p-Type conversion of Si-doped n-type GaN epilayers due to neutron transmutation doping and annealing

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Recently, the successful growth of a high quality p-type GaN epilayer has generated interest in their applications to optoelectronic devices operating from the visible to the ultraviolet spectral region at room temperature [1–5]. The uniform carrier density and the high mobility in the GaN epilayer are very important for improving device efficiency [6, 7]. However, when p-type GaN epilayers are highly doped with Mg, since the deep trap level due to the Mg atoms passivates the carriers [8], it is difficult to achieve a high hole concentration above 4×10^{17} cm^{-3} due to self-compensation [8]. Thus, neutron transmutation doping method is a good technique for obtaining a high carrier density in GaN epilayers because it can dope the impurities uniformly, control the impurity concentration accurately, and activate the carriers with a relatively low-temperature thermal treatment [9, 10]. When neutrons irradiate a semiconductor, defect levels, such as interstitials or antisites, are formed in the semiconductor and those defect levels induce a high resistivity or a type conversion [11–13] due to the existence of non-radiative centers and antisites. However, these inherent problems with neutron-transmutation-doped (NTD) semiconductors can generally be overcome through thermal processes.

This letter reports optical data for NTD and annealed Si-doped GaN epitaxial layers grown on sapphire substrates by using plasma-assisted molecular-beam epitaxy (PAMBE). Photoluminescence (PL) measurements were performed to investigate the behavior of the defect levels formed in neutron-transmutation-doped Si-doped GaN after annealing, and Van der Pauw Hall-effect measurements were performed to determine the carrier density and the mobility of the samples. Secondary-ion mass spectroscopy (SIMS) measurements were carried out in order to investigate the composition of the NTD and annealed GaN epilayer.

The Si^{30} isotope-doped ($n \cong 1 \times 10^{17}$ cm^{-3}) GaN epilayers used in this study were grown on sapphire substrates using a PAMBE system. An inductively coupled radio-frequency plasma source provided the reactive nitrogen from nitrogen gas with a purity of 99.9999% while Ga and Mg with purities of 99.9999% were evaported using conventional effusion cells. Prior to the GaN film growth, the surfaces of chemically cleaned substrates were exposed to an activated nitrogen beam for 10 min in order to cover them completely with nitridated layers. The deposition of the GaN active layer on the 300-Å-thick GaN buffer layer, which was grown at 550 °C, was carried out at a substrate temperature of 750 °C, and its growth rate was approximately 0.28 μm/hr. The typical thickness of the GaN active layer was 600 nm.

To determine the fluences of the thermal neutrons, we inserted an Au-Al wire into the chamber together with the GaN epilayers. A Ge-Li radiation detector (EG & G ORTEC, GMX-25190P) was used to identify the NTD behavior. The fluences of the thermal neutrons relating to the doping of impurities into the GaN epilayer were 1.09×10^{19} and 1.97×10^{20} cm^{-2}. The NTD GaN epilayers were annealed at 1000 °C for between 1 and 6 hrs in a nitrogen atmosphere. To determine the carrier concentration, the mobility, and the resistivity, we performed a four-point probe and van der Pauw Hall effect measurements. Van der Pauw Hall-effect measurements were carried out at room temperature in a magnetic field of 0.5 T using a Keithley 181 nanovoltmeter. Ohmic contacts to the samples for the Hall effect measurements were made by diffusing a small amount of indium through the undoped GaN epilayers at 600 °C in a hydrogen atmosphere for approximately 10 min. The PL measurements were carried out using a 75-cm monochromator equipped with an ultraviolet-sensitive photomultiplier tube. The excitation source was the 3250-Å line of a He-Cd laser, and the power density of the laser was 20 mW. The samples were mounted on a cold finger in a cryostat, and the temperature was controlled at 11 K using a He displex system.

