The Difficulty and Solution of Mg-doped in GaN

Guoting Cheng
College of Physics, Qingdao University, Qingdao, Shandong, 266071, China

Abstract. GaN could be the representative third generation semiconductors, it becomes a significant material in the optoelectronic and microelectronic devices. However, the production of atomic H dramatically increases the resistance of Mg-doped GaN. Large amount of Mg-H complex are produced during the MOCVD process, dramatically reducing the performance of Mg-doped GaN. Low-Energy Electron Beam Irradiation (LEEBI) could eliminate surface H⁺ and thus reduce the resistance. Furthermore, Rapid Thermal Annealing (RTA) could decompose Mg-H complex, increasing the concentration of hole. By studying and improving every method, the electrical properties and optical properties are still not enough. Finally, the research points out the future direction of improving the performance of Mg-doped GaN.

1. Introduction
GaN is a direct bandgap semiconductor with the binary compound of Ⅲ/Ⅴ elements and an extremely stable as well as hard compound with the high melting point. Third generation semiconductors, represented by GaN, are of great advancement due to the special structure characteristic. Because Mg and Ga have similar electronic structural properties, Mg has been used in p-type doping species widely to produce Mg-doped GaN. However, the production of atomic H dramatically increases the resistance of Mg-doped GaN, and intrinsic difficulties due to atomic H seriously limit more application of Mg-doped GaN. Consequently, due to the high resistance of the material, the energy consumption is dramatically increased, and the energy efficiency is to be pretty low. The quality of optoelectronic devices based on GaN, such as LEDs and LDs, are seriously limited, handicapping the development of this kind of devices. According to E. Yamaguchi’s study, the n-type doping technology is relatively simple with Si standing as acceptor, so the drift mobility could exceed 300cm²/(V·s). However, Mg has larger covalent radius, so Mg-H will be produced to make Mg become passive, so the resistance is extremely high[1]. Therefore, in this paper, the difficulty and Solutions of Mg-doped GaN will be discussed in detail, as well as the future direction of development of Mg-doped GaN will be proposed in the end.

2. Current situation of GaN
GaN can be doped with silicon to n-type or with magnesium to p-type. With p-type doping, the performance of GaN could be dramatically improved. Because the deep nature of Mg acceptor has a pretty high doping levels, which is about 1020cm⁻³, Mg-doped p-type GaN has a significant value for the family of devices based on nitride, including photodetectors, light emitting diodes (LEDs), lasers and solar cells. Because of the high thermal conductivity and wide band gap, compared with Si and GaAs, Mg-doped GaN devices can operate at higher temperatures above 200°C, which means that it could tolerate higher energy density, so Mg-doped GaN has higher reliability. Furthermore, the efficiency of GaN could be dramatically increased due to the decreasing of resistance, with more wide band gap and dielectric breakdown electric field. Also, the devices are allowed to operate at high speed with a fast electron saturation speed and high carrier mobility.
3. The mechanism introduction and limitation analysis

3.1. The development and limitation of growing Mg-doped GaN by MOCVD

The growth of Mg-doped GaN is dependent on MOCVD. In 1968, metalorganic chemical vapor deposition (MOCVD) was proposed in America. In the process of MOCVD, the ultrapure gases are injected into the reaction chamber, followed by precisely dosed to deposit an extremely thin layer of doping atoms onto a semiconductor wafer. The condition of reaction to happen on the surface for crystalline growth required compound semiconductors and the epitaxy of materials, with metalorganics and organic compounds and hydrides containing the necessary chemical elements. For example, gallium nitride could be produced in a reactor on heated sapphire substrates, then ammonia (NH$_3$), Trimethylgallium (TMGa) and bicsyclopentadienyl-magnesium (Cp$_2$Mg) are reacted as growth precursors. The Mg-doped layers were produced in a H$_2$ ambient, followed by a post-growth annealing step which was applied to activate the dopants. However, when doping Mg in the epitaxial layer of GaN, because the covalent radium of Mg is larger than Ga and Mg is reacted as deep acceptor, the Mg acceptor in the epitaxial layer will be passivation because of the production of Mg-H, and the atomic H come from H$_2$ reacted as carrier gas and the decomposition of reactant NH$_3$. Therefore, the hole mobility of p-type doping is much low via the conventional metal organic chemical vapor deposition (MOCVD), with high concentrations of Mg which are about $10^{19}$cm$^{-3}$ and the high remaining hydrogen concentration. The remaining hydrogen atoms can be decreased by thermal activation, but under room temperature (RT), there is still considerable quantities of atomic hydrogen with concentration exceeds $10^{18}$cm$^{-3}$ remaining in the films. The consequence of it is that the resistivity of GaN could reach to $10^8$Ω, which extremely limits the conduction of material, the reliabilities of devices such as lasers and light-emitting diodes (LEDs) are reducing, because the diffusion of atomic H is hardly driven by current injection.

