Indication of ferromagnetism in molecular-beam-epitaxy-derived N-type GaMnN

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Growth by molecular-beam epitaxy of the dilute magnetic alloy GaMnN is reported. The GaMnN contains 7.0% Mn as determined by Auger electron spectroscopy, and is single phase as determined by x-ray diffraction and reflection high-energy electron diffraction. Both magnetic and magnetotransport data are reported. The results show the anomalous Hall effect, negative magnetoresistance, and magnetic hysteresis at 10 K, indicating that Mn is incorporating into the GaN and forming the ferromagnetic semiconductor GaMnN. At 25 K the anomalous Hall term vanishes, indicating a Curie temperature between 10 and 25 K. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1397763]

Since the invention of the transistor, all facets of semiconductor electronics technology have been based upon the exploitation of the electron charge. Currently, a large research effort is centered upon methods to also exploit the property of electron spin.[1–6] In recent times, it has been hypothesized that spintronic devices that utilize the quantum properties of the electron spin wave function will allow great advances in the development of electro-optic switches, ultrasensitive magnetic field sensors, and particularly, quantum-based logic and memory for high speed computation.[1–6] However, its has been found that directly mating electronic materials (semiconductors) with spin materials (ferromagnetic metals) leads to interfacial problems due to the dissimilar nature of the materials' crystal structure, bonding, physical and chemical properties of the material.[7] Another solution is the use of dilute magnetic semiconductors (DMS), which consist of semiconductor hosts heavily doped with substitutional magnetic ions. A DMS material could permit direct integration with current semiconductor devices.

Several theories have been presented on the nature of DMS-related ferromagnetism.[8,9] In one theory based on the bound magnetic polaron model, Curie temperatures (T_C) have been calculated for 5% Mn in various III–V and II–VI semiconductors. In this calculation, a concentration of free holes equal to $3.5\times10^{20}/\mathrm{cm}^2$ has been assumed.[9] To date, the best experimental T_C values for InMnAs, GaMnSb, and GaMnAs are in reasonable agreement with theory, but are still well below room temperature.[10–12] The *p*-type III–V DMS material GaMnN is predicted to have a T_C well above room temperature.[9] GaMnN has been produced in powder and crystallite form, but to this point its application has been limited.[13,14] In addition, ferromagnetism has been demonstrated in Mn-implanted *p*-GaN epitaxial layers.[15] In this letter, we demonstrate the thin film growth of ferromagnetic GaMnN.

The GaMnN films were grown by gas source molecular-beam epitaxy (MBE) in an INTEVAC gas source Gen II on In-mounted (0001) Al_2O_3 substrates. A surface nitridation step was performed by exposing the Al_2O_3 to the nitrogen plasma for 5 min at a substrate temperature of 865 °C. After the nitridation, a low-temperature AlN buffer layer was grown at a substrate temperature of 435 °C for 5 min, resulting in 20 nm of material. Following the AlN growth, GaN was grown for 20 min. Finally, GaMnN was grown for 180 min. The total thickness was approximately 1.0 μm. The substrate temperature for the GaN and GaMnN layers was 865 °C. The Al for the low-temperature buffer layer was provided by a dimethylethylamine alane source. Shuttered effusion ovens charged with 7 N (99.99999% pure) Ga and 4 N (99.99% pure) Mn provided the group III and the magnetic dopant fluxes. Reactive nitrogen for all the growth steps was provided by a SVT radio-frequency (rf) plasma source operating at 375 W of forward power and a gas flow rate of 3 sccm N_2. X-ray diffraction (XRD) measurements were performed in a Philips APD 3720 powder diffractometer. Compositional information was provided by Auger electron spectroscopy (AES) in a Perkin–Elmer PHI 6600 system. Magnetic measurements were performed in a Quantum Design superconducting quantum interference device (SQUID) Magnetic Properties Measurement System and a Quantum Design Physical Properties Measurement System with an ac impedance bridge. Hall measurements were also taken at room temperature in a custom built system using a 0.8 T electromagnet. Crystal quality was measured *in situ* using a Staib reflection high-energy electron diffraction (RHEED) gun set to 15 kV.

For the growth of the GaMnN layer, the Mn effusion oven was set to a temperature of 724 °C, resulting in a total Mn concentration of 7.0 at % as determined by AES depth profiling. The Mn cell temperature was determined after a study of Mn flux versus Mn incorporation to be discussed elsewhere.[16] The growth rate of the GaMnN layer was determined to be 54 Å/min. RHEED measurements of the GaMnN surface upon the termination of the layer growth

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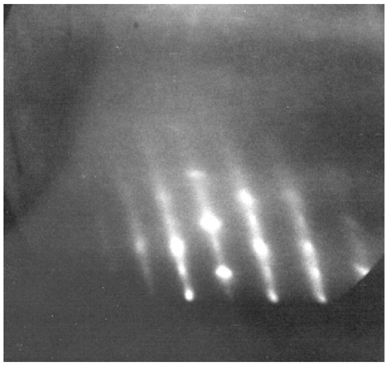

