Room temperature ferromagnetism in N-implanted MgO: synergistic effects of intrinsic and extrinsic defects

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Abstract

N-implanted MgO single crystals were prepared and their magnetic properties were studied. High Resolution x-ray diffraction, photoluminescence, and x-ray photoelectron spectroscopy measurements confirmed that both intrinsic defects (Mg vacancies, oxygen vacancies) and extrinsic defects (N-related defects) were presented in the implanted samples. Ferromagnetism was detected in the samples. The saturation magnetization ($M_s$) of the samples increases with the concentrations of Mg vacancies and N-related defects. We conclude that the enhanced $M_s$ should be ascribed to the synergistic effects of intrinsic and extrinsic defects. The magnetic properties of various composite defects were also studied by first principle calculations. The results suggest that the ferromagnetism is mainly originated from the configurations of $V_{\text{Mg}}$ (Mg vacancy) + $N_O$ (N substituting for O).

1. Introduction

Since Datta et al\textsuperscript{1} proposed the theoretical simulation of a spin field-effect-transistor, semiconductor-based spintronics has undergone decades of development. The essential factor for achieving spintronics devices is to manipulate the degrees of freedom of spin and charge synchronously in one material [2]. That means the materials can contain both ferromagnetic and semiconducting characteristic. And researchers have acquired many novel achievements, such as spin field-effect transistors fabricated from the CdSe colloidal nanowires [3], electric-field controlled FM in MnGe quantum dots [4], nonvolatile memory devices [5] and so on. The major challenge for semiconductor-based spintronics applications is to obtain stable ferromagnetism above room temperature (RTFM). A usual way to accomplish this is to dope transition metal (TM) elements in semiconductors (DMSs). Actually, numerous studies have shown that DMSs can preserve ferromagnetism at room temperature [6–8]. However, TM nanoparticles are inevitably present in the DMSs [9]. These nanoparticles may lead to non-uniform spin density, which will be an obstacle to realize spintronic applications [10]. One approach to solve this problem is doping nonmagnetic elements instead of TM elements to achieve ferromagnetism. Since Pan et al\textsuperscript{11}, experimentally observed RTFM in C-doped ZnO, RTFM has been detected in a wide range of oxides, including C-doped SnO$_2$, N-implanted TiO$_2$, and N-implanted MgO et al\textsuperscript{12–14}.

Due to its special physical and chemical properties, MgO has been recognized as an ideal material for spintronic devices [15]. There have been many theoretical and experimental studies regarding RTFM in MgO [16–19]. However, the mechanisms contributing to the ferromagnetism are still under debate. Li et al\textsuperscript{16} observed room temperature ferromagnetism in MgO thin film prepared by pulsed laser deposition, and the magnetization decreased with the increasing substrate temperature. XPS and PL results showed that the induced ferromagnetism was correlated with Mg vacancies. Nevertheless, Mishra et al\textsuperscript{17} reported that oxygen vacancy enhanced the RTFM in Al-doped MgO, $F^-$ and $F^{2-}$ (color center) mediated ferromagnetism had also been reported in MgO nanosheets [18]. Apart from the intrinsic defects, a few groups suggested that the doping elements were a driving factor for magnetic
To study the magnetic properties of N-implanted MgO, the magnetic 
3.1. Magnetic measurement 
3. Result and discussion 
resultant magnetic order results from the synergistic effects of all defect types in the material. Thus, it is essential to 
investigate the magnetic properties of composite defects in MgO. 

Ion implantation is a non-equilibrium and reproducible method to introduce defects. The concentration 
and depth of defects can be controlled, therefore, this process is widely used in semiconductor technology. 
Implanting nonmagnetic elements such as C and N is a reliable strategy to introduce ferromagnetism in oxides, 
which has been verified by many groups [23, 24]. In this paper, we implanted N ions into MgO single crystal to 
obtain room temperature ferromagnetism. The defect types including V_{Mg}, V_{O}, N_{O}, and N_{int} were investigated 
through various measurements. First-principles calculation revealed that the ferromagnetism is correlated to the 
composite defects.

