Experimental evidence of Ga-vacancy induced room temperature ferromagnetic behavior in GaN films

Basanta Roul,[1,2] Mohana K. Rajpalke,[1] Thirumaleshwara N. Bhat,[1] Mahesh Kumar,[1,2] A. T. Kalghatgi,[2] S. B. Krupanidhi,[1,a)] Nitesh Kumar,[3] and A. Sundaresan[3]
[1]*Materials Research Centre, Indian Institute of Science, Bangalore 560012, India*
[2]*Central Research Laboratory, Bharat Electronics, Bangalore 560013, India*
[3]*Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P. O., Bangalore 560064, India*

(Received 14 July 2011; accepted 28 September 2011; published online 20 October 2011)

We have grown Ga deficient GaN epitaxial films on (0001) sapphire substrate by plasma-assisted molecular beam epitaxy and report the experimental evidence of room temperature ferromagnetic behavior. The observed yellow emission peak in room temperature photoluminescence spectra and the peak positioning at 300 cm^{-1} in Raman spectra confirms the existence of Ga vacancies. The x-ray photoelectron spectroscopic measurements further confirmed the formation of Ga vacancies; since the N/Ga is found to be >1. The ferromagnetism is believed to originate from the polarization of the unpaired 2p electrons of N surrounding the Ga vacancy. © *2011 American Institute of Physics*. [doi:10.1063/1.3654151]

Diluted magnetic semiconductors (DMSs) have been an intense area of research in recent years due to their potential applications in spintronics devices,[1] which exploits both the spin and charge degree of freedom of carriers (electron/holes). A major drawback of making DMSs materials is the low solubility of magnetic elements in the semiconductor compounds.[2] However, if one can find the ferromagnetism in the semiconductor materials without any transition metal doping, this may bring new opportunity to the field of spintronics. For there will be no issues due to clustering of magnetic dopants. The study of (Ga,Mn)N system has provided impetus to the subject of DMS (Refs. 3–7) and it is reported that such system can exhibit ferromagnetism with curie temperature (T_c) varying from liquid helium temperature[6] to 940 K.[7] In the present days, many materials have also been found to exhibit even the ferromagnetic behavior without any magnetic element doping. The observation of room temperature ferromagnetism in various thin films of nonmagnetic oxides (d^0 systems) viz. HfO_2, TiO_2, ZnO, and MgO is interesting.[8–11] The origin of ferromagnetism in such material is attributed to the oxygen vacancies. Recently, room temperature ferromagnetism has been observed by Madhu *et al.*[12] in GaN nanoparticles with different sizes, where the origin of ferromagnetism has been proposed due to the defects confined to the surface of the nanoparticles. Albeit, there is incessant investigation in this direction, the complete knowledge about the origin of ferromagnetism in nonmagnetic semiconductor is still under debate. The theoretical investigation as to GaN predicts the occurrence of induced ferromagnetism in GaN films due to Ga vacancy.[13–16] In spite of that, there is lack of experimental evidence to confirm the theoretical prediction about the origin of ferromagnetism in GaN thin films. In the present work, we have attempted on this issue to understand the manifestation of Ga vacancy induced ferromagnetism in GaN thin films.

