Electronic structure of In$_{1-x}$Mn$_x$As studied by photoemission spectroscopy: Comparison with Ga$_{1-x}$Mn$_x$As

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We have investigated the electronic structure of the p-type diluted magnetic semiconductor In$_{1-x}$Mn$_x$As by photoemission spectroscopy. The Mn 3d partial density of states is found to be basically similar to that of Ga$_{1-x}$Mn$_x$As. However, the impurity-band like states near the top of the valence band have not been observed by angle-resolved photoemission spectroscopy unlike Ga$_{1-x}$Mn$_x$As. This difference would explain the difference in transport, magnetic and optical properties of In$_{1-x}$Mn$_x$As and Ga$_{1-x}$Mn$_x$As. The different electronic structures are attributed to the weaker Mn 3d - As 4p hybridization in In$_{1-x}$Mn$_x$As than in Ga$_{1-x}$Mn$_x$As.

Diluted magnetic semiconductors (DMS) have attracted much attention because of the combination of magnetic and semiconducting properties and hence high potential for new device applications. Recently DMS based on III-V compounds have been extensively studied because of the success in doping high concentrations of transition-metal ions by molecular beam epitaxy (MBE). Most remarkably, Mn doping in InAs and GaAs leads to ferromagnetism and interesting magnetotransport properties. This behavior is generally called “carrier-induced ferromagnetism” because hole carriers introduced into the system mediate the ferromagnetic coupling between the Mn ions, although its microscopic mechanism has been controversial until now. The key to clarify the mechanism of the carrier-induced ferromagnetism is to understand the nature of the doped hole carriers as well as the exchange interaction between the holes in host valence band and the localized d orbitals of the magnetic ions, so-called p-d exchange interaction. For Ga$_{1-x}$Mn$_x$As, previous investigations including photoemission studies have revealed that the basically localized Mn 3d electrons interact with the doped holes through the p-d hybridization which causes the p-d exchange interaction.

As for the closely related system In$_{1-x}$Mn$_x$As, there are several differences from Ga$_{1-x}$Mn$_x$As. (1) The Curie temperature is relatively low: $T_C \leq 45$ K. (2) Optical absorption measurements have indicated that In$_{1-x}$Mn$_x$As shows a Drude-like behavior due to free carriers. For Ga$_{1-x}$Mn$_x$As, on the other hand, a broad peak was observed around 200 meV and there was no clear Drude component. So far, no photoemission study has been reported for In$_{1-x}$Mn$_x$As. Comparative studies of Ga$_{1-x}$Mn$_x$As and In$_{1-x}$Mn$_x$As would provide us with useful information to elucidate the origin of the ferromagnetism in these systems. The electronic structure of In$_{1-x}$Mn$_x$As itself is also interesting because it has been reported that In$_{1-x}$Mn$_x$As grown on GaSb substrate exhibits photo-carrier induced ferromagnetism and field-induced ferromagnetism. Investigation of the electronic structure, especially of the hybridization and the exchange interaction between the host valence band and the localized magnetic ions, as well as the magnetic coupling between the magnetic ions, would give us a useful guideline for further development in functional materials design. Although several theoretical models have been discussed, there are few experimental investigations to clarify the electronic structure and the mechanism of carrier-induced ferromagnetism. The purpose of this paper is to clarify the electronic structure of In$_{1-x}$Mn$_x$As by resonant photoemission spectroscopy (RPES), which yields the Mn 3d partial density of states (DOS), and by angle-resolved photoemission spectroscopy (ARPES), which measures the energy-band dispersions. We compare the present results with those of Ga$_{1-x}$Mn$_x$As.