2. Experimental details 

To minimize the nanoscale effect, MgO single crystals with a thickness of 0.5 mm were prepared through arc 
melting method. The samples were obtained commercially from Hefei Kejing Materials Technology Co., Ltd. 
The sample was cut into a size of 10 × 5 mm². Implantation experiment was carried out at the Institute of 
Semiconductors, CAS, Beijing. N ions were accelerated to 70 keV and injected into MgO samples with the dose 
of 3 × 10^{16} \text{ cm}^{-2} and 2 × 10^{17} \text{ cm}^{-2}. The implants were performed at an angle 7° off normal to minimize the 
channeling effect. The base pressure of the implantation processes was maintained at about 2 × 10^{-5} \text{ Pa} at room 
temperature. The microstructures of samples were characterized by High Resolution x-ray Diffraction 
(HRXRD) in Beijing Synchronous Radiation Facility (BSRF). Qualitative analysis of total elements experiment was 
conducted by x-ray electron spectroscopy (XPS, PHI Quantera) with monochromatic Al Kα, x-ray radiation. The 
magnetization measurements were carried out by superconducting quantum interference device (SQUID, 
Quantum Design) at room temperature. The photoluminescence (PL) emission spectra were carried out by 
using the 235 nm laser diode (LD) as an excitation source with a spectrofluorometer (F55, Edinburgh 
Instruments, UK).

3. Result and discussion 

3.1. Magnetic measurement 

To study the magnetic properties of N-implanted MgO, the magnetic field dependence of magnetization (M-H) 
of pristine and as-implanted samples was measured at room temperature. The M-H curves are shown in figure 1. 
All of the curves are corrected by subtracting the diamagnetic background. As we can see, pristine MgO shows 
typical diamagnetic properties. Nevertheless, N ion implantation leads to a significant change in magnetic 
behavior. For the sample with a dose of 3 × 10^{16} \text{ ions cm}^{-2}, both ferromagnetic and paramagnetic behaviors 
were observed. The M-H curve shows distinct ferromagnetic properties by further increasing the N ion 
implantation dose to 2 × 10^{17} \text{ cm}^{-2}. The saturation magnetization (Ms) is approximately 1.1 × 10^{-4} \text{ emu g}^{-1}, 
nearly 2.5 times as that of 3 × 10^{16} \text{ cm}^{-2} implanted MgO. This magnetic measurement result definitely 
demonstrates that N-implantation plays a crucial role in introducing ferromagnetism in MgO single crystal. A 
high implantation dose can enhance the Ms values, which means the total magnetic moments increase with the 
increasing implantation dose. It is clear that N-implantation produces a high concentration of defects, and 
researchers have reached a consensus that the defect induced ferromagnetism has a positive correlation with the 
defect concentration in the material [25]. However, in the process of N-implantation, besides the implanted N 
ions and N-related defects, the collision ions can also create different kinds of defects. The effects of other types 
of defects on magnetic properties should also be considered.

3.2. Structural properties 

To evaluate the N-implanted effect on the crystal structure, the samples were detected by HRXRD. As shown in 
figure 2, both pristine and as-implanted samples presented highly (200) oriented single crystal structure. No 
peak corresponding to extrinsic impurities or secondary phase was observed. The inset shows that with the 
increasing implantation dose, the diffraction intensity decreases obviously. This indicates that N implantation 
introduces numerous lattice defects. Meanwhile, the shift of (220) peaks toward the lower angle is also observed
in the as-implanted samples, implying that the introduced defects lead to a lattice expansion. The calculation results indicated that N substituted O (NO) can expand the lattice [26], and the interstitial N (Nint) can cause greater lattice expansion than substitute defects do. The peak shift value from pristine to $10^{16}$ cm$^{-2}$ is 0.139°. With increasing the implantation dose from $10^{16}$ to $10^{17}$ cm$^{-2}$, the shift value decreases to 0.086°. This may prove that the incident N ions prefer to occupy the VO site at high defect concentrations.

