Ga-vacancy-induced room-temperature ferromagnetic and adjusted-band-gap behaviors in GaN nanoparticles

Huihui Ren · Jikang Jian · Chu Chen · Dong Pan ·
Abdulezi Ablat · Yanfei Sun · Jin Li · Rong Wu

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Abstract Room-temperature ferromagnetism has been found in Ga-deficient GaN grown using the direct reaction of Ga₂O₃ powder with NH₃ gas. The observed magnetism in GaN induced by Ga vacancies is investigated both experimentally and theoretically. First-principles calculations reveal that the spontaneous spin polarization is created by the 3.0 μ_B local moment for GaN and magnetism originates from the polarization of the unpaired 2*p* electrons of N surrounding the Ga vacancy. At the same time, the band gap can be also adjusted by changing the Ga-vacancy concentration.

1 Introduction

Dilute magnetic semiconductors (DMSs) [1–3] are promising candidate materials in spintronics as they exhibit intrinsic properties of both semiconductor and ferromagnetic materials. GaN is one of the important III–V group semiconductors and much effort has been devoted to grow GaN as nanowires, nanorods, and nanobelts [4–6] synthesized by various routes. As one promising candidate to produce room-temperature ferromagnetism, GaN-based DMSs doped with transition

metal such as Mn [7] and Fe [8] have been reported. However, there is strong evidence that the traditional magnetic components are not the sole cause of ferromagnetism. Indeed, the origin of ferromagnetism in these DMSs is still controversial owing to poor solubility and possible secondary-phase and clustering mechanisms that limit the application of GaN. Recently, room-temperature ferromagnetism of the nonmagnetic component Cu-doped GaN DMSs was reported [9]; ferromagnetism was attributed to *p*–*d* hybridization between Cu and N atoms, which induces delocalized magnetic moments and long-range coupling. If a semiconductor could realize magnetism by itself, this would give a great boost to spintronics. Of late, theoretical studies revealed that defect states in *sp* materials could contribute to the moments and the extended tails of their wave functions mediate long-range magnetic coupling without any dopants. In fact, vacancies were proved capable of inducing ferromagnetic independently in wide band gap semiconductors, such as AlN [10], InN [11], and BN [12]. Chen's group has reported defects and magnetic properties of semi-insulating *p*-type 6H-SiC with neutron irradiations [13], and anion vacancy-induced magnetism in an AlN system revealing that the localized nature of the defect states fostered the formation of local moments at nitrogen vacancies. Moreover, cation-vacancy-introduced magnetization was reported also for CaO [14] and HfO₂ [15], but producing these under thermal equilibrium is extremely difficult as the formation energy of the cation vacancies is too high for any practical utility. Cui et al. [16] reported a significant reduction in their formation energy and thereby induced ferromagnetism in AlN by doping the nonmagnetic element Sc. Recently, attention has been focused on intrinsic defects, hence the study of the intrinsic regime is preferred. Nevertheless, creating cation vacancies in nitrides still remains difficult due to their high formation energies. As is well-known, the Ga vacancy is an intrinsic defect in GaN, thus

H. Ren · J. Jian · C. Chen · A. Ablat · Y. Sun · J. Li · R. Wu (✉)
Key Laboratory of Solid-State Physics and Devices,
Department of Physics, Xinjiang University,
Urumqi, Xinjiang 830046, People's Republic of China
e-mail: renhuihui1105@163.com

R. Wu
e-mail: wurongxju@sina.com

D. Pan
State Key Laboratory of Superlattices and Microstructures,
Institute of Semiconductors, Chinese Academy of Sciences,
P.O. Box 912, Beijing 100083, People's Republic of China

Ga-vacancy-induced magnetism in the GaN system must be intrinsic.

In this paper, we report our result, both theoretical and experimental, on controlling Ga-vacancy-induced magnetism in GaN. First-principles calculations reveal that spontaneous spin polarization is created by a $3.0 \mu_B$ local moment for GaN and the magnetic moment originates from the polarization of the unpaired $2p$ electrons of N surrounding the Ga vacancy. Such vacancies promote room-temperature ferromagnetics in GaN as evident from experimental results, which are consistent with theoretical simulations based on density functional theory. Concurrently, the band gap can be also adjusted by Ga vacancies.

2 Experimental

GaN nanoparticles were synthesized in a horizontal tube furnace. In a typical procedure, Ga_2O_3 powder and NH_3 were used as Ga and N sources. The Ga_2O_3 powder was loaded into a ceramic boat and placed at the center of the quartz tube. The nanoparticles were grown by a two-step process. The first involves growing GaN nanoparticles: the furnace was flushed with argon (Ar, 99.99 %) gas until 950°C , then switched to NH_3 gas flowing at 100–200 sccm, and subsequently the furnace was heated to 980°C . After 3 h thermal activation, the product was allowed to cool naturally to 600°C in NH_3 atmosphere. The second step involves continued growth, but in a reversed sequence: the quartz tube and product were heated again to the same temperature for 2 h in NH_3 atmosphere. Next, the flow was switched to Ar gas and the product was cooled to room temperature naturally.

