


NANO EXPRESS

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Hydrogen Can Passivate Carbon Impurities in Mg-Doped GaN



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Abstract

The effect of unintentionally doped hydrogen on the properties of Mg-doped p-GaN samples grown via metal-organic chemical vapor deposition (MOCVD) is investigated through room temperature photoluminescence (PL) and Hall and secondary ion mass spectroscopy (SIMS) measurements. It is found that there is an interaction between the residual hydrogen and carbon impurities. An increase of the carbon doping concentration can increase resistivity of the p-GaN and weaken blue luminescence (BL) band intensity. However, when hydrogen incorporation increased with carbon doping concentration, the increase of resistivity caused by carbon impurity is weakened and the BL band intensity is enhanced. This suggests that the co-doped hydrogen not only passivates Mg_{Ga}, but also can passivate carbon impurities in Mg-doped p-GaN.

Keywords: Mg-doped GaN, Hydrogen and carbon impurities, BL band

Introduction

GaN-based third-generation semiconductor materials and their alloys have attracted great attention [1] due to their broad applications including light-emitting diodes (LEDs) [2–4] and laser diodes (LDs) [5–7]. Although GaN-based photonic devices are widely commercialized, the relatively low hole concentration and high resistivity of p-type GaN still significantly limit the performance of such devices [8, 9]. Much research has been done to improve the p-type doping efficiency for III-nitrides [10, 11]. Hydrogen and carbon are two main residual impurities existing in the metal-organic chemical deposition (MOCVD)-grown Mg-doped GaN epilayers. It is well known that hydrogen impurities can passivate Mg in p-GaN [12]. On the other hand, carbon impurities can form many kinds of defects and increase the resistivity of Mg-doped p-GaN. Much research has been done to decrease the hydrogen and carbon impurities. However, there are few investigations on the interaction of hydrogen and carbon impurities.

It is known that too much residual impurity of either hydrogen or carbon can cause high resistivity in as-

grown Mg-doped GaN films. On account of the H-containing MOCVD growth environment, Mg is always passivated by hydrogen impurities, and a neutral Mg–H bond complex can be formed during film growth [13]. Fortunately, in a remarkable way, the group of Nakamura et al. [12] has firstly demonstrated that rapid thermal annealing in N₂ ambient at a temperature > 700 °C can successfully dissociate Mg–H complexes and effectively remove the hydrogen atoms from Mg-doped GaN films.

For the past few years, with the research and development of long-wavelength multiple-quantum-well (MQW) devices, high-indium-content InGaN/GaN layers have been widely used as active layers. To avoid the segregation and structural degradation of MQW, relatively low growth temperature (< 1000 °C) and relatively low rapid thermal annealing temperature are required. However, the unintentionally doped carbon impurity concentration increases with decreasing growth temperature, which leads to a higher concentration of carbon impurity-related defects in GaN, existing in the forms of substitutional defects (C_N), interstitial defects (C_i), and complexes [14, 15]. These defects can act as either donors or deep-acceptor species and increase the resistivity of p-GaN significantly [16]. As a result, the low-temperature (LT)-grown Mg-doped p-type GaN films often show a higher resistivity than those grown at higher temperature. Contrary to our expectations, our

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research has found that p-GaN films with both high concentration of hydrogen and carbon impurities show relatively low resistivity.

In this work, three sets of Mg-doped GaN films with different concentrations of hydrogen and carbon residual impurities are investigated through secondary ion mass spectroscopy (SIMS), photoluminescence (PL), and Hall measurements. It is found that hydrogen can passivate the carbon impurities in the p-GaN, which points out a new direction to grow high-quality p-type GaN film.

Experimental Methods

It still remains unknown on how to control the residual hydrogen concentration by setting MOCVD growth conditions. So, our samples are divided in different groups basing on SIMS results rather than growth conditions, similar Mg concentration in each group.

In this work, numbers of Mg-doped GaN films are grown on a 2- μm -thick unintentionally doped GaN layer template in a metal-organic chemical vapor deposition (MOCVD) system. Trimethylgallium (TMGa), ammonia (NH_3), and bis-cyclopentadienyl-magnesium (Cp_2Mg) are used as the precursors for Ga, N, and Mg, respectively. The growth temperature of all p-GaN samples is relatively low at 1020 °C. The Mg doping concentration is mainly adjusted by Cp_2Mg flow rate. The residual carbon impurity concentration is adjusted mainly by NH_3 flow rate during MOCVD—more NH_3 corresponds to less carbon impurity [17]. The rapid thermal annealing is carried out in a nitrogen environment at a temperature of 800 °C for 3 min to de-passivate the Mg–H complexes.

