Effects of proton irradiation on the magnetic properties of GaGdN and GaCrN

J K Hite$^1$, K K Allums$^1$, G T Thaler$^1$, C R Abernathy$^1$, S J Pearton$^{1,5}$, R M Frazier$^2$, R Dwivedi$^3$, R Wilkins$^3$ and J M Zavada$^4$

1 Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA
2 Naval Research Laboratory, WA, DC 20375, USA
3 Center for Applied Radiation Research, Prairie View AM University, Prairie View, TX 77446, USA
4 US Army Research Office, Research Triangle Park, NC 27709, USA
E-mail: spear@mse.ufl.edu

New Journal of Physics 10 (2008) 055005 (8pp)
Received 1 June 2007
Published 23 May 2008
Online at http://www.njp.org/
doi:10.1088/1367-2630/10/5/055005

Abstract. GaGdN and GaCrN films grown by gas source molecular beam epitaxy were irradiated with high energy (10 and 40 MeV) protons at a fluence of $5 \times 10^9 \text{cm}^{-2}$ to examine the effect on magnetization. This dose is equivalent to the exposure expected in 10 years in low-earth orbit space missions. Both photoluminescence intensity and magnetization of the films showed significant decreases with irradiation. The largest response was observed with GaGdN, which experienced a 50–60% loss in band edge luminescence and 11–83% loss in magnetic saturation. After annealing the irradiated samples at 500 °C under a nitrogen plasma ambient, both types of films experienced a complete recovery in magnetic properties. The fact that the introduction of point defects did not increase the magnetization is evidence against unpaired bonds from defects in the film being responsible for the magnetic properties in the films.

$^5$ Author to whom any correspondence should be addressed.
1. Introduction

The GaN family of materials is used in applications ranging from short wavelength (blue–UV) optical emission to power amplifiers capable of uncooled operation at high powers [1]. In particular, the ability of III-N electronic devices to operate in harsh environments makes them attractive for use in space-based systems. However, outside the protection of the earth’s atmosphere, high energy particle bombardment may cause significant degradation in device performance through creation of traps that remove free carriers. This loss of carriers will degrade conventional charge-based devices as well as potential spintronic devices based on nitrides whose magnetic properties depend on carrier density and type. For satellite applications, a major problem is the flux of high energy protons, which make up the majority of galactic cosmic rays. Although the majority of the flux lies outside most satellite orbits, a portion known as the South Atlantic anomaly dips to only 250 km above sea level off the coast of Brazil, posing a hazard for low orbit satellites [2, 3]. This effect is particularly severe in narrower gap semiconductor systems, and as a result has been shown to be responsible for reducing the useful lifetime of satellite systems. Since III-nitride systems have higher displacement energy, they are also more resistant to radiation damage. The majority of radiation studies on GaN have focused on determining the nature of native defects in the lattice [4]–[6], but a few device-based studies have also been reported [7]–[11]. Intentional exposure to high energy protons has been shown to cause slight degradation of the light emitting capabilities of InGaN-based LEDs, along with a decrease in carrier concentration [7], while lower energy protons have shown a similar trend with less change in electrical properties [8]. These effects have been explained by the formation of new recombination centers and traps due to proton displacement damage. In addition, GaN-based high electron mobility transistors (HEMTs) have also shown reduced transconductance and increased threshold voltage after proton irradiation at high energies and fluences (1.8 MeV at $<10^{14}$ cm$^{-2}$ and 40 MeV protons at $5 \times 10^9$ cm$^{-2}$), which are most likely due to carrier removal and scattering by radiation-induced deep traps [9]–[11]. The effects of irradiation of GaN on band edge photoluminescence (PL) are dependent on carrier type. Irradiation of p-GaN increases band edge luminescence, while the opposite effect is seen in n-GaN [12].

