Magnetic properties of P-type GaMnP grown by molecular-beam epitaxy

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Growth by molecular-beam epitaxy of the dilute magnetic alloy GaMnP:C is reported. The GaMnP:C contains 9.4% Mn as determined by Auger electron spectroscopy, and is single phase as determined by x-ray diffraction, reflection high-energy electron diffraction, and transmission electron microscopy. Both magnetization 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 GaP:C and forming the ferromagnetic semiconductor GaMnP:C. Temperature-dependent magnetization and anomalous Hall data show that magnetic behavior persists to at least 200 K, which is a very high value for a III–V based dilute magnetic semiconductor. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1416472]

Currently, a large research effort is centered upon methods to exploit the property of electron spin in device structures.[1–6] Recently, it has been hypothesized that "spintronic" devices that utilize the quantum properties of the electron spin wave function will allow significant 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, it has been found that directly mating electronic materials (semiconductors) with spin materials (ferromagnetic metals) leads to interfacial problems such as the formation of a magnetically dead interfacial layer[7–9] due to the dissimilar nature of the crystal structure, bonding, physical, and chemical properties of the material. Consequently, only low spin injection efficiencies have been reported.[10] Another solution is the use of dilute magnetic semiconductors (DMS), which consist of semiconductor hosts heavily doped with substitutional magnetic ions, for spin injectors.

Several theories have been presented on the nature of DMS-related ferromagnetism.[11,12] 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 $3.5\times10^{20}/\mathrm{cm}^3$ has been assumed.[12] An extremely high experimental T_C value reported for a DMS III–Mn–V material is 110 K for GaMnAs.[13] The *p*-type III–V DMS material GaMnP is predicted to have a T_C of roughly 100 K.[12] Although the T_C is well below room temperature, the close lattice matching between GaP and Si may allow GaMnP layers to be directly integrated as spin injection layers with currently established Si complementary metal–oxide–semiconductor technology. A DMS based upon GaP is also interesting as GaP may be highly doped either *n*-type (using a Si dopant such as $SiBr_4$) or *p*-type (using a C dopant such as CBr_4). This allows the high carrier concentrations required by current DMS theories. In this letter, we demonstrate the growth of thin film ferromagnetic GaMnP:C.

GaMnP:C films were grown on In-mounted (100) epiready GaP substrates by gas source molecular-beam epitaxy (MBE) in an INTEVAC Gas Source Gen II. A surface oxide desorption step was performed by heating the GaP substrate under a P overpressure for 5 min at a temperature of 600 °C. After the oxide desorption, a 150 Å GaP:C layer was grown at a substrate temperature of 600 °C. This layer was grown to buffer the GaMnP:C layer from the substrate/epilayer interface. Following the GaP:C growth, GaMnP:C was grown for 31 min also at a substrate temperature of 600 °C, to a total thickness of approximately 3000 Å. The C flux was provided by the pyrolysis of CBr_4 at the substrate surface. The CBr_4 was introduced into the growth chamber from a bubbler using a He carrier gas at a flow of 1 sccm and a pressure of 10 Torr. The CBr_4 bubbler was held at a temperature of 3.3 °C. Shuttered effusion ovens charged with 7 N (99.999 99% pure) Ga and 4 N (99.99% pure) Mn provided the group III and the magnetic dopant fluxes. Reactive phosphorous was provided by thermally cracking phosphine (PH_3) gas into both P and P_2 species. The cracker was held at a temperature of 1050 °C during the film growth. During the oxide desorption step, a PH_3 flow rate of 5 sccm was used, while the flow rate during the GaP:C and GaMnP:C growth was 2 sccm.

