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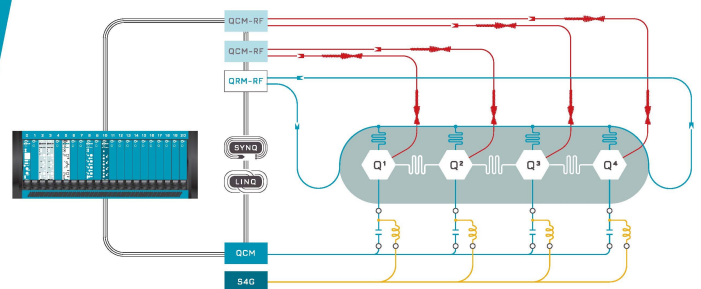
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Clarification of Mn–Zn interaction for InMnP:Zn epilayer by photoluminescence and x-ray photoelectron spectroscopy

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Transition related to the Mn–Zn interaction was observed in photoluminescence (PL) study of the InMnP:Zn epilayer and the peak position blueshifted with increasing Mn concentration. X-ray photoelectron spectroscopy was used to clarify the blueshift of the PL peak. The binding energy shifts of Mn 2*p* and Zn 2*p* core levels indicative of the interaction between Mn and Zn were observed. This mutual interaction between Mn 2*p* and Zn 2*p* agrees with the result that the Mn-related transition in InMnP:Zn codoped with Zn is shifted to the higher energy region in comparison with InMnP without additional doping of Zn. © 2006 American Institute of Physics. [DOI: 10.1063/1.2236201]

InP is one of the representative binary compound semiconductors that have potential applications for optical and high-speed electronic devices.¹ In addition, InP is one of the most promising diluted magnetic semiconductor (DMS) materials although Curie temperature (T_C) of the Mn-doped InP is theoretically predicted to be quite low at ~ 50 K by Dietl *et al.*² DMS based on InP has been receiving attention only very recently even though there is a long history of research on photonic device applications using InP as a host material. Recently reported articles studying InMnP DMS include Mn⁺-implanted InP (Ref. 3) and nanostructured InMnP.⁴ The values of T_C used as a yardstick to determine the degree of ferromagnetism were limited to only 90 and 25 K in those studies, respectively. One of the important problems in materializing DMS characteristics is to increase the T_C up to room temperature for the practical application of spintronic devices. In order to solve this problem, codoping and delta doping were reported as effective methods to increase the T_C .^{5,6} Very recently, we have investigated the effect of codoping on increasing the T_C for both InMnP:Zn bulk and epilayer. In those works, we observed the effect of increasing the T_C value due to the generation of excess holes resulting from codoping of Zn and Mn.^{7,8} In addition, we observed a blueshift of the Mn- and Zn-related emission due to the interaction between Mn and Zn; however, we did not clarify the origin of blueshift in photoluminescence (PL) due to the Mn–Zn interaction.

In this letter, we report the Mn–Zn interaction-related photoemission properties for InMnP:Zn DMS epilayers. The measurements of Hall effect, PL, and x-ray photoelectron spectroscopy (XPS) were carried out to elucidate the origin of Mn–Zn interaction-related photoemission.

The *p*-type InP epilayers doped with Zn were grown on semi-insulating (001) InP substrates at 650 °C by metal organic chemical vapor deposition (MOCVD). The thickness of InP:Zn epilayers was 4 μm . The InP:Zn epilayers showed *p*-type conductivity with the hole concentration of $2.0 \times 10^{18} \text{ cm}^{-3}$ from Hall effect measurements. The resistivity of the samples was approximately $2.92 \times 10^{-2} \Omega \text{ cm}$. After growth of *p*-type InP:Zn epilayers by MOCVD, Mn was evaporated onto the InP:Zn epilayer using a molecular beam epitaxy system. The evaporation of Mn was performed at room temperature for 0.5–3.0 min under base pressure of $\sim 10^{-10}$ Torr. After the evaporation of Mn, the samples were annealed at 300 °C for 30 min in a flowing nitrogen atmosphere. Thereafter, the Hall measurements of InMnP:Zn epilayers showed *p*-type conductivity. The carrier concentration of holes and resistivity were obtained as $1.94 \times 10^{20} \text{ cm}^{-3}$ and $2.18 \times 10^{-4} \Omega \text{ cm}$.

