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The doping of GaN with Mg diffusion

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Abstract

The characteristics of GaN films diffused with Mg were studied. The undoped GaN films were grown by metalorganic chemical vapor deposition (MOCVD). The photoluminescence (PL) spectra of Mg diffused GaN showed a broad violet emission. The Mg-diffused GaN was p-type conductivity with a mobility of 13 cm^2/V-s and a hole concentration of $3 \times 10^{15}/cm^3$ at a diffusion temperature of 1100°C. However, the samples, which were diffused at 1100°C, showed a red emission peak after the annealing process. From the diffusion depth profile observed by secondary ion mass spectrometry (SIMS), we obtained the activation energy of 1.3 eV for Mg diffusion in GaN.

1. Introduction

The wide-band-gap semiconductor GaN shows promise for application in blue light-emitting diodes (LEDs) and laser diodes (LDs). The viability of any photonic or electronic device technology depends on developing controlled doping techniques either during growth or subsequently using diffusion or ion implantation. The formation of p-type GaN films is the key technology in developing these emitting devices. High p-type doping concentration ($10^{18}/cm^3$) has been achieved in GaN, if Mg dopant is injected into the growth chamber during the epitaxial growth [1a–b, 2, 3]. However, the as-grown Mg-doped GaN films show high resistivity and need thermal activation to convert the GaN to be p-type conductivity [1a–b]. In 1991, Nakamura indicated that thermal annealing activated the Mg-doped GaN into p-type conductivity with a hole concentration and mobility of $3 \times 10^{18}/cm^3$ and 9 cm^2/V s, respectively [1a–b]. Doping by diffusion is a conventional integrated circuit processing technique. For GaN, there has been little diffusion study reported. Rubin et al. developed p-type GaN by diffusion of Mg with a hole concentration and mobility of $2 \times 10^{16}/cm^3$ and 12 cm^2/V s, respectively [4]. In this paper, we will report on the observation of photoluminescence (PL), secondary ion mass spectrometry (SIMS) and Hall measurement results of diffusion of Mg dopants in GaN.

2. Experiments

GaN films about 0.48 μm thick were grown on sapphire substrates by metalorganic chemical vapor deposition (MOCVD) with a GaN buffer layer. Vapor phase diffusion was carried out in a furnace with a sealed quartz tube, which was evacuated to be about 1×10^{-5} Torr. The diffusion source was 99.99% Mg. Furthermore, the diffusion temperature was maintained at 1000 or 1100°C for 1 h. After diffusion, the surface was cleaned with HNO_3. The electrical characteristics of GaN were measured by Hall effects at room temperature. The as-grown undoped n-type GaN have an electron concentration of $3 \times 10^{18}/cm^3$ and a mobility of 80 cm^2/V s. Contacts to the diffused GaN were formed using Ni/Au as the metals [5]. Before loading the samples in the evaporating chamber, the samples were cleaned by $HCl:H_2O$ (1:1) solution. Then the metal was deposited sequentially with Ni and Au at the thickness of 15 and 75 nm, respectively. The contacts were alloyed in an AG Associates Heatpulse 410

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rapid thermal annealer (RTA) at 500°C for 60 s in a nitrogen ambient. The experimental apparatus for Hall measurement included a high-impedance current source (Keithley Model 224). The Hall voltage was measured using a digital voltmeter (HP 34401A) whose input impedance was set to be greater than 10 GΩ. The magnetic field was 0.5 T and the input current was 0.1 μA. The photoluminescence (PL) was measured by using a focused beam of a He–Cd 325 nm laser. The incident laser power density on the sample was estimated to be 18 kW/cm^2. The luminescence from the sample was collected into an ARC SP500 monochromator. A Hamamatsu R928 photomultiplier tube (PMT) was utilized to detect the dispersed luminescence, and a Stanford Research Systems SR850 lock-in amplifier with an SR540 optical chopper was used to amplify the signals from the PMT. The sample was mounted on the cold finger of a CTI closed-cycle liquid-helium cryostat. Secondary ion mass spectrometry (SIMS) was used to measure the Mg dopants and depth distributions of diffused GaN.

