The structural, optical and magnetic properties and anomalous Hall effect of InMnP:Zn epilayers

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Abstract. The structural, optical, magnetic and magnetoelectrical transport properties of p-type InMnP:Zn (Mn: 0.019–0.290 at.%) epilayers, which had been prepared by thermal diffusion of Mn through molecular-beam-epitaxial deposition of Mn onto InP:Zn epilayers grown by metal-organic chemical vapor deposition and subsequent annealing of the samples, were systematically investigated. For analyses of structural properties, it was observed that the x-ray diffraction peaks of MnO₂ for InMnP:Zn epilayers coincide with the P4̅32/mmm structure of MnO₂ proved by the electron diffraction analysis of transmission electron microscopy (TEM). For photoluminescence measurements, it was found that broad optical transitions related to Mn appear at 1.247 eV (Eᵥ + 0.173 eV) and 1.261 eV (Eᵥ + 0.159 eV), which are based on a band gap energy of 1.42 eV at 0 K. The samples revealed that in both the experimental pattern of TEM and the calculated diffraction pattern, {010} and {030} spots are missing, indicating that the FCC lattice was still maintained after the Mn doping. The forbidden, regularly spaced spots suggest the presence of a superlattice (a = 11.738 Å), arising from the possible ordering of Mn atoms in the cubic structure of InP. The regularly spaced spots of ordered Mn produce the anomalous Hall

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effect (AHE) showing the characteristics of a diluted magnetic semiconductor (DMS), which is caused by hole-mediated ferromagnetism due to the increase of hole concentration in the tetrahedrally coordinated semiconductor. The transition from the ferromagnetic state to the paramagnetic state observed at \( \sim 150 \) K in AHE measurements was confirmed to be almost consistent with the ferromagnetic transition temperature \( (T_C) \) using superconducting quantum interference device measurements. These results suggest that an InP-based ferromagnetic semiconductor having relatively high \( T_C \) can be successfully formed based on InMnP:Zn epilayers in a category of DMSs.

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1. Introduction

In the field of pure compound semiconductors, InP having good physical properties has been regarded as one of the most representative compound semiconductors. Meanwhile, in the field of diluted magnetic semiconductors (DMSs), although the Curie temperature \( (T_C) \) of InP-based DMSs is theoretically predicted to be low \( (T_C \sim 50 \) K for InMnP), the incorporation of the 3d transition metal Mn into InP is of considerable interest, since they have been theoretically predicted to form a proper DMS [1] based on ferromagnetic correlation mediated by holes. Mn is a well-behaved acceptor suitable for making p-type materials in Mn-doped InP and has small ionization energy in InP compared with the other transition metals [2]. DMSs based on III–V and II–VI compound semiconductors such as GaAs, InAs, GaN and GaP, the digital alloy system based on GaSb, and quantum dots based on InMnAs, AlN and ZnO have been studied since 1989 [3]–[13]. Most of the materials indicated above have shown a high \( T_C \) of about room temperature except for GaAs and InAs \( (T_C \sim 110–170 \) K [14]), which are confirmed by the anomalous Hall effect (AHE) so as to show decisively the accomplishment of DMS without any other precipitates. If any materials based on DMS contain precipitates, it is hard to obtain AHE and to demonstrate the formation of DMS. Therefore, in the field of DMS, exact and overall measurement and analysis including AHE are strongly required. Papers dealing with InP-based DMSs have started being published recently, in particular with regard to InMnP, but reports focused on confirming whether ferromagnetism based on InMnP can be actually formed or not are lacking. In other words, although ferromagnetism has been obtained from InMnP DMSs [15]–[18], further systematic investigations into the more exact physical origin of ferromagnetism have not been carried out.

In this paper, we report our data on the formation of the ferromagnetic semiconductor InMnP:Zn whose \( T_C \) persists up to \( \sim 150 \) K and its various physical properties including structural, microstructural, optical, magnetic and magnetoelectrical transport properties.
The samples were prepared by thermal diffusion of Mn into Zn-codoped p-type InP epilayers, which had been grown by metal–organic chemical vapor deposition (MOCVD), and the physical properties of the samples were investigated by means of x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), photoluminescence (PL), transmission electron microscopy (TEM), AHE and superconducting quantum interference device (SQUID) measurements.

