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Magnetic and structural properties of Mn-implanted GaN

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High doses (10^{15}–5×10^{16} cm^{-2}) of Mn^+ ions were implanted into *p*-GaN at ~350 °C and annealed at 700–1000 °C. At the high end of this dose range, platelet structures of $Ga_xMn_{1-x}N$ were formed. The presence of these regions correlated with ferromagnetic behavior in the samples up to ~250 K. At low doses, the implanted led to a buried band of defects at the end of the ion range. [DOI: 10.1063/1.1376659]

There is tremendous interest in structures involving the manipulation of the spin of the electron in addition to its charge for switching and memory devices with new functionality.[1–10] Applications for these spintronic devices are envisioned in communications technology, data processing, and storage and in photonics. It has been demonstrated in a number of semiconductors (including GaMnAs, InMnAs, and ZnMnSe) that quantum spin states are quite robust and can be transported over very large distances (>100 μm in some cases).[1–10] The ferromagnetism in dilute magnetic III–V semicondcutors is carried induced and is still far from completely understood.[11,12] The Curie temperature (T_C) in these materials is believed to be governed by the interaction between localized ferromagnetic clusters (bound magnetic polarons). Recent calculations[12] suggest that wide band gap semiconductors may have T_C values well above those for GaMnAs (110 K)[10] and InMnAs (<35 K).[10] In particular, GaMnN with ~5 at. % Mn, and high hole concentrations is predicted to have a T_C exceeding 300 K.[12] At present, little is known about doping GaN with Mn, although some initial results have been published on *n*-type $Ga_xMn_{1-x}N$ single crystallites with paramagnetic behavior.[13–15]

In this letter, we report on the magnetic properties of *p*-GaN implanted with high doses (3–5 at. %) of Mn. Under optimized annealing conditions, we observe platelet regions with the same lattice structure as GaN, but different lattice constant, which give rise to Moire fringes and multiple diffraction in a transmission electron microscopy analysis. These regions, which appear to be $Ga_xMn_{1-x}N$, produce ferromagnetic behavior with a T_C of ~250 K. Thus, selected-area Mn implantation into GaN may be useful for creating spin-injection contact regions.

The GaN samples were grown by metal organic chemical vapor deposition on *c*-plane sapphire substrates. At low temperature (540 °C) GaN buffer was grown first (250 Å) followed by 4 μm of undoped GaN and 0.5 μm of *p*-GaN (Mg doped) with a room temperature hole concentration of 2×10^{17} cm^{-3}. Mn^+ ions were implanted at an energy of 250 keV and doses from 10^{15}–5×10^{16} cm^{-2} at an approximate dose rate of 8×10^{12} cm^{-2} s^{-1} to produce average volume concentrations from ~0.1–5 at. % in the top ~2000 Å of the GaN. The samples were held at 350 °C during implantation to avoid amorphization.[16–18] Subsequent annealing at 700–1000 °C was performed for 5 min under flowing N_2 gas with the samples face down on GaN wafers. The structural properties of the implanted material were examined by double crystal x-ray diffraction (XRD), and 200 kV transmission electron microscopy (TEM) with selected area diffraction analysis. The magnetic properties were measured in a Quantum Design PPMS superconducting quantum interference device magnetometer.

Figure 1 shows TEM cross sectional views of the GaN implanted with ~0.1 (top) or ~3 at. % Mn (center and bottom) and annealed at 700 °C. For the low-dose case (top), the implanted regions contain a relatively large density of lattice defects resulting from a agglomeration of point defects created by the nuclear stopping processes of the implanted ions. These samples showed only paramagnetic behavior. By sharp contrast, the samples implanted at higher doses show large (⩽200 Å diameter) platelet structures in addition to a buried band of damage at the end of range of the Mn ions. The end-of-range region is heavily-damaged single crystal. The platelet structures are shown in higher magnification at the bottom of Fig. 1. Similar structures that were on average slightly larger in diameter (⩽250 Å) were observed in the high dose samples annealed at 1000 °C.