3. Results and discussion

The Hall measurement results indicate that the Mg-diffused GaN is a p-type material. Fig. 1 shows the room temperature and 20 K PL spectra of Mg-diffused GaN which were diffused at 1000 and 1100°C. There is no near-band edge emissions and yellow luminescence. These PL spectra show only one broad violet emission at approximately 400 nm for room temperature measurement and about 390 nm at 20 K for 1000°C diffused samples. The full width at half maximum (FWHM) of the violet emissions at 20 K is 96 nm. These emissions might be attributed to the transition between the shallow-level donor state, at about 30 meV below the conduction band [6], and the Mg-related acceptor level which is about 250 meV above the valence band [7–9]. The sample diffused at 1000°C has a hole concentration of 1×10^{14}/cm^3. The resistivity of this sample is very high (~700 Ω cm), thus the derived mobility has the value between 30 to 300 cm^2/V s. Fig. 1 also shows the room temperature and 20 K PL spectra of Mg-diffused GaN which was diffused at 1100°C. The violet emissions are observed to be at approximately 410 nm at room temperature and approximately 400 nm at 20 K. The FWHM of the violet emissions at 20 K is 116 nm. The peak position (wavelength) is longer and the FWHM is wider than the sample diffused at 1000°C. The 20 K PL for an as-grown Mg-doped GaN is similar to these observation with peak wavelength at 430 nm and FWHM of 44 nm [10]. These violet emissions might be attributed to the transition between the interstitial Mg atoms which become impurity donors and the Mg-related acceptor level. A similar phenomenon was observed in Zn-diffused InP [11]. The sample diffused at 1100°C has a hole concentration of 3×10^{15}/cm^3 and a mobility of 13 cm^2/V s. There are weak red emissions (600 nm)

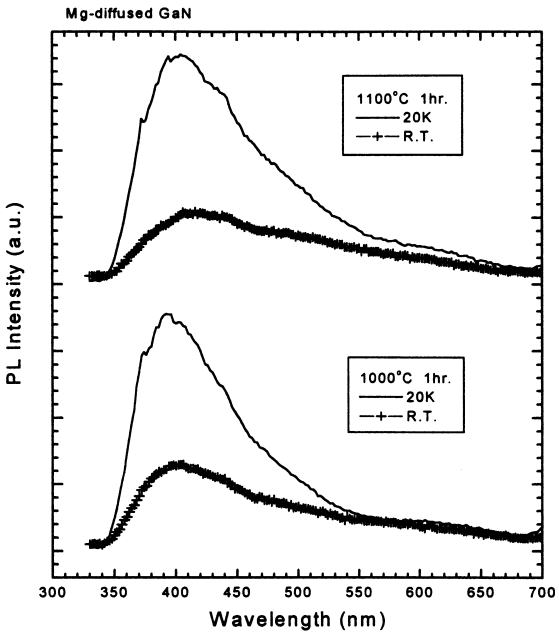

Fig. 1. Room temperature and low temperature photoluminescence spectra for Mg-diffused GaN.