Figure 1 shows PL spectra measured at 16 K for the as-grown sample (inset) and the annealed samples with the Mn concentrations of 0.290%, 0.062%, and 0.019%. For the as-grown sample, the peaks well known as emissions from InP:Zn epilayer appeared. The origins of these peaks can be found in literature.⁸ Among them, we especially focus on the Zn- and Mn-related emission in order to clarify the Mn–Zn interactions in the Mn-doped InP:Zn epilayer. As shown in the inset of Fig. 1, the Zn-related peak was observed at ~ 1.20 eV. After the incorporation of Mn into the InP:Zn epilayer by evaporation of Mn and subsequent annealing at

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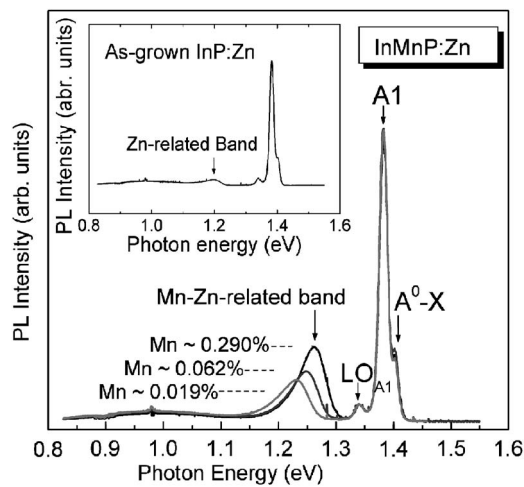


FIG. 1. PL spectra measured at 16 K for the InMnP:Zn epilayers annealed at 300 °C for 30 min with the Mn concentrations of (a) 0.290%, (b) 0.062%, and (c) 0.019%. The inset shows the as-grown InP:Zn epilayer.

300 °C for 30 min, the InMnP:Zn epilayer showed the asymmetrical broadband at 1.231, 1.249, and 1.262 eV together with peaks related to the as-grown epilayer. These asymmetrical broad bands are related to Mn along with the disappearance of the Zn peak. In relation to the Mn-related transitions, there is a ferromagnetic type Mn center possibly formed in III-V compounds. The type of a neutral Mn center (A^0) is $[d^4\text{core}+e(\text{tightly bound electron})]+h(\text{weakly bound hole binding energy}=0.113 \text{ eV in the case of GaAs:Mn})\rightarrow\text{Mn}_{\text{Ga}}^{2+}(d^5)+h$, with the ground state total angular momentum $J=4$ and has the property of a ferromagnetic semiconductor. This feature is found in some bulk GaAs:Mn and InP:Mn samples.^{9–11}

The transition related to Mn at 1.231 eV begins to appear for the sample with Mn of 0.019%. Comparing the ratio of Mn peak intensity to A1 peak intensity, transition related to Mn increases with an increase in the Mn concentration to 0.062% and 0.290%. This result is attributed to the increase of hole carriers by the above neutral Mn center which was confirmed by Hall effect measurements (0.290% = hole of