FIG. 1. RHEED photograph along the (11–20) direction of the GaMnN after growth is shown.

along the $(11\bar{2}0)$ direction, shown in Fig. 1, clearly show a combination of well defined streaks with some evident spots. This mixture of two- and three-dimensional (2D/3D) growth indicates the acceptable quality of the GaMnN layer despite the large fraction of Mn within the material. Subsequent XRD of the GaMnN reveals only the presence of peaks corresponding to hexagonal GaN and Al_2O_3; no second phase peaks were found. Other samples grown using similar conditions utilizing only the Mn cell at the same cell temperature together with the nitrogen plasma were undertaken to determine the stable Mn–N phase at these growth conditions. XRD of this material clearly shows the presence of the (111) and the (222) peaks of Mn_4N, which were not found in the GaMnN. This result shows promise for the future investigation of GaMnN, as low-temperature epitaxy of GaN is not required to obtain the necessary concentration of Mn within the material while avoiding the formation of second phases, as was the case with GaMnAs and InMnAs.[10,11] It also indicates that the relatively high growth temperatures needed for the epitaxial growth of the III nitrides will not prohibit Mn incorporation, despite the high vapor pressure of Mn at these growth temperatures.

Magnetization versus magnetic field (M-H) as measured by SQUID magnetometry is shown in Fig. 2. For this measurement, H was parallel to the sample plane and the

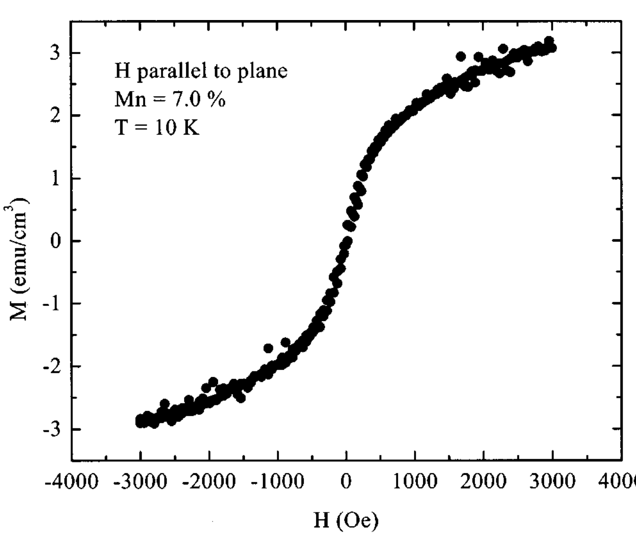

FIG. 2. Magnetization of GaMnN at 10 K with Mn = 7.0% as determined by Auger depth profiling is shown. Magnetic field applied parallel to the sample plane is presented.

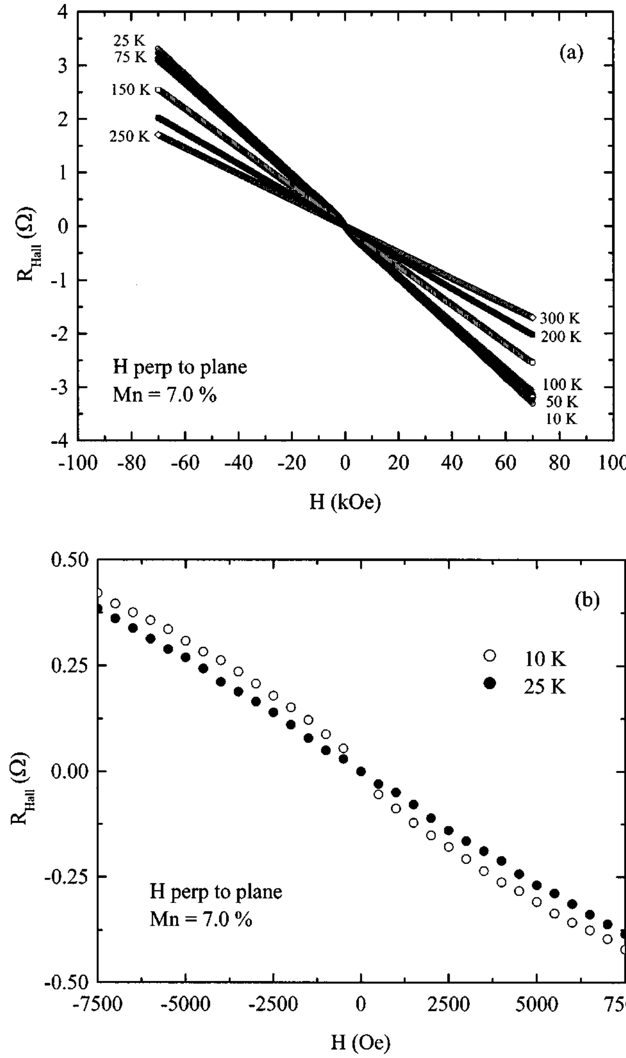

FIG. 3. Magnetotransport Hall resistance data of GaMnN with Mn = 7.0%: (a) for temperatures between 10 and 300 K and (b) 10 and 25 K data showing the onset of anomalous behavior are shown. Magnetic field applied perpendicular to the sample plane is presented.

