Demonstration of defect-defect ferromagnetic coupling in Gd doped GaN epitaxial films: A polarization selective magneto-photoluminescence study

Rajendra K. Saroj,1 Preetha Sarkar,1 Swarup Deb,1 and S. Dhar1,*  
1Department of Physics, Indian Institute of Technology Bombay, Mumbai 400076, India

Magnetic field dependent polarization selective photoluminescence(PL) study has been carried out at 1.5 K on Gd-doped GaN epitaxial layers grown on c-SiC substrates by molecular beam epitaxy technique. It has been found that the incorporation of Gd in GaN leads to the generation of three types of donor like defects that result in neutral donor bound excitonic features in low temperature PL. The study reveals that the rate of spin-flip scattering for all the three excitonic features becomes almost B-independent suggesting that these signals must be stemming from defects which are ferromagnetically coupled with each other. This is further confirmed by the study carried out on a GaN sample co-doped with Si and Gd, where defects are found to be ferromagnetically coupled, while Si-donors do not show any involvement in coupling.

Gadolinium (Gd)-doped GaN (GaN:Gd) remains to be one of the active areas in physics for exhibiting certain intriguing magnetic properties. Ferromagnetism far above room temperature even with doping concentration as low as $\approx 10^{15}$ cm$^{-3}$ as well as several orders of magnitude larger effective magnetic moment per Gd ion as compared to that of a bare Gd$^{3+}$ ion ($\mu_B^Gd$) have been observed in GaN:Gd epitaxial layers$^{1,2}$. Element specific magnetic studies on these layers show a very small polarization for Ga and paramagnetism for Gd ions, indicating that the magnetism does not solely arise from Gd itself.$^3$ Since then, a large volume of work in this field has revealed ferromagnetic like behavior not only in GaN:Gd$^4$-$^6$ but also in other rare-earth doped GaN$^7,8$. Similar magnetic behavior has also been reported in Gd$^9,10$ and Dy$^{11}$-implanted GaN layers. Effective magnetic moment per Gd ion, which is reported to be larger in Gd implanted GaN layers,$^9$ shows a reduction upon annealing$^{10}$, suggesting a defect origin of the magnetism. Formation of multiple type of defects due to Gd incorporation have been demonstrated in molecular beam epitaxy (MBE) grown GaN:Gd layers$^5,12,13$. In these samples, Mishra et al. have also found a connection between the magnetism and the density of certain defects that results in a low temperature photoluminescence(PL) peak at $\approx 3.05$ eV$^{13,14}$. However, the microscopic origin of the defects and their involvement in establishing long range magnetic ordering is still unclear. Theoretical studies have shown that certain defects, such as Ga-vacancies($V_{Ga}$),$^{15-18}$ N-interstitials($N_i$)$^{19}$, O-interstitials($O_i$)$^{19}$ as well as nitrogen vacancy($V_N$)-Ga vacancy complexes$^{20,21}$, which possess magnetic moment, can account for the large effective magnetic moment per Gd ion and explain ferromagnetism in this material. It is noteworthy that ferromagnetism above room temperature has been observed in semiconductors such as HfO, ZnO, TiO$_2$, In$_2$O$_3$, where atoms with partially filled d or f shells are not present at all$^{22}$. Though, crystalline defects are predicted to be the reason for ferromagnetism in these semiconductors, there is no experimental report, which directly evidences coupling between defects.

Here, we have carried out a magnetic field dependent polarization selective photoluminescence(PL) study at 1.5 K on several Gd-doped GaN epitaxial layers grown on c-6H SiC substrates by MBE. The study reveals that the incorporation of Gd in GaN leads to the generation of three types of donor like defects, all of which give rise to neutral donor bound excitonic transitions in low temperature PL. It has been shown that the dependence of spin-flip scattering rate on the magnetic field ($B$) for a given excitonic transition carries the information about the magnetic coupling of the associated defects. Spin-flip scattering rates for all the three excitonic features are found to be almost $B$-independent for samples with Gd concentration more than $\approx 10^{17}$ cm$^{-3}$ suggesting that these signals must be stemming from the defects which are ferromagnetically coupled with each other.

