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Spin Injection, Detection and Magnetoresistive Effects in Organic Systems

A thesis submitted to the University of Dublin, Trinity College
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy
By
Hongjun Xu

School of Physics
Trinity College Dublin
September 2015
Declaration

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Acknowledgments

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Abstract

Because of the weak spin-orbit interaction in organic systems, very long spin lifetimes are intuitively expected. The prospect of cheap and flexible spintronics devices makes organic semiconductors an attractive class of material systems for investigation. Although organic-based spin-valve devices have been widely studied, organic spintronics is still in its infancy. Some fundamental questions, for example the relation between spin injection and magnetoresistance, the exact spin lifetime and carrier mobility in spin-valve devices and the details of the spin relaxation mechanisms, are not well-understood. In this thesis, we investigate the injection of spin-polarized current into organic thin films, prepared following various recipes and relate the possible transport mechanisms with the observed Magnetoresistance (MR) in organic-based spin-valves devices.

In chapter 1, a brief introduction about the background and a motivation of the overall work are presented. Starting with the most conventional MR effect, in chapter 2, we show the origin of conductivity mismatch problem, on the basis of the spin-dependent diffusion model. Possible solutions for this problem are introduced, especially the use of tunnel barriers. Besides the ordinary MR effect, the nonlocal spin-valve measurement for pure spin current detection is described under a similar spin diffusion model. The phenomenon of spin precession is highlighted in the following section. Because for experiments we are often using tunnel barriers, we also illustrate the possible MR phenomena related to inelastic tunneling processes. The magnetic field-modulated resonant tunneling model is employed to understand the Hanle-like MR in a FM/I/NM junction. An experimental overview of organic spintronics is outlined and, in particular, the spin injection in spin-valve devices is treated in more detail. The current status of electric spin injection into organics is that unambiguous experimental evidence is missing from the field.

In chapter 3 & 4, we describe the various recipes for spin-valve devices fabrication and the corresponding magnetotransport results on organic-based spin valves. AlOₓ, MgO, and MgO/AlOₓ tunnel barriers were used in our experiments. Liquid nitrogen cooling and a simply recipe of making small-size junctions were introduced. Both changes are supposed to improve the normally poor quality of the ill-defined interfaces between the organic layers
and top FM electrodes. Because MR vanishes in samples that showed hopping transport features, a multi-step tunneling model is used to explain the temperature dependence of conductance and MR in the AlOx/C60 based devices.

In chapter 5, we turn to a new method, three-terminal spin injection in structures with only one FM electrode. The spin signals due to spin accumulation and precession are actually much lower than the widely-report Hanle like MR (Lorentzian line shape) under a perpendicular magnetic field. The exotic effect from the resonant or multi-step tunneling via the localized states inside the tunnel barrier can nicely explain the behavior. We have found the evidence, from temperature and bias-voltage dependence of conductance and MR, for a multi-step tunneling process in our MgO-based three-terminal devices. We further provide the inelastic tunneling spectroscopy and non-local spin valve observations to support our conclusions.

In chapter 6, results from three-terminal spin injection method applied to organic layers are shown. The very similar result to the case of NM metals indicates that this method is not credible for organics, as well. However, we put forward some alternative methods for injecting and detecting spin currents in organic thin films and even individual molecules.

We finally summarize the main results of the thesis work, in chapter 7, and point out the future work based on those.
<table>
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<tr>
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<th>Definition</th>
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<tbody>
<tr>
<td>3T</td>
<td>Three-Terminal</td>
</tr>
<tr>
<td>AP</td>
<td>Anti-Parallel</td>
</tr>
<tr>
<td>CM</td>
<td>Cassette Module</td>
</tr>
<tr>
<td>EPD</td>
<td>End Point Detector</td>
</tr>
<tr>
<td>EBL</td>
<td>Electron Beam Lithography</td>
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<td>FMR</td>
<td>Ferromagnetic Resonance</td>
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<tr>
<td>FM</td>
<td>Ferromagnetic</td>
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<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>GMR</td>
<td>Giant Magnetoresistance Effect</td>
</tr>
<tr>
<td>HR</td>
<td>High Resistance</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>IETS</td>
<td>Inelastic Electron Tunneling Spectroscopy</td>
</tr>
<tr>
<td>LR</td>
<td>Low Resistance</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>LSs</td>
<td>Localized States</td>
</tr>
<tr>
<td>LE-μSR</td>
<td>Low energy Muon Spins Rotation</td>
</tr>
<tr>
<td>LN</td>
<td>Liquid Nitrogen</td>
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<tr>
<td>MR</td>
<td>Magnetoresistance</td>
</tr>
<tr>
<td>MTJ</td>
<td>Magnetic Tunnel Junction</td>
</tr>
<tr>
<td>NM</td>
<td>Nonmagnetic Materials</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>NLSV</td>
<td>Non-local Spin Valves</td>
</tr>
<tr>
<td>OMT</td>
<td>Orbital Mediated Tunneling</td>
</tr>
<tr>
<td>OMAR</td>
<td>Organic Magnetoresistance</td>
</tr>
<tr>
<td>OS</td>
<td>Organic Semiconductor</td>
</tr>
<tr>
<td>PM</td>
<td>Process Module</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz Crystal Monitor</td>
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<tr>
<td>SCLC</td>
<td>Space-Charge Limited Current</td>
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<tr>
<td>SC</td>
<td>Semiconductor</td>
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<tr>
<td>SCO</td>
<td>Spin-Cross-Over</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-Assembled Monolayers</td>
</tr>
<tr>
<td>TFTs</td>
<td>Thin Film Transistors</td>
</tr>
<tr>
<td>TMR</td>
<td>Tunnel Magneto-Resistance</td>
</tr>
<tr>
<td>TM</td>
<td>Transfer Module</td>
</tr>
<tr>
<td>TAMR</td>
<td>Tunneling Anisotropic Magnetoresistance</td>
</tr>
<tr>
<td>VRH</td>
<td>Variable Range Hopping</td>
</tr>
<tr>
<td>ZBA</td>
<td>Zero Bias Anomaly</td>
</tr>
<tr>
<td>ISHE</td>
<td>Inversed Spin Hall Effect</td>
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Chapter 1 Introduction

1.1 Organic Spintronics

Spintronics, a spin-based electronics, functionalizes the electron's spin degree of freedom in addition to its charge, as in conventional electronic devices\(^1\). The potential advantages of spintronic devices over traditional semiconductor devices are nonvolatility, lower electric power consumption and higher integration densities. Since the first discovery and application of the giant magnetoresistance effect (GMR)\(^2\), research on spintronics has been extended from metal systems to semiconductors, insulators, organic and carbon-based systems, covering the fields of electronics, photonics and magnetism. Besides charge, spin is one of the intrinsic fundamental properties of the electron and it should, in principle, show up in every aspect whenever electrons are used. For nonmagnetic materials, however, the numbers of electrons in the two spin directions are equal, they always counterbalance each other, and the spin properties of electron are thus concealed, except for the two-fold degeneracy of the electron states.

In order to successfully incorporate spins into existing nonmagnetic semiconductors, one needs to create a dynamic imbalance of spins (in other words, a spin-polarization) and detect them before spin relaxation to the equilibrium state\(^3\). The characteristic parameter, the spin lifetime, denotes the time it takes for the spin imbalance to return to equilibrium via different relaxation mechanisms. Potential systems for spintronic applications should possess a relatively long spin lifetime. Usually, spin-orbit interaction is the main mechanism that dominates spin relaxation and determines the spin lifetime. Therefore, the materials that show weak spin-orbit interaction should be favoured for investigations. Organic materials are mainly composed of carbon, hydrogen and oxygen, light elements that are believed to encourage extremely long spin lifetimes (\(\mu s \sim ms\)) compared to their inorganic counterparts\(^4\).
Because of the low cost and the high versatility and flexibility, organic materials attracted a lot of attention during last decade. Before they can be applied, the fundamental physics and basic properties involved in spin injection and detection in organic materials need to be understood. Unfortunately, because of the weak spin-orbit interactions in organic systems, many methods proved effective in inorganic materials for spin injection and detection do not work for organics, for example magneto-optical effects and spin Hall effect.

One notable point is that the expected extremely long spin lifetime in organics has not yet been observed directly in real spintronics devices. The spin relaxation times (up to ms at room temperature) measured by electron paramagnetic resonance actually characterize the spin relaxation process in special sites localized in the organic species. They differ from the case that the extra spins are injected from an external source, transported in the organic channel and relaxed during the transport, which are the ones that need to be measured directly in such systems. Furthermore, it is still controversial whether the external spins can be successfully injected from a ferromagnetic (FM) source into the organic channel and bring about the widely-reported magnetoresistance (MR) effects. The above two issues are closely related.

1.2 This thesis

In this thesis we aim to understand if it is possible to inject, transport and detect spin polarized carriers in organic thin films. In order to clearly show the relation between MR and the transport mechanism, we will first focus on the C₆₀-based spin-valve stacks (FM/I/OS/FM) fabricated using various recipes including: Al₂O₃ and MgO tunnel barriers, big size junctions and small size junctions prepared with and without liquid nitrogen cooling. Obvious MR effects were only observed in the tunneling regime. We have used the multiple-step tunneling model to reproduce the temperature dependence of the MR. In agreement with most of the
reported results, the MR vanishes as the variable range hopping (VRH) emerges in the C_60 layers.

