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ROLE OF C, O AND H IN III-V NITRIDES

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ABSTRACT

The light ion impurities C, O and H have been implanted or diffused into GaN and related compounds and their effect on the electrical properties of these materials measured by Hall, C-V and SIMS as a function of annealing temperatures from 300-1100ºC. While C in as-grown GaN appears to create an acceptor under MOMBE conditions, implanted C shows no measurable activity. Similarly, implanted O does not show any shallow donor activity after annealing at ≤ 700°C, but can create high resistivity regions ($10^6\ \Omega/\square$) in GaN, AlInN and InGaN for device isolation when annealed at 500-700ºC. Finally, hydrogen is found to passivate shallow donor and acceptor states in GaN, InN, InAlN and InGaN, with dissociation of the neutral complexes at >450°C. The liberated hydrogen does not leave the nitride films until much higher annealing temperatures (>800°C). Typical reactivation energies are ~2.0eV for impurity-hydrogen complexes. *

INTRODUCTION

The most common impurities in GaN are probably C, O and H from the growth precursors [$(C_2H_5)_3Ga$ and NH_3] and the ambient. Past work has shown that C has a deep acceptor level in the gap and is an ineffective dopant,(1) although recent theoretical studies suggest it may have utility.(2) There has been one report of p-type GaN grown by Metal Organic Molecular Beam Epitaxy (MOMBE) in which the hole density increased with CCl_4 flow, but a completing parasitic etching reaction by the chlorine reduced the growth rate severely and a maximum role concentration of ~3×10^{17}cm^{-3} was achieved.(3)

Oxygen has been ascribed by some workers to be responsible for at least part of the residual n-type doping in most GaN,(4) although others suggest this is due to nitrogen vacancies.(5) Hydrogen is of course important for its role in passivating the electrical activity of Mg acceptors in GaN grown by Metal Organic Chemical Vapor Deposition. Both e-beam irradiation or simple thermal annealing are found to restore the electrical activity of the Mg by dissociating the neutral Mg-H complexes.(7) We have also recently found that forward bias injection of minority carriers in hydrogenated GaN p-n junctions can reactivate the Mg acceptors, a phenomenon that has also been observed for passivated B in Si and S donors in GaAs.

In this paper we report on some experiments in which C, O or H have been introduced into GaN and related materials by implantation or diffusion and the effects on the electrical properties of the material measured.

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MASTER

EXPERIMENTAL

The nitrides employed in this work were prepared in a Varian Gas Source Gen II system fitted with a Wavemat MPDR 610 ECR plasma source.(8) The nitrogen beam was generated using 200W forward power and nitrogen flows of 1-20 sccm. All layers grown on Al_2O_3 contain an initial 500Å low temperature AlN buffer grown at 425°C using 1 sccm N_2 flow. Triethylgallium III (TEG) was used as the Ga source, trimethylamine alane (TMAA) and dimethylamine alane (DMEAA) were used as the Al sources, and trimethylindium (TMI) and triethylindium (TEI) were employed as In sources.

Some samples were implanted with C^+ or O^+ ions at typical energies of 100keV and doses of 10^{14}-$10^{15}cm^{-2}$ followed by annealing up to 1100°C under a flowing N_2 ambient in an RTA system. Hydrogen was introduced by exposing the samples to either a ^1H or ^2H ECR discharge for 30 mins at 250-400°C. Carrier densities and mobilities were obtained from van der Pauw geometry Hall measurements using alloyed HgIn contacts and impurity profiles obtained from Secondary Ion Mass Spectrometry (SIMS) measurements performed at Charles Evans and Associates.

RESULTS AND DISCUSSION

(a) Carbon

We find that $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys grown by MOMBE are strongly n-type for $x \geq 0.15$ (InGaN) and $x \geq 0.3$ (InAlN), with steadily decreasing conductivity as the In concentration is decreased. High electron concentrations have also been reported for InN grown by other methods,(9) and are usually ascribed to the presence of N vacancies, although this seems less likely in light of trends observed in InN grown using various III/V ratios.(10) Furthermore, ion channeling and AES do not indicate nitrogen deficiency in these films.

