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Hybridization between the conduction band and 3*d* orbitals in the oxide-based diluted magnetic semiconductor $In_{2-x}V_xO_3$

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The electronic structure of $In_{2-x}V_xO_3$ ($x=0.08$) has been investigated by photoemission spectroscopy and x-ray absorption spectroscopy (XAS). The V 2*p* core-level photoemission and XAS spectra revealed that the V ion is in the trivalent state, which is the same valence state as that of In in In_2O_3. The V 3*d* partial density of states obtained by the resonant photoemission technique showed a sharp peak above the O 2*p* band. While the O 1*s* XAS spectrum of $In_{2-x}V_xO_3$ was similar to that of In_2O_3, there were differences in the In 3*p* and 3*d* XAS spectra between the V-doped and pure In_2O_3. The observations give clear evidence for hybridization between the In-derived conduction band and the V 3*d* orbitals in $In_{2-x}V_xO_3$.

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I. INTRODUCTION

Ever since the discovery of carrier-induced ferromagnetism in the III-V diluted magnetic semiconductors (DMS's) $In_{1-x}Mn_xAs$ (Ref. 1) and $Ga_{1-x}Mn_xAs$ (Ref. 2), diluted magnetic semiconductor (DMS) has been one of the key materials for "spin electronics" or "spintronics" because the magnetic interaction between the magnetic ions mediated by carriers enables us to manipulate both the charge and spin degrees of freedom of electrons.[3] Ferromagnetic DMS's having Curie temperatures (T_C's) above room temperature (RT) are strongly desired for realistic spintronic applications of DMS's. A theoretical study based on the *p*-*d*-exchange Zener model has predicted that Mn-doped wide-gap semiconductors GaN and ZnO with high hole concentrations should show ferromagnetism above RT (Ref. 4) and, therefore, DMS's based on wide-gap semiconductors have been studied as candidates for high-T_C DMS's. In fact, RT ferromagnetism in oxide-based DMS's such as $Ti_{1-x}Co_xO_2$,[5] $Sn_{1-x}Co_xO_2$,[6] and $Zn_{1-x}Mn_xO$ (Ref. 7) have been reported so far.

Recently, In_2O_3-based DMS's have attracted much attention because of the observations of RT ferromagnetism not only in light transition-metal(TM)-doped but also in heavy TM-doped In_2O_3 (Refs. 8–20) and also because of the high potential of the host material In_2O_3 for applications. For example, Sn-doped In_2O_3 (ITO) is famous for its high electrical conductivity and transparency.[21,22] Magnetic force microscopy on $In_{2-x}Cr_xO_{3-\delta}$ and $In_{2-x}Ni_xO_3$ has demonstrated that uniform distribution of magnetic domains in these materials.[12,18] The observations of anomalous Hall effects in the In_2O_3-based DMS's suggest that the ferromagnetic properties are related to conducting carriers,[16–20] implying carrier-induced ferromagnetism in the In_2O_3-based DMS's. Here, In_2O_3 has a band gap of 3.5 eV, is an *n*-type semiconductor, and crystallizes in the cubic bixbyite structure, where In atoms are coordinated by six oxygen atoms leading to octahedral (O_h) and orthorhombic (D_{2h}) symmetry and neighboring octahedra are shared with their corners and edges.[23,24]

Photoemission spectroscopy and x-ray absorption spectroscopy (XAS) are powerful tools to investigate electronic structure of materials. In XAS, photoabsorption from a core level to unoccupied states occurs and the electronic structure can be probed in an element-specific way. $2p \rightarrow 3d$ resonant photoemission spectroscopy (RPES) enables us to extract the 3*d* partial density of states (PDOS) in the valence band. In this work, we have performed photoemission and XAS measurements on $In_{2-x}V_xO_3$ (IVO) thin films in order to obtain a fundamental understanding of the magnetic interaction from the electronic structure point of view. The oxidation state of the doped V ion has been determined by core-level x-ray photoemission spectroscopy (XPS) and XAS. Effects of V doping on the electronic structure of the host material In_2O_3 have been revealed by V $2p \rightarrow 3d$ RPES and XAS at the O and In edges.