In view of the reported successes of the new three-terminal spin injection method for inorganic semiconductors, we have performed systematic work on the FM/I/NM to study the possibility of injection and detection of spin with only one FM electrode. Spin lifetime was supposed to be measured by the three-terminal Hanle measurement. Hanle-like MR curves were observed for different NM metals (Al and Au etc.), and a comprehensive body of work was performed to clarify the underlying mechanisms by combining the temperature and bias voltage dependence of the magnetotransport with the tunneling spectroscopy technique. It turned out to be the localized states inside the tunnel barriers (1) that play the main role in the observed Lorentzian line-shape (i.e. Hanle-like) MR curves. On the other hand, four-terminal nonlocal measurement was introduced in the vertical FM/I/NM stacks, which excluded the contribution of spin accumulation in NM to the Hanle-like MR.

The three-terminal spin injection method was applied in the organic case, as well. However, similar results to the case of NM metals were found. The spin lifetime obtained by this method is therefore not credible. We have, thereby, proposed some updated methods for the future study of the intrinsic properties of certain special organic materials. We hope these suggestions can bring us a more fundamental understanding in the transport properties and the role of the electronic spin in organic materials.
Bibliography

Chapter 2 Basic concepts and theory

Conventional electronics is based on the semiconductors like Si, Ge and GaAs, where the charge properties (density and mobility) of the electrons are manipulated. On the other hand, the electron possesses an intrinsic angular momentum with quantum number \( s = 1/2 \), which leads to two spin states, spin up \( \uparrow \) and spin down \( \downarrow \) along any defined direction. The associated projection of the magnetic moment is \( \pm \mu_B = \pm e\hbar/2m_e \), where \( \mu_B \) is Bohr magneton, \( e \) is the electron charge, \( \hbar \) is the reduced Plank constant and \( m_e \) is the electron mass. However, this intrinsic property of electron usually isn't incorporated in conventional electronics because the equal possibility of spin up and spin down of electrons in most non-ferromagnetic semiconductors conceals the spin-related properties.

On the contrary, spin manifests itself in ferromagnetic materials, where the exchange interactions couple the spin of the unpaired electrons parallel with each other, and the collective behavior of electron with the same spin gives rise to the magnetization\(^1\). Especially, for the FM metals (e.g. 3d metals), the s-d interaction polarizes the mobile electrons to give spin-split energy bands at the Fermi level. For the majority of spin direction is parallel to the magnetization. In these systems, the spin-polarization can be defined as\(^2\):\(^2\)

\[
P_n = \frac{\nu^N_{\uparrow}N_1 - \nu^N_{\downarrow}N_1}{\nu^N_{\uparrow}N_1 + \nu^N_{\downarrow}N_1} \quad (2.1)
\]

where \( \nu_f \) is the Fermi velocity and \( N \) is the density of state at Fermi level, \( \uparrow \) and \( \downarrow \) are corresponding to the majority and minority spin electrons with moments parallel and antiparallel to the magnetization direction respectively. The power \( n \) depends on the physical process involved, e.g. \( n = 2 \) for diffusive transport or tunneling at low bias. Assuming that spin-flip scattering can be neglecting in the system, the conductivity can be then expressed as the sum of the conductivity of two channels in parallel, spin up \( \uparrow \) and spin down \( \downarrow \). These
two channels have conductivity: $\sigma_{\uparrow \downarrow} = N_{\uparrow \downarrow} e^2 D_{\uparrow \downarrow}$ where $\sigma_{\uparrow \downarrow}$, $N_{\uparrow \downarrow}$ and $D_{\uparrow \downarrow}$ are spin-dependent conductivity, density of states at Fermi energy and diffusion constant of the two spin channels.

Figure 2.1 An illustration of the GMR effect where the resistances of the spin-up and spin down channels depend on the parallel (left) and antiparallel (right) alignments of the magnetizations of two magnetic layers (top panel). The corresponding resistor model is shown below, where $\rho_{\uparrow \downarrow} = (\sigma_{\uparrow \downarrow})^{-1}$ are the spin-dependent resistances. Current is perpendicular to the plane of the layer.¹

Suppose that two FM layers are separated by a nonmagnetic (NM) spacer layer where the spin-flips can be neglected (current flows perpendicular to the plane, the CPP mode). The magnetizations of the two FM layers can be independently changed to have the configurations with their magnetizations parallel or antiparallel to each other. Electrons of each spin direction transport independently in each layer and experience different scattering there, thus the net scattering events (i.e. resistance) can be different depending on the relative orientation of the two adjacent FM layers (ignoring any spin-independent resistance in the NM layer). As shown in Fig. 2.1, in the parallel state the net resistance is, $R_p = (\sigma_{\uparrow} + \sigma_{\downarrow})/2$, 

¹
where $\sigma_1$ and $\sigma_3$ are the conductance of majority and minority spin electrons that are parallel or antiparallel to the FM magnetization direction, respectively. For the antiparallel state, $R_{ap} = (\sigma_1^{-1} + \sigma_3^{-1})/2$, which is larger than $R_p$. Such trilayer structures are called 'spin valves'; and the MR of a spin-valve is defined as:

$$\frac{\Delta R}{R_p} = \frac{R_{ap} - R_p}{R_p} = (\sigma_1 - \sigma_3)^2/4\sigma_1\sigma_3$$

Hence, MR of such structures is determined by $\sigma_1/\sigma_3$, which is related to the polarization of the conduction electrons in the FM. This simple picture presents the essence of a GMR device. Actually, the first observation of the GMR effect was made in a Fe/(Cr/Fe)$_N$ multilayer structure with the current flowing in the plane of the layers (CIP mode), which triggered the birth of metal spintronics. In real GMR devices, the scattering at the FM/NM interfaces dominate the system resistance. However, a spin-dependent interface conductance can be defined similarly, and the above analysis remains valid.

Like the three-terminal field effect transistor for semiconductors, the spin-valve device is the elementary device for the spintronics. Many other devices are derived from it, such as non-local spin valves (NLSV) and spin-valve transistors. It is also employed to investigate the fundamental properties of new FM and NM materials including half-metals, semiconductors, molecular magnets and even superconductors.

If one replaces the non-magnetic spacer layer in the CPP sandwich structure with a thin insulating layer, where the electron can tunnel through without loss of spin polarization, then a magnetic tunnel junction (MTJ) is formed. The thin tunnel barrier is typically made of 1-2 nm of amorphous AlO$_x$ or crystalline MgO. Depending on the structure of the FM electrodes and the tunnel barrier, the tunneling processes can be different. The tunnel magnetoresistance (TMR) of the MTJ is defined in the same way as in spin-valve devices. Jullière made a simple assumption that the spin-dependent transmission probability can be neglected and the tunneling probability across the barrier is simply proportional to the
product of the densities of states in the two FM electrodes. The TMR is thus given by:

\[
TMR = \frac{(N_1^+N_2^- + N_1^-N_2^+)-(N_1^+N_2^- + N_1^-N_2^+)}{(N_1^+N_2^- + N_1^-N_2^+)} = 2P_1P_2/(1 - P_1P_2) \tag{2.3}
\]

where \(P_i = (N_i^+ - N_i^-)/(N_i^+ + N_i^-)\) \((i = 1, 2)\) is the spin polarization of the FM electrodes. This model seems too simple, but, it can be generalized by replacing the FM spin polarization with an effective polarization (i.e. the averaged interfacial transmission polarization) which is applicable for incoherent tunneling in amorphous 'thick' tunnel barriers. However, for crystalline tunnel barriers with epitaxial FM electrodes, coherent tunneling takes place where the momentum of electron is conserved. The transmission probability does not just depend on the density of states at the Fermi level, but rather on the convolution of the Fermi surfaces of the electrons on either side of the barrier. It is very important to note that crystalline MgO epitaxially grown on bcc Fe (100) can act as a near-perfect spin filter in terms of symmetry of the electronic Bloch function. The \textit{ab initio} calculations showed that the \(\Delta_1\) (\(spd\)-like character) state has the smallest decay rate across the MgO, followed by the \(\Delta_5\) (\(pd\)-like) then the \(\Delta_2\) (\(d\)). Besides, only the majority spin of Fe (100) has the \(\Delta_1\) state. Therefore, in the parallel configuration, the tunneling is expected to be dominated by the propagation of \(\Delta_1\) and \(\Delta_5\) electron but only \(\Delta_5\) electron with a larger decay rate in MgO for antiparallel configuration. Because of the much smaller attenuation rate of majority-spin electrons (\(\Delta_1\)) in the barrier, huge TMR values in excess of 1000\% were predicted for Fe/MgO/Fe in theory and large values are indeed realized in experiments with a slightly different MTJ structure of CoFeB/MgO/CoFeB. The tunneling process in MgO-based MTJs may be still roughly described by the above Julliere formula with \(P\) standing for an average effect of electron density and transmission probability.
2.1 Spin injection and detection

Stimulated by the success of spin-valves and MTJs, some prototype devices, such as spin-transistors were proposed which introduce non-equilibrium spin accumulation in the semiconductor (SC) channel\textsuperscript{10}. Electric field manipulation due to the Rashba effect was suggested to coherently control spin precession of carriers. To realize such a device, the first step is to generate a spin-polarized electron source in the non-magnetic semiconductor, which can be done by direct electric spin injection from a ferromagnetic metal, optical spin injection via the selection rules in semiconductors or dynamic spin pumping. The second point is to transport spin through a suitable medium where the spin information can be preserved over a distance comparable to the devices' feature dimensions when it is possible to manipulate spin by an external field. A spin detector at the second terminal of the device is required to convert the spin signal into another measurable signal by some physical effect such as the magneto-optic effect and the inverse spin-Hall effect or magnetoresistance (MR). MR effect, the change of the device resistance upon the application of an external magnetic field, serves as the standard method to investigate spin-related phenomena. With the MR effect, spin-valve structures of FM/SC/FM are perhaps the most straightforward for electrical spin injection and detection in the SC materials. Therefore, a great deal of effort has been devoted to the MR effect of spin-valve devices, both in experiment and theory. More details will be given in the following parts of this chapter.

