, when the Cp_2Mg flow rate is changed at the same growth pressure, it is found that the residual C concentration in GaN is different. The residual C concentration increases with the increasing Cp_2Mg flow rate. Figure 5 shows the C concentration in samples A, A1, B, and B1. It is obvious that the C concentration in samples A1 and B1 is higher than that in samples A and B. As shown in Table 1, samples A and A1 have the same growth condition except the flow rate of Cp_2Mg, the same is for samples B and B1. The result shown in Fig. 5 indicates that the Cp_2Mg flow rate can affect the residual C concentration in p-GaN samples. The Mg concentration in these samples is 1.04×10^{19} cm^{-3}, 8.37×10^{19} cm^{-3}, 7.06×10^{18} cm^{-3}, and 1.16×10^{20} cm^{-3} for samples A, A1, B, and B1, respectively, as measured by SIMS. Meanwhile we found a strange phenomenon that the growth rate of p-GaN layer increases with the increase of Cp_2Mg flow rate, too. For the growth of GaN epilayer it is easy to understand that the growth rate increases with increasing flow rate of Ga precursor, however, why is it also influenced by the CP_2Mg flow rate? It is known that the Mg atom replaces Ga site and acts as acceptor for p-GaN growth. As the amount of Mg is far less than Ga (for example, only around 0.5 percent when Mg doping concentration is in an order of 10^{20} cm^{-3}), so the increase of growth rate could not be just caused by the increase of the amount of Mg which replaces Ga. We believe there must be some mechanisms playing a role when the flow of Cp_2Mg increases. We think this abnormal growth rate increase with increasing flow rate of Cp_2Mg may be induced by the Ga memory effect, just like the increase of flow rate of TMIn can cause a large increase of the growth rate of InGaN.[24] Along with the increase of flow rate of Cp_2Mg, the Ga atoms which stay residually in the MOCVD system may be replaced by Mg and take part in the p-GaN growth. They are equivalent to adding an extra Ga source, leading the growth rate to increase with the increasing Cp_2Mg flow rate. At the same time, some research found that the extra Ga source will lead to more impurity incorporated in material.[24] Thus, the growth rate increase and the residual Ga joining the reaction will cause an impurity increase in p-GaN layer. From this analysis it is supposed that the Cp_2Mg flow can induce a memory effect to increase the growth rate and introduce more C impurity in material during the p-type GaN growth, so during the growth of heavily Mg-doped samples, we should try to change the growth condition to decrease the memory effect, and the residual C concentration.

Thermal annealing is indispensable to activate Mg acceptor after p-GaN growth. Conventionally, we annealed the p-GaN samples in an annealing furnace with N_2 or N_2/O_2 mixed atmosphere outside of the MOCVD reactor. However, if the thermal annealing process can be *in situ* taken in the MOCVD reactor closely after the p-GaN layer growth, the entire material preparation process would be more convenient. In our study, we compare the samples with same growth condition but different annealing environments, *in situ* or outside of the MOCVD system. As shown in Table 1, the samples A1 and A1* are grown in the same condition but with different annealing atmospheres, i.e., in an annealing furnace outside of the MOCVD system or *in situ* after MOCVD, respectively. The annealing temperature of two annealing processes was set to 680 °C, and the annealing time was fixed to 20 min. After annealing the resistivity and carrier concentration were measured by Hall measurement. From the Hall result it is found that the sample annealed in the annealing furnace has a better performance than the sample annealed *in situ* after MOCVD growth. For sample A1, the resistivity and hole concentration are 9 W·cm and 7.8×10^{16} cm^{-3}, respectively, while for sample A1* they are 63 W·cm and 3.15×10^{16} cm^{-3}respectively. These results mean that annealing outside of MOCVD is far better than that *in situ* MOCVD.

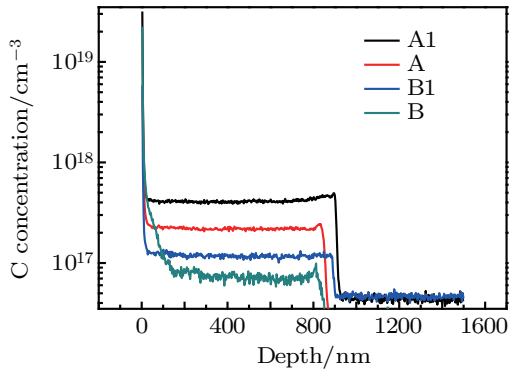


Fig. 5. (color online) The residual C concentration for p-GaN samples grown with different Cp_2Mg flow rates. It is higher in A1 and B1 than in A and B, respectively.

