Ferromagnetism and colossal magnetic moment in Gd-focused ion-beam-implanted GaN

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The structural and the magnetic properties of Gd-focused ion-beam-implanted GaN layers are studied. Gd^{3+} ions were uniformly implanted in molecular beam epitaxy grown GaN layers at room temperature with an energy of 300 keV at doses ranging from 2.4×10^{11} to 1.0×10^{15} cm^{-2} which corresponds to an average Gd concentration range of $2.4 \times 10^{16} - 1.0 \times 10^{20}$ cm^{-3}. The implanted samples were not subjected to any annealing treatment. No secondary phase related to Gd was detected by x-ray diffraction in these layers. Magnetic characterization with superconducting quantum interference device reveals a colossal magnetic moment of Gd and ferromagnetism with an order temperature above room temperature similar to that found in epitaxially grown Gd-doped GaN layers. The effective magnetic moment per Gd atom in these samples is, however, found to be an order of magnitude larger than that found in epitaxially grown layers for a given Gd concentration which indicates that the defects play an important role in giving rise to this effect. *© 2006 American Institute of Physics*. [DOI: 10.1063/1.2267900]

Doping of GaN with different rare-earth elements has gained a lot of attention in recent years not only because of its importance in optoelectronics[1,2] but also due to its potential as a promising material for spintronics. Recently, ferromagnetism with an order temperature T_c above 300 K has been observed in very dilute Gd-doped GaN.[3] The material was found to exhibit ferromagnetism even with a Gd concentration of less than 1×10^{16} cm^{-3}. Moreover, the average value of the effective magnetic moment per Gd atom was found to be as high as $4000\mu_B$ as compared to its atomic moment of $8\mu_B$.[4] While this finding has created exciting opportunities for application in spintronics, the microscopic origin of such an effect is yet to be understood. In order to explain such a colossal magnetic moment one has to consider a long range spin polarization of the GaN matrix by the Gd atoms.[3] It was concluded that the polarization is either directly in the GaN matrix or in a certain type of defects which are present in GaN. The samples, where the above mentioned effects were found, were grown by ammonia molecular beam epitaxy (MBE) and Gd was incorporated in GaN during growth. Gd can also be incorporated in GaN by ion implantation which is a relatively easy and well known technique to dope semiconductors. Implantation of Gd is expected to generate a large number of defects in GaN since neutral Gd has a large atomic size. It is interesting to investigate whether such a long range spin polarization of the matrix is still present in the implanted material or not. Such an investigation would be very helpful in order to understand the role of defects in giving rise to this effect. It is important to mention here that Han *et al.*[5] have recently reported the structural and magnetic properties of Gd-implanted GaN and AlN. They have found hysteretic behavior both in GaN and AlN implanted samples above room temperature. However, their x-ray diffraction study revealed a few Gd related secondary phases in these samples, making it difficult to conclude about the origin of the magnetic behavior.

In this letter, we focus on the structural and the magnetic properties of the GaN films implanted with Gd by focused ion beam implantation (FIB) at different doses. Our study shows that the two effects, namely, the colossal magnetic moment per Gd atom and the ferromagnetism far above room temperature, which were observed before in Gd-doped epitaxial GaN layers, are also present in these films. Moreover, the effective magnetic moment per Gd atom in implanted films is found to be higher than that obtained in Gd-doped GaN epilayers with comparable Gd concentrations.

A 600 nm thick GaN layer, grown directly on Si-face 6*H*-SiC (0001) substrates at a substrate temperature of 810 °C by NH_3 MBE, was cut into four equal (5×7 mm^2) pieces. Piece A-0 was kept as a reference standard. Each of the remaining pieces was implanted with Gd^{3+} ions on a surface area of 4×6 mm^2 using a FIB implanter (Eiko-100). While the energy of the Gd ions was adjusted to 300 keV for all implantations, the dose was varied to incorporate different amounts of Gd in these samples. The implantation doses for pieces A-1, A-2, and A-3 were 2.4×10^{11}, 1.1×10^{13}, and 1.0×10^{15} cm^{-2}, respectively. The liquid metal ion source for the FIB system was consisted of AuGdSi alloy. All implantations were carried out at room temperature and the implanted samples were not subjected to any annealing treatment. The projected ion range was calculated using TRIM code,[6] which predicts the implanted atoms to be distributed mostly within 100 nm from the surface for the ion energy of 300 keV. The average concentration of Gd in these samples was estimated by integrating the profile over the depth and then dividing it by the projected range of 100 nm. The aver-