2.1.1 Conductivity mismatch problem and possible solutions

It was first found from theory by Schmidt \textit{et al}\textsuperscript{11} that there is a fundamental obstacle for electrical spin injection from a FM metal into a SC via an ohmic contact. Based on the assumption that the spin-scattering rate is much smaller than the electron scattering rate, two electrochemical potentials $\mu_1$ and $\mu_2$ can be defined for two spin directions at any point of the FM/SC/FM device. Considering the one-dimensional case for simplicity, they wrote the
following equations, which result from a diffusive model of conduction and reflect Ohm's law and a diffusion equation for the electrochemical difference:

\[
\frac{\partial \mu_{\uparrow \downarrow}}{\partial x} = \frac{\partial j_{\uparrow \downarrow}}{\partial \sigma_{\uparrow \downarrow}} \tag{2.4.1}
\]

\[
\frac{\mu_{\uparrow} - \mu_{\downarrow}}{\tau_{sf}} = D \frac{\partial^2 (\mu_{\uparrow} - \mu_{\downarrow})}{\partial x^2} \tag{2.4.2}
\]

where \(\sigma_{\uparrow \downarrow}\) is the spin-dependent conductivity, \(D\) is a weighted average of the different diffusion constants for both spin directions and \(\tau_{sf}\) is the spin-flip time constant (in other words, the spin lifetime). The spin-polarization of the current is defined as: \(\alpha = (j^\uparrow - j^\downarrow)/(j^\uparrow + j^\downarrow)\) and set the bulk spin-polarizations in the two FM identical far from the interface, \(\alpha_F = \beta\). Hence, \(\sigma_F^\uparrow = \sigma_F(1 + \beta)/2\) and \(\sigma_F^\downarrow = \sigma_F(1 - \beta)/2\). Schmidt considered the ideal case for simplicity but without loss of essential physics: for the semiconductor, set \(\tau_{sf} = \infty\) (i.e. ignore spin relaxation) as the spin diffusion length \(l_s = \sqrt{D\tau_{sf}}\) can be much larger than the SC channel length, \(L\); for the interface assume no spin scattering or interface resistance. Therefore, the general solutions of electrochemical potentials in the diffusion equation in the different regions can be written as:

\[
\mu_{x^\uparrow \downarrow} = \mu_{0} + Ax + B_{x^\uparrow \downarrow} \exp(-|x-x^\uparrow|/l_s) \tag{2.5}
\]

\[
\mu_{x^\uparrow \downarrow} = \mu_{x^\uparrow \downarrow}(0) + C_{x^\uparrow \downarrow} x
\]

Taking account of the boundary conditions that require continuity of \(\mu_{x^\uparrow \downarrow}\) and \(j_{x^\uparrow \downarrow}\) at the interface of \(x_{F1} = 0\) and \(x_{F2} = L\) and \(x \to \pm \infty\) with charge conservation at each site, the electrochemical potentials and the currents in each spin channel can be obtained. Fig. 2.2 shows a schematic drawing of the electrochemical potentials in different regions, which shows that only in the parallel state is the current in the SC spin-polarized (\(j^\uparrow \neq j^\downarrow\)). From the electrochemical potentials, the current density in each spin channel can be calculated and
the total resistances in the parallel and antiparallel configurations are obtained for the MR\textsuperscript{11}:

![Figure 2.2](image)

Figure 2.2 The electrochemical potentials in the three different regions for parallel (left) and (right) antiparallel configurations of the two FM electrode magnetizations.\textsuperscript{11}

\[ \frac{\Delta R}{R_p} = \frac{\beta^2 \frac{l_{sf}^F}{\sigma_F^2} \sigma_s^2}{1 - \beta^2 \left( \frac{2l_{sf}^F \sigma_s}{L \sigma_F + 1} \right)^2 - \beta^2} \]  \hspace{1cm} (2.6)

For the typical values of $\beta \sim 0.6$, $l_{sf}^F \sim 10$ nm, $L \sim 100$ nm, $\sigma_s/\sigma_F \sim 10^4$, the MR is proportional to $(l_{sf}^F/\sigma_F)^2/(L/\sigma_s)^2$ with a value $\sim 3.5 \times 10^{-10}$, which is too tiny to be measured. This reveals the fundamental difficulty in spin injection and detection in the FM/SC/FM structures even if there is no spin relaxation in the SC because of the mismatch term, $(l_{sf}^F/\sigma_F)/(L/\sigma_s) \sim 0$. This is the so-called conductance mismatch problem, which can be qualitatively understood by the resistor model. In the FM the resistances of the two spin channels are spin-dependent and different. However, the resistances in the non-magnetic semiconductor are spin-independent and also much larger than the resistance in FM metals. Because of the series connection, no matter what the spin direction, almost all the electrons experience similar resistance (or change of electrochemical potential) in the semiconductor which also smears the spin accumulation in the SC and thus MR cannot be observed.

As suggested by Rashba, the above problem can be can be solved by introducing a spin-
dependent interface resistance, typically a tunnel junction, on condition that the spin-dependent tunneling resistance is comparable to the resistance of the semiconductor. Later on, Fert and Jaffrès carried out a more detailed calculation and found conditions for efficient spin injection from a FM metal into a SC that are different from the result obtained by Rashba in the upper value of interface resistance. Similar to a CPP-GMR model, the interface resistance is treated as:

\[ r_{\text{t.i.}} = 2\gamma(1 + \gamma) \]  

\[ \mu_{\uparrow,\downarrow}(Z_0^+) - \mu_{\uparrow,\downarrow}(Z_0^-) = r_{\uparrow,\downarrow}(Z_0) \]  

Where \( \gamma \) is the tunneling spin polarization (i.e. \( P \) in Eq. 2.3) and \( \mp \) correspond to the spin up (-) and spin down electrons (+) respectively. With Eq. 2.4, the electrochemical potentials were solved to have the current spin-polarization and MR:

\[ \alpha_{\text{t.i.}} = \left( \frac{J - J}{J} \right) = \frac{\beta r_{\text{F}} + \gamma r_{b}}{r_{\text{F}} + r_{n} + r_{b}} \]  

\[ \Delta R = \frac{4(\beta r_{\text{F}} + \gamma r_{b})^2}{2(r_{b}^* + r_{b}) \cos h(t_{N}/l_{N}^+) + r_{N}(1 + (r_{b}^*/r_{b})^2) \sinh(t_{N}/l_{N}^+)} \]  

\[ R^p = 2(1 - \beta^2) r_{\text{F}} + r_{n} l_{N}/l_{N}^+ + 2(1 - \gamma^2) r_{b}^* + 2(\beta - \gamma)^2 r_{\text{F}} r_{b}^* + 2 r_{N}(\beta^2 r_{\text{F}} + \gamma^2 r_{b}^*) \tan h(t_{N}/2l_{N}^+) \]  

Where \( (\alpha)_{\text{t.i.}} \) is the current spin polarization at the interface, \( \beta \) is FM bulk spin-polarization, \( r_{\text{F}} = l_{N}^F/\sigma_{\text{F}}, \quad r_{n} = l_{N}^n/\sigma_{n} \), \( t_{N} \) is the thickness of non-magnetic layer. Actually, \( r_{\text{F}} \) and \( r_{n} \) are termed spin resistance of FM and NM respectively for characterizing their ability of relaxing spin current. With the typical values of \( r_{\text{F}} = 4.5 \times 10^{-15} \Omega m^2, \beta = 0.46, \gamma = 0.5, r_{n} = 4 \times 10^{-9} \) \( \Omega m^2 \), the dependence of MR \( r_{b}^* \) and \( r_{n} \) (if \( r_{\text{F}} \) is fixed) are plotted in Fig. 2.3. For the case of \( r_{b}^* = 0 \), a sizable MR can be observed only if \( r_{n} \leq r_{\text{F}} \) even if \( l_{N} \) is several times larger than \( l_{N}^\text{F} \), which reproduces the results of metallic CPP-GMR. As indicated in Fig. 2.3 maximum MR,
\( \beta^2(1-\beta^2) \), is obtained when \( t_N \ll l_{sf}^N \) and \( r_N \leq r_F \), hence, \( \Delta R \approx 2\beta^2 \gamma_F \) and \( R^P \approx 2(1-\beta^2)\gamma_F \). On the contrary, MR goes to zero quickly if \( r_N \gg r_F \) regardless of \( t_N \), which represents the conductivity mismatch problem. For non-magnetic semiconductors with a reasonable value of \( r_F \ll r_N \), it shows that only if \( r_N t_N/l_{sf}^N < r_0^* < r_N l_{sf}^N/t_N \), can a clear MR be found in the structure of FM/I/NM/I/FM. In the limit of \( t_N/l_{sf}^N \ll 1 \) and \( r_N t_N/l_{sf}^N \ll r_0^* \ll r_N l_{sf}^N/t_N \), the maximum MR is acquired: \( \Delta R \approx 2\gamma^2 r_0^* \) and \( MR \approx \gamma^2/(1-\gamma^2) \).

The lower edge of the window for obvious MR, \( r_0^* > r_N t_N/l_{sf}^N \), can be understood by the resistor model as before. With the spin-dependent interface resistance being comparable to the dominant spin-independent \( \tau_N \) in the FM/NM/FM structure, the net series resistance also becomes significantly spin-dependent.

