p-type gallium nitride by reactive ion-beam molecular beam epitaxy with ion implantation, diffusion, or coevaporation of Mg

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Gallium nitride is one of the most promising materials for ultraviolet and blue light-emitting diodes and lasers. The principal technical problem that limits device applications has been achieving controllable p-type doping. Molecular beam epitaxy assisted by a nitrogen ion beam produced p-type GaN when doped via ion implantation, diffusion, or coevaporation of Mg. Nearly intrinsic p-type material was also produced without intentional doping, exhibiting hole carrier concentrations of 5×10^{11} cm^{-3} and hole mobilities of over 400 cm^2/V/s at 250 K. This value for the hole mobility is an order of magnitude greater than previously reported.

The control of doping concentration has been a formidable challenge for researchers developing wide band gap semiconductors. To date, only four groups have reported p-type GaN: Amano[1] and Nakamura[2] achieved this goal using atmospheric chemical vapor deposition with *in situ* Mg doping. More recently, Goldenberg at Honeywell[3] achieved this goal using low-pressure chemical vapor deposition with *in situ* Mg doping. Moustakas[4] has also obtained p-type GaN using molecular beam epitaxy (MBE) with an electron-cyclotron-resonance nitrogen plasma source and *in situ* Mg doping. In this letter we show that p-type GaN can be readily formed with Mg doping when starting with nearly intrinsic single-crystal material. We have succeeded in making p-GaN using MBE assisted by a directed nitrogen ion beam together with a variety of doping techniques. p-GaN has been fabricated using conventional integrated circuit processing techniques including ion implantation, diffusion, and coevaporation of Mg. We have also produced nearly "intrinsic" p-type material directly from the chamber without intentional doping. The highest hole mobilities (>400 cm^2/V s) and lowest carrier concentrations (5×10^{11} cm^{-3}) were produced on the nearly "intrinsic" p-type films, as measured at 250 K.

The ion-beam MBE system is equipped with three Knudsen cells, used to evaporate gallium, aluminum, and magnesium, and an ion gun used to produce a beam of nitrogen ions. The Ga and Al sources were W-A Technologies Series-3 Knudsen cells, and the magnesium source is a Riber Knudsen cell. The ion source is a Commonwealth Scientific 3-cm single-grid Kaufman ion gun. The base pressure of this turbopumped system is 1×10^{-8} Torr.

The Kaufman ion gun was used in the single-grid configuration with the accelerator grid grounded, allowing for operation at a typical discharge potential of +25 V and an anode potential of +30 V. Optical emission spectra taken of the ion beam identified N$_2^+$ as the principal ion species present. A moveable Faraday cup is used to measure the ion current delivered at the substrate position. The N$_2^+$ flux from the ion gun was varied between 10^{13} and 5×10^{15} cm^2/s^{-1} during growth. A moveable quartz-crystal oscillator is used to measure the Ga flux at the substrate position which was varied between 5.1×10^{13} and 2.8×10^{14} cm^2/s^{-1}.

Prior to insertion in vacuum, the basal plane (0001) sapphire substrates were degreased in hot acetone followed by an ethanol rinse. The substrates were mounted on a molybdenum heater block using 25-μm-thick platinum foil and molybdenum clamps. Substrates were outgassed at approximately 800 °C and then cooled to the desired growth temperature. In selected experiments, the hot sapphire substrate was exposed to the ion beam with the Ga shutter closed for 15 min. This procedure, however, was not found to be necessary to obtain high-quality samples. Moustakas reported that this technique created a thin AlN surface on the sapphire substrate.[4] After deposition the nitrogen pressure was maintained at 8×10^{-4} Torr until the substrate temperature dropped below 50 °C. Growth rates of 1000–2000 Å/h were typically used to produce films with thicknesses of 3000–10 000 Å. Hall measurements were made in the Van der Pauw geometry with In contacts annealed at 300 °C. In order to perform Hall measurements on high resistivity samples, the experimental apparatus included a Keithley electrometer to monitor current and a high-impedance current source (Keithley Model 220). The Hall voltage was measured using a digital voltmeter (Keithley Model 196DMM) in conjunction with a high-impedance Quad electrometer buffer amplifier (Keithley).