The higher dose samples (⩾3 at. % Mn) displayed a ferromagnetic behavior persisting to ~250 K as shown in Fig. 2 for zero-field cooling (ZFC) and field-cooling (FC) conditions. The difference between these plots essentially subtracts a large diamagnetic background. As further evidence of ferromagnetic behavior, Fig. 3 shows that hysteresis was observed in the magnetic moment of the 3 at. % Mn sample. Assuming the ferromagnetism originates from the platelet

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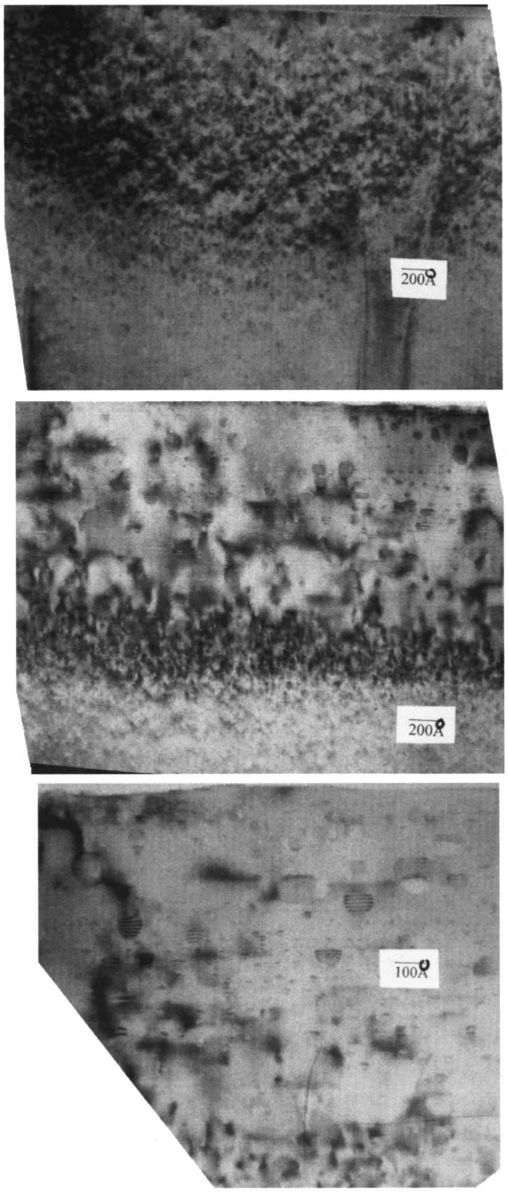

FIG. 1. TEM micrographs taken under dark-file conditions of GaN after Mn^+ implantation and subsequent annealing at 700 °C. The doses were 10^{15} cm^{-2} (top) or 5×10^{16} cm^{-2} (center and bottom) at 250 keV. The scales on the top two micrographs are 200 Å long, while in the bottom micrograph the scale is 100 Å long. The sample surface is at the top of each micrograph.

structures, we can roughly estimate the saturation magnetization to be approximately 3.8 ± 1.3 bohr magnetron per Mn.

Numerous authors have reported on the creation of submicron MnGa and MnAs ferromagnetic crystallites in GaAs by Mn^+ implantation and subsequent heat treatment.[19–23] Both of these phases have T_C values above room temperature (e.g., GaMn has a T_C between 450–800 K depending on the amount of Mn in the alloy). In addition, ferromagnetic MnAs nanoclusters embedded in GaAs can be created by annealing of $Ga_{1-x}Mn_xAs$ films.[24] In some cases, $MnGa_xAs_y$ phases are observed in addition to form ferromagnetic ternary phases. Note that for these GaAs experiments, the Mn implants were performed at room temperature, in contrast to our use of elevated substrate temperatures which should reduce the point defect density.

Figure 4 shows a plan view TEM micrograph of a 5 at. % Mn implanted sample (top), along with selective area

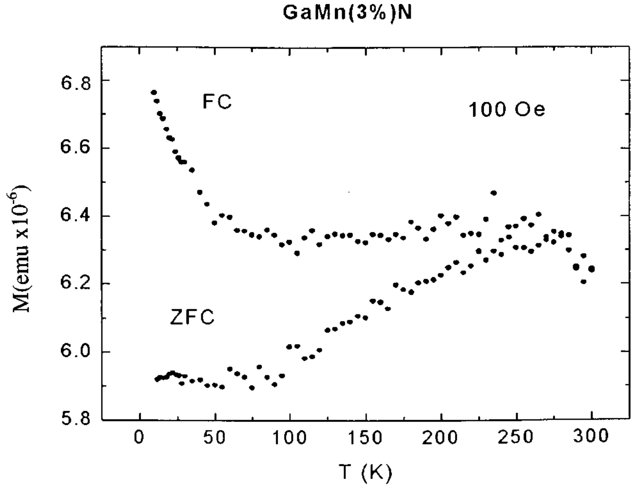

FIG. 2. ZFC and FC magnetization as a function of temperature for GaN implanted with ~3 at. % Mn and annealed at 700 °C.