![Figure 2.3 Magnetoresistance versus \( r_N \) (left panel, with \( r_s^* = 0 \)) and \( r_s^* \) (right panel) with the various values of \( t_N/l_{sf}^N \). The minimum and maximum values of MR are marked by red dashed lines in the plots.](image)

To understand the upper value of \( r_0^* \) for clear MR, one should realize that the dwell time of the spin inside the NM, \( \tau_n \), must be shorter than the spin lifetime, \( \tau_{sf} \). \( \tau_n \) is inversely proportional to the inverse of the transmission coefficient of the interface and hence proportional to the interface resistance. Roughly speaking, when \( r_0^* \) exceeds \( r_N l_{sf}^N/t_N \), the
dwell time exceeds the spin lifetime and the MR vanishes progressively. It was shown that the MR for \( r'_0 \gg r_N \) can be written as \( \text{MR} \approx \left( y^2/(1 - y^2)\right)/(1 + \tau_n/\tau_{sf}) \).\(^{15}\)

Following the above predictions, a great number of experiments were performed employing a tunnel barrier for efficient spin injection and enhancement of the spin accumulation in semiconductors. Successful injection of spin-polarized current from ferromagnets to semiconductors has been demonstrated in many different systems such as GaAs, Si and graphene with various tunnel barriers including the AlO\(_x\), MgO\(^{17}\) and graphene\(^{18,19}\). Note that a Schottky barrier naturally forms between SC and FM and under appropriate conditions the Schottky barrier can work as a spin-dependent interface and sizeable values of spin injection can be realized\(^{20,21}\).

From the above analysis we can find that in order to overcome the conductivity mismatch problem, we can choose FM semiconductors with \( r_F \sim r_N \) (e.g. GaMnAs or the molecular-based magnetic semiconductor, \( \text{V(TCNE)}_2 \)) or perhaps increase the conductivity of the semiconductors up to metallic regions but without significantly decreasing the spin diffusion length. Moreover, use of a spin injector with 100\% spin polarization, such as \( \text{La}_x\text{Sr}_{1-x}\text{MnO}_3 \) (\( 0.2 < x < 0.5 \)), was also thought to be a method to avoid the conductivity mismatch problem. Another alternative scheme is to transport the spin & charge carriers beyond the diffusive regime in the NM channel. As revealed by Fert \textit{et al}\(^{15}\), for ballistic transport, the lower edge of the \( r'_0 \) window disappears and only on condition that \( \tau_n < \tau_{sf} \) persists, which means the tunnel barriers between FM and SC are not necessary in this case.

It is also noticeable that there are some special techniques which circumvent the conductivity mismatch problem and have proved to work nicely for spin injection and detection. Appelbaum \textit{et al} has developed an all-electrical method based on the hot-electron spin transistor to inject spin-polarized hot electrons from a tunnel junction into the conduction-band of undoped single-crystal silicon\(^{23}\) and detect the hot electrons by a second hot-electron
spin transistor. With this method, an unprecedented coherent spin transport distance of up to 350 \( \mu \text{m} \) with spin lifetime over 500 ns at 60 K has been achieved in silicon\(^2\). With the injection of non-equilibrium hot electrons with energy higher than the Fermi level by 1-2 eV, the conductivity mismatch problem is overcome. However, the spin current signals are usually quite small (~ pA), and because of the technical difficulties this method has so far only been successfully applied for silicon.

Another promising method is spin pumping. It can generate pure spin current in the semiconductor through dynamical exchange interaction at the FM/SC interface without electric current flowing across the interface and is thus free from the conductivity mismatch problem\(^3\). In this kind of experiment, the FM is stimulated by a microwave field to excite ferromagnetic resonance (FMR). Under FMR, the damping torque in the FM is suppressed and thus induces pumping of spin into the adjacent NM material because of spin angular momentum conservation\(^4\). The pumped spin causes spin accumulation in the NM and pure spin current is generated and transported in the NM. Such a pure spin current can be converted to electric voltage enabling electric detection by inverse spin Hall effect. This turns out to be a powerful method for efficiently generating a large spin signal in various NM materials including metals\(^5\), semiconductor\(^6\), graphene\(^7\) and even organic materials\(^8\).

**2.1.2 Nonlocal spin valve and spin precession**

**2.1.2.1 Nonlocal spin valves for spin detection**

In previous spin injection and detection schemes based on the CPP-GMR model, the spin relaxation process in the NM layer can be neglected because of the channel length \( L \ll l_0 \) in the vertical geometry. Actually, in order to be compatible with a conventional planar semiconductor, a lateral spin injection and detection geometry that allows more external field manipulation could be more attractive. In this case, a non-local spin-valve geometry (see Fig.
2.4) has provided a more elegant and rigorous way of detecting a pure spin current\textsuperscript{31} and avoiding spurious effects\textsuperscript{32}.

Figure 2.4 Schematic diagram of the nonlocal spin valve geometry and its principle. (a) Geometry for NLSV measurement. (b) Electrochemical potential Profiles of spin up and spin down in the NM/FM (detector) interface, where there is no charge current. (c) Schematic drawing of the spin signals detected by the FM in the parallel and antiparallel states of two FM electrodes\textsuperscript{33}. (d) Typical NLSV signals.

In this geometry, the voltage probes, FM electrodes or Pt electrode utilizing the ISHE effect, are isolated from the current path. Although the spin and charge current sources are provided by the same injector, usually another FM electrode, the spin diffusion lengths are generally much larger than the charge diffusion lengths, therefore, only a pure spin current due to spin accumulation and diffusion is measured. To understand that the pure spin current due to spin accumulation can be detected by a FM electrode, one needs to look in more detail at a single NM/FM interface. In general, we can write the electrochemical potential as:
\( \mu_{\uparrow,\downarrow} = eV + \delta \mu_{\uparrow,\downarrow} \) and the spin accumulation is \( \Delta \mu = \mu_{\uparrow} - \mu_{\downarrow} \) (see Fig. 2.b). Under the boundary conditions of Eq. 2.7 and \( J_x(0) + J_y(0) = 0 \), starting from Eq. 2.4.1, we can derive:

\[
V_{F}^{0^+} - V_{N}^{0^+} = \gamma (\Delta \mu_{N}^{0^+}) / 2e = \gamma (\delta \mu_{N}^{0^+} - \delta \mu_{N}^{0^+}) / 2e
\]  

(2.9.1)

where \( \gamma \) is the tunnelling spin polarization of the tunnel barrier between NM and FM as defined in Eq. 2.7 and as the accumulation in the FM is much smaller than that in the NM, it is neglected. If the FM/NM contact is transparent (i.e. \( r^* = 0 \)), from the boundary condition and current conservation, we have a similar formula:

\[
V_{F}^{0^+} - V_{N}^{0^+} = \beta (\Delta \mu_{N}^{0^+}) / 2e
\]  

(2.9.2)

where \( \beta = (\sigma_{F}^{+} - \sigma_{F}^{-}) / (\sigma_{F}^{+} + \sigma_{F}^{-}) \) is the current spin polarization in bulk FM metal as we mentioned before. Therefore, the spin accumulation in the NM channel can generate a voltage difference between FM and NM to balance the current flowing, which enables us to observe the nonlocal spin signals. As depicted in Fig. 2.4c, we can see that with a spin injector (FM1) of fixed magnetization, the parallel and antiparallel configurations of the spin detectors (FM2) should sense the same voltage magnitude with reversed sign.

For quantitatively calculating the nonlocal spin valve signals, one has to solve the diffusion equation Eq. 2.4 with the boundary conditions at two NM/FM interfaces as in the case of CPP-GMR. We show here the result from Takahashi et al.:

\[
V_{NL} / I = 2R_{N} e^{-2\gamma_{i}} \left( \prod_{i=1}^{2} \left( \frac{\gamma_{i} R_{i}^{0} / R_{N} + \beta R_{i} / R_{N}}{1 - \gamma_{i}^{2}} \right) \right) \left( \frac{\gamma_{1} R_{1}^{0} / R_{N} + \beta R_{1} / R_{N}}{1 - \gamma_{1}^{2}} \right) e^{-2\gamma_{i}} \right)
\]  

(2.10)

where the positive and negative signs correspond to the parallel and antiparallel alignment of the two FM electrodes, \( R_{N,1} = l_{g}^{N,F} / \sigma_{N,F} A_{N,F} \) denotes the spin resistance of the NM and FM layers with corresponding cross sections \( A_{N} = W_{NM} \) and \( A_{1} = W_{NM} W_{F} \), \( t_{N} \) is the thickness of the NM layer and \( W_{N} \) and \( W_{F} \) are shown in Fig. 2.4a. \( \gamma_{1} \) and \( R_{i}^{b} (i = 1, 2) \) are the tunnelling spin polarization and barrier resistance between NM and FM1. The nonlocal spin valve resistance is the change of resistance between \( P \) and \( AP \) states, \( R_{0} = (V_{NL}^{P} - V_{NL}^{AP}) / I \). Fig. 2.5 shows the nonlocal spin signals under various conditions from transparent contact to a spin selective
tunnelling contact between FM and NM. When the two contacts are identical, tunnelling with barrier resistances much larger than the spin resistance of NM channel, then the above formula is simplified to: \( R_s = \gamma^2 R_s e^{-L/L_D^s} \), which has been widely used to calculate the spin diffusion length in the NM channel from the distance dependence of \( R_s \).^35

![Figure 2.5 Nonlocal spin accumulation signals \( R_s \) vs \( L \) for various structures, where \( R_s \) and \( L \) are normalized by the spin resistance and spin diffusion length in the NM channel.]