Figure 1 shows the carrier concentration and mobility as determined by Hall measurements for a series of films grown at different substrate temperatures. At the elevated growth temperatures used in this study, GaN is thermodynamically unstable. Consistent with our earlier analysis,[5] the large kinetic barrier of decomposition allows crystalline film growth up to substrate temperatures of approximately 800 °C. As the temperature was reduced to 600 °C, the carrier concentration decreased to 10^{14}/cm^3 and the mobility rose to 1200 cm^2/V s. This is strong evidence that at the higher substrate temperatures, the enhanced rate of decomposition results in the formation of a significant concentration of the autodoping donor levels, presumably the nonstoichiometric defect, V_N. For substrate temperatures below 600 °C, epitaxial films are not obtained, presumably because the thermal energy was not sufficient to overcome the kinetic barriers of compound formation and epitaxial growth.

In order to minimize ion-impact damage during the film growth, the substrate to anode potential should be as small as possible. The minimum anode potential of +30 V combined with substrate biasing of +18 V is expected to reduce the
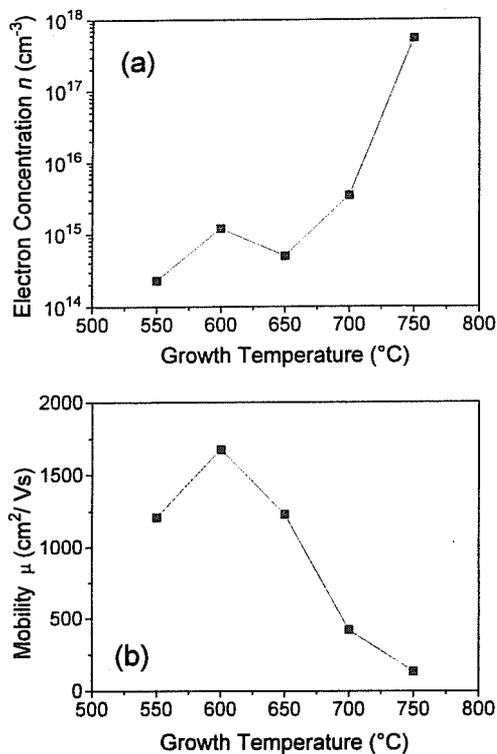
FIG. 1. (a) Hall carrier concentration and (b) Hall mobility vs growth temperature for unbiased undoped n-GaN films.

FIG. 2. (a) Hall carrier concentration and (b) Hall mobility vs measurement temperature for a biased undoped p-GaN film.

impinging N_2^+ ion energy to about 10 V. When this technique was used in combination with low temperature and high N_2^+ flux, p-GaN was obtained without intentional doping. These undoped films have hole concentrations of 5×10^{11} cm^{-3} and hole mobilities of over 400 cm^2/V s at 250 K. From the slope of the carrier concentration versus temperature shown in Fig. 2(a), an activation energy of 0.29 eV is obtained. The strong temperature dependence for the mobility [Fig. 2(b)] indicates that phonon scattering dominates the mobility at room temperature. These electrical parameters compare quite well with values for GaAs when adjusted for the strength of the electron-phonon coupling and the Debye temperature, despite the higher level of impurities in our ion-beam MBE system compared to conventional GaAs MBE and the wider x-ray peaks of the GaN films.

Diffusion of Mg into unintentionally doped n-type GaN films resulted in conversion to p-type material. The films were grown at 600 °C without substrate bias. The diffusion was performed in a sealed ampoule for 80 h at atmospheric N_2 pressures and 800 °C. Hall measurements indicated a hole concentration of 2×10^{16}/cm^3 and a mobility of 12 cm^2/V s at room temperature. Higher diffusion temperatures resulted in the removal of the film by decomposition and evaporation. Lower diffusion temperatures were not successful in converting the material to p-type.

n-type films grown at temperatures of 600 °C without substrate bias were also implanted with large doses (2.02×10^{14} cm^{-2}) of Mg using a metal vapor vacuum arc ion source.[6] High-energy (80–100 keV) Mg implants introduced strain and defects into the GaN films. Even after annealing at 800 °C for 30 min in N_2 the x-ray peaks did not return to

