# Experimental observation of defect-induced intrinsic ferromagnetism in III-V nitrides: The case of BN

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We report the synthesis and magnetic properties characterizations of defective BN obtained from a modified solid-state reaction. X-ray diffraction analysis indicated the presence of two crystalline phases of BN in products. No magnetic impurities, such as Fe, Co, Mn, and Ni were detected by chemical analysis. Transmission electron microscopy observation and photoluminescence spectrum measurement showed the existence of large-scale defects in BN lattices. Magnetic measurement undoubtedly demonstrated the typical ferromagnetic order was established in undoped BN. We consider that the many kinds of defects should be responsible for the long-range magnetic order in the *sp* material of defective BN.

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Recently, search for room temperature (RT) diluted magnetic semiconductors (DMSs) has received much attention due to its potential application in the field of spintronics.[1–5] Traditionally, the DMSs are produced by doping semiconductors with transition metal (TM) elements.[6–8] Partially filled 3*d* or 4*f* subshells in TM, coupled with their high degree of degeneracy, favors spin-polarized electron configurations and leads to the formation of local moments. Collective magnetism is then a result of the coupling between these local moments. Even though ferromagnetism (FM) order has been observed in several DMSs systems,[9–13] previous investigations produced lots of inconsistent results and the nature magnetic origin for FM remains unclear.[14–16] It is found that the traditional TM-doped DMSs often suffer the spurious signals from the precipitates of dopants in the form as clusters or secondary phases, which are detrimental to the performance of spintronics devices.[17,18] If no TM dopants or even no dopants were incorporated into the semiconductor matrix, the DMSs thus produced would not suffer the issues related to precipitates of dopants since they have no contribution for FM order. This scenario has attracted great interests from the science community.[5,14,19] For instance, it was found that the localized defect states in *sp* system may also lead local moments and exhibit collective magnetism.[20] Typically, FM order in various carbon-based materials has been observed and detailed investigations showed that only intrinsic defects could take responsibility for the observed FM order.[19,21,22] In addition, structural defects were also reported to be the possible origin of FM order in some *sp-d* system such as $HfO_2$ (Ref. 23) and *sp* system such as $SnO_2$.[24] Very recently, Dev *et al.*' work suggested that the defects, such the cation vacancies, etc. could induce intrinsic long-range magnetic order in III-V nitrides such as GaN and BN.[25] As an important wide-gap semiconductor (hexagonal BN with a bandgap of 4.0 eV$\sim$5.8 eV), it is therefore of great interests to test the possibility that using defects as a native "dopant" than TM dopants to induce FM order in undoped BN due to its potential applications in spintronics devices. However, the experimental efforts toward producing ferromagnetically interacting BN are still lack until now, which will renew the interests on intrinsic FM mechanism in wide-gap nitrides semiconductor and narrows the gap between theoretical predications and experimental work upon the nature FM origin in III-V nitrides. In Brief Reports, we performed detailed investigations on the structural and magnetic properties features of defective BN. It is confirmed that only the structural defects can also induce FM order successfully in undoped III-V nitrides, the case of BN.

BN for the magnetic measurement was synthesized by modified solid-state metathesis route using boron powder (99.4%, STERM CHEMICALS, Crystalline) and $Li_3N$ (homemade in laboratory) as boron and nitrogen source, respectively.[26] 0.3243 g boron powders and 0.3 g $Li_3N$ were mixed and ground together in an agate mortar. Then the starting materials were pressed to a pellet and put into a stainless steel crucible, followed by placing the crucible into a silica ampule connected to an evacuating system. The silica ampule was evacuated to $3\times10^{-5}$ Pa, then filled with 0.4 MPa high purity nitrogen (99.999%) and sealed. Silica ampule was heated to 820 °C in the conventional muffle and maintained for 4 h. Then the power was shut off and the muffle was cooled down to RT naturally. The desired phase of BN was obtained from the products through a washing process using $HNO_3$ and HF. Then the sample was washed by deionized (DI) water and absolute ethanol, respectively, as described in Ref. 11.