Another possible explanation for the electrical behavior is the presence of unintentionally incorporated carbon. Though carbon has been shown capable of producing p-type GaN, the hole concentrations obtained have been limited to low $\sim 10^{17}cm^{-3}$ even though carbon levels are measured to be $10^{20}cm^{-3}$ or higher. It has been found in other III-V materials that the maximum hole concentration which can be obtained using carbon is related to the difference in bond strength between the group III-carbon case and group V-carbon sites. In the case of InP, the carbon actually sits on the group III site and acts as a donor resulting in n-type material. Based on this simple model, it is expected that carbon will be a donor in InN and high In concentration alloys (see Figure 1). Thus at least some of the conduction observed in these ternary films may be due to carbon. Further, as the composition is reduced in In, the tendency for carbon to act as an acceptor rather than a donor increases, thus possibly explaining the reduction in electron concentration observed with increasing Ga or Al concentration. Clearly more work is needed in this area in order for the role of carbon to be fully understood.

We also implanted C into GaN and annealed at temperatures up to 1100°C, but did not obtain p-type conductivity. Based on the results to date we find that C probably displays amphoteric behavior in the nitrides, with acceptor formation under some conditions (MOMBE-grown GaN) and possible donor action in other cases (implantation in GaN; growth of In-containing alloys).

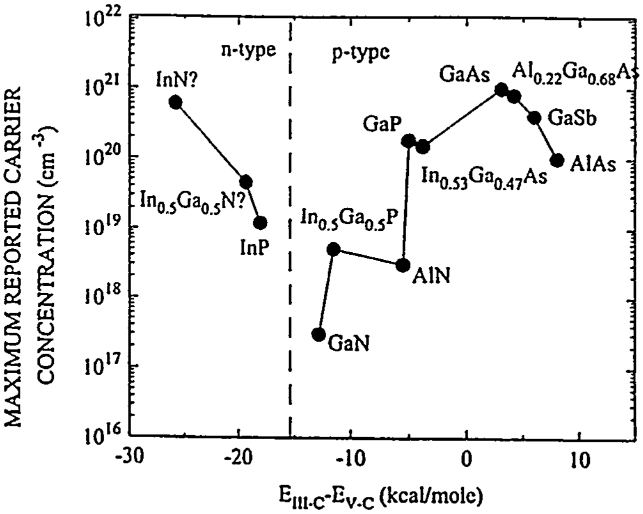

Figure 1. Maximum reported carrier concentration for materials with various group III-carbon and group V-carbon bond strengths as a function of the difference between the two bonds.

(b) Oxygen

Oxygen implantation into initially doped GaN produces damage-related compensation which is thermally stable to ≤ 750°C, and indicates that oxygen does not have a deep acceptor or donor state with high concentration in this material. InGaN which is initially n-type shows less effective implant isolation characteristics, with a maximum of a 100 fold increase(11) in sheet resistance independent of ion species after a 500°C anneal.

As seen in Figure 2, InAlN, in contrast to InGaN, can be highly compensated with N- or O-implantation with over a three order-of-magnitude increase in sheet resistance after a 600 to 700°C anneal while F-implantation produces only one order-of-magnitude increase in sheet resistance. The compensating level in InAlN is also high in the bandgap with the deepest level estimated at 580meV below the conduction band edge in high dose N-isolated material, however it is sufficiently deep to achieve highly compensated material. The enhanced compensation for N- and O-implantation in InAlN may result from a reduction in N-vacancies for N-implantation or the formation of an O-Al complex for O-implantation. An O-Al complex is thought to also be responsible for thermally stable implant isolation in O-implanted AlGaAs.(12)

When O is implanted into GaN and annealed at 1100°C, Zolper has demonstrated it creates n-type doping with an ionization level of ~29meV and poor activation efficiency (≤ 4 %).(13) The diffusivity was $\leq 2.7 \times 10^{-13} cm^2/sec$ at 1125°C.