measurement temperature was 10 K. From Fig. 2, a clear nonlinearity in M is observed with a small amount of hysteresis. The coercive field is approximately 35 Oe and the saturation magnetization correspond to 0.3 Bohr magnetons per Mn atom. Magnetotransport properties of the GaMnN material were investigated in the temperature range between 10 and 300 K for magnetic field sweeps between −7 and +7 T. The Hall (transverse) and sheet (longitudinal) resistances were measured after applying In ohmic contacts to the GaMnN. The magnetotransport data are given in Figs. 3 and 4. The electron carrier density at 300 K was found to be $2.4\times10^{19}/cm^3$, while the carrier density at 10 K was found to decrease slightly to $1.3\times10^{19}\,cm^3$. Normally, as-grown GaN is n-type due to the formation of group V (nitrogen) vacancies during epitaxy. This effect is further accentuated in this case due to the high growth temperature involved, as more of the atomic nitrogen will tend to desorb from the GaMnN surface. The sheet resistance showed clear negative magnetoresistance below 75 K, with the value of $\Delta R/R$ at 10 K equal to 2.3%. Also from Fig. 3, a clear anomalous component to the Hall resistance can be observed in the 10 K measurement. This anomalous nonlinear component is found

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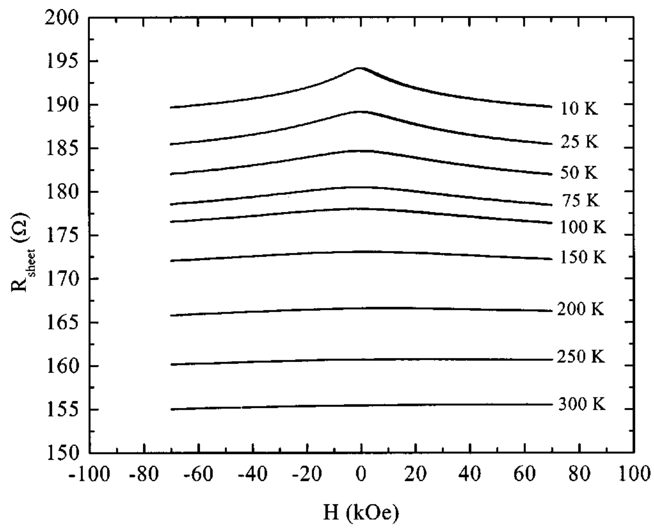

FIG. 4. Magnetotransport sheet resistance data of GaMnN with Mn =7.0% are presented. Magnetic field applied perpendicular to the sample plane is shown.

to vanish at the next measurement temperature of 25 K. From 25 to 300 K, the Hall resistance data is found to be linear with a gradually decreasing slope, indicative of an increasing carrier concentration. The disappearance of the anomalous Hall coefficient between 10 and 25 K indicates that the ferromagnetic phase present within the GaMnN has a T_C between these two temperatures. The linear Hall resistance data from 25 to 300 K is consistent with the absence of magnetic moments due to the thermodynamically stable ferrimagnetic Mn_4N phase, which is reported to have a T_C as high as 745 K.[17] Another possibility is the presence of superparamagnetic clusters of MnGa, or some alloy thereof, with a diameter too small to be seen in the diffraction experiments and with a blocking temperature <25 K. We are currently examining the samples with high resolution transmission electron microscopy, but preliminary results show no clusters to a resolution of ~20 Å.

In summary, we have found that MBE growth of GaN with a high concentration of Mn resulted in the formation of the ferromagnetic phase GaMnN. Negative magnetoresistance was observed below 75 K, while the anomalous Hall effect was observed at 10 K. The disappearance of the anomalous component of the Hall resistance at the 25 K measurement temperature indicates that the T_C for the GaMnN material is between these two temperatures. The lack of any detected second phases by XRD analysis within the GaMnN material in combination with the observed 2D/3D RHEED pattern of the final epitaxial surface indicates that the ferrimagnetic thermodynamically stable Mn_4N phase is not forming within the film. Therefore, we infer that the observed ferromagnetism within the material is due to the formation of GaMnN. This result is significant on several levels. First, ferromagnetism within epitaxial GaMnN is reported. Second, the exchange interaction producing the ferromagnetism in this case is being mediated by electrons and not holes. Although this is possible according to the current theories on DMS ferromagnetism,[9] the predicted T_C's are generally fractions of a degree K. This raises the possibility of further increasing the T_C within the GaMnN material by refining the growth procedure, while not relying on the presence of holes, which is a problematic issue in III-nitride development.

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