3.3. PL measurement

However, HRXRD results can only reflect the average effect of the crystal field. PL is a reliable tool to investigate the defect information in material, and there have a considerable amount of researches which can be used as a reference. Figure 3 shows the PL spectra of pristine and as-implanted samples under the excitation wavelength of 255 nm. The emission peaks located at 400–500 nm are primarily associated with VO (F+, F, or F-centers). An exhibit violet peak at 409 nm is attributed to the F$^+$ centers [27]. The peaks centered at 433 and 455 nm are associated with F$^+$ and F centers [18, 28]. Obviously, the intensity of all these VO-related peaks increases after N-implantation, which indicates that the implantation introduces higher Vo concentration. However, with the implantation dose increasing to $2 \times 10^{17}$, the VO-related emission intensity tends to decrease. This phenomenon may be partially due to the suppressed PL efficiency by the increasing implantation-induced defects [19]. More importantly, since the emission peaks located at 400–500 nm are primarily associated with VO (F+, F or
F-centers), the decrease of intensity can be attributed to the implanted N ions or the interstitial defects substituting the Vo site, resulting in the reduction of Vo-related luminescence centers. Besides, the peak at 373 nm has been attributed to Mg vacancy defects [16]. As is displayed, the peak intensity continuously increases with the increasing implantation dose, suggesting that the concentration of Mg vacancy increases with implantation dose.

3.4. XPS analysis
To further investigate the chemical structure and composition of the samples before and after N-implanted, x-ray photoelectron spectroscopy (XPS) measurement for both pristine and implanted samples was carried out. Figures 4(a)–(c) shows the XPS spectra of N 1 s peak of pristine, $3 \times 10^{16}$ N-implanted, and $2 \times 10^{17}$ N-implanted MgO samples, respectively. Before N-implantation, the N 1 s spectrum reveals a single symmetrical peak at about 398 eV, which can be ascribed to the molecular nitrogen ($\alpha$-N$_2$) [29]. After N-implantation, the N 1 s peak appears to be broadened and asymmetric, indicating the coexistence of multiple nitrogen valences. As displayed in figures 4(b)–(c), both the N 1 s peak of N-implanted samples can be fitted into two symmetric peaks: $N_a$ located at 398.0 ± 0.1 eV and $N_b$ located at 398.8 ± 0.1 eV. The $N_a$ can be obviously assigned to $\alpha$-N$_2$ as the peak in pure MgO. Since XPS is sensitive to the surrounding chemical environment, the $N_b$ is difficult to be assigned unambiguously. However, note that the $N_b$ peak occurs after N-implantation, and the $N_b$ peak intensity contribution to the total increases significantly with the increasing of N-implantation dose. Hence, referring to literature [30], we conclude that $N_b$ peak can be ascribed to N-related vacancies, such as NO and N$_{int}$. Noticeably, the binding energy of $N_b$ is higher than $N_a$, indicating the N-Mg bond barely exists, which means defect pairs such as Mg vacancy and N substituting O coexist in the N-implanted samples. Figures 4(e)–(f) shows the O 1 s XPS spectra of pristine and N-implanted MgO. The O 1 s peak can be fitted into two symmetrical peaks: $O_a$ at about 530.3 eV and $O_b$ at about 531.5 eV. The $O_a$ is ascribed to oxygen bound to Mg in MgO [17]. The $O_b$ is associated with oxygen vacancy [31]. Thus, the peak area of $O_b$ is positively correlated with the concentration of oxygen vacancies. As can be compared in figure 4, the $O_b$ relative area is obviously enlarged after $10^{16}$ ions cm$^{-2}$ N-implantation, but with the implantation dose increasing to $10^{17}$ ions cm$^{-2}$, the $O_b$ relative area slightly decreases. This indicates that the relative content of oxygen vacancy is declining from $10^{16}$ N-implanted sample to $10^{17}$ N-implanted sample, which agree well with the PL results.

3.5. First principle calculations
The experimental results confirm the coexistence of VMg, VO, and N-related defects. To further investigate the correlation between the coexistence vacancies and magnetization, density functional theory was applied on the N-MgO system. The Perdew-Burke-Ernzerhof exchange-correlation function is used to produce the density of states. We used a $2 \times 2 \times 2$ supercell containing 64 atoms to study various vacancies. Both lattice parameters and atomic positions were relaxed until the force on each atom was less than 0.01eV. The electronic structure and magnetic properties were calculated with a $9 \times 9 \times 9$ mesh.
The ion implantation process is non-equilibrium. A series of cascade collisions can directly generate various defects, including VMg, VO, NO, Nint, and anti-site defects. However, the anti-site defects may occur in negligible amounts due to their high formation energy \([32]\). Firstly, we calculated the magnetic moment induced by single point defects. As displayed in Table 1, both VMg and N-related defects can give rise to magnetic moment. Although the experimental results suggest that the concentration of VMg and N-related defects have the same increase tendency with the Ms values, but this is not enough to explain the generation and enhancement of ferromagnetism. In a real crystal field, the direction of spin induced by single defect is random. The

