Origin of high-temperature ferromagnetism in (Ga,Mn)N layers grown on 4H–SiC(0001) by reactive molecular-beam epitaxy

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We report on the growth, structural as well as magnetic characterization of (Ga,Mn)N epitaxial layers grown directly on 4H–SiC(0001) by reactive molecular-beam epitaxy. We focus on two layers grown under identical conditions except for the Mn/Ga flux ratio. Structural characterization reveals that the sample with the lower Mn content is a uniform alloy, while in the layer with the higher Mn content, Mn-rich clusters are found to be embedded in the (Ga,Mn)N alloy matrix. Although the magnetic behavior of both the samples is similar at low temperatures, showing antiferromagnetic characteristics with a spin-glass transition, the sample with higher Mn content additionally exhibits ferromagnetic properties at and above room temperature. This ferromagnetism most likely originates from the Mn-rich clusters in this sample. [DOI: 10.1063/1.1564292]

Growth and magnetic properties of Mn-doped GaN layers are intensely studied in many laboratories, because this class of materials was predicted to exhibit ferromagnetic behavior far above room temperature[1] and could hence be important for spintronic devices.[2] The experimental results, however, show significant discrepancies. While some groups have reported antiferromagnetic behavior for (Ga,Mn)N,[3,4] others observed ferromagnetism with various different values of T_C ranging from 20 to 940 K.[4–8] All values of T_C above room temperature stem from *n*-type or even highly resistive samples.[5–7] The origin of the ferromagnetism observed is far from being understood. We have recently shown[9] that homogeneous ternary (Ga,Mn)N layers, which do not contain any secondary phase, do not exhibit ferromagnetic behavior but represent a Heisenberg spin glass. In this letter we demonstrate that the origin of the frequently observed high-temperature ferromagnetism in (Ga,Mn)N layers is related to the formation of Mn-rich clusters in this ternary alloy. These Mn-rich clusters can be identified by transmission electron microscopy but are extremely difficult to detect with standard structural characterization techniques.

The two samples studied here are grown in a custom designed two-chamber molecular-beam epitaxy (MBE) system equipped with conventional effusion cells and an unheated NH_3 gas injector. A commercial filter purifies NH_3 and a mass-flow controller adjusts its flow into the growth chamber. (Ga,Mn)N layers 350–400 nm thick are grown directly on semi-insulating Si-face 4H–SiC(0001) substrates at a substrate temperature of 710 °C (100 °C lower than the temperature normally used for GaN growth). The NH_3 flux is adjusted to keep the chamber pressure at $4-5\times10^{-5}$ Torr during growth. The Mn/Ga flux ratio is changed in order to adjust the Mn content in the layers (sample A: low Mn content, sample B: high Mn content). Nucleation and growth is monitored *in situ* by reflection high-energy electron diffraction (RHEED). The structural properties of the layers are investigated by x-ray diffraction (XRD), transmission electron microscopy (TEM), and secondary ion mass spectrometry (SIMS). Symmetric high resolution triple crystal x-ray $\omega-2\theta$ scans are taken with a Bede D3 diffractometer utilizing Cu $K\alpha_1$ radiation and equipped with a Bartels-type Ge(002) monochromator and a Si(111) analyzer. TEM is performed using a JEOL3010 microscope operating at 300 kV. The magnetization measurements are done in a Quantum Design superconducting quantum interference device (SQUID) magnetometer with a high temperature oven for measurements up to 750 K. Magnetization loops are recorded at various temperatures for magnetic fields between ±5 kOe. Prior to measuring the temperature dependence of the magnetization, the sample is first cooled from room temperature to 2 K either under a saturation field of 10 kOe (Field cooled: FC) or at zero field (zero field cooled: ZFC). For the high temperature measurements (350–750 K) the sample is magnetized in a field of 10 kOe at room temperature. The magnetic field is applied parallel to the sample surface, i.e., perpendicular to the *c* axis, for all measurements. All data presented below are corrected for the diamagnetic background of the substrate. Both the samples are found to be electrically highly resistive ($\rho\approx1$ MΩ cm) even at room temperature.