X-ray diffraction (XRD) was used to characterize the crystal structure of the products. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analysis were performed on JEOL (JEM-2010) electron microscope to investigate the structural and morphological information of the obtained products. Inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS Intrepid II) was used to determine the im-

 

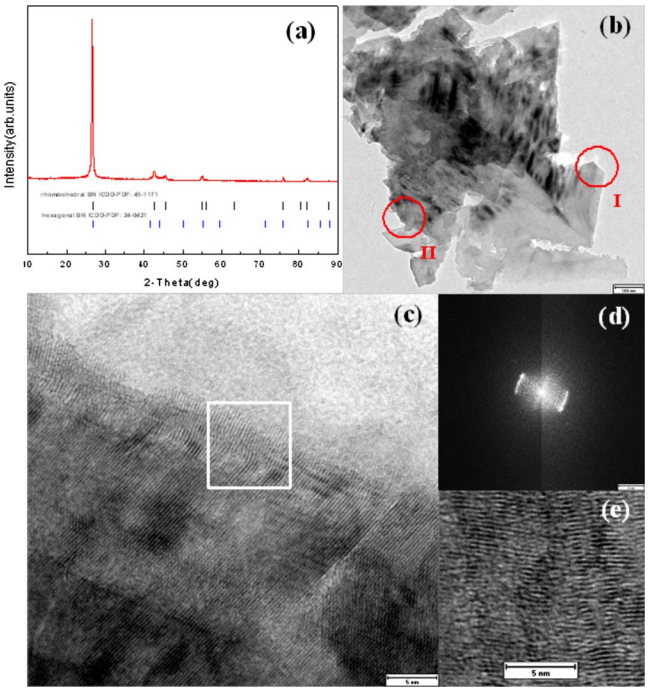


FIG. 1. (Color online) (a) XRD pattern for the products obtained from the reaction after washing process. Vertical bars at the bottom are expected Bragg positions for rhombohedra BN and hexagonal BN phase, respectively. (b) Low magnification TEM image for the overview morphological features of produced BN, and "I" and "II" areas are selected for HRTEM observation randomly. (c) HRTEM image for "I" area. (d) Selected area fast FFT images for the areas as labeled by rectangle in (c). (e) HRTEM image for the spots corresponding to "II" area shown in (b).

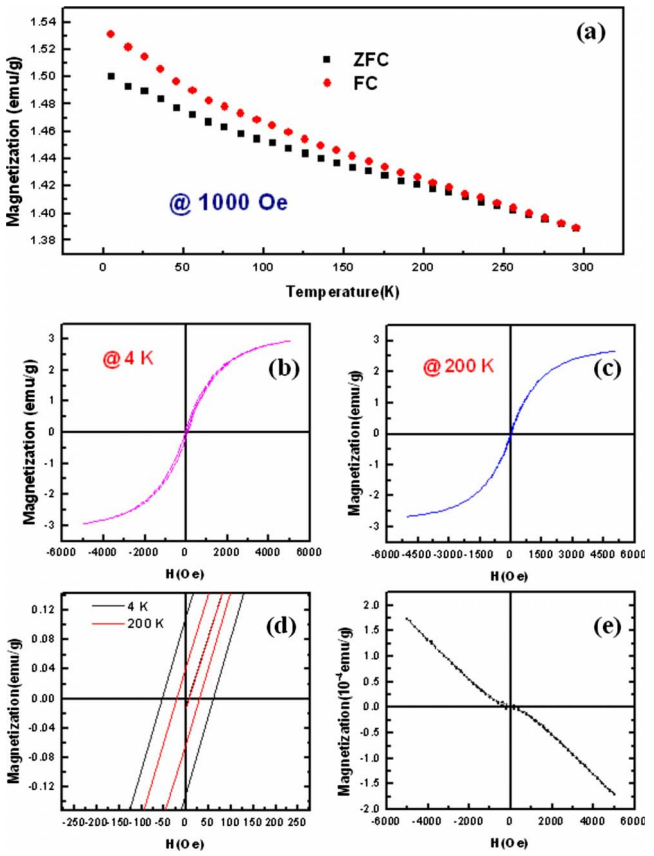


FIG. 2. (Color online) (a) Temperature dependence of FC and ZFC magnetization at 1 kOe for the as-produced BN. 2(b) the magnetization loops for BN at 4 K. 2(c) the magnetization loops for BN at 200 K. 2(d) the magnified magnetization loops for BN measured at 4 and 200 K, respectively. 2(e) the magnetization loops for the reference sample measured at 4 K after the washing process.