$1.94 \times 10^{20} \text{ cm}^{-3}$). It was found that this peak position shifted systematically with increase in the Mn concentration. As the Mn concentration increased from 0.019% to 0.062% and 0.290%, the peak position was observed to shift to the higher energy region: $1.231 \rightarrow 1.249 \rightarrow 1.262 \text{ eV}$. This behavior is considered to originate from the different magnitudes of the interaction between Mn and Zn. It is conjectured that there is little interaction between Mn and Zn at a relatively low Mn concentration, resulting in a peak at a low energy (1.231 eV) while increase of the Mn–Zn interaction progressively shifted the peak to a higher energy. In our previous studies, we observed the transitions at 1.089–1.185 eV, which are typical Mn-related peak positions in unintentionally doped n -type InP bulk implanted with various doses of Mn ($5 \times 10^{12} - 5 \times 10^{16} \text{ cm}^{-2}$)^{3,12} and also observed the transitions around 1.23 eV in p -type InP:Zn bulks and epilayers codoped with Mn.^{7,8} It is especially noted that the Mn-related transition for InMnP:Zn codoped with Zn shifts to the higher energy region ($>1.2 \text{ eV}$) including the present study compared to the InMnP without codoping of Zn. This result is expected to originate from the increase of mutual interaction between Zn and Mn which pushes down the Mn level toward the valence band region. In addition, the codoped sample showed enhancement of ferromagnetic properties compared to the sample without codoping of Zn.

Based on these results, the XPS measurements were performed in order to investigate the mutual interaction between In, P, Mn, and Zn. We discuss only the representative XPS spectra of the Mn concentration of 0.290%, which show all the typical features of the XPS spectra. Figures 2(a) and 2(b) show XPS spectra of In $3d$ and P $2p$ for InMnP:Zn epilayer, respectively. The positions of binding energy (E_b) of In $3d_{3/2}$ and In $3d_{5/2}$ appeared at 452 and 444 eV, respectively. The values of E_b of P $2p_{1/2}$ and P $2p_{3/2}$ were observed at 130 and 129 eV, respectively. The E_b values of both In and P well matched the typical peak positions. In fact, no shift was observed for all XPS spectra of In $3d$ and P $2p$. Furthermore, the weak O $1s$ peak disappeared after sputtering of a few surface layers. These results indicate that oxide phases

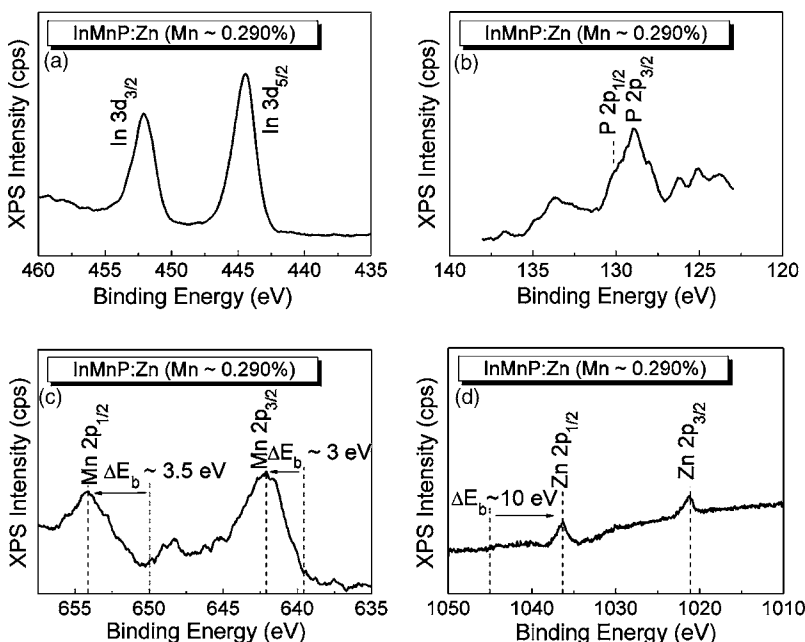


FIG. 2. XPS spectra of (a) In $3d$, (b) P $2p$, (c) Mn $2p$, and (d) Zn $2p$ core levels for InMnP:Zn epilayer (Mn $\sim 0.290\%$).