Hall test is carried out to measure the resistivity of p-GaN samples. To make ohmic contact on p-type GaN, molten indium metal is pointed on a sample surface and acts as a metal electrode. To check the concentrations of magnesium, hydrogen, carbon, and oxygen impurities, [Mg], [C], [H], [O], secondary ion mass spectroscopy (SIMS) measurements of these p-GaN samples are taken. Seven samples are selected because of the suitable Mg concentration and divided in three groups, similar Mg concentration in each group, named as A1, A2, A3, B1, B2, and C1, C2.

Room temperature photoluminescence (PL) measurements of all samples are carried out by the 325-nm wavelength of a He–Cd laser at an excitation density of about 0.4 W/cm². The luminescence intensity is normalized by the near-band-edge emission luminescence intensity (at around 3.44 eV)¹ for the sake of analysis.

Results and Discussion

The results of Hall test and SIMS measurement are exhibited in Table 1. Based on the SIMS results of Mg, C, and H concentration measurements, the seven samples

Table 1 Resistivity and Mg, C, H, and O concentrations for Mg-doped p-GaN samples

Sample	Resistivity (Ω cm)	Mg (cm^{-3})	C (cm^{-3})	H (cm^{-3})
A1	1.39	2.87E+19	1.17 E+17	1.70E+18
A2	4.95	3.14E+19	8.00E+17	8.70E+17
A3	47.7	2.39E+19	1.12E+19	4.11E+17
B1	1.49	1.10E+19	2.40E+16	4.60E+17
B2	2.35	1.08E+19	4.13E+17	2.81E+18
C1	1.95	1.60E+19	2.90E+17	1.50E+18
C2	2.95	1.40E+19	4.20E+17	4.59E+18

are divided into three groups A, B, and C. Samples in each group has to be similar to Mg concentration, because Mg is the major acceptor in p-GaN and the conductivity of p-GaN is mostly caused by Mg. So, if we want to investigate the influence of H and C impurity on resistivity, we should keep Mg concentration invariability in each group. The joint influence of doping concentrations of these impurities on the sample property, mainly the p-type electrical resistivity, is analyzed. The doping concentration of magnesium in these samples is very high (in $10^{19}\sim 3\times 10^{19}\text{ cm}^{-3}$) and has no remarkable difference for the samples in each group. The concentration of oxygen is low enough (10^{16} cm^{-3}) and can be taken out of further consideration.

In group A, the rise of carbon impurities causes a tremendous resistivity increase of the p-GaN, while in group B, the increase of hydrogen along with carbon impurities is found to weaken this trend. And group C is employed to further investigate the influence on BL band.

It can be seen in Table 1 and Fig. 1 that for samples A1–A3, the concentration of carbon impurity increases dramatically, changing two orders of magnitude from 1.17×10^{17} to $1.12\times 10^{19}\text{ cm}^{-3}$, but the concentrations of magnesium, hydrogen, and oxygen change only little. From the previous research, we realized that though the doping concentration of magnesium is very high, actually the hole concentration is still two orders of magnitude lower than magnesium because of the low ionization rate and high possibility of self-compensation [18, 19]. In GaN, Mg_{Ga} has an acceptor ionization energy of 260 meV [20], an order of magnitude more than $k_{\text{B}}T$ (about 26 meV) in room temperature, and defects and impurities exist in GaN can compensate or passivate Mg_{Ga} , so the hole concentration in Mg-doped GaN is about two orders of magnitude lower than magnesium. In addition, the residual carbon impurities can also cause negative effects to p-type GaN conductivity [16]. The resistivity of p-GaN samples in series A raised obviously with increasing carbon concentration (from 1.39 to $\sim 47.7\ \Omega$ cm). Therefore, the differences between samples A1–A3 can be attributed to the difference of carbon

