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Characterizations of n-type ferromagnetic GaMnN thin film grown on GaN/Al_2O_3 (0 0 0 1) by metal-organic chemical vapor deposition

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ABSTRACT

A high-quality ferromagnetic GaMnN (Mn = 2.8 at%) film was deposited onto a GaN buffer/Al_2O_3(0 0 0 1) at 885 °C using the metal-organic chemical vapor deposition (MOCVD) process. The GaMnN film shows a highly *c*-axis-oriented hexagonal wurtzite structure, implying that Mn doping into GaN does not influence the crystallinity of the film. No Mn-related secondary phases were found in the GaMnN film by means of a high-flux X-ray diffraction analysis. The composition profiles of Ga, Mn, and N maintain nearly constant levels in depth profiles of the GaMnN film. The binding energy peak of the Mn $2p_{3/2}$ orbital was observed at 642.3 eV corresponding to the Mn (III) oxidation state of MnN. The presence of metallic Mn clusters (binding energy: 640.9 eV) in the GaMnN film was excluded. A broad yellow emission around 2.2 eV as well as a relatively weak near-band-edge emission at 3.39 eV was observed in a Mn-doped GaN film, while the undoped GaN film only shows a near-band-edge emission at 3.37 eV. The Mn-doped GaN film showed n-type semiconducting characteristics; the electron carrier concentration was $1.2 \times 10^{21}/cm^3$ and the resistivity was $3.9 \times 10^{-3}\,\Omega$ cm. Ferromagnetic hysteresis loops were observed at 300 K with a magnetic field parallel and perpendicular to the *ab* plane. The zero-field-cooled and field-cooled curves at temperatures ranging from 10 to 350 K strongly indicate that the GaMnN film is ferromagnetic at least up to 350 K. A coercive field of 250 Oe and effective magnetic moment of 0.0003 μ_B/Mn were obtained. The n-type semiconducting behavior plays a role in inducing ferromagnetism in the GaMnN film, and the observed ferromagnetism is appropriately explained by a double exchange mechanism.

1. Introduction

Dilute magnetic semiconductors (DMSs) are potential candidate materials for spintronic devices such as spin-field effect transistor (spin-FET) and ultra dense nonvolatile semiconductor memory (MRAM) [1,2], which could utilize the spin degree of freedom of the charge carriers. Recently, the Mn-doped III–V semiconductors have attracted extensive attention due to its ferromagnetic ordering properties. Most researches were focused on developing Mn-doped GaAs materials with the Curie temperature (T_C) lower than room temperature. The highest T_C for GaMnAs was reported at 150 K, restricting its practical applications for spintronics devices [3].

GaN-based DMSs have drawn much attention since they could have a high T_C above room temperature [4]. Many research groups reported room-temperature ferromagnetic ordering in GaMnN. However, its origin for ferromagnetic ordering was controversial. One can be charge carriers (e^-,h^+) generated by either Mn dopant, N vacancy, or extrinsic ferromagnetic secondary phases (Mn_xN_y or Mn_xGa_y compounds), and the other can be Mn-induced impurity band hybridized with the N 2p orbital [5–8]. These contradictable results may come from the different film fabrication methods and experimental conditions.

Molecular beam epitaxy (MBE) has been adopted extensively for epitaxial GaMnN film growth due to their ability to fabricate well-defined structures with atomically abrupt interfaces at temperatures below 800 °C [9–11]. On the other hand, metal-organic chemical vapor deposition process (MOCVD) has been also used for thin film growth technique in the semiconductor industries to produce economically feasible large films with well-controlled composition and good crystallization, but has rarely been adopted for ferromagnetic GaMnN film growth.

In this work, the MOCVD is proposed as a potential thin film growth technique for ferromagnetic GaMnN thin film fabrication, and the magnetic properties is discussed in terms of structural, electronic, and optical properties.

2. Experimental procedures

A GaMnN film is grown on a GaN buffer layer/Al_2O_3(0 0 0 1) substrate at 885 °C with a MOCVD method. Prior to the GaMnN

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film, the GaN buffer layer is deposited with the supply of 0.2 sccm Ga, 170 sccm NH_3, and 200 sccm H_2. NH_3 and H_2 gases were employed after passing through in-line gas purifier to remove H_2O, O_2, CO, and CO_2 impurities down to less than 1 ppb (SAES Pure Gas. Inc.). An epi-ready sapphire substrate ($10 \times 10\,mm^2$) was loaded on a SiC-coated graphite susceptor (60 mm in diameter and 80 mm length cylindrical shape, situated coaxially under the shower head). The chamber was initially evacuated to 5×10^{-3} Torr. The susceptor was heated inductively to 1075 °C at the rate of 1 °C/s and sustained at that temperature for 10 min to keep uniformity on a substrate. H_2 gas of 500 sccm was then introduced for 10 min to remove any residual contaminants on the substrate, followed by nitridation with 500 sccm NH_3 for another 10 min at 1050 °C. The 40-nm-thick GaN buffer layer at low temperature (500 °C) and the 1-μm-thick GaN buffer layer at high temperature (1025 °C) were grown, followed by 200 nm GaMnN film growth at 885 °C with the addition of 0.006 sccm Mn vapor (Mn/Ga = 0.03). $(CH_3)_3Ga$ (trimethyl gallium) and $(CH_3C_5H_4)Mn(CO)_3$ (Methylcyclopentadienyl tricarbonylmanganese) were used for Ga and Mn metal-organic sources. The total pressure in a chamber was maintained at 100 Torr with the aid of an exhaust throttle valve during the whole deposition process.