During nucleation of the layers, a spotty (1×1) RHEED pattern is initially observed, reflecting a purely three-dimensional (3D) growth mode. After the deposition of 10 monolayers of (Ga,Mn)N, the RHEED pattern becomes streaky, reflecting two-dimensional (2D) growth. For sample A with lower Mn content, the RHEED pattern remains entirely streaky throughout growth. Figure 1 shows the RHEED patterns along the $\langle 11\bar{2}0\rangle$ azimuth for sample B with higher Mn content during growth. The pattern remains streaky for the first 100 nm of deposition [Fig. 1(a)], after which a superimposed 2D/3D pattern evolves [Fig. 1(b)].

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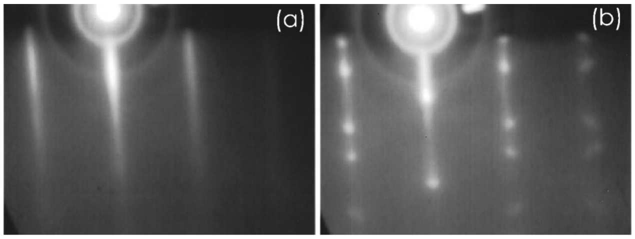

FIG. 1. RHEED pattern along the $\langle 11\bar{2}0\rangle$ azimuth of sample B during (a) and after (b) the first 100 nm of deposition.

The position of the diffraction spots is consistent with rotational twinning of cubic GaN(111),[10] indicating that a high concentration of Mn triggers the formation of cubic inclusions similar to what has been observed for GaN:Fe.[11]

The Mn content as measured by SIMS is 7.6% and 13.7% for samples A and B, respectively, and is constant over the entire thickness ruling out any accumulation of Mn on the surface during growth. XRD of samples with various Mn content reveals a linear decrease of the *c* lattice constant with increasing Mn content, indicating a substitutional incorporation of Mn. Symmetric (0002) and asymmetric $(11\bar{2}4)$ x-ray rocking curves for the samples under investigation exhibit a width of 300 and 900 arcsec., respectively. These values are lower than values we observe for equally thin pure GaN layers grown under identical conditions, and are comparable to values reported for high-quality GaN grown by MBE in general. All these results suggest the formation of a uniform (Ga,Mn)N alloy with a good crystalline quality.

Figure 2 shows the TEM micrographs of both samples. Sample A is seen [Fig. 2(a)] to be a homogeneous layer without any evidence for a secondary phase. For sample B, in contrast, nm-size clusters are observed in the micrograph [Fig. 2(b)]. Preliminary high-resolution TEM investigations (not shown here) indicate that these clusters have wurtzite structure and are coherent to the surrounding matrix, suggesting that the cubic reflections observed in Fig. 1 are not directly related to the clusters. Further investigations are under way to explore the structural and chemical properties of these clusters. We note that we were unable to detect the presence of these clusters by XRD, presumably because of

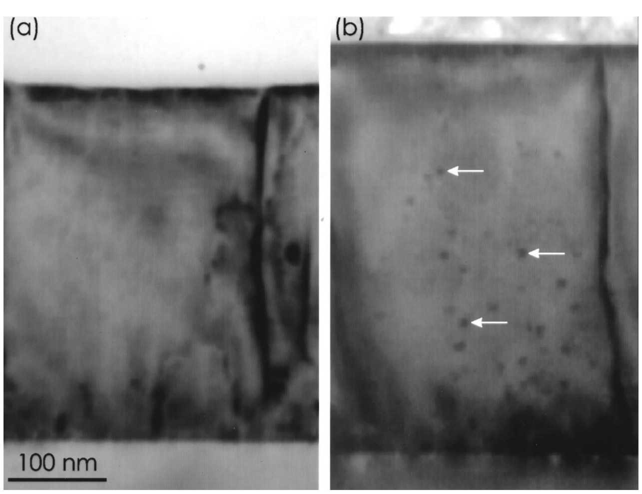

FIG. 2. Bright-field TEM micrographs of (a) sample A and (b) sample B. Note the presence of nm-scale clusters, some of which are highlighted by arrows, in sample B.