2. Experimental details

The p-type InP epilayers doped with Zn were grown on semi-insulating (001) InP substrates at 650 °C using trimethylindium (TMIn) and phosphine (PH$_3$) by MOCVD. Diethylzinc (DEZn) was used as a precursor of acceptor dopants. The thickness of InP:Zn epilayers was ∼3 µm. After the growth of InP:Zn, the samples showed p-type conductivity with a hole concentration of $2.0 \times 10^{18}$ cm$^{-3}$ for Hall effect measurements. The resistivity of the samples was approximately $2.92 \times 10^{-2}$ Ω cm. Onto the p-type InP:Zn epilayers, high-purity Mn (99.9999%) was evaporated using molecular beam epitaxy (MBE) in an ultra-high vacuum ($\sim 10^{-10}$ Torr) system. Before the Mn deposition in the MBE system, similar to the deoxidation process during the growth of GaAs epilayers using MBE, a thermal etching process at $\sim 500$ °C was performed in order to remove the surface oxide that might be formed during the transfer of the sample from the MOCVD chamber to the MBE chamber. After the deoxidation process, the evaporation of Mn was carried out for various times (30–180 s) at room temperature. Subsequently, the samples were annealed at 300 °C for 30 min in N$_2$ atmosphere. Low-temperature annealing at the growth temperature (650 °C) of InP:Zn epilayers was undertaken in order to suppress the interdiffusion of In and P in the InP:Zn epilayer and consequently to prevent the formation of precipitates such as InMn and MnP. After the formation of InMnP:Zn epilayers, the samples showed very high p-type conductivity with a hole concentration of $\sim 10^{19}$ cm$^{-3}$ for Hall effect measurements at room temperature. Here, it should be noted that the obtained value of hole concentration is not exactly correct but roughly estimated. This is because it is difficult to determine the exact carrier concentration even if an extremely high magnetic field ($> 22$ T) is applied when the carrier concentration is high, in particular for ferromagnetic semiconductor layers [19]. Furthermore, our samples consist of a bilayer system of thin InMnP/thick InP. The thickness of the Mn-incorporated layer was confirmed to be ∼20 nm by means of Auger electron spectroscopy measurements. The compositional fraction of Mn components was confirmed by XPS measurements, and in this study, we show data on two samples having different Mn concentrations. One is InMnP:Zn (Mn ∼ 0.062 at.%), and the other is InMnP:Zn (Mn ∼ 0.290 at.%). XRD patterns were measured in order to confirm the existence of possible secondary phases, and TEM measurements were carried out so as to investigate lattice structures. Temperature-dependent PL measurements at 10–200 K for determining the energy level of Mn acceptors were performed using a 75 cm monochromator with an RCA31034 photomultiplier tube, and the excitation source was a 632.8 nm line of a He–Ne laser. Magnetoelectrical transport properties were examined by AHE measurements and magnetic properties were characterized by SQUID measurements.

3. Results and discussion

Figure 1 shows the XPS spectra measured after the thermal doping of Mn into the InP:Zn epilayers subsequent to the evaporation of Mn onto the InP:Zn epilayers using MBE. Indeed,
we prepared several kinds of samples with various Mn concentrations ranging from 0.019 to 0.290%. Among those samples, the ones with Mn concentrations of 0.290 and 0.062% showed ordered Mn-related spots in the electron diffraction pattern and the AHE, revealing the characteristics of DMS, whereas other samples did not show ordered Mn-related spots and the AHE. Thus, our discussion will be focused on those two samples. As represented in figure 1, the sample with Mn evaporation for 3 min exhibits Mn 2p peaks from which the molar concentration was determined to be 0.290%, and the sample with Mn evaporation for 1 min had an Mn molar concentration of 0.062%. The samples with Mn 2p concentrations of 0.290 and 0.062% showed O 1s peaks, but the intensities of the O 1s peaks were very small. MnO$_2$ analyzed by XRD and TEM, which will be discussed later, is caused by O 1s and Mn 2p. The intensity of O 1s with an Mn concentration of 0.062% is much smaller than that of O 1s with an Mn concentration of 0.290%. These results agree with the result that the intensity of MnO$_2$ measured by XRD is reduced because of the lower concentrations of O 1s and Mn 2p.