(c) Hydrogen

By analogy with the models for neutral hydrogen-dopant complexes in other III-V semiconductors, Figure 3 shows schematic representations of the likely configurations in GaN. For donor dopants, the H occupies an antibonding position either attached to the dopant in the case of group IV donors or attached to the Ga neighbor in the case of a group IV donor.

For acceptor dopants, the H is at a bond-centered position, bonded predominantly either to the acceptor or a N neighbor, respectively, depending on whether the acceptor is from column IV or II of the Periodic Table.

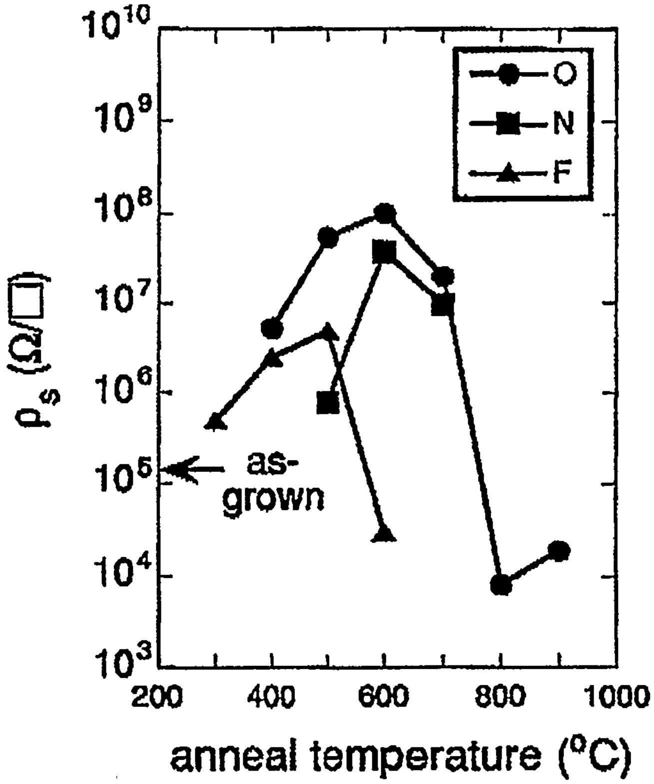

Figure 2. Sheet resistance versus anneal temperature for autodoped $In_{0.75}Al_{0.25}N$ implanted with O, N or F with an average ion concentration = $5x10^{18}cm^{-3}$.

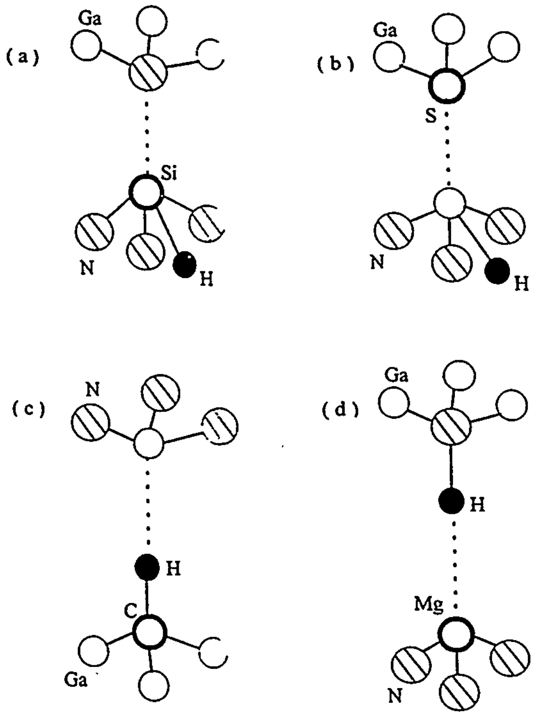

Figure 3. Schematic representation of hydrogen-dopant complexes in GaN.