2.1.2.2 Spin precession and Hanle effect

In vertical spin-valve (or MTJ) stacks, the MRs are normally measured under an external magnetic field swept in the plane of the FM electrode’s magnetization. In contrast, for lateral spin-valves, because of the relatively longer transport distance and transport time, one can introduce spin precession by applying a magnetic field perpendicular to the plane of the FM electrode’s magnetization (i.e. the injected spin direction). The spin precession modifying the MR signals in both local and nonlocal geometries is called Hanle effect, and it is usually considered as conclusive evidence for spin injection and transport in the NM channel. Note that to observe the Hanle effect, efficient spin injection, spin precession in the channel and adequate spin detection are all required. In this situation, not only spin diffusion and relaxation but also spin precession should be considered:
\[
\frac{\partial \mu_z}{\partial t} = D \nabla^2 \mu_z - \frac{\mu_z}{\tau_s} + \gamma_e (B \times \mu)_z; \quad \frac{\partial \mu_\perp}{\partial t} = D \nabla^2 \mu_\perp - \frac{\mu_\perp}{T_\perp} + \gamma_e (B \times \mu)_\perp
\]

(2.11)

where \( z \) and \( \perp \) represent the external magnetic field direction and the FM magnetisation plane, \( \mu, D \) and \( \gamma_e \) denote the chemical potential, diffusion constant and gyromagnetic ratio respectively. \( \tau_s \), the spin relaxation time, is the time it takes for the spins to reach the equilibrium state along the longitudinal magnetic field direction. \( T_\perp \), the spin dephasing time, is the time that for the ensemble of transverse spins to lose their phase when precessing about the longitudinal magnetic field. In the Eq. 2.11, the first term describes the spin diffusion; the second term describes the spin relaxation and the third term the spin precession. If a strong electric field is present, a spin drift term should be added. When the system is isotropic and the correlation time, \( \tau_c \), is much shorter than the Larmor period, the spin relaxation time equals the spin dephasing time. In this case, the spin transport behaviour can be described by a one-dimensional Bloch equation in a steady state:

\[
D \frac{d^2 \mu}{dx^2} - \frac{\mu}{\tau_s} + \gamma (B \times \mu) = 0
\]

(2.12)

In the spin precession experiment, a magnetic field along the easy-axis of the spin injector and detector (\( y \)-axis in Fig. 2.6) is first applied to align the magnetizations of the two FM electrodes (parallel or antiparallel). After proper magnetisation alignment, the field is removed and one can measure the nonlocal spin resistances as a function of a second relatively small magnetic field along \( z \)-direction (see Fig. 2.6). The above Bloch equation can be solved strictly for the spin transport experiment in the presence of spin precession with the boundary condition that at \( x = 0 \) there is a spin current injected into the region \( x > 0 \) with the spin direction along \( \hat{y} \). The diffusion constant and spin relaxation time can be thus extracted.

Jedema et al. provided a concise physical picture for attaining the right answer for the diffusive spins as follow. For an infinite diffusive channel, the travel time for a distance \( L \) between two FM electrodes has a broad distribution, \( (L/\sqrt{4\pi D t}) \exp[-L^2/(4Dt)] \), which gives the proportion of spins that, once injected at \( FM_1 \), arrive at the \( FM_2 \) after a diffusion time \( t \) (see Fig. 2.6 c). Within the spin transport time, \( t \), there is an in plane rotation angle, \( \omega_0 t, (\omega_0 \).
\( \gamma B \) is the Larmor frequency, relative to the initial spin direction \((\hat{y})\) (Fig. 2.6 b). The relaxation factor, \( \exp(-t/\tau_s) \), was added to account for spin relaxation. Because of the distribution broadening, each spin has a different precession angle, therefore the total

![Diagram](image)

**Figure 2.6** The spin precession in the nonlocal spin valve geometry (a) and the typical Hanle signal (e). (b), (c) and (d) show the contributions due to the terms of angle rotation, diffusion travel time distribution and magnetic field effect respectively.

The resistance measured at the detector is the sum of all contributions from every spin over all diffusion times \( t \):

\[
R(B) = \pm R(0) \frac{2D}{l_d} \exp(-L/l_d) \int_0^\infty \frac{1}{\sqrt{4\pi Dt}} \exp(-L^2/4Dt) \cos(\sigma \tau) \exp\left(-\frac{t}{\tau_s}\right) dt
\]

where \( \pm \) corresponds to the parallel/antiparallel alignments of the FM magnetization respectively, \( R(0) \) is the nonlocal spin signal without perpendicular field (in the case of two identical spin-polarized tunnelling contacts between FM and NM, \( R(0) = \gamma^2 R_N e^{-L/l_d} \) (see Eq. 2.10), where \( \gamma \) is tunneling spin polarization, \( R_N = l_d/\sigma N A_N \), \( D \) is the diffusion constant,
$l_s = \sqrt{D\tau_s}$ is the spin diffusion length. The standard Hanle spin precession curves are shown in Fig. 2.6d. Fitting the curves observed from experiment, the important spin transport parameters in the NM channel e.g. $D$ and $l_s$ can be obtained. In the case of applying a large perpendicular field, the magnetization directions of the FM electrodes are tilted out of the plane at an angle $\theta$. Therefore, the above formula can be modified to:

$$R(B_z, \theta) = R(B_z)\cos^2\theta + R(0)\sin^2\theta$$

which indicates that the precession signal is reduced and a positive background signal increases as $\theta$ increases.

2.1.3 Tunneling magneto-resistance phenomenon

2.1.3.1 From direct tunneling to resonant and multi-step tunneling

Tunneling is a quantum-physics phenomenon that exists when a particle is transmitted between two states isolated by a high energy barrier compared with the kinetic energy of the particle. The transmission would be impossible in classic physics. It is the essential physics for MTJs and also plays an important role in spin injection & detection as we have shown before. In this part, we will present some more details about magneto-resistance phenomena related to the tunneling process in the FM/I/FM, FM/I/NM and NM/I/NM structures.

The tunneling processes can be classified as elastic tunneling and inelastic tunneling according to the energy change in process. Elastic tunneling includes direct tunneling and resonant tunneling. The former refers to tunneling process without any scattering or energy exchange inside the barrier so the initial and final stats have the same energy. In this case, the current density at 0 K can be calculated from the formula:

$$j(V) = \frac{e}{4\pi^2\hbar} \sum_{\sigma} \int d\epsilon \int_0^\infty k_x d k_x |t_{K\sigma}|^2 \left( \frac{\epsilon - \hbar^2 k_x^2 / 2m - V_{lo}}{\epsilon - \hbar^2 k_x^2 / 2m - V_{lo}} \right)^{1/2} \left[ f(\epsilon) - f(\epsilon - eV) \right]$$

(2.14)

where $k$ is the in-plane component of the electron wave-vector, $\epsilon$ is the electron energy, $t_{K\sigma}$ is the transmission amplitude for an electron with wave vector $k$ and spin $\sigma$, $V_{lo}$ and $V_{ro}$ are the
spin-dependent energy band edges on the left and right electrodes respectively and \( f(e) \) is the Fermi-Dirac distribution function\(^{10}\). The sum and integrations in this formula account for the conservation of spin, energy and in plane wave-vector (specular transmission).

![Figure 2.7](image)

Figure 2.7 The tunneling process in a tunnel junction: red regions, electrodes; grey region, tunnel barrier; direct tunneling, resonant tunneling and inelastic tunneling with the excitation of a phonon in the tunnel barriers are shown.

The transmission probability can be calculated by the Wentzel-Kramers-Brillouin (WKB) method and the well-known parabolic bias voltage dependence of conductance for a tunnel junction is obtained (i.e. Brinkman-Rowell-Dynes (BDR) model)\(^41\):

\[
\frac{G(V)}{G(0)} \approx 1 - \left( \frac{A_0 \Delta \phi}{16 \bar{\phi}^{3/2}} \right) e^V + \left( \frac{9 A_0}{128} \frac{\Delta \phi}{\bar{\phi}} e^V \right)^2
\]  

(2.15)

where \( \Delta \phi = \varphi_2 - \varphi_1 \), \( \bar{\phi} = (\varphi_2 + \varphi_1)/2 \), \( A_0 = 4(2m)^{1/2} d/3h \), and \( \varphi_1 \) and \( \varphi_2 \) are the barrier heights for the two electrodes, \( d \) is the barrier width and

\[
G(0) = (3.16 \times 10^{10} \bar{\phi}^{1/2} / d) \exp(-1.025d\bar{\phi}^{1/2})
\]  

(2.16)

For \( T > 0 \) K, the thermal smearing of Fermi distribution leads to a simplified approximation\(^42\):

\[
G(T) \approx G(0) \times CT/\sin(CT), \quad C = 1.387 \times 10^{-4} d/\sqrt{\bar{\phi}}
\]  

(2.16)
where $G(0)$ is the conductance at 0 K, $d$ and $\bar{\varphi}$ are defined as before. Usually, for an MTJ, the highest TMR ratio is achieved in the direct tunneling regime as the other tunneling processes decrease the TMR ratio due to incoherent or spin-flip processes.