Figure 2 shows the XRD patterns measured so as to confirm the unwanted secondary phases such as Mn$_3$In, MnP, MnO and MnO$_2$ for the InMnP:Zn epilayers. The possible precipitates in InMnP:Zn include MnP, Mn$_2$P and MnP$_4$. MnP and Mn$_2$P are ferromagnetic with a $T_C$ of 291 K and antiferromagnetic with a Neel temperature ($T_N$) of 103 K, respectively. MnP$_4$ is diamagnetic. The compound Mn$_3$In has a $\beta$-brass-type crystal structure and is weakly ferrimagnetic below its Curie point at 583 K. The Mn oxides of MnO, MnO$_2$ and Mn$_2$O$_3$ are antiferromagnetic with a $T_N$ of 116, 84 and 90 K, respectively. As shown in figure 2, the InMnP:Zn samples with Mn concentrations of 0.290 and 0.062% show some additional peaks, in contrast with the reference sample of InP:Zn. The peaks at 41.464°, 46.840° and 56.885° correspond to MnO$_2$ indexed to (211), (311) and (402), respectively, suggesting the presence of MnO$_2$ for the InMnP:Zn samples.

The XRD peaks coincide with the P4$_2$/mmm structure of MnO$_2$, also proved by the electron diffraction analysis of TEM. These data are typical of all samples without showing
any other precipitates. MnO$_2$ is a rutile-type magnetic oxide. Rutile is the name of the oxide TiO$_2$. Replacing Ti by 3d transition metal ions such as Cr and Mn, we have the rutile-type magnetic oxides and a typical example is CrO$_2$, which is ferromagnetic with the Curie point at 390–400 K, but MnO$_2$ is antiferromagnetic. The presence of antiferromagnetic MnO$_2$ weakened the ferromagnetism in InMnP and, as a result, led to a $T_C$ of about 150 K and the weak ferromagnetic hysteresis loop, which will be discussed later. However, the observed $T_C$ is still higher than the theoretical value ($\sim$50 K) calculated with the Mn concentration of 5% per cation in 2$^+$ charge state and $3.5 \times 10^{20}$ holes cm$^{-3}$ [1].

Figure 3 shows the electron diffraction patterns of TEM taken from samples of (a) a bare InP:Zn epilayer (reference sample) and InMnP:Zn epilayers with Mn concentration of (b) 0.062% and (c) 0.290% in the 001 zone direction. Except for the bare InP:Zn epilayer, all the diffraction patterns contain a ring pattern due to the presence of MnO$_2$ on the surface. The ring patterns indexed in figures 3(b) and (c) correspond to the P$_{4/2}/mmm$ structure of MnO$_2$ in agreement with the XRD measurements. In addition, the diffraction patterns from figures 3(b) and (c) also exhibit regularly spaced extra spots, some of which have been indicated by the red circles for clarification. It was noted that these spots are absent from the other samples, which did not exhibit the DMS characteristics as demonstrated by AHE. InMnP:Zn epilayers reveal regularly spaced extra spots and this result indicates that Mn ions are well incorporated into the host InP lattice, which will lead to the Mn-related PL emission as discussed later. InP lattice has a zinc-blende structure (F43m, $a = 5.869$ Å), in which the In atoms occupy the normal FCC lattice with the P atoms occupying one-half of the available tetrahedral interstitial sites on the body diagonal. With the usual extinction rule for a FCC lattice, $\{100\}$ and $\{110\}$ and their odd multiple peaks should be absent from the diffraction pattern. The forbidden extra spots in figures 3(b) and (c) suggest the presence of a superlattice, arising from possible ordering of Mn atoms in the cubic structure of InP [20].
Figure 3. (a–c) Electron diffraction patterns of TEM taken from (a) the as-grown InP:Zn and the InMnP:Zn epilayers with Mn concentrations of (b) 0.062% and (c) 0.290%. (d) Schematic diagram of 1/2 of the BCC superlattice unit cell related to Mn order. Dotted lines show the original InP unit cell. (e) Schematic projection of the InP lattice in the [001] direction with Mn atoms lying on the 000 site of every other InP unit cell (Mn atoms with ‘+’ sign lie 5.869 Å below the ‘−’-labeled atoms). (f) Calculated diffraction pattern resulting from the ordered incorporation of Mn. (g) Cross-sectional TEM with the Mn concentration of 0.290%.
The intensity of a diffracted beam from a \((hkl)\) plane is proportional to the square of the structure factor as below:

\[
I_{\text{diffracted}} \propto |F_{hkl}|^2,
\]

\[
F_{hkl} = \sum_i f_i \exp \left[2\pi i \left(hx + ky + lz\right)\right],
\]

(1)

where \(f_i\) is the atomic scattering factor and \(x, y\) and \(z\) are the fractional coordinates of each atom. The diffracted beam intensity can be estimated using equation (1). The structure factor of the \((\bar{3}10)\) peak in a normal InP lattice can be calculated with In atoms at 000, 0\(\frac{1}{2}\)\(\frac{1}{2}\), \(\frac{1}{2}\)\(\frac{1}{2}\), \(\frac{1}{2}\)0 and P atoms at \(\frac{1}{2}\)\(\frac{1}{2}\)\(\frac{1}{2}\), \(\frac{1}{2}\)\(\frac{1}{2}\)\(\frac{1}{2}\) and \(\frac{1}{2}\)\(\frac{1}{2}\)\(\frac{1}{2}\):

\[
F_{\bar{3}10} = f_n \left[ e^{2\pi i (0)} + e^{2\pi i (1/2)} + e^{2\pi i (-3/2)} + e^{2\pi i (-1)} \right]
+ f_p \left[ e^{2\pi i ((-3/4)+(1/4))} + e^{2\pi i ((-3/4)+(3/4))} + e^{2\pi i ((-9/4)+(1/4))} + e^{2\pi i ((-9/4)+(3/4))} \right] = 0.
\]

(2)

Thus, \(F_{\bar{3}10}\) is zero in a normal InP lattice so that the \((\bar{3}10)\) peak should be a forbidden peak in the InP lattice as expected. Excitation of such forbidden peaks in figures 3(b) and (c) is indicative of a superlattice in which Mn atoms are substituted into In sites in an ordered manner. One possible solution for the diffraction pattern is provided if Mn atoms were to replace In on the 0,0,0 site of every other InP unit cell, creating a superlattice BCC unit cell \((a = 11.738\ \text{Å})\) related to Mn order, as shown in figure 3(d). In such a structure, \(F_{\bar{3}10}\) would no longer be zero as can be seen from equation (2). Based on experimental data and analysis, figure 3(e) shows the schematic projection of the InP lattice in the [001] direction with Mn atoms occupying the 000 site of every other InP unit cell. Normal InP unit cell without the Mn atoms, outlined by dotted lines in cyan color, would produce the calculated spot pattern (black spots labeled in blue) in figure 3(f), which matches the experimental diffraction patterns in figures 3(a)–(c). If Mn atoms were to ideally occupy the 000 site of every other InP unit cell, these new Mn site occupations in the original InP lattice would create a BCC superlattice. The BCC superlattice will generate extra spots in the reciprocal space, which are forbidden in the normal FCC lattice as the real space lattice in figure 3(e) is Fourier-transformed. The calculated diffraction pattern resulting from the ordered incorporation of Mn is shown in figure 3(f) with its indexed extra spots (gray spots). The calculated diffraction pattern in figure 3(f) assuming an ideally ordered Mn site occupation closely matches the experimental diffraction patterns in figures 3(b) and (c). The diffraction patterns in figures 3(b) and (c) suggest that most of the doped Mn atoms in the samples with Mn at 0.062 and 0.290% formed an ordered structure. In addition to the plan view TEM analysis, cross-sectional TEM analysis was carried out to check the presence of secondary phases. The cross-sectional image shown in figure 3(g) verifies that secondary phases resulting from the Mn incorporation were not produced.

