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中国激光

碳杂质对 p-GaN 电阻率的补偿作用研究

吴昕宁[1]，刘昭阳[1]，刘明佳[1]，赵云涛[1]，齐浩然[1]，周梅[1*]，沈慧星[1**]，赵德刚[2]

[1]中国农业大学理学院应用物理系，北京 100083；

[2]中国科学院半导体研究所集成光电子国家重点实验室，北京 100083

摘要 研究了碳杂质对 p-GaN 的补偿作用。采用金属有机化学气相沉积法生长 GaN∶Mg 材料，实验发现，当生长温度从 1000 ℃提高到 1050 ℃时，p-GaN 的电阻率减小，空穴浓度增大。通过光致发光测试，发现随着生长温度的升高，尽管 p-GaN 的电阻率减小，但是 Mg 杂质的自补偿效应增强。进一步结合二次离子质谱测试，发现高温生长的 p-GaN 材料中碳杂质浓度更低，碳杂质在 p-GaN 中可能形成施主，从而补偿受主，增大 p-GaN 的电阻率。因此，在 p-GaN 中，碳杂质补偿相对于 Mg 杂质自补偿具有更重要的作用，抑制碳杂质对 p 型掺杂 p-GaN 非常重要。

关键词 材料；p-GaN；补偿作用；碳杂质；二次离子质谱

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1 引言

氮化镓(GaN)及其合金因其在发光器件中的广泛应用和广阔的市场前景而备受关注[1-6]。p-GaN 是 GaN 基光电器件结构的重要组成部分。然而，低空穴浓度和高电阻率往往限制了 p-GaN 的应用[7-9]。迄今为止，Mg 是 GaN 中最有效的 p 型受主杂质，对于金属有机化学气相沉积(MOCVD)生长的 GaN∶Mg 层，由于 H 钝化了 Mg 受主[10-11]，需要经过如热退火等工序来激活 GaN 中的 Mg 受主。适当的 Mg 掺杂浓度是获得高质量 p-GaN 的必要条件，但过量的 Mg 掺杂具有自补偿效应，不利于获得高空穴浓度和低电阻率的 p-GaN[12-15]。此外，位错密度、非故意掺杂杂质、碳和氧的浓度也对 p-GaN 的电阻率有重要影响[16-23]。p-GaN 材料的补偿中心很多，厘清补偿作用及机制，对于 GaN、AlGaN 材料的 p 型掺杂技术发展非常重要。

本文研究了 p-GaN 材料的补偿特性。采用 MOCVD 在不同生长温度下生长了 p-GaN 材料。实验发现，随着生长温度的升高，样品的电阻率减小，空穴浓度增加。光致发光(PL)和二次离子质谱(SIMS)测试结果表明，高温生长的 p-GaN 样品中 Mg 杂质自补偿更严重，同时高温生长的 p-GaN 样品中碳杂质浓度也更低。碳杂质在 p-GaN 中起着施主作用，从而补偿 Mg 受主、破坏 p 型导电，而高温生长的 p-GaN 样品电阻率更低，说明碳杂质的补偿比 Mg 杂质自补偿在 p-GaN 中占据更主导的作用。较高的生长温度有助于抑制碳杂质，从而减小施主补偿，获得高质量的 p-GaN 材料。

2 实验

采用型号为 Aixtron 3×2 的 MOCVD 设备进行 p-GaN 生长，具体过程如下：在 540 ℃条件下，在蓝宝石基底上生长 20 nm 厚的低温 GaN 缓冲层，随后在 1060 ℃生长了厚度为 2 μm 的非故意掺杂 GaN 层；然后，在 1000～1050 ℃范围内生长出一系列厚度为 0.7 μm 的 Mg 掺杂 GaN 层；最后，所有样品在 800 ℃下，在相同的氮气退火环境中退火 3 min，激活 Mg 受主[24]。在 MOCVD 生长过程中，TMGa、NH_3 和 Cp_2Mg 分别是 Ga、N 和 Mg 源。所研究的 5 个 p-GaN 样品 A～E，在生长过程中只有生长温度变化，其他生长条件均保持不变。X 射线衍射仪测试结果表明，A～E 样品的位错密度基本一致。

