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Fabrication of (Ga,Mn)N nanowires with room temperature ferromagnetism using nitrogen plasma

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Ferromagnetic properties of (Ga,Mn)N nanowires were examined by treating with nitrogen plasma at 200 °C. Nanowires grown by chemical vapor deposition were n-type and no secondary phases were found. The magnetic moment increased and was maintained at room temperature by this treatment. Synchrotron radiation photoemission spectroscopy revealed that Ga vacancies significantly increased, but N vacancies decreased by plasma treatment, leading to a decrease of Mn_{Ga}–V_N complex and the enhancement of Mn activation. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1999862]

GaN-based diluted magnetic semiconductors (DMSs) doped with transition metals such as Mn have attracted a great deal of attention because their Curie temperatures (T_c) were higher than room temperature according to the theoretical calculation of Dietl *et al.*[1,2] Highly Mn-doped GaN film showing ferromagnetic behavior above room temperature was grown on sapphire (0001) by molecular beam epitaxy (MBE).[3] The ferromagnetic properties were also reported in Mn-implanted GaN and by subsequent annealing.[4] This material is a suitable candidate for spin-field effect transistors, spin-light emitting diodes, and biodetectors.[5] To date, most works to obtain ferromagnetic properties of (Ga,Mn)N have focused on the microcrystalline, epitaxial, bulk, Mn implanted, and Mn-diffused (Ga,Mn)N.[3–6] However, no results on ferromagnetic properties of nanometer-sized (Ga,Mn)N such as nanowires have been reported.

The effects of atomic nitrogen on the magnetic properties of (Ga,Mn)N are of interest since magnetic properties significantly depend on the relative atomic concentration of nitrogen and gallium. In (Ga,Mn)N, atomic nitrogen reduces the number of nitrogen vacancies, leading to a decrease of Mn acceptor–donor (D–A) pairs.[6] The enhancement of Mg activation in GaN using nitrogen plasma, containing atomic nitrogen, was also reported.[7] These results suggest that ferromagnetic properties with high T_c could be obtained using nitrogen plasma. In addition, compared to bulk (Ga,Mn)N materials, nitrogen plasma treatment of (Ga,Mn)N nanowires could have a larger influence due to their larger surface area/volume ratio.

In this work, we reported on the fabrication of (Ga,Mn)N nanowires showing ferromagnetic behaviors above room temperature using nitrogen plasma. The morphology of nanowires was analyzed using field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM). Synchrotron radiation photoemission spectroscopy (SRPES) was also employed to identify secondary phases and chemical bonding states in nanowires. The optical properties of samples were analyzed through photoluminescence spectroscopy. From these, we interpreted the origin of ferromagnetic properties in (Ga,Mn)N nanowires.

A (0001) sapphire substrate was used as a starting substrate. Before the growth of GaN nanowire, the substrate was cleaned with acetone, ethyl-alcohol, and deionized water. A thin layer of 30-Å-thick Au was evaporated to enhance the formation of GaN nanowire.[8] A (2:1) mixture by weight of pure Ga and $MnCl_2$ powders (99.95%) was introduced into the middle of the quartz boat. The quartz boat was then placed in a horizontal furnace, evacuated to 10 mTorr and purged with a constant nitrogen flow of 500 sccm. The furnace temperature was then increased to 900 °C. A high purity NH_3 (99.995%) of 150 sccm was introduced into the reaction chamber for 2 h under a pressure of 1 atm. After the reaction, a layer of light-yellow products was visible on the surface of the substrate in the quartz boat. The (Ga,Mn)N nanowires were then exposed to nitrogen plasma for 10 min at 200 °C in a radio-frequency reactor operating at 800 mTorr pressure and 50 W.

