ABRIDGED DOCTORAL DISSERTATION

博士論文（要約）

Studies on New Narrow-gap III-V Magnetic Semiconductors

(新規狭ギャップ III-V 族磁性半導体の研究)

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1. Introduction

"Semiconductor spintronics" is an emerging field which aims to manipulate the electron spin in addition to its charge for future electronics and information technology. By introducing the spin degrees of freedom into semiconductors, we can obtain many new devices with attractive functions such as spin transistors, reconfigurable logic circuits, and quantum computing using spin states, that are unavailable with conventional materials and devices. To fulfill this purpose, ferromagnetic semiconductors (FMSs) have been widely studied, because they exhibit both semiconducting and ferromagnetic properties, which may be used for non-volatile and low-power-consumption electronic devices. Among FMS families, Mn-based III-V FMSs such as (In,Mn)As and (Ga,Mn)As have been intensively studied,[1, 2, 3] because they show hole-induced ferromagnetism. However, those materials are always *p*-type. For realizing spintronic devices, not only *p*-type but also *n*-type FMS materials are required. Furthermore, the maximum Curie temperature T_C of (Ga,Mn)As and (In,Mn)As are 200 K and 90 K, respectively, which are much lower than room temperature. [4, 5] In addition, the origin of ferromagnetism in Mn-based III-V is a long-debated issue and not fully understood yet. So far it is difficult to utilize the conventional Mn-based FMSs for practical devices. Therefore, we need to look for new FMSs, and we have found that narrow-gap Fe based FMSs can give a solution.

In this study, in order to explore other possibilities of narrow gap FMSs and to understand the origin of ferromagnetism in narrow gap FMSs. We have fabricated and investigated the properties of *n*-type (In,Co)As and *p*-type (Ga,Fe)Sb, which have not been grown and investigated so far. *Firstly,* we compare magnetic properties of (In,Co)As with other InAs-based FMSs such as (In,Mn)As and (In,Fe)As. By fixing host semiconductor (InAs) and changing transition metal (Mn, Fe, and Co), we can clarify the magnetism trend in InAs-based MSs and understand the role of transition metal. *Secondly,* we compare magnetic properties of (Ga,Fe)Sb with (Ga,Fe)As and (In,Fe)As. In such case, transition metal was fixed, and host semiconductor was changed to understand the origin of ferromagnetism in narrow gap FMSs.

2. Experiments

We have grown $(In_{1-x},Co_x)As$ (x = 3 – 18%) and $(Ga_{1-x},Fe_x)Sb$ (x = 3.9 – 20%) thin films by low-temperature molecular beam epitaxy (LT-MBE) on GaAs (001) substrates. We employed transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), transmission electron diffraction (TED), and X-ray diffraction spectroscopy (XRD) to characterize their crystal structure and quality. The magneto-transport measurements of (In,Co)As and (Ga,Fe)Sb layers were carried out by using Hall-bars with size of 200 µm × 50 µm. Their magneto-optical properties were characterized by magnetic circular dichroism (MCD) spectroscopy. The magnetization of (Ga,Fe)Sb layers were further investigated by superconducting quantum interference device (SQUID).

3. Results

3.1. Properties of new n-type magnetic semiconductor (In,Co)As

RHEED patterns during the MBE growth and TEM images indicate that (In,Co)As layers have zinc-blende crystal structure with a small fraction of embedded CoAs nanoclusters. However, those CoAs nanoclusters do not affect the electrical and magnetic properties of the (In,Co)As layers. The electron concentration of the (In,Co)As layers can be changed in the range of 1.9×10^{18} to 2.4×10^{19} cm^{-3} by changing the Co concentration. The metal-insulator transition of $(In_{1-x},Co_x)As$ is observed at x = 5%. Furthermore, large negative magnetoresistance (up to -17.5% at 0.95 Tesla) is observed at low temperature and can be attributed to spin-disorder scattering in the (In,Co)As matrix. From the MCD analysis, (In,Co)As is paramagnetic and has the band structure of zinc-blende type semiconductors. The absence of ferromagnetism in (In,Co)As indicates that the *s-d* exchange interaction is very weak. This is contrasting to the strong *s-d* exchange and *p-d* exchange interactions observed in (In,Fe)As and (In,Mn)As, respectively.

3.2. Properties of new p-type ferromagnetic semiconductor (Ga,Fe)Sb

RHEED patterns during the MBE growth and XRD spectra indicate that the crystal structure of (Ga,Fe)Sb layers are of zinc-blende type without any visible second phases. STEM image and TED pattern of representative samples with x = 13.7% and 20% indicate that the crystal structure of (Ga,Fe)Sb layers are of zinc-blende-type without any visible second phases. The MCD spectra of the $(Ga_{1-x},Fe_x)Sb$ samples (x = 3.9 – 20%) with a magnetic field H of 1 T applied perpendicular to the film plane show strongly enhanced peaks at E_1 (2.19 eV) and $E_1 + \Delta_1$ (2.63 eV) corresponding to the GaSb band structure,[6] indicating that (Ga,Fe)Sb maintains the zinc-blende crystal structure with large spin-split band structure due to the *s,p-d* exchange interactions. MCD-H characteristics of $(Ga_{1-x},Fe_x)Sb$ samples (x = 3.9 – 20%) show clear hysteresis at low temperature, demonstrating the presence of ferromagnetic order at low temperature. Furthermore, Hall resistance vs. magnetic field (R_{Hall}–H) characteristics also show clear hysteresis curves at low temperature, indicating the ferromagnetic order. At 300 K, the R_{Hall}–H characteristics are linear with positive slopes, indicating that all samples are p-type. The T_C values estimated by the Arrott plots of R_{Hall}–H and MCD–H characteristics are in good agreement, thus further supporting intrinsic ferromagnetism of (Ga,Fe)Sb. The T_C values of the $(Ga_{1-x},Fe_x)Sb$ samples increases as x increases. However, T_C is not linearly proportional to x. Instead, T_C seem to be proportional to $xp^{1/3}$. This suggests that T_C also depends on p as in the case of other FMSs with hole-induced ferromagnetism. Noted that the obtained T_C (230 K) at x = 20% is the highest in III-V FMSs.

