Hybridization between the conduction band and 3d orbitals in the oxide-based diluted magnetic semiconductor In$_{2-x}$V$_x$O$_3$

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The electronic structure of In$_{2-x}$V$_x$O$_3$ ($x = 0.08$) has been investigated using photoemission spectroscopy (PES) and x-ray absorption spectroscopy (XAS). The V 2p core-level PES and XAS spectra revealed trivalent electronic state of the V ion, consistent with the substitution of the V ion for the In site. The V 3d partial density of states obtained by the resonant PES technique showed a sharp peak above the O 2p band. While the O 1s XAS spectrum of In$_{2-x}$V$_x$O$_3$ was similar to that of In$_2$O$_3$, there were differences in the In 3p and 3d XAS spectra between V-doped and pure In$_2$O$_3$. The observations give clear evidence for hybridization between the In conduction band and the V 3d orbitals in In$_{2-x}$V$_x$O$_3$.

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Diluted magnetic semiconductors (DMS’s) have been studied intensively since the discovery of ferromagnetism in the III-V DMS Ga$_{1-x}$Mn$_x$As because the ferromagnetic interaction between the Mn ions mediated by hole carriers enables us to manipulate both the charge and spin degrees of freedom of electrons. Ferromagnetic DMS’s having Curie temperature ($T_C$) above room temperature have been strongly desired for realistic spintronic applications. Ever since the theoretical prediction by Dietl et al. that Mn-doped GaN and ZnO with high hole concentrations should show ferromagnetism above room temperature, wide-gap semiconductors have become promising host materials for high-$T_C$ DMS. In fact, there have been many reports on room temperature ferromagnetism in oxide-based DMS’s such as Co-doped TiO$_2$, Co-doped SnO$_2$, and Mn-doped ZnO.

Recently, In$_2$O$_3$-based DMS’s have attracted much attention because of the reports of room temperature ferromagnetism in not only light transition-metal (TM) but also heavy TM doped In$_2$O$_3$ and of the potential of the host material In$_2$O$_3$ for applications. Here, In$_2$O$_3$ has a band gap of $\sim 3.5$ eV, is an n-type semiconductor, and crystallizes in the cubic bixbyite structure, where In atoms are coordinated by six oxygens forming octahedral (Ok) and orthorhombic (D$_{2h}$) octahedra and neighboring octahedra are shared with their corners and edges, and Sn-doped In$_2$O$_3$ (ITO) has been famous for its high electrical conductivity and transparency. Magnetic force microscopy observations of In$_{2-x}$Cr$_x$O$_3$ and In$_{2-x}$Ni$_x$O$_3$ have demonstrated that the topological undulations correspond to the strength of magnetic response, indicating a uniform distribution of magnetic domains in these materials. Reports of In$_2$O$_3$-based DMS’s have suggested relationship between the electrical conductivity and ferromagnetism through measurements of, e.g., anomalous Hall effects. As In$_2$O$_3$-based DMS’s are candidates for room-temperature ferromagnetic DMS’s, the knowledge of their electronic structure is necessary to understand the origin of the ferromagnetism.

Photoemission spectroscopy (PES) and x-ray absorption spectroscopy (XAS) are powerful tools to investigate electronic structure of materials. XAS, which means photon absorption from a core-level electron into unoccupied states, is an element specific technique to study the electronic structure. $2p \rightarrow 3d$ resonant photoemission spectroscopy (RPES) enables us to extract the 3d partial density of states (PDOS) in the valence band. In this work, we have performed PES and XAS measurements on In$_{2-x}$V$_x$O$_3$ (IVO) thin films in order to obtain a fundamental understanding of the electronic structures. The valence state of the doped V ion has been determined by core-level x-ray photoemission spectroscopy (XPS) and XAS. Effects of doping on the electronic structure of the host material have been approached by V $2p \rightarrow 3d$ RPES and XAS at the O and In edges.

