

A Hydrogen-Free Doping Process by Mg and N₂ Diffusion for Fabrication of P-Type GaN

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Abstract:

A hydrogen-free doping process is adapted in this experiment which is revealed by put Mg with the un-doped WZ-GaN[0001] film into the diffusion ampoule. Diffusion process is taken place at 900°C and 1000°C for three hours. The 900°C diffused GaN film has a strong A-exciton line at 355 nm (~3.493 eV) which is the highest value by now, and the 1000°C diffused GaN film has a strong A-exciton line at 356 nm (~3.483 eV) which is as high as ever being measured.¹ Both exist free exciton line, I₁(exciton bound to the neutral acceptor) line and D-A pair with its LO-phonon replicas. PL measurement are taken under different temperature and excitation power with a 325.5 nm He-Cd laser. The ex-situ and hydrogen-free doping technique is proven to be valid in our work. And we have the highest A-exciton (free exciton) peak frequency than ever being reported. The emission mechanism seem to be different at different temperature. The deep-level-related yellow band emission dominate at 20 K. The emission intensity decay rapidly when the temperature exceeding 160 K.

Introduction:

The III-V nitride wide band gap semiconductors have become a promising material for the fabrication of the green-blue to the UV region.¹ However, a classical MOCVD grows GaN film with NH₃ as a nitrogen source, which will dissociate hydrogen atoms and produce acceptor-hydrogen complex. So it needs an annealing process to dissociate the acceptor-hydrogen complex and activate the dopant as real acceptor. The annealing process can be revealed either by low-energy electron-beam irradiation (LEEBI) treatment or simple thermal annealing at a temperature above 500°C.^{2,3,4,5}

To avoid the formation of Mg-H complex, we don't dope the GaN film by furnishing Cp₂Mg into reaction chamber. Instead, we dope Mg into GaN film by diffusion

method. The GaN film and Mg and N₂ gas are put into a sealed diffusion ampoule, and proceed a constant-temperature diffusion process. The reason for using Mg with N₂ atmosphere as a Mg source is to avoid too much V_N produced. The N₂ in the diffusion ampoule is then as the atmosphere inhibiting the dissociation of the GaN and avoid the formation of Mg-H complex.

Experiment :

The diffusion ampoule is made of a quartz tube which was cleaned by 1% HF solution for 2 hour and rinsed by DI water for 4 hours. Then the tube was dried by pure N₂ purge. The un-doped GaN film and the diffusion source are put into the quartz tube as a whole to form a diffusion ampoule. In this experiment the diffusion

process are taken place in a tube furnace at 900 °C and 1000 °C for 3 hours. All of the diffusion ampoules suffer an uniform thermal profile, i.e., no thermal gradient occurred. After diffusion, PL spectrum is measured at variant temperature and power. The exciting source is 325.5 nm KIMMON IK series He-Cd CW Laser with a maximum power output of 60mW and 2 mm beam size in diameter. After focusing, the power density can reach up to about 20 W/cm². The monochromator is ARC Spectrapro-750. Thorton EMI PMT and SRS830 Lock-in Amplifier are used to amplify the signal and reduce the noise. CTI-Cryogenic compressor and Model 22 Refrigerator are used to supply a low-temperature environment. Laser power is adjusted by attenuation filter.

Results and Discussion:

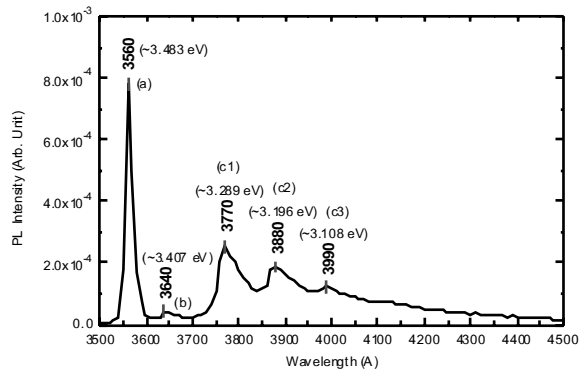


Fig.1. A PL spectrum measured at 10 K for Mg-diffused GaN film at 1000 °C. (a) The main peak at 356 nm (~3.483 eV) responses to the A-exciton (free-exciton) which is as the same as observed by K. Naniwae, e.a. (b) The 364 nm line represents the exciton bound to the neutral acceptor. (c1~3). The D-A pair with its three LO-phonon replicas.

Figure 1 is a typical PL spectrum measured at 10 K for this experiment which is obtained. It shows that a sharp peak at 355.0nm (~3.492 eV) which corresponds to the A-exciton which attributed to the decay of the free

excitons⁶ and 27 meV high than observed than in-situ doped.⁷ The 365 nm (~3.397 eV) is attributed by the LO phonon replica of the A-exciton line and a strong no-phonon D-A pair band at 377.0 nm (~3.289 eV) accompanied by a series of phonon replicas.

Figure 2 represents the temperature dependence of the intensity for the A-exciton (free-exciton) and exciton bound to neutral acceptor (Ex-A). In the case of diffusing at 1000 °C, as can be seen in figure 2, when the measuring temperature increases, the peak intensity tends to decrease except for that at 20 K. We suppose that the luminescence mechanism at 20 K is different with other temperatures, maybe relating to the deep level emission, we can not make sure. We can not read out the yellow band emission signal to a significant value due to the limitation of lens and read-out instrument. But we suppose that the yellow emission is stronger at 20 K.

