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Coexistence of Mn²⁺ and Mn³⁺ in ferromagnetic GaMnN

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Abstract

Considerable efforts have been devoted recently to synthesizing diluted magnetic semiconductors having ferromagnetic properties at room temperature because of their technological impacts for spintronic devices. In 2001 successful growth of GaMnN films showing room temperature ferromagnetism and p-type conductivity was reported. The estimated Curie temperature was 940 K at 5.7% of Mn, which is the highest among diluted magnetic semiconductors ever reported. However, the electronic mechanism behind the ferromagnetic behaviour has still been controversial. Here we show experimental evidence using ferromagnetic samples that Mn atoms are substitutionally dissolved into the GaN lattice and they exhibit mixed valences of +2 (majority) and +3. The p-type carrier density decreases significantly at very low temperatures. At the same time, magnetization dramatically decreases. The results imply that the ferromagnetic coupling between Mn atoms is mediated by holes in the mid-gap Mn band.

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1. Introduction

Fundamental knowledge on the electronic structure of transition metal elements in host semiconductors is essential for design and development of new spintronic devices. The ferromagnetic III–V diluted magnetic semiconductor (DMS) was first recognized in InMnAs and GaMnAs [1–3]. The mean-field Zener model has been adopted to explain the ferromagnetism in these systems [4]. Based on the model, room temperature ferromagnetism in GaMnN and ZnMnO has been predicted [4]. After the discovery of GaMnN with an extremely high Curie temperature, T_C [5, 6], the mechanism of ferromagnetism in GaMnN has been discussed from a comparative view with GaMnAs [7–9]. Dietl *et al* [10] proposed that the high temperature ferromagnetism in GaMnN can be explained within their mean-field Zener model, similar to the case of GaMnAs. This model is based on the idea that the Mn^{3+}/Mn^{2+} level is located within or near the valence band and holes are thereby introduced. Mn should be in the charge state of Mn^{2+} . The experimental result by Mn K NEXAFS (near edge x-ray absorption fine structure) [11] was taken as evidence for Mn^{2+} in GaMnN. Mn-L_{2,3} NEXAFS of GaMnN [12] seems to support the presence of Mn^{2+} . On the other hand, first principles calculations have predicted that the local electronic structure of Mn in GaN significantly differs from Mn in GaAs [11, 13, 14]. A deep Mn^{3+}/Mn^{2+} level appears in the bandgap in GaN, while the Mn^{3+}/Mn^{2+} state in GaAs is shallow, making a significant overlap between Mn 3d and As 4p valence states. However, a recent first principles study failed to predict high temperature ferromagnetism in GaMnN [14].

A typical argument for the unexplained ferromagnetism has been formation of ferromagnetic clusters or segregations. Rao and Jena [15] proposed that the formation of Mn_xN type clusters brings about the ferromagnetism through first principles calculations. More recent calculations, however, suggested that such clustering decreases the T_C [16]. It is true that Pearton *et al* [17] reported that Ga_xMn_y type crystalline secondary phases having T_C exceeding room temperature were found by x-ray diffraction (XRD) in GaMnN film (5% Mn) when grown under ‘unoptimized’ conditions. However, the formation of such clusters has never been verified by XRD in our ferromagnetic samples. The presence of nano-scale ferromagnetic inclusions cannot be ruled out only by the XRD result. In the present study, we adopt x-ray absorption spectroscopy to identify the physical and chemical states of Mn atoms.

2. Results and discussion

The GaMnN films in the present study were grown by molecular beam epitaxy using NH_3 as nitrogen source. The procedure is the same as those reported in earlier papers [5, 18]. Here we report results for thicker films such as 1 μm and higher Mn concentrations up to 8.2 at.% as determined by electron probe microanalyser (EPMA). The XRD shown in figure 1(a) does not exhibit any crystalline secondary phases even in the 8.2 at.% Mn film.

The yellowish film 1 μm in thickness remains transparent as can be seen in the photograph in figure 1(b). The optical absorption spectrum obtained at room temperature is also shown in figure 1(b). Corresponding to its yellowish colour, an absorption peak was observed at around 1.5 eV followed by a broad absorption started at around 1.8 eV. The spectrum is similar to those reported by Graf *et al* [19] on a GaN:Mn film with 0.23% Mn, and that by Wolos *et al* [20] on a GaN:Mn + Mg bulk crystal with 0.009% Mn. The peak at around 1.5 eV was found to be absent in Si-codoped GaN:Mn in which Si atoms were expected to act as electron donors [19]. The 1.5 eV peak is a signature of the presence of Mn^{3+} , since Mn^{2+} with a half filled 3d level does not contribute to spin-allowed d–d absorption in this energy range.

