博士論文(要約)

Epitaxial growth and characterizations of Fe doped ferromagnetic semiconductors and their nanostructures

(Fe 添加強磁性半導体とナノ構造のエピタキシャル成長と物性評価)

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The main objective is to develop new structures of Fe-doped ferromagnetic semiconductors with very high Curie temperature (TC) (ideally over 500K so that it can be used in wide range of applications without temperature control), which are crucial to realize practical spin devices. In order to archive this goal, it is indispensable to i) elucidate the mechanism of ferromagnetism, and ii) explore new material engineering strategies to improve the TC of Fe based ferromagnetic semiconductors (FMSs). We choose (Ga,Fe)Sb as the starting point of its high TC and not much has been known about its properties.

In chapter 1, we first investigate the band structure of (Ga,Fe)Sb, using magnetic circular dichroism (MCD) spectroscopy. The band structure of an FMS play a central role in elucidating the mechanism of ferromagnetism and material design, as clearly demonstrated in the case of (Ga,Mn)As. We found that the position of Fermi level (EF) is in the band gap and confirmed the presence of an impurity band in (Ga,Fe)Sb. By combining with other evidence from X-ray MCD (XMCD), Angle resolved Photo Emission Spectroscopy (ARPES), and first principles calculation, we concluded that a band model with the Fe-related impurity band at the valence band top is applicable for the case of (Ga,Fe)Sb. These studies also indicate that the way to increase TC in this material is to increase the Fe concentration and reduce the Fe-Fe atom distance. Theoretical calculations of our collaborators also predict that Zinc Blende (ZB) FeSb and FeAs structures show extraordinarily high TC (>1000K) if successfully grown.

To realize a high concentration of Fe in III-V semiconductors, however, is highly challenging even with low-temperature molecular beam epitaxy (MBE) growth. If we just keep doping more and more Fe the crystal structure deteriorates and does not lead to increased TC. After many trials, we found that it is very hard to grow highly doped Fe FMSs (~50% Fe) on regular GaAs (001) substrates.

We suggested and followed two lines of strategy: 1) Growing these highly-doped Fe doped FMS structures on GaAs (111) substrates, where a uniform distribution of magnetic impurities was shown to be achievable. 2) Growing Fe-doped nano-scale structures such as quantum dots (QDs). Another motivation for the growth of QDs is the high tunability of the carrier density using electrical gating, due to the low dimensionality. From the theoretical prediction, on tuning the EF in Fe-doped FMSs, giant magnetic response following a transition between ferromagnetic to anti-ferromagnetic could be expected. We hope to achieve these novel functionalities for the first time in the case of Fe-doped QDs.

Therefore, in chapter 2, we first try the growth of Fe doped GaSb quantum dot (QD) structures which could result in increased local Fe concentration due to the extreme conditions during growth. We were successful in increasing the TC (>400K). However, we discovered a completely new phase, which was cubic, of Fe and Ga, which precipitate towards the top of the dots. Although the high TC in these structures is encouraging, we need some first principles calculations to elucidate the mechanism for this new phase.

Then in chapter 3, we try a similar approach but instead of Sb-based GaSb we use As-based InAs and try growth of Fe doped InAs QDs. This time we were successful in maintaining a ZB structure throughout the QD. Interestingly, this time the Fe was precipitated towards the bottom of the dot like a thin layer, which is different from the case of GaSb. This might also be the reason why a MCD signal albeit a small one was observed in this case. Though we have only doped 12% Fe, it might be possible that we were successful in increasing the local Fe concentration which led to high TC (>300K).

The growth mechanisms for both of the above structures are believed to be Stranski-Krastanov mechanism modified by the presence of Fe which acts as a surface catalyst. In the first case, the Fe-Ga phase being formed might be energetically favorable than forming the usual ZB (Ga,Fe)Sb and hence it gets precipitated at the top of the dot. In the second case, it might be energetically favorable for the formation of Fe-Ga bonds rather than Fe-In bonds which results in the accumulation of Fe at the bottom of the dot.