purity concentration. Zero-field-cooled (ZFC) and field-cooled (FC) temperature dependent magnetization ($M$-$T$) were performed in the temperature range from 5 to 300 K with a superconducting quantum interference device (SQUID, MPMS-7). Magnetization versus applied magnetic field ($M$-$H$) below 300 K were measured on SQUID in the range of $0 \sim \pm 5000$ Oe. $M$-$H$ curves in the temperature range of 300 K $\sim$ 400 K were measured on physical property measurement system. The contribution from capsule was subtracted from the original data. The photoluminescence (PL) measurements were performed using a Xe lamp as the excitation source with a Hitachi F-4700 spectrofluorometer.

XRD pattern (Fig. 1(a)) indicates that the products are composed of two crystalline phases, that is, rhombohedra BN (ICDD-PDF: 45-1171) as main phase, and hexagonal BN (ICDD-PDF: 34-0421) as secondary phase. The cell parameters calculated from XRD pattern are $a_1=0.2505$ nm and $c_1=1.011$ nm for main phase rhombohedra BN, and $a_2=0.25061$ nm and $c_2=0.66813$ nm for secondary phase hexagonal BN, and no other peaks from impurities were detected under the x-ray diffractometer's resolution (Philips X'PERT MPD). Figure 1(b) shows the typical morphological features of as-prepared BN products. The products were micrometer powder with irregular morphological features. HRTEM images as shown in Fig. 1(c), which corresponds to the "I" area as marked in Fig. 1(b), unravel more detailed structural and morphological information. One can see clearly that there were large scales of dislocations and lattice defects presenting in the as-produced BN, showing a relatively poor crystallinity quality. The selected area fast Fourier transform (FFT) images [Fig. 1(d)] corresponding to the areas labeled by rectangle as shown in Fig. 1(c) displays a typical blurry diffraction dots for the products with worse crystalline quality, confirming the corresponding HRTEM results. Further, Fig. 1(e) shows the HRTEM image of the spots corresponding to "II" area. The points for HRTEM observation were selected at random, and these morphological characteristics thus represented the average level of crystalline quality. In addition, energy dispersive spectrometer analysis showed the as-prepared BN was B-rich (not shown here). Figure 2(a) shows the ZFC and FC temperature dependence of dc magnetization in the field of 1 kOe for obtained BN. The smooth and featureless $M$-$T$ curve indicates the absence of any secondary or tiny parasitic magnetic phase, in agreement with the previous XRD result. Figures 2(b) and 2(c) displays the $M$-$H$ curves measured at 4 K (upper-right inset) and 200 K (middle-right inset), respectively. Both of them show a clear and well-defined hysteresis for typical DMSs. Figure 2(d) displays the magnified coercive field of $H_{c4\ K}=80.58$ Oe and $H_{c200\ K}=25.96$ Oe, respectively.

The robust FM signals from Fig. 2 indicated that the Cu-

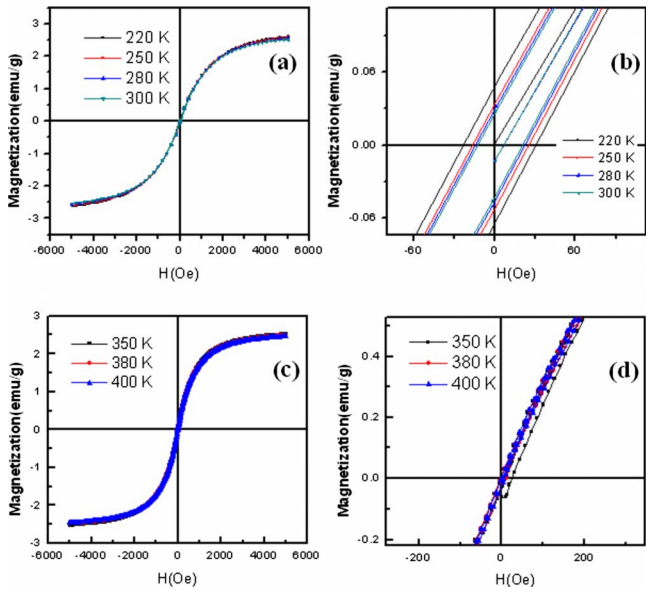


FIG. 3. (Color online) (a) The magnetization loops for BN measured at 220, 250, 280, and 300 K, respectively. 3(b) the magnified loops for BN as shown in (a). (c) The magnetization loops for BN measured at 350, 380, and 400 K, respectively. (d) The magnified loops for BN as shown in (c).