NEXAFS provides element-specific information of local environment of atoms. Samples for NEXAFS need not be bulk crystals. Nano-crystalline or amorphous materials can also

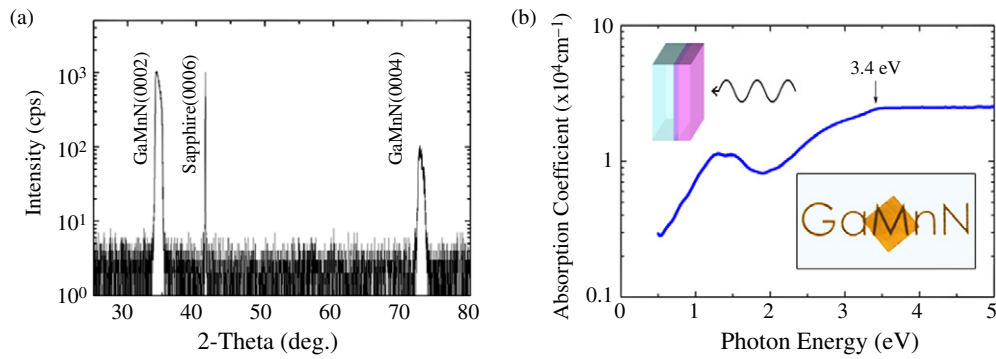


Figure 1. (a) XRD patterns of the GaMnN film (Mn 8.2%) (θ - 2θ scan) and (b) optical absorption spectrum of the GaMnN (Mn 8.2%) with a photograph of the present GaMnN film. Although the film is as thick as $1\ \mu\text{m}$, letters below the film can be read because of its good transparency.

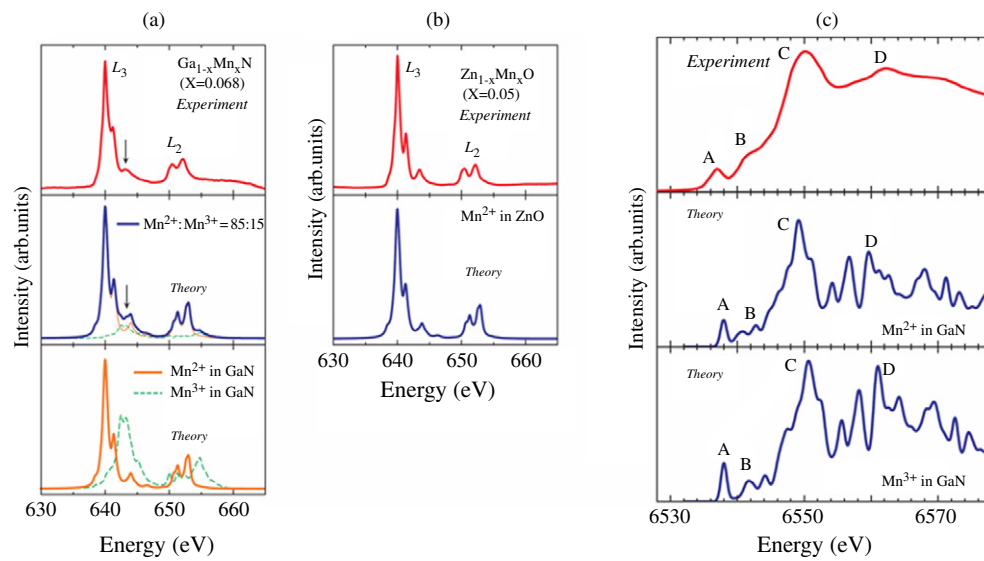


Figure 2. (a) Mn $L_{2,3}$ -NEXAFS of GaMnN (Mn 6.8%). The top panel shows an experimental spectrum. The bottom one presents calculated spectra for Mn^{2+} (orange) and Mn^{3+} (green) using the first principles multi-electron method. The middle one is composed of 15% of Mn^{3+} and 85% of Mn^{2+} calculated spectra, which shows the best agreement to the experimental spectrum. (b) Mn $L_{2,3}$ -NEXAFS of ZnMnO with 5% Mn. (c) Mn K-NEXAFS of GaMnN. The lower two panels are the calculated spectrum for Mn^{2+} and Mn^{3+} in GaN using the FLAPW + l_0 method [24] and the upper panel is the experimental spectrum.

be examined. In the present study, we made a series of NEXAFS experiments on our ferromagnetic samples and analysed the results with the aid of first principles calculations. Mn- $L_{2,3}$ NEXAFS of the films were measured at ALS (Advanced Light Source, Berkeley) BL8.0.1 with the total electron yield method at room temperature. The shape of the spectrum is found to be independent of the Mn concentration. A typical spectrum shown in figure 2(a) is the same as that reported by Edmonds *et al* [12] for GaMnN with 3% Mn. However, no detailed information on the properties of their sample was available. No interpretation of the spectrum was provided, either, except that the valence state of Mn is +2, based on fingerprints of some