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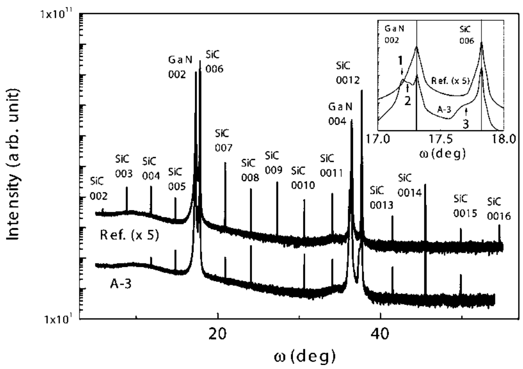

FIG. 1. X-ray diffraction ω-2θ symmetric scans taken with a 1 mm slit in front of the detector for samples A-0 and A-3. The inset shows the region covering GaN (0002) and SiC (0006) reflections in an expanded scale.

age Gd concentrations N_{Gd} in samples A-1, A-2, and A-3 were 2.4×10^{16}, 1.1×10^{18}, and $1.0\times10^{20}\ \mathrm{cm}^{-3}$, respectively, with a maximum estimation of error of 5% for all samples.

The structural properties of the layers were investigated by x-ray diffraction using a Philips X'pert Pro™ diffractometer with Cu $K\alpha_1$ radiation. The magnetization measurements from 2 up to 360 K were performed in a Quantum Design superconducting quantum interference device magnetometer. The magnetization loops were recorded at various temperatures for magnetic fields between ±50 kOe with the magnetic field applied parallel to the sample surface, i.e., perpendicular to the *c* axis. Prior to measuring the temperature dependence of the magnetization, the sample was cooled from room temperature to 2 K either under a saturation field of 50 kOe [field cooled (FC)] or at zero field [zero field cooled (ZFC)]. In the case of ZFC measurements the sample was demagnetized under an oscillatory magnetic field at room temperature before cooling it down to 2 K.

Figure 1 compares the symmetric x-ray ω-2θ scans taken within a wide angular range of ω from 5° to 55° with a 1 mm slit in front of the detector for samples A-0 and A-3. The inset shows the region covering the GaN (0002) and SiC (0006) reflections in an expanded scale. Apart from the reflections of the substrate and the GaN layer, no additional reflections were detected in sample A-0 as expected. The ω-2θ scans for Gd-implanted samples A-1 and A-2 (not shown in the figure) look very similar to that obtained for sample A-0 without revealing any additional reflection. However, in sample A-3, which was implanted at the highest dose, a few additional features (indicated by arrows) around the GaN (0002) peak can clearly be seen in the inset of the figure. The broad feature appearing at the left side of the GaN (0002) reflection is expected to have originated from the Gd-implanted top layer. The Bragg angle associated with this peak is smaller than that for the GaN (0002) reflection, which indicates an increase of the *c*-lattice constant in the Gd-implanted layer. The origin of this splitting (indicated by arrows 1 and 2) is not clear yet. The broad feature (indicated by arrow 3) appearing as a solder to the substrate peak might stem from a few nm of the surface layer which is expected to be highly defective in this sample because of the damages created by heavy implantation doses. It is worth to be noted that the possibility of the formation of other Gd related phases as clusters cannot be ruled out in this particular sample. In sample A-3, the GaN (0002) peak appears almost at the same position and has a very similar width as that from the reference sample, suggesting that the peak must be associated with the bottom part of the GaN layer which remains unaffected by the implantation.