Figure 4 shows PL spectra measured at 16 K for the as-grown InP:Zn epilayer (inset) and the InMnP:Zn epilayers with Mn concentrations of 0.290 and 0.062%. For the as-grown InP:Zn epilayer, the peak at 1.40 eV belongs to the acceptor-bound exciton (\(A^0\)-X). The peak at 1.38 eV is regarded as the donor–acceptor (D–A) pair transition. The peak at 1.38 eV, which is usually referred to as the A1 peak, frequently appears in InP grown by various methods and until recently was attributed to carbon as the acceptor. The peak at 1.38 eV is usually an unidentified donor–carbon acceptor pair transition. With regard to the above transition, the first phonon replica appeared near 1.34 eV. In view of the XPS result, the candidate for donor is the phosphorus vacancy because the molar concentration of P is slightly lower than that of In. The peak related to Zn appeared around 1.20 eV. After doping of Mn, the InMnP:Zn epilayers
showed an asymmetrical broad band at $\sim$1.25 eV related to Mn along with the disappearance of peak from the Zn-related band. In relation to Mn-related transitions, there are ferromagnetic types of Mn centers possibly formed in III–V compounds.

Type I: the first type of neutral Mn center (A$^0$) is substitutional Mn$^{3+}$Ga (d$^4$) with the ground-state spin $S$ = 2 and its related transition was found mainly in GaP:Mn [21].

Type II: the second type of neutral Mn center (A$^0$) is [d$^4$ core + e (tightly bound electron)] +h (weakly bound hole, binding energy = 0.113 eV in the case of GaAs:Mn) $\rightarrow$ Mn$^{2+}_{Ga}$ (d$^5$) + h with the ground state total angular momentum $J$ = 4 and has the properties of ferromagnetic semiconductors, and was found in some bulk GaAs:Mn and InP:Mn samples [21]–[23].

Type III: the third type of Mn center is the ionized Mn$^{2+}_{Ga}$ center (A$^-$) with the ground-state spin $S$ = 5/2, dissociation of hole from type II, and was found in GaP:Mn, GaAs:Mn bulks, and GaAs:Mn, InAs:Mn epilayers: i.e. Mn$^{3+}_{Ga}$ (3d$^4$) + h$\nu$ $\rightarrow$ Mn$^{2+}_{Ga}$ (3d$^5$) + hole = A$^0$ + h$\nu$ $\rightarrow$ A$^-$ + hole.

The peak position of the transition related to the Mn band blue-shifts, and the intensity of the peak increases with increasing Mn concentration. This result was confirmed to be due to type II, because the increase of hole carrier concentration was confirmed by Hall effect, by comparing the ratio of A1 peak intensity with the ratio of Mn peak intensity.

We confirmed the existence of Mn-related bands [(e,Mn) and (D,Mn)] for GaAs and GaN doped with Mn and Fe [24]–[28], where (e,Mn) and (D,Mn) mean a conduction band–Mn acceptor transition and a donor–Mn acceptor pair transition (D–A pair), by the analysis of temperature-dependent PL spectra and multiple oscillator fittings. We observed the transition at 1.185 eV in unintentionally doped n-type InP bulk implanted with various doses ($5 \times 10^{12}$–$5 \times 10^{16}$ cm$^{-2}$ = 10%) of Mn [15, 29] and we also observed the transitions around 1.2 eV in p-type

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**Figure 4.** PL spectra measured at 16 K for the as-grown InP:Zn (inset) and the InMnP:Zn epilayers with Mn concentrations of 0.062 and 0.290%. 

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Figure 5. Energy level schemes for Mn and Fe acceptor bands in (a) GaAs, (b) GaN and (c) InP. The $E_c$ and $E_v$ denote the conduction band minimum and valence band maximum, respectively.

InP:Zn bulks and epilayers doped with Mn [16, 17]. A range of binding energies from 0.14 to 0.40 eV for the Mn center was reported [30]. Figure 5 shows the total energy level schemes for (a) GaAs, (b) GaN and (c) InP doped with Mn or Fe studied until now. For Mn-doped InP, the broad peaks at 1.247 eV and 1.261 eV appear to arise from the recombination of free electrons or electrons bound to donors with holes bound at a state that is at the energies of 0.173 and 0.159 eV above the valence band edge in terms of an energy level scheme for Mn, namely peaks at 1.247 eV ($E_v + 0.173$ eV) and 1.261 eV ($E_v + 0.159$ eV) based on a band gap energy of 1.42 eV at 0 K.

