ORNL/CP-98016

DOPING OF GaN BY ION IMPLANTATION: DOES IT WORK?

A. SUVKHANOV [*], J. HUNN [**], W. WU [***], D. THOMSON [****], K. PRICE [*]
N. PARIKH [*], E. IRENE [***], R.F. DAVIS [****], L. KRASNOBAEV [*****]

[*]Department of Physics & Astronomy, University of North Carolina, Chapel Hill, NC 27599
[**]Metals and Seramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6376
[***]Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599
[****]Department of Materials Science & Engineering, NC State University, Raleigh , NC 27695
[*****]Implant Center, San-Jose, CA 95131

CONF-980405--

RECEIVED
JUN 10 1998
OSTI

ABSTRACT

Epitaxially grown GaN by metal organic chemical vapor deposition (MOCVD) on SiC were implanted with 100 keV Si^+ (for n-type) and 80 keV Mg^+ (for p-type) with various fluences from $1x10^{12}$ to $7x10^{15}$ ions/cm^2 at liquid nitrogen temperature (LT), room temperature (RT), and 700 ^{0}C (HT). High temperature (1200 ^{0}C and 1500 ^{0}C) annealing was carried out after capping the GaN with epitaxial AlN by MOCVD to study damage recovery. Samples were capped by a layer of AlN in order to protect the GaN surface during annealing. Effects of implant temperature, damage and dopant activation are critically studied to evaluate a role of ion implantation in doping of GaN. The damage was studied by Rutherford Backscattering/Channeling, spectroscopic ellipsometry and photoluminescence. Results show dependence of radiation damage level on temperature of the substrate during implantation: implantations at elevated temperatures up to 550 ^{0}C decrease the lattice disorder; "hot implants" above 550 ^{0}C can not be useful in doping of GaN due to nitrogen loss from the surface. SE measurements have indicated very high sensitivity to the implantation damage. PL measurements at LT of 80 keV Mg^+ ($5x10^{14}$ cm^{-2}) implanted and annealed GaN showed two peaks : one ~100 meV and another ~140 meV away from the band edge.

INTRODUCTION

In recent years attention to GaN related materials have risen because of potential and present applications, such as blue and ultraviolet light emitting diodes [1,2], blue lasers [3], UV detectors [4] and high-power and high-temperature FETs [5]. Regardless of the great success in the fabrication of optoelectronic and electronic devices, group III-nitrides suffer from difficulties in exhibiting the desired n- and p- type conduction [6-9]. Successful doping of GaN by ion implantation would be advantageous for device fabrication and therefore recovery of the implantation induced damage needs to be studied. So far there have been studies on ion damage generation and its partial recovery [10,11]. Additional studies are necessary to address the problem of effective doping of GaN by ion implantation. In this work we have performed implantations of Si^+ and Mg^+ in highly resistive epitaxially deposited GaN. Magnesium was chosen as the acceptor having low reported ionization energy, ~160 meV [12]. Silicon was chosen as potential n- type dopant with reported ionization level 30 - 65 meV [13,14]. Implantations of silicon and magnesium were carried out at energies so that projected range of dopants would be ~70 nm from the GaN surface. Implanted samples were capped by a layer of AlN grown epitaxially at 1000 ^{0}C by MOCVD. Subsequently, samples were annealed at 1200 ^{0}C and 1500 ^{0}C in conventional furnace for 2 hours in the argon ambient. Activation of the implanted dopants after high temperature annealing was studied by Rutherford

DISCLAIMER

Backscattering/Channeling (RBS/C), photoluminescence (PL) , and spectroscopic ellipsometry (SE).

EXPERIMENT

Epitaxial GaN films grown on AlN buffer layers previously deposited on 6H-SiC (0001) wafers and having dislocation densities on the order of 10^7 cm/cm^3 beyond 0.5μm from the initial growth interface have been achieved via chemical vapor deposition (CVD). An absence of stacking faults and twinning in the implantation regions of the films make them the best materials available for the implantation doping study. Details of growth process and resulting films parameters are discussed elsewhere [15]. The deposited films were characterized by RBS/C with 1.6 MeV and 2.0 MeV He^+ with scattering angle 165^0, and PL at low temperature (77K) in vacuum and room temperature.