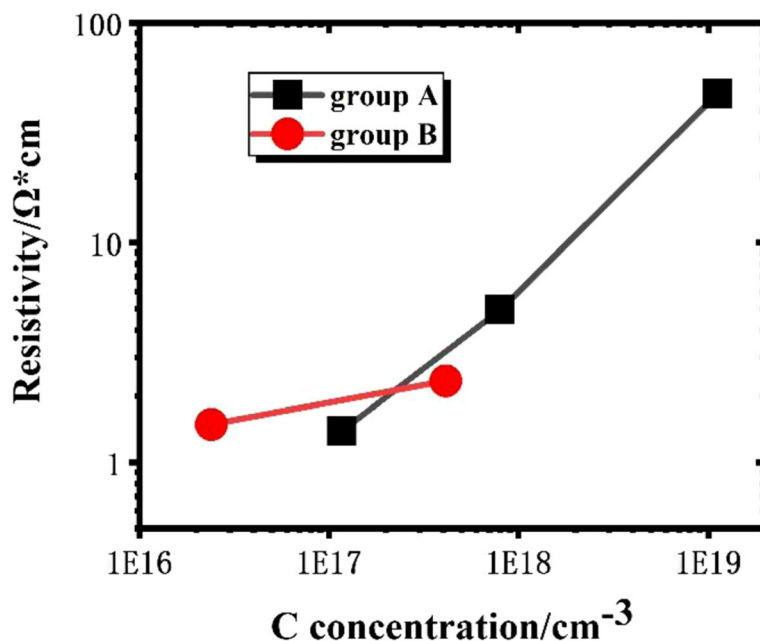


Fig. 1 The resistivity of samples changes with the C concentration in groups A and B

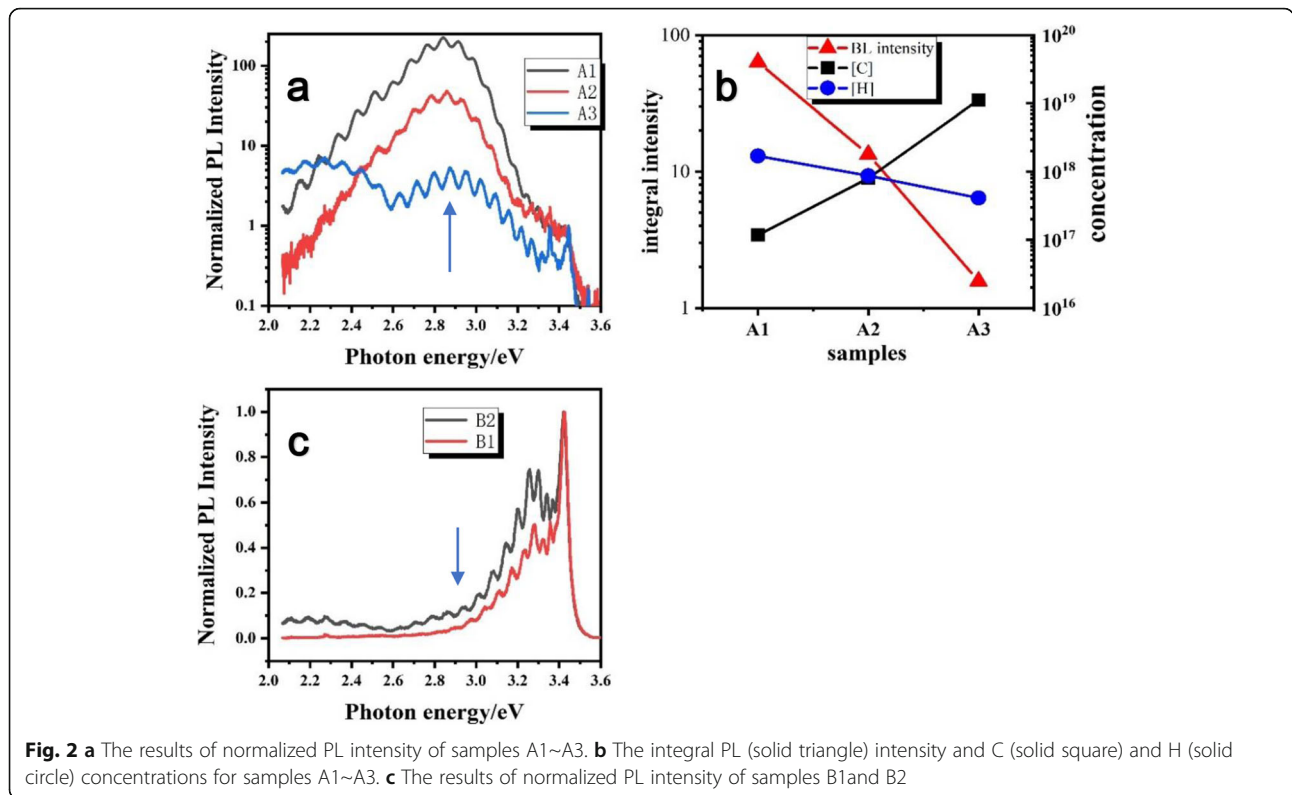
impurities. As described in our previous study [16], carbon impurities may preferentially play the role of donor-type compensation centers in Mg-doped GaN films. The donors can compensate magnesium acceptors. Therefore, the resistivity of p-GaN increases with the rise of residual carbon impurities concentration.