In order to finally identify the Mn-related band and to find the activation of Mn$^{2+}$In$^{(3d^5)}$ + hole by the above type II process, we have carried out temperature-dependent PL measurements. Figure 6 shows the temperature-dependent PL spectra of the sample with the Mn concentration of 0.290%. With an increase in the temperature, the band of 1.261 eV ($E_v + 0.159$ eV) related to Mn disappeared gradually and simultaneously the D–A pairs (A1 peak) at 1.38 eV also disappeared gradually. The Mn-related band persists up to about 150 K and the transition entirely disappears above 150 K. These results confirm the activation of Mn$^{2+}$In$^{(3d^5)}$ + hole up to about 150 K.

The magnetoelectrical transport properties for InMnP:Zn were characterized by AHE measurements at various temperatures. The AHE means the effect of spin–orbital interaction.
by spin-polarized carriers and is expressed by the following formula:

\[ \rho_{xy} = R_H B + R_A M, \]  

where \( R_H \) is the ordinary Hall coefficient, \( R_A \) is the anomalous Hall coefficient and \( M \) is the magnetization [31]. Figure 7(a) shows the Hall resistivity of the sample with the Mn concentration of 0.290%. The sample reveals p-type conductivity with a hole concentration of approximately \( \sim 6 \times 10^{19} \text{ cm}^{-3} \). The AHE appears and is dominant up to 150 K and is saturated above an external magnetic field of 1 T. AHE disappears above 150 K and only the ordinary Hall effect appears due to the ordinary Hall coefficient, \( R_H \). Figure 7(b) shows the Hall resistivity of the sample with the lower Mn concentration of 0.062%. The sample also reveals p-type conductivity. The sample with the lower Mn concentration of 0.062% shows a similar trend to the sample with 0.290%, but AHE persists up to the lower temperature of 100 K. With regard to the interpretation of the origin of ferromagnetism in DMS materials, indeed there are so many arguments and these are still controversial. So, at the moment, it is difficult to find out the exact mechanism behind the observed ferromagnetism in our samples. However, from an experimental viewpoint, we think that the observed ferromagnetism in our samples follows the trend of some theoretical results. According to the mean-field model of ferromagnetism in
p-type zinc-blende semiconductors, which contain a sizable concentration of magnetic ions, the strong spin–orbit and k-p couplings in the valence band as well as the influence of strain on the hole density of states strongly affect ferromagnetism in the semiconductors. In addition, it has been argued that over the relevant range of hole densities, the ferromagnetic coupling between the localized spins is primarily mediated by delocalized or weakly localized holes residing in a p-like valence band. Therefore, based on AHE results, one can expect that the $T_C$ values of the two samples are about 100 and 150 K, respectively. It is confirmed that the $T_C$ of InMnP:Zn epilayers is about 150 K by the AHE showing spin–orbital interaction by spin-polarized holes to date. In addition, we indeed found that other samples show neither AHE nor regularly spaced spots of ordered Mn in the electron diffraction patterns of TEM. Therefore, these results of AHE appearing in only two samples agree with the electron diffraction pattern in which the spots of ordered Mn appeared only in the same sample as above. Namely, the regularly spaced spots of ordered Mn produce the AHE of spin–orbital interaction by spin-polarized holes. In relation to the observed ferromagnetism with some possible secondary phases, we know that the possibility

**Figure 7.** Magnetic field dependence of resistivity as a function of temperature for InMnP:Zn epilayers with (a) 0.062% and (b) 0.290%.

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of ferromagnetism from nanosized ferromagnetic clusters, such as MnP or MnIn, cannot be totally ruled out. However, the AHE may not be observed in our samples if the ferromagnetism in our samples were predominately from those phases. This is because metastable clusters in the host semiconductor lattice would generally not reveal the AHE even if we assume that the host material is not ferromagnetic but only clusters are ferromagnetic. Thus, we believe that the observed ferromagnetism is from InMnP DMS layers.