A p-type In$_{1-x}$Mn$_x$As/GaSb sample of 30 nm thickness was grown by MBE. The sample had a Curie temperature of 35 K and the Mn content was estimated to be $x = 0.09$ based on the calibration of beam fluxes during MBE growth. Experiments were performed at beamline BL 18-A of Photon Factory, High Energy Accelerator Research Organization, using an ADES-500 analyzer for ARPES and a CLAM-II analyzer for angle-integrated RPES. The total energy resolution was set to 100 meV, comparable to the thermal broadening at the room temperature where all experiments were carried out. The angular resolution of the ADES-500 and CLAM-II analyzers were $\pm 1^\circ$, $\pm 4^\circ$, respectively. To remove oxidized surface layers and other contamination, we made repeated Ar-ion sputtering (1 kV) and annealing. The annealing temperature was limited to 200°C to avoid the segregation of MnAs clusters.
surface showed a 1×1 LEED pattern. We checked the chemical composition of the sample by measuring x-ray photoemission spectra of In, As, and Mn core levels. For angle-integrated RPES in the Mn 3p to 3d absorption region, photons of $h\nu = 46 - 55$ eV were used. In the case of ARPES, electrons emitted in the direction normal to the surface, which come from the $\Gamma - \Delta - X$ line in the Brillouin zone, were collected. We compared the $\text{In}_{1-x}\text{Mn}_x\text{As}$ spectra with those of the reference p-type InAs. The identical procedure of surface cleaning was performed also for the InAs sample. Binding energies are referenced to the Fermi edge of Ta spectra in electrical contact with the sample.

Figure 1 shows RPES spectra recorded using photon energies of $h\nu = 46 - 55$ eV. The spectra have been normalized to the photon flux. Resonant enhancement occurred at $h\nu=50$ eV and off-resonance spectra were taken at $h\nu=48$ eV. The difference between the two curves yields the Mn 3d-derived spectra as in the case of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$. The difference spectrum shows a sharp peak at $\sim 4$ eV binding energy as well as a broad peak at $\sim 7$ eV binding energy. There is little intensity at the Fermi level ($E_F$). Such a spectral line shape is almost identical to that of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, which has been interpreted in terms of configuration-interaction cluster-model calculations. From that analysis, the ground state has been found to be dominated by the $3d^5$ configuration. These spectra also indicate strong hybridization between the Mn 3d electrons and the As 4p-derived valence band.

As shown at the bottom of Fig. 1, we compare the experimental Mn 3d partial DOS of $\text{In}_{1-x}\text{Mn}_x\text{As}$ with configuration-interaction cluster-model calculations. For comparison, we also show the result for $\text{Ga}_{1-x}\text{Mn}_x\text{As}$. The parameters for the cluster-model calculations are the charge-transfer energy $\Delta$ from the ligand $p$ level to the transition-metal $d$ level, the on-site Coulomb energy $U$ between two Mn 3d electrons, and the hybridization strength ($p\sigma$) between the ligand $p$ orbital and the transition-metal $d$ orbitals defined by Slater-Koster parameters. The details of the calculations are given in Ref. 21. The Mn 3d-derived spectrum has been reproduced using parameters with a smaller ($p\sigma$) value compared to that for $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ as summarized in Table I. According to the cluster-model calculations, the $\sim 2$ eV feature predominantly consists of $d^0L^4$ final states, while the satellite structure comes from the $d^4$ final-state configuration because $E(d^4) - E(d^0L^4)\sim U - \Delta > 0$. Using the above parameters, we have estimated the $p\sigma$ exchange interaction in $\text{In}_{1-x}\text{Mn}_x\text{As}$ to be $N\beta = -0.7$ eV. This value is smaller than that of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ ($N\beta = -1.0$ eV). The depressed intensity at $E_F$ in the difference spectrum compared to the valence-band intensity at $E_F$ for various photon energies both for $\text{In}_{1-x}\text{Mn}_x\text{As}$ and $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ indicates that the Mn 3d DOS are not dominant at $E_F$ and suggests that hole carriers of As 4p character contribute to the transport.

The difference spectrum between $\text{In}_{1-x}\text{Mn}_x\text{As}$ and pure InAs taken at $h\nu = 70$ eV has also been used to obtain the Mn 3d partial DOS as shown in Fig. 2. The spectra have been normalized to the In 4d core-level peaks taking into account the composition difference between In and Mn. Because of the Cooper minimum of the As 4p states at $h\nu\sim 70$ eV, the ionization cross section of As 4p reaches a minimum, and the Mn 3d component is relatively enhanced. The lineshape of the difference spectrum is almost the same as that in Fig. 1, which guarantees that the Mn 3d density of states deduced from RPES is valid to discuss the electronic structure.