X-ray diffraction (XRD) measurements were performed in a Philips APD 3720 powder diffractometer. Transmission electron microscopy (TEM) measurements were performed in a JEOL 200 CX. Compositional information was provided by Auger electron spectroscopy (AES) in a Perkin–Elmer PHI 6600 system. Magnetization and magnetotransport measurements were performed respectively in a Quantum Design superconducting quantum interference device (SQUID) Magnetic Properties Measurement System and in a Quantum Design Physical Properties Measurement System equipped with a Linear Research LR700 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.

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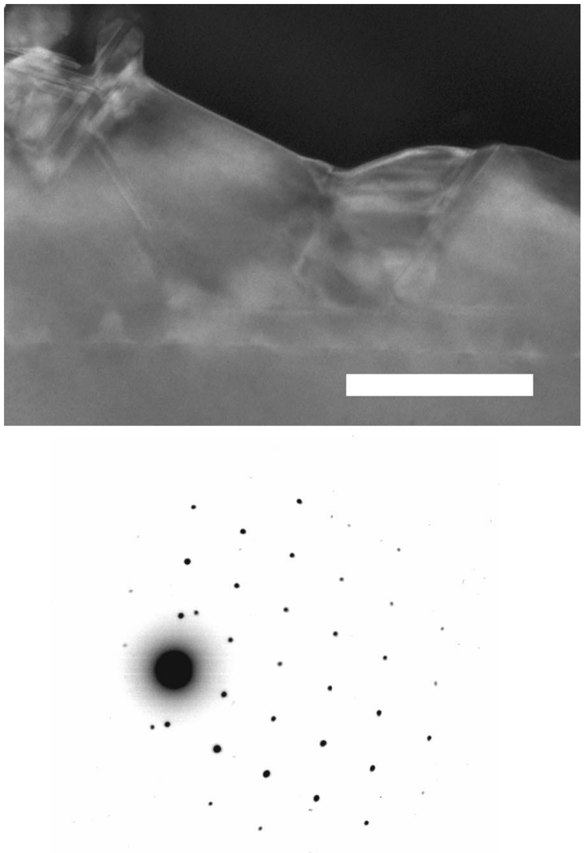

FIG. 1. Cross sectional TEM photograph of the GaMnP:C after growth (top). The length scale is 4000 Å. SAD pattern (bottom) from the same sample.

