

## Electronic structure investigation of III-nitrides based dilute magnetic semiconductors by high-energy photoemission spectroscopy

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Transition-metal (TM) doped III-nitrides have been received much attention because the material system is one of promising candidates for novel spintronics device. It is important to study electronic structure near the Fermi level in order to understand their material properties. We have investigated the electronic structure of  $Ga_{1-x}Cr_xN$  ( $x=0.06, 0.1$ ) by hard x-ray photoemission spectroscopy (HX-PES) at BL29XU of SPring-8. It was revealed that Cr  $3d$  orbital strongly hybridized with the second nearest neighbored Ga  $4s$ .  $Ga_{0.987}Cr_{0.015}N$  shows dominant ferromagnetic property, while higher Cr content  $Ga_{1-x}Cr_xN$  ( $x = 0.06, 0.1$ ) shows coexistence of a paramagnetic-like behavior and ferromagnetic one. It can be speculated that the  $Ga_{0.987}Cr_{0.015}N$  may show different electronic structure compared to higher Cr content GaCrN. On the other hand, it is theoretically predicted that TM-doped InN shows ferromagnetism with high Curie temperature. However, the band gap of InN itself changes depending on growth conditions, and origin of the variation is still under discussions. In this study we performed HX-PES on  $Ga_{0.987}Cr_{0.015}N$  and on InN grown by MBE at different growth temperatures.

HX-PES experiment was accomplished at BL47XU. Hard X-rays of 5.95keV was used. The large escape depth at the energy allows bulk sensitive measurements with negligibly small contribution from the surface. Therefore, no specific surface treatment was employed. Photoelectrons were collected by SES2002 electron analyzer, which is modified to accommodate higher photoelectron kinetic energies up to 6keV. Energy resolution was estimated to be 310meV by the Fermi energy ( $E_F$ ) of Au plates.

Figure 1 shows the photoemission spectra

of the valence band of the  $Ga_{0.987}Cr_{0.015}N$  measured at room temperature. Similar to the high Cr content  $Ga_{1-x}Cr_xN$ , one can clearly see the in-gap state caused by the hybridization between Cr  $3d$  and Ga  $4s$ . Based on first principle band calculation, we expected some structures for the in-gap states of the  $Ga_{0.987}Cr_{0.015}N$ . But we couldn't observe it within experimental error.

Figure 2 shows the photoemission spectra of the valence band of the InN grown at different growth temperature. Valence band maximum (VBM) shifts to higher binding energy side with the increase of growth temperature. The tendency is consistent with results of optical absorption. In addition, we observed an energy state across the  $E_F$ . This state extended with the decrease of growth temperature. The shift of VBM seems related to the extension of the state on the  $E_F$ .

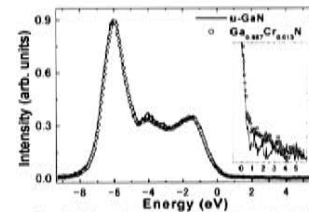


Fig. 1. Valence band photoemission spectra of the undoped GaN and  $Ga_{0.987}Cr_{0.015}N$ .

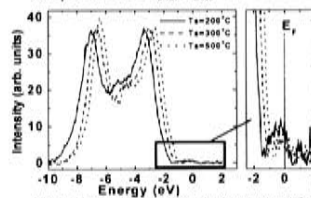


Fig. 2. Valence band photoemission spectra of InN's, which are grown at different growth temperature

## 3D observation of Cu-based monotectic solidification for micro- and nano-porous media

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Porous materials have potential for various practical applications because of their characteristic features. For example, they have large surface area with respect to their volume, permeation of fluids, an ability to hold fluids in their pores, and high strength to weight ratio.

A novel process to fabricate porous media in which deep pores are regularly aligned, has been proposed by our group [1]. The process consists of two parts. The first is the solidification process under a magnetic field to produce an aligned structure in which the minor phase with rod shape is regularly aligned in the matrix phase. The second is the electrochemical dissolution of the minor phase.

3D observation of the rods and the pores is required to evaluate the aligned structure and the electrochemical dissolution. X-ray computerized tomography with a high spatial resolution enables the observation of the aligned structure and the pores fabricated by the electrochemical dissolution. In the previous project of Spring8, Al porous media in which the pores with diameters of 10-20  $\mu m$  are regularly aligned were characterized by the micro X-ray CT.

The X-ray computed micro-tomography was performed at a beam line BL47XU. The format of the transmission X-ray images was 1000x1018 pixels and the effective pixel size was 0.5  $\mu m$  x 0.5  $\mu m$ . X-ray energy was 15 keV and the exposure time for every transmitted image was 1.5s.

Figure 1 shows 3D images of the Cu-15.5at%Pb monotectic alloys which were unidirectionally solidified under a magnetic field of 10T. In the figure, the Cu matrix was removed to observe the Pb rods.

Comparing to the In rods in the Al-In monotectic alloys (previous project), degree of the alignment in the Cu-Pb system was relatively low. As shown in Fig.1(b), the Pb rods were created and they often joined together. Furthermore, no branch of the Pb rod was observed in the growth direction. The result suggested that the Pb liquid phase was pushed by the solidifying Cu phase.

On the basis of the observation, we examined the alloy system to produce the regularly aligned structure. The addition of the Al significantly reduced the frequency in the joining of the Pb rods, resulted in the regular structure. Porous Cu was preliminarily fabricated by the selective dissolution of the Pb phase.

### References

[1] H. Yasuda, I. Ohnaka, S. Fujimoto, A. Sugiyama, Y. Hayashi, M. Yamamoto, A. Tsuchiyama, T. Nakano, K. Uesugi, K. Kishio, Materials Letter, 58(2004) 911-915.

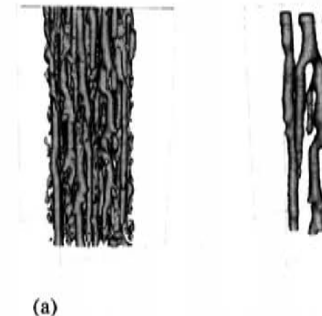


Fig.1 Reconstructed images of the Cu-15.5at%Pb alloy unidirectionally solidified at a magnetic field of 10T. Size: (a) 250x250x400  $\mu m^3$ , (b) 100x100x250  $\mu m^3$  Growth direction: from bottom to top.