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Room temperature ferromagnetic (Ga,Mn)N epitaxial films with low Mn concentration grown by plasma-enhanced molecular beam epitaxy

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Abstract

We report on the crystal structures, magnetic and magnetotransport properties of epitaxial $(Ga_{1-x}Mn_x)N$ films with low Mn concentration ($x = 0.06$–0.5%) grown by plasma-enhanced molecular beam epitaxy, exhibiting n-type conductivity and ferromagnetism with Curie temperature in the range 550–700 K. Transmission electron microscopy studies revealed that Mn ions substitute for Ga ions in the epitaxial structure, leading to the expansion of the lattice parameter *a* of the hexagonal (wurtzite) structure. The temperature dependence of the sheet resistance is found to show negative magnetoresistance in the temperature range 4–300 K, indicative of ferromagnetic semiconducting (Ga,Mn)N films. © 2002 Elsevier Science Ltd. All rights reserved.

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In recent years, ferromagnetic semiconductors have been of great interest scientifically and technologically to both theorists and experimentalists due to potential applications for spintronics, in which the spin of charge carriers (electrons or holes) delivers prospects for fundamentally novel functionality with respect to semiconductor device physics [1,2]. Comprehensive studies have focused on the (Ga,Mn)As [3,4], (In,Mn)As [5,6], and MnGe [7] systems, which exhibit very intriguing magnetic and transport properties for spintronics, but suffer from low Curie temperatures (T_c) for practical device applications, i.e. ~110 K for (Ga,Mn)As [3,4], ~35 K for (In,Mn)As, and 116 K for MnGe [7]. Wide bandgap semiconductors are of particular importance in this context, since Dietl et al. [8] predicted T_c exceeding room temperature for GaN and ZnO containing 5% of Mn and a high hole concentration ($3.5 \times 10^{20}\ cm^{-3}$) on the basis of the mean-field Zener model of ferromagnetism. More recent reports have attracted significant attention on the room temperature ferromagnetic p-type (Ga,Mn)N [9] prepared by Mn diffusion into MOCVD-grown GaN epitaxial layer and n-type (Ga,Mn)N [10,11] grown by MBE. However, nature of ferromagnetic (Ga,Mn)N with T_c above room temperature is still far from complete understanding for spintronic device applications.

In this paper, we present the crystal structures, magnetic and magnetotransport properties in the epitaxial (Ga,Mn)N films with low Mn concentration grown by plasma-enhanced molecular beam epitaxy (PEMBE). The epitaxial

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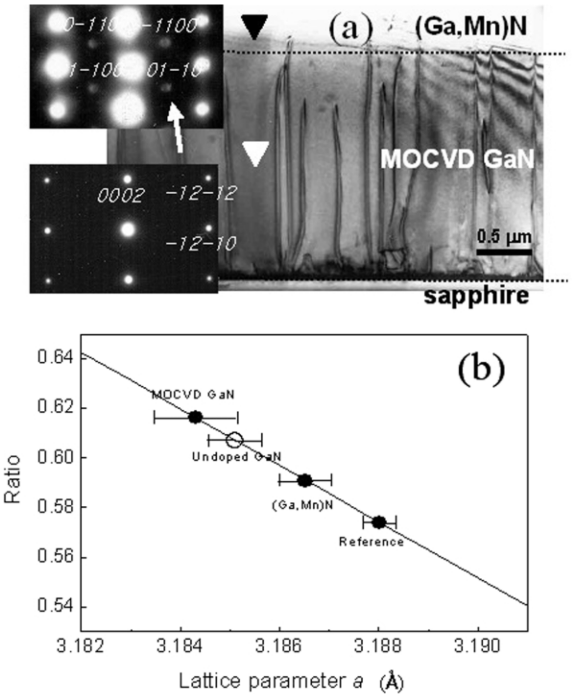

Fig. 1. (a) Cross-sectional TEM micrograph for the (Ga,Mn)N with $x = 0.2\%$/GaN (MOCVD)/sapphire(0001), electron diffraction patterns for the (Ga,Mn)N (upper) and MOCVD-grown GaN (lower), and (b) the lattice parameters a for the (Ga,Mn)N, the MOCVD-grown GaN, a Mn-undoped GaN, and a reference sample, obtained from HOLZ measurements. The arrow indicates the additional diffraction spots for the (Ga,Mn)N.

