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学位論文題目 Spin Dependent Transport in Ferromagnetic Double Tunnel Junctions with Non-ferromagnetic Nanoparticles （非強磁性ナノ粒子を含む強磁性２重トンネル接合素子におけるスピン依存伝導に関する研究）
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論 文 内 容 要 旨

1. Introduction

Spintronics is a multidisciplinary field whose central theme is the active *manipulation of the spin degree of freedom of electrons* in solid-state devices. Developments of spin sources, manipulators and detectors can open new functionalities in solid-state devices, which could overcome the scale down issue in current solid-state devices that are operated via the manipulation of the charge of electrons.

Spin accumulation in non-magnetic materials is one of the key phenomena for the design of spintronics devices. This phenomenon is strongly influenced by spin relaxation in non-magnetic materials, which is mainly affected by spin-orbit interaction.

A ferromagnetic double tunnel junction with non-ferromagnetic nanoparticles shows spin-dependent single electron tunneling at low temperature due to the spin accumulation and the increase in the charging energy in non-ferromagnetic nanoparticles. This structure gives a model system to study the spin relaxation in non-ferromagnetic nanoparticles. In this structure, spin accumulation in the non-ferromagnetic nanoparticle is induced for the antiparallel configuration of the ferromagnetic electrodes due to the difference of the tunneling probabilities of conduction electrons that come into and go out from the non-ferromagnetic nanoparticle. This spin accumulation in non-ferromagnetic nanoparticles with the antiparallel configuration of the ferromagnetic electrodes changes the total tunneling probability compared to the parallel configuration in this structure, which induces tunnel magnetoresistance (TMR). Since this spin accumulation in non-ferromagnetic nanoparticle is non-equilibrium state, this state is going to change to equilibrium state due to spin relaxation. Thus, in this structure, TMR appears when the spin relaxation time in non-ferromagnetic nanoparticles is sufficiently long compared with the time interval between successive tunneling events.

Several previous papers revealed that the spin relaxation time in metallic nanoparticles was remarkably enhanced compared to that of bulk [1]. The enhancement of spin relaxation time is attractive for spintronics. However, it is noted that no experimental results have been reported on the temperature and/or size dependence to date. The systematic investigation on the temperature and/or size dependence of spin relaxation time will be able to give the significant information on the origin for its enhancement.

The main purpose of this study is to investigate the mechanism based on a systematic study for the enhanced spin relaxation time in non-ferromagnetic nanoparticles. More specifically, the systematic study includes nanoparticle size dependence and temperature dependence of spin relaxation time.

We chose two types of non-ferromagnetic materials: Au and Cr nanoparticles. Spin accumulation, i.e., the spin-dependent Fermi level shift in nanoparticles is required for the appearance of TMR. This shift is inverse proportional to the density of states at the Fermi level. Both elements have relatively low electronic density states at the Fermi level.

2. Experimental

A typical sample structure is shown in Figure 1. All layers were grown on a polished MgO (100) single crystal substrate using molecular beam epitaxy (MBE). A typical film structure was MgO (100) substrate/MgO buffer, 5nm/Fe buffer, 40nm/1st MgO barrier, 1.5nm/ Au or Cr nanoparticles/ 2nd MgO barrier, 3nm/Fe, 10nm/Au capping layer. Au or Cr nanoparticles were formed on the MgO barrier due to the Volmer-Weber mode. The size of nanoparticles was controlled by changing the nominal thickness.

Nano size pillars were fabricated using the combination of electron beam lithography and Ar ion etching techniques. Electronic transport properties were measured with the two-terminal method in various temperatures.
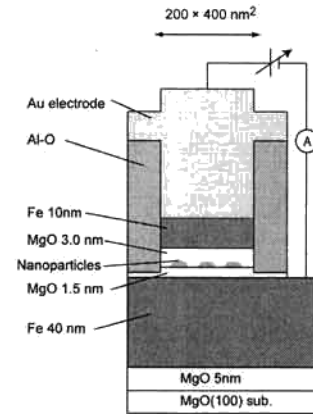

Fig.1 Typical sample structure of a ferromagnetic double tunnel junction with non-ferromagnetic nanoparticles.