II. EXPERIMENTAL

Each of In_2O_3 and $In_{2-x}V_xO_3$ ($x=0.08$) thin films was highly oriented normal to the plane of a sapphire (0001) substrate by the pulsed-laser-deposition technique, using sintered ceramic targets In_2O_3 and $In_{1.9}V_{0.1}O_3$, respectively. During the depositions of V-doped and pure In_2O_3 thin films, the substrate temperatures were kept at 673 and 400 °C, respectively, under 1.0 mbar oxygen atmosphere.[14] The total thickness of the deposited layers was several hundred nm. X-ray diffraction confirmed that the thin film had the cubic bixbyite structure and no secondary phase was observed. The V concentration *x* in the film was estimated from the intensity ratio between the V 2*p* and O 1*s* core-level photoemission spectra by comparing with that in V_2O_3. Ferromagnetism above RT in IVO thin film was confirmed by magnetization measurements using a superconducting quantum interference device magnetometer (Quantum Design, Co. Ltd.).

RPES and XAS measurements were performed at the soft x-ray beamline BL23SU of SPring-8.[25] The monochromator

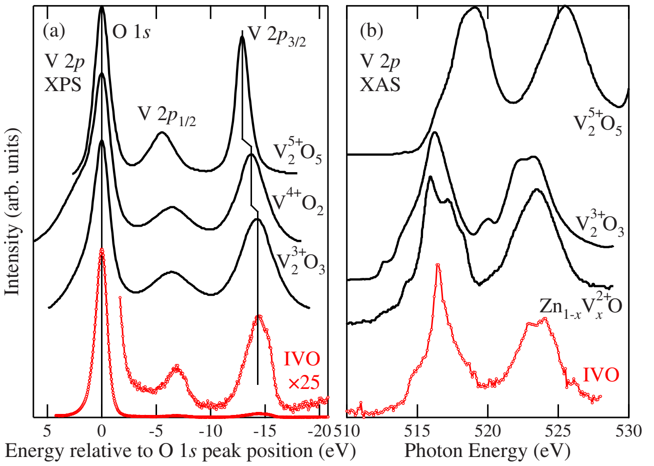

FIG. 1. (Color online) V 2*p* core-level spectra of $In_{2-x}V_xO_3$ (IVO) with $x=0.08$. (a) V 2*p* XPS spectra compared with those of other vanadium oxides (Ref. 27). (b) V 2*p* XAS spectra compared with those of other vanadium oxides $Zn_{1-x}V_xO$ (Ref. 29), V_2O_3 (Ref. 28), and V_2O_5 (Ref. 30).

resolution was $E/\Delta E > 10\,000$. XAS signals were measured by the total-electron-yield method. An Mg-$K\alpha$ x-ray source ($h\nu = 1253.6$ eV) was employed for the XPS measurements. The RPES and XPS measurements were performed in a vacuum below 1.0×10^{-7} Pa using Gammadata Scienta SES-2000 and SES-100 hemispherical analyzers, respectively. The total resolution of the RPES and XPS measurements including temperature broadening were ~300 and ~800 meV, respectively. Sample surfaces were cleaned by repeated Ar^+-ion sputtering.[26] Cleanliness of the sample surface was checked by the absence of a high binding-energy shoulder in the O 1*s* spectrum and C 1*s* contamination. The position of the Fermi level (E_F) was determined by measuring photoemission spectra of evaporated gold which was in electrical contact with the samples.

III. RESULTS AND DISCUSSION

First, we discuss the oxidation state of the V ions in IVO. Figure 1 shows the V 2*p* core-level spectra of IVO and various vanadium oxides. In general, the binding energy (E_B) of a core-level peak position is related to its charge state and becomes larger with increasing oxidation state. Indeed, it has been reported that the E_B of the V $2p_{3/2}$ peak increases with oxidation state of V as shown in Fig. 1(a).[27] By comparing the V $2p_{3/2}$ core-level peak position of IVO with those of the other vanadium oxides, the V $2p_{3/2}$ peak position of IVO is almost the same as that of V_2O_3 (V^{3+}). 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_2O_3 (V^{3+}) (Ref. 28) rather than that of $Zn_{1-x}V_xO$ (V^{2+}) (Ref. 29) and V_2O_5 (V^{5+}) (Ref. 30) consistent with the observation from the V 2*p* XPS. The results suggest that the electronic structure of the V ion in IVO is close to that in V_2O_3, i.e., the V ion is in the trivalent V^{3+} (d^2) state octahedrally coordinated by oxygen atoms. Therefore, it is likely that the doped V ions substitute for the In sites.