The GaN films were grown on c-sapphire substrate by plasma-assisted molecular beam epitaxy (PAMBE) system. The substrates were thermally cleaned at 750 °C for 30 min followed by nitridation treatment for 30 min at 700 °C. After substrate nitridation, the films were grown by using two step processes: growth of low temperature GaN buffer layer of thickness 20 nm at 500 °C followed by high temperature (780 °C) epilayer. The thickness of the GaN samples investigated in this study was ~150 nm. During the growth, the RF power of nitrogen plasma and the Gallium beam equivalent pressure was fixed at 350 W and 5.6×10^{-7} mbar, respectively, while the nitrogen flow rate was varied. The nitrogen flow rate for the samples were 0.5 (sample-A) and 0.3 (sample-B) sccm. The structural characterization of the as-grown samples was carried out by high-resolution x-ray diffraction (HRXRD). The x-ray photoelectron spectroscopy (XPS) analysis was carried out with a Thermo Scientific Multilab-2000 spectrometer using a monochromatic Al Kα ($h\upsilon = 1486.6$ eV) source. The stoichiometry of the GaN films was determined by comparing the integrated area of the Ga $2p_{3/2}$ and N 1s photoelectron lines using the appropriate atomic sensitive factors. The room temperature photoluminescence (PL) was carried out on GaN films by using He-Cd laser with 325 nm wavelength. Raman spectroscopy measurements were carried out by using Ar+ laser with 514 nm wavelength. The magnetization measurements, as a function of magnetic field, at different temperatures, were carried out by using a superconducting quantum interference device (SQUID) magnetometer.

Figure 1(a) shows a typical $2\theta - \omega$ HRXRD scan of GaN film (sample-B) grown on c-plane sapphire substrate. The peaks at $2\theta = 34.56°$ and 72.81° are assigned to the (0002) and (0004) planes of the GaN films, respectively. The strong peak at $2\theta = 41.69°$ is assigned to the Al_2O_3 (0006) reflection. The HRXRD pattern confirms the c-direction growth of GaN film with hexagonal structure. In order to get information on the presence of Ga vacancies in the GaN films, we have studied the room temperature PL and Raman

a)Electronic mail: sbk@mrc.iisc.ernet.in.

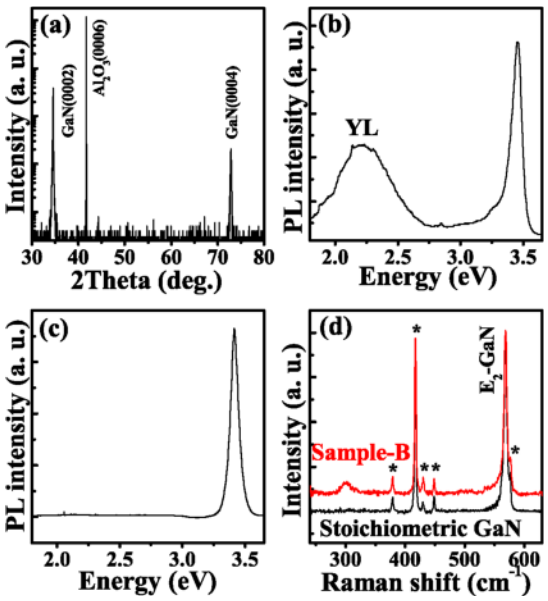

FIG. 1. (Color online) (a) $2\theta-\omega$ HRXRD scanning curve of GaN film (sample-B) grown on c-sapphire. (b) Room temperature PL spectra of Ga deficient GaN film (sample-B). (c) PL spectra of typical stoichiometric GaN film and (d) Raman spectrum of GaN films.

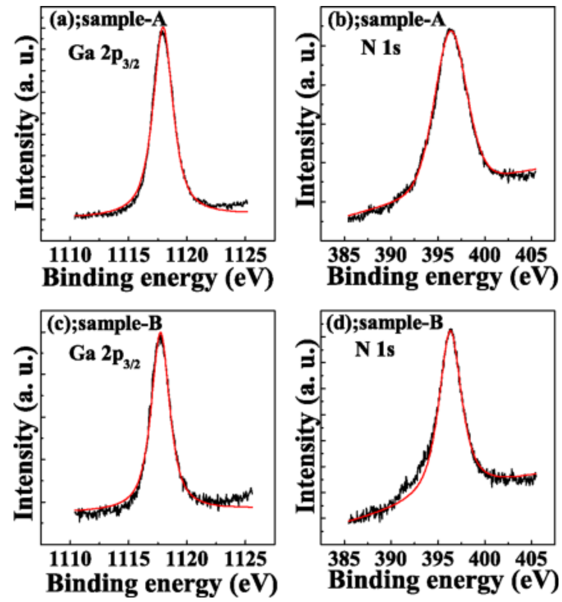

FIG. 2. (Color online) (a)-(b) XPS spectra of Ga $2p_{3/2}$ and N 1s core level of sample-A and (c)-(d) XPS spectra of Ga $2p_{3/2}$ and N 1s core level of sample-B.