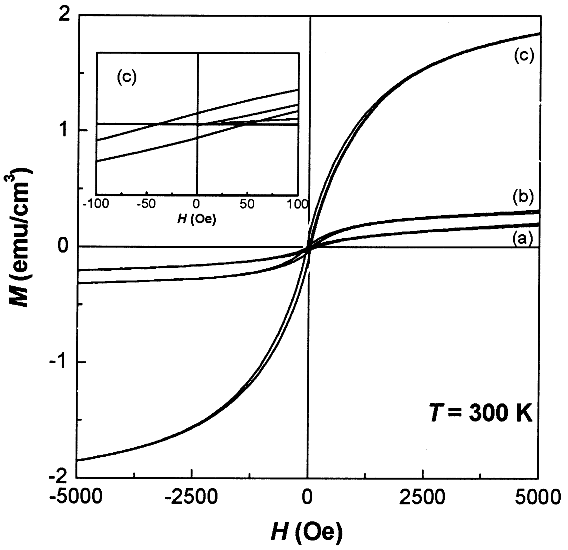

Fig. 2. Representative hysteresis loops for the (Ga,Mn)N films with low Mn concentration (0.06–0.5 Mn%) as a function of Mn cell temperature, obtained with magnetic fields applied parallel to the plane of the samples at room temperature by AGM. Mn cell temperatures are (a) 630 °C, (b) 650 °C, and (c) 670 °C. The non-magnetic contributions of the GaN buffer layer and sapphire substrate have been subtracted from the data for all the films.

(Ga,Mn)N films were found to exhibit n-type conductivity, negative magnetoresistance (MR) in the range of 4–300 K and ferromagnetic ordering with T_c exceeding room temperature. Transmission electron microscopy (TEM) studies confirmed that a (Ga,Mn)N film with low Mn concentration is a ferromagnetic single-phase solid solution without secondary phases or clusters, suggesting the possibility of applying for spintronic devices.

The Mn-doped GaN films were grown by PEMBE system under ultrahigh vacuum conditions (UHV) with a base pressure of $\sim 2 \times 10^{-10}$ Torr. High-purity Mn metal (5N5) was used as a source material. As a nitrogen source, high-purity (6N) nitrogen gas was supplied through an rf plasma source. For the epitaxial growth, MOCVD-grown 2 μm-thick GaN templates on sapphire (0001) [12] were prepared as substrates prior to the deposition of the Mn-doped GaN layers. The (Ga,Mn)N films were grown at various Mn-cell temperatures ranging from 600–700 °C and at a fixed Ga-cell temperature of 1000 °C. All the films were grown using plasma power of 350 W at 700 °C. The Mn profiles were found to be uniform for the films throughout the entire thickness in the range 0.7–1.0 μm with no appreciable segregation by secondary ion mass spectroscopy (SIMS). The homogeneous distribution of Mn in the film was also confirmed by electron probe microanalysis (EPMA). The van der Pauw Hall and MR measurements were performed by applying a magnetic field up to 9 T in the temperature range 4–300 K. Hysteresis loops were measured at temperatures ranging from 4–300 K using a superconducting quantum interference device (SQUID) and a high-sensitivity (10^{-8} emu) alternating gradient magnetometer (AGM). In the present work, Mn concentration was estimated from calculations using the total magnetic moment, provided each Mn atom has the theoretical magnetic moment of 3 μ_B [7], since quantitative determination is difficult due to very low Mn concentration ($x = 0.06$–0.5%).

The cross-sectional TEM micrograph for the ($Ga_{1-x}Mn_x$)N with $x = 0.2\%$/GaN (MOCVD)/sapphire (0001) is shown in Fig. 1(a). A number of threading dislocations are seen to initiate at the interface between the substrate and MOCVD GaN buffer layer. The dislocations extend up toward the (Ga,Mn)N layer, and develop to accommodate the large lattice mismatch of 16% with the sapphire substrate. It is observed that the electron diffraction pattern for the (Ga,Mn)N differs from that for the MOCVD-grown GaN as seen in the insets of Fig. 1(a). As reported in previous TEM studies [9], the additional diffraction spots were found in the zone axis of $B = [01-10]$ for the (Ga,Mn)N, due to a single twin orientation in the closed packed hexagonal matrix, implying a substitutional solid solution (Ga,Mn)N structure.

