Role of hydrogen in room temperature ferromagnetism of GaMnN films

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Abstract
X-ray photoemission of the valence band and Mn 3s of hydrogenated/dehydrogenated GaMnN films and as-grown ferromagnetic GaMnN films is investigated. The Fermi level is shifted upward by the hydrogenation. Larger energy splitting in Mn 3s peaks after the hydrogenation indicates that Mn ions obtain additional electrons in 3d states. The ferromagnetism of the hydrogenated film disappears after dehydrogenation. As-grown ferromagnetic films contain 10^{21} cm^{-3} hydrogen. We conclude that hydrogen is responsible for the ferromagnetism of GaMnN films.

(Some figures in this article are in colour only in the electronic version)

Recently, considerable efforts have been devoted to realizing semiconductors with carrier-induced ferromagnetism and Curie temperatures (T_C) exceeding room temperature (RT) because of their potential for spintronic applications. Among the materials predicted to have RT ferromagnetism, the GaN-based ferromagnetic (FM) semiconductor is one of the most attractive materials: using GaN, blue LEDs and LDs have already been commercialized, and high-power and high-temperature field-effect transistors have been achieved and rapidly improved.

Since the first report on FM Mn-doped GaN (GaMnN) films with the highest T_C of 940 K [1–6], the authors have reported thermally activated conductivity [3], mixed valence (2+ and 3+) of Mn [7] and vanishing ferromagnetism at low temperatures, where resistivity shows a steep increase with decreasing temperature [7, 8]. These results imply that the ferromagnetism is induced by carrier conduction in an impurity band formed by mainly Mn 3d states in the mid-gap of GaN: the additional 3d electron in the band mediates FM coupling when Mn^{2+} and Mn^{3+} coexist. This is consistent with the model suggested by Kronik *et al* [9]. In the previous paper [7], we mentioned that interstitial hydrogen (H) from NH_3, which is the nitrogen source for growth by molecular beam epitaxy (MBE), is one of the candidates for the formation of Mn^{2+}. Based on this hypothesis, we attempted to grow paramagnetic (PM) GaMnN films by applying relatively high substrate temperatures during the growth to avoid residual interstitial H. Actually, the grown films show paramagnetism at RT, and the H concentration is as low as the detection limit ($1 \times$

10^{19} cm^{-3}) of secondary ion mass spectroscopy (SIMS). In the films, Mn^{3+} is predominant [10]. Subsequent to this successful growth of PM GaMnN films, the PM–FM transition of GaMnN films was attempted and realized by hydrogenation with atomic H exposure resulting in $\sim 10^{21}$ cm^{-3} H incorporation. It was confirmed by Mn $L_{2,3}$-x-ray absorption spectroscopy (XAS) measurements that the majority of the Mn valence is 2+ in the hydrogenated films [10].

Regarding the interaction between magnetism and carriers in GaMnN, it has also been reported that charge transfer across adjacent layers in $Ga_{1-x}Mn_xN$/p–GaN:Mg and $Ga_{1-x}Mn_xN$/n–GaN:Si heterostructures changes their ferromagnetic properties [11]. Freeman *et al* reported bulk-incorporated Mn in a hybridized d^4–d^5 configuration, which is weakly ferromagnetically coupled due to a filling of the Mn^{3+}–Mn^{2+} impurity band by surface donors [12].

As described, there has been a gradual accumulation of data that support carrier-induced ferromagnetism in GaMnN, however, no result has ever been reported on the direct observation of the behavior of the Fermi level, which is expected to shift when the magnetic properties are changed in the carrier-induced ferromagnetic system. For example, when electrons are added to Mn 3d states forming an impurity band in mid-gap of GaN, the Fermi level (E_F) is expected to be slightly shifted upward. The primary purpose of this study was to investigate the change of E_F accompanying the magnetic state transition.