To obtain more information about the electronic structure around $E_F$, we have measured ARPES spectra along the $\Gamma - \Delta - X$ line for both $\text{In}_{1-x}\text{Mn}_x\text{As}$ and InAs. As shown in Fig. 3, by changing the photon energy in the normal emission set up from the (001) surface, the energy band dispersions along the $\Gamma - \Delta - X$ line were observed. According to the direct-transition model for ARPES with an appropriate inner potential (10 eV), the $\Gamma$ point is measured at $h\nu\sim 10$ eV and the $X$ point is measured at $h\nu\sim 32$ eV. The peaks in Fig. 3 (a) correspond to the $\Delta_1$ band (split-off band) and $\Delta_3 + \Delta_4$ band (heavy- and light-hole bands, respectively) along the $\Gamma - \Delta - X$ line. The clear dispersion curves are almost the same as those for GaAs and InAs. Due to the Mn 3p-3d resonant effect, the line shape changes drastically around $h\nu = 50$ eV, almost in the same way as in the RPES result. Comparison of the spectra near $E_F$ between $\text{In}_{1-x}\text{Mn}_x\text{As}$ and InAs shown in Fig. 3 (b) reveals no clear differences in spite of Mn doping. This is quite different from the case of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ and GaAs, where impurity-band-like new states were found to form near the valence-band maximum (VBM) by Mn doping as shown in Fig. 3 (c). Although Mn doping in GaAs induces split-off states above the VBM through hybridization with As 4p and forms the impurity band-like states, Mn in InAs does not induce such states, probably because of the weaker hybridization strength ($p\sigma$) than in GaAs. In fact, in the dilute limit of Mn in InAs (Mn: 8×10^{16} cm^{-3}), Mn doping leads to the formation of an acceptor level of primarily As 4p character at 30 meV above the VBM, which is much smaller than that for Mn in GaAs (100 meV).

Now we discuss the origin of the differences between the electronic structure of $\text{In}_{1-x}\text{Mn}_x\text{As}$ and $\text{Ga}_{1-x}\text{Mn}_x\text{As}$. Comparing Mn 3d spectral features in $\text{In}_{1-x}\text{Mn}_x\text{As}$ and $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, we find that the main peak in $\text{In}_{1-x}\text{Mn}_x\text{As}$ has a lower binding energy compared to that in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, suggesting a lower $\Delta$ in $\text{In}_{1-x}\text{Mn}_x\text{As}$. There are two possible reasons for the decrease of the hybridization strength ($p\sigma$) in $\text{In}_{1-x}\text{Mn}_x\text{As}$ compared to that in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$. One is the differences in the Mn-As distance in these two systems. Extended x-ray-absorption fine-structure (EXAFS) measurements were performed and the Mn-As distance was reported to be 2.44 Å for $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ and 2.54-2.58 Å for $\text{In}_{1-x}\text{Mn}_x\text{As}$. The longer Mn-As distance in $\text{In}_{1-x}\text{Mn}_x\text{As}$ would lead to a decrease in the $p\sigma$ hybridization.
bridization strength. Second, because of the smaller band gap in InAs (0.4 eV) than that in GaAs (1.5 eV), the In $5s$ states in the unoccupied part is more strongly mixed with the As $4p$ states in the valence band than in the case of Ga $4s$ states in GaAs. Through the mixing with the In $5s$ states, the As $4p$ weight in the valence band is reduced and hence the hybridization between the valence band and the Mn $3d$ state would decrease. Due to the weaker hybridization between the host valence band and Mn $3d$, the acceptor levels in In$_{1-x}$Mn$_x$As are not so strongly split off from the valence band maximum (VBM) and the Mn ions become difficult to bind holes. The bound hole picture (Mn$^{2+} + $ bound hole) is therefore less appropriate for In$_{1-x}$Mn$_x$As than for Ga$_{1-x}$Mn$_x$As, and holes in In$_{1-x}$Mn$_x$As behave as free carriers. This would naturally explain the difference in the optical properties of In$_{1-x}$Mn$_x$As and Ga$_{1-x}$Mn$_x$As.