spectroscopy. Figure 1(b) shows the room temperature PL spectra of the GaN film (sample-B). The spectra exhibit two distinct features namely ultra-violet emission at 3.4 eV and the yellow broad band emission centered around 2.2 eV.[17] The peak at around ~3.4 eV is usually attributed to the free excitonic transition with radiative emission between valence and conduction bands of GaN. The broad yellow luminescence (YL) peak arises because of the Ga vacancy which forms at high growth temperature with low nitrogen flow rate.[18] At the high temperature, the Ga desorption rate is higher in the presence of lesser nitrogen pressure, which will lead to formation of Ga vacancy. The PL spectrum of a typical stoichiometric GaN sample is shown in the Fig. 1(c), which shows emission only at 3.4 eV. Figure 1(d) shows Raman spectra of sample-B and a stoichiometric GaN sample. Raman spectra displays E_2(high) phonon peaks of the GaN films along with substrate peaks assigned by asterisk (*). Raman spectrum of sample-B exhibited a peak positioning at 300 cm^{-1}, which is attributed to Ga vacancies.[19,20] In essence, the PL and Raman spectroscopy confirms the existence of Ga vacancies in the GaN films.

In order to quantify the percentage of elements present on the surface of the films, we have carried out XPS studies. Figure 2 represent the XPS spectra of core level electrons associated with different elements in GaN. Shifting of the electron binding energies due to charging of the sample was corrected by assuming the C 1s peak at 285 eV for the determination of binding energy of different elements. Figures 2(a) and 2(b) show the XPS spectra of Ga $2p_{3/2}$ and N 1s core level in sample-A, while Figs. 2(c) and 2(d) represent for sample-B. The areas of the Ga $2p_{3/2}$ and N 1s peaks are determined and then normalized using atomic sensitivity factors (3.341 for Ga and 0.477 for N). The elemental ratio (*N:Ga*) in the samples can be determined by the relation, $N{:}Ga = A_N F_{Ga}/A_{Ga} F_N$, where *A* and *F* are the area of the elemental peak and atomic sensitivity factor, respectively. Using the above mentioned relation, the elemental ratio (N/Ga) in the sample-A and sample-B was found to be 2.1 and 4.3, respectively. Hence, the XPS study evidently demonstrates the presence of Ga deficiency in both the GaN films. The induced room temperature ferromagnetic behavior of GaN films because of Ga vacancy will be discussed in the following paragraph.

Figure 3 shows the magnetization versus applied magnetic field (*M-H*) plots for the GaN films recorded at room temperature for both sets of samples. The magnetization measurement was carried out with field applied parallel to the plane of the sample. The diamagnetic contribution of the sapphire substrate has been subtracted from the measured magnetization and then the magnetization is normalized by the area of the sample. It is distinct from Fig. 3 that both sets of samples exhibit well defined hysteresis loop signifying the

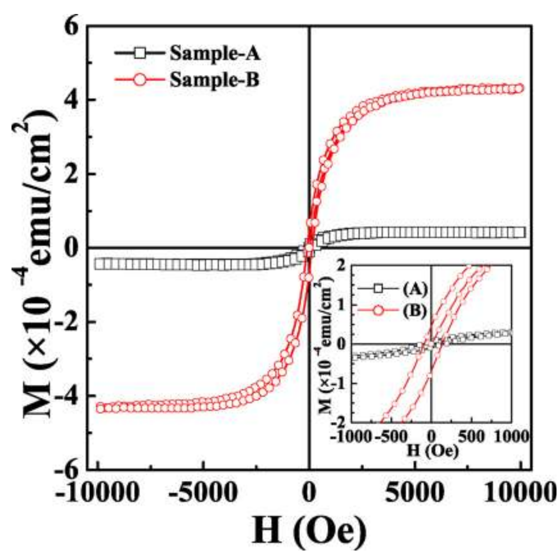

FIG. 3. (Color online) Magnetization versus magnetic field (*M-H*) at RT for GaN films with N:Ga ~ 2.1:1 (sample-A) and 4.3:1 (sample-B). The inset presents the zoomed view of the *M-H* plot.