The crystalline structure was ascertained by a high-resolution X-ray diffraction (HRXRD) [Philips X'Pert PRO-MRD] using the triple crystal diffractometry (TCD) with monochromatic Cu Kα radiation ($\lambda = 0.154056$ nm) as well as a high-flux X-ray diffraction (HFXRD) [Rigaku D/max-2500/PC & Huber 4-circle goniometry]. The vibrating sample magnetometer (VSM) was used to investigate the magnetic properties as functions of temperature and magnetic field. A photoluminescence (PL) spectroscopy analysis was carried out with a He–Cd laser (325 nm) at 300 K to characterize the optical properties. Electronic structures were characterized by the X-ray photoelectron spectroscopy (XPS) [VG scientific Co. ESCALab 220IXL] using a monochromatic Mg Kα radiation (1253.6 eV) at a typical energy resolution of 0.47 eV full-width at half-maximum. The charge-shifted spectra were corrected using the maximum of the C 1s photoelectron signal at 284.6 eV. The pass energy of 50 eV and the X-ray power of 100 W were adopted. During the compositional depth profile measurements by XPS, the Ar ions accelerated at 3 KeV were utilized for film sputtering. The surface morphology and thickness of GaMnN films were determined through the field emission scanning electron microscopy (FESEM) [JSM 6330F], whose operating voltage was 15 KeV. Table 1 shows the film compositions and thicknesses of GaN and GaMnN films ascertained by the XPS and FESEM. The root mean square (RMS) roughness was measured with the atomic force microscope (AFM) [DI Multi mode]. The Hall-effect measurements were carried out to identify the carrier type and its density at 300 K using the standard Van der Pauw technique.

Table 1
The compositions and thickness of GaN and GaMnN films determined by XPS.

Specimen	Ga (at%)	Mn (at%)	N (at%)	Thickness (nm)
GaN buffer layer	43.05		56.95	1000
GaMnN	57.43	2.8	39.77	200

3. Results and discussion

Fig. 1 shows the images of the surface morphology for as-grown and Mn-doped GaN films. The surface morphology of the as-grown film shows a flat mirror-like surface with several tens of nano-sized hexagonal hollows in Fig. 1(a). RMS roughness of 10 nm for the as-grown film implies a very flat surface suitable for the following GaMnN film growth. In contrast to the flat surface of GaN, GaMnN film grown on GaN buffer shows a rough and moon-like surface with a shape of craters (Fig. 1(b)).

Fig. 2(a) shows a magnetic field dependence of magnetic susceptibility (M/H) measured at 10 and 300 K for GaMnN films. The magnetic field ranging from -5 to 5 kOe was applied with perpendicular ($H \perp ab$ plane) and parallel ($H \| ab$ plane) to the plane of the film. The diamagnetic signal from GaN buffer/sapphire substrate was subtracted from the measured M/H curve in the high magnetic field region. The typical ferromagnetic hysteresis loop is observed at 300 K. The coercive field and effective magnetic moment are $H_C = 250$ Oe and $\mu_{eff} = 0.003\,\mu_B$/Mn, respectively. The H_C is three times bigger than the previously reported ones for GaMnN film grown by MBE and implantation methods, while the μ_{eff} is one order smaller [12,13]. The values of H_C with $H \| ab$ plane are bigger than that with $H \perp ab$ plane as shown in the inset of Fig. 2(a). This result indicates that the easy magnetization axis is the in-plane direction for the present GaMnN film grown by MOCVD. The field-cooled (FC) and zero-field-cooled (ZFC) magnetization data measured in a field of 10 kOe are plotted as a function of temperature in Fig. 2(b). The difference between FC and ZFC curves at the temperatures above 50 K indicates a room-temperature ferromagnetism of the GaMnN film. The magnetization increases significantly with decreasing temperatures below 50 K due to the paramagnetic contribution, which corresponds to the previous report. [14] These results suggest that the GaMnN film possesses both ferromagnetic and paramagnetic interactions among Mn ions. Previous research groups reported different origins for ferromagnetism in GaMnN. Ham and Myoung [15] and Lee et al. [16] reported that hole or electron carriers played a key role for the ferromagnetism in GaMnN, while Nakayama et al. [17] and Baik et al. [18] insisted that ferromagnetic secondary phases such as Mn_xN_y or Mn_xGa_y mainly contribute the observed ferromagnetism in GaMnN. Therefore, the HRXRD, HFXRD, XPS, PL and Hall measurements

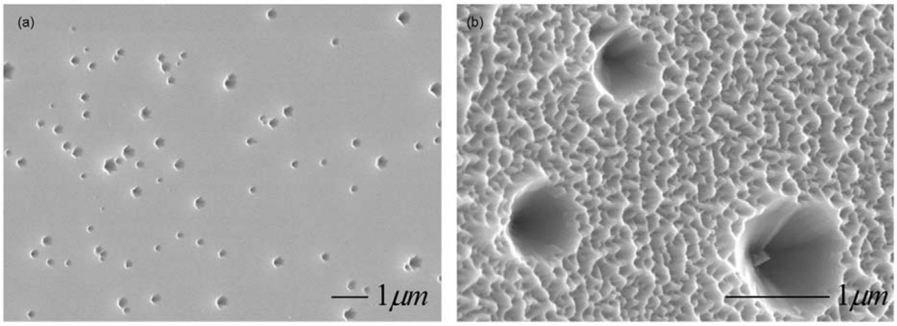

Fig. 1. FESEM images for (a) GaN buffer grown at 1025 °C and (b) GaMnN (Mn = 2.8 at%) film grown at 885 °C.