Effect of defects on magnetic properties of O+-implanted AlN films by positron annihilation spectroscopy

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Abstract

Room-temperature ferromagnetism is observed in the O+-implanted AlN films with O+ doses of 5 × 1016 cm-2 (AlN:O5$×$1016) and 2 × 1017 cm-2 (AlN:O2$×1017).*Theobservedmagneticanisotropyindicatethattheferromagnetismisattributedtotheintrinsic* *−implantedAlNfilms.Theout−of−planesaturationmagnetization(MS)oftheAlN* : *O*5×1016*isabout*0.68*emu/g*, *muchhigherthanthatofAlN* : *O*2×$1017, 0.09 emu/g, which is due to the excessively high O+ dose made more O+ ions occupy adjacent Al3+ positions in forms of antiferromagnetic coupling. Doppler broadening of positron annihilation radiation measurements demonstrate the existence of Al vacancies in the O+-implanted AlN films. The first-principles calculations suggest that the ferromagnetism originates mainly from the Al vacancies.

Full Text

Preamble

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Effect of Defects on Magnetic Properties of O^+-Implanted AlN Films by Positron Annihilation Spectroscopy

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Abstract: Room-temperature ferromagnetism is observed in O^+-implanted AlN films with doses of 5×10^{16} cm^{-2} ($AlN{:}O_{5\times10^{16}}$) and 2×10^{17} cm^{-2} ($AlN{:}O_{2\times10^{17}}$). The observed magnetic anisotropy indicates that the ferromagnetism is an intrinsic property of the O^+-implanted AlN films. The out-of-plane saturation magnetization (M) of $AlN{:}O_{5\times10^{16}}$ is approximately 0.68 emu/g, significantly higher than that of $AlN{:}O_{2\times10^{17}}$ (0.09 emu/g). This difference arises because the excessively high O^+ dose causes more O^+ ions to occupy adjacent Al^{3+} positions, forming antiferromagnetic coupling configurations.

Doppler broadening of positron annihilation radiation measurements demonstrate the existence of Al vacancies in the O^+-implanted AlN films. First-principles calculations suggest that the ferromagnetism originates primarily from Al vacancies. Meanwhile, the formation of divacancies or vacancy clusters at high concentrations of Al vacancies leads to a transformation of V –V coupling from ferromagnetism to antiferromagnetism, ultimately weakening the ferromagnetism of the sample.

Keywords: positron annihilation spectroscopy; ion implantation; semiconductors; ferromagnetism
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1 Introduction

AlN, a wide-bandgap III-V semiconductor, has attracted considerable attention over the last decade due to its high thermal conductivity, high electron mobility, and excellent chemical stability [1-2]. The induction of magnetism in AlN enables simultaneous manipulation of both charge and spin degrees of freedom of electrons, making it a promising candidate for spintronic applications [3]. AlN becomes a diluted magnetic semiconductor (DMS) when doped with transition metals that induce ferromagnetism [4-6].

Recently, ferromagnetism has been observed in AlN doped with non-magnetic elements such as Cu [7], Mg [8], and C [9]. As one of the most common elements, oxygen can readily become an impurity in samples, thereby affecting their properties. However, magnetic O-doped AlN has rarely been investigated [10]. Generally, AlN films doped with non-magnetic elements or transition metals contain numerous defects that are not uniformly distributed, particularly when prepared by ion implantation. Probing the defect structure and identifying defect types are therefore crucial for understanding the origin of ferromagnetism in AlN DMS films.

Positron annihilation spectroscopy has proven to be a unique method for investigating nanometer-scale defects in materials [11-12]. By controlling the energy of incident positrons, depth profiles of samples can be obtained by detecting annihilation gamma rays. A high-purity Ge detector was used to detect γ-rays produced by positron annihilation to reconstruct the Doppler broadening of annihilation radiation (DBAR) spectra. The obtained DBAR spectrum is characterized by S and W parameters. The S parameter is defined as the ratio of the central area of the annihilation peak (511 $\pm$ 0.81 keV) to the total peak area, reflecting information about positron annihilation with low-momentum electrons (valence or conduction electrons). The W parameter is the ratio of the wing area (505.92–509.16 keV, 512.84–516.08 keV) to the total peak area, reflecting information about positron annihilation with high-momentum electrons (core electrons). When positrons are trapped by vacancy-type defects in samples, the S parameter increases and the W parameter decreases due to the higher fraction of valence electrons around defects compared to defect-free regions. Leveraging DBAR measurements, the defect distribution in AlN films can be obtained. In this work, we prepared O^+-doped AlN films by ion implantation and investigated their structural and magnetic properties.