rie temperature ($T_c$) of the as-prepared BN should exceed 200 K. Figure 3(a) shows the magnetization loops for BN measured at 220, 250, 280, and 300 K, respectively. One can see clearly that four *M-H* curves all exhibited typical FM order, indicating the long-range magnetic order still dominated the BN even at RT. With the increasing of temperature, the coercive field decreased from 31 Oe (at 220 K) to 20.9 Oe (at 300 K) as shown in Fig. 3(b). Further, Fig. 3(c) shows the similar *M-H* curves measured at 350, 380, and 400 K, respectively, indicating that $T_c$ must be higher than 400 K. Figure 3(d) shows the magnified magnetization loops as shown in Fig. 3(c). Here, we pay attention to origin of FM order than the precise $T_c$.

To investigate the intrinsic origin of FM order of the as-prepared BN, we first take account of the purity of the starting materials, which is critical to determine the magnetic order of the bulk sample, as there have been several reports on the discovery of organic magnets but included the trace amount of FM metal nanoclusters. In this study, the most convincing evidence against the impurity role is that all the pristine, that is, neither boron powder nor $Li_3N$ exhibited FM signal. In addition, hexagonal BN (99.9%) from Alfa Aesar was selected as contrast sample to test whether the treating process involved $HNO_3$ and HF solution should be responsible for the observed FM order since some magnetic impurities may be introduced. The *M-H* curve [Fig. 2(e)] measured at 4 K after washing showed that no FM impurity or insufficient magnetic impurities were involved via the washing process. Furthermore, within the resolution of IRIS Intrepid II spectrometry, no magnetic impurities such as Fe, Co, Mn, and Ni were detected in as-prepared BN during the ICP-AES analysis, indicating the magnetic impurities content should be less than 100 ppm. The saturation magnetic moment per unit mass caused by 100 ppm magnetic impurities (Fe, Co, Ni, etc.) is estimated to be for about 0.01364 emu/g, that is, two orders of magnitude less than the magnetization measured in as-prepared BN. This excludes the possibility that the magnetic effect is due to FM clusters formed by magnetic atoms as described in previous reports on "organic magnets" that included trace amounts of ferromagnetic metals.[22] Thus, the more higher precision characterization means for chemical composition such as secondary ion mass spectrometer and glow discharge mass spectrometer is not required in this study. There should be another effective magnetic mechanism than the traditional magnetic impurities take responsibility for the nature origin of FM order in undoped BN. However, the conventional models for FM order in DMSs, such as Ruderman-Kittel-Kasuya-Yosida,[2] bound magnetic polarons,[27] and *d-d* double exchange mechanism, are not applicable for the as-obtained BN in this study in which no magnetic impurity or doping elements including TM or no TM elements were involved.[28]

