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A comparative study on ferromagnetic C/O-implanted GaN films by positron annihilation spectroscopy

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ABSTRACT

Room temperature ferromagnetism was observed in both C- and O-implanted GaN films, which were irradiated by 80 keV C/O-ions with respective dose of 5×10^{16} and 2×10^{17} ions/cm^2. Positron annihilation spectroscopy was used to explore the magnetic origin and the correlation between the magnetism and structural features. The results reveal that carbon-ions play an important role in the stable ferromagnetism in C-implanted GaN films, while oxygen has no effect on the magnetic properties, even than a weak hysteresis loop was observed in O-implanted sample. This weak ferromagnetism is demonstrated as originated from Ga-related vacancies which induced by implantation. With first-principle calculations, we confirmed that substitutional C-ion at N-site can introduce magnetic moment for 0.8 μ_B and stabilize ferromagnetic coupling with adjacent Ga-vacancy at room temperature. Moreover, the effect of O-ions was clearly ruled out. Our discussion gives an experimental and theoretical insight of the different origin of ferromagnetism between acceptor and donor non-metal-doped GaN materials.

1. Introduction

In the past decade, ferromagnetic behavior with Curie temperature above 300 K was widely observed in semiconductors, which are referred as dilute magnetic semiconductors (DMSs) and considered to be most promising materials in spintronic devices [1–2]. Many researchers focused their efforts on transition metal-doped oxides such as Co–ZnO, Mn–ZnO and Mn–TiO2 [3–5]. Recently, GaN-based DMSs also received increasing interests from scientists due to their outstanding properties such as direct bandgap and blue light-emitting, which guarantee GaN as promising material in integrated controlling of spin, charge and photon [6–7]. However, the related reports are still relatively few and the results are under stuck debate. For instance, Gao et al. observed ferromagnetism in Er^+-implanted GaN films and concluded it as magnetic coupling between Er^{3+} ions and electrons [8]. However, it is also possible that the weak ferromagnetism in semiconductors probably arise from magnetic clusters which may be doped unintentionally or by pollution [9]. On the other hand, ion-implantation usually used as an effective way of particle-doping in the DMSs field, thus the induced-defects will inevitably affect the ferromagnetic performance in implanted samples. Some studies demonstrated that intrinsic defects could introduce magnetic behavior in un-doped GaN materials [10–12]. Importantly, doping-induced magnetisms were considered to arise from p-type particles [13–15]. Recently some observations suggested that donor doping also induced spontaneous magnetization in BN and AlN with N vacancy [16–17]. In addition, carbon substitution for either single boron or nitrogen atom in the BN nanotubes, a spontaneous magnetization was always induced [18]. Since spin-splitting at top of valence band (normally induced by localized polarized electrons) is the intrinsic origin of magnetic coupling in semiconductors, dose the localized moments can be introduced into GaN by donor particles? Also, the affect from lattice defects should be considered in whatever ions-doped GaN samples.

To void the clusters interference, C- and O-ions were selected as acceptor and donor doping particles because of its non-magnetic nature to implant into GaN films. In this paper, the possible magnetic action of C/O and the effect of defects on ferromagnetic behavior were clearly demonstrated. Positron annihilation technique as an effective way was employed to probe the implantation induced defects in samples. Furthermore, the first-principle calculations based on density functional theory (DFT) were also used to provide further insight in the magnetic properties in implanted

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GaN samples. This work may provide some valuable results for further theories and applications of GaN-based spintronic devices.

2. Experiment

GaN wafers based on sapphire substrate were grown by hydride vapor phase epitaxy method with thickness of about 30 μm. They were cut into seven parts with the size of $6 \times 8\ mm^2$ and washed by ultrasonic vibration cleaner for 30 min. To estimate the unexpected magnetism, possible trace elements were carefully detected by Laser Ablation Inductively Coupled Plasma Mass Spectroscopy. The outcomes show that magnetic elements like Fe, Co, Ni, Gr, Mn et al. are totally about 60 ppm that provides the magnetic moment is about 0.01 emu/g in the whole wafer, which has been reported in our previous work [12]. C/O-implantation was performed using ions implanter at college of Nuclear Science and Technology center, Beijing Normal University. The carbon and oxygen ions were accelerated to 80 keV and implanted into different GaN wafers with dose being divided into $5 \times 10^{16}\ cm^{-2}$ and $2 \times 10^{17}\ cm^{-2}$, respectively. The injection processes maintained at 2×10^{-4} Pa at about room temperature. No immediate annealing was performed after implantation. For comparison, N-irradiated GaN crystals with a dose of $2 \times 10^{17}\ cm^{-2}$ were also prepared under the identical conditions. Another N/O complex-implanted sample with nearly same total dose was maintained as a reference. After implantation, 18 kW rotating anode X-ray diffraction diffractometer was used for structure analysis, no extra second-phase was observed within detection limit.