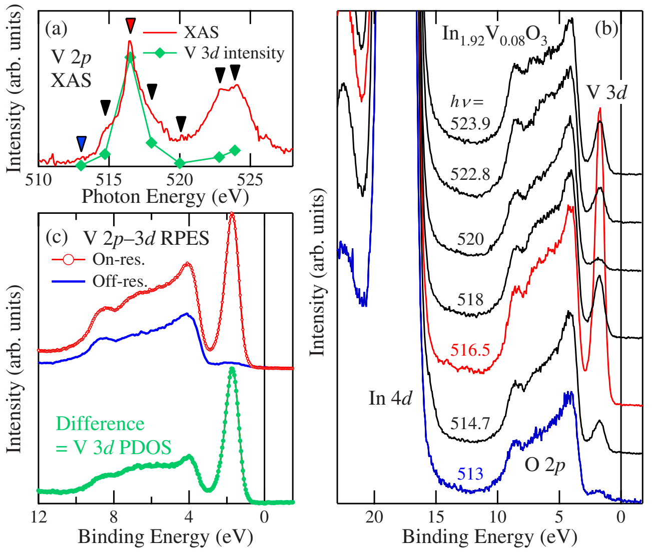

FIG. 2. (Color online) V $2p \rightarrow 3d$ resonant photoemission spectra in the valence band of $In_{2-x}V_xO_3$ ($x=0.08$). (a) V 2*p* XAS spectrum and the intensity of the V 3*d* peak at $E_B = 1.7$ eV as functions of photon energy ($h\nu$). (b) A series of spectra measured at $h\nu$'s denoted by triangles in (a). (c) Top: On-($h\nu = 516.5$ 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).

In order to study the electronic structure of the V 3*d* states in the valence band, we measured V $2p \rightarrow 3d$ RPES spectra of IVO. Figure 2 shows the V $2p \rightarrow 3d$ RPES spectra of the valence band of IVO. As shown in Fig. 2(b), the valence-band spectra demonstrate clear V $2p \rightarrow 3d$ resonant enhancement. The photoemission intensity as a function of photon energy ($h\nu$), i.e., constant-initial-state (CIS) spectrum, at $E_B = 1.7$ eV shows that the enhancement is nearly proportional to the intensity of the V 2*p* XAS as shown in Fig. 2(a). Although the relative intensities of different spectral features change with photon energy due to the effects of transition-matrix elements, the position of the dominant peak at $E_B \simeq 2$ eV in the V $2p \rightarrow 3d$ absorption region is independent of photon energy, implying that the V ions are in a single electronic state. The spectra measured at $h\nu = 516.5$ eV and 513 eV were chosen as the on- and off-resonance spectra, respectively. The V 3*d* PDOS has been extracted from the difference between the on- and the off-resonance spectra [Fig. 2(c)]. The V 3*d* PDOS shows a peak at $E_B \simeq 2$ eV, i.e., in the middle of the band gap of In_2O_3. The narrow width (full width at half maximum is of ~1.04 eV) and strong intensity of the peak imply the localized nature of the V 3*d* electrons in the valence band, i.e., weak V 3*d*-O 2*p* hybridization in IVO.

Energy difference between the top of the O 2*p* bands and E_F is ~3.0 eV as shown in Fig. 2(b) and is comparable to the band gap of In_2O_3 3.5 eV, indicating that E_F is located near the bottom of the conduction band in the IVO thin film. With regard to *n*-type DMS's, it is likely that electronic states near the bottom of the conduction band are important for carrier-induced ferromagnetism. XAS spectra measured at the absorption edges of the host semiconductor reflect the

