APPLIED PHYSICS LETTERS VOLUME 79, NUMBER 21 19 NOVEMBER 2001

Characterization of high dose Fe implantation into *p*-GaN

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(Received 13 June 2001; accepted for publication 11 September 2001)

High concentrations (3–5 at. %) of Fe were incorporated into *p*-GaN by direct implantation at elevated substrate temperature (350 °C). Subsequent annealing at 700 °C produced apparent ferromagnetic behavior up to ~250 K for the 3 at. % sample. Selected area diffraction patterns did not reveal the presence of any other phases in the Fe-implanted region. The direct implantation process appears promising for examining the properties of magnetic semiconductors with application to magnetotransport and magneto-optical devices. *© 2001 American Institute of Physics.* [DOI: 10.1063/1.1420406]

The interest in the carrier-induced ferromagnetism in dilute magnetic compound semiconductors such as (In, Mn)As and (Ga, Mn)As has increased recently because of their potential application to new classes of devices based on spin-polarized transport or integration of magnetic, optical, and electronic functions on a single chip.[1–9] The ability to control the magnetic properties through application of an electric field (i.e., field gating to manipulate the carrier density) to the material has recently been demonstrated by Ohno *et al.*[10] The Curie temperatures, T_C, of (In, Mn)As (Ref. 11) and (Ga, Mn)As (Refs. 4 and 12) are relatively low (~35 and 110 K, respectively) and from practical considerations it is desirable to find materials with higher values. Recent calculations based on a Zener model of ferromagnetism predict the possibility that wide band gap systems such as (Ga, Mn)N and (Zn, Mn)O might have T_C values above room temperature.[13] Mean-field theory models suggest that the T_C's in Mn-doped compound semiconductors would be proportional to the valence band density-of-states in the host.[14]

At present, little is known about the properties of GaN heavily doped with impurities that might induce ferromagnetic behavior. Some initial reports have appeared on microcrystalline $Ga_{1-x}Mn_xN$ with Mn contents up to $x=0.05$ which exhibited ferromagnetic behavior.[15,16] Akinaga *et al.*[17] reported ferromagnetic properties at <100 K in heavily Fe-doped GaN grown by low temperature (380 °C) molecular-beam epitaxy. We have found apparent ferromagnetic behavior in Mn-implanted *p*-GaN at temperatures up to ~250 K for implanted Mn concentrations of 3–5 at. %.[18] The implantation process is a simple approach for introducing magnetic ions into different host materials and could readily be used for making selected-area contact regions for injection of spin-polarized current into device structures.

In this letter, we report on the properties of *p*-GaN implanted with Fe at doses designed to produce concentrations of 3–5 at. % at the peak of the implanted profile. The samples were annealed at 700 °C and under these conditions, they do not show any evidence of secondary phase formation, at least to the 20 Å sensitivity of transmission electron microscopy (TEM) and selected area diffraction pattern (SADP) analysis. Ferromagnetic behavior was observed in the implanted samples that is consistent with published results on epitaxial Fe-doped GaN.[17]

The *p*-GaN samples were grown by metalorganic chemical vapor deposition on Al_2O_3 substrates using triethylgallium and ammonia as precursors and Cp_2Mg as the Mg dopant source. The acceptor concentration measured by capacitance–voltage was $\sim 2\times 10^{19}\,\mathrm{cm}^{-3}$, with a hole concentration of $\sim 3\times 10^{17}\,\mathrm{cm}^{-3}$ at 25 °C due to the deep ionization level of the Mg (~170 meV). The total epilayer thickness was 4 μm. Fe^+ ions were implanted at an energy of 250 keV at a dose of $\sim 3-5\times 10^{16}\,\mathrm{cm}^{-2}$ to produce average volume concentrations of ~3–5 at. % in the top ~2000 Å of the GaN. Amorphization of the implanted region was avoided by holding the samples at ~350 °C during the implantation.[19,20] Annealing was performed at 700 °C for 5 min under flowing N_2 gas with the samples face down on another GaN wafer. The crystalline quality of the implanted regions was examined by TEM and SADP analysis, while the magnetic properties were measured in a Quantum Design MPMS superconducting quantum interference device magnetometer.

