Effect of Gd implantation on the structural and magnetic properties of GaN and AlN

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Gd⁺ ions were implanted at total doses of $3\text{--}6 \times 10^{14} \text{ cm}^{-2}$ into single-crystal GaN or AlN epilayers grown on sapphire substrates and annealed at 700–1000 °C. The implanted Gd showed no detectable diffusion in either material after annealing, as measured by secondary ion mass spectrometry, corresponding to a diffusion coefficient $< 8 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. Under all annealing conditions, x-ray diffraction shows the formation of second phases. In the case of GaN, these include Gd₃Ga₂, GdN, and Gd, while for AlN only Gd peaks are observed. Both the GaN and AlN show high saturation magnetization after annealing at 900 °C ($\sim 15 \text{ emu cm}^{-3}$ for GaN and $\sim 35 \text{ emu cm}^{-3}$ for AlN). The magnetization versus temperature characteristics of the Gd-implanted GaN show a blocking behavior consistent with the presence of precipitates, whereas the AlN shows a clear difference in field-cooled and zero-field-cooled magnetization to above room temperature which may also be due to Gd inclusions. © 2006 American Institute of Physics.
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There is a strong interest in the properties of implanted rare-earth ions in wide band-gap nitrides for application in light-emitters and spintronics.^{1–15} The large band gaps of GaN and AlN allow exploitation of regions of the emission spectrum of some rare earths that are hidden in smaller band-gap host materials, and thus may have application in white-light systems that employ either color combining or phosphor pumping. Gd-implanted AlN shows intense ultraviolet cathodoluminescence at 318 nm,¹ while Er³⁺, Eu³⁺, Tb³⁺, Yb³⁺, and Tm³⁺ have also been investigated in this material, both for light emission and crystal-field splitting experiments on the high-energy states of the rare-earth ions.^{1,3,4,6,16–19} The most widely examined implanted rare-earth metal ion in GaN is Er³⁺ because of the interest in developing a temperature stable light emitter at 1.5 μm for pumping of optical fiber.^{4–11} The doping of nitrides with partially filled 4f rare-earth ions metals is also of interest as an alternative to transition metal doping for spintronics because of the possibility of above room-temperature ferromagnetism mediated either by carriers or by conduction through bands induced by the substitutional ions. Reports of Curie temperatures above 400 K and extremely large magnetic moments (much higher than the atomic moment) in Gd-doped GaN^{12–14} suggest that more understanding is needed of the behavior of this rare-earth element in the wide band-gap nitrides.¹⁵

In this letter, we report on the structural and magnetic properties of GaN and AlN implanted with subamorphization doses of Gd at room temperature. In both cases, Gd-related phases appear after annealing and may contribute to the ob-

served magnetization, especially in the case of GaN.

The GaN samples were $\sim 3 \mu\text{m}$ thick, Si-doped layers ($n \sim 10^{18} \text{ cm}^{-3}$) grown by metalorganic chemical vapor deposition on *c*-plane sapphire substrates at 1140 °C. The undoped AlN layers were grown by rf-plasma-assisted molecular-beam epitaxy at 900 °C on *c*-plane sapphire substrates and were insulating ($> 10^6 \Omega \text{ cm}$) as determined by Hall measurements. The samples were implanted using a HVEE 2 MV ion implanter with Gd ions at two energies (250 and 500 keV) with doses of either 1.15×10^{14} (250 keV) plus 2.52×10^{14} (500 keV) cm^{-2} or 2.3×10^{14} (250 keV) plus 5.4×10^{14} (500 keV) cm^{-2} . The samples were held near room temperature during the implantation, which was performed with typical beam currents of $0.1 \mu\text{A cm}^{-2}$. From visual inspection, the implanted regions were not amorphous under our conditions, as expected from

FIG. 1. SIMS profile of Gd implanted into GaN at 250 keV/ $2.3 \times 10^{14} \text{ cm}^{-2}$ and 500 keV/ $5.4 \times 10^{14} \text{ cm}^{-2}$.

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FIG. 2. XRD spectra from Gd-implanted GaN($250 \text{ keV}/2.3 \times 10^{14} \text{ cm}^{-2}$ and $500 \text{ keV}/5.4 \times 10^{14} \text{ cm}^{-2}$) annealed at either (a) 700°C and (b) 900°C .

previous reports by Kucheyev *et al.*^{20–24} on the temperature, dose, and dose rate dependence of amorphization in nitrides. Annealing was performed for 5 min under flowing N_2 gas at temperatures of 700 – 1000°C for GaN and 900°C for AlN. Powder x-ray diffraction (XRD) was used to determine the phase composition of the films. Magnetic behavior of the Gd-implanted films and their unimplanted companions was investigated using a Quantum Design Magnetic Properties Measurement System superconducting quantum interference device magnetometer. Magnetization versus applied field and magnetization versus temperature measurements were taken up to the limit of the sample holder ($\sim 350 \text{ K}$). Background effects were subtracted from the raw data and the subsequent data were normalized to volume to ensure proper comparison between films.