RBS/C measurements for the deposited GaN resulted in χ_{min} less than 3% (ratio of aligned to random yield right after the surface peak) indicating excellent quality of MOCVD grown films. Mg^+ and Si^+ were implanted at liquid nitrogen (LT) and room temperatures (RT) , and 700 °C (HT) to study the effect of implant temperature on the generation of disorder in the film. Implantation fluences were varied from 10^{12} to $7x10^{15}$ ions/cm^2. The energies of dopants are calculated using TRIM code [16] to give an ion projected range of ~70nm. As-implanted samples were analyzed with RBS/C, PL, and SE. Selected samples were capped with ~30 nm AlN thereby preventing volatile component escape from the GaN. Capped samples were characterized with PL and SE. After this the capped samples were annealed at 1200 ^{0}C and 1500 ^{0}C in a conventional furnace in flowing Ar for 2 hours. Annealed samples were again characterized with PL and SE. He-Cd laser was used as the photoexcitation source (325 nm) for the PL experiment. The laser power was less than 100 mW. The spectrometer was a 0.85 m double-grating instrument with a GaAs PMT. The slits were 500 microns. The LT measurements were performed using a Joule-Thompson refrigirator.

RESULTS

RBS/C study of as-deposited samples of GaN showed very good channeling along the C axis. The RBS/C data demonstrated that even at the highest fluence $7x10^{15}$ ions/cm^2, a comparatively high dose, the implantation damage did not reach the random level. The Mg^+ implants showed a lower damage level compared to Si^+ implants, however the lowest dose of Mg^+ was enough to generate enough lattice damage to suppress the PL signal.

Fig. 1 (a). and Fig. 1 (b). demonstrate dependence of the level of disorder χ on the implant temperature. In the case of LT implants the induced damage level is higher than that at RT suggesting that RT implantation undergoes partial annealing. From the measured χ the HT implants reveal different processes for the generation of disorder in film with the production of a higher density of defects on the surface. This can be explained by considering a gradual degradation of the GaN surface layer with the loss of nitrogen. Thus, "hot implants" at temperatures higher than 550 °C can not be utilized to dope GaN.