Figure 1 (top and center) shows some cross sectional TEM micrographs of the 3 at. % Fe-implanted GaN at different magnifications. There is residual disorder in the form of

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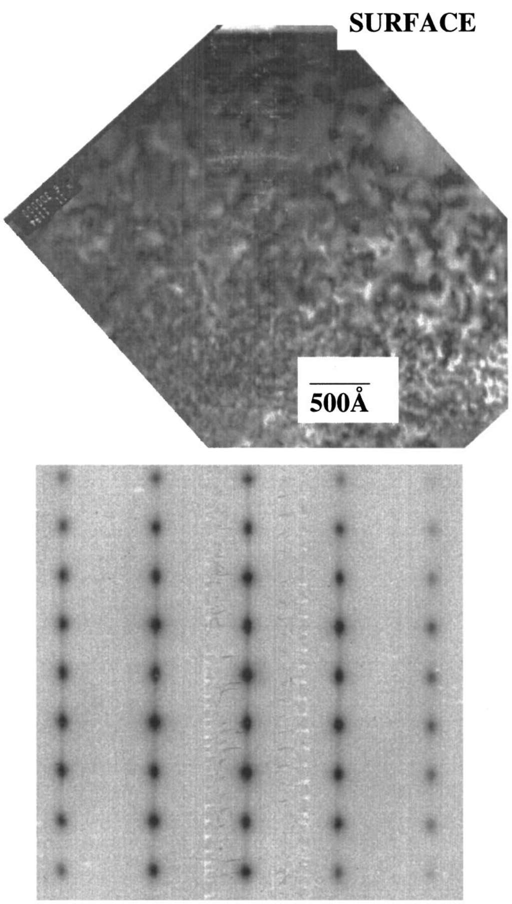

FIG. 1. Cross section TEM micrographs from GaN implanted with $3 \times 10^{16}\,\mathrm{cm}^{-2}$ Fe^{+}, after annealing at 700 °C (top and center) and SADP from the implanted region (bottom).

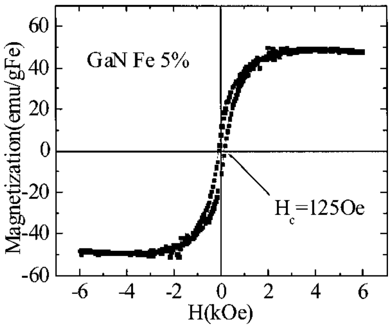

FIG. 3. Magnetization curve at 10 K of GaN implanted with $5 \times 10^{16}\,\mathrm{cm}^{-2}$ Fe^{+} and annealed at 700 °C. The coercive field is 125 Oe.

dislocation loops extending throughout the implanted region, with an increased intensity toward the end-of-range of the Fe. The total damage depth is ~0.22 μm, which correlates fairly well with the Fe incorporation depth obtained from transport-of-ions-in-matter (TRIM) simulations. The bottom of Fig. 1 shows the SADP from the implanted region. There are no obvious extra spots from secondary phase formation and only the diffraction from the GaN hexagonal crystal structure is observed. This is similar to the case of SiC single crystals implanted with Fe under the same conditions, where we also did not observe secondary phases after annealing.[21] The apparent ferromagnetic behavior cannot be attributed to superparamagnetism since we did not observe aggregation of particles within the 20 Å sensitivity of TEM. (If the size of the superparamagnetic Fe particles was 20 Å, the blocking temperature would be of the order of 1 K.) Our results are consistent with the previous molecular-beam epitaxy-grown GaN (Fe) results in which ~1 at. % of Fe was incorporated substitutionally on the Ga site and no other phases such as $\mathrm{Fe}_x\mathrm{N}$ precipitates were observed.[17] Note that it is difficult to directly compare the results here with those from Ref. 17 because we quote the total concentration of Fe introduced, which is most likely not all contributing to the magnetization.

