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ION IMPLANTATION OF EPITAXIAL GaN FILMS: DAMAGE, DOPING AND ACTIVATION

Nalin Parikh, Agajan Suvkhanov, and Mike Lioubtchenko
Department of Physics and Astronomy
University of North Carolina, Chapel Hill, NC 27599-3255

9500473

Eric Carlson, Michael Bremser, David Bray and Robert Davis
Department of Materials Science and Engineering
North Carolina State University, Raleigh, NC 27695-7907

9521822

John Hunn
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6376

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ION IMPLANTATION OF EPITAXIAL GaN FILMS: DAMAGE, DOPING AND ACTIVATION, Nalin Parikh, Agajan Suvkhanov, and Mike Lioubtchenko, Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599-3255; Eric Carlson, Michael Bremser, David Bray and Robert Davis, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695-7907 and John Hunn, Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831- 6376.

Monocrystalline 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 0.5 μm from the initial growth interface have been achieved via chemical vapor deposition (CVD). The absence of low angle grain boundaries invariably extant in GaN films deposited on sapphire substrates and the relatively low dislocation densities and absence of stacking faults and twinning in the implantation regions of the films make them the best materials available for the study of implantation doping.

In our initial study, 160 keV Si (n-type) and 120 keV Mg (p-type) with projected range $\sim 110 \text{ nm}$ and fluences of 1×10^{14} , 5×10^{14} and $1 \times 10^{15} \text{ cm}^{-2}$ were implanted at both room temperature and 550°C . The samples were characterized by Rutherford backscattering (RBS)/channeling and photoluminescence (PL) techniques before and after implantation. RBS/channeling results of virgin and as-implanted GaN for 120 keV Mg at 550°C and $1 \times 10^{15} \text{ cm}^{-2}$ fluence showed that even at this comparatively high dose the implantation damage is very little. However the characteristic PL signal which was present before the implantation disappeared even for the lowest dose ($1 \times 10^{14} \text{ cm}^{-2}$). These samples were annealed in a rapid thermal annealing furnace at 1000°C , and damage recovery and dopant activation were measured by PL, RBS/channeling and Cross-Sectional TEM (XTEM).

INTRODUCTION:

Recent successful fabrication of first blue-green¹ and blue² injection laser diodes (LD's), high-efficiency blue light-emitting diodes³ (LED's) and field effect transistors⁴ have generated a lot of interest in III-VI compound semiconductors particularly in GaN. One of the long-standing problems in GaN research has been how to introduce shallow p-type dopant. Most potential dopants have been observed to be compensated in GaN, yielding highly resistive materials. One of the limitations in the development of wide band gap semiconductors has been the difficulty in finding suitable level dopants. Dopants may be introduced into semiconducting materials either during growth or by ion implantation. In planar device technology, ion implantation is a most promising doping technique for these materials because it allows the selective doping of certain regions and, therefore, the isolation of devices from each other. Ion implantation also offers advantages already known from silicon technology, including the introduction of nearly all elements of the periodic table and the precise control of dopant concentration and depth distribution. The major drawback of the technique is related to the lattice damage produced by the energetic ions. However, this damage can also be used beneficially as a gettering layer. For elemental semiconductors, lattice damage recovery via solid phase epitaxy has been successful; however, in a compound semiconductors native defects, e.g., antisite complexes, may be formed during the annealing which can compensate or trap charge carriers.

In early work Pankove and Hutchby^{5,6} implanted 35 elements in GaN and measured photoluminescence spectra. Out of these elements Zn, Mg, Cd, C, Li and Si (in decreasing order) gave most efficient emission when implanted with relatively low doping concentration (5×10^{18} atoms/cm³). Recently, Pearton et. al.⁷ produced n- and p-type conduction in GaN by implanting Si and Mg/P respectively. Mg implantation alone did not produce p-type conduction but when co-implanted with P produced n-to-p conversion after annealing at 1050-1100° C. The p-type conduction was determined by the sign of the Hall effect and thermal probe measurements. The authors determined that only 62% of Mg ions were activated. The effect of co-implantation was to increase Mg substitution on Ga sites relative to N sites, presumably by filling up N vacancies with the P atoms. The quality of these devices needs improvement to make them commercially acceptable. This can be achieved by optimizing implantation and annealing conditions. In this work we have attempted to address this issue by implanting potential dopants Si and Mg in epitaxial GaN samples.

