Abstract of Dissertation

論文の内容の要旨

# A New Group-IV Ferromagnetic Semiconductor $Ge_{1-x}Fe_x$: Epitaxial Growth, Crystal Structure, Magnetic Properties, and Heterostructures

(新しい IV 族強磁性半導体 $Ge_{1-x}Fe_x$ 薄膜の研究：

エピタキシャル成長、結晶構造、磁性、およびヘテロ構造)

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Abstract:

Si-based spintronics will lead to a new progress beyond the conventional Si technology, because spin degrees of freedom provide new and unimaginable functionalities in well-established Si devices and systems. Here, injection and detection of spin-polarized current in actively-controlled channels are indispensable fundamental operations to obtain new functionalities in Si-based spintronic devices such as spin MOSFETs. Group-IV ferromagnetic semiconductors have many advantages to achieve these operations in comparison with commonly-used ferromagnetic metals, because they can be grown on Si platform with atomically flat and abrupt interfaces, they are compatible with Si device processes, and the conductivity mismatch problem does not have to be considered. Thus, group-IV ferromagnetic semiconductors are promising for emerging Si-technology-based spintronic devices.

Ferromagnetic semiconductors have been given simultaneously dual advantages of the semiconductor properties and the magnetic properties. Fundamental properties of "intrinsic" ferromagnetic semiconductors have been investigated in III-V-based ferromagnetic semiconductors $Ga_{1-x}Mn_xAs$ and $In_{1-x}Mn_xAs$. The magnetic ions were substituted for the lattice sites of host semiconductors keeping the single crystal structure of the type of hosts, and as a result, the band structure of ferromagnetic semiconductors reflects that of hosts. Ferromagnetic ordering is induced by the *s*,*p*-*d* exchange interactions, not by the intermetallic precipitates. The *s*,*p*-*d* exchange interactions provide unique properties such as large magneto-optical effects induced by spin-splitting of the band-edge, and controllability of their magnetism by varying the hole density. When a new candidate material is fabricated, investigation of these fundamental characters is indispensable to test whether it is an intrinsic ferromagnetic semiconductor or not.

The first successful growth of group-IV ferromagnetic semiconductor was reported by Park *et al*. They demonstrated the control of ferromagnetic ordering in gated $Ge_{1-x}Mn_x$ films by applying an electric field. Although this result implied that $Ge_{1-x}Mn_x$ had the behavior of intrinsic

ferromagnetic semiconductors, the investigation of fundamental properties was not enough. Then controversy arose over the origin of the ferromagnetism in epitaxial $Ge_{1-x}Mn_x$ films, since some reports suggested that the $Ge_2Mn$ nanocolumn structures, the intermetallic $Mn_5Ge_3$, and amorphous $Ge_{1-y}Mn_y$ clusters were easily formed in epitaxial $Ge_{1-x}Mn_x$ films.

In this thesis, Fe was chosen as magnetic dopants in place of commonly used Mn atoms. Fe-doped Ge ($Ge_{1-x}Fe_x$) films have been grown on Ge(001) and Si(001) substrates by low-temperature molecular beam epitaxy (LT-MBE) and thoroughly investigated their crystal structure and magnetic properties. Furthermore, by studying group-IV magnetic heterostructures, possibility of using $Ge_{1-x}Fe_x$ films in actual spintronic devices is explored.