The SRPES measurements were carried out at the 8A1 undulator beamline at the Pohang Accelerator Laboratory (PAL). A hemispherical electron energy analyzer with 16 energy-detecting channels/windows was used, and the energy separation/resolution per window was 0.05 eV. An incident photon energy of 700 eV was used to measure the core-level spectra of Ga 3*d* and Mn 2*p*. The binding energy of the core-level spectrum was calibrated using the Au 4*f* core level of Au foil. The Fermi level was determined by linearly extrapolating the sloped region with a base line in the valence-band spectrum of the Au foil. FESEM with a high spatial resolution of 1.50 nm was used to characterize product morphology. The HRTEM images were collected using a JEOL 2010F operated at 200 kV. Its spatial resolution was 0.19 nm.

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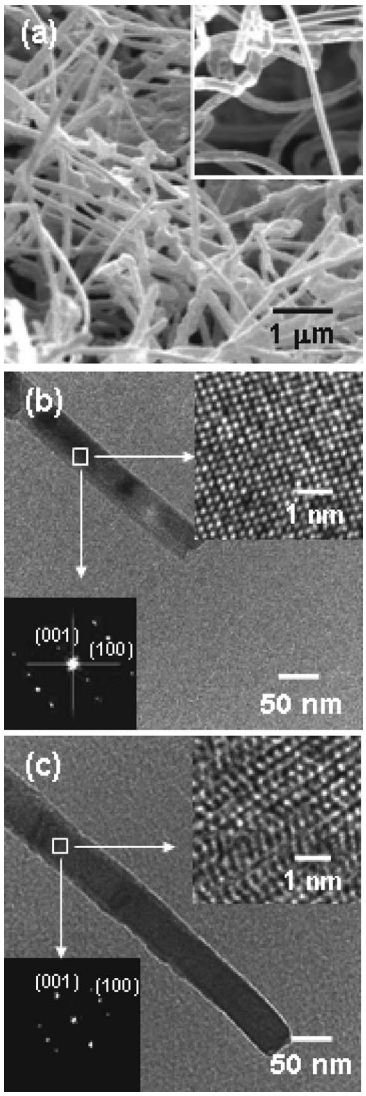

FIG. 1. (a) FESEM image of (Ga,Mn)N nanowires with random orientation. The SEM image of GaN nanowires is also shown in the inset; (b) cross-sectional TEM image of a single GaN nanowire and corresponding electron diffraction patterns recorded along the [010] zone axis and lattice image; (c) cross-sectional TEM image of a single (Ga,Mn)N nanowire and corresponding electron diffraction patterns recorded along the [010] zone axis and lattice image.

PL measurements were carried out using a 0.75 m monochromator equipped with an ultraviolet-sensitive photomultiplier. Magnetization measurement was carried out using a superconducting quantum interference device (SQUID) magnetometer (MPMSXL, Quantum Design Co., Ltd).

The SEM image of (Ga,Mn)N nanowires is shown in Fig. 1(a). The image is the same as the image of GaN nanowires, as shown in the inset of Fig. 1(a). The nanowires exhibited a length of a few micrometers and a mean diameter of 80 nm. In Fig. 1(b), a bright-field TEM image of GaN nanowires is displayed. The selected area electron diffraction patterns from a single nanowire, shown in the inset of Fig. 1(b), confirmed that the nanowire was a single-crystalline wurzite structure and its growth direction was [002]. From the high-resolution lattice image of selective area of a nanowire, it was found that the lattice is well aligned without lattice distortion. Figure 1(c) is a bright-field TEM image of (Ga,Mn)N nanowires. The growth direction was also [002] and no Mn-related secondary phases were found. However, the lattice image was partially distorted as shown in the inset of Fig. 1(c), compared with the lattice image of GaN nanowires in Fig. 1(b). After nitrogen plasma treatment, no change in the lattice image, including growth direction, was found in (Ga,Mn)N nanowires.