The native donors in InGaN and InAlN are also passivated by association with atomic hydrogen. Figure 4 shows the fraction of passivated donors remaining in both alloys as a function of post-hydrogenation annealing temperature. Both samples displayed a decrease in carrier concentration of approximately an order of magnitude after H plasma exposure. On subsequent annealing the passivated donors begin to reactivate around 500°C. The reactivation was fit to the relation

$$No/N = 1-exp[-t\nu exp(Ed/kT)] \qquad (1)$$

where No/N is the fraction of passivated centers reactivated by annealing at temperature T for time t, ν is the attempt frequency (assumed to be $10^{14}s^{-1}$) and Ed is the activation energy for reactivation. The recovery of the donor activity occurred over a broader temperature range than generally observed for passivated dopants and was consistent with the presence of a Gaussian distribution of activation energies. We obtained values for Ed around 2.4eV with a FWHM of ~0.3eV. The hydrogen does not leave the crystal at these temperatures, but probably associates with other hydrogen atoms to form molecules and larger clusters. At much higher temperatures (> 800°C) these clusters are evolved from the sample.

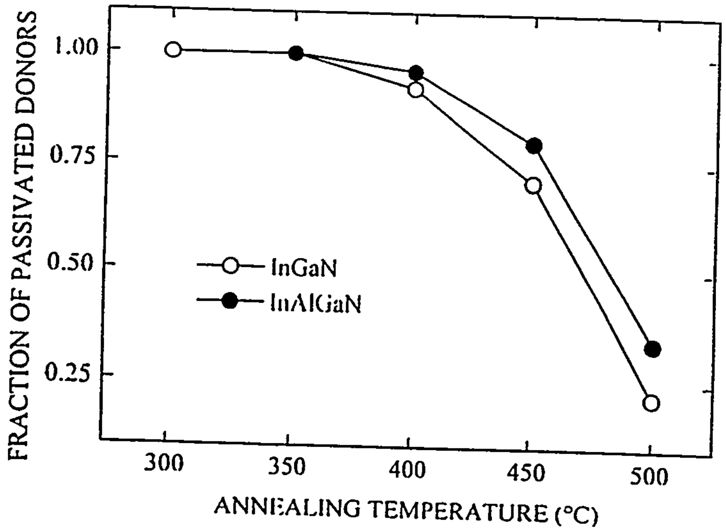

Figure 4. Fraction of passivated donors remaining in InAlN or InGaN after deuteration at 250°C and subsequent annealing at different temperatures.

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REFERENCES

1. J. I. Pankove and J. A. Hutchby, J. Appl. Phys. 47 5387 (1976).

2. S. Strite, Jap. J. Appl. Phys. 33 1699 (1994).

3. C. R. Abernathy, J. D. MacKenzie, S. J. Pearton and W. S. Hobson, Appl. Phys. Lett. 66 1969 (1995).

4. B. C. Chung and M. Gershenzon, J. Appl. Phys. 72 651 (1992).

5. R. J. Molnar, K. B. Nichols, P. Maki, E. R. Brown and I. Melngailis, Mat. Res. Soc. Symp. Proc. Vol. 378 479 (1995).

6. H. Amano, M. Kito, K. Hiramatsu and I. Akasaki, Jap. J. Appl. Phys. 28 L2112 (1989).

7. S. Nakamura, N. Iwasa, M. Senoh and T. Mukai, Jap. J. Appl. Phys. 31 1258 (1992).

8. C. R. Abernathy, J. D. MacKenzie, R. J. Shul, A. Howard and J. S. Williams, Proc. Electrochem. Soc. 95-211 (1995).

9. T. L. Tansley and C. P. Foley, Electron. Lett. 20 1066 (1984).

10. C. R. Abernathy, P. Wisk, F. Ren and S. J. Pearton, J. Vac. Sci. Technol. B11 179 (1993).

11. J. C. Zolper, S. J. Pearton, C. R. Abernathy and C. B. Vartuli, Appl. Phys. Lett. 66 3042 (1995).

12. J. C. Zolper, A. G. Baca and S. A. Chalmers, Appl. Phys. Lett. 62 2536 (1993).

13. J. C. Zolper et al. (to be published).

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