Photoemission and X-ray absorption studies of the electronic structure of GaN-based diluted magnetic semiconductors

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We have investigated the electronic structure of Cr- and Mn-doped GaN using photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS). Cr and Mn XAS at the L-edge have indicated that the Cr and Mn ions are in the tetrahedral crystal field and that their valences are trivalent and divalent, respectively. Upon Cr and Mn doping into GaN, new states were found to form in the band-gap region of GaN. Resonant photoemission spectroscopy (RPES) has revealed that the main structure of the Cr 3d partial density of states (PDOS) appears within the band gap of GaN while that of the Mn 3d PDOS appears within the valence band of GaN and as a shoulder above the valence-band maximum of GaN, indicating that the character of the doping-induced states is different between Ga1–xCrxN and Ga1–xMnxN.

1 Introduction

Diluted magnetic semiconductors (DMSs) have recently attracted much interest because of novel functions and potential applications utilizing the combination of magnetism caused by the local spins of transition-metal ions and semiconducting properties of the itinerant carriers of the host materials. In the III–V DMSs such as Ga1–xMnxAs, the ferromagnetism is induced by the hole carriers created by the substitution of the divalent Mn ions for the trivalent cations. This ferromagnetism is therefore called “carrier-induced ferromagnetism”. From the view point of applications, it is required to synthesize DMSs with a Curie temperature (Tc) above the room temperature. So far, the Tc of the III–V DMSs has been mostly below the room temperature. In recent theoretical studies, it has been predicted that the ferromagnetic state is stable in DMSs based on wide-gap semiconductors such as Ga1–xCrxN and Ga1–xMnxN [1, 2] and that ferromagnetism with a very high Tc is realized in p-type Ga1–xMnxN [3]. After the successful Mn doping into GaN [4, 5], several groups have reported the growth of ferromagnetic Ga1–xMnxN [6–10]. However, these results have been quite diverse between different reports and the mechanism of ferromagnetism remains controversial [4, 5, 8, 9]. Cr doping into GaN has also been achieved. Hashimoto et al. has reported that Ga1–xCrxN indicates ferromagnetism with Tc exceeding room temperature [11]. It

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is therefore desirable to characterize the electronic structures of Ga$_{1-x}$Mn$_x$N and Ga$_{1-x}$Cr$_x$N, which is necessary to study the mechanism of the ferromagnetism.

High-energy spectroscopic methods such as photoemission spectroscopy (PES) and soft X-ray absorption spectroscopy (XAS) are powerful techniques to investigate the electronic structure of solids. In the studies of DMSs, too, these techniques have played important roles [12, 13]. In this work, we have investigated the electronic structures of Ga$_{1-x}$Mn$_x$N and Ga$_{1-x}$Cr$_x$N using PES and XAS.

2 Experimental

The PES experiments were performed at BL-18A of Photon Factory, High Energy Accelerator Research Organization (KEK) and BL-23SU of SPring-8. The total energy resolution including the monochromator, the electron analyzer and the temperature broadening was ~200 meV as estimated from the Fermi edge of gold. The photoemission spectra were referenced to the Fermi edge of gold in electrical contact with the sample. Also, the Au 4f$_{7/2}$ core-level binding energy 84.0 eV was used as the reference. All the measurements were made in an ultra-high vacuum below 5 \times 10^{-10} Torr at room temperature. The XAS measurements were performed at the soft X-ray beam line BL-23SU of Spring-8. Absorption spectra were measured by the total electron yield method with the energy resolution $E/\Delta E$ higher than 10000.

Ga$_{1-x}$Mn$_x$N (0001) thin films with $x = 0.042$ were grown by molecular beam epitaxy with an RF-plasma nitrogen source on a sapphire (0001) substrate using elemental sources of Ga and Mn [14]. The sample was paramagnetic from room temperature down to 4 K. Ga$_{1-x}$Cr$_x$N (0001) thin films with $x = 0.015$ were grown by molecular beam epitaxy with an ECR plasma-enhanced nitrogen source on a sapphire (0001) substrate using elemental sources of Ga and Cr [11]. The sample was ferromagnetic with $T_C$ above 400 K.

3 Results and discussion

Figure 1 shows XAS spectra (dashed line) at the Cr $L$-edge and the Mn $L$-edge compared with atomic multiplet calculations including the crystal field (solid curves) [15]. Comparing the experimental line shape with the calculation, one can obtain the information about the valence and the crystal field of Cr.

![Fig. 1 Transition-metal $L_{2,3}$-edge XAS spectra.](image)

(a) XAS Cr $L$-edge Ga$_{0.958}$Cr$_{0.042}$N. Calculations for the d$^4$ and d$^5$ ground state in a tetrahedral crystal field (solid curves) are compared with experimental data (dashed curve). The line shape of the experimental data is close to the calculated spectra assuming the d$^5$ ground state with the crystal field $\sim -0.5$ eV. (b) Mn $L_{2,3}$-edge XAS of Ga$_{0.985}$Mn$_{0.015}$N. Calculations for the d$^3$ and d$^4$ ground state in a tetrahedral crystal field (solid curves) are compared with experimental data (dashed curves). The line shape of the experimental data is close to the calculated spectra assuming the d$^3$ ground state with the crystal field $\sim -1.5$ eV.
Fig. 2 Resonant photoemission spectra. (a) Photoemission spectra of Ga$_{0.985}$Cr$_{0.015}$N for various photon energies around the Cr 2p–3d core excitation threshold. The difference curve at the bottom represents the Cr 3d PDOS. (b) Photoemission spectra of Ga$_{0.958}$Mn$_{0.042}$N for various photon energies around the Mn 3p–3d core excitation threshold. The difference curve at the bottom represents the Mn 3d PDOS. The inset shows the Mn 3p–3d absorption spectra of $x = 0.0$ and $0.042$ recorded by the total electron yield method.