GaN layers with different Gd concentrations were grown directly on 6H-SiC(0001) substrates using reactive molecular-beam epitaxy (RMBE) technique. A Gd-undoped GaN layer was also grown as the reference standard (sample R). One of the samples (sample E) was co-doped with both Gd and Si. More details about the growth can be found elsewhere$^{1,2}$. Magnetization measurements show ferromagnetic like behavior even above 300 K in all of the Gd-doped samples. One of the Gd doped sample (sample D) was rapid thermally annealed at 600°C for 30 s in flowing N$_2$ gas. See Tab. I to know more about these samples. A commercial grade hydride vapor phase epitaxy (HVPE) grown Si doped ($N_{Si} \approx 1 \times 10^{18}$ cm$^{-3}$) c-plane GaN(3 $\mu$m)/sapphire sample from

| Sample | $t$ (nm) | $N_{Ga}$ (cm$^{-3}$) | $N_{Si}$ (cm$^{-3}$) | $M_S$ (2 K) (emu/cm$^3$) | $M_S$ (300 K) (emu/cm$^3$) |
|--------|---------|---------------------|---------------------|------------------------|------------------------|
| C      | 700     | 6\times10^{16}     | 0                   | 0.52                   | 0.41                   |
| D      | 700     | 2.45\times10^{17}  | 0                   | 0.8                    | 0.54                   |
| D*     | 700     | 2.45\times10^{17}  | 0                   | -                      | 0.22                   |
| E      | 200     | 1\times10^{18}     | 2\times10^{19}      | 4                      | 2.5                    |
Note that the magnitude of PL polarization $|P|$ for $X_1$ peak is much weaker than those for $X_2$ and $X_3$ peaks [see Figure 2(b)].

FIG. 2. (a) PL spectra recorded at 1.5 K for samples with different Gd concentrations. Inset compares the PL spectra normalized with respect to the band edge transition for Gd-doped/undoped GaN samples and a piece of bare SiC substrate. PL spectra recorded at 1.5 K in $\sigma^+$ and $\sigma^-$ polarized states under a magnetic field of 7 T for (b) $X_1$, $X_2$, $X_3$ peaks in sample D and (c) $D^oX$ peaks in sample E. Red curves in panel (b) and (c) represent the magnitude of $P = (I^+ - I^-)/(I^+ + I^-)$ as a function of the photon energy.

FIG. 1. (a) Schematic depiction of the polarization selective magneto-photoluminescence (PL) spectroscopy setup. (b) Zeeman splitting of the conduction(valence) band minimum(maximum). Allowed optical transitions along with their polarization directions are also shown.
1.5 K, for $B > 1$ T. Polarization $P_i$ can thus be written as $P_i = -1/(\gamma_i/\beta_i + 1)$ for $B > 1$ T, meaning the ratio $\gamma_i/\beta_i = 1/|P| = -1$ can be obtained for Si-$D^{0}X$, and all the $X$-features, separately. Note that $\beta_i$ is expected to depend upon the magnetic field\cite{27}. However, $\gamma_i$ should be $B$-independent. If the i-th type of $X$-defects are ferromagnetically coupled, Zeeman splitting of the valence band like state of the exciton can be given by $\Delta E_{\text{h}}(B) = g_i\mu_B B + \alpha_i M(B)$, where $M(B)$ is the magnetization and $\alpha_i$ is the magnetic coupling coefficient. This means that each of the defects experiences an overall magnetic field of $B_F = B + B_E$. Saturation of magnetization $M_s$ leads to the saturation of the molecular field at $B_{Es} = w_i M_s$, where $w_i$ the coupling constant for the defects. If $X_i$-feature is stemming from a region of ferromagnetically coupled i-th defects, where $B_{Es}$ prevails over $B$, $\beta_i$ is expected to show much weaker $B$-dependence beyond the saturation field. Therefore, the ratio $\gamma_i/\beta_i$ as a function of $B$ can carry the information about the involvement of individual defect types in ferromagnetic coupling.