In the case of GaSb QDs the phase is new and the mechanism of ferromagnetism is not known. Therefore, it is difficult to comment on the quantum effects. In the case of InAs QDs as seen in the MCD signal there is a peak at around 1000 nm which is different from the usual (In,Fe)As spectrum probably resulting from the quantum effects. The quantum size effect in InAs QDs is well known and the band-gap has been enhanced to about 1eV in previous studies. By controlling the size of QDs it has also been observed that the emission wavelength can be controlled and by optimizing the growth conditions the linewidth of emission can be controlled as well leading to almost homogenous radiation. This is promising because it shows that the MCD spectrum of (In,Fe)As QDs is possibly coming from the band gap of the QDs and by optimizing the growth conditions we can further fine tune the spectrum which can lead to room temperature spin LED formation.

Another possible way to increase the Fe concentration without deteriorating the crystal structure is the growth on (111) surface. (Ga,Fe)Sb in particular, it has been found that on doping more Fe it forms nanocolumn like pillars in the film which leads to out of plane anisotropy and on doping more Fe the crystal quality deteriorates which does not lead to higher TC. In previous research on another material, GeMn showed pillar like structures by growth on (001) surface which dispersed and led to more even distribution of Fe by growth on (111) surface.

So, in chapter 4, we investigated the growth of (Ga,Fe)Sb on GaAs (111)B substrate. We were successful in growth of (Ga,Fe)Sb with 20% Fe doping on the (111) plane and this showed very beautiful satellite peaks in the XRD. However, the TC of this sample was not so high and does not cross room temperature. So, we tried to dope more Fe and we were successful in increasing the Fe concentration up to 50% with clear RHEED patterns. This sample showed room temperature ferromagnetism. Also, a point to be noted is that the anisotropy of (Ga,Fe)Sb changed on doping more Fe and changed from out of plane to in plane anisotropy. This might suggest that the Fe is not forming nanopillar like structures and is being distributed more uniformly.

Finally, we decided to increase the Fe concentration further and found that we were also successful in growth of FeSb and FeAs with a possible cubic/ZB structure. The FeSb needs more optimization for its growth but the growth of FeAs has been achieved with very clean streaky RHEED pattern. To confirm this further we have measured the scanning tunneling electron microscopy (STEM) of FeAs and saw that the crystal structure is zinc blende with clear boundary between GaAs and FeAs. Also, the energy dispersive X-rap spectroscopy (EDS) mapping showed that there is no intermixing of Fe in the GaAs and no new phases precipitated. The transmission electron diffraction (TED) patterns also showed ZB patterns for both the buffer and the FeAs phase without any spots from a different phase which provide further confirmation that FeAs is of a ZB phase. The ratio of Fe to As however is not 1:1 and more than 1 which suggests that though the crystal is ZB there might be some irregularities such as antisite defects or interstitial Fe in the FeAs lattice. The XRD and X-ray reflectivity (XRR) measurements show that there is only one peak corresponding to GaAs which means that the FeAs lattice has the same lattice constant as that of GaAs and the density of the FeAs layer is higher than GaAs suggesting that there is extra Fe in the lattice. The magnetic properties have also been measured which showed that it has very clear square like hysteresis and a very high TC with M-T curve showing remanent magnetization even at 400K. The MCD signal shows a very high value of about 250mdeg at room temperature and a spectrum which does not resemble the other FMSs. However, the hysteresis is not open suggesting that the origin of ferromagnetism is different compared to the III-V Fe doped FMSs. Transport properties show that the FeAs film is metallic albeit a weak one with not even a factor of 2 difference between the room temperature and low temperature resistance. The magnetoresistance however corresponds to the magnetism measurements from SQUID showing anisotropic magnetoresistance (AMR) with a 2-fold and a 6-fold anisotropy which can be thought to be appearing from the crystal symmetry.

In conclusion, the growth of Fe doped QDs with high TC provide new opportunities to understand more about the origin of ferromagnetism and the growth of FMSs and the growth of ZB FeAs epitaxially over GaAs provides exciting opportunities for room temperature spintronics such as TMR devices and spin transistor devices. The discovery of PMR in (Ga,Fe)Sb/InAs structure and the capability of these materials in combination with epitaxial superconductors or topological materials which led to the renaissance of FMSs followed by these results means that these materials is still very much alive and kicking.