Each of In$_2$O$_3$ and In$_{2-x}$V$_x$O$_3$ ($x = 0.08$) thin films was highly oriented normal to the plane of a sapphire(0001) substrate by the pulsed laser deposition technique. During the deposition, the substrate temperature was kept at $\sim 400$ °C. The total thickness of the deposited layer was $\sim 500$ nm. X-ray diffraction confirmed that the thin film had the cubic bixbyite structure and no secondary phase was observed. Details of the sample fabrication are given in Ref. 14. The V concentration $x$ in the thin films was estimated from the intensity of the V $2p$ core-level PES spectrum. Ferromagnetism above room temperature was confirmed by magnetization mea-

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RPES and XAS measurements were performed at the soft x-ray beam line BL23SU of SPring-8. The monochromator resolution was $E/\Delta E > 10,000$. XAS signals were measured by the total electron yield method. The background of the XAS spectra was assumed to be a hyperbolic tangent function. The RPES and XPS measurements were performed in a vacuum below $1 \times 10^{-7}$ Pa using Gammadata Scienta SES-2000 and SES-100 hemispherical analyzers, respectively. A Mg-Kα x-ray source ($h\nu = 1253.6$ eV) was employed for the XPS measurements. In the PES measurements, photoelectrons were collected in the angle integrated mode at room temperature. The total resolution of the RPES and XPS measurements including temperature broadening were $\sim 300$ and $\sim 800$ meV, respectively. Sample surface was cleaned by cycles of Ar$^+$-ion sputtering. Cleanliness of the sample surface was checked by the absence of a high binding-energy shoulder in the O 1s spectrum and C 1s contamination by XPS. The position of the Fermi level ($E_F$) was determined by measuring PES spectra of evaporated gold which was electrically in contact with the samples.

First, we discuss about the valence state of the V ions in IVO. Figure 1 shows the V 2p core-level spectra of IVO and various vanadium oxides. The binding energy ($E_B$) of a core-level peak position is related to its charge state and, in general, becomes larger with increasing valency. In fact, it has been reported that the $E_B$ of the V 2$p_{3/2}$ peak increases with valency of V as shown in Fig. 1(a). By comparing the peak position of the V 2$p_{3/2}$ core level of IVO with those of the other vanadium oxides, the valence state of V in In$_2$O$_3$ is found to be trivalent V$^{3+}$ ($d^2$). Figure 1(b) shows the V 2$p$ XAS spectra of IVO and several vanadium oxides. The line shape of the V 2$p$ spectrum of IVO is similar to that of V$_2$O$_3$ (V$^{3+}$) rather than that of Zn$_{1-x}$V$_x$O (V$^{2+}$) and of V$_3$O$_5$ (V$^{5+}$) $^{28}$, consistent with the observation of the V 2$p$ XPS. The results suggest that the electronic structure of the doped V ion in IVO is close to that of the V ion in V$_2$O$_3$, i.e., V is in the trivalent V$^{3+}$ state octahedrally coordinated by oxygens. Therefore, it is likely that the doped V ions are substituted for the In sites.

In order to obtain an understanding of the electronic structure of the V ion in the valence band, we measured V 2$p \rightarrow 3d$ resonant photoemission spectra of IVO. Figure 2(b) shows the valence-band PES spectra of IVO taken at various photon energies in the V 2$p \rightarrow 3d$ core-excitation region. Energy difference between the top of the O 2$p$ bands and $E_F$ is $\sim 3.0$ eV, comparable to the band gap of In$_2$O$_3$. The results suggest that the electronic structure of the doped V ion in IVO is close to that of the V ion in V$_2$O$_3$, i.e., V is in the trivalent V$^{3+}$ state octahedrally coordinated by oxygens. Therefore, it is likely that the doped V ions are substituted for the In sites.

![FIG. 1: V 2$p$ core-level spectra of In$_{2-x}$V$_x$O$_3$ (IVO) with $x = 0.08$. (a) V 2$p$ XPS spectra compared with those of other vanadium oxides. $^{28}$ (b) V 2$p$ XAS spectra compared with those of other vanadium oxides Zn$_{1-x}$V$_x$O, $^{29}$ V$_2$O$_3$, $^{28}$, and V$_3$O$_5$ ($^{30}$).](image)

