In-situ photoemission study of the room-temperature ferromagnetism in $ZnGeP_2$: Mn

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After the successful synthesis of III-V-based ferromagnetic diluted magnetic semiconductors (DMS or DFS), it is now crucial to increase the T_C above the room temperature (RT) for practical applications. There are several reports of RT-DFS such as TiO_2:Co, ZnO:Co, and ZnO:V. Among them is the intriguing report of the Mn incorporated II-IV-V_2-type chalcopyrite semiconductors $CdGeP_2$ and $ZnGeP_2$, which show ferromagnetism above 350 K [1]. High concentration of Mn ions are incorporated in the surface region by depositing Mn on the surface of $ZnGeP_2$ single crystals annealed at 400℃. Chemical reaction and the composition in the densely Mn-deposited surface region are still to be clarified.

In order to study the chemical and electronic structures of $ZnGeP_2$:Mn interface, we performed extensive *in-situ* photoemission measurements. Core-level and valence-band spectra were taken for various amounts of Mn deposition on the $ZnGeP_2$ surface. As the Mn was deposited, Zn signal quickly disappeared while the Ge and P were always present even after depositing the nominal Mn thickness of 500 A. The magnetization curve measured by SQUID for this 500 A Mn deposited surface showed a two component ferromagnetic behavior, one vanishing at 290 K, and the other showing ferromagnetism even above 375 K. The former component may be assigned to MnP (T_C = 290 K), while the latter is attributed to some ternary compound(s) of Mn, Ge, and P.

The valence band spectra showed a prominent Mn 3p-3d resonant peak up to the nominal Mn thickness of 30 A, while the Mn $M_{23}VV$ Auger decay replaced the resonant behavior for further Mn deposition (Fig. 1). A clear Fermi edge was observed after 10 A Mn deposition, and its intensity was enhanced for further Mn deposition up to 100 A, beyond which both the ratio of the core-level intensities and the valence-band feature drastically changed. This indicates successive transitions from a DMS-like chemical state to other metallic compounds with Mn deposition on the $ZnGeP_2$:Mn interface.

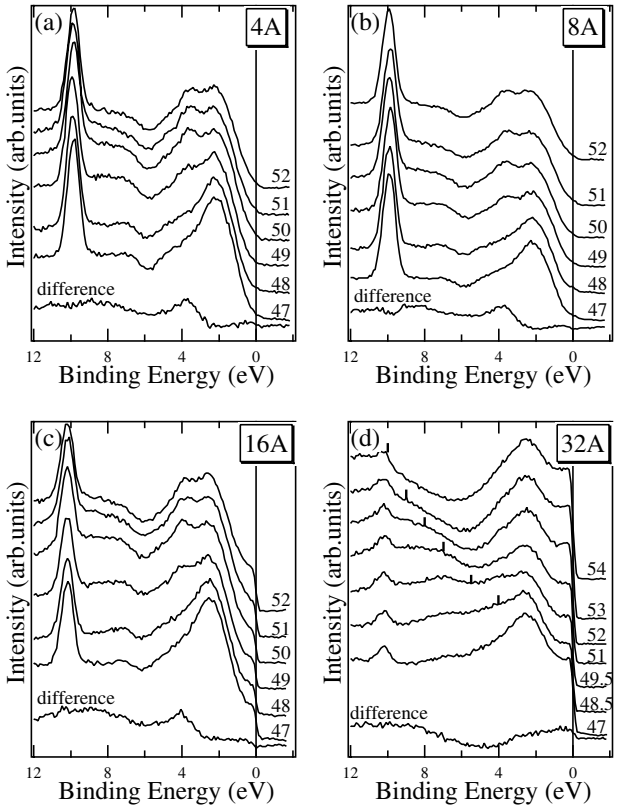

Fig. 1. Valence-band spectra of the nominal Mn thickness of 4, 8, 16, and 32 A in the Mn 3p-3d core excitation reigion. Every spectrum is normalized to the photon flux. The difference spectra are taken between on-resonance (hν =51eV) and off-resonance (hν =48eV). The difference specrta below 30 A Mn deposition represent the Mn 3d partial DOS. The vertical bars in (d) denote the Mn $M_{23}VV$ Auger peak.

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