On the other side, in series B, the concentrations of magnesium and oxygen change little in each group as shown in Table 1 and Fig. 1. The carbon concentration of sample B1 is much higher (about 20 times) than that of sample B2. However, the resistivity of sample B2 is quite close to and not much larger than that of sample B1. This trend is different from what we have observed for group A. Hence, it suggests that this different trend of resistivity variation in two groups may be attributed to the difference in the concentration of hydrogen impurity. For samples A1–A3, hydrogen impurity concentration decreases little, with a factor of $\sim 1/3$, while carbon impurity concentration increases nearly two orders of magnitude. On the contrary, for samples B1–B2, the concentration of hydrogen impurity increases along with the carbon impurity. Thus, the obtained result suggests that hydrogen incorporation may weaken the influence of carbon on the resistivity of Mg-doped p-GaN, producing a counteraction effect.

In order to further investigate how carbon impurity compensates magnesium acceptors and why hydrogen can weaken this process, the room temperature photoluminescence measurements were carried out. In Fig. 2a, as shown by the results of PL measurement of samples A1–A3, a luminescence peak at about 2.9 eV can be seen

obviously. This blue luminescence (BL) band has been already studied for decades. It is known that the BL band in p-GaN PL spectra around 2.9 eV has a distinct donor–acceptor pair luminescence character. For the candidate of acceptor, isolated Mg substitute of Ga defect (Mg_{Ga}) is the natural choice. And the most possible candidate for the deep donor in very heavily Mg-doped GaN is a nearest neighbor complex, which is an associate of Mg_{Ga} and nitrogen vacancy (V_{N}), formed by self-compensation [21]. As the integral intensity of BL band decreases with higher doping of carbon impurities (Fig. 2b), we can assume that carbon impurities may decrease the number of relevant donor–acceptor pairs by compensating magnesium acceptors, because carbon impurities may preferentially play the role of donor-type compensation centers in Mg-doped GaN films [16]. The appearance of a strong 2.2-eV peak for sample A3 indicates that there is a larger number of carbon-related defects in sample A3 [15].

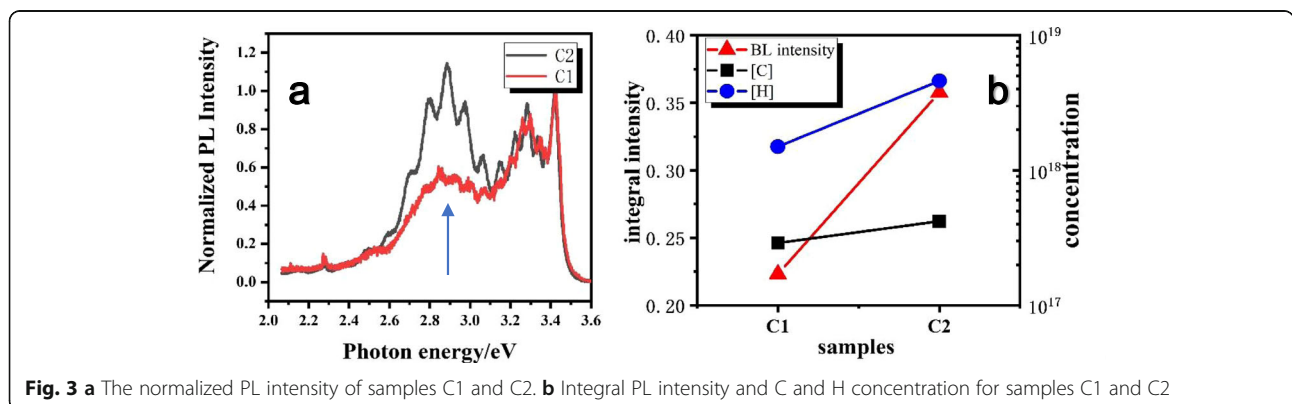
Meanwhile, regardless of a large increase of both carbon and hydrogen concentrations from B1 to B2 in sample group B, the PL spectra of these two samples are quite similar to each other. Actually, there is no obvious BL band in sample B1 and only a small BL peak in sample B2 (Fig. 2c), perhaps because of the relatively lower concentration of magnesium in series B samples (nearly $1 \times 10^{19} \text{ cm}^{-3}$) in comparison with group A samples. Therefore, the data of samples C1 and C2 are employed to check the interaction between hydrogen and carbon impurities further.