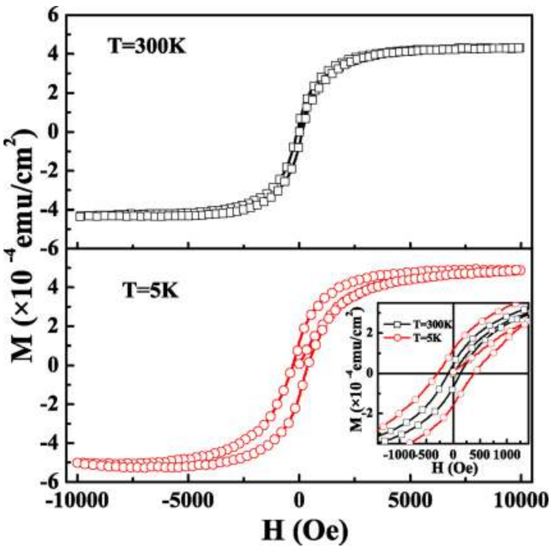

FIG. 4. (Color online) Magnetization versus magnetic field (*M-H*) for GaN film with N:Ga ~ 4.3:1 (sample-B) at RT and 5 K. The inset shows the close up view of the *M-H* plot.

characteristic of ferromagnetic behavior. The value of saturation magnetization (M_s) was found to be 0.44×10^{-4} and 4.31×10^{-4} emu/cm^2 for sample-A and sample-B, respectively. The observed higher value of saturation magnetization in sample-B strongly suggests that the Ga vacancies are the source of ferromagnetism in the GaN films. Such intrinsic ferromagnetism is naively believed to have a genesis associated with Ga vacancies that releases holes into the system. It has to be noted here that the spin polarized band structure calculation by Larson and Satpathy[15] predicts the formation of three distinct spin polarized states above the Fermi level (E_F) where three holes associated with each Ga vacancy are shared by four neighboring N atoms of GaN. The asymmetry of density of states at the Fermi level [$D(E_F)$] results a finite spin polarization (P) and characterize the system to be ferromagnetic in nature since for conventional ferromagnets, $P = \frac{D_\uparrow(E_F) - D_\downarrow(E_F)}{D_\uparrow(E_F) + D_\downarrow(E_F)} \neq 0$. In a nutshell, the polarization of unpaired electrons associated with Nitrogen ($N = 1s^2 2s^2 2p_x{}^1 2p_y{}^1 2p_z{}^1$) around the Ga vacancy gives rise to induced local magnetic moment and these induced magnetic moment interact cooperatively to exhibit the ferromagnetism.[13] The zoomed view of the room temperature *M-H* plot for the Ga deficient GaN films is shown in inset of Fig. 3. The remanent magnetization (M_R) obtained for the sample-A and sample-B was found to be 0.06×10^{-4} and 0.45×10^{-4} emu/cm^2, respectively.

Figure 4 shows the *M-H* curves for sample-B (N:Ga ~ 4.3:1) at two different temperatures (5 and 300 K). The inset in Fig. 4 shows the close up view of the *M-H* plot. It is clear from the inset that the M_R and coercive field (H_C) at 5 K show an enhanced value ($M_R \sim 1.18 \times 10^{-4}$ emu/cm^2 and $H_C \sim 390$ Oe) compared to the value at 300 K ($M_R \sim 0.45 \times 10^{-4}$ emu/cm^2 and $H_C \sim 136$ Oe), as expected for ferromagnetic materials.