Figure 2 shows the magnetization curve at 10 K for the 3 at. % Fe-implanted GaN annealed at 700 °C. A coercive field of 100 Oe was measured after subtracting out a diamagnetic background. Figure 3 shows the magnetization curve at 10 K from the 5 at. % Fe-implanted GaN. The coercive field for the 5 at. % Fe implanted GaN sample is slightly larger (125 Oe). The Fe implantation clearly induces a major change in the magnetic properties of the GaN, because the unimplanted material is diamagnetic. The inset of Fig. 4 shows the magnetization as a function of temperature for both field-cooled (FC) and zero-field-cooled (ZFC) conditions for the 3 at. % Fe implanted GaN, whereas the main part of Fig. 4 shows the difference in magnetization between the two conditions. The ferromagnetic contribution is present up 250 K in these samples. Our previous results on Mn-implanted GaN found a ferromagnetic contribution present below ~250 K as well, but in that case platelet-type regions were observed which were suggested to be $\mathrm{Ga}_x\mathrm{Mn}_{1-x}\mathrm{N}$.[18] The origin of the magnetic behavior in the Fe-implanted GaN is less clear, since the effective hole concentration is certainly less than the 2

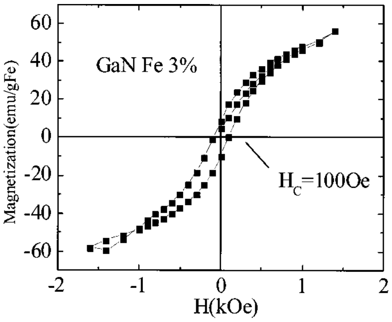

FIG. 2. Magnetization curve at 10 K of GaN implanted with $3 \times 10^{16}\,\mathrm{cm}^{-2}$ Fe^{+} and annealed at 700 °C. The coercive field is 100 Oe. For comparison, the saturation magnetization of Fe is 220 emu/g.

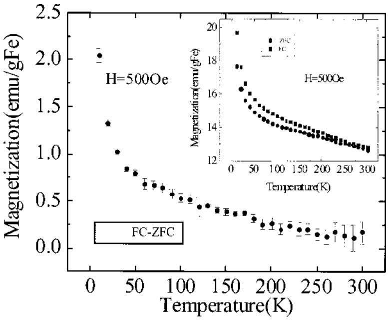

FIG. 4. Temperature dependence of the difference in magnetization per g of Fe for the 3 at. % Fe-implanted GaN sample calculated by subtracting the ZFC from the FC data. The inset shows the separate FC and ZFC curves taken at 500 Oe.

$\times 10^{17}\,\mathrm{cm}^{-3}$ present in the starting sample due to residual implant damage. The trapping of holes by these damage-related centers and the donor nature of residual damage both lead to reduced carrier concentrations. Theory suggests much higher hole densities ($\geqslant 10^{20}\,\mathrm{cm}^{-3}$) are necessary for carrier-mediated ferromagnetism.[13]

The difference between FC and ZFC curves for the 5% sample extrapolates to zero at a somewhat lower temperature. The decrease in apparent Curie temperature relative to the 3 at. % Fe-implanted GaN may be due to a lower hole concentration as a result of more residual implant-induced donor levels. Past work on the electrical effects of implant damage in GaN have established its donor nature,[22] which would reduce the hole concentration in the samples.

Since the origin of the ferromagnetism in Fe-implanted GaN is still not clear, it is difficult to compare the T_C values observed experimentally with those predicted by theory.[13] In particular, the hole concentrations in implanted material with residual damage are many orders of magnitude lower than assumed in the theoretical predictions. Hall measurements on our samples showed the hole concentration to be $\leqslant 10^{16}\,\mathrm{cm}^{-3}$. The other question is how high levels of Fe incorporation would affect the hole concentration, even in epitaxially grown material. If the Fe has a deep level energy state in the gap with a significant capture cross section for holes, then at room temperature most of the holes in the GaN would be trapped at these centers. Since the T_C is expected to be a strong function of both the Fe ion concentration and the hole density, it would be necessary to have both as high as possible. At the very least, ion implantation of different impurities into GaN is an efficient method for examining their effectiveness in creating ferromagnetism and can be used as a way of screening the various impurities and finding the most likely ones to succeed during epitaxial growth.

In summary, high dose implantation of Fe into *p*-GaN produced apparent ferromagnetism up to approximately 250 K. This behavior is consistent with previous results on epitaxial GaN(Fe). Future work should focus on the improvement in Curie temperature by increasing both Fe solubility and the hole concentration in the GaN.

The work at the University of Florida is partially supported by NSF (DMR-0101438 and DMR-9705224), while the work of one of the authors (R.G.W.) is partially supported by ARO.

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