For the purpose of a further analysis, we have made an additional annealing treatment outside of the MOCVD reactor to the sample A1*. The Hall measurement result shows that the p-type performance of this sample has a large improvement. The resistivity and hole concentration are 15 W·cm and 7.1×10^{16} cm^{-3}, respectively, but it is still lower than the sample A1 which is just annealed outside of MOCVD system. The H concentrations in these samples are checked by SIMS measurement, as shown in Fig. 6. It is shown that the H concentration for the sample annealed in the MOCVD reactor (sample A1*) is higher than that annealed outside the MOCVD system (sample A1), and after an extra annealing process outside of the MOCVD system, the H concentration in sample A1* becomes almost the same as sample A1. The SIMS result suggests that the difference in the p-type conductivity of these samples may be caused by different efficiency of releasing H and activating the Mg acceptor in the annealing processes, and the annealing condition used in the annealing furnace may be more suitable for the H release from the Mg-doped GaN samples.

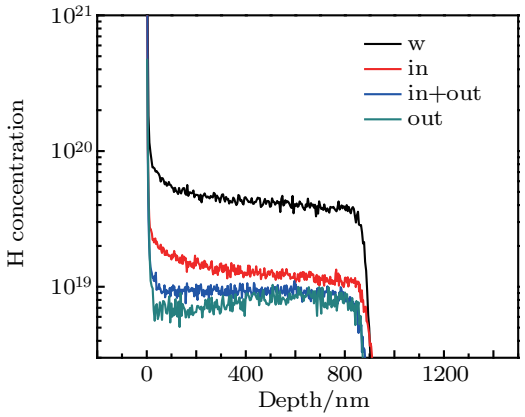


Fig. 6. (color online) The H concentration measured by SIMS in the samples after different annealing ways. The curve w represents the H concentration without any annealing treatment, while the curves in, in + out and out respectively represent: the H concentration in sample A1* annealed *in situ* in the MOCVD reactor, sample A1* with additional annealing process outside of MOCVD reactor, and in sample A1 annealed outside of the MOCVD reactor.

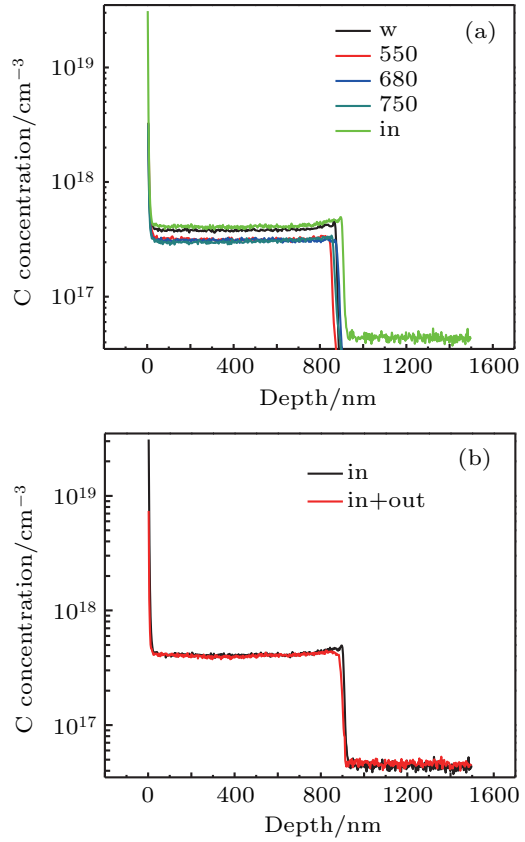


Fig. 7. (color online) The C concentration in samples after different annealing treatments. In Fig. 7(a) the curve w displays the C concentration without any annealing treatment, while the curves 550, 680, and 750 represent the C concentrations annealed outside the MOCVD system with the annealing temperature 550, 680, and 750 °C, respectively, and the curve in means the C concentration annealing in MOCVD. In Fig. 7(b) the curves in and in + out represent the C concentration annealed in MOCVD and annealing in MOCVD with another extra outside annealing process, respectively.

At the same time, we have also examined the residual C concentration contained in these samples. From the SIMS measurement, an interesting phenomenon is found that the C concentration is different in the samples annealed in two different annealing ways, as shown in Fig. 7. The C concentration in the sample annealed *in situ* in the MOCVD reactor (sample A1*) is almost unchanged, while the C concentration has an obvious decrease after annealing outside the MOCVD reactor (sample A1). In addition, it is found that the C concentration does not change when an extra outside annealing process is taken for the sample A1* as shown in Fig. 7(b). In order to check whether this phenomenon is caused by the experimental error or not, several other annealing temperatures are taken in the outside annealing experiment. It is found that the C concentration is always lower when annealing is made outside the MOCVD reactor than when the sample is annealed *in situ* in the MOCVD reactor and the sample is without any annealing treatment. So we can conclude that annealing outside MOCVD reactor has an advantage to releasing H concentration, which is the main reason that the conductivity of p-GaN annealing outside is much better than those annealed *in situ* in the MOCVD reactor. In addition, when an extra annealing process is taken out of the MOCVD system, the p-type conductivity can be improved, but is still a little lower than the sample which has not taken any *in situ* annealing treatment earlier. It may be caused by the difference in the residual C concentration: the C concentration decreases when annealed outside the MOCVD system, and the annealing *in situ* MOCVD reactor has an immobilization effect on C atoms; the C concentration thus could not decrease further when an extra annealing process is taking place outside of the MOCVD system.