At first, $Ge_{1-x}Fe_x$ films were epitaxially grown on Ge(001) substrates by low-temperature molecular beam epitaxy (LT-MBE). During growth, the surface morphology of the samples was monitored by *in-situ* reflection high energy electron diffraction (RHEED) observations. RHEED patterns of the samples showed the diffraction pattern of the diamond-type lattice structure without extra spots caused by the formation of Fe-Ge precipitates. Detailed crystallographic analyses were carried out by transmission electron microscopy (TEM), transmission electron diffraction (TED), energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction spectroscopy (XRD) observations. Epitaxially-grown $Ge_{1-x}Fe_x$ films on Ge(001) substrates maintained the diamond-type lattice structure including the fluctuation of Fe distribution and tiny stacking fault defects without any other ferromagnetic Fe-Ge precipitates, when they were grown at the substrate temperature ($T_S$) of less than 200 °C. The lattice constant (along the growth direction) evaluated from XRD spectra of the samples linearly decreased with increasing the Fe content ($x$) up to 13.0% and was saturated at $x$ more than 13.0%. This behavior indicates that Fe atoms were substituted for the lattice sites of host Ge up to at least $x$ = 13.0%. Magneto-optical measurements were carried out by magnetic circular dichroism (MCD) technique. The MCD spectra of $Ge_{1-x}Fe_x$ films reflected the band structure of host Ge and the MCD peak at the critical point (especially $E_1$ transition energy) was largely enhanced by Fe doping, although broad offset-like MCD signals were observed. This indicates that the band-edge spin-splitting was induced by the *s*,*p*-*d* exchange interactions as described above. Magnetic field dependence of MCD intensity at any photon energies including $E_1$ and other points exhibited clear ferromagnetic hysteresis loops, and these shapes were identical with one another, indicating that the MCD spectral features and ferromagnetic ordering of the samples came from a magnetically-homogeneous single ferromagnetic phase, without any other ferromagnetic Fe-Ge precipitates. The Curie temperature ($T_C$) of the $Ge_{1-x}Fe_x$ films on Ge(001) evaluated from the temperature dependence of MCD hysteresis loops linearly increased with increasing $x$ up to 13.0%, and was saturated at $x$ more than 13.0%. The behavior of $T_C$ had a good correlation with the behavior of lattice constant as a function of $x$. This correlation indicates that $T_C$ increases in proportion to the number of substitutional Fe atoms, and that the crystal structure and the magnetic properties of

$Ge_{1-x}Fe_x$ films on Ge(001) have linear relation with each other, which is one of the essentials for intrinsic ferromagnetic semiconductors. All the results presented here confirm that epitaxial $Ge_{1-x}Fe_x$ films on Ge(001) are “intrinsic” ferromagnetic semiconductor.

Next, $Ge_{1-x}Fe_x$ films were epitaxially grown at $T_S$ = 200 °C on Si(001) substrates by LT-MBE. To establish the epitaxial growth of $Ge_{1-x}Fe_x$ films on Si is the next important step for realizing group-IV-based spintronic devices integrated into Si CMOS platform. *In-situ* RHEED during growth showed only the diffraction pattern of the diamond-type lattice structure. Crystallographic analyses revealed that the crystal quality of the $Ge_{1-x}Fe_x$ layer was deteriorated including not only the fluctuation of Fe distribution and tiny stacking fault defects as well as the films on Ge(001) but also threading dislocations induced by large lattice mismatch between $Ge_{1-x}Fe_x$ and Si, although there were no formation of intermetallic Fe-Ge precipitates within $Ge_{1-x}Fe_x$ layer. The lattice constant (along the growth direction) evaluated from XRD spectra linearly decreased with increasing $x$ up to 13.0% and was saturated at $x$ more than 13.0%. MCD measurements indicate a largely enhancement of MCD peak intensity at $E_1$, a magnetically-homogeneous single origin of their ferromagnetism, linear increase of $T_C$ depending on $x$, and good correlation between $T_C$ and the lattice constant. All the results of $Ge_{1-x}Fe_x$ films on Si(001) were consistent with the case of $Ge_{1-x}Fe_x$ films on Ge(001), confirming that epitaxial $Ge_{1-x}Fe_x$ films on Si(001) are also intrinsic ferromagnetic semiconductor. Furthermore, magneto-transport properties were examined in the $Ge_{1-x}Fe_x$ films on Si(001). Anomalous Hall effects (AHE) with ferromagnetic hysteresis loops was clearly observed at the temperature lower than $T_C$ evaluated from MCD, and the shapes of AHE was consistent with those of MCD. This means that anomalous Hall effect and MCD measurements detected the same ferromagnetic phase, that is, the intrinsic ferromagnetic semiconductor phase.

Finally, the observation of tunneling magneto-resistance (TMR) effect was attempted in tri-layer magnetic tunnel junction (MTJ) structures with ferromagnetic $Ge_{1-x}Fe_x$ films as ferromagnetic electrode. TMR-like behaviors were observed at low temperature (~3K) in the tri-layer structure of top Fe / $Si_{0.2}Ge_{0.8}$ barrier / bottom $Ge_{1-x}Fe_x$ ($x$ = 13.0%), although TMR changed negatively and these TMR ratio were very low (~ 0.3%). This behavior indicated that $Ge_{1-x}Fe_x$ films can actually function as a spin injector and detector in Si-technology-based spintronic devices.