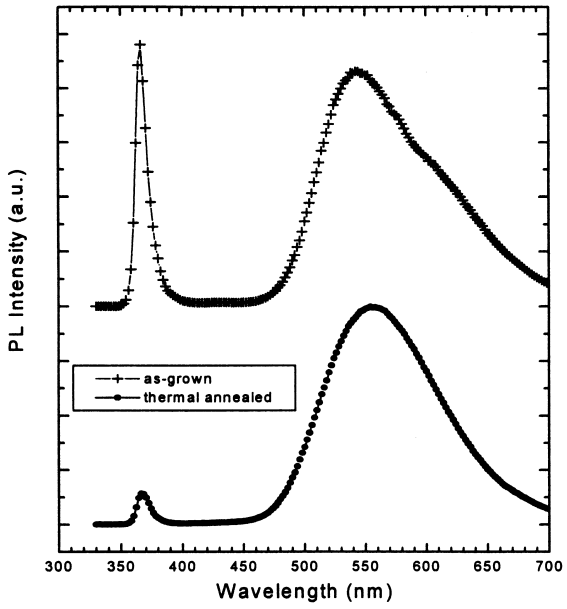

Fig. 2. Room temperature photoluminescence spectra for as-grown undoped GaN and GaN treated with diffusion at 1100°C without Mg source.

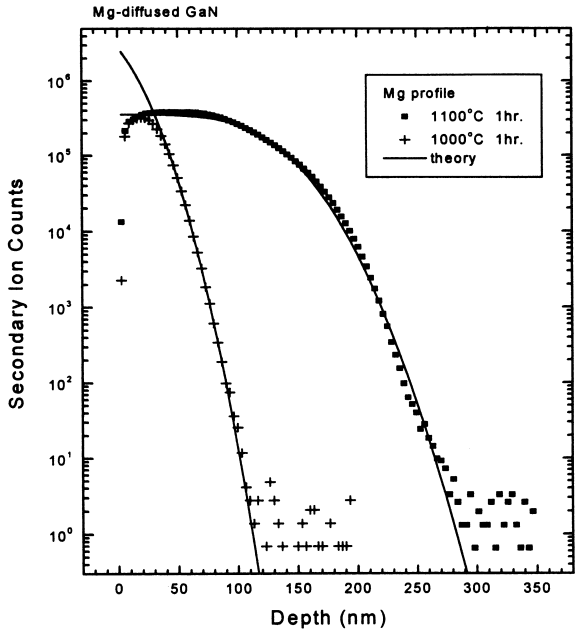

Fig. 3. The SIMS profiles for Mg-diffused GaN.

shown in 20 K PL spectrum for the sample diffused at 1100°C. The red emissions might be associated with the annealing induced thermal damage [7]. Samples diffused at 1100°C generate more surface damage than samples diffused at 1000°C.

Fig. 2 shows the room temperature PL spectrum of GaN which was treated with the same diffusion process (annealed at 1100°C) without Mg source. The PL spectrum of as-grown undoped GaN was also shown in Fig. 2. There are near-band-edge emissions and yellow luminescence for both samples. The intensity ratio between the 365 nm and the 550 nm emission line is changed due to thermal annealing. For the annealed sample, the near-band-edge emissions peak is less than the yellow luminescence. This result might be associated with the damaged surface, since the diffused sample went through the high temperature and low pressure annealing processing.

Fig. 3 shows the SIMS profiles of diffused GaN. The curved part of every profile can be fitted with a complementary error function. Based on this error function fitting, we obtain the diffusion constant D of diffusion at 1000 and 1100°C to be 4.6 and 10.5 nm^2/min, respectively. In general, the diffusion constant can be described by the following equation [12]:

$$D = D_0 \exp\left(-\frac{E}{kT}\right)$$

where D_0, E, k and T are the frequency factor, the activation energy, the Boltzmann's constant and the temperature, respectively. From our experimental results, we derived the activation energy to be 1.3 eV. In cubic structure, the activation energy for interstitial diffusion is between 0.5 and 1.5 eV and the activation energy for vacancy diffusion is between 3 and 5 eV [12]. The diffusion mechanism in GaN therefore might be an interstitial diffusion process.

4. Summary

In conclusion, we report the PL, SIMS and Hall measurement results of Mg-diffused GaN at a diffusion temperature of 1000 or 1100°C for 1 h. The Mg-diffused GaN displays a violet photoluminescence similar to an as-grown Mg-doped GaN PL spectrum. The sample diffused at 1100°C has a higher hole concentration and more surface damage than the sample diffused at 1000°C. The activation energy of the Mg dopants of diffusion is 1.3 eV.

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