4. Discussion

In order to explain the observed paramagnetism in (In,Co)As and ferromagnetism in (Ga,Fe)Sb, we have proposed a "resonant *s,p-d* exchange interaction" model in narrow gap FMSs. It has been known that the s,p-d exchange interaction energy is given by Anderson Hamiltonian:[7] $_0\alpha\ or\ N_0\beta = -2\left|V_{s,p-d}\right|^2\left(\frac{1}{E_{C,V}-\varepsilon_d}+\frac{1}{U-E_{C,V}+\varepsilon_d}\right)$. Here, N_0 is the density of cation sites, α and β are the *s,p-d* exchange integral, $E_{C,V}$ are the energy at the bottom of the conduction band (the top of the valence band), ε_d is the energy level of d-states, U is the Coulomb repulsion between opposite-spin electrons in a d-state, and $V_{s,p-d}$ is the s,p-d mixing potential. Therefore, *s,p-d* exchange interaction ($N_0\alpha\ or\ N_0\beta$) is strongly depends on the relative position of the *d*-level of the transition metals in the host semiconductor band structure $E_{C,V}-\varepsilon_d$.

From our model, (In,Co)As is paramagnetic because the *d*-level of Co is far away from the band edges of InAs. Here, *d*-level of Co is deeper under the valence band top of InAs. Thus, $E_{C,V}-\varepsilon_d$ is large and *s,p-d* exchange interaction is small to induce the ferromagnetism. This may be the same for the case of (Ga,Fe)As, in which *d*-level of Fe is also far away from the band edges of GaAs (in band-gap of GaAs). Thus, (Ga,Fe)As is paramagnetic[8]. In contrast, (Ga,Fe)Sb and (In, Fe)As[9] are ferromagnetic, since *d*-level of Fe lie near to the conduction band bottom of InAs and valence band top of GaSb, respectively. Furthermore, this model also agrees with the ferromagnetism trend in Mn-based FMSs. Mn *d*-level tends to be far away from valence top with narrowing the band-gap of the host semiconductor. Thus, T_C of narrow gap Mn-based III-V FMSs is lower due to the larger E_C - ε_d term. Our result indicates that the position of the *d*-level of the transition metals in the host semiconductor band structure plays an important role to induce the ferromagnetism

5. Conclusion

New ferromagnetic semiconductors $(In_{1-x},Co_x)As$ (x = 3 – 18%) and $(Ga_{1-x},Fe_x)Sb$ (x = 3.9 – 20%) have been successfully grown by low-temperature molecular beam epitaxy (LT-MBE) on GaAs(001) substrates.[10] [11] Crystal structure analysis (TEM or XRD) indicates that both (In,Co)As and (Ga,Fe)Sb have zinc-blende crystal structure. Carrier concentration and conductivity were enhanced by doping transition metals (TMs). The (In,Co)As layers with high Co concentrations ($x \geq 5\%$) are metallic and show large negative MR Magnetic circular dichroism (MCD) spectroscopy and magneto-transport data indicate that (In,Co)As is paramagnetic due to small *s-d* exchange interaction, and (Ga,Fe)Sb is an intrinsic ferromagnetic semiconductor induced by large *p-d* exchange interaction. Curie temperature (T_C) of $(Ga_{1-x},Fe_x)Sb$ sample reaches 230 K at $x = 20\%$, which is the highest reported value so far and promising for room temperature ferromagnetism. This study indicates that the position of the *d* level of the transition metals in the host semiconductor band structure plays an important role to induce ferromagnetism.

6. Impact and significances

Firstly, we provided a possibly promising material for semiconductor-based magnetic sensors. Because magnetoresistance values observed in (In,Co)As (-17.5%) is much larger than those of (In,Mn)As (-0.14%)[12] and (In,Fe)As (- 0.55%).[13] *Secondly*, we demonstrated a new intrinsic p-type ferromagnetic semiconductor (Ga,Fe)Sb. T_C (230 K) of (Ga,Fe)Sb ($x = 20\%$) is the highest in III-V FMSs, and much higher than that of other FMSs. Our results show that Fe-based FMSs are promising for semiconductor spintronic devices. *Thirdly*, our result helps to understand the origin of ferromagnetism in narrow-gap FMSs. We indicate that the position of the *d*-level of the transition metals in the host semiconductor band structure plays an important role to induce ferromagnetism. *Finally*, this research opens a new approach towards high T_C FMSs. Based on our model, we can obtain FMSs with high T_C by designing a suitable material, which has the *d*-level of transition metals near valence band top (or conduction band bottom) of the host semiconductor.

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