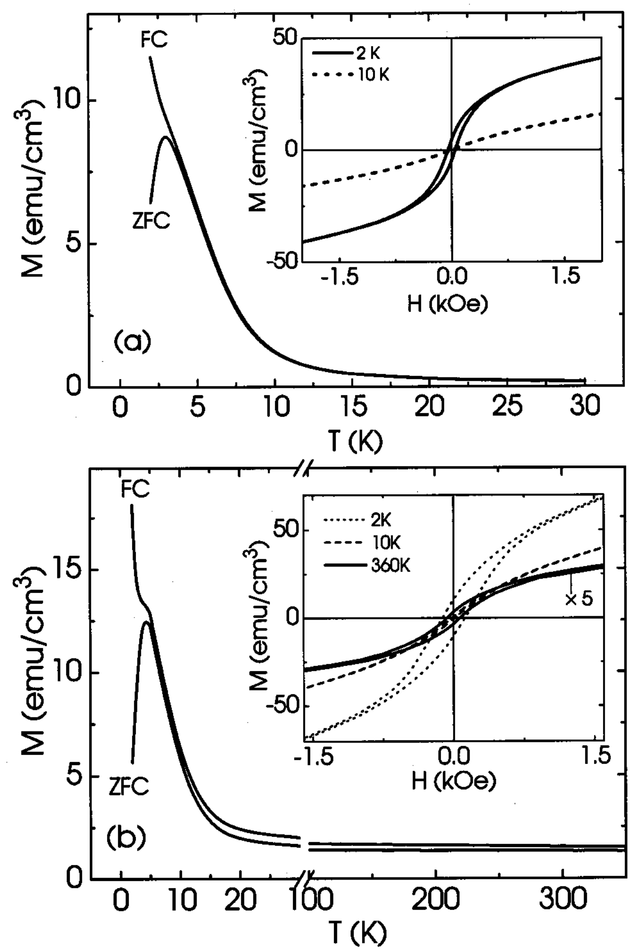

FIG. 3. Temperature dependence of magnetization at field-cooled (FC) and zero-field-cooled (ZFC) conditions for (a) sample A and (b) sample B at a magnetic field of 100 Oe. Hysteresis loops obtained at various temperatures in these samples are shown in the insets of the respective figures.

their minuscule size resulting in a significant broadening of the reflection.

Figure 3 shows the temperature dependence of the magnetization for samples A and B. Clearly, the low-temperature behavior of both samples is similar, which is characterized by a FC-ZFC irreversibility and a sharp cusp in the ZFC curves. These two features are fingerprints for spin-glass systems. We have investigated the low-temperature behavior in great detail using frequency and field dependent ac susceptibility measurements,[9] which demonstrate that the material indeed represents a Heisenberg spin glass below 6 K. At higher temperatures, sample B is ferromagnetic as seen from the separation of the FC and ZFC curves above 10 K. The inset of Figs. 3(a) and 3(b) shows the magnetization loops for samples A and B, respectively. Both samples show a hysteresis below 6 K, as expected from the FC and ZFC curves. Sample A is paramagnetic at higher temperatures, whereas sample B remains hysteretic again at high temperatures demonstrating the existence of ferromagnetism.

To further explore this ferromagnetic characteristics of sample B we perform magnetization measurements up to 750 K which are depicted in Fig. 4. Although the oven enhances the magnetic background signal and more noise is picked up, a clear hysteresis loop is observed at 650 K (cf. inset of Fig. 4). Furthermore, the temperature dependent magnetization

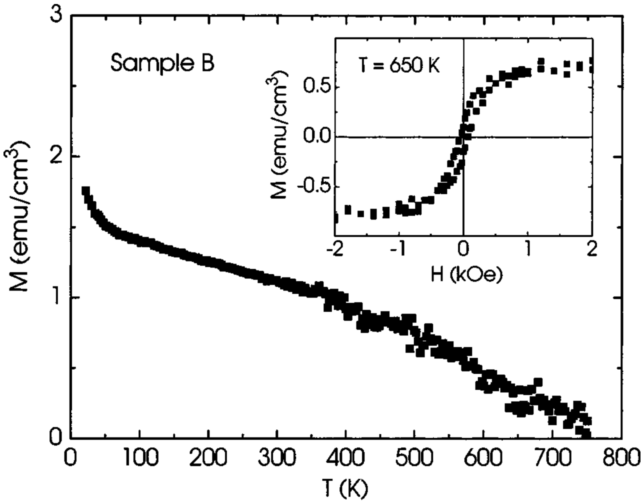

FIG. 4. Temperature dependence of the magnetization of sample B at 50 Oe. The inset shows the magnetization loop of this sample measured at 650 K.