For any real tunnel barrier, it is inevitable that there are defects, impurities and localized states (LSs). With alignment of one electrodes' Fermi level with a localized state inside the tunnel barrier, the transmission coefficient of the particles from one electrode to another can be distinctly enhanced. This is resonant tunneling and the conductance due to the elastic transition from the left electrode ($\varepsilon$) to the right electrode ($\varepsilon'$) via a localized state ($\varepsilon_i$) is given by the formula:

$$g(\varepsilon \to \varepsilon') = \frac{e^2}{4\pi \hbar} \frac{4\Gamma_L \Gamma_R}{(\varepsilon - \varepsilon_i)^2 + \Gamma^2} \delta(\varepsilon - \varepsilon')$$

(2.17)

where $\Gamma_{L(R)} = E_0 \exp(-2\alpha Z_{L(R)})$ is the coupling between impurity states and the left (right) electrode, $\alpha^{-1}$ is the localization length and $Z_{L(R)}$ is the distance from the LS to the left (right) electrode. $E_0$ is the binding energy of the LS. In this formula, the Lorentzian shape stems from the quantum-mechanically coherent nature of the process. The width of this resonance is related to the lifetime $\tau$ of an electron on the LS by $\tau \sim \hbar/\Gamma$ according to the Heisenberg's uncertainty principle. The conductance is maximum, $e^2/2\pi \hbar$, when $\Gamma_L = \Gamma_R$ (i.e. $Z_L = Z_R$, if left and right electrodes are identical) and $\varepsilon_i = \varepsilon = \varepsilon'$. If $\alpha d \gg 1$, the width of this resonance is sharp, being confined in space to within $\alpha^{-1}$ of the center position of the barrier and in energy to within $\Gamma$ of the resonant energy. Thus for the zero-bias conductance of a tunnel junction, only LSs of energy within $\sim \Gamma$ of the Fermi energy make a contribution. Assuming a uniform distribution of LSs in space and in energy near the Fermi level with a density $g$, the sum of the conductance through all the resonant states gives:

$$G_{1}^{rs} = \frac{\pi e^2}{\hbar} gS\alpha^{-1} E_0 e^{-ad} \propto e^{-ad}$$

(2.18)
where \( S \) is the area of the junction. This tunnel barrier thickness dependence differs characteristically from that of direct tunneling: \( G_0^{\text{str}} \propto e^{-2\alpha d} \)

It is obvious that \( G_1^{\text{res}} > G_0^{\text{str}} \) for a sufficiently large barrier thickness, \( d \). Although resonant tunneling may not be good for high TMR, it can bring out many interesting behaviors such as oscillation of the TMR\(^4\) and inversion of the TMR\(^5\). The temperature dependence of \( G_1^{\text{res}} \) also has the form of \( G_1^{\text{res}}(T) \propto CT / \sin(CT) \) due to the thermal broadening of the Fermi surface of the electrodes.

As the thickness of the tunnel barrier and temperature increase, inelastic tunneling processes will occur, even at zero bias voltage. Glazman and Matveev investigated the process of inelastic tunneling through \( N \) localized states \((N \geq 2)\). Fig. 2.8 shows the case of \( N = 2 \). They found that in the limit, \( eV \ll k_B T \), the conductance due to hopping via a series of LSSs is:

\[
g_N = \frac{e^2}{2k_B T} \frac{1}{\Gamma_{l1}} \left[ 1 + \sum_{i=1}^{N-1} \frac{2}{\gamma_i} + \frac{1}{\Gamma_{RN}} \right]^{-1}
\]  

(2.19)
Where $\Gamma_{ll} \approx E_0 \exp(-2\alpha Z_{ll})$ and $\Gamma_{NN} \approx E_0 \exp(-2\alpha Z_{NN})$ are the elastic transition rates between the left electrode and LS-1 and between LS-N and the right electrode respectively. 

$$\gamma \approx \lambda \left[ \frac{\Delta E}{E_0} \right] \left[ E_0 \exp(-2\alpha r_{ll+1}) \right]$$

is the transition rate between the two adjacent LSs which are coupled via electron-phonon interaction. $\Delta E$ is the energy difference between the two states, $\lambda$ is a dimensionless electron-phonon interaction. As these constituent transitions are incoherent, their rates add in a serial fashion and the maximum is attained when all these rates are equal:

$$g_{\text{max}} \approx \frac{e^2}{h} \frac{\Delta E}{k_B T} \left[ \frac{\Delta E}{E_0} \right]^{(N-1)/(N+1)} E_0 \exp \left( -\frac{2\alpha d}{N+1} \right)$$

(2.20)

Summing all the possible hopping, compared with the resonant tunneling conductance, the average zero-bias conductance due to hopping via $N$-LSs is:

$$G_N^{\text{hop}}(T)/G_1^{\text{res}} \propto \left( k_B T \right)^{N-2/(N+1)} \exp \left( \frac{N-1}{N+1} \alpha d \right)$$

(2.21)

The total conductance at any temperature is the sum of the contributions from all the channels:

$$G(T) = G_0^{\text{dir}} + G_1^{\text{res}} + \sum_{N=2} G_N^{\text{hop}}(T)$$

Compared to the inelastic hopping, the temperature dependence of the elastic tunneling can generally be ignored, and the contribution of high order inelastic tunneling (i.e. hopping) can dominate the conductance at high temperature and in thicker tunnel barriers. In the high-bias and low temperature limit, where $eV \gg k_B T$, there is a similar expression for the voltage-dependent correction to the conductance due to the $N$-LS hopping channels: $G_N^{\text{hop}}(V)/G_1^{\text{res}} \propto (V)^{N-2/(N+1)}$, where the resonant conductance is voltage-independent.

Xu et al confirmed the above prediction in a prototype system composed of a metal/amorphous silicon/metal tunnel junction\textsuperscript{43}. In such a system, the LSs are distributed evenly and densely throughout the barrier both in space and in energy sufficiently close to the Fermi level. They found that the increasingly nonlinear dependence of conductance on
temperature, bias voltage and barrier thickness can be quantitatively described by the Glazman-Matveev theory. It was found by the same group that the Coulomb blockade effect on the resonant tunneling and inelastic hopping process has a distinct MR in such nonmagnetic tunnel systems. We will return to this work later.

2.1.3.2 Inelastic tunneling process in MTJs

![Schematic drawing of a spin-polarized inelastic transport process in a MTJ of CoFeB/MgO/CoFeB](image)

In the work of Glazman and Matveev, resonant tunneling and inelastic hopping were generally treated as spin-independent processes, which is not directly applicable for MTJs. Lu et al. suggested the existence of spin-conserving inelastic processes in their relatively thick MgO barrier, which observably reduced the TMR (Fig. 2.9). They extended the Glazman-Matveev theory by considering a spin-conserving hopping process. Replacing $\Gamma_{L}$ and $\Gamma_{RN}$ in formula (2.19) with $\Gamma_{L}^{\gamma} \exp(-2\alpha Z_{L})$ and $\Gamma_{R}^{\sigma} \exp(-2\alpha Z_{R})$, defining

$$P_{L(R)} = \frac{\Gamma_{L(R)}^{\gamma} - \Gamma_{L(R)}^{\sigma}}{\Gamma_{L(R)}^{\gamma} + \Gamma_{L(R)}^{\sigma}}$$

as the tunneling spin polarization between two FM electrodes and two nearby LSs and assuming an identical spin polarization $P = \sqrt{P_{L}P_{R}}$ for both contacts, they minimized the series resistance by equalizing all the resistance contributions:

$$\Gamma_{N}^{\sigma} = \frac{1}{N+1} \left[ \Gamma_{L}^{\gamma} \Gamma_{R}^{\gamma} \gamma^{N-1} \right]^{1/N+1} \exp \left( -\frac{2\alpha d}{N+1} \right),$$

where $\gamma \propto k_{B}T$ is the inelastic interaction between two LSs with phonons, which was assumed to be spin-independent. Besides, the optimal configuration number scales like

$$\xi_{N} \propto [g^{LS}k_{B}T]^{N} \alpha^{-2N+1}d^{N},$$

where $g^{LS}$ is the
density of localized states. Hence, the conductance of $P$ and $AP$ configurations and the corresponding TMR are:

\[ G_N^{P} \propto (k_n T)^{v_N} \times [(1 + P)^{\beta N} + (1 - P)^{\beta N}] \times \exp \left( -\frac{2\alpha d}{N + 1} \right) \]  

\[ G_N^{AP} \propto (k_n T)^{v_N} \times [2(1 - P^2)] \times \exp \left( -\frac{2\alpha d}{N + 1} \right) \]  

\[ \text{TMR}(N) = \frac{(1 + P)^{2\beta_N} + (1 - P)^{2\beta_N}}{2(1 - P^2)^{\beta_N}} - 1 \]

where $v_N = N - 2/(N + 1)$, $\beta_N = 1/(N + 1)$. We can see that for $N = 0$ (direct tunneling), TMR is highest and the Jullière formula is reproduced. As $N$ increases, even for the spin-conserving inelastic hopping process, the TMR gradually decreases. It can be understood in the series resistor picture: the parts of hopping resistances due to $\gamma$ is magnetic-field independent, the contributions to MR only relate to the first and final tunneling steps between two LSs and the spin-polarized FM electrodes. The weights of these two terms decrease as $N$ rises. A special case is that the TMR of resonant tunneling ($N = 1$) is half that of direct tunneling. It also predicts the same power law dependence of conductance as for the unpolarized system. This model was employed to explain the experimental result that for samples with thicker MgO tunnel barriers, a much more pronounced decrease of TMR with temperature was observed. They found that tunneling via a $N = 3$ LSs chain can dominate the junction conductance and that it is responsible for the increase of $\Delta G$, $\Delta G(T) = G^{P}(T) - G^{AP}(T)$, with temperature, which is impossible for direct tunneling.