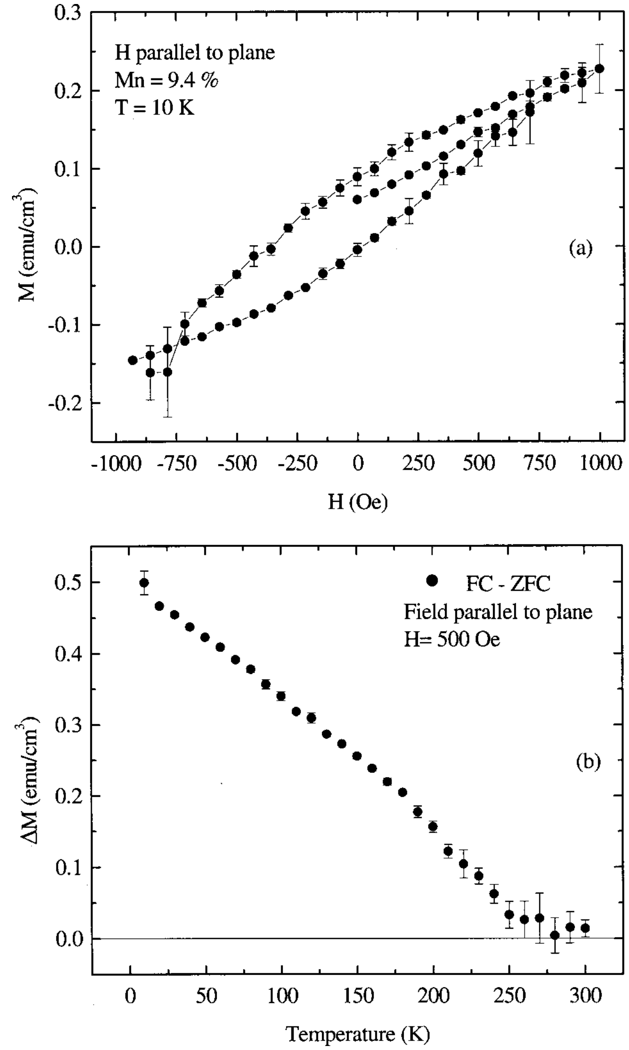

FIG. 2. Magnetization of GaMnP:C with Mn=9.4% as determined by Auger depth profiling, versus (a) field at 10 K and versus (b) temperature at 500 Oe. Magnetic field applied parallel to the sample plane.

For the growth of the GaMnP:C layer, the Mn effusion oven was set to a temperature of 724 °C, resulting in a total Mn concentration of 9.4 at % as determined by AES depth profiling. The Mn cell temperature was chosen after a study of Mn flux versus Mn incorporation to be discussed elsewhere.[14] The growth rate of the GaP:C layer was determined to be 72 Å/min, while the growth rate of the GaMnP:C layer was determined to be 93 Å/min. RHEED measurements of the GaMnP:C surface clearly showed a spotty pattern. This three-dimensional (3D) growth indicates the acceptable quality of the GaMnP:C layer despite the large fraction of Mn within the material. Subsequent XRD of the GaMnP:C revealed only the presence of peaks corresponding to cubic GaP; no second phase peaks were found. All the peaks seen in the x-ray scan have previously be seen in GaP and GaP:C epilayers grown in the same Varian Gen II. A cross sectional TEM photograph of the GaMnP:C is given in Fig. 1 (top). No spots indicating second phase precipitates or superparamagnetic Mn clusters are visible, to a resolution of 50 Å. The lack of precipitates is also evident when investigating the selected area diffraction (SAD) pattern of the GaMnP:C layer (Fig. 1, bottom). One extra set of spots (in addition to those from GaP) was found in the SAD photograph of the GaMnP:C layer. However, this set of spots was found to correspond to a shift of the GaP pattern, indicating that there exists a degree of tilt to the GaMnP:C grains. The TEM photograph also shows a rough GaMnP:C surface, which produces the 3D pattern seen by RHEED. This result shows the need for continued optimization of the GaMnP:C growth conditions. Homoepitaxial GaP is normally grown at 600 °C. Therefore, low-temperature epitaxy of GaP 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.[13]

Magnetization versus magnetic field ($M-H$) and versus temperature ($M-T$), measured by SQUID magnetometry, are shown in Fig. 2. For the M vs H measurement, H was parallel to the sample plane and the measurement temperature was 10 K. From Fig. 2, a nonlinearity in M is observed with a clear amount of hysteresis. The coercive field is ~195 Oe and the saturation magnetization corresponds to 0.005 Bohr magnetons/Mn atom. M vs T was determined by taking the difference of field-cooled and zero-field-cooled measurements at 500 Oe. These data indicate that the observed ferromagnetism persists to approximately 250 K. While MnP has a ferromagnetic phase with T_C as high as 291 K,[15] there is no evidence for its presence in our samples, provided the Mn content is kept below 10% at a growth temperature of 600 °C. Magnetotransport properties of the GaMnP:C material were investigated in the temperature range between 10 and 350 K for magnetic field sweeps between -7 and $+7$ T. The Hall (transverse) and sheet (longitudinal) resistances