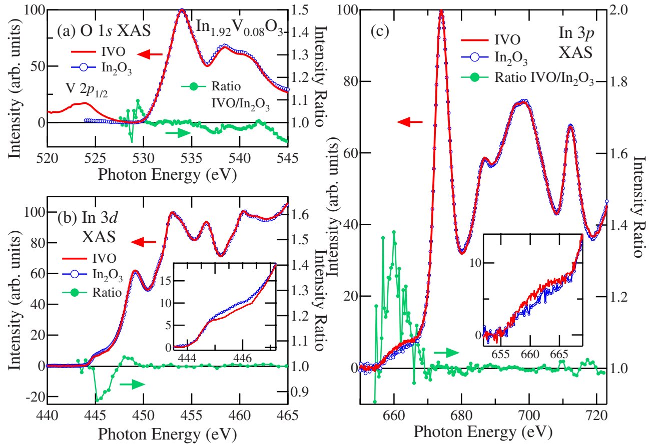

FIG. 3. (Color online) X-ray absorption spectra of $In_{2-x}V_xO_3$ (IVO) with $x=0.08$ measured at the In $3p$, In $3d$, and O $1s$ absorption edges. The ratio of intensity between IVO and In_2O_3 are also plotted. (a) O K XAS spectra. (b) and (c) In $3d$ and $3p$ XAS spectra, respectively. The insets show enlarged plots in the pre-edge region.

unoccupied electronic states, namely, the conduction band. Figure 3 shows XAS spectra of V-doped and pure In_2O_3 measured at the In $3p$, In $3d$, and O $1s$ absorption edges, and the ratio of XAS intensity between IVO and In_2O_3. The O $1s$ XAS spectrum of IVO is nearly identical to that of In_2O_3, and the ratio of intensity between IVO and In_2O_3 is nearly unity within the noise level [Fig. 3(a)]. It has been reported that the O $1s$ XAS spectrum of Fe-doped In_2O_3 differs from that of pure In_2O_3 and that the difference is induced by hybridization of the Fe $3d$ orbitals with the O $2p$ band.[15] The present 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 $In_{2-x}Fe_xO_3$, consistent with the result of the V $2p \rightarrow 3d$ RPES. In contrast, as shown in Figs. 3(b) and 3(c), the In $3p$ and $3d$ XAS spectra change with V doping, i.e., there are finite differences between the XAS spectra of IVO and those of pure In_2O_3. The intensity ratios clearly indicate that the changes of electronic structure occur in the In $3p$ and $3d$ pre-edge regions. The observations suggest hybridization between the In $5sp$-derived conduction band and the V $3d$ orbitals in IVO.

Based on the hybridization between In-derived conduction band and V $3d$ orbital described above, we shall discuss the electronic structure of the In_2O_3-based DMS's. The $3d$ levels of a TM atom octahedrally coordinated by oxygen atoms split into twofold-degenerate e_g and threefold-degenerate t_{2g} levels. In IVO, the V^{3+} ($3d^2$) ion substituting for the In site has two electrons in the t_{2g} levels (or the two lowest levels split 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, the O $2p$ band hybridizes with the e_g orbitals more strongly than the t_{2g} orbitals. Actually, 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] From the observation of the O $1s$ XAS spectra unaffected by V doping, hybridization between the O $2p$ band and the e_g orbitals is probably weak. In contrast to the e_g orbitals, the t_{2g} orbitals are directed toward the In atoms [Fig. 4(b)] and then it is likely that the t_{2g} orbitals hybridize strongly with the In band. Note that light TM ions such as Ti^{3+} and Cr^{3+} in the O_h crystal field only have electron(s) in the t_{2g} levels. Since the extent of $3d$ orbitals diminishes with increasing number of $3d$ electrons, the hybridization between In-derived conduction band and $3d$ orbital may be weakened in heavy TM-doped In_2O_3 DMS's such as $In_{2-x}Fe_xO_3$. It follows from those arguments that for light TM-doped In_2O_3, hybridization between the In-derived conduction band and the $3d\ t_{2g}$ orbitals should be taken into consideration to understand their electronic properties.