![Figure 1. Illustration of MOCVD process.](image1)

![Figure 2. MOCVD apparatus](image2)

Accounting for that there is a 2.8 eV photoluminescence band in metalorganic chemical vapor deposition grown GaN, Kaufmann proposed a viewpoint of donor–acceptor (D–A) pair recombination character. He claims that blue band is produced by the recombination of dependent acceptor M$_{Ga}$ and deep donor energy level, the deep donor level refers to M$_{Ga}$V$_n$, which is recombined by acceptor M$_{Ga}$ and nearby vacancy of nitrogen V$_n$V$_n$ is the defection produced in the process of MOCVD with high pressure of nitrogen balance, the concentration of V$_n$ reaches the highest point in the 1000 °C temperature[2].

Young pointed out that the increase of p-type doping is relative with the density of dislocation, dislocation becomes the migration path of hydrogen atom[3].
With the purpose of increasing the conductivity of hole and obtaining low resistance p-type GaN, researchers invented many new doping techniques. T. Yamamoto proposed co-doping method. Both of n-type and p-type dopant are doped at the same time, then the donor level is reduced and the acceptor level is increased, which will produce higher hole concentration. Meanwhile, the hole mobility is going to be increased, because short-range dipole scattering substitutes long-range Coulomb scattering of isolated impurity charges and the intensity of scattering is weakened[4].

3.2. The development and limitation Low-Energy Electron Beam Irradiation (LEEBI)

When the single-crystalline GaN is prepared to produce, a sapphire substrate is used to work as heteroepitaxial growth. However, because of huge difference in the thermal expansion coefficient between sapphire and GaN, as well as the huge lattice mismatch and the high-quality epitaxial growth must operate on a flat surface free from cracks, which is much difficult. Therefore, low-energy electron beam irradiation is applied before the growth of GaN by MOVCD. After handling with LEEBI, crystalline quality, the film uniformity, luminescence and electrical properties of GaN films are greatly improved, and resistance of p-type doped GaN is dramatically reduced. The hall effect measurement of Mg-doped GaN which had been treated with Low-Energy Electron Beam Irradiation at room temperature (RT) showed that the hole concentration is $2 \times 10^{16}$ cm$^{-3}$, the resistivity is $35 \Omega \cdot$ cm and the hole mobility is $8 \text{cm}^2/\text{V} \cdot \text{s}$ approximately[5].

J. A. Van Vechten did research about the mechanism of this treatment, proposing that a large quantity of electron-hole pairs are produced in the GaN by the low energy electron beam irradiation, and there pairs are tend to assemble to the area where acceptors and donors H$^+$-Mg complex are aggregated, therefore, the interstitial ion H$^+$ is neutralized by electron forming neutron H, and some of the neutron diffuse to the surface of GaN, then it forms H$_2$ with other neutron H to escape outside, leaving much activated acceptor[6]. The resistance of Mg-doped GaN could be reduced by this process. However, the resistance of Mg-doped GaN is far depended on the penetration depth of LEEBI, only on the area with very thin surface of GaN could present p-type characteristic distinctively.