It is noted that the Mg and C concentrations in sample C1 are similar to those in sample C2, and the resistivity of the two samples is also similar to each other. But it is interesting to note that BL band changes obviously in the PL spectra of sample group C.

The H concentration in sample C2 is three times higher than that in sample C1. Figure 3a shows that the BL band intensity is quite different for samples C1 and C2. The intensity of BL band of C2 is much larger, which is attributed to the larger hydrogen concentration in this sample. In addition, the integral intensity of BL band increases clearly with the rise of the concentration of hydrogen, even though carbon impurity (can decrease BL band) concentration also increases a little at the same

time (Fig. 3b). It implies that the reason for the increase of BL band is the increase of hydrogen impurities instead of carbon. It suggests that hydrogen and carbon may have an opposite effect on BL band of p-GaN. For hydrogen impurities, we assume that the most probable way to enhance the BL band is to form more relevant donor-acceptor pairs by forming C-H complexes with carbon impurity and passivating the carbon impurities in Mg-doped GaN. So, it is speculated that hydrogen can form complexes with carbon in the Mg-doped p-GaN sample, leading to a smaller concentration of donor-type compensation centers. In other words, hydrogen can passivate carbon and improve the conductivity of Mg-doped p-GaN. Further investigation is needed to figure



out how to control hydrogen incorporation to preferentially passivate carbon impurity instead of Mg acceptors.

Conclusion

In summary, the effects of carbon and hydrogen impurities on Mg-doped GaN films were investigated. It is found that carbon impurities may preferentially play the role of donor-type compensation centers and compensate Mg acceptor in Mg-doped GaN films. An increase of the carbon doping concentration can increase resistivity of the p-GaN and weaken blue luminescence (BL) band intensity. However, when hydrogen incorporation increased with carbon doping concentration, the increase of resistivity caused by carbon impurity is weakened and the BL band intensity is enhanced, which suggests that hydrogen not only can passivate Mg_{Ga} acceptors, but also may passivate carbon by forming C–H complex with carbon impurity.

Abbreviations

GaN: Gallium nitride; InGaN: Indium gallium nitride; InN: Indium nitride; LD: Laser diode; LED: Light-emitting device; Mg_{Ga}: Mg substitute of Ga defect; MOCVD: Metal-organic chemical deposition; MQW: Multiple quantum well; NH₃: Ammonia; SIMS: Secondary ion mass spectroscopy; TMGa: Trimethylgallium; TMI: Trimethylindium; V_N: Nitrogen vacancy

Acknowledgements

The authors acknowledge the support from National Key R&D Program of China (Grant Nos. 2016YFB0401801 and 2016YFB0400803), Science Challenge Project (Grant No. TZ2016003), and National Natural Science Foundation of China (Grant Nos. 61904172, 61974162, 61674138, 61674139 and 61604145).

Authors' Contributions

YZ and DJ were major contributors in writing the manuscript. FL, DZ, JZ, ZL, JY, and SL help in collecting and analyzing the data. All authors read and approved the final manuscript.

Funding

All sources of funding for the research reported have been declared.

Availability of Data and Materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing Interests

The authors declare that they have no competing interests.