Further direct evidence is shown in Fig. 1(b), exhibiting

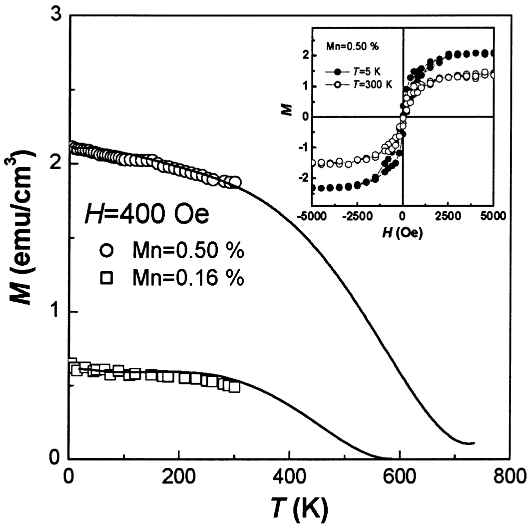

Fig. 3. Temperature dependence of magnetization for the (Ga,Mn)N films with $x = 0.16$ and 0.5%, respectively, obtained by SQUID magnetometry with a magnetic field of 400 Oe. The inset presents M–H loops for (Ga,Mn)N film $x = 0.5\%$, measured at 5 and 300 K.

the lattice parameters a for the (Ga,Mn)N, the MOCVD-grown GaN, a Mn-undoped GaN and a reference sample,[1] obtained from high-order Laue zone (HOLZ) measurements [13]. The average value of the ratio for the reference sample is 0.570, corresponding to $a = 3.1884$ Å. For the MOCVD-grown GaN, the lattice parameter is calculated to be $a = 3.1854$ Å, due to the lattice mismatch (16%) with the sapphire substrate. By contrast, the lattice parameter for the (Ga,Mn)N is found to be $a = 3.1865$ Å, lager than that for the MOCVD-grown GaN, reflecting the expansion of a due to Mn ions substitution for Ga ions in the (Ga,Mn)N structure. It is also found that the lattice parameter for a Mn-undoped GaN grown on the MOCVD GaN is very close to that for the MOCVD GaN. The further detail is given elsewhere [13].

The magnetic behavior for the (Ga,Mn)N films has been studied as a function of Mn cell temperature. In Fig. 2, shown are representative hysteresis loops for the $(Ga_{1-x}Mn_x)N$ films with very low Mn concentration ($x = 0.06$–0.50%) obtained with magnetic fields applied parallel to the plane of the films at room temperature by AGM. Obviously, the hysteresis loops are indicative of ferromagnetic ordering at room temperature for all the samples with Mn concentration in the range 0.06–0.5%. A clear Mn cell temperature dependence of magnetic behavior was found for the (Ga,Mn)N films grown with cell temperatures of (a) 630 °C, (b) 650 °C, and (c) 670 °C, illustrating that saturation magnetization (M_s) increases with increasing Mn cell temperature or higher Mn incorporation in the films.

[1] The 200 μm-thick GaN film as a reference were grown on the sapphire substrate by hydride vapor phase epitaxy and were liberated from the substrate to exclude the lattice mismatch strain.

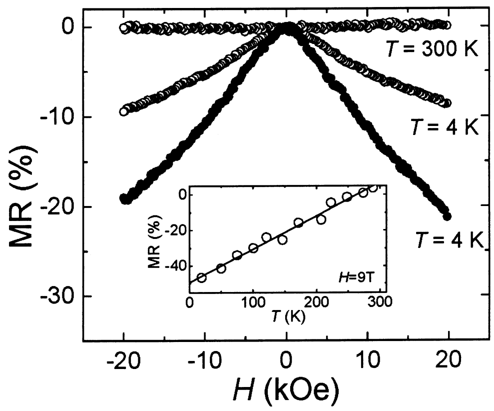

Fig. 4. Sheet MR ($\Delta R/R$) against magnetic fields applied perpendicular to the sample plane for the (Ga,Mn)N films with $T_{Mn} = 600$ °C (open circle) and $T_{Mn} = 650$ °C (closed circle). The inset shows the variation of MR with temperature for the (Ga,Mn)N film with $T_{Mn} = 600$ °C, obtained with a magnetic field of 9 T.

