Structural, optical, and magnetic properties of Ho-implanted GaN thin films

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Abstract. Ho ions were implanted into highly-resistive molecular-beam-epitaxy grown GaN thin films with a 100kV focused-ion-beam implanter at room temperature (RT). The implantation doses of Ho ions ranges from $10^{14}$ to $10^{16}$ cm$^{-2}$. Without thermal annealing, the structural, optical, and magnetic properties of the Ho-implanted thin films were investigated. Structural properties studied by x-ray diffraction revealed Ho incorporation into GaN matrix without secondary phase. The overall photoluminescence of any implanted sample is weaker than that of the non-implanted one. The spectra show neutral-donor-bound exciton emission and defect-related blue luminescence. Blocked superparamagnetic behavior was identified from Ho-implanted samples at temperatures below RT by measurements with a superconducting quantum interference device. The highest ordering temperature is 100 K.

1. Introduction

Rare earth doped III-V nitride semiconductor materials have received considerable attention primarily for potential use in optoelectronic applications in visible displays or in white light systems that employ color-combining techniques. Recently, rare earth doped GaN and AlN thin films have also shown potential impact for application in spintronics. Among them, Gd-doped GaN attracted great interest because it was reported to be ferromagnetic above room temperature (RT) and have large colossal magnetic moment [1-3]. Holmium (Ho) has the atomic magnetic moment of 10.4 $\mu_B$, which is the second largest value among rare earth elements, and therefore, it would be interesting to incorporate Ho into GaN and compare the properties between Ho- and Gd-doped GaN.
In this paper, we investigate the structural, optical, and magnetic properties of GaN thin films implanted with Ho by focused-ion-beam (FIB) implantation at different doses. Our results show well-incorporation of Ho into GaN, and the impurity-related emission in photoluminescence spectra. The magnetic ordering occurs at temperatures lower than 130 K.

2. Experimental

Wurtzite GaN thin films grown by ammonia-source molecular beam epitaxy on a c-oriented sapphire substrate were implanted with Ho ions at three different doses (1×10^{14}, 1×10^{15}, and 1×10^{16} cm^{-2}, and labeled as sample A, B, and C, respectively) at RT by using a FIB implanter (EIKO-100). For samples A and B, the ion energy of Ho is 300keV, and the projected range simulated by SRIM code [4] is 52.6nm. For sample C, the ion energy and the simulated projected range are 200keV and 38.2nm, respectively.

The structural, optical, and magnetic properties of the samples were investigated after implantation without performing thermal annealing. The structural properties of the samples were investigated by x-ray diffraction (XRD) at RT. The optical properties were studied by photoluminescence (PL) spectroscopy with an excitation wavelength of 325 nm. PL spectra in the range of 2.0 to 3.6 eV were recorded with standard lock-in technique at two temperatures, 10 and 300 K, respectively. The magnetic properties were measured with a Quantum Design superconducting quantum interference device (SQUID) magnetometer in the temperature range from 2 to 300 K. The magnetization loops (m-H curves) of each sample were taken at T = 5 and 300 K in the magnetic field between ±50 kOe. The temperature dependence of the magnetization between 2 and 300 K was studied by recording field-cooled (FC) and zero-field-cooled (ZFC) curves at a magnetic field of 100 Oe. The magnetic field was applied parallel to the surface of the samples for all SQUID measurements, and all the data presented here are corrected for the artifacts and the diamagnetic background.

3. Results and discussions

3.1. Structural properties

Wide range ω-2θ scan of the Ho-implanted samples were carried out with a Phillips X’Pert MRD diffractometer. No diffraction peaks other than sapphire(0006) and GaN(0002) were detected from the implanted samples, which shows that no secondary phase were formed during FIB implantation. Figure 1 compares the high-resolution x-ray diffraction rocking curves of the Ho-implanted and non-implanted thin films obtained by using Bede D3 diffractometer, and the intensity is normalized to the peak intensity of GaN(0002). The GaN(0002) peak of sample A has no shift in peak position but with a slight broadening at the lower-angle side. GaN(0002) peak of sample B broadens on both sides, where lower-angle side has stronger broadening than the higher-angle side. However, the peak position is not shifted. For sample C, the GaN(0002) peak shifts to the lower-angle side and with pronounced broadening on both sides.

Figure 1 Comparison of rocking curves of Ho-implanted GaN thin films to a non-implanted one. The intensity is normalized to the peak intensity of GaN(0002). (a) Sample A, (b) sample B, and (c) sample C.
The slight broadening on the lower-angle side of GaN(0002) peak of samples A and B and the shift of peak position of sample C are the evidence of incorporation of Ho into GaN matrix, and the reasons are the following: (i) Ho-doped GaN would have larger lattice constant because Ho has larger ionic radius than Ga; and (ii) the GaN(0002) peak is the superposition of the diffraction peaks of the thin Ho-doped GaN and the underneath thick undoped GaN layers. Therefore, the GaN(0002) broadens slight on the lower-angle side for low Ho doses and shifts to lower angle for high Ho dose. The broadening of on the higher-angle side of GaN(0002) peak of sample B and C is attributed to implantation-induced local amorphization of the thin films, which becomes pronounced with doses above $1 \times 10^{15}$ cm$^{-2}$.