3. Spin-dependent transport in Au nanoparticles

We prepared the samples with several different sizes of Au nanoparticles and measured electric transport properties in various temperatures. The samples showed clear Coulomb blockade at 7 K. The size of Au nanoparticle was estimated to be 1.5 to 2.2 nm in diameter from the threshold voltage of Coulomb blockade. The samples showed clear TMR when the bias voltage expected a critical voltage. Since this TMR is induced by the spin accumulation in Au nanoparticles, the critical bias voltage exists for the appearance of TMR as explained.

Spin relaxation time was estimated using the following relation $\tau_{SF} \approx e/I_C^{TMR}$. Here, τ_{SF}, e and I_C^{TMR} are spin relaxation time, electron charge and critical current for the appearance of TMR, respectively. The estimated spin relaxation of Au nanoparticles with the diamter of 1.5 nm was 800 ns, which is much longer than that of Au bulk. The temperature dependence of spin relaxation time of Au nanoparticle with the diameter of 1.5 nm showed unique behavior as shown in Figure 2. The spin relaxation time showed an almost constant value of 800 ns below the temperature of 70 K, then decreased monotonically with temperature and TMR disappeared at around 130 K. Single electron tunneling (SET) governed the electronic transport due to the small size of Au nanoparticle and SET disappeared at around 220 K, indicating that SET did not directly correlate with the spin relaxation.

Since the estimated Au nanoparticle size was 1.5 nm in diameter, it is reasonable to think about the electronic energy level quantization in the Au nanoparticle [2] ; the spacing of the energy level δ was evaluated to be about 30 meV from the size of the Au nanoparticle. The energy level quantization plays a dominant role if the condition $\delta > 3.5 k_B T$ [3] is satisfied, where k_B is the Boltzmann constant and T is temperature. For our experiments, this temperature was found to be about 100 K, which is close to the temperature for the disappearance of TMR,
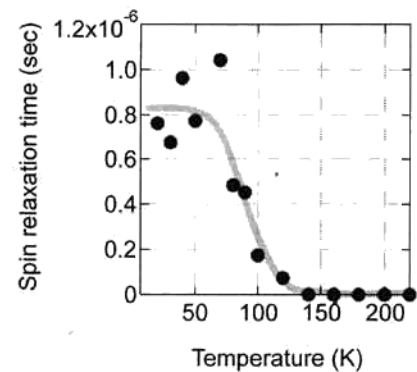

Fig.2 Temperature dependence of spin relaxation time of Au nanoparticle with the diameter of 1.5 nm.

corresponding to the temperature for the drastic decrease of spin relaxation time.

Spin relaxation time showed a drastic decreased above a critical temperature. The critical temperatures for the appearance of TMR decreased rapidly with increasing the size of the particle as shown in Figure 3. The curve for the condition of the appearance of the effect of electronic energy level quantization is also plotted. This curve is consistent with the data points, indicating that the energy level quantization strongly enhances the spin relaxation time in nanoparticles. Thus, we can explain the temperature dependence of spin relaxation time shown in Figure 2 as follows. Below 60 K, the electronic discrete energy level is much larger than that the thermal broadening of each level. Above about 60 K, the thermal broadening effect is not negligible, and the effective spacing between electronic discrete energy levels decreases with temperature, which reduces the spin relaxation time with

Fig.3 Size dependence of the temperature for the appearance of TMR. The red curve shows the condition for the appearance of quantum size effect.

temperature. Above 130 K, the thermal broadening is larger than spacing between electronic discrete energy levels and the effect of discrete electronic energy levels does not work.