4. Conclusion

We have confirmed that the residual C concentration in p-GaN layer has a negative influence on the performance of low-temperature growth p-GaN. Several growth and annealing parameters have been found to have remarkable influence on the residual C concentration of p-GaN material. In order to improve the p-type performance we need to increase the growth pressure, suitably increase the Cp_2Mg fluxes along the pressure increase and anneal outside the MOCVD system to decrease the residual C concentration.

References

[1] Cao K W, Fu B L, Liu Z, Zhao L X, Li J M and Wang J X 2016 *J. Semicond.* **37** 014008
[2] Jiang L R, Liu J P, Tian A Q, Cheng Y, Li Z C, Zhang L Q, Zhang S M, Li D Y, Ikeda M and Yang H 2016 *J. Semicond.* **37** 111001
[3] Li J M, Liu Z, Liu Z Q, Yan J Q, Wei T B, Yi X Y and Wang J X 2016 *J. Semicond.* **37** 061001
[4] Lei Y, Liu Z Q, He M, Yi X Y, Wang J X, Li J M, Zheng S W and Li S T 2015 *J. Semicond.* **36** 054006
[5] Sun Q, Yan W, Feng M X, Li Z C, Feng B, Zhao H M and Yang H 2016 *J. Semicond.* **37** 044006
[6] Xian Y l, Huang S J, Zheng Z Y, Fan B F, Wu Z S, Jiang H and Wang G 2011 *J. Crystal Growth* **232** 325
[7] Takeya M and Ikeda M 2001 *Jpn. J. Appl. Phys.* **40** 6260
[8] Youn D H, Lachab M, Hao M S, Sugahara T, Takenaka H, Naoi Y and Sakai S 1999 *Jpn. J. Appl. Phys.* **38** 631
[9] Amano H, kito M, Hiramatsu K and Akasaki I 1989 *Jpn. J. Appl. Phys.* **28** L2112

[10] Obloh H, Bachem K H, Kaufmann U, Kunzer M, Maier M, Ramakrishnan A and Schlotter P 1998 *J. Crystal Growth* **195** 270
[11] Yang J, Zhao D G, Jiang D S, Chen P, Liu Z S, Le L C, Li X J, He X G, Liu J P, Zhang S M, Wang H, Zhu J J and Yang H 2014 *J. Appl. Phys.* **115** 163704
[12] Tansley T L and Egan R J 1992 *Phys. Rev. B* **45** 10942
[13] Waki I, Fujioka H and Oshima M 2001 *Appl. Phys. Lett.* **78** 2899
[14] Chuo C C, Lee C M and Chyi J I 2001 *Appl. Phys. Lett.* **78** 314
[15] McCluskey M D, Romano L T, Krusor B S, Johnson N M, Suski T and Jun J 1998 *Appl. Phys. Lett.* **73** 1281
[16] Yang J, Zhao D G, Jiang D S, Chen P, Liu Z S, Zhu J J, Le L C, Li X J, He X G, Zhang L Q and Yang H 2016 *Chin. Phys. B* **25** 027102
[17] Chen J T, Forsberg U and Janzen E 2013 *Appl. Phys. Lett.* **102** 193506
[18] Kaufmann U, Kunzer M, Obloh H, Maier M, Manz C, Ramakrishnan A and Santic B 1999 *Phys. Rev. B* **59** 5561
[19] Kaufmann U, Kunzer M, maier M, Obloh H, Ramakrishnan A, Santic B and Schlotter P 1998 *Appl. Phys. Lett.* **72** 1326
[20] Amano H, Kitoh M, Hiramatsu K and Akasaki I 1990 *J. Electrochem. Soc.* **137** 1639
[21] Eunsoon O, Park H and Park Y 1998 *Appl. Phys. Lett.* **72** 70
[22] Kaufmann U, Schlotter P, Obloh H, Kohler K and Maier M 2000 *Phys. Rev. B* **62** 10867
[23] Parish G, Keller S, Denbaars S P and Mishra U K 2000 *Electron. Mater.* **29** 16
[24] Hiroki M, Oda Y, Watanabe N, Maeda N, Yokoyama H, Kumakura K and Yamamoto H 2013 *J. Crystal Growth* **382** 36