EXPERIMENTAL:

As-received vicinal 6H-SiC(0001) wafers oriented 3° - 4° off-axis toward $\langle 11\bar{2}0 \rangle$ were cut into 7 mm squares. These pieces were degreased in sequential ultrasonic baths of trichloroethylene, acetone and methanol and rinsed in deionized water. The SiC substrates were then dipped into a 10% HF solution for 10 minutes to remove the thermally grown oxide layer and blown dried with N_2 before being loaded onto a SiC-coated graphite susceptor contained in a cold-wall, vertical, pancake-style, OMVPE deposition system. The system was evacuated to less than 3×10^{-5} Torr prior to initiating growth. The continuously rotating susceptor was RF inductively heated to the AlN deposition temperature of 1100°C (optically measured on the susceptor) in 3 SLM of flowing H_2 diluent. Hydrogen was also used as the carrier gas for the various metalorganic precursors. Deposition of AlN was initiated by flowing triethylaluminum (TEA) and ammonia (NH_3) into the reactor at $23.6 \mu\text{mol/min}$ and 1.5 SLM, respectively. The system pressure was 45 Torr. Each AlN buffer layer was grown for 30 minutes resulting in a thickness of ~ 100 nm. The TEA flow was subsequently terminated, the substrate temperature decreased to 950°C and the system pressure increased to 90 Torr for GaN growth. The flow rate of triethylgallium (TEG) was maintained at $24.8 \mu\text{mol/min}$. The growth rate for GaN was $\approx 0.9 \mu\text{m/hr}$. These films had a background carrier concentration of less than $1 \times 10^{16} \text{ cm}^{-3}$ as measured by capacitance-voltage. Details of the growth process and resulting films parameters are discussed elsewhere⁸. As deposited films were characterized by RBS/channeling with 1.6 MeV He^+ with scattering angle at 165° , and photoluminescence (PL) at low temperature (20 K) in UHV ambient.

After as-deposited films were characterized, the samples were implanted with 120 keV Mg^+ , and 160 keV Si^+ with fluences of 1×10^{14} , 5×10^{14} and $1 \times 10^{15} \text{ cm}^{-2}$ at 550°C and room temperature. Mg and Si were selected because of their low ionization energies for p-type and n-type conversion of GaN. The energies of Mg and Si are calculated using TRIM code⁹ to give an ion projected range of 110 nm. As-implanted samples were again analyzed with RBS/channeling, C-V, PL, and XTEM. The cross-sectional TEM samples were made after implantation by cutting two pieces of the specimen and gluing them together face on. The samples were then ground down, polished, dimpled, and ion milled. The specimen was then imaged using a TOPCON EM0002B electron microscope and a Philips CM200FEG. All cross-sectional images were taken in a $[11\bar{2}0]$ orientation.

After this the samples were annealed at 1000°C in a Rapid Thermal Anneal (RTA) furnace in Ar ambient for 60 s. During the annealing, the samples were covered by undoped GaN so that the two surfaces remained in close proximity, thereby not letting any

volatile component escape from the surface. Afterward the RTA samples were again characterized by the above-mentioned techniques.

RESULTS and DISCUSSION:

The GaN films deposited were single crystalline with very smooth surfaces except for a few random pinholes possibly caused by incomplete coalescence, as observed in plan view SEM. The PL spectra of GaN (taken at 10, 20, 30 and 40 K) shown in Fig.1 revealed an intense near-edge emission at 3.46 eV, which has been attributed¹⁰ to an exciton bound to a neutral donor. The FWHM of this peak was 3 meV.