样品 A～E 的生长条件和部分霍尔实验结果见

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* **E-mail**：mmmzhou@126.com；** **E-mail**：huixingshen@163.com

表1。所有样品的电阻率和空穴浓度均采用室温霍尔法测量。通过光致发光测试、二次离子质谱测试和样品对比,研究了生长过程中碳杂质对 p-GaN 的补偿作用及物理机制。

表1　p-GaN 样品的生长条件和霍尔测试结果

Table 1　Growth condition and Hall test results for p-GaN samples

Sample	Growth temperature /℃	Reaction chamber pressure /kPa	NH_3 flow /($L \cdot min^{-1}$)	TMGa flow /($mL \cdot min^{-1}$)	Cp_2Mg flow /($mL \cdot min^{-1}$)	Resistivity /($\Omega \cdot cm$)	Hole mobility /($cm^2 \cdot V^{-1} \cdot s^{-1}$)	Hole concentration /(10^{17} cm^{-3})
A	1000	13.3	5	18	110	2.16	13.4	2.15
B	1020	13.3	5	18	110	2.22	8.6	3.27
C	1030	13.3	5	18	110	1.49	10.3	4.07
D	1040	13.3	5	18	110	1.51	9.3	4.46
E	1050	13.3	5	18	110	1.43	9.1	4.81

3　分析与讨论

从表1可以看到,随着生长温度的升高,p-GaN的空穴浓度增大,电阻率减小。为了阐明其物理机制,测试了室温光致发光(PL)光谱,激发光源为325 nm波长的He-Cd激光器,测试结果如图1所示,其中曲线波动是由光的干涉现象引起的。可以看到,样品C、D和E的蓝色发光带(BL)的峰值波长在430 nm左右(2.8 eV),而样品A和B的蓝光发光带很弱。已有的研究结果[25-26]表明,2.8 eV蓝光带发光来源于施主-受主对(DAP)跃迁。

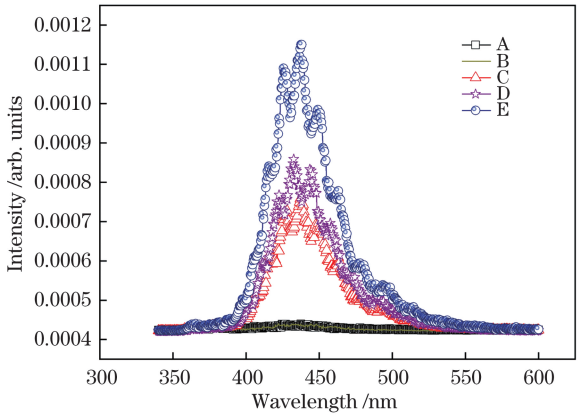

图1　样品A、B、C、D、E的室温PL光谱

Fig. 1　Room-temperature PL spectra for samples A, B, C, D, and E

p-GaN中的施主-受主对发光是Mg自补偿的有力证据,其中施主浓度的增加主要是由Mg杂质自补偿(Mg杂质浓度超过 1×10^{19} cm^{-3})引起的。施主-受主对中的受主是 Mg_{Ga},而施主可能是 Mg_{Ga}-V_N 或其他相关缺陷[14]。一般来说,BL峰越强,施主-受主对密度越高。较高的Mg掺杂浓度会导致施主-受主对的浓度升高,从而导致p-GaN的空穴浓度降低、电阻率升高。然而,在这5个样品中,强BL发光的C、D和E样品的电阻率并不是最高的,意味着除了Mg的自补偿外,可能还有其他更重要的原因导致在较低温度下生长的p-GaN具有较高的电阻率。