3.2. Optical properties

Before the PL spectra are discussed, it is worthy to note that the overall integrated emission intensity of any of the four samples is weak – without focusing the laser beam, there was no observable spectrum even for the non-implanted sample. Figure 2 compares the PL spectra of the non-implanted sample to the Ho-implanted ones at $T = 10$ K. For non-implanted sample (black curves), PL spectra show only the near-band-edge emissions, but the typical yellow luminescence was not observed at both temperatures. The near-band-edge emissions consist of neutral-acceptor-bound exciton ($A^0X$) and its longitudinal phonon replica ($A^0X$-LO), and donor-acceptor-pair (DAP) emissions. After implantation, near-band-edge emission was observed only for sample A, and it has only one contribution, which is the neutral-acceptor-bound exciton emission [5] – indicating the majority of the optically active defects is acceptor-like, possibly due to either the magnesium impurity or gallium vacancy. For samples B and C, the near-band-edge emission disappeared completely, and the reason can be implantation-induced local defect formation and amorphization. Local amorphous material and the defects modify the band structure and create absorption centers, which render the near-band-edge emission invisible.

Furthermore, a broad but weak blue luminescence (BL) emission, whose peak is around 2.9 eV, is barely visible as background for the non-implanted sample and becomes clearer for the Ho-implanted samples. According to Ref. 6, this BL can be related to stacking-fault type of defects, and this indicates good crystal quality of our as-grown GaN thin films and the increase in density of such defects to Ho implantation.

3.3. Magnetic Properties

At $T = 5$ K, $m$-$H$ curves, shown in Fig. 3, of the all Ho-implanted samples show only paramagnetic-like behavior without saturation at $H = 50$ kOe after all the artifacts and the diamagnetic background are corrected. Surprisingly, the $m$-$H$ curves of samples A and B overlap completely. In small magnetic fields, $|H| \leq 3$ kOe, no hysteresis loop was observed from all Ho-implanted samples, and the remanent magnetic moment of samples A and B are at the resolution limit of our SQUID. The non-saturation feature indicates that the magnetic moment of all samples has two contributions, one from the (Ga,Ho)N thin films and the other from defects in the thin films, whether intrinsic or
implantation-induced. The latter becomes dominant at high magnetic fields, and the defect density can be quite large. The magnetization loops at T = 300 K do not show any hysteretic behavior for all the implanted samples and are not depicted.

Figure 4 shows the temperature dependence of FC and ZFC magnetic moment curves under a magnetic field of 100 Oe for all three Ho-implanted samples. The FC and ZFC curves of sample B coincide each other – representing no long-range magnetic ordering. Separation between FC and ZFC curves were observed only for samples A and C, and this indicates long-range magnetic ordering in these two samples. The long-range ordering of the samples looks like blocking type because the FC curves show the temperature dependence of a paramagnet, and the ordering temperatures are around 100 K and 80 K for samples A and C, respectively. Because both Ho and HoN have the Curie temperature at around 20 K [7,8], the long-range magnetic ordering comes from (Ga,Ho)N.

The surprising magnetic properties of sample B (Ho-dose of 1×10^15 cm^{-2}) – (i) having the same m-H curve as sample A (Ho-dose of 1×10^{14} cm^{-2}), and (ii) showing no long-range magnetic ordering while the other two do – prompted us to postulate that there is possible change in ordering mechanism for GaN implanted with a Ho-dose at around 1×10^15 cm^{-2}. For lower Ho doses, where the separation between the Ho ions is large, the magnetic ordering is by blocking. For higher Ho doses, where the Ho density is in the percentage range, the magnetic properties of (Ga,Ho)N tend toward HoN, and the magnetic ordering mechanism is ferromagnetic – in our case, it could be impurity-mediated mechanism [9] or exchange mechanism. However, the FC curve shows no (clear) step-wise behavior, and it requires further investigations to verify our postulate.

4. Conclusions
Ho ions were implanted into wurtzite GaN thin films at room temperature with a dose ranging from 10^{14} to 10^{16} cm^{-2}. Without any thermal treatment on the samples, X-ray diffraction showed Ho-incorporation into the GaN matrix without any secondary phase. PL spectra revealed the presence of acceptor-like defects in Ho-implanted GaN with the dominant neutral-acceptor-bound-exciton emission. Ho-implanted GaN shows superparamagnetic behavior at low temperatures for implantation doses of 1×10^{14} cm^{-2} and 1×10^{16} cm^{-2}. The ordering temperature of the samples is around 100 K and 80 K, respectively. The sample implanted with a dose of 1×10^{15} cm^{-2} shows paramagnetic behavior with no magnetic ordering.

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