In particular, the (Ga,Mn)N film with $T_{Mn} = 670$ °C exhibits $M_s = 1.9$ emu/cm^3, which is comparable with that ($M_s = 3.2$ emu/cm^3) for (Ga,Mn)N film with $x = 6\%$ grown by MBE using ammonia [10]. More importantly, the (Ga,Mn)N film with $T_{Mn} = 670$ °C shows a coercivity of $H_c = 69$ Oe, as seen in the inset of Fig. 2. Clearly, the (Ga,Mn)N film does not exhibit a superparamagnetic behavior due to nano-clusters [11,14] as a secondary phase, e.g. MnSb nano-clusters in (Ga,Mn)Sb, giving rise to no hysteresis [14]. Again, our results demonstrate that the (Ga,Mn)N films are single-phase solid solutions without appreciable nano-clusters, showing ferromagnetic ordering at room temperature.

Temperature dependence of magnetization for the (Ga,Mn)N films with $x = 0.16$ and 0.50%, respectively, is shown in Fig. 3. Ferromagnetic ordering for both the films is clearly seen in the temperature range 4–300 K, contrasting to antiferromagnetic behavior for (Ga,Mn)N films with 5% Mn in previous work [11]. The M–T curves were fitted with theoretical equations based on the mean field theory [15] in order to estimate Curie temperature (T_c), providing $T_c \approx 550$ and 700 K, respectively, for the (Ga,Mn)N films with $x = 0.16$ and 0.50%. In the inset of Fig. 3, the M–H loops are shown for (Ga,Mn)N film $x = 0.50\%$, measured by SQUID magnetometry at 5 and 300 K, showing ferromagnetic ordering for both the temperature.

All the films were found to show n-type characteristics ($n \approx 10^{16}$–10^{17} cm^{-3}, $\mu_H \approx 10^3$ cm^2/Vs, $\rho \approx 0.2$ Ω cm). Although the electron concentration in the (Ga,Mn)N films is as low as in the range 10^{16}–10^{17} cm^{-3}, our results supports that the ferromagnetic ordering in the (Ga,Mn)N is due to the coupling of electron spins and localized Mn moments, as theoretically predicted in the low carrier density regime [16].

Fig. 4 shows the variation of MR ($\Delta R/R$) against magnetic fields applied perpendicular to the sample plane for the (Ga,Mn)N films with $T_{Mn} = 600$ and 650 °C. The variation of MR with magnetic fields for both the films is hardly seen at room temperature, whereas the negative MR are remarkable at 4 K, reaching ~10, and 20%, respectively. The negative MR ratios are much higher than that ($\Delta R/R = 2.3\%$ at 10 K with 7 T) for (Ga,Mn)N film with Mn = 7% in previous work [17]. The negative MR gradually increases with decreasing temperature in the temperature range 4–300 K as seen in the inset of Fig. 4, in contrast to previous work [17], in which negative MR was observed below 75 K only. Such negative MR has been found in (Ga,Mn)As [18] and (Ga,Mn)Sb [14]. The origin of the negative MR in (Ga,Mn)As [18] is believed to be either the formation of magnetic polaron consisting of a hole carrier and a cloud of Mn spins or the Zeeman shift of the Fermi energy, related to metal–insulator boundary depending on Mn concentration. It should be noted that for the (Ga,Mn)N film with $T_{Mn} = 600$ °C, no humps indicating T_c [9] were found in the R_{sheet}–T curves in the temperature range 4–300 K and that the temperature dependence of R_{sheet} is similar to that for undoped semiconducting GaN [9].

In summary, we have investigated the crystal structures, magnetic and magnetotransport properties in epitaxial (Ga,Mn)N films with low Mn concentration, showing electron induced ferromagnetic ordering with Curie temperature in the range 550–700 K. TEM. Magnetic studies confirmed that (Ga,Mn)N is a single-phase substitutional solid solution without secondary phases or clusters. The temperature dependence of sheet resistance shows negative MR in the temperature range 4–300 K, indicative of ferromagnetic semiconducting (Ga,Mn)N films.

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