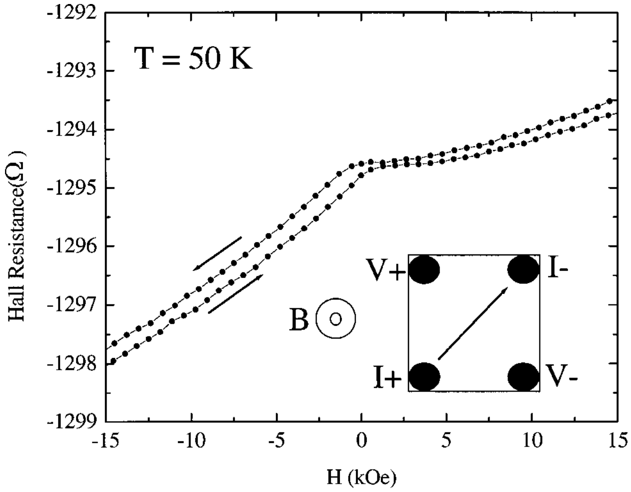

FIG. 3. Hall resistance data of GaMnP:C with Mn=9.4% at 50 K. The magnetic field was applied perpendicular to the sample plane. The contact configuration is indicated.

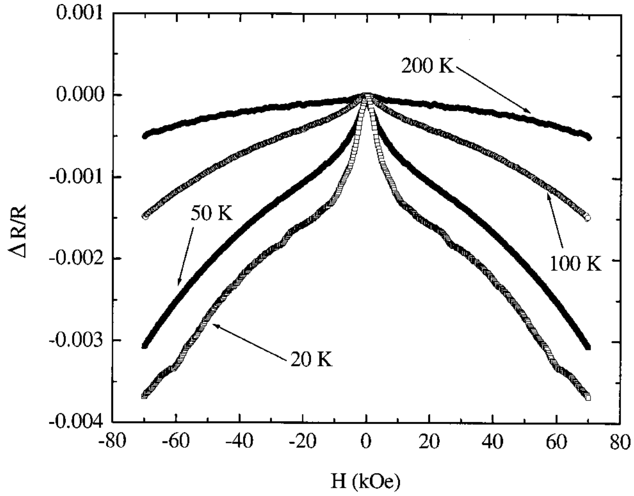

FIG. 4. Magnetotransport sheet resistance data of GaMnP:C with Mn =9.4%. Magnetic field applied perpendicular to the sample plane.

were measured after applying In ohmic contacts to the GaMnP:C. The magnetotransport data are given in Figs. 3 and 4. The concentration of holes at 300 K was found to be $3.0\times10^{18}/\mathrm{cm}^3$. The sheet resistance showed clear negative magnetoresistance up to 200 K, with the value of $\Delta R/R$ at 20 K equal to 0.35%. For the Hall resistance measurements, hysteresis is observed in the data at 50, 100, and 200 K. At 200 K, there is a time-dependent drift in the measurement of comparable value, that is believed to be due to either contact resistance or a surface potential due to a nonohmic component to the contacts. The hysteresis at 50 and 100 K is consistent with the existence of an anomalous component to the Hall resistance. The Hall resistance data given in Fig. 3 show the shift in the data as the field is ramped to +7 T and then reversed, indicating the existence of hysteresis consistent with the SQUID magnetometry data.

In summary, we have found that MBE growth of GaP:C with a high concentration of Mn resulted in the formation of the ferromagnetic phase GaMnP:C. Negative magnetoresistance was observed up to 200 K, while the anomalous Hall effect was observed at 50, 100, and 200 K. The lack of any detected second phases by XRD analysis and cross sectional TEM of the GaMnP:C material in combination with the observed 3D RHEED pattern of the final epitaxial surface indicates that the ferromagnetic MnP phase is not forming within the film. Therefore, we infer that the observed ferromagnetism within the material is due to the formation of GaMnP:C. This result is significant on several levels. First, ferromagnetism within epitaxial GaMnP:C is reported. Second, the experimental results show that the ferromagnetism persists to at least 200 K, far greater than predicted by current theories. This raises the possibility of further increases in the T_C within the GaMnP:C material by refined growth procedures to: improve the film morphology, optimize the degree of Mn incorporation, and optimize the concentration of free holes. By incorporating GaMnP:C layers with current Si-based structures, room temperature spintronic devices may be possible.

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