Mn compounds. In the present study, we use a novel first principles multi-electron method to calculate the Mn- $L_{2,3}$ NEXAFS. Because of the strong correlation between 3d electrons and a 2p core hole, the spectrum shows clear multiplet structures that cannot be reproduced by a simple one-electron calculation. In the present study, we firstly optimized atomic positions by a plane-wave pseudopotential method [21] using supercells of $(\text{Ga}_{35}\text{Mn}_1\text{N}_{36})$. Then the multi-electron calculations were made employing all configuration interactions among Mn 3d and N 2p electrons together with Mn 2p core electrons using MnN_4^{9-} and MnN_4^{10-} models, that correspond to Mn^{3+} and Mn^{2+} , respectively. Details of the multi-electron method can be found elsewhere [22]. Comparison of theoretical spectra with experimental ones shows that the majority of Mn atoms are substitutionally dissolved into GaN as Mn^{2+} . Similar comparison has been made for Mn- $L_{2,3}$ NEXAFS of ZnMnO with 5% Mn, that shows no ferromagnetism at room temperature. The ZnMnO sample was made by the pulsed laser deposition process. Details of the preparation procedure can be found in [23]. Excellent agreement between experimental and theoretical spectra with Mn^{2+} can be seen in ZnMnO. A small but clear difference between experimental spectra of ZnMnO and GaMnN is recognized at the small satellite peak as indicated by arrows in figure 2(a). This can be ascribed to the presence of the Mn^{3+} component only in GaMnN. Indeed, the experimental spectrum of GaMnN is better reproduced when 15% of Mn atoms are assumed to be in the 3+ state. The difference between magnetic properties of ZnMnO and GaMnN can be ascribed to the presence of the Mn^{3+} component. On the basis of two spectroscopic results, we can conclude that Mn^{2+} and Mn^{3+} are coexistent in the present GaMnN sample with Mn^{2+} as a major component.

The Mn K NEXAFS of the film was also measured and compared with theoretical calculations (figure 2(c)) [24]. It agrees well with those in the literature [11, 25]. However, clear interpretation of the experimental spectrum has not been provided thus far. Main conclusions by the Mn K NEXAFS are twofold.

- (1) Excellent agreement between theory and experiment shows that Mn atoms are substitutionally present at Ga sites. Signature of other sites of Mn, much as in metallic or clustered Mn, is not evident. Soo *et al* [11] mentioned that peak A may be ascribed to Mn clusters. This assertion can be discounted because peak A is clearly seen in the present theoretical spectrum.
- (2) Although Mn at different hosts shows different fingerprints in general, it is very difficult to distinguish the difference in valence between Mn^{2+} and Mn^{3+} in GaMnN only by the Mn K NEXAFS if they are present at the substitutional sites. Instead, Mn- $L_{2,3}$ NEXAFS can reveal the valence states with the assistance of reliable theoretical calculations.

Both results by optical absorption and $L_{2,3}$ NEXAFS unambiguously show the coexistence of the two valence states in the present GaMnN samples. This implies that the electronic level of $\text{Mn}^{2+}/\text{Mn}^{3+}$ stays in the mid-gap, which is consistent with the results by first principles calculations [13]. The assumption of the mean-field Zener model is therefore not valid in the case of GaMnN.

Figure 3(a) shows the magnetic field dependence of magnetization ($M-H$ curve) of the 6.8 at.% Mn sample measured by superconducting quantum interference device (SQUID) magnetometer at 400 K in the magnetic field parallel and perpendicular to the film plane. As can be seen, the film is ferromagnetic even at 400 K with the easy axis in the plane. The Curie temperature of this sample is 720 K by extrapolating the $M-T$ curve.

In order to find out the origin of ferromagnetism, the temperature dependence of the magnetization has been examined. Firstly, a magnetic field of 1 T was applied parallel to the film at 300 K. At this temperature, this film is fully magnetized with 1 T. After decreasing the applied magnetic field to 0 T, the magnetization of this film was measured while cooling

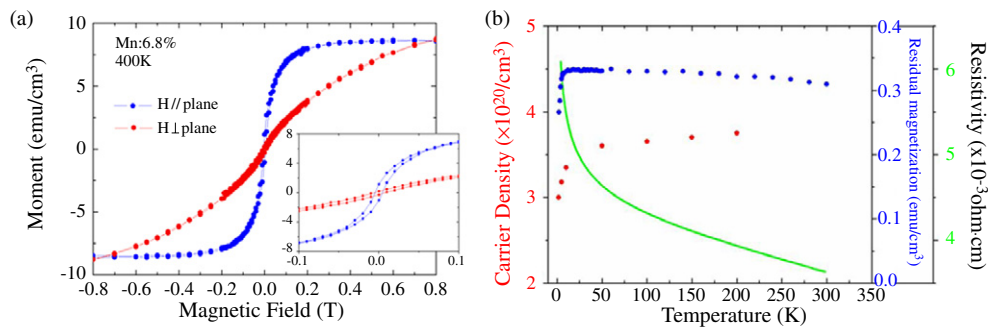


Figure 3. (a) Magnetic field dependence of magnetization ($M-H$ curve) of GaMnN (Mn 6.8%) film at 400 K in the magnetic field parallel and perpendicular to the film. The inset is the magnified $M-H$ curve at around 0 T. (b) Temperature dependences of residual magnetization (M_r-T curve) of the GaMnN film (Mn 6.8%), and its carrier density and electric resistivity.