3.3. The development and limitation of Rapid Thermal Annealing (RTA)

Despite the hydrogen removing was first achieved with a low energy electron beam irradiation, subsequent work showed that a thermal anneal of 700℃ for 20 minutes could still activate Mg acceptors. The contact of metal/GaN and film properties are influenced by different thermal annealing temperature and time. Therefore, different thermal annealing is used based on the difference of necessary.

Recently, there is a method of using Rapid Thermal Annealing (RTA) at temperatures about 1150℃ to activate Mg-doped GaN in a light emitting diode (LED) structure. Compared with conventional
thermal annealing, RTA works in a higher temperature. The high temperature step could improve the samples photoluminescence. If an excellent conductivity neither n-type or p-type, a rapid thermal annealing temperature of more than 1000℃ is required to achieve.

The high-temperature rapid thermal anneals effectively improve the morphology of surface and photoluminescence of GaN growing on sapphire. Particularly, GaN samples rms roughness is reduced when annealed in an N₂ ambient at 1100℃ for 15s, the average value of roughness, originally 3.9nm, could reach to 1.1nm[7]. Therefore, the band-edge photoluminescence emission also increases correlated with the improvements of surface morphology. Furthermore, the electron mobility is also reduced by thermal annealing, partly because the two bands conduction mechanism or an increasing of compensation ration.

The thermal annealing of GaN film growth usually occupies in the growth room, and the ohmic contact and rectifying contact in the production of GaN devices occupy in the special annealing furnace. With the purpose of protecting the surface of GaN film surface, the overpressure method is usually adopted. Hydrogen is usually adopted as carrier gas to transport NH₃ to growth room, providing overpressure of nitrogen, so the purpose of protecting surface could be achieved. However, this method could bring two-sided problems. The first one is that the volume of growth room is large normally, which is lead to require long process to warming and cooling. The another one is that NH₃ is inevitably decomposed worked as annealing gas atmosphere, and H could disperse to material, causing hydrogen passivation.

M. W. Cole has researched the impact of rapid thermal annealing temperature to the mass of film crystal. The annealing occupied in nitrogen atmosphere, lasting for 1 minute and the temperature range is 600~ 800℃observed by TEM, the quality of GaN film surface is dramatically enhanced, and the crystallographic defect of GaN film surface is reduced approximately 25% ~ 30% compared with the interface of substrate and buffer layer. The annealing temperature higher, the less flat defect, dislocation mostly, extend to surface. Furthermore, Mg-H complex still be found in the Mg-doped GaN after rapid thermal annealing, because H⁺ are not be totally neutralized after annealing, so Mg-h could reproduce once temperature fall to the room temperature[8]. Theoretically, less defect could increase the mobility of carrier, but researchers hasn’t observed any increasing of carrier mobility after annealing, partly because the negative influence of impurities including H and C cannot be removed by thermal annealing.

With purpose of obtaining better quality devices, scholars have studied the passive effect of Mg-H complex, the mechanism of acceptor stimulation, the relationship between the condition of thermal annealing and the concentration of external surface of GaN, the crystal quality, the luminescence character. Meanwhile, they have also proposed some invented doping method. The research of Kim indicated that when annealing temperature is 800℃, deep energy band originated from Mg-N-H complex concentrates on 0.22 eV, and more hydrogen atom will come out from complex with high annealing temperature[9]. K S Ahn applied Two-step Rapid Annealing Process, which means that GaN firstly is annealed under low temperature of 600℃ for 5 min, then it is annealed under high temperature of 900℃ for 1 min. The electric quality, crystal quality and surface smoothness of GaN are apparently improved[10]. Waki I invented that plating Ni which thickness of 1.5 nm with chemical vapor deposition (CVD), followed by annealing in the atmosphere of N₂. Observed by SIMS, atomic hydrogen is effectively ejected and the absorption of atomic hydrogen is apparently improved by Ni[11].