The O/C-implanted average profiles and defect distributions were simulated by Stopping and Ranges of Ions in Matter (SRIM) program, and the results are shown in Fig. 1.The thickness of incident O-ion layer is estimated about 150 nm in the range of 50–200 nm. Since the radius of C is slightly smaller than that of O, the average – depth for C ions is larger than that of O ions. The atomic concentrations of C-ions were estimated using the density of samples which gave impurity peak of 4.8 at.% and 18 at.% for $5 \times 10^{16}\ cm^{-2}$ and $2 \times 10^{17}\ cm^{-2}$ doses, respectively. The blue and red shadows represent the content of vacancy type defects caused by implantation O and C, respectively. The defect profiles depend on the incident ions which interact with target atom by nuclear collisions. The injected ions continuously lose their energy by collision and finally stopped at certain sites when their energy was exhausted. Therefore, the vacancies distribute from surface into implanted region, and the profiles are different from that of the

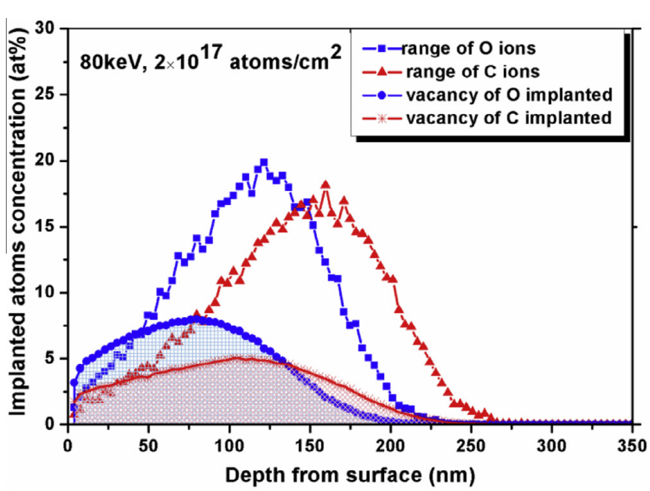

Fig. 1. Depth profiles of injected O/C-ions with $2 \times 10^{17}/cm^2$ dose and the induced defects estimated by SRIM.

injected O/C-ions. Unsurprisingly, the defect profile caused by C-ions is slightly deeper and the content of vacancies is normally smaller than that caused by O-ions.

The real structure and defects of implanted samples were characterized by positron annihilation spectroscopy (PAS), which has proven to be an effective tool for detecting vacancy-type defects in materials [19]. Positrons have a high affinity to be trapped by vacancy defects, which result in a narrowing of 511 keV annihilation peak compared to the bulk annihilation. S-parameter was defined as a fraction of counts in the central region of annihilation peak [20]. It reflects on Doppler broadening of 511 keV peak and detected by an HPGe detector. Therefore, increase in S-parameter indicates that positrons were annihilated in vacancy defects. In our work, Doppler broadening measurements were carried out using energy-variable slow positron beam with ranging from 0.25 to 20 keV at State Key Laboratory of Particle Detection and Electronics, University of Science and Technology of China. By varying the positron energy, the depth-dependent S-parameter curves were obtained. These curves were analyzed with VEPFIT program to obtain diffusion length of positrons and the thickness of the damaged layer [21]. Besides, magnetic properties of the samples were determined by Vibrating samples magnetometer (VSM) with a high accuracy of 10^{-7} emu.

3. Results and discussion

As shown in Fig. 2(a), the raw GaN film shows a rigorous diamagnetism behavior and was treated in all other curves to subtract background influences like substrate, straws and possible impurities, thus the curve of the raw wafer displays as a horizontal line in patterns. For higher dose N- and O-implanted samples, the field-dependent magnetization (M–H) curves show distinct S-shaped magnetic changes. The saturation moment (M_S) in N-implanted sample is estimated about 0.7 emu/g and the coercive force (H_C) is about 120 Oe, as shown in inset of Fig. 2(a). Since the ferromagnetism is greatly larger than that caused by total possible impurities, we consider the observed ferromagnetism should contribute to inject-induced defects in GaN wafer [12]. Similar to other reports, we observed room temperature ferromagnetism in O-implanted GaN wafer. With the same dose, the H_C and M_S of O-implanted sample almost exactly equal to that of N-implanted sample. The inset display identical low-field hysteresis loops in them and only a slight difference of paramagnetism was observed. We also carried N/O co-implantation sample as a reference shown in Fig. 2(b), and without any change in performance of ferromagnetism. Since ion-irradiation will inevitably introduce defects, we should characterize the defect situations in N- and O-implanted samples before further discussion. Fig. 2(c) and (d) indicates the S-parameters as a function of incident positron energy (S–E curves) for these samples. Based on VEPFIT, the implanted samples should divide into three layers: surface, irradiated region and substrate. The irradiated layer is about 17–165 nm, which has a good agreement with the simulation result of SRIM mentioned above. After ions-implantation, all the samples display increased S-parameters in irradiation layers than that of raw GaN film, which indicate the emergence of induced defects. Cation vacancies are dominant positron trapping defects in materials, thus significant S-increase in irradiated layers definitely due to induced Ga-vacancy related defects. The largest S-parameters in surface layer (corresponding to positron energy range of 0.25–2 keV) were normally due to the formation of positronium atoms at material surface [22]. Compared with the O-implanted sample, both N-implantation and N/O co-implantation samples show almost identical S-curves, indicates that the Ga-related vacancies are basically in the same type and content in these three samples. As the