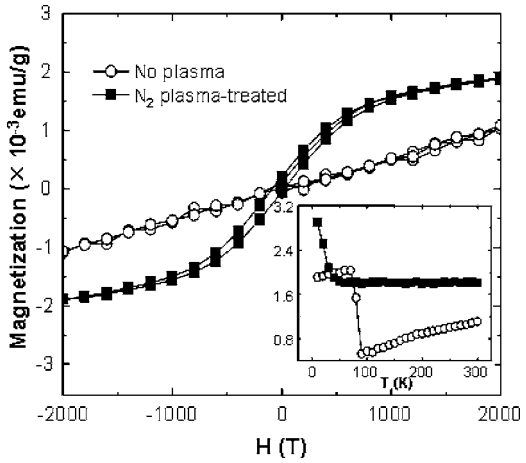

FIG. 2. Magnetization curves at 300 K for (Ga,Mn)N nanowires with nitrogen plasma treatment. The temperature dependence of the magnetic moment is plotted in the inset.

Figure 2 shows the magnetization curves at 300 K for the as-grown and nitrogen plasma-treated (Ga,Mn)N samples. For the as-grown sample, a paramagnetic behavior was observed because its T_c was lower than 300 K. However, a clear ferromagnetic curve with H_c of 53 Oe and $M_s \approx 2.0 \times 10^{-3}$ (emu/g) was obtained in the nitrogen plasma-treated sample. The magnetic moment also increased with plasma treatment in the temperature range between 100 and 300 K, shown in the inset of Fig. 2.

Figures 3(a), 3(b), and 3(c) display the SRPES spectra of Mn 2*p*, N 1*s*, and Ga 3*d* core levels, respectively. The Mn 2*p*

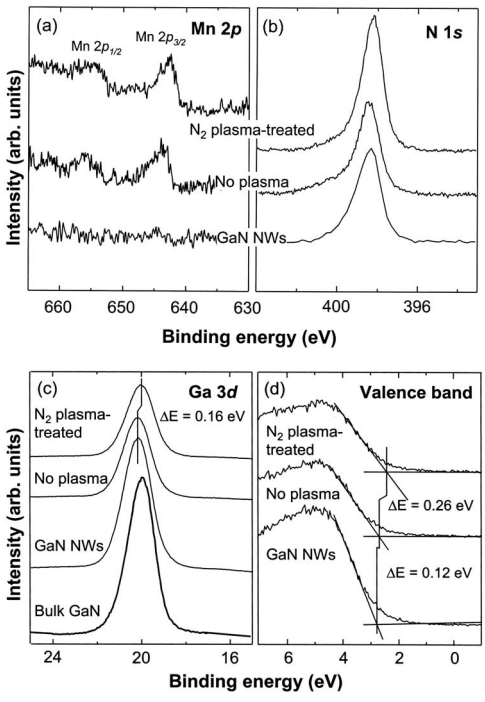

FIG. 3. SRPES spectra of (Ga,Mn)N nanowires with nitrogen plasma treatment: (a) Mn 2*p*; (b) N 1*s*; (c) Ga 3*d* core levels; and (d) valence band spectra.

TABLE I. Change of Ga/N atomic ratio. The GaN and (Ga,Mn)N nanowires were grown at an ammonia flow rate of 150 sccm.

Sample	Ga/N ratio
as-grown GaN NWs	1
as-grown (Ga,Mn)N NWs	0.82
N_2 plasma treated (Ga,Mn)N NWs	0.70

spectrum was observed in (Ga,Mn)N nanowires and the peak intensity remained unchanged with plasma treatment. No additional chemical bonds due to Mn-related secondary phases were found. The peak intensity of N 1*s* spectra significantly increased with the treatment. This indicates that the nitrogen plasma treatment introduced atomic nitrogen to the nanowires, resulting in the decrease of n vacancies. In the SRPES spectra of Ga 3*d*, the peak intensity in bulk GaN was larger than that in GaN nanowires. From the integration of peak intensities of the N 1*s* and Ga 3*d* spectra, it was found that the relative atomic ratio of Ga/N decreased with the treatment, summarized in Table I. It was also observed from the valence band spectra in Fig. 3(d) that the surface band bending of (Ga,Mn)N nanowires changed with nitrogen plasma treatment. In (Ga,Mn)N nanowires, the Fermi level shifted about 0.12 eV toward the valence band maximum (VBM) in comparison with the GaN nanowires. After the plasma treatment, the Fermi level shifted about 0.26 eV toward the VBM. This means that net hole concentration increased due to the increase in the number of Ga vacancies, consistent with the change of the Ga 3*d* spectrum in Fig. 3(c).