Figs 1 and 2 show PL intensities at 12 K for (a) as grown Si-doped GaN epilayer and the NTD (fluences = 1.09×10^{19} and 1.97×10^{20} cm^{-2}) Si-doped GaN epilayers annealed at 1000 °C for (b) 1 hr, (c) 2 hrs, (d) 3 hrs, (e) 4 hrs, (f) 5 hrs, and (g) 6 hrs. The PL spectra at 12 K for the as-grown Si-doped GaN epilayers show only the luminesence peak corresponding to the donor-acceptor pair (DAP) transition [14]. The DAP transition peak disappears after NTD treatment. When

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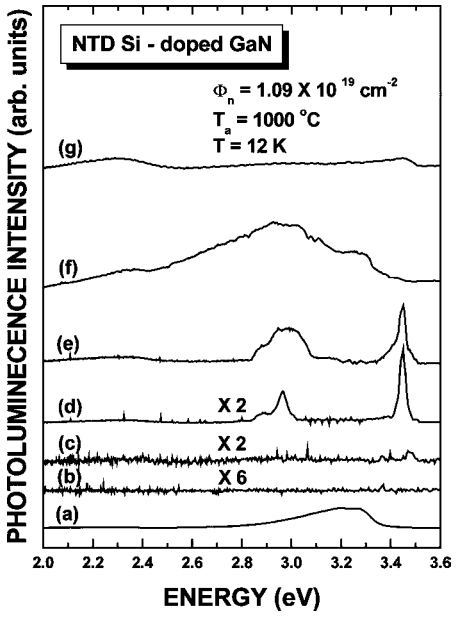

Figure 1 Photoluminescence intensity at 12 K for (a) the as grown Si-doped GaN epilayers the NTD (fluences = 1.09×10^{19} cm^{-2}) Si-doped GaN epilayers annealed at 1000 °C for (b) 1 hr, (c) 2 hrs, (d) 3 hrs, (e) 4 hrs, (f) 5 hrs, and (g) 6 hrs.

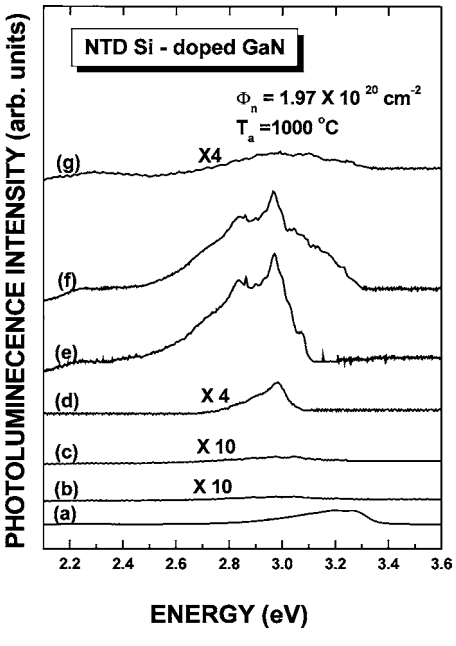

Figure 2 Photoluminescence intensity at 12 K for (a) the as grown Si-doped GaN epilayers and the NTD (fluences = 1.09×10^{19} cm^{-2}) Si-doped GaN epilayers annealed at 1000 °C for (b) 1 hr, (c) 2 hrs, (d) 3 hrs, (e) 4 hrs, (f) 5 hrs, and (g) 6 hrs.

neutrons enter into a Si-doped GaN epilayer, they interact with either impurities or carriers bound in the complex level inside the GaN epilayer [15]. When the NTD samples are annealed at 1000 °C, a new peak at 2.97 eV appears. When the NTD Si-doped GaN epilayers are annealed at 1000 °C for 3 hrs, a peak at 3.44 eV, which is attributed to neutral acceptor-bound excitons (A^0, X) [16], appears together with the DAP transition peak. The peak intensity of the (A^0, X) increases with increasing annealing time. The peak at 2.97 eV is attributed to neutron-transmuted acceptors, and this behavior is related to Ga_N atoms being transmutated to Ge_N atoms during neutron irradiation [17]. Since N vacancies are easily created as the annealing time or temperature increases, Ga or Ge atoms move into the N vacancies rather than the Ga sites.

The resistivity, the carrier concentration, the mobility, and the carrier type at 300 K for as-grown Si-doped GaN epilayers and Si-doped GaN epilayers after NTD at fluences = 1.09×10^{19} and 1.97×10^{20} cm^{-2} and annealing at 1000 °C are summarized in Table I. The carrier densities of the NTD and annealed Si-doped GaN epilayers determined from the Hall-effect measurements are much smaller than the magnitudes of the total irradiated fluxes, and this behavior originates from low transmutation efficiency. Furthermore, n-type GaN epilayers are transformed to p-type GaN epilayers due to NTD and annealing treatment, which is confirmed by the PL measurements. The resistivity of the NTD and annealed GaN epilayer is much larger than that of the undoped GaN epilayers, and is due to the transformation from an n-type to a p-type layer.