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Received: 22 September 2019 Accepted: 20 January 2020

Published online: 10 February 2020

References

- Pankove JI, Moustakas TD (1997) Chapter 1 introduction: a historical survey of research on gallium nitride. *Semiconduct Semimet* 50:1–10
- Morkoç H (2008) *Handbook of nitride semiconductors and devices*, vol 1–3. Wiley, New York
- Amano H (2016) Development of GaN-based blue LEDs and metalorganic vapor phase epitaxy of GaN and related materials. *Prog Cryst Growth CH* 62: 126–135
- Zhao DM, Zhao DG (2018) Analysis of the growth of GaN epitaxy on silicon. *J Semicond* 39(3):033006. <https://doi.org/10.1088/1674-4926/39/3/033006>
- Murayama M, Nakayama Y, Yamazaki K, Hoshina Y, Watanabe H, Fuutagawa N, Kawanishi H, Uemura T, Narui H (2018) Watt-class green (530 nm) and blue (465 nm) laser diodes. *Phys Status Solidi A* 215:1700513
- Liang F, Yang J, Zhao DG, Liu ZS, Zhu JJ, Chen P, Jiang DS, Shi YS, Wang H, Duan LH, Zhang LQ, Yang H (2019) Room-temperature continuous-wave operation of GaN-based blue-violet laser diodes with a lifetime longer than 1000 h. *J Semicond* 40(2):022801. <https://doi.org/10.1088/1674-4926/40/2/022801>
- Zhao DG, Yang J, Liu ZS, Chen P, Zhu JJ, Jiang DS, Shi YS, Wang H, Duan LH, Zhang LQ (2017) Fabrication of room temperature continuous-wave operation GaN-based ultraviolet laser diodes. *J Semicond* 38:051001
- Glaser ER, Carlos WE, Braga GC, Freitas JA Jr, Moore WJ, Shanabrook BV et al (2002) Magnetic resonance studies of Mg-doped GaN epitaxial layers grown by organometallic chemical vapor deposition. *Phys Rev B* 65(8):085312
- Xian Y, Huang S, Zheng Z et al (2011) Effects of growth pressure on the properties of p-GaN layers. *J Cryst Growth* 325(1):32–35
- Li S, Zhang T, Wu J, Yang Y, Wang Z, Wu Z, Chen Z, Jiang Y (2013) Polarization induced hole doping in graded Al_xGa_{1-x}N (x = 0.7 ~ 1) layer grown by molecular beam epitaxy. *Appl Phys Lett* 102. <https://doi.org/10.1063/1.4792685>
- Li S, Ware M, Wu J, Minor P, Wang Z-G, Wu ZM, Jiang YD, Salamo G (2012) Polarization induced pn-junction without dopant in graded AlGa_N coherently strained on GaN. *Appl Phys Lett* 101:3. <https://doi.org/10.1063/1.4753993>
- Nakamura S, Mukai T, Senoh M et al (1992) Thermal annealing effects on P-type Mg-doped GaN films. *Jpn J Appl Phys* 31(2B):L139–L142
- Amano H, Kito M, Hiramatsu K et al (1989) P-Type conduction in Mg-doped GaN treated with low-energy electron beam irradiation (LEEBI). *Jpn J Appl Phys* 28(Part 2, 12):L2112–L2114
- Wright AF (2002) Substitutional and interstitial carbon in wurtzite GaN. *J Appl Phys* 92(5):2575
- Lyons JL, Janotti A, Van de Walle CG (2010) Carbon impurities and the yellow luminescence in GaN. *Appl Phys Lett* 97(15):152108
- Yang J, Zhao DG, Jiang DS et al (2014) Investigation on the compensation effect of residual carbon impurities in low temperature grown Mg doped GaN films. *J Appl Phys* 115(16):163704
- Liang F, Zhao D, Jiang D, Liu Z, Zhu J, Chen P, Yang J, Liu S, Xing Y, Zhang L, Li M, Zhang Y, Du G (2018) Carbon-related defects as a source for the enhancement of yellow luminescence of unintentionally doped GaN. *Nanomaterials* 8:744
- Obloh H, Bachem KH, Kaufmann U, Kunzer M, Maier M, Ramakrishnan A, Schlotter P (1998) Self-compensation in Mg doped p-type GaN grown by MOCVD. *J Cryst Growth* 195:270–273
- Miceli G, Pasquarello A (2016) Self-compensation due to point defects in Mg-doped GaN. *Phys Rev B* 93(16):165207
- Lyons J, Janotti A, Chris VDW (2012) Shallow versus deep nature of Mg acceptors in nitride semiconductors. *Phys Rev Lett* 108(15):156403
- Kaufmann U, Kunzer M, Maier M, Obloh H, Ramakrishnan A, Santic B et al (1998) Nature of the 2.8 eV photoluminescence band in Mg doped GaN. *Appl Phys Lett* 72(11):1326–1328

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