4. Result analysis
One of the most important reason of handicapping the development of GaN is that p-type GaN with high quality is hard to obtained, which far limited further the application of GaN devices. Although scientists have deeply studied the concrete mechanism of p-type GaN and invented several doping methods, the electric quality, photoluminescence and crystal characteristic of p-type GaN still remain in poor condition. In the future, more attempt should focus on activating the dopant of GaN, achieving higher concentration of hole carrier and lower resistivity and finding more proper acceptor dopant. The fact is that, there are only 1%~2% of Mg atoms in GaN could be acted as acceptor, so the amount of Mg atoms should be added to two orders of magnitude higher than hole concentration. However, with such
huge amount, the surface of GaN will be rough, reducing the performance of materials. Therefore, only to find more active acceptor could reduce the amount of acceptor dopant.

5. Conclusion
In summary, this paper contains only a theoretical analysis of the development and limitation of MOCVD, LEEBI and RTA technology, lacking concrete experimental operation. Therefore, the proposition is based on theoretical deduction. In practical operations, the results will be influenced by several factors, including operation accuracy and material quality. In the subsequent research, the theory and practical operation will combine together, and the theory will be modified based on experiment results, also, the operation will be improved with the development of theoretical knowledge. With the deeper cognition of doping mechanism and improvement of doping techniques, the technique of p-type doping tends to be more improved, so meet more high-quality requirements. Therefore, the performance of optoelectronic and microelectronic devices will be significantly increased, embracing a bright future of microelectronic world.

References
[1] Yamaguchi, E., Junnar, M. R. (1998) Effects of nitrogen vacancy on optical properties of nitride semiconductors. J. Cryst. Growth., 189:570
[2] Kaufmann, U., Kunzer, M., Maier, M., Obloh, H., Ramakrishnan, A., Santic, B., Schlotter, P. (1998) Nature of the 2.8 eV photoluminescence band in Mg doped GaN. J. Appl. Phys. Lett., 72(11): 1326–1328.
[3] Youn, D., Laehab, M., Hao, M., et al. (1999) Investigation on the p-type activation mechanism in Mg-doped GaN films grown by metalorganic chemical vapor deposition. Jpn. J. Appl. Phys., 38(2): 631–634.
[4] Yamaoto, T., Katayama-Yoshida, H. (1998) Electronic structures of p-type GaN co-doped with Be or Mg as the acceptors and Si or O as the donor condopants. J. Cryst. Growth., 189: 532.
[5] Amano, H., Kito, M., Hiramatsu, K., Akasaki, I. (1998) P-Type Conduction in Mg-Doped GaN Treated with Low-Energy Electron Beam Irradiation (LEEBI). J. Journal of Applied Physics, pp. 2112–2114.
[6] Van Vechten, J. A., Zook, J. D., Horning, R. D., et al. (1992) Defeating compensation in wide gap semiconductors by growing in H that is removed by low temperature de-ionizing radiation. Jpn. J. Appl. Phys., 31(11): 3662–3664.
[7] Zolper, J. C., Crawford Hagerott, M., Howard, A. J., Ramer, J., Hersee, S. D. (1996) Morphology and photoluminescence improvements from high temperature rapid thermal annealing of GaN. J. Appl. Phys. Lett., 68: 200.
[8] Cole, M. W., Ren, F., Pearton, S. J. (1997) Post growth rapid thermal annealing of GaN. The relationship between annealing temperature, GaN crystal quality, and contact- GaN interfacial structure. J. Applied Physics Letters, 71: 3004.
[9] Kim, K., Harrison, J. G. (2003) Critical Mg doping on the blue-light emission in p-type GaN thin film grown by meta-organic chemical-vapor deposition. J. Vac. Sci. Technol., A21:134–139.
[10] Ahn, K. S., Kim, D. J., Moon, Y. T. (2001) Rapid thermal annealing method of p-GaN thin film growth. J. Vac. Sci. Technol, B19(1):215–217.
[11] Waki, I., Fujioka, H., Oshima, M. (2001) Doping Mg on UHCVD add Ni research. J. Appl. Phys. Lett., 78(4): 2899–2900