Photoemission study of the diluted magnetic semiconductor $\text{Zn}_{1-x}\text{Co}_x\text{O}$

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Introduction
Diluted magnetic semiconductors (DMSs) are key materials in spintronics (spin plus electronics), which is intended to manipulate both the spin and charge degrees of freedom. ZnO-based DMS have been predicted to be a candidate for a room temperature ferromagnet by theoretical studies [1]. In n-type Co-doped ZnO thin films, Ueda et al. succeeded to observe room temperature ferromagnetism [2]. In DMS, Photoemission spectroscopy (PES) and configuration-interaction (CI) analysis using the cluster model are powerful tools to investigate the electronic structure of the substituted transition metal ion [3].

Experimental
A Zn$_{1-x}$Co$_x$O ($x=0.05$) thin film was prepared on a Al2O3 (0001) substrate by the pulsed laser deposition technique using an ArF excimer laser at the substrate temperature of ~300°C in an ambient oxygen pressure of 1.0x10$^{-5}$ mbar. The total thickness of the Zn$_{1-x}$Co$_x$O layer was ~200nm on a 50nm ZnO buffer layer.

Ultraviolet photoemission (UPS) measurements were performed at BL-18A of Photon Factory. Spectra were taken in an ultrahigh vacuum below 7.5x10$^{-10}$ Torr. Photoelectrons were collected in the angle integrated mode at room temperature. The total resolution of the spectrometer with a VG CLAM hemispherical analyzer including temperature broadening was about 200 meV. Sample surface was cleaned by Ar$^+$-ion sputtering at 1.5 kV and annealing at 250°C. Cleanliness was checked by low energy electron diffraction (LEED) and the absence of a high binding-energy (EB) shoulder in the O 1s spectrum and of C 1s contamination by x-ray photoemission spectroscopy (XPS).

Results
Absorption spectrum measured in the total yield mode shows that Co 3p $\rightarrow$ 3d absorption occurs at h$\nu$ ~61 eV. Figure 1 (a) shows the Co 3d partial density of states (PDOS) of Zn$_{0.95}$Co$_{0.05}$O, which has obtained by subtracting the off-resonance spectrum (h$\nu$=60.0 eV) from the on-resonance one (h$\nu$=61.5 eV) that have been normalized to the integrated valence band (VB) intensity of ZnO (integration range: 0<EB<9 eV). The Co 3d PDOS shows a peak at E$_{B}$ ~ 3.0 eV, and a satellite at E$_{B}$ ~ 7.0 eV.

By applying the CI cluster-model analysis to the Co 3d PDOS in the VB, electronic structure parameters are obtained as the ligand to 3d charge transfer energy $\Delta=5.0\pm0.5$ eV, the d-d Coulomb interaction energy $U=6.0\pm0.5$ eV and the Slater-Koster parameter (p)=-1.6 $\pm$ 0.1 eV (a transfer integral between O 2p and Co 3d).

These parameters are consistent with the chemical trend in II-VI DMSs [4]. Figure 1(b) shows that the main structure of the spectrum dominantly consists of the charge-transferred electronic states, i.e. $d^7L$ where $L$ denotes a ligand 2p hole. These results mean that it is important to consider the strong correlation effects for the electronic structure of Co.


Fig. 1. (a) On-resonance (h$\nu$=61.5 eV) and off-resonance (h$\nu$=60.0 eV) spectra normalized to the integrated valence band intensity of ZnO. Difference between these spectra represents the Co 3d PDOS.
(b) CI cluster model analysis for the Co 3d PDOS.

References

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