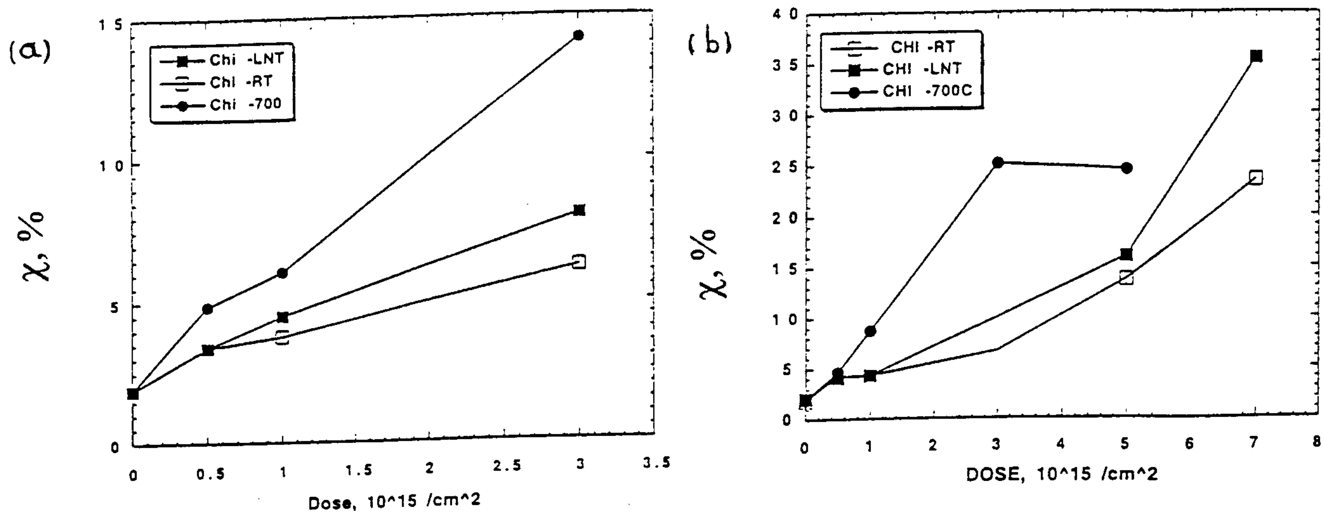

Fig. 1. Disorder (χ) from channeling for LNT, RT and 700 °C 80 keV (a) Mg^+ and (b) Si^+ implantations respectively as a function of fluence.

The RT photoluminescense of unimplanted GaN is shown in Fig. 2 (a).

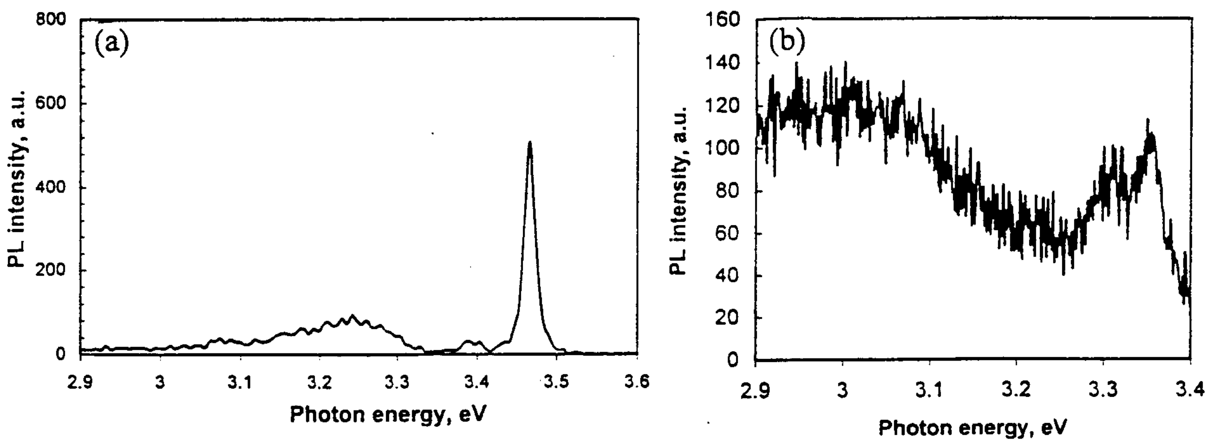

Fig. 2. PL spectra taken (a) at room temperature for as-deposited 2.3 micron thick GaN and (b) at LT for 80 keV Mg^+ implanted, dose $5x10^{14}$ cm^{-2}. The sample was capped by ~30 nm epitaxial AlN prior to annealing (1200 °C, 30 min in Ar).

As-implanted GaN sample did not give any PL signal. The peak at 3.465 eV is attributed to the recombination of excitons at neutral donors. The FWHM of the peak was 186 meV.

Mg-implanted and annealed GaN (Fig. 2 (b)) resulted in two peaks near the band edge. First peak is located ~100 meV (3.348 eV) from band edge, the second is ~140 meV (3.31 meV) away from band edge. The first peak can be related to a Mg acceptor-bound exciton. The nature of the second peak needs to be investigated. Low intensity can be justified by partial recovery of lattice damage. According to the spectra the ionization level is less than previously reported 160-200 meV [12]. We think that the the broad peak at ~3 eV is due to defect luminescence in the substrate.