In summary, we have grown Ga deficient GaN epitaxial films on (0001) sapphire substrate by PAMBE and report the experimental evidence of room temperature ferromagnetism, induced by Ga vacancies. The observation of broad yellow emission peak at 2.2 eV in PL spectra and a peak positioning at 300 cm^{-1} in Raman spectra confirm the existence of Ga vacancies in the films. The x-ray photoelectron spectroscopic measurements further confirmed the formation of Ga vacancies. The magnetization as a function of magnetic field measured on Ga deficient GaN films exhibited room temperature ferromagnetism and the saturation magnetization is found to increase with increasing Ga vacancy. Such manifestation is strongly believed to originate from the polarization of unpaired 2 p electrons of N surrounding the Ga vacancy.

[1] Y. Ohno, D. K. Young, B. Beschoten, F. Matsukura, H. Ohno, and D. D. Awschalom, Nature (London) **402**, 790 (1999).
[2] H. Ohno, Science **281**, 951 (1998).
[3] N. Theodoropoulou, A. F. Hebard, M. E. Overberg, C. R. Abernathy, S. J. Pearton, S. N. G. Chu, and R. G. Wilson, Appl. Phys. Lett. **78**, 3475 (2001).
[4] J. M. Baik, Y. Shon, T. W. Kang, and J. L. Lee, Appl. Phys. Lett. **84**, 1120 (2004).
[5] E. Sarigiannidou, F. Wilhelm, E. Monroy, R. M. Galera, E. Bellet-Amalric, A. Rogalev, J. Goulon, J. Cibert, and H. Mariette, Phys. Rev. B **74**, 041306 (2006).
[6] S. Dhar, O. Brandt, A. Trampert, K. J. Friedland, Y. J. Sun, and K. H. Ploog, Phys. Rev. B **67**, 165205 (2003).
[7] S. Sonodaa, S. Shimizua, T. Sasakib, Y. Yamamotob, and H. Horia, J. Cryst. Growth **237–239**, 1358 (2002).
[8] M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey, Nature (London) **430**, 630 (2004).
[9] N. H. Hong, J. Sakai, N. Poirot, and V. Brizé, Phys. Rev. B **73**, 132404 (2006).
[10] N. H. Hong, J. Sakai, and V. Brize, J. Phys.:Condens. Matter **19**, 036219 (2007).
[11] M. Kapilashrami, J. Xu, K. V. Rao, L. Belova, E. Carlegrim, and M. Fahlman, J. Phys.: Condens. Matter **22**, 345004 (2010).
[12] C. Madhu, A. Sundaresan, and C. N. R. Rao, Phys. Rev. B **77**, 201306 (2008).
[13] P. Dev, Y. Xue, and P. Zhang, Phys. Rev. Lett. **100**, 117204 (2008).
[14] J. Hong, J. Appl. Phys. **103**, 063907 (2008).
[15] P. Larson and S. Satpathy, Phys. Rev. B **76**, 245205 (2007).
[16] H. Jin, Y. Dai, B. Huang, and M. H. Whangbo, Appl. Phys. Lett. **94**, 162505 (2009).
[17] J. Neugebauera and C. G. Van de Walle, Appl. Phys. Lett. **69**, 503 (1996).
[18] G. Koblmüller, F. Reurings, F. Tuomisto, and J. S. Speck, Appl. Phys. Lett. **97**, 191915 (2010).
[19] M. Katsikini, K. Papagelis, E. C. Paloura, and S. Ves, J. Appl. Phys. **94**, 4389 (2003).
[20] P. J. Huang, C. W. Chen, J. Y. Chen, G. C. Chi, C. J. Pan, C. C. Kuo, L. C. Chen, C. W. Hsu, K. H. Chen, S. C. Hung, C. Y. Chang, S. J. Pearton, and F. Ren, Vacuum **83**, 797 (2009).