The crystal, microstructures, and chemical components of the samples were analyzed using X-ray diffraction (XRD, M18XHF22-SRA, MAC Science Co. Japan) with a $\text{CuK}\alpha$ radiation source, scanning electron microscopy (SEM, 1430VP, LEO, Germany), and high-resolution transmission electron microscopy (HRTEM), (JEM-2100, JEOL Ltd, Japan). The optical transmittance measurements were performed using an ultraviolet (UV) absorption spectrophotometer, (U-3010, Hitachi, Japan). Photoluminescence spectra (PL) were collected at room temperature using a spectrofluorometer (RF-5301, Shimadzu, Japan). Raman spectra were recorded at room temperature using a laser Raman spectrometer (JY-HR800, Horiba Jobin Yvon SAS) under a back-scattering configuration mode using a 532-nm solid-state laser as excitation source. The X-ray absorption spectra (XAS) were measured at the BL08U beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The magnetic properties were measured with a vibrating sample magnetometer (VSM, 7410 Series, Lake Shore, USA) and superconducting quantum interference device magnetometer (SQUID, MPMS-7, Quantum Design Inc., USA).

3 Results and discussion

Figure 1a shows the XRD pattern of the as-synthesized GaN nanoparticles (the sample of GaN-1). All diffraction peaks in the pattern can be indexed to a hexagonal wurtzite-structure with lattice constants $a = b = 3.189 \text{ \AA}$ and $c = 5.186 \text{ \AA}$ (ICDD-PDF: 50-0792, space group $\text{P6}_3\text{mc}$). Within the XRD sensitivity, no contributions from impurities or secondary phases were detected. This result was also supported by the corresponding EDS spectrum which contained only Ga and N signals (Fig. 1a inset).

The Ga/N ratio is 0.90. Typical SEM image of the GaN-1 product (Fig. 1b) shows that the nanoparticles have similar spindle shapes. These nanoparticles can be obtained in high yields with lengths of several hundred nanometers and diameters of 100–200 nm. The microstructural analysis of the nanoparticles, performed using HRTEM image of GaN-1 sample (upper inset Fig. 1b), revealed a clear lattice spacing of 0.231 nm, which is in agreement with the spacing of wurtzite GaN (ICDD-PDF: 50-0792). The lower inset is the corresponding fast Fourier transform (FFT) spectrum which confirms that the GaN nanoparticle is a single crystal.

Figure 1c shows the PL spectrum of the GaN-1 nanoparticle upon excitation at 325 nm recorded at room temperature. The spectrum exhibits three distinct features: a blue emission at 413 nm, another broad-band blue emission centered on 467 nm and a yellow luminescence band emission centered on 516 nm. The peak around 413 nm is usually attributed to the free excitonic transition with radiative emission between valence and conduction bands of GaN [17]. The strong peak located at 467 nm has been observed before in GaN nanocrystallite solids [18] and cylindrical GaN nanowires [19]. Here, the band at 467 nm is probably attributed to the conduction band to V_{Ga} , or some residual impurities [20]. The peak around 516 nm was attributed to cation vacancy (Ga vacancy) as reported in a previous work [21]. At the high growth temperature, the Ga desorption rate is higher in the presence of lesser nitrogen pressure, which will lead to the formation of Ga vacancy. The Raman spectrum of the GaN-1 (Fig. 1d) was obtained at room temperature. Three main peaks centered at 531, 566, and 727 cm^{-1} are correlated with the first-order vibrational modes of A_1 (TO), E_2 (high), and A_1 (LO) for GaN-1 nanostructures, respectively. One extra peak seen at 260 cm^{-1} is attributed to the zone-boundary phonon activated by the surface disorders and finite-size effect [22]. Another peak at 420 cm^{-1} is attributed to the overtones of transverse acoustic phonons [23,24]. The Raman mode at 300 cm^{-1} is ascribed to the cation vacancy (Ga vacancy), a host-lattice atom [25,26]. Both PL and Raman spectroscopy confirm the existence of these Ga vacancies in the GaN nanoparticle.