The above multi-step tunneling process described is more evident for ‘thick’ tunnel barriers. However, even for a thin tunnel barrier, where the direct tunneling is dominant, the inelastic processes inevitably play a role as the temperature and bias voltage increase. Zhang et al proposed that itinerant tunneling electrons ($s$ electrons) with excess energies above the Fermi level can produce collective excitations of local spins ($d$ electron) at the interface between the tunnel barrier and the magnetic electrodes (magnons) via $s$-$d$ exchange interaction. Due
to conservation of angular momentum, the creation and annihilation of magnons leads to the electron spin-flips, which are responsible for the reduction of MR with increase of temperature and bias voltage. One of the basic processes, tunneling of electrons from the left to the right electrode with an emission of a magnon at the interface of the barrier with the right (R) electrode can be written as:

$$ j_{i}^{(1)} = \frac{4\pi e}{hN_{s}} \sum_{q} \left[ d\omega 2 |T|^{2} S_{r} \rho_{r}^{m}(\omega) \rho_{r}^{m}(\omega + eV - \omega_{q}) f_{r}(\omega)[1 - f_{r}(\omega + eV - \omega_{q})] \langle a^{\dagger}_{q} a_{q}^{+} \rangle \right] $$

(2.23)

where $N_{s}$ is the number of spins at the interfaces, $T^{r}$ is spin-dependent transfer matrix, $S_{r}$ is the spin quantum number, $V$ is the applied voltage across the junction, $\rho_{r}^{m}$ and $\rho_{r}^{M}$ are density of states for itinerant minority and majority electrons of the left and right electrodes respectively, $\omega_{q}$ is the magnon spectrum at the interfaces. $\langle a^{\dagger}_{q} a_{q}^{+} \rangle = 1 + n_{q}^{R(L)}$ and $n_{q}^{R(L)}$ denote the thermodynamic average number of interface magnons with wave vector $q$. Summing all the similar terms with suitable simplifications, the temperature dependence of the resistance of $G_{P}$ and $G_{AP}$ states at zero bias can be expressed as:

$$ G_{r}(T, 0) = G_{r}(0, 0) \left[ 1 + \xi \frac{2SQ}{k_{B}T} \ln \left( \frac{k_{B}T}{E_{c}} \right) \right], \quad \xi = \begin{cases} \frac{\xi_{P}}{\xi_{AP}}, & \xi_{P} > \xi_{AP} \\ \frac{\xi_{AP}}{\xi_{P}}, & \xi_{P} < \xi_{AP} \end{cases} $$

(2.24)

where the parameter $Q$ describes the excitation probability of a magnon in the tunneling process, $\xi = 2\rho_{m}^{a}(\rho_{m}^{2} + \rho_{m}^{2})$ represents the ratio of the density of states products for AP and P configurations, $E_{c}$ is the magnon cutoff energy. The conductance $G_{P}$, $G_{AP}$ and TMR ratio at zero temperature ($n_{q}^{P} = 0$) and low bias voltage $V$ can be also derived in a simplified form:

$$ TMR(0, V) = TMR(0, 0) - \frac{QSeV}{E_{m}} \frac{G_{P}(0, 0)}{G_{AP}(0, 0)} \left( \frac{1}{\xi} - \xi \right) $$

(2.25)

This magnon excitation model was widely used to explain bias voltage and temperature dependence of TMR in MTJs with good tunnel barriers. Self-consistent fits of $Q$ and $E_{c}$ were
performed to obtain the properties of the magnons in the MTJs. This was done not only for amorphous AlOx tunnel barriers but also for crystalline MgO tunnel barriers, where the coherent tunneling process occurs. Moreover, in the case of thicker or defective tunnel barrier junctions, in order to improve the fitting, a small but non-negligible temperature dependence of direct tunneling conductance and the extra spin-independent hopping conductance (Eq. (2.16)) via localized states were also taken into account:

\[ G_r(T, 0) = G_r(0, 0) \sin(CT) \left[ 1 + \frac{2S_Q}{E_m} k_B T \ln \left( \frac{k_B T}{E} \right) \right] + G_r^{\text{imp}}(T) \]  

(2.26)

### 2.1.3.3 MR in FM/I/NM and NM/I/NM junctions

![Diagram of MR in FM/I/NM and NM/I/NM junctions](image)

Figure 2.10 Resonant tunneling via (c) type A or (d) type B impurities for spin injection (electrons flow from F to N). Calculated MR via an impurity with \( \alpha = 0.1 \) embedded in a FM/I/NM junction with \( p = 1/3 \). MR due to resonant tunneling via an (a) \( E' \) and (b) \( P_d \) defect in silicon-oxide interfaces. (c) MR in the presence of molecular fields due to exchange between nearest-neighbour impurities.

Recently an MR effect with a Lorentzian line shape has been reported in the FM/I/NM system (three-terminal geometry, see details in Chapter 5). The signals were larger than the values expected from spin injection by several orders of magnitude. It has been increasingly realized such MR depends much more on the tunneling process rather than on the spin accumulation in a NM material. Yang Song et al proposed that the large MR signals and their dependence on temperature are set by resonant tunneling via the impurities with large on-site Coulomb repulsion energies. Modifying the Anderson impurity model, they wrote the system Hamiltonian for an \( s = 1/2 \) impurity as:
\[ H = \sum_{i=\alpha,\beta} \left[ \varepsilon_{i\sigma} a_{i\sigma}^\dagger a_{i\sigma} + \left( T_{ij} a_{i\sigma}^\dagger d_{j\sigma} + H.c. \right) \right] + U n_i n_i + \varepsilon_i(\theta) n_i + \varepsilon_{\pi}(\theta) n_i + \varepsilon_B \sin \theta (d_i^+ d_i + d_i^d_i) \]

where \( \varepsilon_B = \frac{g \mu_B B}{2} \) and \( \varepsilon_{\pi}(\theta) = \varepsilon_0 \pm \varepsilon_B \cos \theta \). \( \varepsilon_0 \) is the resonance energy of the singly occupied state, \( T_{ij} \) denotes the impurity-electrode interaction, \( U \) is the on-site Coulomb interaction energy. The off-diagonal terms, \( d_i^+ d_i \), are most notable, which results from spin precession on the impurity states (assuming the spin lifetimes of electrons on the impurity are much longer than the average tunneling time). The impurities are classified as type A and type B: in type A (B), the filling energy for the first (second) electron is within the bias window. Under the limit of \( eV \gg k_B T \gg \varepsilon_B \) the resonant currents were obtained from the steady-state solution of the master equations:

\[ i_A^{N \rightarrow F} = -i_B^{F \rightarrow N} = \frac{2e}{\hbar} \frac{\Gamma_F \Gamma_N}{\Gamma_F + 2\Gamma_N} \frac{1 - p^2 \chi(B)}{1 - \alpha p^2 \chi(B)} \]  

\[ i_B^{N \rightarrow F} = -i_A^{F \rightarrow N} = \frac{2e}{\hbar} \frac{\Gamma_F \Gamma_N}{2\Gamma_F + \Gamma_N} \]  

where \( \chi(B) = \frac{(B_i^2 + B^2 \cos^2 \theta)/(B_i^2 + B^2)}{\alpha = \Gamma_F / (\Gamma_F + 2\Gamma_N)} \) and \( B_i = \Gamma_F / g \mu_B \). \( \Gamma_{F(N)} \) denotes the coupling between the impurity and the FM (NM) electrodes, \( P \) is the interface current polarization \( p = (\Gamma_{F+} - \Gamma_{F-}) / (\Gamma_{F+} + \Gamma_{F-}) \). It shows that the injection (extraction) current from FM to NM depends on the magnetic field only when tunneling through type B (A) impurities, which reflects the symmetry of electrons and holes. The magnetic field dependence of the resonance current via type A and B impurities is best perceived by considering the FM as half metallic and the junction under an out-of-plane magnetic field. For the resonant tunneling, without a magnetic field, injection via type B impurities (or extraction via type A impurities) is completely blocked because only the spin orientation that is opposite to that of the occupied electron is allowed to tunnel via this site. Under a large out-of-plane field, the blockade is lifted in both cases due to depolarization of the impurity spin by Larmor precession and the two opposite directions are mixed. Although Eq. 2.27 presents a modulation of current and thus a Lorentzian-shape MR under the out-of-
plane magnetic field \( \theta = 90^\circ \), \( \Delta R \propto B^2 \dot{P}^2 / (B^2 + B_\pi^2 (1 - P^2)) \), the effect vanishes for an in-plane external field \( (\chi_B = 1) \). This is not consistent with the experimental results. In order to eliminate the discrepancy, the authors considered the ubiquitous spin interactions, which tend to randomize the spin orientation at the impurities. These internal interactions include hyperfine fields due to interaction with the nuclear spins, exchange interactions with nearby impurities as well as the stray field of the FM electrodes. An effective magnetic field, \( B = B_e + B_i \), on the impurity site was thereby introduced and the resonant current can be rewritten as:

\[
\frac{i}{i_0} = 1 - (1 - \alpha) P^2 \int d\Phi \int d\cos \theta \int d\phi \frac{B^2 f(B, \theta, \phi)}{B_i^2 + (1 - \alpha P^2) B_e^2}
\]  

Where \( i_0 = 2 eG \sqrt{\gamma} / h \) and \( f(B, \theta, \phi) \) is the normalized distribution for the internal field, \( B^2 = B_e^2 + (B_x + B_i) \) and \( B_x^2 = B_i^2 + B_e^2 + 2 B_i B_e \cos(\phi - \phi_i) \) are the components of effective field along and normal to the FM respectively. Fig. 2.10 b and 2.10 c show the solution of Eq. 2.28 under hyperfine fields of some defects centers in Si-oxide interfaces. It thereby reproduces the experimental observations. Although the internal magnetic field, \( B_i \), is important to explain the MR evolution with external magnetic field along different directions, \( \Delta R \) measured at a sufficiently large magnetic field is independent of the details of the internal field (\( B_e \gg B_i \) & \( B_T \)):

\[
\Delta R = \frac{\sum_n (\Delta i_n(0) - \Delta i_n(\pi))}{I_f} = \frac{1}{I_f} \sum_n \frac{(1 - \alpha_n) P^2}{1 - \alpha_n P^2} \frac{i_{b,n}}{I_f}
\]

Where \( n \) runs over type A (B) impurities in the tunnel barrier for spin extraction (injection). The amplitude of the MR depends on the tunneling polarization of FM, the density of impurities and their coupling to the electrodes. There are some important points to note from this model: the MR effect is stronger for impurities located closer to the NM than to the FM electrode (i.e. \( \Gamma_N \gg \Gamma_F \)); The width of the MR curves are set by the internal field rather than \( B_T \) (as \( \Gamma_F \) is small and \( B_T \ll B_e \)); the interplay between \( U \) and \( eV \) (\( U \gg eV \)) between \( k_B T \) and the activation energy \( E_a \) (\( E_a \gg k_B T \)) make the temperature dependence of the MR
typically follows an Arrhenius law; the numbers of type A and B impurities in the bias voltage window determine the amplitude of the MR for positive and negative bias respectively; the above MR is also applicable for multi-step tunneling via several LSs if the series resistance picture is working; without a spin polarized source from the FM electrode, the spin lifetime is not concerned, a pair of A-B configuration localized in optimal energy and space positions can also generate an obvious MR, which was extended to tunneling via two localized states. It is worthwhile to compare the MR effect from this model with the Coulomb correlation effect of resonant tunneling and inelastic hopping that we mentioned before and the huge MR reported by one group in doped polymers (see details in Chapter 5). Without including any FM electrodes in their devices, much larger MR effect than that of the three-terminal devices were claimed in both system. However, for the former, a large magnetic field is required to split the resonant states and lift the blockade; for the later, a spin-selective reaction between spin-carrying excitations are needed and strictly one-dimensional transport is supposed to greatly enhance the effect.