At this moment, the mechanism of the PM–FM transition is not completely understood, but it can at least be stated

that it is not attributable to the segregated phase since the local crystallographic structure around Mn clearly is not changed [10]. In this case, two possible ways of creating Mn^{2+} ions for the PM–FM transition remain: one possibility is that the treatment introduces nitrogen vacancies (V_N) in the film, which can supply electrons to Mn ions. Larson and Satpathy have reported the effect of V_N on magnetism in GaN:Mn from first principles [13]. The band structure of $Ga_{15}MnN_{15}V_N$ is quite different from $Ga_{15}MnN_{16}$, especially in the shape of Mn d partial density of states (pDOS): with V_N, the Mn d pDOS are spread over the band gap of GaN, while the Mn d pDOS of $Ga_{15}MnN_{16}$ clusters in the middle of the band gap of GaN. We have observed the multiplet splitting of Mn L-edge XAS spectra with rich structures in our GaMnN films, which are typical for localized 3d states surrounded by four nitrogen ions [7, 10]. We also have found an optical absorption peak at around 1.5 eV in the as-grown FM GaMnN. These observations are inconsistent with the calculated band structure of $Ga_{15}MnN_{15}V_N$ [7].

Another possibility for creating Mn^{2+} is that the introduced interstitial H itself gives an additional electron to the Mn ion. There is no report of the band structure of GaMnN with interstitial H, and we are is not able to validate this possibility only through the XAS study. If this were the case, however, an inverted transition, that is, FM–PM transition, would be expected to occur upon dehydrogenation. Another purpose of this study was to examine the effect of dehydrogenation on ferromagnetism. In this paper, we report the results of x-ray photoemission spectroscopy (XPS) near the valence band maximum (VBM) region and of magnetization measurements at RT for hydrogenated/dehydrogenated films and as-grown FM films.

Wurtzite GaMnN films were grown by MBE using NH_3 as the nitrogen source without cracking as described elsewhere [1–8]. To introduce H into the films, mild hydrogenation treatment with atomic H was applied [10]. As references, n-GaN:Si (electron concentration: 2×10^{18} cm^{-3}) and p-GaN:Mg (hole concentration: 3×10^{17} cm^{-3}) films having wurtzite structure grown by metal–organic chemical vapor deposition were exposed to H under the same conditions as in the case of the GaMnN films. For dehydrogenation, the GaMnN films were annealed in N_2 atmosphere at 550 °C for 5 min. It was confirmed that the crystal structure retains the wurtzite structure by x-ray diffraction and reflection high-energy electron diffraction analyses. XPS was performed on a Shimadzu KRATOS AXIS-165 using monochromatic Al Kα ($h\nu = 1486.6$ eV). The spectra were referenced to the C 1s photoelectron line (284.6 eV). The distributions of H were monitored by SIMS (ULVAC PHI, ADEPT-1010). Magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer. Magnetic field dependences of the magnetization (M–H curve) of the samples were in the field parallel to the film. All the measurements were made at RT.

The valence band XPS spectra of n-GaN, p-GaN, and H-exposed p-GaN films are shown in figure 1. All the GaN films have two peaks (peak 1 and peak 2) with about 4.4 eV energy
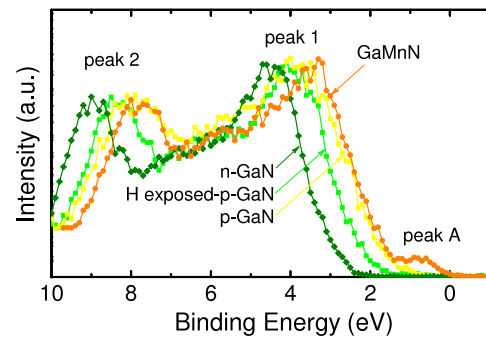

Figure 1. The valence band photoemission spectra of n-GaN, p-GaN, H-exposed p-GaN and as-grown FM GaMnN (Mn: 8.2%). These spectra were normalized against the intensities of peak 2.

separations, which agree with the spectrum of wurtzite GaN reported by Lambrecht *et al* [14]. As expected, the VBM of p-GaN was lower than that of n-GaN in the binding energy. It should be noted that the VBM of H-exposed p-GaN appears at a higher binding energy, indicating the rise of E_F upon hydrogenation as a result of the passivation of acceptors [15].