2 Experiment

One-micrometer-thick unintentionally doped AlN films (marked as as-grown AlN) prepared on c-plane (0001) sapphire substrates (500 m thick) by hydride vapor phase epitaxy were purchased from Hefei Kejing Materials Technology Co., Ltd. The $AlN{:}O_{5\times10}{}^{16}$ and $AlN{:}O_{2\times10}{}^{17}$ samples (where the subscript denotes the dose of implanted O^+ ions in cm^{-2}) were obtained by implanting O^+ ions with an energy of 80 keV into two as-grown AlN films. The ion implantation experiments were performed using an ion implanter at room temperature, with a base pressure of approximately 2×10^{-4} Pa.

Crystal structure analysis was conducted using an X-ray diffractometer (PANalytical X'Pert PRO MPD) in Bragg-Brentano geometry (240 mm radius) with Cu-Kα radiation (λ = 1.5406 Å). Raman spectra were measured at room temperature using a LabRamHR Evolution Raman system with an Ar ion laser (wavelength centered at 514.5 nm) in backscattering geometry as the excitation source. Doppler broadening of annihilation radiation (DBAR) measurements were performed using a slow positron beam with variable energy from 0.25 to 25 keV at the University of Science and Technology of China. The magnetic properties of AlN films were investigated using a Superconducting Quantum Interference Device (MPMS3, Quantum Design) with an accuracy of 10^{-8} emu. Magnetic hysteresis loop measurements were carried out at room temperature with magnetic fields applied both parallel and perpendicular to the sample plane.

3 Results and Discussion

3.1 Structural Characterization

The crystal structures of the AlN samples were investigated by XRD. The XRD spectra were normalized with respect to the intensity of the (0006) peak of the sapphire substrate for the as-grown AlN sample. As shown in Fig. 1 [Figure 1: see original paper], typical (002) peaks of AlN are observed, which can be indexed to hexagonal AlN. No peaks related to metallic Al are found in the

AlN patterns. As shown in the inset of Fig. 1, the intensity of the (002) peak decreases after ion implantation, indicating that the implantation process introduced numerous lattice defects in AlN:$O_5 \times_{10}{}^{16}$ and AlN:$O_2 \times_{10}{}^{17}$. The XRD results for the AlN samples are summarized in Table 1 . The AlN (002) peak shifts toward larger 2 after implantation, suggesting lattice contraction along the c-axis for AlN microcrystals in AlN:$O_5 \times_{10}{}^{16}$ and AlN:$O_2 \times_{10}{}^{17}$, which is likely attributed to the substitution of N^+ or Al^{3+} by O^+ ions due to the smaller covalent radius of oxygen [13].

The Raman spectra of as-grown AlN, AlN:$O_5 \times_{10}{}^{16}$, and AlN:$O_2 \times_{10}{}^{17}$ are shown in Fig. 2 [Figure 2: see original paper]. For as-grown AlN, first-order phonon modes located at 250 cm^{-1} [E_2(low)], 659 cm^{-1} [E_2(high)], and 889 cm^{-1} [A_1(LO)] were observed, which agree well with values reported for AlN films [14-15]. Five additional peaks (marked with asterisks) are attributed to vibrational modes from the sapphire substrate. For AlN:$O_5 \times_{10}{}^{16}$ and AlN:$O_2 \times_{10}{}^{17}$, the E_2(high) peaks at 659 cm^{-1} are also clearly visible. The FWHM of the E_2(high) peak for as-grown AlN, AlN:$O_5 \times_{10}{}^{16}$, and AlN:$O_2 \times_{10}{}^{17}$ are approximately 7.4, 11.1, and 12.1 cm^{-1}, respectively. The broadening of the E_2(high) peak after O^+ implantation suggests a high density of defects in AlN:$O_5 \times_{10}{}^{16}$ and AlN:$O_2 \times_{10}{}^{17}$. With increasing O^+ concentration, the intensity of the E_2(high) peak decreases and the peak becomes asymmetric, indicating lattice distortion of the AlN wurtzite structure. Furthermore, the E_2(low) and A_1(LO) components in AlN:$O_5 \times_{10}{}^{16}$ and AlN:$O_2 \times_{10}{}^{17}$ disappear, replaced by broad bands. In general, Raman band broadening and the absence of local vibrational modes are associated with lattice disorder, defects, and substitutional impurities, which can lead to photon confinement and loss of periodicity [16-17]. The vacancies and substitution of O^+ ions for N^+ or Al^{3+} ions are responsible for these changes in peak shape.