There is also potential for GaN-based materials as ferromagnetic semiconductors for spintronics applications. The use of spin-based transport opens up the possibility of devices that are nonvolatile and have increased processing speed, decreased power consumption and increased integration density [13]–[15]. The addition of dopants such as Mn or Cr at atomic per cent levels or Gd at much lower levels results in single-phase dilute magnetic semiconductors exhibiting room temperature ferromagnetism [16]–[27]. Gd doping is attractive
precisely because at these low concentrations there is less change in the basic electrical and optical properties of the GaN itself. It is important to study the effects of radiation on dilute magnetic semiconductor (DMS) materials because of the strong influence of carrier type and density. Understanding the effect of particle irradiation on magnetic behavior may help to shed light on the mechanisms responsible for the magnetic ordering observed in these materials. For example, there is a huge effective magnetic moment per Gd atom in GaN at dilute concentrations if calculated from superconducting quantum interference device (SQUID) magnetometry, which is even more pronounced in Gd-ion-implanted GaN [24]–[27]. Some recent reports have suggested that part of the large magnetization observed in GaGdN might therefore result from magnetically polarized defects [28]. In this paper, the effects of high energy (10 and 40 MeV) proton irradiation on the magnetic and optical properties of two DMS materials, GaCrN and GaGdN, are discussed. These two materials represent the two basic approaches to obtaining ferromagnetic GaN.

2. Experimental

GaCrN and GaGdN were grown by gas source molecular beam epitaxy (GSMBE) on commercially available free-standing GaN substrates. These consist of \( \sim 200 \mu \text{m} \) of undoped GaN that was initially grown on a sapphire substrate and then removed from this substrate by differential heating. These substrates are paramagnetic when tested in a Quantum Design magnetic properties measurement system SQUID magnetometer. Solid 7N gallium, 6N chromium, and 4N gadolinium heated in effusion cells, along with RF nitrogen plasma served as the source materials for growth. The films were grown to thicknesses of 2500 Å. In addition to the choice of transition metal dopant, these materials also differed in dopant concentration. The Cr content was 3 at.\%, while Gd was \( \sim 10^{16} \text{ atom cm}^{-3} \). The films were irradiated with 10 and 40 MeV protons to a total fluence of \( 5 \times 10^9 \text{ cm}^{-2} \) at the PrairieView AM Cyclotron. This fluence was chosen to be commensurate with expected radiation doses during low orbit space missions of over 10 years, and proton radiation testing is an accepted method for determining the tolerance of electronic devices to the space radiation environment [29]. At these energies, the projected range of the protons (\( >40 \mu \text{m} \) at 40 MeV) is much greater than the thickness of the epitaxial films, so they are expected to traverse into the substrate. The samples were also annealed under a \( \text{N}_2 \) plasma within the MBE chamber after irradiation to determine whether the materials would recover from irradiation damage.

The PL spectra at room temperature were taken before and after radiation using a HeCd excitation source. Magnetic behavior of the material was determined using a SQUID. All magnetic measurements were performed with the applied field parallel to the sample surface. To facilitate comparison between the films, background effects were subtracted out and the data were further normalized to volume.

3. Results and discussion

The PL spectra of the as grown films are similar to undoped MBE GaN with a broad yellow luminescence band at 2.2 eV and band edge transitions between 3.4 and 3.45 eV (inset of figure 1). The only other notable feature is an additional peak at about 1.7 eV in the GaGdN spectra. Zhou et al [30] saw a similar peak for GaGdN attributed to \( f \) level transitions, only the entire spectra was blue shifted, perhaps from the larger concentration of Gd (6\%) used in
Figure 1. Band edge luminescence normalized to as-grown values versus proton irradiation energy. The normalizing values were 1.3 for GaGdN and 0.17 for GaCrN. The inset shows a PL spectrum for as-grown GaGdN.

that study. In addition, the GaGdN signal was much larger than the GaCrN, probably due to the higher crystal quality of the GaGdN. This is a major advantage of the use of Gd doping for spintronics, compared to transition metals, in that much lower impurity concentrations are needed and this produces less compromise in material quality. Proton irradiation reduced the luminescence intensity of the samples. After irradiation, the emission from the band edge decreased with increasing irradiation energy for both materials, along with a slight red shift. GaCrN showed a less marked change in band edge emission than the GaGdN. After the 10 MeV proton exposure, the GaGdN band edge emission was cut in half, and was reduced further after the 40 MeV exposure. These results are illustrated in the plot of proton energy and band edge luminescence normalized to as grown values (figure 1). This is the same response that has been reported in n-type and undoped GaN [12]. The fact that the high Cr concentration forms an impurity band may be the reason GaCrN is less sensitive to irradiation than GaGdN, where the Gd concentration is dilute.