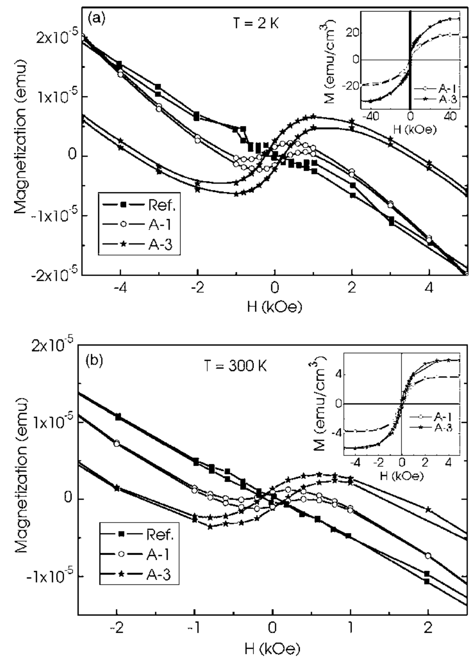

FIG. 2. Magnetization loops obtained for samples A-0, A-1, and A-3 at (a) 2 K and (b) 300 K. The insets show the loops corrected for the diamagnetic background.

Figure 2 compares the field dependence of the magnetization for the reference sample A-0 and the Gd-implanted samples A-1 and A-3 at 2 and 300 K. Both at 2 and 300 K, the reference sample exhibits the expected diamagnetic behavior in the whole magnetic field range between ±50 kOe, while the Gd-implanted samples clearly exhibit a hysteresis (at lower fields) superimposed on a diamagnetic background. The contribution from this additional phase can be extracted by subtracting the diamagnetic background from the data. In the insets, these contributions are plotted for samples A-1 and A-3. At 300 K, the magnetization clearly saturates at high magnetic fields in these samples, indicating a ferromagneticlike behavior. However, at 2 K, the magnetization appears to be still not saturated even at a magnetic field of ±50 kOe which suggests that an additional paramagnetic phase is present at low temperatures. It should be noted that a similar magnetic hysteretic behavior with an order temperature above 300 K has been observed in epitaxially grown Gd-doped GaN layers.[3]

Figure 3 shows the temperature dependence of the FC and ZFC magnetizations under a magnetic field of 100 Oe for samples A-1 and A-3. Clearly, the FC and ZFC curves are qualitatively similar for these samples, featuring a strong temperature dependence below 10 K followed by a slow component at higher temperatures, suggesting the coexistence of a paramagneticlike and a ferromagneticlike phase in these samples. This finding is consistent with the observation in Fig. 2. It is noteworthy that unlike in epitaxially grown Gd-doped GaN layers, the FC curves in these samples do not show any step at around 70 K.[3] In all samples the FC and ZFC curves are separated throughout the entire temperature range of 2–360 K. The separation between the FC and ZFC curves indicates a hysteretic behavior which is consistent with the observations shown in Fig. 2.

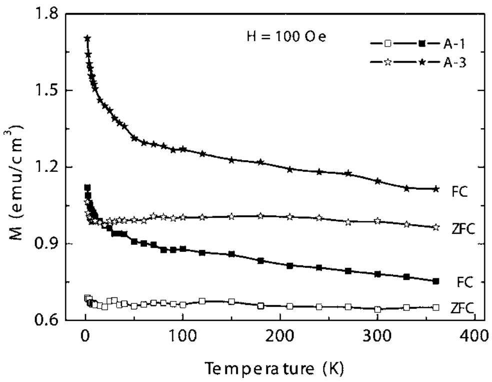

FIG. 3. Temperature dependence of magnetization at field-cooled (solid symbols) and zero-field-cooled (open symbols) conditions at a magnetic field of 100 Oe for samples A-1 and A-3.