We examined a possible microscopic origin of enhanced spin relaxation time due to the existence of discrete electronic energy level. Previously Kawabata [4] proposed the relation between spin relaxation time τ_{SF} and the particle diameter d,

$$\frac{1}{\tau_{SF}} = \frac{\Delta g(d)^2 V_F}{d}$$

$$\Delta g(d) \approx \frac{V_{SO}}{\delta}$$

where $\Delta g(d)$ is the conduction electron g-shift from the g factor of free electrons with the particle size d, V_F is the Fermi velocity and V_{SO} is the spin-orbit coupling constant. Since Δg is proportional to the cube of diameter, the spin relaxation time is inversely proportional to the fifth of diameter. This expression can explain the extremely enhanced spin relaxation time in nanoparticle compared to that in bulk.

The nanoparticle size changes not only electronic energy levels but also phonon modes in materials. In a nanoparticle, the lowest mode of phonon is determined by the perimeter of the particle, and a half-wavelength is the same as the particle diameter. This phonon mode restriction affects momentum scattering of conduction electrons by phonons, which influences spin relaxation process. Our analysis reveals that the temperature for the lowest phonon mode in Au nanoparticle with the diameter of 1.5 nm is close to the temperature for the appearance of TMR, suggesting that the size induced phonon modulation in Au nanoparticles also affects spin relaxation and contributes to the unique temperature dependence of spin relaxation time.

4. Spin-dependent transport in Cr nanoparticles

We successfully obtained a double tunnel junction with Cr nanoparticles. The average size of Cr nanoparticles was around 4 nm in diameter with the size distribution of 20 % estimated from an atomic force microscope observation.

Electronic transport properties were evaluated at 7 K. Current-voltage characteristics showed that the current was well suppressed in the low bias voltage range, indicating that SET governed the electronic transport properties. The threshold voltage for Coulomb blockade was found to be 40 mV. TMR was observed only in the bias voltage range over 0.25 V and the MR ratio increased with increasing the bias voltage up to 0.35V, indicating that this TMR is induced by the spin accumulation in Cr nanoparticle.

Spin relaxation time in Cr nanoparticles was found to be of the order of tens of nano seconds, which is shorter than that in Au nanoparticles. A possible reason of the difference of spin relaxation time between Cr and Au nanoparticles is due to the interface state
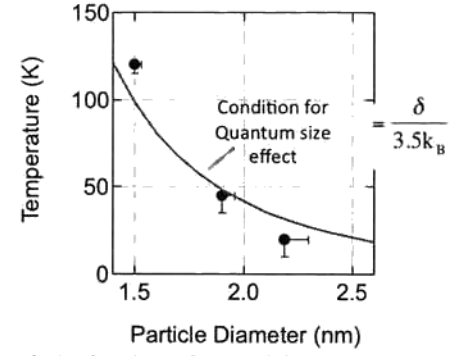
of Cr nanoparticle. Cr oxide could exist at the interface between the Cr and MgO interface, which suppresses spin accumulation in Cr nanoparticles due to the spin scattering at the interface and reduces the spin relaxation time in Cr nanoparticle.

5. Conclusions

In order to understand the mechanism of enhanced spin relaxation time in nanoparticles, we have performed a systematic study of spin relaxation time using double tunnel junctions with non-ferromagnetic nanoparticles. We used two types of elements, Au and Cr nanoparticles. The conclusions of the whole study are as follows.

1) To investigate temperature and size dependence of spin relaxation time, ferromagnetic double tunnel junctions with Au nanoparticles were successfully prepared. We observed clear Coulomb blockade in those samples. The estimated nanoparticle size from the threshold voltage of Coulomb blockade was in the range of 1.5 to 2.2 nm in diameter. Those samples appeared clear TMR induced by spin accumulation in Au nanoparticle. The estimated spin relaxation time of Au nanoparticles were several hundreds of ns, which was much longer than that of Au bulk (10 ps). The spin relaxation time with the diameter of 1.5 nm showed an almost constant value of 800 ns below the temperature of 70 K, then decreased monotonically with temperature and TMR disappeared at around 130 K. It should be noted that single electron tunneling (SET) governed the electronic transport below 220 K, indicating that SET does not directly influence the spin relaxation. Spin relaxation time showed a drastic decrease above a critical temperature and TMR disappeared. We also found that this critical temperature decreased rapidly with the increase in the size of Au nanoparticles. Our analysis reveals that the critical temperature agrees with that where the thermal broadening of discrete electronic energy levels shows considerable effect.