it without the external magnetic field (blue dots in figure 3(b)). Down to around 10 K, the magnetization remains almost unchanged. But it drops significantly with further decrease of temperature. The magnetization behaviour is almost reversible against temperature. Such a temperature dependence of the residual magnetization in a GaMnN sample is reported for the first time in this study. In parallel to the magnetic measurements, electric transport has been examined. The resistance was measured by the four-terminal method, and the carrier density was evaluated from Hall resistance. The major carrier in these samples is p type. The carrier concentration (red dots in figure 3(b)) is found to decrease remarkably below 10 K. The electric resistivity of the sample as shown by a green curve shows the reciprocal tendency.

The decrease of the residual magnetization in the low temperature region corresponds well to the decrease of the hole density, which clearly implies good correlation between ferromagnetism and mobile holes. It should be emphasized that the weakening of the ferromagnetism at the low temperature and the reversibility of magnetization with temperature cannot be explained by the presence of ferromagnetic clusters such as Mn_xN_y or Ga_xMn_y .

Because Mn^{2+} and Mn^{3+} are coexistent, the Fermi level should be located at the Mn 3d band as in the case of colossal magnetoresistance manganites, not in the valence band. The p-type conductivity in the present sample may take place with d electrons hopping between Mn^{2+} and Mn^{3+} . The ferromagnetic coupling between Mn atoms may be driven by a double exchange that is mediated by the hole in the Mn band. The carrier density of $3.8 \times 10^{20} \text{ cm}^{-3}$ corresponds to about 13% of the total number of Mn atoms in the 6.8 at.% Mn sample. This agrees well with the fraction of Mn^{3+} as assumed for the analysis of the Mn- $L_{2,3}$ NEXAFS. The saturation magnetization is $0.3 \mu_B/\text{Mn}$ when the magnetic field is applied parallel to the film. This corresponds to $2.1 \mu_B$ per hole or Mn^{3+} ion.

The reader may be puzzled by the coexistence of Mn^{2+} and Mn^{3+} in p-type GaMnN materials since the Mn^{2+}/Mn^{3+} level is deep from the top of the valence band. It is true that Mn should have the charge of +3 not merely +2 within this scenario. We have to think of the presence of donor-type defects that contribute to the formation of Mn^{2+} . There are at least two strong candidates for such donors. One is the nitrogen vacancy, V_N . Recent careful first principles calculations have concluded that positive charge states are energetically favourable for V_N irrespective of the Fermi level, indicating that it always acts as a donor or compensates acceptor-type defects [26]. A high energy electron irradiation study of hydride vapour phase epitaxy-grown GaN films has also shown the donor nature of V_N [27]. Another candidate is hydrogen. As in the case of V_N , donor-like behaviour of hydrogen has been suggested by

both experimental and theoretical works [28, 29]. A large amount of hydrogen is known to be incorporated in GaN films grown by MOCVD utilizing NH_3 as nitrogen source and H_2 as carrier gas. In fact, we have observed the existence of 10^{19} cm^{-3} hydrogen in the film with 8.2% of Mn by SIMS (secondary ion mass spectroscopy). Baik *et al* [30] examined the effect of H in GaMnN on the magnetization. They irradiated n-type GaMnN film containing 3% Mn with H plasma and indeed observed the increase of residual magnetization. This behaviour seems to support the mechanism that was recently proposed by Coey *et al* [31], who assumed the presence of long range ferromagnetic coupling via donors associated with the n-type conductivity. However, their theory cannot be used to explain our experimental data, because our samples show clear p-type conductivity rather than n type.

3. Conclusion

The present study has confirmed that the high temperature ferromagnetism of GaMnN is a behaviour intrinsic to Mn ions substitutionally dissolved into GaN. There is no need to think of an external source of ferromagnetism such as precipitates. The coexistence of $\text{Mn}^{2+}/\text{Mn}^{3+}$ resulting in p-type conductivity via d-electron hopping is suggested to play a very important role in the ferromagnetism. The mechanism we propose may be valid for other wide-gap semiconductors doped with transition elements showing mid-gap redox levels and p-type conductivity thereon.

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