So, the very robust and clear FM signals as shown in Fig. 2 can only be convincingly explained by its intrinsic features of the sample, that is, the large scale of extended defects and dislocations in the as-prepared defective BN may induce the long-range magnetic order. If the long-range magnetic order naturally arises from BN itself, two facts should be taken into account. First, how the unpaired spins formed? For the case of undoped BN, it is speculated that the unpaired spins have two possible sources: (1) originated from the conversion from $sp^3$ to $sp^3$-$sp^2$ hybridization. Since the existence of large scales of defects, the ideal B-N bonds in $sp^3$ configuration were destroyed with the formation of $sp^3$ and $sp^2$ hybridization, named as mixture hybridization. Unpaired electron is thus prompted to a higher orbital enabling it to participate in the magnetic ordering as proposed by Song *et al.*[5] for the possible FM origin in Al-doped 4H-SiC; (2) the other possible origin for the unpaired spin electrons was ascribed to the as-produced defects, such as neutral cation vacancies which could result in a net moment.[25] Other types of defects such as dislocations, anion vacancies ($V_N$), and interstitial defects ($B_i$, $N_i$) were also considered to be responsible for the formation of unpaired spins.[29,30] As seen from HR-TEM observations, the defects in as-prepared BN do not confine themselves to one special type but exhibit in the complex types as reported by Madhu *et al.*[28] That is to say, the defects in as-prepared BN are bulk nature in fact and this may be the reason for why the observed saturation moment is seemingly much higher than other defects induced FM systems including nanoparticles[31] or thin films.[32] Second, which served as the "effective correlation" between these spins moments to induce long-range FM order? Extensive structural defects were speculated to serve as this crucial role.[5] The striking feature of defects in undoped BN thus may serve as dual roles: (1) produced unpaired spin electrons; (2) acted as the effective relation to induce the long-range FM order. Our study demonstrated that only defect states can also result in collective magnetism in undoped III-V nitrides: the case of BN, a very important *sp* semiconductor material.

So, it is very necessary to investigate the status of defects in the as-prepared BN. As one powerful characterization mean, PL spectrum is often used to investigate the defects

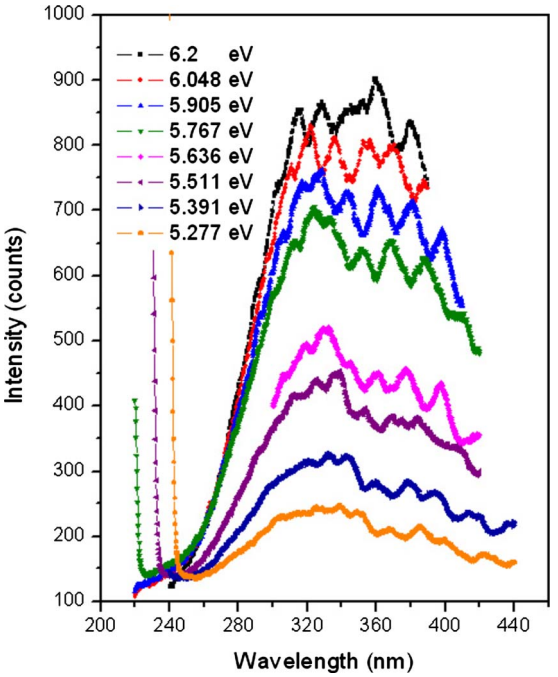


FIG. 4. (Color online) PL spectra of the produced BN excited at room temperature from 6.2 to 5.277 eV.

information. Figure 4 shows the PL spectra of the as-produced BN measured at RT. A very broad band ranging from 2.5 to 5.0 eV was observed. This broad band contains a series of emission peaks located at 380, 360, 329, and 315 nm, respectively. It is expected that these emission peaks could display the defects levels of the BN. In the case of B-rich BN, there existed large quantities of defects, in the form as N vacancies $V_N$, B interstitial $B_i$, and the B antisite $N_B$. In addition, the incorporation of O impurities was also inevitable since the treating process was performed in strong acids solution in which the absorption of $O_2$ and $H_2O$ cannot be prevented. It is well known that the oxygen point defects in BN have two forms, i.e., $O_N$ (O substituting for N) and $O_i$ (isolated O interstitials).[33] It has been demonstrated that the formation energy for $O_N$ is several electronvolts lower than for $O_i$. Hence, $O_N$ was easily formed regarding its low formation energy.[34] However, the detailed defects level for BN is not unclear at present, the PL spectra undoubtedly demonstrated that the presence of large-scale defects, which should be responsible for the observed robust FM order in undoped BN.

In summary, the ideal pristine sample: undoped BN with large scales of defects was successfully obtained by the modified solid-state reaction. The as-produced BN was thoroughly characterized by various techniques. TEM and PL spectra observation showed the presence of large-scale defects. Magnetic measurement showed the typical FM order was successfully established. Observation of long-range magnetic order is consistent well with the theoretical prediction proposed by Dev *et al.* that only the defects in III-V nitrides can also give rise to a FM ground state.

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