为了寻找可能的补偿机制,对B、C、D样品进行二次离子质谱(SIMS)测量,结果如图2所示。Mg、C、H的浓度如表2所示。结果表明:这3个样品的碳浓度有很明显的差异,其他杂质浓度几乎没有变化;样品D的碳浓度最低。这说明碳杂质对p-GaN的电阻率有很大的影响。事实上,GaN中含有多种形式的碳杂质。碳杂质可以取代N作为杂质的受体(C_N)或取代Ga作为杂质的施主(C_{Ga})[27];它们也可以是间隙杂质(C_i)或与其他杂质形成复合物。p-GaN中的碳杂质主要是形成施主,从而补偿Mg受主,也可以作为非辐射复合中心或诱导黄色发光带(YL)[17]。本研究发现它作为非辐射复合中心,引起了BL强度的降低,因此认为p-GaN中的碳杂质可以形成施主并补偿Mg受主,导致p-GaN的电阻率增加、电学性能变差。

表2　二次离子质谱测量得到的镁(Mg)、碳(C)和氢(H)的粒子浓度

Table 2　Particle concentration of magnesium, carbon, and hydrogen, which measured by secondary ion mass spectra

Sample	Concentration of particles /(10^{19} cm^{-3})			Growth temperature /℃
	Mg	C	H	
B	1.60	0.0400	0.220	1020
C	2.16	0.0357	0.275	1030
D	2.00	0.0170	0.150	1040

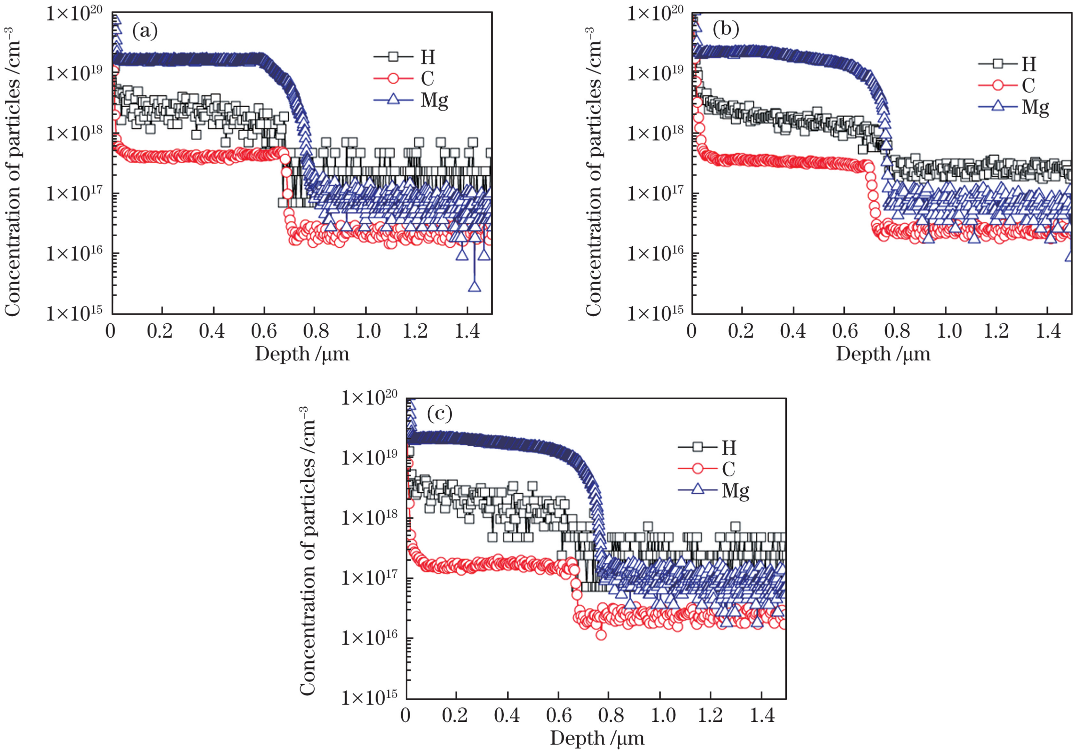

图 2 3 种样品的二次离子质谱测量结果。(a)样品 B;(b)样品 C;(c)样品 D

Fig. 2 Measuring results of secondary ion mass spectroscopy for three samples. (a) Sample B; (b) sample C; (c) sample D