In Fig. 4, In(1/|P| - 1) is plotted as a function of $B$ for $X_1$ [Panel (a)], $X_2$ [Panel (b)], $X_3$ [Panel (c)] and $D^{0}X$ [Panel (d)] excitonic peaks in these samples. Evidently, in all cases, the data show a linear variation at high fields, which suggests that $\beta_i \propto B^{\nu_i}$ for all these NDBX. It is interesting to note that for all the $X$-features, the slope substantially decreases in samples with $N_{Gd} > 10^{17}$ cm$^{-3}$. Moreover, in sample D, the slope is increased for all the $X$-features upon annealing. Note that the saturation magnetization of the sample decreases by about 50% after annealing (see Tab. I)\cite{13}. On the other hand, the slope for the $D^{0}X$ exciton in the Si doped reference sample RS is very much the same as that of the sample E, which is co-doped with both Si and Gd. These results thus suggest that the defects associated with $X$-features in Gd doped GaN samples must be experiencing an overwhelmingly large $B_{Es}$ field, meaning these defects are ferromagnetically coupled. Interestingly, for the co-doped sample, $D^{0}X$ excitons associated with Si shallow donors do not experience any $B_{Es}$ field, which suggests that they are not involved in the ferromagnetic coupling. Role of the internal field in governing the slope of these plots becomes more explicit from the fact that upon annealing, $M_s$ (and hence $B_{Es}$) decreases and at the same time the slope increases in sample D.

Note that these defects are likely to be generated surrounding each Gd ion, whereas Si shallow donors are randomly distributed over the entire lattice as shown schematically in Fig. 5(a). Close proximity of the defects in the regions surrounding the Gd sites leads to defect-defect ferromagnetic coupling\cite{13}. This results in the formation of ferromagnetic domains surrounding every Gd site. Beyond a percolation threshold, a long range ferromagnetic order sets in. In this framework, the saturation magnetization can be expressed as $M_s = p_{Gd}N_{Gd} + p_o N_o[1-\exp(-v/N_{Gd})]$, where $p_{Gd}$ and $p_o$ are the bare magnetic moments per Gd ion and defect, respectively, $N_o$ the defect density within the cluster and $v=4/3\pi r_c^3$ the volume of each cluster. In one of our earlier works, we have estimated $p_o N_o = 4.68 \times 10^{19} \mu_B$ cm$^{-3}$ and $r_c = 22$ nm by fitting the experimental data from Ref. 1 with the above expression\cite{13}. If an average magnetic moment $\approx 3 \mu_B$ (predicted for N-interstitials\cite{19}) is attributed per

FIG. 3. (a) PL intensities recorded at $X_1$, $X_2$, $X_3$ peaks for sample D and at $D^{0}X$ peak for sample RS at 0 and 7 T magnetic field as a function of time as the polarization selection is abruptly switched between $\sigma^+$ or $\sigma^-$ states at two time points.

FIG. 4. Plots of In(1/|P| - 1) vs ln($B$) for (a) $X_1$, (b) $X_2$, (c) $X_3$ and (d) $D^{0}X$ peaks of the samples with different Gd concentrations ($N_{Gd}$). $D^*$ represents the sample D after annealing.
defect site, \( N_o \) comes out to be \( 1.56 \times 10^{19} \text{ cm}^{-3} \). It is noteworthy that a same order of magnitude of defect density has been estimated by Roever \textit{et al.} in their MBE grown Gd:GaN samples\(^{28}\). However, the actual distribution of \( N_o(r) \) may not be uniform inside the defect sphere. Rather a reduction of \( N_o(r) \) from the center to the surface is more realistic a scenario. Note that in the co-doped sample (sample E), \( N_{Si} \) is comparable with \( N_o \). If radial variation of \( N_o \) is taken into account, one can find a defect dominated zone (DDZ) around every Gd site, where \( N_o > N_{Si} \) as shown schematically in the figure. X-excitons are thus expected to be mostly present in DDZs, whereas Si-\( D^nX \) signal is arising from the regions outside these zones as depicted in Fig. 5(b). Because of their non-involvement in ferromagnetic coupling, Si-donors do not experience any strong molecular field, even though they are located in the regions where the back ground X-defects are ferromagnetically coupled. This can explain why \( \ln(1/|P| - 1) \) shows almost a \( B \)-independent behavior for all the X-features for this sample, while it decreases faster with increasing \( B \) for the Si-\( D^nX \) feature [see Fig. 4]. It should be mentioned that even though the saturation magnetizations are comparable for sample D and C, variation of \( \ln(1/|P| - 1) \) with \( B \) is much faster in sample C than in sample D. The reason might be the strength of the molecular field \( wM_s \), where \( w \) could depend upon the overlap of the defect clusters. Since in sample D, \( N_{Gd} \) is more than that in sample C, the overlap and hence \( wM_s \) is expected to be higher. We believe that \( wM_s \) prevails over \( B \) in sample D, while in sample C, the field \( B \gg wM_s \).