diffraction pattern (bottom). The sample was thinned from the back side and the data are typical of all samples implanted with 3–5 at. % Mn and annealed at 700 °C or 1000 °C. Electron diffraction did not show any four-fold symmetry patterns, which would be expected to be present if either tetragonal (GaMn, $Mn_{0.6}Ga_{0.4}$, and Mn_3N_2) or cubic (Ga_5Mn_8, Mn_4N, and $Ga_{7.7}Mn_{2.3}$) phases were formed. The diffraction pattern shows multiple diffraction spots around those of GaN with a six-fold symmetry, indicating the platelet regions are $Ga_xMn_{1-x}N$ with the same lattice structure as GaN but with a different (smaller) lattice constant which gives rise to the Moire fringes and multiple diffractions. This was confirmed by a qualitative simulation of [0001] double diffraction for a stack of two hexagonal-close-packed lattices with different lattice constants, in analogy for a previous analysis of the cubic system GaAs on InP.[25] Similar diffraction results were obtained from cross-section samples, confirming that the Al_2O_3 substrates play no role. The only possible hexagonal phase present could be Mn_3Ga, but this was not found either in XRD spectra or in energy dispersive x-ray spectroscopy analysis of the platelets. Moreover, we could expect the samples to display T_C values above room temperature if the binary GaMn phases were present.

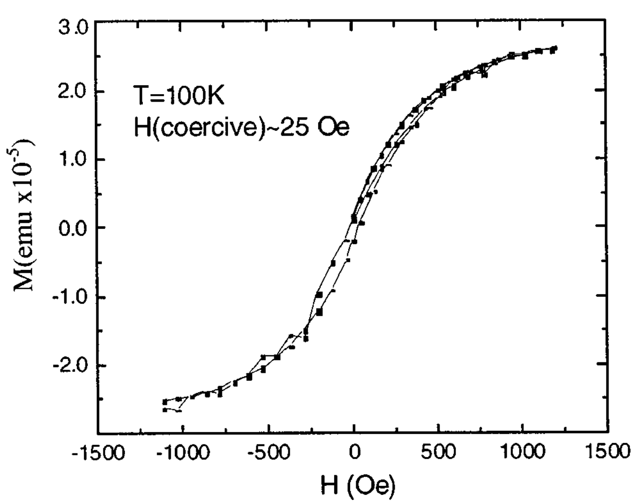

FIG. 3. Hysteresis measured at 100 K in the magnetic moment of a sample implanted with ~3 at. % Mn and annealed at 700 °C.

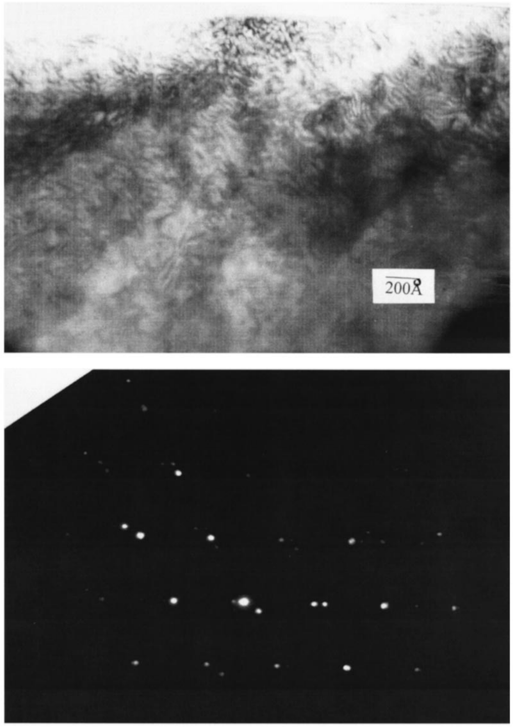

FIG. 4. Plan view TEM micrograph of 5 at. % Mn-implanted GaN (dose 5×10^{16} cm^{-2} at 250 keV) sample annealed at 1000 °C (top) and selected area diffraction pattern (bottom). The scale is 200 Å long.

In conclusion, high-dose Mn^+ implantation at elevated temperatures into *p*-GaN appears to be a promising method for producing ferromagnetic behavior and may be useful for creating selective-area spin-injection regions in device structures. The observed Curie temperature is below theoretical predictions, but may be affected by the low hole density in heavily implanted *p*-GaN. Considerable work needs to be done to understand the solubility limits of Mn under these conditions and the thermal stability of the phases created.

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