博士論文（要約）

Band structure and ferromagnetism in III-V ferromagnetic semiconductor GaMnAs
(III-V族強磁性半導体GaMnAsにおけるバンド構造と強磁性)

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Conventional semiconductor devices use only the charge degree of freedom of electrons and holes, while the spin of carriers remains untouched. Spintronics on semiconductors is aiming to introduce spin-related functions to semiconductor devices by utilizing the spin degrees of freedom of carriers and atoms. The most widely studied materials to realize semiconductor spintronics are ferromagnetic semiconductors (FMSs), which have the properties of both semiconductors and ferromagnets. The most intensively investigated FMS is the III-V ferromagnetic semiconductor GaMnAs, which has the zinc-blende crystal structure where a part (typically a few %) of the Ga atoms in GaAs is replaced by Mn. The Mn atoms act as both acceptors and localized spins. GaMnAs is known to show ferromagnetism when the Mn content is over 1%. This concentration is not enough to show the ferromagnetism by a direct exchange interaction between two neighboring Mn, but holes mediate the indirect exchange interaction, which induces the ferromagnetism in GaMnAs.

In Chapter 2, the survey of the recent research on the band structure and the ferromagnetism in GaMnAs is described. The problem in GaMnAs is that the band structure and the origin of the ferromagnetism are not understood. At the beginning, the holes were believed to be in the valence band, which is spin split by the p-d exchange interaction between the holes and 3d electrons. However, recent experiments have shown that the valence band is filled with electrons (no holes) and is highly ordered. These new findings raise three unsolved problems: (i) The position of the Fermi level which is located in the impurity band in the band gap contradicts the conventional understanding that in non-magnetic p-type GaAs the Fermi level crosses over the valence band as doping concentration increases. (ii) The highly-ordered valence band is against the simple expectation that the heavy doping and p-d hybridization will result in the disordered valence band. (iii) The detail about the impurity band in GaMnAs is not understood at all because it was believed so far that the impurity band did not exist in the metallic GaMnAs. In the following three Chapters, these three problems are addressed, respectively.

In Chapter 3, the Fermi level position in GaMnAs is precisely determined. It was believed that the Fermi level in GaMnAs crosses over the valence band as the Mn content increases, which is based on the conventional understanding of the non-magnetic p-type GaAs: Whereas the holes are bound by the acceptor ions and the narrow impurity states or band are formed when the acceptor concentration is low (light doping), the impurity band vanishes or merges with the valence band when the acceptor concentration is high (heavy doping) because of the screening effect, which results in free holes in the valence band. However, recent experimental results strongly indicate that the Fermi level is not in the valence band, but in the impurity band in the band gap, which requires reconsideration of the conventional scenario. In order to clarify the Fermi level position and the valence band structure of GaMnAs, it is necessary to clarify the Mn content dependence of the Fermi level position. In particular, the Mn content region around 1% is important, because based on the conventional scenario the

impurity band and the valence band merge in that region. Here, the Mn content dependence of the Fermi level position in GaMnAs is systematically investigated by the resonant tunneling spectroscopy in GaMnAs quantum-well heterostructures. The quantum levels of the valence band with respect to the Fermi level are obtained from the resonant tunneling spectroscopy. Since the quantum levels converge on the bulk valence band top as the quantum-well thickness increases, the energy offset between the Fermi level and the valence band top can be precisely estimated. The Fermi level is found to be always in the band gap and the closest to the valence band top at the Mn content 1%, where the ferromagnetism starts to occur. However, the Fermi level moves away from the valence band top as the Mn content decreases or increases from 1%. This anomalous behavior of the Fermi level is completely different from that of the non-magnetic p-type GaAs. These results means that the impurity states still exist in the band gap even when the Coulomb potential of the Mn ions is completely screened. The origin of the impurity states in the ferromagnetic GaMnAs is thought to be the weakly-bound states due to the p-d hybridization, which is different from the Coulomb potential of the Mn ions. The holes bound by the d-related impurity states are thought to induce the ferromangeitsm in GaMnAs.

In Chapter 4, the valence band ordering in GaMnAs is studied. The Fermi level in GaMnAs has been found to be inside the impurity band, which is different from the one in non-magnetic p-type GaAs. The disordered impurity band is theoretically predicted to originate from the strong p-d exchange interaction with the p-d hybridization. Considering the large modification of the charge wave functions of the conductive holes due to the strong p-d exchange interaction, one might simply expect that the valence band becomes disordered or merges with the impurity band. However, our resonant tunneling spectroscopy experiments show that the valence band in GaMnAs has highly ordered. Moreover, recent results of the angle-resolved photoemission spectroscopy show that the ***k***-dispersion of the valence band in GaMnAs is the almost same as GaAs one. The band structure under the strong p-d exchange interaction is not yet understood in GaMnAs, in particular how much ordered or disordered depending on the Mn concentration. Measuring the valence band ordering is a key to understand the coexistence of the disordered impurity band and the highly-ordered valence band under the strong p-d exchange interaction in GaMnAs. Although the mean-free path is often estimated by Hall measurements to evaluate the conductive-band ordering, the Hall measurement in GaMnAs does not provide the mean-free path of the valence band because the Fermi level in GaMnAs is always in the impurity band. On the other hand, the valence band ordering can be estimated from the resonant tunneling of the valence band in the quantum well because the resonant tunneling depends on the valence band ordering as well as the quantum-well thickness. Since the increase in the quantum-well thickness weakens the resonant tunneling, the maximum thickness where the resonant tunneling can be observed is an indicator of the valence band ordering. Here, the Mn content dependence of the valence band