![FIG. 2: V 2$p \rightarrow 3d$ resonant photoemission spectra in the valence band of of In$_{2-x}$V$_x$O$_3$ ($x = 0.08$). (a) V 2$p$ XAS spectrum and the intensity of the V 3$d$ peak at $E_F = 1.7$ eV as functions of photon energy. (b) A series of spectra measured at $h\nu$s denoted by triangles in (a). (c) Top: On-res. ($h\nu = 516.5$ eV) and off-resonance ($h\nu = 513$ eV) spectra. Bottom: On- and off-resonance difference spectrum representing the V 3$d$ partial density of states (PDOS).](image)
3d PDOS are independent of photon energy, implying that the V ions are in a single electronic state. The V 3d PDOS shows a peak above the O 2p band, that is, in the middle of the band gap of In2O3, as shown in Fig. 2(c). The narrow width and strong intensity of the peak imply the localized nature of the V 3d orbitals in the valence band, i.e., weak V 3d − O 2p mixing in IVO.

In n-type DMS’s, electronic states near the bottom of the conduction band are expected to be important for carrier-induced ferromagnetism since $E_F$ is located there. Because the valence band of the host semiconductor is usually occupied, XAS spectra measured at the absorption edges of the host semiconductor reflect the unoccupied electronic states, namely, the conduction band, and are useful for the investigation of the electronic structure of n-type DMS’s. Figure 3(a) shows XAS spectra measured at absorption edges of In and O, and compares them between V-doped and pure In2O3. The O 1s XAS spectrum of IVO is nearly identical to that of In2O3 as shown in Fig. 3(a). It has been reported that the O 1s XAS spectrum of Fe-doped In2O3 differs from that of pure In2O3, and that the difference is induced by hybridization of the Fe 3d orbitals with the O 2p band [15]. The observation implies weaker hybridization between the O 2p band and the V 3d orbitals in IVO than that between O 2p and Fe 3d in In2−xFe2O3, consistent with the result of the V 2p → 3d RPES. In contrast, the In 3p and 3d XAS spectra were changed by V doping, i.e., there are differences between the XAS spectra of IVO and those of pure In2O3 in both pre-edge regions as shown in Figs. 3(b) and 3(c). The observations clearly indicate hybridization between the In 5p conduction band and the V 3d orbitals in IVO.

Based on the above findings, we shall discuss about the electronic structure of In2O3-based DMS’s, in particular, those doped with light-TM atoms. Electronic structure of a TM atom octahedrally coordinated by oxygens splits into two-fold degenerate $e_g$ and three-fold degenerate $t_{2g}$ levels due to ligand crystal fields. In IVO, the $V^{3+}$ (3d2) ion substituting for the In site has two electrons in the $t_{2g}$ levels (or the two lowest levels splitted from the $t_{2g}$ level due to the $D_{2h}$ symmetry) as shown in Fig. 4(a). Because the $e_g$ orbitals are directed toward the O atoms as shown in Figs. 4(b) and 4(c), the O 2p band can hybridize with the $e_g$ orbitals stronger than the $t_{2g}$ orbitals. Indeed, the Slater-Koster parameter ($pd\sigma$), which represents transfer integrals between the 3d $e_g$ and ligand $p$ orbitals, has an absolute value about twice larger than ($pd\pi$), which represents transfer integrals between the 3d $t_{2g}$ and ligand $p$ orbitals [31]. Considering the result of O 1s XAS, hybridization between the O 2p band and the $e_g$ orbitals is expected to be weak. It is probable that the $t_{2g}$ orbitals hybridize dominantly with the In band. Light TM ions Ti$^{3+}$ and Cr$^{3+}$ under the O$_h$ crystal field only have electron(s) in the $t_{2g}$ levels, too [Fig. 4(a)]. It follows from those arguments that for light TM-doped In2O3, hybridization between the host conduction band and the 3d $t_{2g}$ orbitals should be taken into consideration to understand their electronic properties.