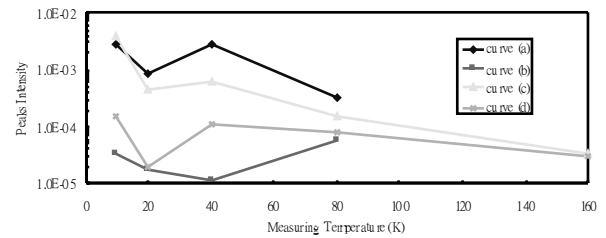


fig. 2. Temperature dependence of emission intensity for each peak. Curve (a): The free exciton (355 nm) for sample diffused at 900 °C. Curve (b): The free exciton (356 nm) for sample diffused at 1000 °C. Curve (c): The exciton bound to neutral acceptor (Ex-A) for sample diffused at 1000 °C. Curve (d): The exciton bound to neutral acceptor (Ex-A) for sample diffused at 900 °C. Note that this is plotted with logarithm scale.

Another interesting phenomenon is its free exciton line decays in a faster rate than the Ex-A. The temperature dependence of the A-exciton is more sensitive than the Ex-A. As the temperature get higher and higher, both the free exciton and the Ex-A diminish.

In the case of diffusing at 900 °C, there exists

different trend for the variation of peaks intensity. It seems that the Ex-A emission is getting to dominate and the free-exciton emission is getting extinguished as the temperature is increasing.

Figure 3 shows the power density dependence of peak position for the free exciton and Ex-A line. As can be seen from the plot, the free exciton keeps at 3.483 eV when the power varies from 0.2 to 0.8. This is because the temperature variation is not very large. If we measured the PL until room temperature, it is believed that the peak will shift toward the direction of long wavelength⁹ at higher temperature..

$$E_g = 3.503 + (5.08 \times 10^{-4} T^2) / (T - 996) \quad (1)$$

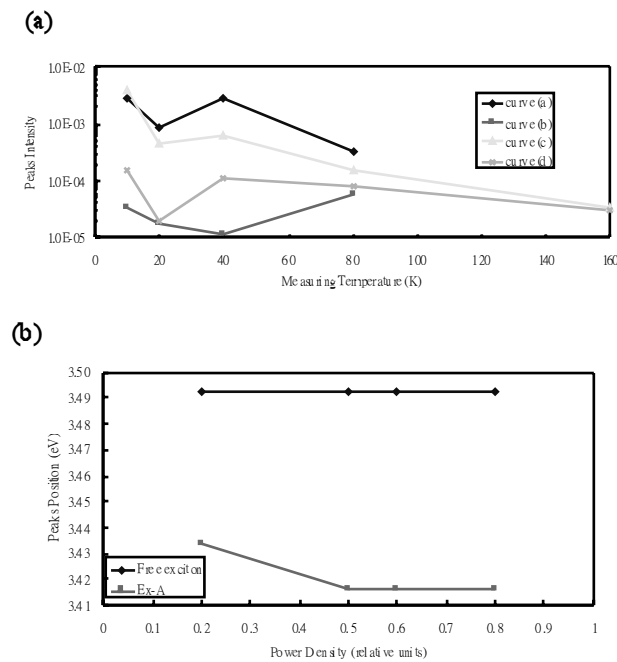


Fig 3. (a) The excitation power dependence of peaks position for free exciton and Ex-A lines. This plot is obtained by measured the 1000°C diffused GaN film at 10 K. The power density is relative units. (b) The same but diffusion at 900 °C and measured at 80 K.

However the Ex-A mode doesn't show the same

result. It tends to decay as power is increasing and has a minimum value at 0.5 unit in this experiment. This phenomenon is very similar to the Cd-doped GaN made by VPE⁸, but the photon energy of free-exciton in Fig3-(b) is higher than ever reported. The binding energy of D-A pair can be calculated to be ~22.7 meV by the following equation:

$$E_B = E_g - E_D + E_C - E_{peak} \quad (2)$$

Figure 4 represents the excitation power dependence of the PL intensity. The free exciton line is increasing as the excitation is increasing. But the Ex-A line has a minimum intensity at 0.4 power unit. It means that the different excitation power may result in different emission mechanism.

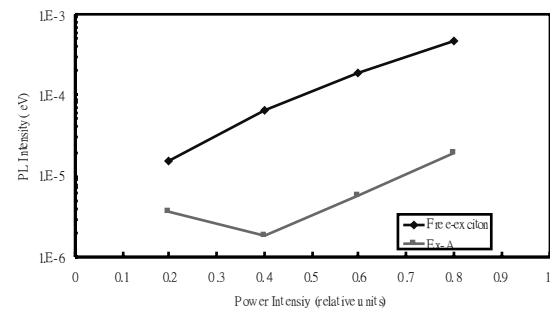


Fig 4 The power density dependence of PL intensity for the 1000°C diffused GaN film which is measured at 20 K. Note that this is plotted with logarithm scale.

Conclusions:

An ex-situ doping technique of GaN is adapted in this experiment which is proven to be valid. PL measurement at variant temperatures and excitation power density are made systematically. The results show that the free-exciton emission in our works is higher (3.493 eV at 10 K) than any being reported. The Ex-A emission has lower intensity when the excitation power is at 0.4 power unit. And the deep level related yellow band emission is the main mechanism at 20 K. The diffusion

occured at 900 °C and 1000 °C both have a D-A pair binding energy of 22.8 meV.

Acknowledgement:

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