Materials Science : Electronic & Magnetic Properties

HYBRIDIZATION OF Cr 3*d*-N 2*p*-Ga 4*s* IN THE WIDE-BAND-GAP DILUTED MAGNETIC SEMICONDUCTOR Ga$_{1-x}$Cr$_x$N

Diluted magnetic semiconductors (DMS) have been of much interest because of their potential application to spintronics. In semiconductor spintronics, two degrees of freedom, charge and spin, have been explored to realize novel functionalities in semiconductors [1]. For practical device applications, it is desirable to synthesize materials with high Curie temperatures. Transition-metal-doped group-III nitrides have been considered to be one of the promising candidates for high-temperature ferromagnetic DMS. However, the origin of magnetism in the material system is still controversial. In order to get insight into the mechanism of the magnetism, an electronic structure investigation of GaN-based DMS is necessary.

We report on the electronic structure of Ga$_{1-x}$Cr$_x$N observed by hard X-ray photoemission spectroscopy (HX-PES) at the excitation energy of 5.95 keV to understand a possible origin of the magnetism. Soft X-ray PES is very surface sensitive due to the short mean free paths of electrons at measurable kinetic energies. There is no method of forming an ideal surface after exposure to atmosphere even once. This problem is more critical for the case of epitaxial thin films because surface cleaning procedures are not well established. The photoemission spectra of Ga$_{1-x}$Cr$_x$N in this research are actually bulk sensitive, and also almost free from distortion due to inelastic scattering at high energies [2,3]. Thus, we are able to precisely analyze the difference of the spectra between doped and undoped GaN.

The HX-PES experiments were performed at **BL29XU** and **BL47XU**. The large escape depth at a high energy allow determination of bulk electronic states with high precision owing to the negligibly small contribution from the surface; therefore, no surface cleaning was done. Photoelectrons were collected using a Gammadata Scienta SES2002 electron analyzer, which is modified to accommodate higher photoelectron kinetic energies up to 6 keV.

Figure 1 shows the energy distribution curves (EDC) of undoped GaN and that of Ga$_{0.899}$Cr$_{0.101}$N, and the difference spectrum between them. The origin of binding energy (BE) is set to the valence band maximum (VBM). Cr doping introduces new electronic states in the band gap (**A**) and causes some change in the valence band structure (**B** and **C**). In addition, the intensity of the in-gap state increases in proportion to the Cr concentration (inset in Fig. 1).

Thus, the in-gap states should be related to the doped Cr.

In order to elucidate the origin of the new electronic states, we have calculated the electronic band structure for Cr-doped GaN by the first-principles calculation based on the density functional theory using the generalized gradient approximation. On the basis of the calculation considering the intensity ratio of the atomic subshell photoionization cross sections of Cr 3*d* and Ga 4*s* at the high excitation energy [4], the observed in-gap state is interpreted to originate dominantly from Ga 4*s* states by hybridization with Cr 3*d* [5].

Core level spectra of N 1*s* and Ga 2*p*$_{3/2}$ are also modified by Cr doping. Open circles, solid gray circles, and solid black circles in Fig. 2(a) show N 1*s* core level spectra of undoped GaN, Ga$_{0.937}$Cr$_{0.063}$N, and Ga$_{0.899}$Cr$_{0.101}$N, respectively. Gray and black solid lines are the difference spectra between the undoped
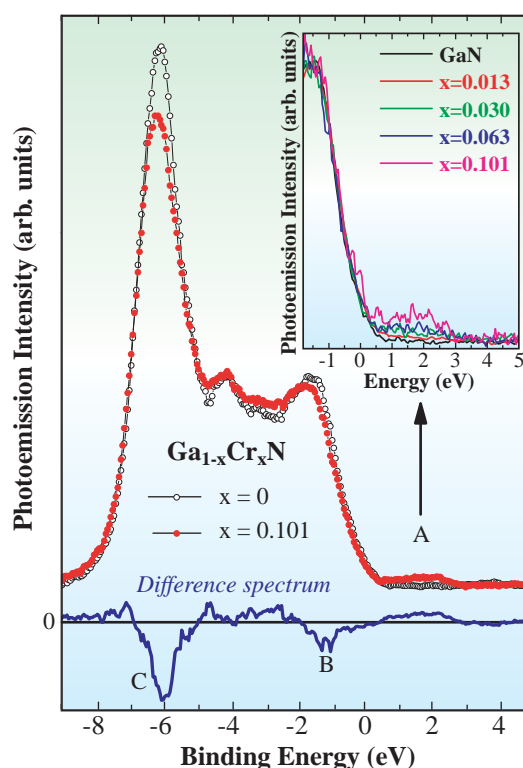

Fig. 1. EDCs for undoped GaN (open circles) and Ga$_{0.899}$Cr$_{0.101}$N (filled circles) at h*ν* = 5.95 keV. These EDCs are obtained by subtracting the trivial background from the experimental spectra. The solid line at the bottom panel shows the difference spectrum. The inset shows the intensity of the in-gap state *versus* Cr concentration.