indicates a Curie temperature of about 750 K. It is important to note that there exist several Ga–Mn and Mn–N phases, some of which are ferromagnetic up to very high temperatures (for example, MnGa: ferromagnetic, $T_C > 600$ K;[12] Mn_4N: ferrimagnetic, $T_C = 738$ K[13]). Furthermore, a recent theoretical work suggests that molecular Mn_xN clusters exhibit ferromagnetic coupling and giant magnetic moments.[14] In the wurtzite GaN matrix, it is conceivable that up to four Mn atoms substitute Ga while retaining the tetrahedral configuration in the wurtzite lattice, which might explain our high-resolution TEM results.

In Fig. 5, the inverse of the dc susceptibility χ is plotted versus temperature for sample A. A fit of the Curie–Weiss law to the high-temperature data[15] returns a value of $\theta = -10.4$ K, revealing the antiferromagnetic Mn–Mn interaction in insulating (Ga,Mn)N. In fact, in the absence of free carriers in the crystal, the Mn–Mn interaction is expected to be antiferromagnetic. Only the presence of an adequate density of free carriers can turn the antiferromagnetic interaction into ferromagnetic, as has been postulated for (Ga,Mn)As.[16] Since Mn forms a relatively shallow acceptor level in GaAs (100 meV),[17] free holes may be generated at high Mn concentrations resulting *p*-type conductivity.[16] In contrast, Mn in GaN has been experimentally observed by Korotkov *et al.*[18] to form a very deep acceptor state within the gap (1.4 eV). Mn will thus merely act as a compensating center and render the (Ga,Mn)N alloy into a semi-insulating material, as experimentally observed for our samples.

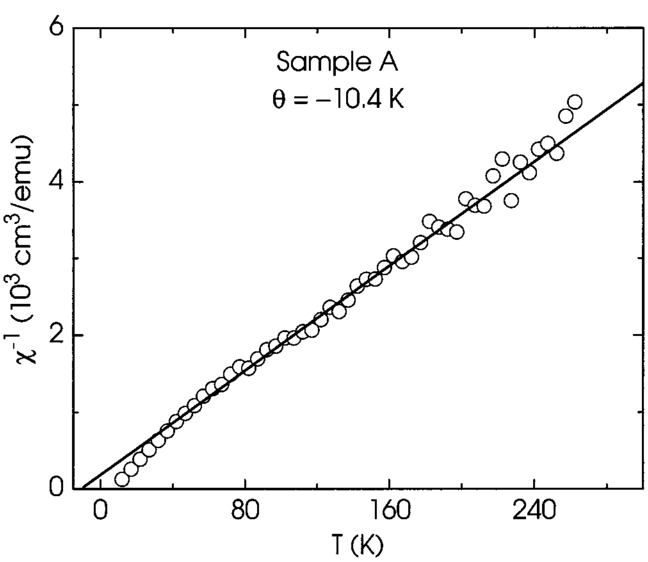

FIG. 5. Inverse of dc susceptibility measured at 100 Oe for sample A as a function of temperature (open circles). The line shows the fit to the data with the Curie–Weiss law $[\chi = C/(T-\theta)]$.

To summarize and conclude, the homogeneous alloy (Ga,Mn)N exhibits antiferromagnetic Mn–Mn interaction and undergoes a spin-glass transition at temperatures around 5 K. On the other hand, ferromagnetism is observed at room temperature and above for insulating (Ga,Mn)N with a Mn content of 14%. This ferromagnetism is not an intrinsic property of (Ga,Mn)N but originates from nm-scale Mn-rich clusters formed during growth.

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