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 3d or 4f subshells in TM, coupled with their high degree of degeneracy, favors spin-polarized electron configuration 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 of 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 Li3N (homemade in laboratory) as boron and nitrogen source, respectively.26 0.3243 g boron powders and 0.3 g Li3N 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 $3 \times 10^{-5}$ Pa, then filled with 0.4 MPa high purity nitrogen (99.999%) and sealed. Silica ampule was heated at 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 HNO3 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-
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 temperature dependent magnetization loops for BN at 4 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.

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 in (c). (e) HRTEM image for the spots corresponding to “II” area shown in (b). XRD pattern (Fig. 1(a)) indicates that the products are composed of two crystalline phases, that is, rhombohedral 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 rhombohedral 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 in (c). (e) HRTEM image for the spots corresponding to “II” area shown in (b). XRD pattern (Fig. 1(a)) indicates that the products are composed of two crystalline phases, that is, rhombohedral 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 rhombohedral 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 in (c). (e) HRTEM image for the spots corresponding to “II” area shown in (b). XRD pattern (Fig. 1(a)) indicates that the products are composed of two crystalline phases, that is, rhombohedral 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 rhombohedral 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
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 possible origins 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 BN. In this study, the most convincing evidence against the impurity role is that all the possible origins 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

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.31 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 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 $sp^3$-$sp^3$ 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 $sp^3$ 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 ($B_0$, $N_0$) were also considered to be responsible for the formation of unpaired spins.29,30

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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_x (O substituting for N) and O_y (isolated O interstitials).

It has been demonstrated that the formation energy for O_x is several electronvolts lower than for O_y. Hence, O_x was easily formed regarding its low formation energy. However, the detailed defects level for BN is not clear 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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