The Ga L-edge XAS of three sets with different Ga vacancies, Ga foil (99.9999 %), and stoichiometric GaN (from Alfa

Fig. 1 **a** XRD pattern of the GaN nanoparticles obtained using CuK α radiation. Inset is corresponding EDS image. **b** SEM image of the GaN nanoparticles. Inset is the corresponding HRTEM and FFT patterns.

c Room-temperature photoluminescence spectrum of the GaN-1 sample excited at 325 nm. **d** Raman scattering of the GaN-1

Fig. 2 Ga L-edge XAS spectra of Ga foil, stoichiometric GaN, and three sets of different Ga vacancies of GaN nanoparticles. Spectra are normalized to the integrated spectral area between 1,115 and 1,160 eV

Aesar, wurtzite, 99.999 %) are shown in Fig. 2. The XAS yield information on the core electron excitations into unoccupied states as a function of photon energy; that is, it gives the cross-sectional variation of the measured photoelectron density of states (DOS) versus photon energy. The Ga L-edge

XAS result from electron excitations from the $2p$ orbital to the ($4s$, $4d$) orbitals in the conduction band and provide the DOS for unoccupied s and d states. In Fig. 2, the spectral features and absorption edges of all samples are very similar to the Ga L-edge XAS of the stoichiometric GaN and hexagonal GaN [27], whereas these are quite distinct from those of Ga 0 for the Ga foil. Thus, we conclude that the Ga ions are in trivalent states in samples with hexagonal crystal structure. The structural confirmation from XAS is consistent with the XRD measurements. Further work shall be conducted to determine the origin of each peak and variation of the s – d hybridization strength in different samples and corresponding results will be presented elsewhere.

The magnetization measurements, performed on a VSM with 10^{-6} -emu sensitivity, give the dependence of magnetization on applied magnetic field (M – H) for three sets of GaN samples recorded at 300 K (Fig. 3a). All the M – H curves are in the shape of a distinct hysteresis loop, indicating these samples have room-temperature ferromagnetism. Their saturation magnetizations (M_s) and coercive fields (H_c) are about 13.62×10^{-3} , 9.53×10^{-3} , 5.97×10^{-3} emu/g, and 150.31, 89.21, 108.32 Oe, respectively. The quantitative analysis indicates that the atomic ratios of Ga/N in GaN-

Fig. 3 **a** Magnetic hysteresis loops of the sample at $T = 300$ K: GaN-1, GaN-2 and GaN-3. The inset is enlargement of the hysteresis loops. **b** Temperature dependence of magnetization at $B = 0$ T for the GaN-1 sample. The inset is corresponding temperature dependence FC/ZFC curve image. **c** The strong polarization results in a complete separation

between majority- and minority-spin states. The Fermi level is indicated by the dashed vertical line. **d** Isosurface spin density plot of the net spin states associated with a V_{Ga} in a 72-atom GaN supercell, Ga atoms are shown in brown stick and N atoms in blue, blue ball represents the spin density

1, GaN-2, and GaN-3 different values are estimated to be 0.90, 0.95, and 0.98, respectively. Obviously, M_s is found to increase with increasing Ga-vacancy concentration. Figure 3b displays the temperature dependence of the magnetic properties in the absence of an applied magnetic field for the GaN-1 nanoparticles in the temperature range from 5 to 300 K with a SQUID. Temperature dependence of remanent magnetization showed that the ferromagnetic transition temperature was beyond 300 K. In addition, the smooth and featureless $M-T$ curve indicates the absence of any secondary or residual parasitic magnetic phase, in agreement with the previous XRD result. The temperature dependence of the magnetic properties was also investigated by zero field cooled-field cooled (ZFC-FC) measurements, which were obtained by applying a magnetic field of 100 Oe for GaN-1 sample (see inset of Fig. 3b). The ZFC-FC curves have a clear separation ($\Delta M > 0$) at 300 K further indicating that the sample has room-temperature ferromagnetism. Indeed, although our samples are N-rich as determined by EDS, clusters or second phases have not been observed from XRD and XAS measurements. To further detect the magnetic impurity level, in particular, the concentration of Fe,

Co and Ni, ICP-MS measurements have been carried out in our GaN samples (not shown here). It is found that the total magnetic moments estimated from the detected impurity concentration of Fe, Co and Ni, are very small to account for the observed magnetism by at least one order of magnitude. PL and Raman spectroscopy confirm the existence of Ga vacancies in the samples. Thus, we consider the characteristic associated with room-temperature ferromagnetic behavior is the intrinsic properties of the GaN samples, and the ferromagnetism can be induced by Ga vacancies. In other words, Ga vacancies modify the room-temperature ferromagnetic behavior in GaN.