![Figure 4. XPS spectra of N 1 s and O 1 s for (a), (d) the pristine, (b), (e) \(3 \times 10^{16}\) ions cm\(^{-2}\), and (c), (f) \(2 \times 10^{16}\) ions cm\(^{-2}\).](image)

| System | VMg | VO | NO | Nint | VMg-VO | VMg-NO | VMg-Nint | VO-NO | VO-Nint |
|--------|-----|----|----|------|--------|--------|----------|--------|----------|
| \(m(\mu_B)\) | 1.83 | 0.00 | 0.98 | 3.00 | 3.00 | 0.98 | 0.99 | 2.99 |
ferromagnetism originates in the exchange-correlation of these spins, thus it is essential to explore the interaction of different defect types.

Based on the above-mentioned experimental results, we considered the following configurations: VO–NO, VO–Nint, VMg–NO, VMg–Nint. Figure 5 shows the Density of State (DOS). All of the four configurations can contribute to magnetic moment in the N-MgO system. The asymmetry of spin polarized density mainly comes from the O 2p and N 2p orbitals, indicating the introduction of N ions changes the local electronic structure. For the VO–N0 and VO–Nint configurations, the total induced magnetic moment is 0.99 $\mu_B$ and 2.99 $\mu_B$, with little change than the single N0 and Nint defect. This is because VO can not induce any local magnetization, thus has no correlation interaction with the magnetic moment induced by N-related defects. For the VMg–N0, VMg–Nint configurations, as is shown in figures 5(c)–(d), the EF passes through the spin states, presents a half-metallic characteristic. Furthermore, the calculation results indicate that there is an apparent magnetic coupling between VMg and N-related defects. In the case of VMg+NO configuration, the total magnetic moment increases significantly compared to single VMg and NO, which means that the magnetic moment induced by VMg and NO favors parallel spin alignment. While for VMg+Nint, the induced magnetic moment by single VMg and Nint is suppressed by each other, indicating that the exchange interaction favors the unpaired electrons with anti-parallel spins. These results demonstrate that the VMg+NO configuration can contribute to both magnetic moment values and ferromagnetism, while the VMg+Nint configuration may only contribute to the magnetic moment values. Previous literature reported that Nint was not stable in MgO system \[33\]. We also calculated the total energy of VMg–NO (−367.55 eV), VMg–V0–Nint (−365.22 eV) and VO–N0 (−366.56 eV), VM0–V0–Nint (−356.06 eV). The results suggest that in the presence of VMg–V0 or VO–V0–Nint prefers to occupy the VO site. Accordingly, we speculate that the configuration of VMg–N0 and VO–N0 are most likely exist in N-implanted MgO. Obviously, comparing with VO–N0, the magnetic coupling in VMg–N0 can make more contribution to the magnetization. This is inconsistent with our experimental results.

According to the experimental and calculation results, the induced ferromagnetism in N-implanted MgO can be explained by Heisenberg exchange model. Ion implantation introduces large amounts of intrinsic and extrinsic defects, generating unpaired electrons that can hold magnetic moment. There is no exchange correlation between unpaired electrons at low defect concentration, therefore the material is paramagnetic. With the increasing implantation dose, more defects are introduced, thus the Ms values enhance. Meanwhile, the defects exist in the form of composite defects. Take VMg+NO for example, the exchange interaction favors the unpaired electrons with parallel spins, resulting local magnetic ordering. In an external magnetic field, N-implanted MgO shows ferromagnetic characteristics.

4. Conclusion

In summary, ferromagnetism was observed in N-implanted MgO single crystal at room temperature. The HRXRD, PL, and XPS results showed the coexistence of VMg, VO, and N-related defects. The experimental results...
also indicated that the concentration of VMg and N-related defects had the same increasing tendency with the M value. The first-principle calculations reveal that the configuration of VMg+N0 play a leading role in mediating the ferromagnetism in MgO. This work provides a new perspective to understand the effect of composite defects on the magnetic properties.

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