Figure 2 shows the dependence of saturation magnetization of GaGdN and GaCrN with increasing proton energy. After irradiation, the GaCrN films show similar degradation in magnetic saturation for the two proton energies, dropping to approximately half of the original value. The GaGdN films also show a degradation in magnetization after proton damage, especially at 40 MeV where the signal is only about 17% of the as-grown value. This contrast is further illustrated in the hysteresis loops for GaGdN before and after exposure to 40 MeV protons, shown in figure 3.

After undergoing a 30 min anneal at 500°C under nitrogen plasma, the irradiated films show a strong recovery in magnetic saturation (figure 2). This is also illustrated in the zero-field-cooled and field-cooled curves, and shows that irradiation causes a decrease in magnetic ordering for GaGdN (figure 4). The fact that point defects are induced by the proton irradiation and did not lead to an increase in magnetization is contrary to the view that defects play a role in the large magnetization observed for Gd-doped GaN. A similar degree of improvement in magnetization is also observed after annealing the non-irradiated GaCrN. Only the as-grown
GaGdN did not improve with annealing. For all samples, the remanent magnetization values of the annealed samples are slightly larger, while the coercivities of the annealed samples are slightly reduced.

The origin of magnetization in DMS films like GaCrN and GaGdN has been explained by several theories, including localized polarization of the matrix by the magnetic ions for Gd. The addition of a deep trap into the material would reduce the number of electrons, and their
Figure 4. Magnetization versus temperature curves for GaGdN exposed to 10 MeV proton irradiation before and after annealing. The curves were taken at an applied field of 200 Oe. Irradiated traces are shown as circles, and those further annealed are denoted as squares. Error bars are shown on all points.

spins, that could be incorporated into the polarization field of Gd or Cr atoms, reducing the overall magnetic moment of the samples. In this case, the dramatically lower Gd concentration would make the GaGdN material more susceptible to this effect than GaCrN. Dalpian and Wei [31] suggested from theory that electron doping from oxygen impurities was needed to stabilize ferromagnetism in Gd-doped nitrides and thus if deep traps were created by the proton damage, the conductivity and hence magnetization of the films would be reduced. In this case, additional competition for electrons by the addition of traps would make GaGdN more sensitive to radiation. The response to annealing shows that this is a recoverable process. Increasing the energy of the protons should correspond to a decrease in magnetization and luminescence, which fits the experimental data.

4. Conclusions

In conclusion, GaCrN and GaGdN films have been irradiated with high energy protons, leading to a decrease in both magnetization and PL emission intensity which was more pronounced in the case of GaGdN. Post-irradiation annealing at 500 °C recovered the magnetization to the original levels. The results are consistent with creation of deep traps that alter the conductivity of the films and reduce the radiative efficiency from the GaN.

Acknowledgments

The authors at UF acknowledge the US Army Research Office for their support of this work under contract no. W911-NF-04-10296. The authors at PVAMU would like to acknowledge the assistance of S Shojah-Aradalan, H Baffour-Awuah and the staff of the Texas AM Cyclotron

*New Journal of Physics* 10 (2008) 055005 (http://www.njp.org/)
Institute in preparing and executing the radiation experiments. The work performed by PV AMU is supported through the NASA Texas Institute for Intelligent Bio-Nano Materials and Structures for Aerospace Vehicles (NCC-01-02003), and the NASA Center for Applied Radiation Research (NCC-9-114).

References

[1] Nakamura S and Chichibu S F (ed) 2000 Introduction to Nitride Semiconductor Blue Lasers and Light Emitting Diodes (London: Taylor and Francis)

Pearton S J (ed) 1997 GaN and Related Materials (Amsterdam: Gordon and Breach)

Manesreh M O and Pearton S J 1997 GaN and Related Materials (Optoelectronic Properties of Semiconductors and Superlattices vol 2) (Amsterdam: Gordon and Breach)

[2] Stassinopoulos E G and Raymond J P 1988 Proc. IEEE 76 1423

[3] Barth J L, Dyer C S and Stassinopoulos E G 2003 IEEE Trans. Nucl. Sci. 50 466

[4] Entsev M M, Davydov V Y , Haller E E, Klochikhin A A, Koslovskii V V, Oganesyan G A, Poloskin D S, Shmidt N M, Vekshin V A and Usikov A S 2001 Physica B 308–10 58

[5] Look D C, Reynolds D, Hemskey J W, Sizelove J R, Jones R L and Molnar R J 1997 Phys. Rev. Lett. 79 2273

