Core-level photoemission study of Ga$_{1-x}$Mn$_x$As

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We have studied the electronic structure of Mn impurities in GaAs by Mn $2p$ core-level photoemission spectroscopy. From cluster-model analysis assuming the neutral (Mn$^{3+}$) or negatively ionized (Mn$^{2+}$) ground state, electronic structure parameters have been obtained. In either case, the Mn $d$ electron number is evaluated to be $\sim 5$ using the obtained parameters, meaning that the neutral Mn$^{3+}$ impurity, if it exists, consists of the Mn $3d^5$ configuration and a valence hole bound to it through $p-d$ hybridization and/or Coulomb interaction. We discuss the exchange interaction between the Mn local spin and the valence hole as well as the stability of the neutral impurity against the ionization of the valence hole. [S0163-1829(98)52532-5]

The recent success of doping III-V semiconductors with magnetic impurities using the molecular-beam epitaxy technique has opened up, to the best of our knowledge, a new field in the research of diluted magnetic semiconductors (DMS).$^{1,2}$ Because one can introduce both magnetic moments and charge carriers in DMS, they have the possibility of combining magnetics and electronics. So far, II-VI based DMS such as Cd$_{1-x}$Mn$_x$Te, in which magnetic ions, particularly Mn$^{2+}$, can be doped up to high concentration, have been extensively studied.$^{3,4}$ Cd$_{1-x}$Mn$_x$Te is now used as optical isolators because of their strong magneto-optical effects.$^5$ In II-VI based DMS, Mn impurities substituting 2+ cations are stable as 2+ ions and therefore there are few carriers, making them insulators. Owing to the presence of conducting carriers, III-V based DMS show "carrier-induced ferromagnetism" in $p$-type samples.$^6,7$ In recent years, a III-V based DMS system Ga$_{1-x}$Mn$_x$As has attracted considerable interest because of its relatively high Curie temperature ($T_C \sim 110$ K).$^8$ Also, magnetotransport properties such as anomalous Hall effect and large magnetoresistance,$^9,10$ as well as photoinduced ferromagnetism$^{11}$ have been reported for the GaAs-based DMS.

In order to understand those anomalous properties associated with the strong coupling between the magnetism and the charge transport in the III-V based DMS, we must first characterize their electronic structure, especially interaction between the localized Mn $d$ electrons and the delocalized band electrons of the host semiconductor. In order to understand such a system, theoretical framework beyond a one-electron band picture is necessary because electron correlation at the Mn site should be quite substantial. Different models have been suggested for the III-V based DMS$^{12,13}$ and there has been no consensus on their electronic structure. Photoemission spectroscopy is a powerful technique in the investigation of the electronic structure of solids, especially of correlated-electron systems such as $3d$ transition-metal compounds.$^{14}$ Indeed, the electronic structure of II-VI based DMS, including Cd$_{1-x}$Mn$_x$Te, has been studied by photoemission spectroscopy combined with configuration-interaction (CI) cluster-model calculation and their optical properties, $p-d$ exchange interactions and donor and acceptor ionization energies have been explained on a unified ground.$^{15,16}$ In this paper, we present a study of the electronic structure of the Mn impurity in Ga$_{1-x}$Mn$_x$As by core-level photoemission spectroscopy and subsequent cluster-model calculations. We discuss the $p-d$ exchange interaction between the Mn impurity and the host semiconductor as well as the stability of the neutral impurity A$^0$ (Mn$^{3+}$) against the negatively ionized state A$^-$ (Mn$^{2+}$).

The sample was prepared by molecular-beam epitaxy at low growth temperature as follows. We grew a Ga$_{1-x}$Mn$_x$As (001) single-crystal thin film on the GaAs (001) surface at the growth temperature of $250^\circ$C. The Mn concentration was estimated to be $x = 0.074$ by x-ray diffraction. We estimated the Curie temperature to be $T_C = 55-60$ K from anomalous Hall effect, the details of which are reported in Refs. 17 and 18.

We performed x-ray photoemission spectroscopy (XPS) experiments using a VG CLAM hemispherical analyzer and a Mg x-ray source. The measurements were made in an ultrahigh vacuum of $10^{-11}$ Torr at room temperature. The resolution of XPS was estimated to be $\sim 0.7$ eV from the Au $4f$ core-level spectrum. For sample cleaning, we repeated Ar ion sputtering (1 kV) and annealing at 200°C. It is known that if Ga$_{1-x}$Mn$_x$As samples are heated above $400^\circ$C after the growth, ferromagnetic MnAs clusters appear. Therefore, we took caution by controlling the annealing temperature below 240°C so that MnAs did not appear. We obtained an
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and its cluster-model analysis