GaN and $Ga_{1-x}Cr_xN$ (x = 0.063 and 0.101, respectively). The main peak at 394.5 eV decreases and the tail at 393.8 eV increases with Cr doping. The rates of the decrease and the increase are proportional to the Cr concentration. Namely, Cr doping causes a decrease of N 1s in the matrix and introduces a new chemically shifted component at the low BE region. Because the electronegativities (EN) of Ga, Cr, and N atoms are 1.81, 1.56, and 3.07, respectively, the EN difference of the Cr-N bond is larger than that of the Ga-N bond. Therefore, the N atoms bonded with Cr are more shielded by electrons than the N atom bonded with Ga atoms. Accordingly, Cr doping causes a chemical shift of N 1s to the low BE region.

Figure 2(b) shows Ga 2$p_{3/2}$ core level spectra. Gray and black solid lines are the difference spectra between undoped GaN and $Ga_{1-x}Cr_xN$ (x = 0.063 and 0.101, respectively). The intensity of the peak decreases with Cr doping. The decrease of the intensity is almost linearly proportional to the increase of Cr content. The line shape in difference spectra is evidently asymmetric, suggesting the existence of an unresolved chemically shifted component at the low BE side. This is reasonably expected from the EN differences between Ga-Cr and N-Cr. The linear increase of the full width at half maximum (FWHM) with increasing Cr content (inset in Fig. 2(b)) is taken as further evidence of the existence of the increasing chemically shifted component, supporting the Ga-Cr hybridization discussed above.

We have investigated the electronic structure of $Ga_{1-x}Cr_xN$ by bulk-sensitive HX-PES. We have observed for the first time the electronic states in the GaN band-gap region induced by Cr doping. This is the Ga 4s contribution raised by the hybridization with Cr 3d. We have also observed that the Cr doping influences the second neighbor Ga via the formation of Cr-N bonds.
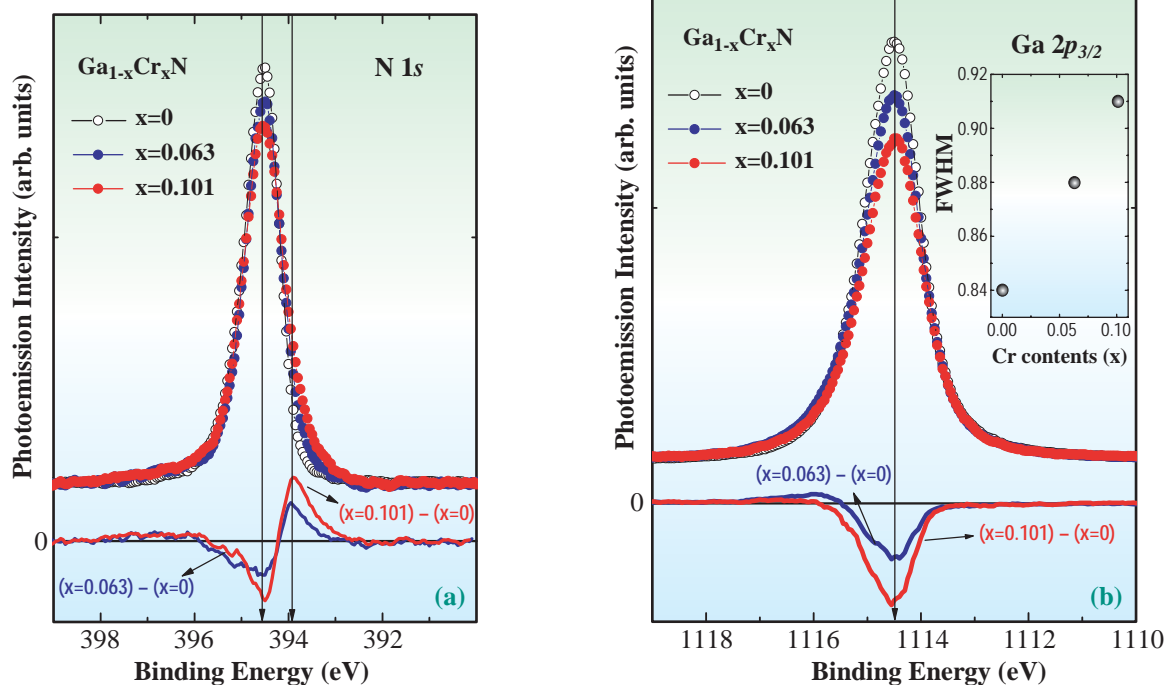

Fig. 2. Core-level photoemission spectra of **(a)** N 1s and **(b)** Ga 2$p_{3/2}$ of undoped GaN (open circles) and $Ga_{1-x}Cr_xN$ (x = 0.063 (solid blue circles), 0.101(solid red circles). The inset on the right in (b) shows the FWHM variation of the Ga 2$p_{3/2}$ spectra with Cr concentration. The more Cr doped, the broader the FWHM of Ga 2$p_{3/2}$ spectra.

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