A spectrum of the as-grown FM GaMnN (Mn: 8.2%) is shown in figure 1. Two main observations are that (1) the VBM of GaMnN is close to that of p-GaN, and that (2) only GaMnN has peak A just above the VBM. The observation of (1) means that the E_F is shifted downward by Mn doping, the same as in the case of Mg doping. Observation (2) indicates that new states are formed within the band gap of GaN upon Mn doping. These findings agree with the results reported by Hwang *et al* [16]. They explained that the new states above the VBM are the acceptor levels occupied by compensating electrons, because acceptor levels which formed above the VBM would remain empty and hence would not be observed in the spectra. Actually, most of the Mn atoms in their $Ga_{1-x}Mn_xN$ samples appeared to be in the d^5 state, as determined by the analysis of M $L_{2,3}$-XAS spectra. In our samples, however, the observed new states are considered to be a result of forming Mn 3d impurity levels in the band gap of GaN, since similar states are observed in the spectra for both as-grown PM GaMnN films with most of the Mn in the d^4 state and H-exposed GaMnN films with Mn in the d^5 state, as shown in figure 2(a). Assuming the compensated acceptor level model by Hwang *et al* [16], the new states within the band gap would not be observed in the spectrum of GaMnN with Mn in the d^4 state. As for E_F, H-exposed GaMnN has a slightly higher binging energy than as-grown film does, meaning E_F is shifted upward by hydrogenation accompanied by PM–FM transition.

In this study, we monitored the exchange splitting of the Mn 3s core level peaks, as it is thought to be a direct indicator of the Mn valence [17]. Figure 2(b) shows Mn 3s XPS spectra of as-grown PM film and H-exposed FM film. The exchange splitting of the Mn 3s spectra of H-exposed GaMnN is 0.7 eV larger than that of the as-grown film, indicating that the formal valency of Mn decreases after H exposure. At this moment, the quantitative analysis of the Mn valency is impossible in GaMnN because of the lack of information. Qualitatively, however, it can be stated that Mn ions obtain
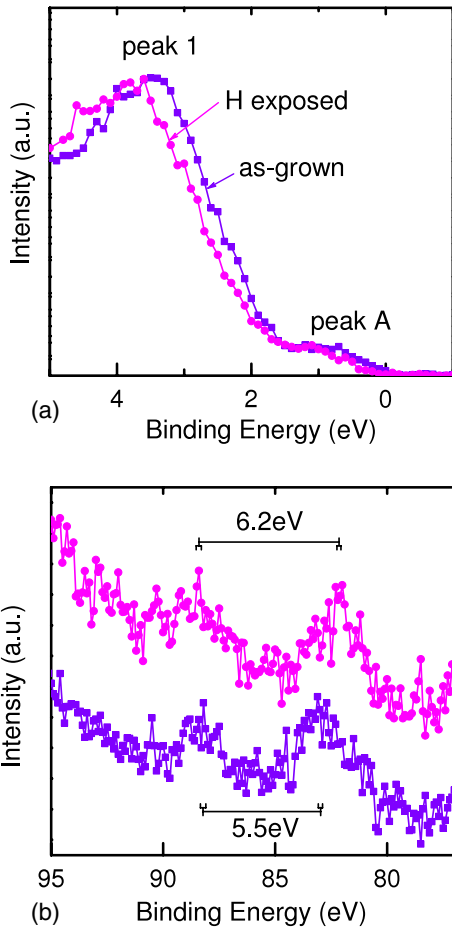
Figure 2. (a) The valence band photoemission spectra of as-grown PM and H-exposed FM GaMnN (Mn: 6.0%) films. (b) The Mn 3s photoemission spectra of as-grown PM (upper) and H-exposed FM (lower) films.

Figure 3. (a) H depth profiles and (b) magnetic field dependence of magnetization ($M-H$ curves) of as-grown, H-exposed and annealed H-exposed GaMnN (Mn: 6.0%) films at room temperature.

Figure 4. H depth profiles of as-grown FM GaMnN films with 5.7% and 6.8% of Mn.

additional electrons via H exposure. In the case of the Mn oxide, a change from 5.5 to 6.2 eV corresponds to a change from Mn^{3+} to almost Mn^{2+} [17]. From these results, we can conclude that the increase in Mn 3s splitting energy is due to addition of electrons to Mn^{3+} ions leading to a shift of E_F upward.

Next, we show the effects of dehydrogenation on the magnetic properties. Magnetization curves and H depth profiles are shown in figures 3(a) and (b), respectively. It is obvious that the H concentration increases in the near-surface region after hydrogenation [10]. The film after hydrogenation shows an obvious hysteresis loop [10]. Upon annealing the hydrogenated film, the H concentration drastically decreases to almost the same level as that of the as-grown film. This dehydrogenation brings about the FM–PM transition, as shown in figure 3(b). This reversible magnetic state transition leads to a conclusion that the magnetic state transition is attributed to interstitial H.