Considering the present observations, we shall discuss about the mechanism of the ferromagnetism in In$_{2−x}$V$_x$O$_3$. The bottom of the conduction band of In$_2$O$_3$ are mainly composed of the In 5s bands [21]. For n-type DMS’s, the electronic structure near the bottom of the conduction band is important, i.e., s-d exchange interaction may play an essential role rather than the p-d exchange interaction. It is possible that hybridization between the In 5s and V 3d orbitals as observed In 3p XAS strengthens the s-d exchange interaction, as in the case of the host conduction band in Co 3d orbital exchange interaction in Ti$_{1−x}$Co$_x$O$_2$ [32]. Generally speaking, be-

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**FIG. 3**: X-ray absorption spectra of In$_{2−x}$V$_x$O$_3$ (IVO) with $x = 0.08$ measured at In and O absorption edges related to the host In$_2$O$_3$. (a) O K XAS spectra, (b), (c) In 3d and 3p XAS spectra, respectively. The insets show enlarged plots in the pre-edge region.

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**FIG. 4**: 3d electronic structure of the V ion of In$_{2−x}$V$_x$O$_3$. (a) A schematic representation of the electronic structure in the V ion. Those of the Ti$^{3+}$ and Cr$^{3+}$ ion in an O$_h$ crystal field are also presented. (b) Octahedral coordination of the O atoms. (c) $e_g$ orbitals.
cause in wide-gap semiconductors the effective mass \( m^* \) is large, the magnetic splitting due to the exchange term in Hamiltonian \((s,p,d)\) exchange interaction\) is greater than the spin splitting of the host valence and conduction bands predicted by ordinary \(sp\) band theory, and the exchange contribution can be expressed as a large effective \( g\) factor, which is given by

\[
\begin{align*}
g_{\text{eff}} &= g^* + \Delta g_{\text{ex}}, \\
\Delta g_{\text{ex}} &= \alpha M/\left( g_{\text{TM}} \mu_B^2 H \right),
\end{align*}
\]

where \( g^* \) is the band \( g \) factor, \( g_{\text{TM}} \) is the \( g \) factor of the 3d ions, \( \alpha \) is the exchange constant, and \( \mu_B \) is the Bohr magneton, that is, \(|\Delta g_{\text{ex}}| > |g^*|\) for wide-gap semiconductors \[33\]. Therefore, the \( s,d\) exchange interaction accompanied by the spin splitting of the conduction band is expected to be dominant in \( \text{In}_{2-x}\text{V}_x\text{O}_3 \). In such a case, magnetic circular dichroism signal at the optical absorption edge should be measurable. Additional measurements which are related to the spin splitting of the 3d orbitals in the valence band. There are differences of XAS spectra measured at In 3p and 3d edges although the O 1s XAS spectrum is independent of V doping. Based on the findings, it is likely that the \( s,d\) exchange interaction is dominant for the ferromagnetism in \( \text{In}_{2-x}\text{V}_x\text{O}_3 \). For light TM-doped \( \text{In}_2\text{O}_3 \), the role of oxygen vacancy has been discussed. The present results point to a need for taking into account hybridization between the host conduction band and 3d orbitals in \( \text{In}_2\text{O}_3\)-based DMS’s, especially for light TM doped ones. We believe that the findings will promote further systematic studies of \( n\)-type oxide-based DMS’s.

In conclusion, we have performed PES and XAS studies of \( \text{In}_{2-x}\text{V}_x\text{O}_3 \) thin films in order to investigate their electronic structure and its relationship with ferromagnetism. From comparison with previous reports, the V 3d ions are expected to be trivalent states, indicating that the V ion substitutes for the In site. The V 3d PDOS in valence band has been observed using RPES technique and shows a sharp peak within the band gap of \( \text{In}_2\text{O}_3 \), implying the localized nature of the V 3d orbitals in the valence band. There are differences of XAS spectra measured at In 3p and 3d edges although the O K XAS spectrum is independent of V doping. Based on the findings, it is likely that the \( s,d\) exchange interaction is dominant for the ferromagnetism in \( \text{In}_{2-x}\text{V}_x\text{O}_3 \). For light TM-doped \( \text{In}_2\text{O}_3 \), the role of oxygen vacancy has been discussed. The present results point to a need for taking into account hybridization between the host conduction band and 3d orbitals in \( \text{In}_2\text{O}_3\)-based DMS’s, especially for light TM doped ones. We believe that the findings will promote further systematic studies of \( n\)-type oxide-based DMS’s.

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