d the Mn 3d electrons and hybridization between the Mn 3d and other valence orbitals. One can see from Fig. 1 that the satellite intensity is weak compared with those of the II-VI compounds. In this case, the ground state is given by a linear combination of d^5, d^6L, d^6L^2, ... configurations. We have fitted the XPS spectrum by varying \( \Delta \), (pd\( \sigma \)) and U, as shown by solid curves in Fig. 1. The Coulomb interaction between the core hole and the d electron is assumed to be Q = 1.25U, as usual. The Gaussian and Lorentzian broadenings were applied with full width at half maximum (FWHM) of 1.5 and 1.0 eV, respectively, to simulate the measured spectra. The integral background is shown by dashed curves in Fig. 1. The \( j = \frac{1}{2} \) part of the spectrum was used for the fitting because the \( j = \frac{1}{2} \) part is broadened by a Coster-Kronig decay into the \( j = \frac{3}{2} \) and is also obscured by the overlapping Auger feature and the high background level.

The parameters thus obtained are listed in Table I and are compared with those of II-VI based DMS. The \( U \) value

FIG. 1. Photoemission spectrum of the Mn 2p core level (dots) and its cluster-model analysis (solid curves) assuming the negatively ionized Mn^{2+} (a) and neutral Mn^{3+} (b) ground states. The vertical bars are unbroadened spectra. The calculated background is shown by dashed curves.

ordered surface as confirmed by a clear 1×1 low-energy electron diffraction (LEED) pattern. We presume that on the energy scale of the core-level photoemission spectroscopy, the spectra are not affected by magnetic ordering and therefore that they do not depend on the temperature appreciably.

Figure 1 shows the XPS spectrum of the Mn 2p core level in Ga_{0.93}Mn_{0.07}As. The spectrum shows a spin-orbit doublet \((j = \frac{1}{2}, \frac{3}{2})\), each component of which shows a charge-transfer satellite on the higher binding energy side of the main peak. The broad peak at 667 eV is due to the Mn L\( _2 \)M\( _3 \)M\( _{4.5} \)Auger emission and is not considered here. The presence of the satellite structure indicates strong Coulomb interaction between the Mn 3d electrons and hybridization between the Mn 3d and other valence orbitals. One can see from Fig. 1 that the satellite intensity is weak compared with those of the II-VI based DMS. We have analyzed the satellite structure using the CI cluster model to obtain the electronic structure parameters as described below.

In the CI picture, the wave functions are given as linear combinations of d^5, d^6L, d^6L^2, ... configurations, where L stands for a hole in the ligand orbitals. We have considered a MnAs_4 cluster with the central Mn atom, concentrating on energy levels arising from the hybridized Mn 3d and ligand As 4p orbitals. The cluster contains the following parameters: The ligand-to-3d charge-transfer energy is defined by \( \Delta = E(d^{n+1}) - E(d^n) \). The on-site 3d-3d Coulomb interaction energy is defined by \( U = E(d^{n-1}) + E(d^{n+1}) - 2E(d^n) \), where \( E(d^nL_m) \) is the center of gravity of the d^nL_m multiplet. The multiplet splitting is expressed using Racah parameters B and C, which are fixed at the values of the free Mn ion. One-electron transfer integrals between the Mn 3d and As ligand p orbitals are expressed in terms of Slater-Koster parameters (pd\( \sigma \)) and (pd\( \pi \)). We have utilized the relationship between (pd\( \sigma \)) and (pd\( \pi \)): (pd\( \sigma \)) = -2(pd\( \pi \)).

![Diagram](Image)

FIG. 2. Schematic energy-level diagrams of the MnAs_4 cluster in the initial states for the negatively ionized Mn^{2+} (a) and neutral Mn^{3+} (b) models.

In the analysis, we have assumed the ground state of formally Mn^{2+} or Mn^{3+} configuration. For the Mn^{3+}, i.e., neutral impurity ground state, the wave function is expanded by a linear combination d^4, d^6L, d^6L^2, ... configurations as shown in Fig. 2. We also consider the case where the Mn impurity is negatively ionized (A^-) and becomes Mn^{2+} as in the II-VI compounds. In this case, the ground state is given by a linear combination of d^5, d^6L, d^6L^2, ... configurations. We have fitted the XPS spectrum by varying \( \Delta \), (pd\( \sigma \)) and U, as shown by solid curves in Fig. 1. The Coulomb interaction between the core hole and the d electron is assumed to be Q = 1.25U as usual. The Gaussian and Lorentzian broadenings were applied with full width at half maximum (FWHM) of 1.5 and 1.0 eV, respectively, to simulate the measured spectra. The integral background is shown by dashed curves in Fig. 1. The \( j = \frac{1}{2} \) part of the spectrum was used for the fitting because the \( j = \frac{1}{2} \) part is broadened by a Coster-Kronig decay into the \( j = \frac{3}{2} \) and is also obscured by the overlapping Auger feature and the high background level.