3.2 Positron Annihilation Spectroscopy Analysis

Figure 3(a) [Figure 3: see original paper] shows the S parameters versus positron energy (S–E curves) measured for the AlN films. For as-grown AlN, positron energies of 0–2 keV correspond to the surface layer, where large S parameters result from positron annihilation and formation of positronium atoms at the surface [18]. In this surface layer, S parameters decrease with increasing positron energy. The S values saturate at positron energies of 2–10 keV, indicating that positrons annihilate in the AlN layer. The obtained bulk S parameter (S_b) for as-grown AlN is approximately 0.439. For energies $E > 10$ keV, the S parameters decrease due to annihilation of positrons in the sapphire substrate. Compared to as-grown AlN, the O^+-implanted AlN films exhibit much higher S parameters across the entire energy range, attributed to annihilation of positrons at trapping centers that are Al-related vacancies (negatively charged). The defect types in AlN:$O_5 \times_{10}{}^{16}$ and AlN:$O_2 \times_{10}{}^{17}$ can be determined from the S parameters. The S values for the defect layer (S_d) are 0.461 for AlN:$O_5 \times_{10}{}^{16}$ and 0.454 for AlN:$O_2 \times_{10}{}^{17}$, giving S_d/S_b values of approximately 1.050 and

1.034, respectively. These ratios indicate that the implantation-induced defects in AlN:$O_5\times_{10}{}^{16}$ and AlN:$O_2\times_{10}{}^{17}$ are likely mono-vacancies (V_{Al}) or divacancies according to previous reports [19-20].

To further investigate positron annihilation characteristics in the AlN films, the S–E curves were fitted using VEPFIT software [21] to resolve the defect depth profiles and depth structures of the implanted AlN layers. The S parameter measured at different positron energies E can be expressed by the following formula:

$$S(E) = S_S F_S(E) + \sum_{i=1}^{n} S_i F_i(E)$$

where S_S and S_i are the S parameters for positrons annihilated at the surface and in the ith layer, respectively, while F_S and F_i denote the fractions of positrons annihilated at the surface and in the ith layer, with the relation F_S(E) + Σ_{i=1}^{n} F_i(E) = 1. As shown in Fig. 3(a), the solid lines are in good agreement with the experimental data.

According to previous work [22], the region sampled by annihilated positrons was divided into two blocks for as-grown AlN and three blocks for AlN:$O_5\times_{10}{}^{16}$ and AlN:$O_2\times_{10}{}^{17}$. The defect depth profiles for the AlN films are shown in Fig. 3(b) [Figure 3: see original paper]. In the first block of approximately 60 nm, AlN:$O_5\times_{10}{}^{16}$ and AlN:$O_2\times_{10}{}^{17}$ exhibit high S values due to ion implantation and high O^+ concentration. However, the S value of AlN:$O_5\times_{10}{}^{16}$ is much higher than that of AlN:$O_2\times_{10}{}^{17}$, which is attributed to reverse diffusion of implanted ions. During implantation, vacancy defects are formed while some O^+ ions diffuse toward the surface of the AlN films and accumulate. At lower implantation doses, fewer O^+ ions occupy Al vacancies, whereas more O^+ ions occupy Al vacancies at higher doses, leading to higher vacancy defect densities at lower doses compared to higher doses within the first 60 nm of film thickness. This anomalous result has also been observed in C^+-implanted AlN films [9]. In the second block of approximately 350 nm, high S values for AlN:$O_5\times_{10}{}^{16}$ and AlN:$O_2\times_{10}{}^{17}$ are due to Al-related vacancies. The third block at approximately 950 nm depth corresponds to the AlN thickness, where S values converge due to annihilation of the vast majority of positrons in the sapphire substrate.