Figure 4 shows the PL spectra of (Ga,Mn)N nanowires with nitrogen plasma treatment. For an as-grown sample, only one peak appeared at an energy of 3.25 eV. This PL peak was commonly observed in low-temperature PL measurements, which might be due to the shallow donor–acceptor pair transitions (DAP).[7] After plasma treatment, the peak intensity was slightly changed and two PL peaks occurred at 2.35 and 3.04 eV. The PL peak centered at 2.35 eV was a typical yellow luminescence band, corresponding to the PL band due to Ga vacancies.[9] This means that concentration of Ga vacancies increased by the treatment, consistent with the results in Fig. 3(c). The PL band observed at 3.04 eV corresponded to a conduction band-shallow Mn acceptor (e, Mn) transition.[6] The band acceptor transition, E_{eA}, is given by $E_{eA}=E_G-E_A+1/2kT$. From this equation, the Mn acceptor binding energy is about 370 meV. The increase in the peak intensity after plasma treatment implies the enhancement of Mn activation in (Ga,Mn)N nanowires.

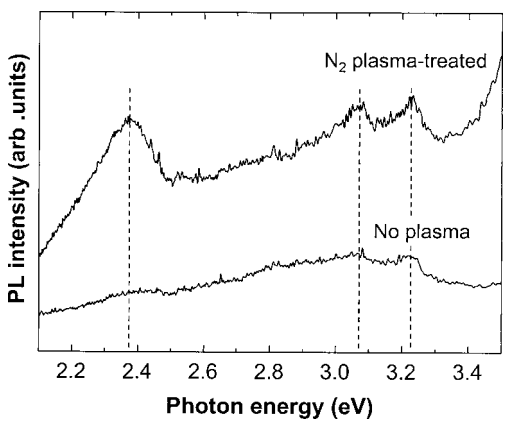

FIG. 4. PL spectra at 10 K for (Ga,Mn)N nanowires with nitrogen plasma treatment.

In (Ga,Mn)N thin films previously reported in the literature,[3–6,10] experimental results showed significant discrepancies due to the formation of nanosized Ga–Mn and Mn–N compounds. However, such secondary phases were not observed in (Ga,Mn)N nanowires, meaning the dissolution of Mn atoms to form a solid solution in GaN nanowire. The magnetic properties enhanced by nitrogen plasma treatment can be explained by ferromagnetic coupling between Mn ions mediated by Mn-bound holes.[8] When the nanowires were exposed to nitrogen plasma, the concentration of Ga vacancies relatively increased, but N vacancies decreased. In (Ga,Mn)N, Mn ions occupied at Ga vacancies.[11] Thus, the nitrogen plasma treatment might lead to an increase of Mn concentration occupying Ga sites. In the meantime, N vacancies and Mn acceptors, which are oppositely charged, attract each other and tend to form Mn_{Ga}–V_N complex.[6] From electron spin resonance measurements, Mn in (Ga,Mn)N was found to be mostly present in the neutral acceptor state, Mn^{3+} or $Mn^{2+}+h^+$ with spin $S=2$.[12] Nitrogen vacancies in GaN are donors for electrons. Thus, a number of Mn^{2+} ions, which were responsible for the paramagnetic behavior of n-type (Ga,Mn)N semiconductors, could be produced due to the increase of n vacancies. Therefore, ferromagnetic properties could be enhanced with nitrogen plasma treatment.

In conclusion, we reported on the fabrication of (Ga,Mn)N nanowires showing ferromagnetic behavior above room temperature using nitrogen plasma. With nitrogen plasma treatment, Ga vacancies significantly increased, but N vacancies decreased, leading to the decrease of Mn_{Ga}–V_N complex and enhancement of the activation of Mn atoms. As a result, the ferromagnetic signal and Curie temperature significantly increased.

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