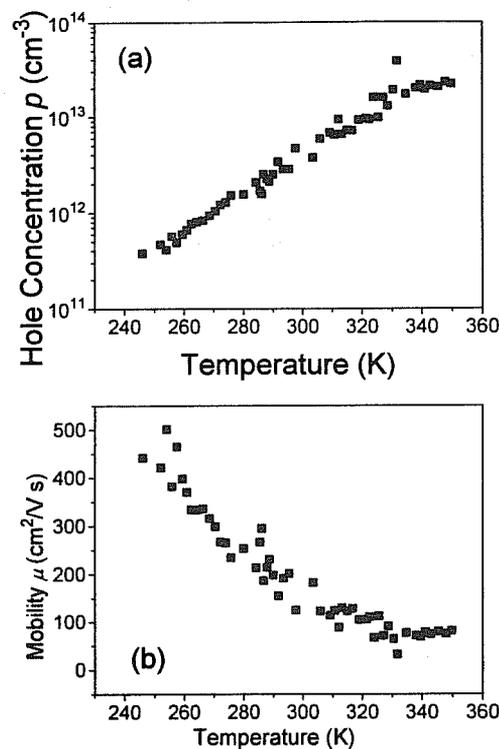their initial positions. A high concentration of midgap states were detected with optical absorption, presumably preventing the material from becoming p type by the shallow Mg dopant. Films implanted with Mg ions at lower energies (40–60 keV) recovered their original lattice parameter after annealing at 800 °C, as determined by x-ray diffraction (see Fig. 3). Hot-point probe tests confirmed that these lower energy implants produced p-type conduction. This is the first report of p-type GaN using ion implantation. Pankove implanted GaN with Mg and obtained a binding energy of 250 meV using photoluminescence,[7] but never achieved hole conduction. Room temperature resistivities of the implanted films are 4 Ω/cm. This work will be described in much greater detail in a forthcoming article.[8]
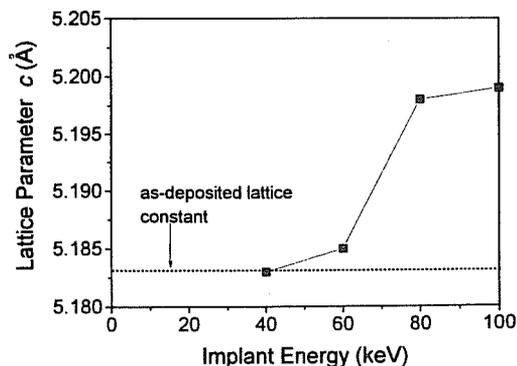

FIG. 3. Strained lattice parameters of films implanted with Mg at various energies.

Finally, a Knudsen cell for direct *in situ* coevaporation of Mg was used. At a Mg source temperature of 180 °C and a substrate bias of 18 V, the films were found to exhibit hole conduction. Hall measurements indicated a hole concentration of 2×10^{17} cm^{-3} and hole mobilities of <1 cm^2/V s at room temperature.

In summary, *p*-type conduction was obtained in ion-beam MBE films by a variety of doping methods including ion implantation, diffusion, and coevaporation of Mg. These results clearly indicate that the key to the control of hole doping lies primarily in reducing the defects in the base material.

[1] H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, Jpn. J. Appl. Phys. **28**, L2112 (1989).

[2] S. Nakamura, T. Mukai, and M. Senoh, Jpn. J. Appl. Phys. **30**, L1998 (1991).

[3] B. Goldenberg, J. D. Zook, and R. J. Ulmer, Appl. Phys. Lett. **62**, 381 (1993).

[4] T. D. Moustakas and R. J. Molnar (unpublished).

[5] N. Newman, J. Ross, and M. Rubin, Appl. Phys. Lett. **62**, 1242 (1993).

[6] I. G. Brown, J. E. Galvin, and R. A. MacGill, Appl. Phys. Lett. **47**, 358 (1985).

[7] J. I. Pankove and J. A. Hutchby, J. Appl. Phys. **47**, 5387 (1976).

[8] J. Ross, M. Rubin, X. Yao, N. Newman, and A. Moll, Ion Implantation of Mg and C into GaN Films Grown by Ion-Assisted MBE, LBL Preprint 34414, 1993 (unpublished).