To characterize changes in vacancy type, S–W analysis was performed for all AlN films as shown in Fig. 4 [Figure 4: see original paper]. Data for positron energies below 2 keV were subtracted. The fitting curves of the S–W data for as-grown AlN, AlN:$O_5\times_{10}{}^{16}$, and AlN:$O_2\times_{10}{}^{17}$ are straight lines that approximately overlap, indicating that these samples contain the same types of defects. Therefore, increasing the O^+ ion dose increases the density of Al-related vacancies but does not change the defect type.

3.3 Magnetic Properties

The variations of magnetization (M) as a function of applied magnetic field (H) for $AlN:O_5{\times}_{10}{}^{16}$ and $AlN:O_2{\times}_{10}{}^{17}$, measured with magnetic field perpendicular ( ) to the sample plane, are shown in Fig. 5(a) [Figure 5: see original paper]. In our previous work, as-grown AlN exhibited an almost zero hysteresis phenomenon and showed diamagnetic character, indicating the absence of magnetic impurities [9]. Ferromagnetic behavior has been observed for $AlN:O_5{\times}_{10}{}^{16}$ and $AlN:O_2{\times}_{10}{}^{17}$. The saturation magnetization (M_S) of $AlN:O_5{\times}_{10}{}^{16}$ is approximately 0.68 emu/g, much higher than that of $AlN:O_2{\times}_{10}{}^{17}$ (0.09 emu/g). This difference may be due to the excessively high O^+ dose increasing the number of O^+ ions occupying adjacent Al^{3+} positions, resulting in antiferromagnetic coupling [7,23]. This finding is consistent with the DBAR results. The magnetic properties of $AlN:O_5{\times}_{10}{}^{16}$ were measured with magnetic fields applied both parallel (//) and perpendicular ( ) to the sample plane, as shown in Fig. 5(b) [Figure 5: see original paper]. Much stronger ferromagnetism is observed in the perpendicular direction (0.68 emu/g) than in the parallel direction (0.29 emu/g). This magnetic anisotropy can be considered evidence of intrinsic ferromagnetism in O^+-implanted AlN films [24].

To further investigate the origin of ferromagnetism in O^+-implanted AlN films, we calculated their electronic and magnetic properties using DFT methods [9]. For a supercell containing a single Al vacancy, the total magnetic moment is 3.00 _B. Furthermore, the calculated total energy of the spin-polarized state is approximately 556 meV lower than that of the non-spin-polarized state, indicating that a single Al vacancy prefers the spin-polarized state. The magnetic coupling of Al divacancies (V_{Al}–V_{Al}) with different separations was also investigated [25]. The results suggest that the energy difference between antiferromagnetic and ferromagnetic phases rises sharply with increasing distance between two Al vacancies, leading to a crucial transformation of V_{Al}–V_{Al} coupling from antiferromagnetism to ferromagnetism. When the V_{Al}–V_{Al} distance is less than 9.96 Å, the magnetic coupling between them tends to form antiferromagnetic interaction. Thus, for ion implantation with higher dose, divacancies or vacancy clusters will weaken the ferromagnetism of AlN films, which is consistent with the magnetic measurement results.

Based on these results, we propose that the intrinsic ferromagnetism in O^+-implanted AlN films is related to Al vacancies. O^+ ions occupying adjacent Al^{3+} positions and Al divacancies or vacancy clusters jointly play an important role in regulating magnetic properties through antiferromagnetic alignment.

4 Summary

Room-temperature ferromagnetism was observed in O^+-implanted AlN films. The saturation magnetization (M_S) decreased with increasing O^+ dose due to the excessively high O^+ dose causing more O^+ ions to occupy adjacent Al^{3+} positions in antiferromagnetic coupling configurations, as determined by DBAR experiments. First-principles calculations and DBAR experiments revealed that the ferromagnetism originates mainly from Al vacancies. The formation of divacancies or vacancy clusters at high concentrations of Al vacancies leads to a transformation of V_{Al}–V_{Al} coupling from ferromagnetism to antiferromagnetism, ultimately weakening the ferromagnetism of the sample. This work reveals the roles of cation vacancies and substitutional atoms in ferromagnetism within nonmagnetic element-implanted DMSs and demonstrates once again that positrons are a very useful probe for nanometer-scale defects in materials that will be widely used in semiconductor research.

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Note: Figure translations are in progress. See original paper for figures.