The effective magnetic moment per Gd atom p_{eff}, obtained from the value of magnetization at ±50 kOe [$p_{\mathrm{eff}}=M$ (50 kOe)$/N_{\mathrm{Gd}}$], is plotted as a function of N_{Gd} at 2 and 300 K in Fig. 4. These values are extraordinarily large as compared to the Gd atomic moment of $8\mu_B$, particularly for low Gd concentrations (samples A-1 and A-2). Here, it is important to state that instead of calculating p_{eff} from M (50 kOe), it is derived from the remanent magnetization M_r; a very large value of p_{eff} is still obtained for samples A-1 and A-2. For example, if one calculates p_{eff} from the FC magnetization which is obtained at 100 Oe of the magnetic field, it comes out to be around $5000\mu_B$ and $3300\mu_B$ at 2 and 300 K, respectively, for sample A-1. While a similar effect has already been observed in epitaxially grown Gd-doped GaN layers,[3] in samples A-1 and A-2, p_{eff} is found to be even larger (more than an order of magnitude) than those found in epitaxially grown GaN with comparable Gd concentrations. Both at 2 and 300 K, p_{eff} decreases with the increase of N_{Gd}. It is interesting to note that at 300 K, p_{eff} is found to be very close to the Gd atomic-moment value of $8\mu_B$ in the highest Gd-implanted sample (A-3). However, p_{eff} is found to be much larger than $8\mu_B$ in this sample at 2 K. A similar tendency has been found in epitaxially grown Gd-doped GaN layers.[3] When temperature is varied between 2 and 300 K, the change of p_{eff} is much larger in implanted samples than that in the case of epitaxially grown layers for a given Gd concentration. In the insets, the magnetization obtained at 50 kOe, which can be considered as the saturation magnetization (M_s) at least at 300 K, is plotted as a function of N_{Gd} at these temperatures. It is clear that both at 2 and 300 K, it increases with N_{Gd}. However, the difference of M (50 kOe) between A-1 and A-2 is smaller than that obtained between A-2 and A-3. Particularly at 2 K, this tendency is clearly visible. It should be noted that in case of epitaxially grown Gd-doped GaN layers M_s was also found to exhibit a similar M_{Gd} dependence which indicates that a very similar mechanism is involved in giving rise to the effect in both cases.

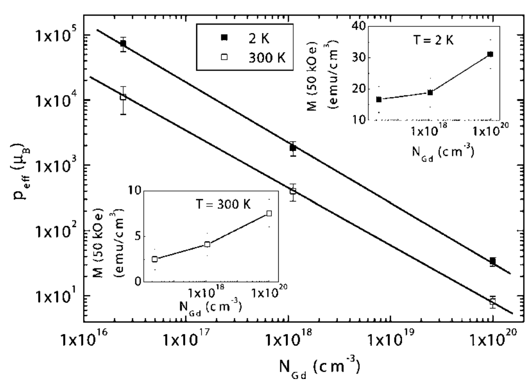

FIG. 4. Magnetic moment per Gd atom (p_{eff}) as a function of Gd concentration at 2 K (solid squares) and 300 K (open squares). Insets show the magnetization obtained at 50 kOe as a function of Gd concentration at 2 K (upper-right corner) and 300 K (lower-left corner). Straight lines are guides to the eyes.

In order to explain such a colossal magnetic moment one has to consider a Gd induced spin polarization either of the GaN matrix atoms (Ga or/and N) or of a certain type of defects residing in the GaN matrix. In Ref. 3, the effect was explained in terms of a phenomenological model assuming that Gd induces a magnetic moment in all the matrix atoms covered by a sphere of its influence. Here, we observe about an order of magnitude larger magnetic moments per Gd atom in implanted samples as compared to epitaxially grown layers for a given concentration of Gd. This suggests that either (i) the density of the polarization sites or (ii) the magnitude of polarization per site in implanted samples is more than that in epitaxially grown layers. Since the concentration of defects in implanted samples is expected to be higher than in epitaxial layers, possibility (i) would mean that the polarization is not in the matrix atoms but in a certain type of defects present in GaN. On the other hand, possibility (ii) would suggest that a certain type of defects in GaN plays a mediator role in giving rise to the coupling between the matrix atoms and the Gd atoms. The magnitude of polarization per matrix atom might be more in the implanted samples than that in epitaxially grown layers, since the defect density in the former case is expected to be larger than that in the latter. In either way, defects play an important role in manifesting this effect.

In conclusion, our study has found that the effect of colossal magnetic moment of Gd and a ferromagneticlike behavior with T_c above room temperature with Gd concentration as low as 10^{16} cm^{-3}, which has already been observed in epitaxially grown Gd-doped GaN layers, is also present in Gd-implanted GaN samples. The magnetic moment per Gd atom in implanted samples is, however about an order of magnitude larger than that found in epitaxially grown layers for a given concentration of Gd which suggests that the defects play an important role in giving rise to this effect. This finding could provide a vital clue in understanding the microscopic origin of this effect which is still lacking.

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