[6] Chow K H, Watkins G D, Usui A and Mizuta M 2000 Phys. Rev. Lett. 85 2761

[7] Khanna R, Allums K K, Abernathy C R, Pearton S J, Kim J, Ren F, Dwivedi R, Fogarty T N and Wilkins R 2004 Appl. Phys. Lett. 85 3131

[8] Osinski A, Perlin P, Schoen H, Paxton A H and Taylor E W 1997 IEE Electron. Lett. 33 1252

[9] Cai Y et al 2000 IEEE Trans. Electron Devices 47 304

[10] Luo B et al 2002 J. Electron. Mater. 31 437

[11] Hu X, Karmarkar A P, Jun B, Fleetwood D M, Schimpf R, Geil R, Weller A, White B D, Batiaev M, Brillson L J and Mishra U K 2003 IEEE Trans. Nucl. Sci. 50 1791

[12] Allums K K 2006 Proton Radiation and Thermal Stability of Gallium Nitride and Gallium Nitride Devices (Gainesville, FL.: University of Florida) Online at http://purl.fcla.edu/fcla/etd/UFE0013123

[13] von Molnar S 2003 J. Supercond. 16 1

[14] von Molnar S and Read D 2003 Proc. IEEE 91 715

[15] Awerbuch D W, Buhrman R A, Daughton J M, von Molnar S and Roukes M L (ed) 2004 Spin Electronics (London: Kluwer)

[16] Reed M L, El-Masry N A, Stadelmaier M, Ritums M E, Reed N, Parker C A, Roberts J C and Bedair S M 2001 Appl. Phys. Lett. 79 3473

[17] Thaler G T et al 2002 Appl. Phys. Lett. 80 3964

[18] Frazier R M, Thaler G, Overberg M E, Gila B, Abernathy C R and Pearton S J 2003 Appl. Phys. Lett. 83 1758

[19] Thaler G T, Frazier R M, Abernathy C R and Pearton S J 2005 Appl. Phys. Lett. 86 131907

[20] Frazier R M, Thaler G T, Leifer J Y, Hite J K, Gila B P, Abernathy C R and Pearton S J 2005 Appl. Phys. Lett. 86 52101

[21] Asahi H, Zhou Y K, Hashimoto M, Kim M S, Li X J, Emura S and Hasegawa H 2004 J. Phys.: Condens. Matter 16 S5555

[22] Teraguchi N, Suzuki A, Nanishi Y, Zhou Y K, Hashimoto M and Asahi H 2002 Solid State Commun. 122 651

[23] Dhar S, Brandt O, Ramsteiner M, Sapega V F and Ploog K H 2005 Phys. Rev. Lett. 94 037205

[24] Dhar S, Kammermeier T, Ney A, Perez L, Ploog K H, Melnikov A and Wieck A D 2006 Appl. Phys. Lett. 89 062503

[25] Han S Y, Hite J, Thaler G T, Frazier R M, Abernathy C R, Pearton S J, Choi H K, Lee W O, Park Y D, Zavada J M and Gwilliam R 2006 Appl. Phys. Lett. 88 042102

[26] Hite J K, Frazier R M, Davies J, Thaler G T, Abernathy C R, Pearton S J and Zavada J M 2006 Appl. Phys. Lett. 89 092119

New Journal of Physics 10 (2008) 055005 (http://www.njp.org/)
[27] Dhar S, Perez L, Brandt O, Trampert A, Ploog K H, Keller J and Beschoten B 2005 Phys. Rev. B 72 245203
[28] Ney A, Kammermeier T, Manuel E, Ney V, Dhar S, Ploog K H, Wilhelm K and Rogalaev A 2007 Appl. Phys. Lett. 90 252515
[29] Schwank J R, Shaneyfelt M, Paillet P, Beutler D E, Ferlet-Cavrois V, Draper B, Loemker R A, Dodd P E and Sexton F W 2001 IEEE Trans. Nucl. Sci. 48 2152
[30] Zhou Y, Kim M S, Li X, Kimura S, Kaneta A, Kawakami Y, Fujita S, Emura S, Hasegawa H and Asahi H 2003 J. Phys.: Condens. Matter 16 S5743
[31] Dalpian G M and Wei S 2005 Phys. Rev. B 72 115201