and Mn in GaN. From the Cr L-edge spectra shown in Fig. 1(a), one can see that the calculation assuming the d$^3$ ground state with the crystal field $10Dq \sim -1.5$ eV well reproduces the experimental spectrum. The positive and negative $10Dq$ means a crystal field due to the octahedrally and tetrahedrally coordinated anions, respectively. This indicates Cr in GaN has the valence of $3^+$ in the tetrahedral-crystal field. From the Mn L-edge spectra shown in Fig. 1(b), one can see that the calculation assuming the d$^5$ ground state with the tetrahedral-crystal field $10Dq \sim -0.5$ eV well represents the experimental spectrum. This leads us to conclude that Mn is in the d$^5$ state in the tetrahedral crystal field, namely, the valence of Mn is $2^+$ different from the case of Cr in Ga$_{1-x}$Cr$_x$N. This indicates that in the case of Ga$_{1-x}$Mn$_x$N doped Mn ions are positively ionized in the GaN.

We have also investigated the valence band region using resonant photoemission spectroscopy (RPES) to extract the Cr 3d and Mn 3d partial density of states (PDOS). In RPES, because Cr 2p-to-3d (Mn 3p-to-3d) absorption occurs at photon energies above 576 eV (50 eV), interference between the normal photoemission and 2p-to-3d (3p-to-3d) photoabsorption followed by a 2p–3d–3d (3p–3d–3d) super-Coster–Krönig decay generates a resonance enhancement of the Cr 3d-derived (Mn 3d-derived) photoemission. Figure 2 shows the valence-band spectra taken at various photon energies in the Cr 2p-to-3d and the Mn 3p-to-3d core excitation regions. The intensities have been normalized to the photon flux and the photon energy dependence of the cross section of the N 2p atomic orbital has been considered. All binding energies are referenced to the Fermi level ($E_F$). In Fig. 2(a), in going from $h\nu = 573$ to $576$ eV, one can see that the peak at the binding energy of 2.5 eV grows in intensity. By subtracting the off-resonant spectrum ($h\nu = 573$ eV) from the on-resonant one ($h\nu = 576$ eV), we obtain the Cr 3d derived spectrum as shown in the bottom panel of Fig. 2(a). The difference spectrum representing the Cr 3d PDOS is mainly distributed in the band gap of GaN. The intensity of the Cr 3d PDOS in the band gap is weak at $E_F$ and no clear Fermi edge has been observed.

Figure 2(b) shows the valence-band spectra of Ga$_{1-x}$Mn$_x$N taken at excitation energies in the Mn 3p-to-3d core excitation region. The inset of Fig. 2(b) shows the absorption spectra near the Mn 3p–3d core excitation threshold, indicating that a peak representing the Mn 3p-to-3d absorption appears at 50 eV and grows in intensity. In Fig. 2(b), in going from $h\nu = 47$ to 50 eV, the peak at the binding energy of 5 eV grows in intensity. By subtracting the off-resonant spectrum from the on-resonant spectrum, we obtain the Mn 3d derived spectrum as shown in the bottom panel of Fig. 2(b). The difference spectrum which corresponds to the Mn 3d PDOS reveals a peak at $E_B = 5$ eV and a shoulder at $E_B = 2$ eV well below the $E_F$, suggesting the occurrence of charge compensation. The satellite also appears at $E_B = 9–13$ eV.
For the Cr 3d PDOS, agreement between the experiment and the theoretical calculation within the local density approximation (LSDA) [1], in which the Cr 3d PDOS mainly appeared in the band gap of GaN, is fairly good except for the absence of the Fermi edge in experiment. Because the Cr-induced state in the band gap is mainly composed by Cr 3d, the carriers should have d character. The absence of the Fermi edge imply that the carriers are localized and is consistent with the non-metallic, hopping conduction with the Coulomb gap at the Fermi level reported in Ref. [16]. The ferromagnetic coupling between Cr ions may be driven by the hopping electrons through the double exchange coupling. In order to test this possibility, more detailed study on the electronic structure near the $E_F$ is needed.

For the Mn 3d PDOS, on the other hand, the experimental line shapes of the Mn 3d PDOS are not in accordance with the calculation. In the present experiment, the main structure of the Mn 3d PDOS appears below the valence-band maximum while in the calculation the Mn 3d PDOS appears within the band gap as in the case of the Cr 3d PDOS. We have therefore analyzed the Mn 3d PDOS based on configuration interaction (CI) calculation on the cluster model [17]. In the analysis, it has been revealed that the Mn-induced states should have p character and the p–d exchange constant was estimated as $-1.6$ eV, larger than that of Ga$_{1-x}$Mn$_x$As [12]. Therefore this suggests that if the charge compensation is avoided in some way and a sufficient amount of holes are doped into the system, strong ferromagnetism would be expected in Ga$_{1-x}$Mn$_x$N [18].

In conclusion, we have investigated the electronic structures of Ga$_{1-x}$Cr$_x$N and Ga$_{1-x}$Mn$_x$N using high-energy spectroscopic methods. Comparing the electronic structures between Ga$_{1-x}$Cr$_x$N and Ga$_{1-x}$Mn$_x$N, it has been revealed that the character of the transition-metal-induced states is different between Ga$_{1-x}$Cr$_x$N and Ga$_{1-x}$Mn$_x$N.

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