Observation of Fig. 4 suggests that the defects associated with all the X-features have neutral donor like states. Among all the defects, which are theoretically predicted to have magnetic moment, \( O_i \), \( V_{Ga} \) and \( V_N-V_{Ga} \) complexes do not contribute any donor like state at a position matching with those of \( X_1 \), \( X_2 \) and \( X_3 \)\(^{29,30}\), meaning that the \( D_{X_1}, D_{X_2} \) and \( D_{X_3} \) defects are unlikely to be either of the three. In fact, Roever \textit{et al.} using positron annihilation spectroscopy have shown that there is no direct correlation between Ga-vacancy and ferromagnetism observed in this material\(^{28}\). Nitrogen split interstitials, whose formation energy is one of the lowest among all point defects and their complexes, can have a 0/-1 state at about 0.48 eV below the conduction band minimum\(^{29}\). This position matches quite well with that of \( X_1 \) feature. Moreover, each \( N_i \) is expected to contribute 3 \( \mu_B \) of magnetic moment\(^{19}\). Our finding, therefore, indicates that \( D_{X_1} \) defects are N-interstitials. Positions of \( X_2 \) and \( X_3 \) do not match with those of any known point defect contributing neutral donor like states. It is noteworthy that upon annealing, PL intensity of \( X_1 \)-feature reduces quite significantly as compared to those of \( X_2 \) and \( X_3 \)\(^{13,14}\), implying that \( D_{X_2} \) and \( D_{X_3} \) defects have better thermal stability than \( D_{X_1} \) defects. It is plausible that \( D_{X_2} \) and \( D_{X_3} \) defects are also \( N_{Si} \)s that make complexes with certain other point defects/impurities, which has better thermal stability than isolated \( N_i \).

In conclusion, incorporation of Gd in GaN produce three types of donor like defects, which result in three neutral donor bound excitonic (NBDX) features appearing at about 3.05, 3.15 and 3.25 eV in the low temperature PL spectra. It has been shown that the dependence of spin-flip scattering rate on the magnetic field (\( B \)) for these NDBX features carry the information about the involvement of the associated defects in magnetic coupling. Our study shows that all the three signals must be stemming from those defects, which are ferromagnetically coupled with each other.

**ACKNOWLEDGEMENTS**

The authors acknowledge the financial support of this work by the Department of Science and Technology of the Government of India under the Project Code SR/S2/CMP-71/2012. We also would like to thank Paul-Drude-Institute, Berlin, Germany for the samples and Prof. S. Ghosh of TIFR, Mumbai for help in certain characterizations.

---

\* dhar@phy.iitb.ac.in

1. S. Dhar, O. Brandt, M. Ramsteiner, V. F. Sapega, and K. H. Ploog, \textit{Phys. Rev. Lett.} \textbf{94}, 037205 (2005).

2. S. Dhar, L. Pérez, O. Brandt, A. Trampert, K. H. Ploog, J. Keller, and B. Beschoten, \textit{Phys. Rev. B} \textbf{72}, 245203 (2005).