实验结果表明,在较低的生长温度下,Mg 对 p-GaN 生长的自补偿效应较弱,但在较低的生长温度时碳杂质浓度较大,从而导致电阻率增大。而在较高的生长温度下 Mg 自补偿效应较强,碳杂质浓度较低。我们注意到,高温生长的样品,尽管 Mg 杂质的自补偿效应增强,但是电阻率依然较低,说明碳杂质的补偿在 p-GaN 中具有更重要的作用。要想得到电阻率低、空穴浓度高的 p-GaN 材料,必须抑制碳杂质并入。高温生长的 p-GaN 电学性能更好,其物理本质还是碳杂质浓度低。

值得注意的是,在 InGaN/GaN 多量子阱光电器件的生长过程中,通常需要高质量的 p-GaN 层。在这种情况下,p-GaN 层的生长温度不宜过高,以免发生 InGaN 层的分解,破坏量子阱层。p-GaN 层生长温度的选择是折衷的结果,在蓝绿光发光器件中一般应低于 1050 ℃,此时必须通过其他生长条件的调控来抑制碳杂质,才能获得高质量的 p 型层。一般情况下,GaN/AlGaN 多层器件中的 p-GaN 层应该选择相对较高的温度进行生长。

4 结　　论

通过 SIMS、霍尔测试和光致发光测试,研究了碳杂质对 Mg 掺杂 p-GaN 薄膜的补偿作用和机理。实验发现,随着生长温度的升高,p-GaN 的 Mg 杂质自补偿效应增强,但是电阻率反而降低。进一步研究发现,高温生长的 p-GaN 样品中碳杂质浓度更低,碳杂质可以补偿 Mg 受主,引起电阻率增大。研究表明,碳杂质的补偿在 p-GaN 中相对于 Mg 自补偿具有更重要的作用,适当提高生长温度可以抑制碳杂质并入,从而获得高质量的 p-GaN 薄膜。由此可见,抑制碳杂质对 GaN 的 p 型掺杂非常重要。

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Compensation Effect of Carbon Impurities on the Resistivity of p-GaN

Wu Xinning[1], Liu Zhaoyang[1], Liu Mingjia[1], Zhao Yuntao[1], Qi Haoran[1], Zhou Mei[1*],
Shen Huixing[1**], Zhao Degang[2]

[1] *Department of Applied Physics, College of Science, China Agricultural University, Beijing* 100083, *China*;
[2] *State Key Laboratory of Integrated Optoelectronics, Institute of Semiconductors, Chinese Academy of Sciences,*
Beijing 100083, *China*

Abstract

Objective Gallium nitride (GaN) and its ternary alloys have drawn considerable attention because of their broad applications and promising market prospects for light-emitting devices. p-type doped GaN is an important part of GaN-based optoelectronic device structure. However, the applications of p-GaN are often limited by the low hole concentration and high resistivity. Until now, only Mg has been successfully employed as an effective and practical acceptor impurity in GaN for achieving useful p-type conduction. Post-growth treatment, such as thermal annealing, is required to activate the Mg acceptors in GaN in case of layers grown via metal-organic chemical vapor deposition (MOCVD). Further, there is convincing evidence that hydrogen passivates Mg acceptors in the as-grown state of the materials. An appropriate Mg doping concentration is required for obtaining high-quality GaN. The usage of a considerably high or low Mg doping concentration does not allow for a high hole concentration because of the self-compensation effect associated with heavy Mg doping. In addition, the dislocation density and the concentration of unintentionally doped impurities (e.g., carbon and oxygen) have an important effect on the resistivity of p-GaN. Overall, the compensation mechanisms and functions of the p-doped GaN and AlGaN materials must be clarified for their further development.

Methods A series of Mg-doped p-GaN films was grown in a vertical MOCVD system under different growth temperatures. An Aixtron 3 × 2 MOCVD system was used for growing p-GaN films. A 20-nm thick GaN buffer layer was initially grown at 540 ℃ on a sapphire substrate. Then, a 2-μm thick unintentionally doped GaN layer was grown by increasing the temperature to 1060 ℃. Subsequently, a series of 0.7-μm thick Mg-doped GaN layers was grown at 1000–1050 ℃. Each sample was annealed at 800 ℃ for 3 min under the same nitrogen environment for activating the Mg acceptors. Trimethylgallium (TMGa), ammonia (NH_3), and Cp_2Mg were used as sources of Ga, N, and Mg, respectively, when using MOCVD. All the conditions were maintained constant for each sample (A–E), except the growth temperature. X-ray diffraction was performed to confirm that the dislocation density in each sample was approximately identical. Further, the resistivity and hole concentration of each sample were measured using the room-temperature Hall method. In addition, the photoluminescence (PL) was measured and secondary-ion mass spectrometry (SIMS) was performed to study the compensation effect of the carbon impurities on p-GaN and its physical mechanism.