To understand the nature of the observed magnetism mentioned above, we carried out first-principles calculations based on density functional theory using Dmol³ code. The ideal GaN crystal, as well as the defective structures with Ga vacancies and N interstitials, was studied. Because of N interstitial formation, our calculation predicted magnetism in GaN and revealed that it resulted from Ga vacancies. The local density approximation (LDA) [28] with the Perdew-Wang (PWC) approximation [29] was employed with the exchange-correlation functional. All structures were opti-

Fig. 4 **a** UV-vis spectra of the three samples with different concentrations of Ga vacancies. **b** $(\alpha h\nu)^2$ versus energy for the three samples. The band structure of GaN semiconductor in different supercells from periodic DFT calculations: **c** $\text{Ga}_{36}\text{N}_{36}$; **d** $\text{Ga}_{35}\text{V}_{\text{Ga}}\text{N}_{36}$; **e** $\text{Ga}_{53}\text{V}_{\text{Ga}}\text{N}_{54}$ and **f** $\text{Ga}_{63}\text{V}_{\text{Ga}}\text{N}_{64}$

mized given the symmetry restriction. The spin-unrestricted self-consistent field calculation was done with a convergence criterion of 10^{-4} a.u. The values of total energy, maximum force, and maximum displacement are estimated to be 1.0×10^{-4} Ha (1 Ha = 27.2 eV), 0.02 Ha/Å, and 0.05 Å, respectively. The lattice constants of the structure were fixed from the experimental values of GaN crystal, $a = b = 3.189$ Å and $c = 5.186$ Å. Three concentrations of Ga vacancies (2.8, 1.8, and 1.6 %) corresponding to a neutral cation vacancy (Ga vacancy) in the 72-atom ($\text{Ga}_{35}\text{V}_{\text{Ga}}\text{N}_{36}$) (Fig. 3c), the 108-atom ($\text{Ga}_{53}\text{V}_{\text{Ga}}\text{N}_{54}$), and

the 128-atom ($\text{Ga}_{63}\text{V}_{\text{Ga}}\text{N}_{64}$) cubic supercells, respectively, confirmed that all spontaneous spin polarizations created a local magnetic moment of $3.0 \mu_B$ for all three Ga-vacancy concentrations, in good agreement with an earlier report [28]. Figure 3c shows that the p -orbital electrons split near the Fermi energy. Figure 3d, in which the blue ball indicates the location of the magnetic moment source, reveals that the magnetic moment mainly originates from the polarization of unpaired $2p$ electrons from N atoms surrounding the Ga vacancy, with each N atom contributing a $0.678 \mu_B$ magnetic moment.

The optical absorption of the three sets of samples is plotted in Fig. 4a. The absorption measurement was performed at wavelengths 200–800 nm. As the concentration of Ga vacancies increase, the UV absorption edge moves to longer wavelengths (red-shifted). The plots $(\alpha h\nu)^2$ show the band gaps in GaN-1, GaN-2, and GaN-3 have different values of 3.15, 3.17, and 3.20 eV, respectively, as shown in Fig. 4b. The band-gap energy was observed to be a maximum for a Ga/N ratio = 0.98 composition. Increasing the Ga vacancies in GaN nanoparticles causes an increase in density of states in the valance band. The addition of Ga vacancies also creates a localized state in the band gap. This behavior leads to a shift in the absorption edge towards lower photon energies; the decrease in the optical energy gap follows a similar explanation given in report [30].

The calculated results also indicate an almost identical relationship between the energy band and Ga vacancies. The calculated lattice constants a and c of wurtzite GaN are 3.189 and 5.186 Å, respectively. GaN is a direct semiconductor with an experimental gap of 3.4 eV, and our result produces a direct band gap of 2.312 eV in the G position (Γ point) which is close to the experimental value (Fig. 4c). For the other supercell, the calculated band gaps for $\text{Ga}_{35}\text{V}_{\text{Ga}}\text{N}_{36}$, $\text{Ga}_{53}\text{V}_{\text{Ga}}\text{N}_{54}$, and $\text{Ga}_{63}\text{V}_{\text{Ga}}\text{N}_{64}$ (as shown in Fig. 4d, e, and f) are 0.381, 0.680, and 0.843 eV. These results confirm that the band gap decreases with increasing Ga-vacancy concentration, which is also in good agreement with our experimental results.

4 Conclusion

In summary, Ga-deficient GaN nanoparticles have been synthesized. PL and Raman spectroscopy confirmed the existence of Ga vacancies in the GaN nanoparticles. The $M-H$ and $M-T$ curves of GaN nanoparticles showed that nanoparticles exhibited room-temperature ferromagnetism; the associated behavior is an intrinsic property of the GaN samples. The ferromagnetism can be induced by Ga vacancies and the result was proved experimentally and theoretically. First-principles calculations revealed that spontaneous spin polarization is created by the $3.0 \mu_B$ local moment for GaN and the magnetism originated from the polarization of unpaired $2p$ electrons of N surrounding the Ga vacancies. Concurrently, the band gap can be tuned by changing the Ga-vacancy concentration and decreases with increasing Ga-vacancy number.

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