3. A. Ney, T. Kammermeier, K. Ollefs, V. Ney, S. Ye, S. Dhar, K. Ploog, M. Röver, J. Malindretos, A. Rizzi, F. Wilhelm, and A. Rogalev, \textit{Journal of Magnetism and Magnetic Materials} \textbf{322}, 1162 (2010), proceedings of the Joint European Magnetic Symposia.
4 J. K. Hite, R. M. Frazier, R. Davies, G. T. Thaler, C. R. Abernathy, S. J. Pearton, and J. M. Zavada, Applied Physics Letters 89, 092119 (2006).
5 A. Bedoya-Pinto, J. Malindretos, M. Roever, D. D. Mai, and A. Rizzi, Phys. Rev. B 80, 195208 (2009).
6 H. Asahi, Y. K. Zhou, M. Hashimoto, M. S. Kim, X. J. Li, S. Emura, and S. Hasegawa, Journal of Physics: Condensed Matter 16, S5555 (2004).
7 J. Hite, G. T. Thaler, R. Khanna, C. R. Abernathy, S. J. Pearton, J. H. Park, A. J. Steckl, and J. M. Zavada, Applied Physics Letters 89, 092119 (2006).
8 L. Sun, C. Liu, J. Li, J. Wang, F. Yan, Y. Zeng, and J. Li, Materials Letters 65, 667 (2011).
9 S. Dhar, T. Kammermeier, A. Ney, L. Pérez, K. H. Ploog, A. Melnikov, and A. D. Wieck, Applied Physics Letters 89, 062503 (2006).
10 M. A. Khaderbad, S. Dhar, L. Pérez, K. H. Ploog, A. Melnikov, and A. D. Wieck, Applied Physics Letters 91, 072514 (2007).
11 S. Wang, X. Xie, H. Liu, Q. Hao, Y. Li, L. Liang, and C. Liu, Journal of Alloys and Compounds 712, 482 (2017).
12 J. Mishra, S. Dhar, and O. Brandt, Solid State Communications 150, 2370 (2010).
13 T. Kammermeier, A. Ney, L. Pérez, K. H. Ploog, and A. D. Wieck, Applied Physics Letters 89, 062503 (2006).
14 Y. Gohda and A. Oshiyama, Phys. Rev. B 78, 161201 (2008).
15 Y. Gohda and A. Oshiyama, Phys. Rev. B 78, 161201 (2008).
16 L. Liu, P. Y. Yu, Z. Ma, and S. S. Mao, Phys. Rev. Lett. 100, 127203 (2008).
17 A. Thiess, S. Blügel, P. H. Dederichs, R. Zeller, and W. R. L. Lambrecht, Phys. Rev. B 92, 104418 (2015).
18 C. Mitra and W. R. L. Lambrecht, Phys. Rev. B 80, 081202 (2009).
19 Z. Zhang, U. Schwingenschlögl, and I. S. Roqan, Journal of Applied Physics 116, 183905 (2014).
20 Y. Gohda and A. Oshiyama, Journal of the Physical Society of Japan 79, 083705 (2010).
21 S. Sun, P. Wu, and P. Xing, Applied Physics Letters 101, 132417 (2012), and references therein.
22 A. V. Rodina and B. K. Meyer, Phys. Rev. B 64, 245209 (2001).
23 A. V. Rodina, M. Dietrich, A. Göldner, L. Ecken, A. Hoffmann, A. L. Efros, M. Rosen, and B. K. Meyer, Phys. Rev. B 64, 115204 (2001).
24 See supplementary materials for the derivation of polarization associated with luminescence arising from neutral donor bound excitons.
25 G. Bacher et al., Advances in Solid State Physics, Vol. 41 (Springer, Springer-Verlag Berlin Heidelberg, 2001) pp 51-62.
26 B. Beschoten, E. Johnston-Halperin, D. K. Young, M. Poggio, J. E. Grimaldi, S. Keller, S. P. DenBaars, U. K. Mishra, E. L. Hu, and D. D. Awschalom, Phys. Rev. B 63, 121202 (2001).
27 I. C. Diallo and D. O. Demchenko, Phys. Rev. Applied 6, 064002 (2016).
28 A. F. Wright, Journal of Applied Physics 98, 103531 (2005).