Results and Discussions The results obtained from the room-temperature Hall method (Table 1) indicate that the hole concentration increased and the resistivity decreased with the increasing growth temperature. To find possible causes for these phenomena, room-temperature PL spectra (Fig. 1) were obtained using a 325-nm laser beam excitation. The undulation of the PL spectral curves can be attributed to the interference caused by the Fabry-Perot effect owing to flat epitaxial films, which can be eliminated via a line-shape simulation treatment. Samples B, C, and D exhibited a blue luminescence (BL) band peak at approximately 430 nm (2.8 eV), whereas samples A and B did not exhibit such a peak. Detailed investigations have proven that the 2.8-eV BL is caused by donor-acceptor pair (DAP) recombination, where a strong BL peak indicates a high density of DAPs. A considerably high Mg doping concentration may induce a high concentration of DAPs, which can decrease the hole concentration and increase the resistivity. However, in this study, samples B, C, and D exhibited a high BL intensity but not the highest resistivity, implying that factors other than the self-compensation of Mg resulted in the high resistivity of GaN grown at low temperatures. By performing SIMS on samples B, C, and D (Fig. 2), we can observe that the carbon concentration in sample D was the lowest, implying that the concentration of carbon impurities considerably influences the resistivity of p-GaN by acting as a nonradiative recombination center and thereby decreasing the intensity of the BL band peak. Thus, the carbon impurities in p-GaN can form deep donors and compensate for the

Mg acceptors, resulting in the deteriorated resistivity and poor mass of p-GaN. The experimental results presented in Table 2 indicate that the self-compensation effect of Mg in case of p-GaN growth was weaker at a lower growth temperature. However, a lower growth temperature can increase the density of carbon impurities, increasing the resistivity. Further, a higher growth temperature resulted in a stronger self-compensation effect and a lower carbon impurity concentration. The samples grown at high temperatures exhibited low resistivity despite the enhanced self-compensation effect of the Mg impurities, indicating that the compensation of carbon impurities played a more important role in p-GaN. Therefore, carbon impurities must be suppressed to obtain p-GaN materials with low resistivity and high hole concentrations. The p-GaN samples grown at high temperatures were of high quality because of their low concentrations of carbon impurities. High-quality p-GaN conduction layers are required for the growth of InGaN/GaN multiple quantum well optoelectronic devices. However, tradeoffs must be considered because the growth temperature of the top p-type GaN layer must not be considerably high to avoid thermal instability and the decomposition of the InGaN layers. It must be considerably lower than 1050 ℃ in a blue or green light-emitting device. Carbon impurities must be suppressed by regulating other growth conditions to obtain a high-quality p-type layer. Generally, the p-GaN layer in GaN/AlGaN multilayer devices must be grown at high temperatures.

Conclusions The effect of the growth temperature of heavily Mg-doped p-GaN films is studied based on the SIMS and PL measurements as well as the Hall method. Experimental results show that the self-compensation of the Mg impurity in p-GaN increased with the increasing growth temperature; however, its resistivity decreased. Further study indicated that the concentration of carbon impurity in the p-GaN sample grown at high temperatures was low. Carbon impurities can compensate for the Mg acceptor and increase the resistivity. The presented results indicate that the compensation of carbon impurities plays a more important role in the development of p-GaN films than the self-compensation of Mg. Thus, high-quality p-GaN films can be obtained by increasing the growth temperature appropriately to inhibit the incorporation of carbon impurities.

Key words materials; p-GaN; compensation effect; carbon impurities; secondary ion mass spectroscopy

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