formed with In and P such as In_2O_3 , P_2O_5 , and InPO_3 , which are generally known to be produced by oxidation of InP, did not precipitate, and therefore, the mutual interaction of core levels among In $3d$, P $2p$, and O $1s$ did not take place. Figure 2(c) shows XPS spectra of Mn $2p$ for InMnP:Zn epilayer. The peaks of Mn $2p_{1/2}$ and Mn $2p_{3/2}$ were observed at 653.5 and 642.0 eV, respectively. The peak position of Mn $2p_{1/2}$ shifted from 650 eV which is the original peak position of Mn $2p_{1/2}$ to 653.5 eV, and the peak position of Mn $2p_{3/2}$ shifted from 639 eV which is the original peak position of Mn $2p_{3/2}$ to 642 eV so that both peaks shifted by ~ 3 eV. Figure 2(d) shows XPS spectra of Zn $2p$ for InMnP:Zn epilayer. The peaks of Zn $2p_{1/2}$ and Zn $2p_{3/2}$ were detected at 1,036.3 and 1,021.1 eV, respectively. The peak positions of Zn $2p_{1/2}$ and Zn $2p_{3/2}$ shifted from 1,045.0 and 1,022.0 eV to 1,036.3 and 1,021.1 eV, respectively. The values of E_b shift for Zn $2p_{1/2}$ and Zn $2p_{3/2}$ peaks are 8.7 and 0.9 eV, respectively. In short, the E_b shifts of Mn $2p$ and Zn $2p$ were observed whereas those of In $3d$ and P $2p$ were not shifted. Although the E_b shifts of Zn $2p$ and Mn $2p$ were observed, the secondary phases such as MnP, MnO, ZnP, and/or ZnO are not expected to exist because no shift of P $2p$ peak and no existence of O $1s$ peak were observed for the InMnP:Zn main layer. Considering the above results, only the interaction between Mn $2p$ and Zn $2p$ took place, but the interactions of Mn $2p$ and Zn $2p$ with In $3d$ and P $2p$ did not occur. The shifts of XPS peak position mean that there are interactions between elements making up solid states because the binding energy changes due to reorientation of lattice distribution resulting from the incorporation of extra dopants. Therefore, it can be inferred that there exists an interaction between Mn and Zn rather than those between other components. The interaction between Mn $2p$ and Zn $2p$ is caused by the interaction between core levels of covalently bonded $\text{Mn}_{\text{In}}^{2+} [i.e., \text{Mn}_{\text{In}}^{2+}(d^5)+h]$ and $\text{Zn}_{\text{In}}^{2+} [i.e., \text{Zn}_{\text{In}}^{2+}(d^{10})+h]$. This mutual interaction of Mn_{In} and Zn_{In} agrees with the result that the Mn-related transition for ferromagnetically enhanced InMnP:Zn codoped with Zn shifts to higher energy (<1.26 eV) in comparison with InMnP without additional incorporation of Zn.^{3,12}

In summary, PL and XPS measurements were carried out to confirm the variation of Zn- and Mn-related emissions and binding energies of In, P, Zn, and Mn components for InMnP:Zn epilayers, respectively. The results of PL revealed that

the Mn-related peak position was systematically shifted to higher energy region (i.e., $1.231 \rightarrow 1.249 \rightarrow 1.262$ eV) with an increase in the Mn concentration (i.e., $0.019\% \rightarrow 0.062\% \rightarrow 0.290\%$). This result is attributed to the increase of the mutual interaction between Zn and Mn due to the increase of the incorporated Mn concentration, because the increased interaction between Zn and Mn pushes down the Mn level toward the valence band region. This mutual interaction was confirmed by XPS measurements. The E_b shifts indicative of interactions between Mn $2p$ and Zn $2p$ core levels were observed for InMnP:Zn epilayers. The interaction between Mn $2p$ and Zn $2p$ is originated from the interaction between core levels of covalently bonded $\text{Mn}_{\text{In}}^{2+} [i.e., \text{Mn}_{\text{In}}^{2+}(d^5)+h]$ and $\text{Zn}_{\text{In}}^{2+} [i.e., \text{Zn}_{\text{In}}^{2+}(d^{10})+h]$.

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