ordering in GaMnAs is systematically investigated by the resonant tunneling in GaMnAs-based quantum-well heterostructures, where the Mn content of the GaMnAs quantum well is varied from ~0.03% (the paramagnetic region) to a few of % (the ferromagnetic region). It is found that the valence band loses its ordering in the paramagnetic region as the Mn content increases from ~0.03% to 1%, but as the Mn content increases over 1% the valence band ordering is restored at the onset of ferromagnetism. This result shows that, while the paramagnetic impurity band merges with the valence band, the disordered impurity band due to the strong p-d exchange interaction is independent of the valence band. The paramagnetic impurity band is composed of the bound states due to the Coulomb potential of the Mn impurities. As the Mn content increases, these impurity bound states spread out of the Mn impurities because of the screening effect. These delocalized impurity states can merge with the Γ point of the valence band, whose states are well broadened over the crystal. In contrast to the delocalized impurity states in the paramagnetic region, the disordered impurity states in the ferromagnetic region do not merge with the valence band because those states are localized around the Mn impurities owing to the strong p-d exchange interaction. As a result, the disordered impurity band and the highly-ordered valence band appear in the ferromagnetic GaMnAs.

In Chapter 5, the anisotropy of the disordered impurity band is studied. Although it has been clarified that the ferromagnetism in GaMnAs comes from the impurity band, the detailed structure of the impurity band has not been investigated experimentally, which is necessary for understanding the mechanism of the ferromagnetism. Tunneling anisotropic magnetoresistance (TAMR) can be used for clarifying the anisotropy of the wave functions in ferromagnetic semiconductors, and TAMR observed in GaMnAs tunnel junctions has been thought to originate from the valence-band-like hole-bound states in GaMnAs. However, the studies on the Fermi level described in the above two chapters show that the valence-band-like hole-bound states should vanish in the metallic GaMnAs because of the screening effect, and the strong p-d exchange interaction gives rise to the hole-bound states made of the disordered impurity band. Therefore, it is more natural to think that TAMR originates from the disordered impurity band in the ferromagnetic GaMnAs. Here, we study the Mn content dependence of the anisotropy of the disordered impurity band by measuring the hole-energy dependence of TAMR in GaMnAs single-barrier heterostructures. We measured the *I-V* characteristics at 3.5 K with applying a magnetic field of 8 kG in various in-plain directions θ, where θ is the angle between the magnetic field (// magnetization) and the [100] direction. At 8 kG, the magnetization of the GaMnAs layer is parallel to the magnetic field $\boldsymbol{H}$. dI/dV at each bias voltage V, which is proportional to the density of states at each energy, was obtained numerically from the *I-V* characteristics. Since the spatial anisotropy of the wave functions induces the dependence of the density of states on the magnetization direction because of the spin-orbit interaction, TAMR symmetry provides the anisotropy of the disordered impurity band. TAMR data show

two-fold symmetry with peculiar and complicated features in the band gap region, which are considered to be related to the anisotropy of the disordered impurity band. This result indicates that the multiple impurity levels have the wave functions with the different spatial anisotropies, and that the Fermi level position in the disordered impurity band determines the magnetic anisotropy in GaMnAs.

In summary, the Mn content dependence of the Fermi level position and the valence band ordering are investigated by the resonant tunneling spectroscopy in the GaMnAs quantum-well heterostructures. By comparing the paramagnetic and ferromagnetic GaMnAs, these results directly show that the ferromagnetism in GaMnAs originates from the disordered impurity band formed by the strong p-d exchange interaction, which is different from the paramagnetic impurity band formed by the Coulomb potential of the Mn impurity ions. Also, the anisotropy of the disordered impurity band was investigated by means of TAMR in the GaMnAs-based tunnel junctions. It is found that the disordered impurity band have the anisotropic wave functions, which depend on the energy levels. This indicates that the disordered impurity band is related to the magnetic properties such as the magnetic anisotropy in the ferromagnetic GaMnAs. These results indicates that the detail of the band structure, such as the Fermi level position and the merging or separation of the valence and impurity bands, plays an important role in the magnetic properties of the prototype FMS GaMnAs, such as ferromagnetism, Curie temperature, and magnetic anisotropy. The methods investigated in this study can be applied to other FMSs such as GaMnP and GaMnSb, where the strength of the p-d exchange interaction is different. Comprehensive and deep understanding of the relationship between the band structure and ferromagnetism in FMSs is necessary for FMSs to be utilized for real semiconductor spintronics devices.