Spectroscopic ellipsometry (SE) was used to measure n (refractive index) and k (damping coefficient) for virgin, as-implanted and annealed samples. The sensitivity of SE to the implantation induced damage level can be observed in Fig. 3 (a) (100 keV Si^+ implantation at LT) and Fig. 3 (b) (80keV Mg^+ implantation at LT).

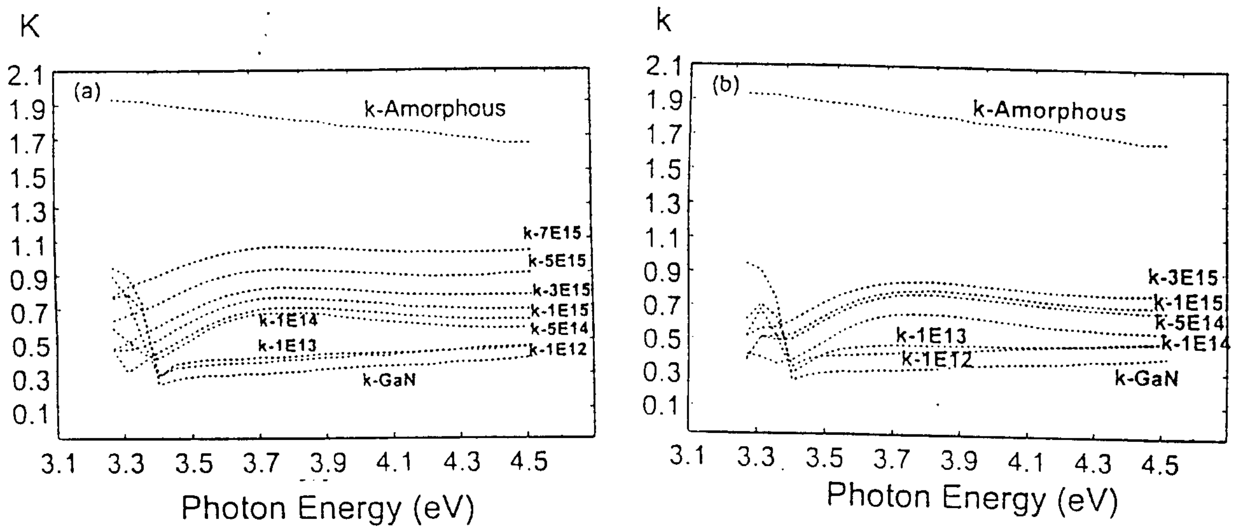

Fig. 3. Spectroscopic ellipsometry data for k for LT (a) 100 keV Si^+ and (b) 80 keV Mg^+ implanted GaN as a function of dose.

Both figures show the absorption (or damping) coefficient plotted as a function of photon energy. k increases with the implantation fluence as is expected since damage creates more photon absorbing sites. In ongoing experiments we have reduced the ion energies [17] thus making the implant shallower in order to get the SE response near vicinity (~40 nm) the implant distribution peak, so that it would give better correlation with RBS/C results. Selected implanted samples were annealed at 1200 ^oC and 1500 ^0C after capping with AlN. Our past annealing up to 1100 ^oC did not restore the PL signal. However, RBS/C results showed significant annealing at 1100 ^oC. As the temperature of the sample was increased during implantation, the damage level was reduced [17] as is shown in Fig. 4. This is expected since at high temperature one expects dynamic annealing during implantation. It presents dose dependence of k as a function of photon energy. The coefficient k can be related to damping level of the material, level of implant induced disorder. SE measurements are sensitive enough to distinguish difference in defect density created by implant fluence of $1x10^{12}$ cm^{-2} from the virgin measurements.

Fig. 4 presents the absorption coefficient k (taken at 3.7 eV) vs. implant dose for various implantation temperatures . For higher fluences dependence on implantation temperature is pronounced. The values of k presented in Figures 3- 5 were collected at the photon energies higher than E_g: GaN is almost transparent for photon energies below E_g; at energies higher than E_g the film becomes opaque, and absorption spectra for the material show features. Fig. 5. shows the influence of capping on the improvement of k values for Si and Mg implanted samples.