Figure 1 shows the secondary ion mass spectroscopy (SIMS) profile from the as-implanted GaN sample (total dose $7.7 \times 10^{14} \text{ cm}^{-2}$). The projected ranges determined by SIMS were consistent with the values expected from a stopping-and-range-of-ions-in-matter (SRIM) simulation.²⁵ No significant redistribution of the Gd could be determined in either nitride at 1000°C (GaN) or 900°C (AlN). Based on the experimental depth resolution of $\sim 100 \text{ \AA}$, this translates to an effective diffusivity of $< 8 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for Gd in the two materials at the highest anneal temperatures used for each.

Figure 2 shows the XRD spectra from the GaN implanted with Gd at a total dose of $7.7 \times 10^{14} \text{ cm}^{-2}$ and annealed at either 700°C (top) or 900°C (bottom). In both cases, there are second phases present; namely, Gd_3Ga_2 , GdN, and Gd. Based on the best available information on the heat of formation of these compounds^{26,27} and previous reports from Xiao *et al.*²⁸ on the reaction of Gd with GaN, it is expected that the reaction $\text{Gd} + \text{GaN} \rightarrow \text{Ga} + \text{GdN} + \text{Ga}_x\text{Gd}_y\text{N}$ will occur, and that the Ga can then form alloys of Gd_xGa_y .²⁷ Clearly, the Gd may then be present in a number of forms within the GaN and not simply as substitutional dopant occupying the Ga site.

FIG. 3. (a) FC/ZFC magnetization measurements with each T_B labeled for Gd-implanted GaN annealed at different temperatures ($H=100 \text{ Oe}$) and (b) M vs H at 5 and 300 K for the sample annealed at 900°C .

The magnetic properties of Gd-implanted GaN are summarized in Fig. 3. The plots on the top show all of the zero-field-cooled (ZFC)/field-cooled (FC) measurements of various annealed samples implanted with $3.67 \times 10^{14} \text{ cm}^{-2}$ total dose. We express magnetization as emu/cc using the SIMS profile calibration of Gd incorporation distance. The 900°C anneal is optimal in terms of total magnetization. The lower anneal temperatures may produce a lower magnetization through incomplete annealing of the implant damage. Previous reports have shown the importance of crystalline quality in achieving strong magnetization in transition metal-doped nitrides.²⁹ Higher anneal temperatures may lead to loss of Gd from solution. An interesting feature is the change in the “blocking temperature” (T_B) or where ZFC/FC curves meet. If we interpret the T_B as arising from superparamagnetic precipitates, we would expect the T_B to increase with annealing temperature as precipitates increase in size. However, we observe the opposite behavior, from the lowest to the highest annealing temperatures considered, which may possibly suggest a more favorable formation of non-magnetic Gd-rich alloys at higher annealing temperatures as well as loss of Gd from solution. Figure 3 (bottom) shows the magnetization (M) versus field behavior (H) at 5 and 300 K for Gd-implanted samples annealed at 900°C . Hysteretic behavior is clearly observed, consistent with ferromagnetism. Other possible explanations for hysteretic M versus H behavior that are remotely possible include superparamagnetism and spin-

FIG. 4. (a) FC/ZFC magnetization from Gd-implanted AlN annealed at 900 °C and (b) M vs H at 5 and 300 K for the same sample.

glass effects as T_B for the particular sample is found to be ~ 360 K. Magnetization measurements were also performed on the unimplanted GaN samples to eliminate the possibility that spurious transition metal impurities might be responsible for the magnetic response. These exhibited no magnetic hysteresis, showing that the Gd doping is responsible for the observed magnetization. Bulk Gd is a ferromagnetic material with Curie temperature of 308 K, while rocksalt-phase GdN is also ferromagnetic with T_C of 72 K. The observed magnetic properties may come from Gd precipitates which are likely to have a different Curie temperature than bulk Gd or from the Gd_3Ga_2 , whose magnetic properties are not known. We also cannot rule out a contribution from a true GaGdN alloy component.

The XRD spectrum from Gd-implanted AlN annealed at 900 °C showed only Gd in addition to the AlN peaks. The formation of Gd_xAl_y compounds is less energetically favored in the Gd+AlN system relative to their Gd_xGa_y counterparts.^{26,27} The magnetic data from the Gd-implanted AlN are shown in Fig. 4. Once again the magnetization shows a difference between the FC and ZFC plots to above room temperature and clear hysteretic behavior at 300 K. Dhar *et al.*¹³ suggested that Gd causes a long-range polarization of the GaN matrix, while Dalpain and Wei¹⁵ suggested from theory that electron doping was needed to stabilize fer-

romagnetism in Gd-doped nitrides. Of course, our AlN is insulating and does not contain a significant concentration of carriers. Future work should investigate whether altering the implantation temperature can reduce the tendency for Gd to remain out of solution after annealing. It is critical for most potential spintronic applications that a true dilute magnetic semiconductor forms with polarized carrier population.

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