Lastly, we show the H depth profiles of as-grown FM films in figure 4. It is found that the as-grown FM films contain 10^{21} cm^{-3} H in the near-surface region, and the H concentrations decrease with depth, similar to the hydrogenation films. This result implies that the
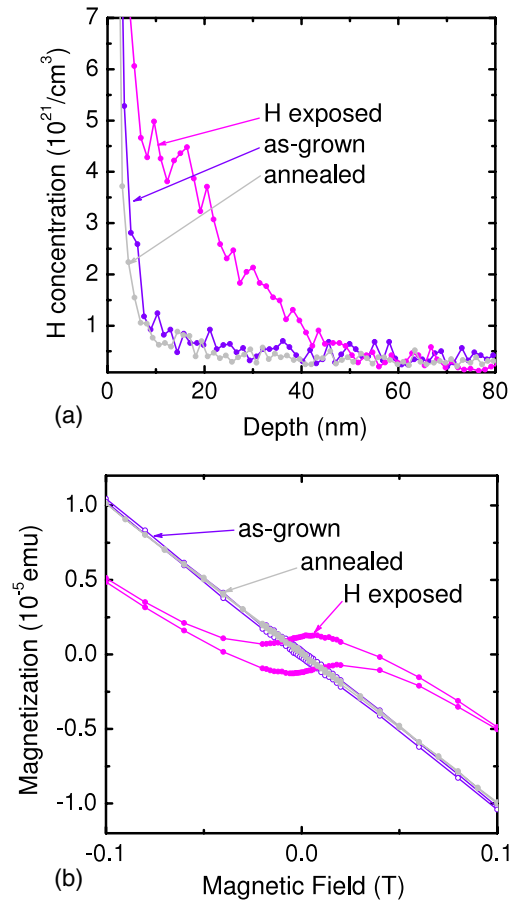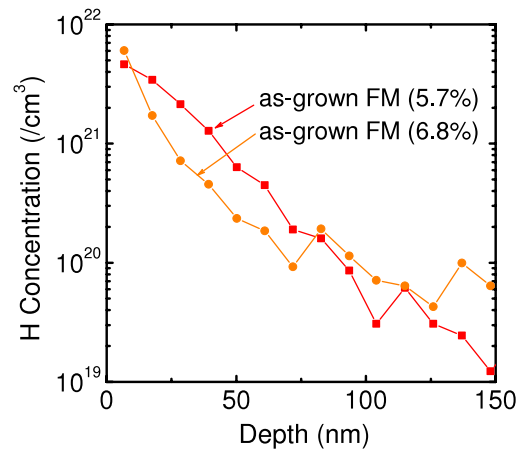
ferromagnetism of the as-grown films is attributable to the high concentration of residual H, the same as that of the hydrogenated FM films. An additional remark that should be made here concerns the inhomogeneity of H. This means the inhomogeneity of the magnetic property; in other words, the FM films are *not perfect single ferromagnets*.

In this work, the observed new states in the mid-gap of GaN in all GaMnN films and the larger energy splitting

of Mn 3s after hydrogenation demonstrate that (1) doped Mn forms impurity bands in the band and (2) H supplies electrons to the Mn 3d band, which cause E_F to shift upward and Mn^{2+} creation. These findings suggest that the PM–FM magnetic state transition can be attributed to the impurity band conduction where the added electrons mediate the FM coupling between Mn atoms. The observed FM–PM transition upon dehydrogenation provides evidence that the incorporated H itself supplies additional electrons to Mn^{3+}. This model is strongly supported by the observation of a high concentration (10^{21} cm^{-3}) of H in as-grown FM films.

On the basis of this impurity band conduction model, it is conceivable that there are contradictions in the electric conduction of the FM samples reported by other groups: p-type and/or n-type are observed for GaMnN films [18–21]. For the material with impurity band (hopping) conduction, it is very difficult to judge the conduction type from only Hall measurements under the assumption of the classic Lorentz force arc as the path of charged particles. Frequently it is also argued that the wide variation in reported T_c would be evidence of the existence of dopant clustering or secondary FM phase [22]. These arguments require a reexamination: the magnetism of GaMnN depends both on concentrations of Mn and donor that can give additional electrons to Mn^{3+}.

Acknowledgments

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