RBS/channeling study of as-deposited samples showed very good channeling along the C axis of the GaN. The $\chi_{\min}$ (ratio of aligned to random yield near the surface) of as-deposited samples were below 3%, indicating a very high quality of epitaxial film. Fig.2 shows RBS/channeling spectra of as-implanted GaN for 120 keV Mg⁺ at 550° C with fluences of 1e14, 5e14 and 1e15 cm⁻². The figure shows that even at 1e15, a comparatively high dose, the implantation damage (near channel # 340) was very little. However the characteristic PL signal which was present before the implantation disappeared even for the lowest dose (1e14 cm⁻²). The 160 keV Si⁺ samples implanted at 550°C also showed a low damage, again even the smallest fluence (1e14 cm⁻²) was enough to extinguish the PL signal. The samples implanted at room temperature (120 keV Mg) of same fluences showed higher damage compared to samples implanted at 550°C (Fig.3). This was expected since there is some dynamic annealing of the implantation damage that occurs during the implantation.

To recover the crystalline quality and activate the dopants, samples were annealed at 1000° C for 60 s in argon ambient. RBS/channeling study revealed that some damage is removed as shown in Fig.4 for 160 keV Si implanted at 550° C and annealed at 1000° C. Even the smallest fluence implanted samples of Mg or Si after RTA at 1000° C did not show PL signal. It seems that implanting at higher temperature helps to minimize damage. However, unfortunately GaN can not be implanted much higher than 550° C since nitrogen will start escaping the film above this temperature. In this case, one needs to go to a higher annealing temperature and at the same time minimize damage by implanting in several small fluences and anneal in between.

The XTEM study of as-implanted samples (1e15 Si/cm² at 550° C) showed small damage clusters extended to ~300 nm, which is a much larger than projected range for these ions (110 nm) as shown in Fig.5. The exact nature of the damage cluster, however, could not be determined using high resolution TEM.

SUMMARY:

Single crystalline GaN films grown on AlN buffer layers previously deposited on 6H-SiC (0001) were studied for radiation damage and its recovery using RBS/channeling, PL and XTEM. The highest fluence of ($1 \times 10^{15} \text{ cm}^{-2}$) 110 keV Mg and 160 keV Si produced little damage at an implantation temperature of 550° C. The room temperature damage was higher for the same fluences compared to implantation done at 550° C. The damage was partially annealed by RTA at 1000°C, however, this was not enough to recover the PL signal even for the lowest fluence ($1 \times 10^{14} \text{ cm}^{-2}$). XTEM study of as-implanted samples revealed small clusters of defects extended beyond the projected range of the ions. To recover damage completely perhaps one needs to go either much higher RTA temperature and/or implant samples in a smaller fluence increment and anneal in between the implants to recover the damage.

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Figure caption:

Fig. 1 PL spectra of a typical GaN film at low temperatures (10, 20, 30 and 40 K) film.

Fig. 2 RBS/channeling spectra of GaN implanted at 550 °C with 120 keV Mg⁺ fluences of 1e14 (--▲--), 5e14 (--■--) and 1e15 (--●--) cm⁻².

Fig. 3 RBS/channeling spectra of GaN implanted with 120 keV Mg⁺ fluence of 5e14 cm⁻² at room temperature (--●-) and 550 °C (--▲--).

Fig. 4 RBS/channeling spectra of GaN implanted with 160 keV Si⁺ fluence of 1e15 cm⁻² at 550 °C (--●--) and RTA annealed at 1000° C for 60 s (--▲--).

Fig. 5 TEM micrograph of damaged layer of GaN implanted with 110 keV Si fluence of 1e15 cm⁻² at 550° C.

PL of a 3.7 μm GaN at 10,20,30 and 40 K

Fig. 1

Fig. 2

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Fig. 2

Fig. 3

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 Fig. 3

Fig. 4

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Fig. 4

Fig. 5

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Fig. 5

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