The parameters thus obtained are listed in Table I and are compared with those of II-VI based DMS. The \( U \) value

<table>
<thead>
<tr>
<th>Material</th>
<th>( \Delta )</th>
<th>( U )</th>
<th>(pd( \sigma ))</th>
<th>( n_d )</th>
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<td>4.0</td>
<td>1.1</td>
<td>Ref. 15</td>
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<td>4.0</td>
<td>1.3</td>
<td>Ref. 15</td>
</tr>
<tr>
<td>Ga_{1-x}Mn_xAs (A^-; Mn^{2+})</td>
<td>1.5</td>
<td>3.5</td>
<td>1.1</td>
<td>5.3</td>
</tr>
<tr>
<td>Ga_{1-x}Mn_xAs (A^0; Mn^{3+})</td>
<td>-1.5</td>
<td>3.5</td>
<td>1.0</td>
<td>5.1</td>
</tr>
</tbody>
</table>

TABLE I. Electronic structure parameters for substitutional Mn impurities in semiconductors. \( \Delta \), U, and (pd\( \sigma \)) are given in units of eV. Error bars are ±0.5 eV for \( \Delta \) and U and ±0.1 eV for (pd\( \sigma \)).
Figure 3 shows the energy diagram of the XPS final state in GaAs. The great similarity between the two calculated spectra obtained by subtracting the valence-band width from $\Delta_{eff}$. To deduce $\Delta_{eff}$ and $U_{eff}$ from $\Delta$ and $U$, we have used Kanamori parameters $j$, $j'$, and $u$ evaluated from Rach parameters $B=0.119$ eV and $C=0.412$ eV as described elsewhere. The details of the calculation are given in Ref. 22. The value thus evaluated is $N\beta = 1.2 \pm 0.2$ eV for $S = \frac{1}{2}$. This means that the $p-d$ interaction is antiferromagnetic, consistent with the recent magnetic circular dichroism (MCD) measurement of the interband transition for $x=0.074$. In another MCD study of very dilute ($x=0.001\%$) samples, however, $N\beta$ has been estimated to be positive and large, $+2.5$ eV. It has also been reported that $|N\beta|$ is $3.0$ eV from magnetotransport measurements.

It should be noted here that the $N\beta$ value depends on whether the Mn impurity is $2+$ or $3+$. For the Mn $2+$ state, the spin-up states are fully occupied and only the valence electrons which have spins antiparallel to the Mn $2+$ state, move between the Mn $3+$ and Mn $2+$ ground states. It is not clear, however, whether the Mn $3+$ ($A^0$) state is stable, i.e., whether the hole created on the As $p$ orbitals behaves as a bound hole around the Mn $2+$ impurity to form the Mn $2+$ state or is extended throughout the crystal leaving the Mn $2+$ state. The great similarity between the two calculated spectra is attributed to the fact that the Mn impurity has five $d$ electrons in either case because the difference between $\Delta$(Mn $2+$) and $\Delta$(Mn $3+$) nearly equals the $d-d$ Coulomb interaction $U$. Figure 3 shows the energy diagram of the XPS final state in the CI picture. Because of the core-hole potential, the $2pd^5L$ state is pulled down below the $2pd^5$ state with the separation $\Delta - Q$, where $2p$ denotes a hole in the $2p$ core level. The main peak is composed of $2pd^5L$ in the Mn $3+$ state and $2pd^5L^2$ in the Mn $2+$ state. Excited states, which correspond to the satellite, consist of $2pd^6$ and $2pd^5L$ configurations for the Mn $2+$ and Mn $3+$ cases, respectively.

Using the above parameter values, one can estimate the exchange constant $N\beta$ between the Mn $2+$ ion and the electron at the top of the valence band of the host semiconductor. We treated the hybridization as a perturbation in the CI picture. In the second-order perturbation, with respect to the charge transfer, the $N\beta$ is given by

$$N\beta = -\frac{16}{3}\left(1 - \frac{1}{\delta_{eff} + U_{eff} + \delta_{eff}}\right) \times \left(\frac{1}{3} (pd\sigma) - 2\sqrt{3}(pd\pi)\right)^2.$$
find no bound state within the band gap of GaAs using these parameters within the Anderson impurity model and propose that the bound-state formation is made possible by the long-range Coulomb interaction.

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7 If free holes can be introduced into II-VI compounds, ferromagnetism can be induced as demonstrated for a quantum-well system Cd$_{0.976}$Mn$_{0.024}$Te/Cd$_{0.66}$Mg$_{0.27}$Zn$_{0.07}$Te:N. [A. Haury et al., Phys. Rev. Lett. 79, 511 (1997).]