The formation of the impurity-band-like states around $E_F$ would be important for the magneto-transport properties of the Mn doped DMS. According to the electron paramagnetic resonance (EPR) measurements, the Mn $3d$ signals of Ga$_{1-x}$Mn$_x$As showed that the Mn impurities in this system were predominantly in the ionized state (Mn$^{2+}$, $A^-$). Similar picture was also obtained for n-type In$_{1-x}$Mn$_x$As in which incorporated Mn in ionized by the excess donors. From the view point of photoemission spectroscopy, the Mn $3d$ spectrum in Fig. 1 is analyzed using of the cluster model with the Mn$^{2+}$ ground state as in the case of Ga$_{1-x}$Mn$_x$As. These results support that the Mn $3d$ electronic configuration is similar between Ga$_{1-x}$Mn$_x$As and In$_{1-x}$Mn$_x$As. However, it is difficult to distinguish between the Mn$^{2+}$ states with a weakly bound hole and with a free hole. In both In$_{1-x}$Mn$_x$As and Ga$_{1-x}$Mn$_x$As, the itinerant holes obviously mediate the ferromagnetic order.

The ferromagnetism in the double-perovskite compound Sr$_2$FeMoO$_6$ is also considered to be caused by the same mechanism as the Mn-doped DMS in the sense that the O $2p$ doped hole mediates the ferromagnetism through the gain in kinetic energy in the ferromagnetic state.

The peculiar feature in Ga$_{1-x}$Mn$_x$As is that impurity-band-like states are split off from the VBM, suggesting virtually bound holes rather than simple free carriers of In$_{1-x}$Mn$_x$As. The formation of these states may help to increase the $T_c$ of Ga$_{1-x}$Mn$_x$As compared to In$_{1-x}$Mn$_x$As but more studies are necessary to clarify the mechanism for this.

In conclusion, we have investigated the electronic structure of In$_{1-x}$Mn$_x$As using ARPES and RPES and compared it with Ga$_{1-x}$Mn$_x$As. Although the Mn $3d$ states are in the Mn$^{2+}$ configuration in both systems, impurity-band-like states are not observed in In$_{1-x}$Mn$_x$As unlike Ga$_{1-x}$Mn$_x$As. We attribute this to the weaker hybridization in In$_{1-x}$Mn$_x$As than in Ga$_{1-x}$Mn$_x$As, that is not sufficient to split off states from the VBM to form the impurity-band-like states.

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TABLE I. Electronic structure parameters $\Delta$, $U$ and $(pd\sigma)$ and the exchange coupling constant $N\beta$ for substitutional Mn impurities in InAs and GaAs in units of eV. Error bars from the lineshape analyses are $\pm 0.5$ eV for $\Delta$, $U$ and $N\beta$, and $\pm 0.1$ eV for $(pd\sigma)$.

| Material      | $\Delta$ | $U$   | $(pd\sigma)$ | $N\beta$ | Ref. |
|---------------|----------|-------|---------------|----------|------|
| Ga$_{1-x}$Mn$_x$As | 1.5      | 3.5   | 1.0           | 1.0      | this work |

FIG. 1. A series of photoemission spectra of In$_{0.9}$Mn$_{0.1}$As at various photon energies in the Mn 3$p$ - 3$d$ core excitation threshold. The difference spectra between the on-resonant ($h\nu=50$ eV) and off-resonant (48 eV) spectra, which is a measure of the Mn 3$d$ partial density of states, is shown at the bottom and is compared with configuration interaction cluster calculation results assuming the Mn$^{2+}$ ground state configuration. Similar comparison is shown for Ga$_{1-x}$Mn$_x$As (Ref. 6).

FIG. 2. Angle-integrated photoemission spectra of In$_{0.9}$Mn$_{0.1}$As and InAs at $h\nu = 70$ eV, where the Mn 3$d$ cross section is large compared with As 4$p$, and their difference spectrum representing the Mn 3$d$ partial density of states.

FIG. 3. Angle-resolved photoemission spectra of In$_{1-x}$Mn$_x$As along the $\Gamma - \Delta - X$ direction. (a) Wide-range spectra. Vertical bars show peak or shoulder positions. (b) Narrow-range spectra near the Fermi level for In$_{0.9}$Mn$_{0.1}$As (solid curves) and InAs (dashed curves). (c) Corresponding spectra for Ga$_{1-x}$Mn$_x$As and GaAs taken from Ref. 7.