Fig. 3 shows SIMS profiles of N^+ Ga, Ge, and P for the NTD and annealed Si-doped GaN epilayer. The annealing temperature and time are 1000 °C and 5 hrs, respectively. Ga^{71} and Si^{30} are transformed into Ge^{72} and P^{31} due to neutron doping, as shown in Fig. 3. While the atomic concentration of Ge^{72} is very uniform regardless of the depth, that of the P^{31} drops by five decades with increasing depth and then rises. This behavior originates from the transformation sensitivity of the P^{31} dependency on the depth. Since the Ga^{71} atoms are transformed into Ge^{72} during the NTD process, together with the formation of N vacancies, the sum of the N and Ga atomic density is much lower than the correct value of GaN. The carrier concentration of the annealed and NTD Si doped GaN epilayers, as determined from the Hall-effect measurements, is larger than the concentration of the P obtained from the SIMS

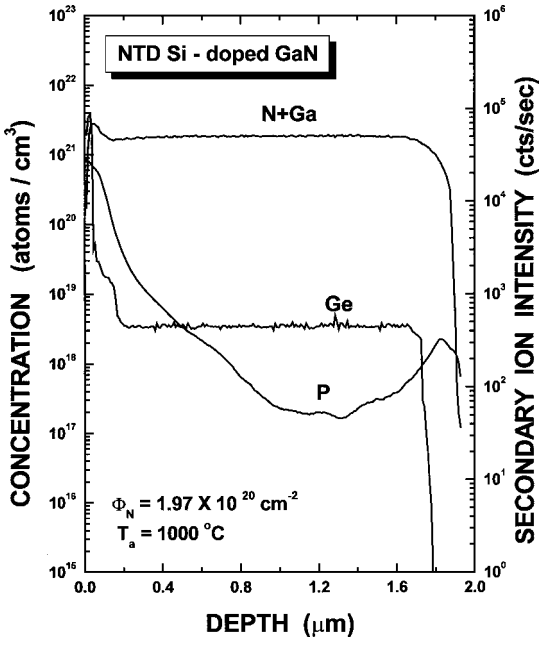

Figure 3 Secondary-ion mass spectroscopy profiles of N+Ga, Ge, and P for the NTD and annealed Si-doped GaN epilayers. The annealing temperature and time are 1000 °C and 5 hrs, respectively.

TABLE I Resistivity, carrier concentration, mobility, and carrier type at 300 K for as-grown Si-doped GaN epilayers and Si-doped GaN epilayers after neutron transmutation doping (fluences = 1.09×10^{19} and 1.97×10^{20} cm^{-2}) and annealing at 1000 °C

Annealing temperature (°C)	Annealing time (h)	Total irradiated flux (cm^{-2})	Resistivity (Ω cm)	Carrier concentration (cm^{-3})	Mobility (cm^2/Vs)	Carrier type
As-grown			2.5×10^3	7.21×10^{17}	810	n
1000	3	1.09×10^{19}	1.1×10^5	4.17×10^{16}	19	p
1000	4	1.09×10^{19}	1.1×10^4	9.76×10^{16}	11	p
1000	4	1.97×10^{20}	8.7×10^3	3.57×10^{17}	7	p
1000	5	1.97×10^{20}	5.1×10^2	8.89×10^{17}	4	p

profile. This result indicates that Ge atoms are majority carriers in the sample acting as p-type dopants.

When thermal and fast neutrons are injected into GaN epilayers, the NTD semiconductors form defect levels due to several phenomena, such as collision displacement of the core neutron, γ-recoil, and β-recoil [18]. Thus, when Si atoms are doped into GaN epilayers, some Si^{30} atoms transmute to P^{31} atoms, which occupy Ga sites with the remaining Si atoms also occupying Ga sites. The extra electrons act as donors as a result of the existence of the P at the Ga site, and the collision displacement created in the lattice due to fast neutrons changes the atomic position to antisites or interstitial sites. When an interstitial site moves to a substitutional site, the transformation from Ga^{71} to Ge^{72} during this process occurs at the Ga site, and the movement probability of the Ge^{72} for the Si-doped GaN epilayer is smaller than that for the undoped GaN epilayer. The defaults created are thought to be N vacancies due to Si doping and thermal treatment donors. Since the majority carriers of the neutron-transmuted Ge (due to thermal treatment) act as acceptors, the annealed and NTD GaN epilayers become p-type semiconductors. When the P and the Ge atoms are significantly activated by increasing the thermal treatment time, the GaN epilayer shows a high resistivity during its compensation. When the compensation process of the GaN epilayer causes a p-type GaN epilayer to be formed slowly, the resistivity of the GaN epilayer decreases, and the GaN epilayer activates electrically.