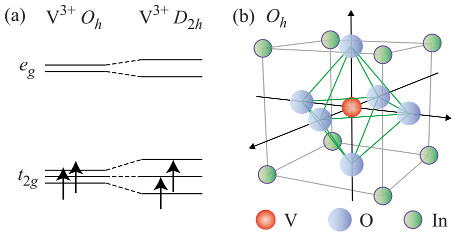

FIG. 4. (Color online) $3d$ electronic structure of the V ion of $In_{2-x}V_xO_3$. (a) A schematic representation of the electronic structure in the V ion. (b) Octahedral coordination of the O atoms to the V atom and the nearest-neighbor In atoms.

Now we shall discuss the mechanism of the ferromagnetism in $In_{2-x}V_xO$ and In_2O_3-based DMS. For n-type DMS's, s-d exchange and/or donor-impurity band exchange interactions are considered as origins of the carrier-induced ferromagnetism.[32,33] In the donor-impurity band exchange model,[32] when the $3d$ orbitals hybridize with the impurity band formed by donor defects such as oxygen vacancies and E_F is located within the impurity band, the binding of electron carriers around the defects leads to the formation of bound magnetic polarons. However, since no indication of impurity band near E_F is observed in the RPES and XAS spectra, we consider that the donor-impurity band exchange is hardly effective in IVO. The spin splitting of the conduction band is proportional to the s-d-exchange constant $N_0\alpha$.[34] The bottom of the conduction band of In_2O_3 is mainly composed of the In $5s$ states.[23] Taking into account the n-type nature of IVO, the conduction-band minimum composed of the In states, and the hybridization between the In-driven conduction band and the V $3d$ orbitals, the s-d-exchange interaction accompanied by the spin splitting of the conduction band will be dominant in the magnetism of $In_{2-x}V_xO_3$.

In II-VI DMS's, the s-d-exchange constant $N_0\alpha$ is small and weakly dependent both on the magnetic ion and the host semiconductor.[34] The typical value of $N_0\alpha$ in II-VI DMS's is of ~ 0.2 eV while the value of p-d-exchange constant $N_0\beta$ in $Ga_{1-x}Mn_xAs$ ($T_C < 200$ K) is of ~ -1.0 eV.[35] In the case of IVO, hybridization between the In-derived conduction band and the V $3d$ orbital may increase the strength of s-d-exchange interaction. As in the present case, carrier-induced ferromagnetic interaction in n-type $Ti_{1-x}Co_xO_2$ is considered to be caused by hybridization between the host conduction band and the Co $3d$ orbital.[36] In addition, there is a possibility that oxygen vacancies strengthen the hybridization in the In_2O_3-based DMS, where oxygen vacancies are major defects and act as double donors. A first-principles electronic-structure calculation of In_2O_3 has predicted that when electrons are localized around the oxygen vacancy, the In-In bond is reinforced remarkably while the In-O bond is significantly weakened.[23] Considering this result together with the experimental findings, it is possible that besides the increase in electron-carrier concentration, the presence of oxygen vacancy augments the exchange interaction between the In-derived conduction band and the TM 3*d* orbitals in In_2O_3-based DMS's. In fact, for light TM-doped In_2O_3 DMS's, there are several studies demonstrating relationship between ferromagnetism and oxygen vacancies.[18,37] On the other hand, there is a report that the saturation magnetization of IVO increases with higher-growth oxygen pressure which is expected to suppress the generation of oxygen vacancies[14] and the report is inconsistent with this consideration. In order to resolve this apparent inconsistency, further systematic studies of In_2O_3-based DMS's with independently controlled oxygen vacancies and carrier concentrations are desirable.

IV. CONCLUSION

We have performed photoemission and XAS studies of $In_{2-x}V_xO_3$ thin films in order to investigate their electronic structure and its relationship with ferromagnetism. From comparison with previous reports, the V 3*d* ions are expected to be trivalent. The V 3*d* PDOS in the valence band has been obtained using RPES technique. The PDOS shows a sharp peak within the band gap of In_2O_3, implying the localized nature of the V 3*d* orbitals in the valence band. In going from In_2O_3 to IVO, there were changes in the XAS spectra measured at the In 3*p* and 3*d* edges while the O *K* XAS spectrum remained almost unchanged. Therefore, it is likely that the *s*-*d*-exchange interaction is dominant and is responsible for the ferromagnetism in $In_{2-x}V_xO_3$. The present results point to a need for taking into account hybridization between the host conduction band and 3*d* orbitals in In_2O_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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