In view of the results of XRD, TEM, PL and AHE, the magnetic property was finally characterized by SQUID magnetometer measurements. Figure 8 shows temperature-dependent magnetization (M–T) curves of the samples with an Mn concentration of 0.290%. The sample displayed a ferromagnetic behavior persisting up to ∼150 K and this value corresponds to that obtained by AHE measurements, indicating that the Tc of the sample is ∼150 K. The ferromagnetic state can also be confirmed by observing the magnetic hysteresis behavior. The inset of figure 8 shows the magnetic field-dependent magnetization (M–H) curves measured at 10 K for the samples with Mn concentrations of 0.062 and 0.290%. A relatively weak ferromagnetic hysteresis loop appears in the sample with an Mn concentration of 0.062%, and the coercive field (Hc) and the remanent magnetization (Mr) were 196 Oe and 0.55µB/Mn site, respectively. This result is attributed to the contribution of antiferromagnetic MnO2 appearing in XRD and TEM and also agrees with the result that the Tc of AHE is low, ∼100 K. With increasing the Mn concentration from 0.290%, increased ferromagnetic hysteresis loop appears in comparison with the previous sample. Hc and Mr are increased to 238 Oe and 0.67µB/Mn site, respectively, and the saturation magnetization is 2.47µB/Mn site. Although this sample also involves the antiferromagnetic MnO2 shown in XRD, the improved ferromagnetic hysteresis loop is caused by the increase of Mn concentration and is also supported by the fact that the Tc of the AHE increases to about 150 K. Furthermore, the contribution of the magnetic moment of each Mn ion to the InMnP:Zn solid-state system is comparable with the values observed usually for zinc-blende GaMnAs ferromagnetic semiconductor epilayers [32]–[34]. As a result, based
on the results of XRD, TEM, PL, AHE and SQUID, we can conjecture that ferromagnetism in our samples is carrier-mediated by holes and that an InP-based DMS with increased $T_C$ ($\sim 150$ K) can be formed in the form of Mn- and Zn-codoped InMnP:Zn epilayers.

4. Conclusions

The MnO$_2$ of XRD peaks observed from InMnP:Zn epilayers with Mn concentrations of 0.062 and 0.290% coincide with the P4$_1$/2/mmm structure of MnO$_2$ proved by the electron diffraction analysis of TEM without showing any other precipitates. PL transitions related to Mn acceptor bands at 1.247 eV ($E_v + 0.173$ eV) for the InMnP:Zn epilayer with an Mn concentration of 0.062% and 1.261 eV ($E_v + 0.159$ eV) for the InMnP:Zn epilayer with an Mn concentration of 0.290% are activated due to the increase of holes. Both in the experimental pattern and in the calculated diffraction pattern, the FCC lattice was still maintained after the Mn doping, and hence, the ordered site occupation of Mn can be regarded as the creation of a superlattice ($a = 11.738$ Å). The samples showing the regularly spaced spots of ordered Mn produce the AHE of spin–orbital interaction by spin-polarized holes. The sample with an Mn concentration of 0.290% reveals p-type conductivity with a hole concentration of $\sim 6 \times 10^{19}$ cm$^{-3}$. The $T_C$ of AHE persists up to 150 K. The sample with the lower Mn concentration of 0.062% also reveals p-type conductivity, but the $T_C$ of AHE persists up to the lower 100 K in comparison with the sample with the Mn concentration of 0.290%. The increase of $T_C$ is caused by the increase of Mn concentration. The $M$–$T$ curve of the sample with an Mn concentration of 0.290% also showed a $T_C$ of about 150 K. Relatively weak ferromagnetic hysteresis appears in the sample with an Mn concentration of 0.062% compared with the sample with an Mn concentration of 0.290%, and this result is attributed to the contribution of antiferromagnetic MnO$_2$ appearing in XRD and TEM and agrees with the lower $T_C$ (100 K) of AHE. Increased ferromagnetic loop appears in the sample with the Mn concentration of 0.290% and is caused by the increase of Mn concentration and is also supported by the fact that the $T_C$ of AHE increases to about 150 K. It is found that a ferromagnetic semiconductor mediated by holes at 150 K can be successfully formed based on InMnP:Zn epilayers discovered to date.

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