In summary, the results of the PL measurements on annealed and NTD GaN epilayers showed that the peak intensity related to NTD acceptors increased with increasing thermal treatment time. Hall-effect measurements on the samples showed that n-type Si-doped GaN epilayers were converted into p-type epilayers after NTD and annealing. SIMS depth profiles demonstrated that Ge and P atoms acted as p-type dopants. These results indicate that n-type Si-doped GaN epilayers are effectively converted into p-type GaN epilayers after NTD and annealing treatment.

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References

1. T. MORI, T. KOZAWA, T. OHWAKI, Y. TAGA, S. NAGAI, S. YAMASAKI, S. ASAMI, N. SHIBATA and M. KOITE, *Appl. Phys. Lett.* **69** (1996) 3537.
2. J. M. DELUCCA, H. S. VENUGOPALAN, S. E. MOHNEY and R. F. KARLICEK JR., *ibid.* **73** (1998) 3402.
3. J. S. JANG, I. S. CHANG, H. K. KIM, T. Y. SEONG, S. LEE and S. J. PARK,*ibid*. **74** (1999) 70.
4. J. K. HO, C. S. JONG, C. C. CHIU, C. N. HUANG, C. Y. CHEN and K. K. SHIN, *ibid*. **74** (1999) 1275.
5. TAE WON KANG, CHANG SUN CHI, SEUNG HO PARK and TAE WHAN KIM, *Jpn. J. Appl. Phys*. **39** (2000) 1062.
6. F. REN, M. HONG, S. N. G. CHU, M. A. MARCUS, M. J. SCHURMAN and A. BACA, *Appl. Phys. Lett*. **73** (1998) 3893.
7. M. S. SHUR, A. D. BYKHOVSKI, R. GASKA, M. A. KHAN and J. W. YANG, *ibid* **76** (2000) 3298.
8. U. KAUFMANN, M. KUNZER, M. MAIER, H. OBLOH, A. RAMAKRISHNAN, B. SANTIC and P. SCHLOTTER, *ibid*. **72** (1998) 1326 .
9. J. M. MEESE (ed.), in Proc. 2nd Internat. Conf. Transmutation Doping in Semiconductors, Missouri, 1979 (Plenum Press, New York, 1981).
10. J. GULDBUG (ed.), in Proc. 3rd Internat. Conf. Transmutation Doping in Silicon, Copenhagen, 1980 (Plenum Press, New York, 1981).
11. M. SATOH, K. KURIYAMA, K. YAHAGI, K. IWAMURA, C. KIM, T. KAWASKUBO, K. YONEDA and I. KIMURA, *Appl. Phys. Lett*. **50** (1987) 580.
12. M. SATOH, K. KURIYAMA and Y. MAKITA, *J. Appl. Phys*. **65** (1989) 2224.
13. P. BOGUSLAWSKI, E. L. BRIGGS and J. BERNHOLC, *Phys. Rev*. B **51** (1995) 17255 .
14. M. J. SKROMME, *MRS Internet J. Nitride Semicond. Res*. **4** (1999) 15.
15. M. S. BRANDT, N. M. JOHNSON, R. J. MOLNAR, R. SINGH and T. D. MOUSTAKES, *Appl. Phys. Lett*. **64** (1994) 2264.
16. M. SMITH, G. D. CHEN, J. Y. LIN, H. X. JIANG, M. ASIG KAHN and C. J. SUN, *ibid*. **67** (1995) 3295.
17. S. GOIN, *Phys. Rev*. **132** (1963) 178 .
18. H. D. CHO, Y. SHON, T. W. KANG, H. J. KIM, H. S. SHIM and T. W. KIM, *Phys. Stat*. (a) **146** (1994) 603.

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