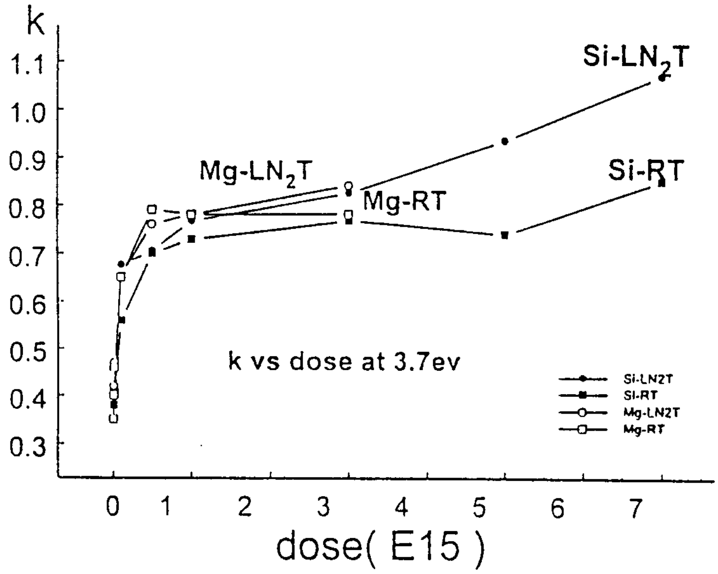

Fig. 4. Spectroscopic ellipsometry data for k for 100 keV Si^+ LT and RT implants and 80 keV Mg^+ LT and RT implants as a function of dose.

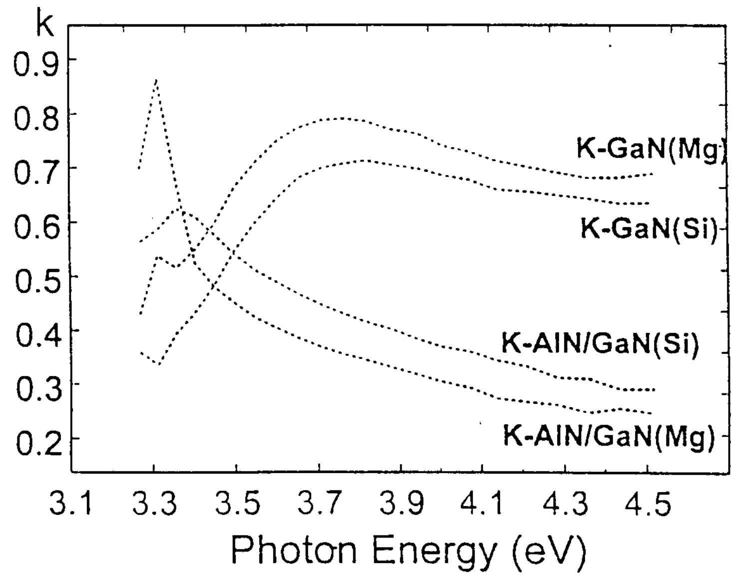

Fig. 5. Spectroscopic ellipsometry data for k for capped and uncapped GaN as a function of photon energy.

CONCLUSIONS

100 keV Si^+ and 80 keV Mg^+ with various fluences from $1x10^{12}$ to $7x10^{15}$ ions/cm^2 were implanted at liquid nitrogen temperature, room temperature, and 700 ^{0}C. RBS/C measurements showed high resistance of GaN to radiation damage. Recovery of implantation damage for high fluences are very difficult, hence to get high activation efficiency one needs to implant small fluences and anneal in between to recover the damage. Also, to optimize the damage recovery we are exploring recoil implantation concept through AlN capped layer. The HT implants, according to the measured χ_{min}, reveal different processes in the generation of disorder in the film, the production of higher density of defects on the surface due to gradual degradation of the GaN surface layer, and loss of nitrogen. Thus, "hot implants" at temperatures

higher than 550 °C can not be utilized to dope GaN. PL data for annealed capped Mg-implanted GaN resulted in two peaks near the band edge: 100 meV and 140 meV. The first peak can be related to Mg acceptor-bound exciton. The nature of the second peak needs to be investigated. This level of ionization is less than previously reported (160-200 meV). SE measurements are sensitive enough to distinguish difference in defect density for even very low (1×10^{12} cm^{-2}) implant doses.