2) To investigate enhanced spin relaxation time in non-ferromagnetic transition metal nanoparticles, double tunnel junctions containing Cr nanoparticles were successfully obtained. The electronic transport properties are measured at 7 K. The Cr nanoparticles showed clear Coulomb blockade and TMR appeared above the bias voltage of 0.25 V due to the spin accumulation. Estimated spin relaxation time in Cr nanoparticles is of the order of tens of nano seconds, which is shorter than that in Au nanoparticles.

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論文審査結果の要旨

　電子の電荷とスピンという2つの自由度を活用したスピントロニクスが、新しいエレクトロニクスとして現在関心を集めている。スピン緩和時間は、スピントロニクスデバイスを動作させる為の重要な因子の一つである。近年、幾つかの研究グループから、金属ナノ粒子のスピン緩和時間がバルクに比べて著しく増大することが報告され、注目されている。しかし、スピン緩和時間がナノ粒子のサイズや温度に対してどのように変化するかを系統的に研究した例はなく、したがってスピン緩和時間増大のメカニズムも十分に解明されていない。本論文は、非強磁性金属ナノ粒子を強磁性電極で挟んだ2重トンネル接合素子を作製し、そのスピン依存単電子トンネル伝導に関して、ナノ粒子のサイズ及び温度に対する変化を系統的に評価し、ナノ粒子中で生じるスピン緩和時間の増大現象について考察したものであり、全編5章から成る。

　第1章は序論であり、本研究の背景および目的を述べている。

　第2章では、本研究における試料の作製法と評価法について述べている。

　第3章では、MgO トンネル障壁を介して Au ナノ粒子を2つの Fe 電極で挟んだ試料のスピン依存単電子トンネル伝導について、Au ナノ粒子のサイズ及び温度依存性の実験結果と考察を述べている。低温で Au ナノ粒子内のスピン蓄積に起因するトンネル磁気抵抗効果（TMR）が観測され、スピン緩和時間はバルクに比較して顕著に増大していることがわかった。温度を上昇させると、スピン緩和時間はある温度から急激に減少し、TMR も消失するが、その温度はサイズに強く依存することが示された。また、スピン緩和時間とクーロンブロッケードの閾値電圧の温度依存性を比較すると、両者の間に特別な相関は見られなかった。Au ナノ粒子のサイズが 1.5-2.2 nm と非常に微小であることから、電子エネルギーの離散効果を考慮して実験結果を解析したところ、スピン緩和時間と電子エネルギーの離散化に強い相関があることが見出された。以上の結果から、スピン緩和時間が低温で増大する要因として、電子エネルギーの離散化に伴い、スピン軌道相互作用がバルクよりも抑制されることを説明している。さらに、スピン緩和時間の温度依存性の考察から、ナノ粒子内のフォノンモードにもサイズ効果が現れることを指摘し、フォノンモードのサイズ効果もスピン緩和時間の増大に関与することが示唆されている。

　第4章では、MgO トンネル障壁を介して Cr ナノ粒子を2つの Fe 電極で挟んだ試料のスピン依存単電子トンネル伝導に関する実験結果及び考察を述べている。Cr ナノ粒子の場合も Au ナノ粒子と同様に、低温でスピン蓄積に起因する TMR が観測され、スピン緩和時間がバルクと比較して増大していることがわかったが、スピン緩和時間は Au ナノ粒子より小さいことが示されている。

　第5章は総括である。

　以上要するに本論文は、非強磁性ナノ粒子のスピン緩和時間の増大現象について、スピン依存単電子トンネル伝導を用いて、系統的かつ詳細な研究を行い、その起源に関する重要な知見を得たもので、スピントロニクスに関わる材料物性学の発展に寄与するところが少なくない。

　よって，本論文は博士（工学）の学位論文として合格と認める。