## Photoemission study of the room-temperature ferromagnet Zn<sub>1-x</sub>V<sub>x</sub>O

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Diluted ferromagnetic semiconductors have become one of the key materials for the 'spintronics' devices, which aim at the integrated use of spins and carriers in the semiconductors. Recently, Saeki et al. [1] succeeded in the fabrication of ferromagnetic  $Zn_{1-x}V_xO$  whose Curie temperature exceeds well above the room temperature. We have studied the electronic structure of  $Zn_{1-x}V_xO$  by use of photoemission spectroscopy.

Resonant photoemission has been successfully applied to obtain the Mn 3*d* partial density of states in the Mnbased diluted magnetic semiconductors (DMSs), e.g.,  $Cd_{1-x}Mn_xTe_{2}$ ,  $Ga_{1-x}Mn_xAs_{3}$ , and  $Zn_{1-x}Mn_xO_{4}$ , and subsequent analyses provided the strength of *p-d* exchange interaction and the on-site Coulomb interaction and hence the *p-d* exchange interaction. Here, we have investigated the electronic structure of  $Zn_{1-x}V_xO$  by resonant photoemission and compared it with those of the Mn-doped DMSs.

 $Zn_{0.95}V_{0.05}O$  and ZnO with Ga dopant were prepared by pulsed-laser deposition on  $Al_2O_3$  (0001) substrates as reported in the literature [1]. Ferromagnetic  $Zn_{1-x}V_xO$ samples show metallic conductivity while semiconducting samples always remain non-magnetic. Optical transmission spectra indicate that the V ions are largely in the divalent state [1].

Photoemission measurements at room temperature were performed at BL 18-A of Photon Factory. The total energy resolution including the VG CLAM analyzer and the temperature broadening was ~200 meV. Repeated Arion sputtering at 1.0 kV and subsequent annealing at 250°C for 10 min were used for sample cleaning. Surface cleanliness was checked by the weakness of the C 1s core-level signal. Ferromagnetism of the  $Zn_{1-x}V_xO$  sample was confrimed before and after the photoemission measurements using a SQUID magnetometer.

Figure 1(a) shows the total electron yield spectra of  $Zn_{0.95}V_{0.05}O$  and Ga-doped ZnO measured. Compared to the spectrum of the undoped ZnO, the spectrum of  $Zn_{0.95}V_{0.05}O$  shows a broad enhancement around hv = 45 eV, which corresponds to the V  $M_{2,3}$  absorption edge in the V-doped ZnO spectrum [Fig. 1(a) hatched area]. Since V is an early transition metal, a broad absorption edge compared to those obtained in Mn-doped diluted magnetic semiconductors is observed [3].

Figure 1(b) shows the valence-band spectra of  $Zn_{0.95}V_{0.05}O$  near the V  $M_{2,3}$  absorption edge. All the spectra have been normalized to the post-focusing Au mirror current. The Fermi level has been calibrated using

the Fermi cut-off of a metal in contact with the sample. The main structure of the V 3*d* band ( $E_B \sim 1.8 \text{ eV}$ ) appeared within the band gap of ZnO, and is well separated from the O 2*p* band. Although the ferromagnetic sample showed metallic conductivity, no Fermi edge was observed in the photoemission spectra. Even the main structure of V 3*d* is located well below the Fermi level as seen in Fig.1(b). This may suggest that the metallic charge is mainly of Zn 4*s* character whose crosssection is too weak to be detected in the photoemission spectra in the present experiment. Corresponding to the enhancement in the total yield spectra [Fig. 1(a)], there is a resonance around hv = 47 eV of the E<sub>B</sub> ~ 1.8 eV structure.



Fig 1. Total electron yield of  $Zn_{0.95}V_{0.05}O$  and  $Zn_{0.95}Ga_{0.05}O$  [(a)], and the photoemission spectra of  $Zn_{0.95}V_{0.05}O$  near the V  $M_{2,3}$  absorption edge [(b)].

## **References**

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