ACKNOWLEDGMENTS

The authors are grateful to Holger Knauss, Chris Bower and Sean Rubio for their help with high temperature annealing. Special thanks to Dr. Steve Withrow (ORNL) for assistance and valuable discussions. The authors would also like to acknowledge partial support of SURA-ORAU/ORNL 1997 Summer Cooperative Research Program. Research is sponsored in part by the division of Materials Science , U.S. Department of Energy, **under contract no. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.**

References

1. H. Sakai, T. Koide, H. Suzuki, M. Yamaguchi, S. Yamasaki, M. Koike, H. Amano and I. Akasaki , Jpn. J. Appl.., 34, L1429 (1995).
2. S. Nakamura, M. Senoh, N. Iwasa and S. Nagahama, 1995 Appl. Phys. Lett., 67, 1868 (1995).
3. S . Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku and Y. Sugimoto, Jpn. J. Appl. Phys., 35, L74 (1996).
4. M. Razeghi and A. Rogalski, J. Appl. Phys., 79, 7433 (1996).
5. M. A. Khan, M. S. Shur, J. N. Kuznia, Q. Chen, . J. Burm and W. Schaff, Appl. Phys. Lett., 66, 1083 (1995).
6. B. Goldenberg, J. D. Zook and R. J. Ulmer, Appl. Phys. Lett., 62, 381 (1993).
7. C. R. Abernathy, J. D. Mackenzie, S.J. Pearton and W. S. Hobson, Appl. Phys. Lett., 66, 1969 (1995).
8. R. Kaplan, S. M. Prokes, S. C. Binari and G. Kelner, Appl. Phys. Lett., 68, 3248 (1996).
9. K. Wongchotigul, N. Chen, D. P. Zhang, X. Tang and M. G. Spencer, Mater. Letter, 26, 223 (1996).
10. H. H. Tan, J. S. Williams, C. Yuan and S. J. Pearton, MRS Symp. Proc. Vol. 395, 807 (1996).
11. J. C. Zolper, J. Of Crystal Growth, 178, 157 (1997).
12. I. Akasaki, H. Amano, M. Kito and K. Hiromatsu, J. Lumin., 48/49, 666 (1991).
13. W. Gotz, N. M. Johnson, C. Chen, H. Liu, C. Kuo and W. Imler, Appl. Phys. Lett., 68, 22 (1996).
14. J. C. Kim, A. C. Frenkel, H. Liu and R. M. Park, Appl. Phys. Lett., 65, 91 (1994).
15. T.W. Weeks, Jr., M.D. Bremser, K.S. Alley, E. Carlson, W.G. Perry and R.F. Davis, Appl. Phys. Lett. 67 (1995) 401.
16. J.F. Zeigler, J.P. Biersak and U. Littmark, in :The Stopping and Range of Ions in Matter, Vol. 1 (Pergamon, New York, 1985).
17. N. Parikh, A. Suvkhanov, M. Lioubtchenko, E. Carlson, M. Bremser, D. Bray, R. Davis and J. Hunn, Nucl. Instr. and Meth. in Phys. Res. B 127/128 (1997) 463

M98005655

Report Number (14) ORNL/CP--98016
CONF-980405--

Publ. Date (11) 199804
Sponsor Code (18) DOE/ER, XF
UC Category (19) UC-400, DOE/ER

19980702 045

DOE