2.2 Organic spintronics

2.2.1 Basic concepts in organic conductor

Consisting mostly of light elements (C, H, N or O), organic semiconductors (OS) are considered as a potential system for spintronic because of their relatively weak spin-orbit interaction. The OS are mainly \( \pi \)-conjugated materials, usually divided into polymers and small molecules with 1.5-3.5 eV band gap. The OS backbone is formed by carbon atoms, whose \( s \) orbitals combine with two \( p^x \) and \( p^y \) orbitals to create hybrid \( sp^2 \) orbitals (see top panel of Fig. 2.11). Overlapping of the \( sp^2 \) orbitals and \( p^z \) orbitals result in \( \sigma \)-bonds and \( \pi \)-bonds respectively. In the conjugated molecules, the overlap of one \( p^z \) orbital with another across an intervening \( \sigma \) bond allows a delocalization of the \( \pi \) electrons across all the adjacent aligned \( p^z \) orbitals. For such \( \pi \)-conjugated molecules, the superposition of adjacent carbon atomic \( p^z \) orbitals gives rise to the molecule’s orbital levels which are responsible for the
electrical and optical properties of the molecule (see bottom panel of Fig. 2.11): the in-phase combination of $p^z$ orbitals has a lower energy level and is occupied in the ground state of the molecule, whereas the out-of-phase combination of $p^z$ orbitals have higher energy and are unoccupied. Among them, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are most important in the ground-excitation state transition, which brings about the colour of the organic, and electric transport.

In the thin films and bulk OS materials, molecules bond together by weak van der Waals' intermolecular forces, which are much weaker than the binding force of covalent and ionic bonds in inorganic crystals. Such an interaction weakens the electronic coupling between the
molecules and considerably reduces the bandwidth (~ 0.1 eV) of the HOMO and the LUMO levels in OS (compared to ~10 eV for the valance & conduction bands in Si). Because of this, OS show very low carrier mobility in electric transport. Moreover, organic materials are much less rigid than their inorganic counterparts. The propagating charge carriers are able to locally distort the potential by polarizing the molecules around them, forming a quasi-particle known as a polaron. Such effects greatly increase the effective mass of the charge carriers and also contribute to their reduced mobility. For these reasons, the carrier mobilities in organics are considerably lower than in their inorganic counterparts: even one of the highest carrier mobilities reported so far in OS, the hole mobility in single crystal of rubrene is only about 40 cm²V⁻¹s⁻¹ at room temperature and it is normally 3 to 8 orders of magnitude lower for polycrystalline and amorphous organic materials, whereas the mobility of p-type Si is about 450 cm²V⁻¹s⁻¹. It is worth mentioning that a polaron carries spin one-half, whereas two nearby condensed polarons, form a bipolaron, which is spinless.

The transport mechanisms of polarons in organic materials are therefore quite different from those in inorganics: hopping is dominant in most cases. The band-type transport is emerging in some specific cases, for example in highly-ordered materials at low temperatures. In those materials, the valence and conduction bands are formed from overlapping HOMO and LUMO levels of the molecules, respectively. For disordered systems, charge transport between the localized molecular states is via phonon-assisted hopping which strongly depends on temperature, electric field, trap states and carrier concentration. Usually, vapor-deposited organic thin films are amorphous, and the charges are localized on the molecular sites due to the disorder. The conduction is dominated by phonon-assisted tunneling from one localized site to another site. In Mott’s variable range hopping (VRH) model, the hopping probability, \( P_{ij} \), from one site, \( i \), to another site, \( j \), is:

\[
P_{ij} \approx \begin{cases} 
  e^{-2aR_{ij} - (E_j - E_i)/k_B T} & \text{if } E_j > E_i \\
  e^{-2aR_{ij}} & \text{if } E_j \leq E_i 
\end{cases}
\]

where \( R_{ij} \) is the distance between the two sites, \( E_i \) and \( E_j \) are the energy levels of an electron at the two sites and \( a \) corresponds accounts for exponential decay of the wave function in the
potential barrier between two sites. From this equation one can deduce that the transport of carriers is affected by disorder of the hopping sites in position and energy. In such a disordered system, the conductance is proportional to the average probability of hopping between two sites, in the space and energy coordinates. From VRH model, the conductance, as a function of temperature $T$ is given by

$$G \propto e^{-(2aR)} \approx \exp \left[ -\left( \frac{T_0}{T} \right)^{\frac{1}{1+d}} \right]$$

(2.31)

where $T_0$ is the characteristic temperature and $d$ is the dimension. The model predicts that the variable-range-hopping length, $R$, increases with decreasing temperature as $T^{(1+d)}$, and in three dimensions, the index is $1/4$. A similar exponential formula applies for the electric field dependence of conductance at low temperature.

It turns out that in real organic-based electronic devices, two different processes can govern the device performance, namely, carrier injection limitation at the interfaces and space-charge limited current (SCLC) in the organic channel. The former usually plays a key role in thin-film-based devices at low bias voltage, where the possible charge injection mechanisms include Fowler-Nordheim tunneling and Richardson-Schottky thermionic emission. The latter manifests itself in the devices with thicker organic media with low contact barriers at high bias voltage, where trap-free SCLC described by the Mott-Gurney equation and trap-charge limited current density together with or without considering the electric field-dependence of carrier mobility (Poole-Frenkel relation) may be applicable, respectively.

### 2.2.2 GMR or TMR in organics? An experimental overview

As we have seen in previous part, for $\pi$-conjugated molecules, $\pi$ electrons are delocalized in these individual molecules. However, for disordered molecule systems, the very small transfer rate of these $\pi$ electrons between different molecules via incoherence tunnelling (hopping) actually 'localize' them at each individual molecular site. An important question concerning spin relaxation process in such a system is that of the difference of the spin lifetimes between the 'localized' and 'mobile' $\pi$ electrons. It is noted that when referring to
spin lifetime for organic spintronics application there is no such a distinction as in a real conductive organic system even the 'mobile' electrons are still localized in a few molecules sites. In principle, a pure tunnelling event between different molecules doesn't change the spin of \( \pi \) electron. If only considering the hyperfine interaction as the main spin relaxation mechanism for organics, we would not expect significant difference for spin relaxation of the \( \pi \) electron on different molecular sites, where the molecules are identical: even the background of hyperfine interaction in a molecule can be different from one atom to another. Evidence for this viewpoint can be found in a field-induced electron spin resonance (FESR), where the ESR signal originates from the gate-induced carriers \( (S = 1/2) \) in a field effect transistor (FET) device. It was reported that in a pentacene FET, the spatial extent of wave function of the carriers is in the order of 10 molecules (~ 10 nm) where the carriers change between localized and mobile states by a multiple trap-and-release process. It was further confirmed that the linewidth of ESR signals (related to the spin relaxation) becomes narrower as the carrier mobility increases, which reflected a large spin-lattice relaxation time, \( T_1 \), in the order of 10-100 \( \mu \)s is maintained in this process (of trapping time decrease from 2 ns to 0.7 ns). Compared with inorganic system such as silicon \( (T_1 \sim \text{ns}) \), organic materials indeed present a considerable large spin lifetime.

In spite of the large spin lifetimes, the extremely low carriers mobility \( (\mu \sim 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \text{ for Alq3 amorphous thin films}) \) pose the question of how far the spins can propagate in such systems, assuming that a spin current can be injected. Making use of Einstein relation for diffusion constant \( D = \mu k_B T / e \) and \( l_{sf} = \sqrt{D \tau_{sf}} \), we can estimate the spin diffusion length, \( l_{sf} \sim 5 \text{ nm} \) at room temperature (with \( \mu \sim 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) and \( \tau_{sf} \sim 1 \mu\text{s}, \) which is significantly smaller than the spin diffusion length in inorganic semiconductors (e.g. for Si, \( l_{sf} \sim \mu\text{m} \)).
Figure 2.12 Organic spintronic devices. (a) Lateral spin device with two ferromagnetic LSMO electrodes separated by 70-500 nm and bridged by a T6 channel. (b) Magnetoresistance \( \mu_0 H = 0.3 \, T \), where \( H \) is the magnetic field) of the lateral spin device depicted as a function of the channel length\(^7\). (d) Vertical LSMO/Alq3/Co spin-valve and the corresponding MR at low temperature (c)\(^7\).

It has been more than ten years since organic material was firstly introduced into the spintronics. Dediu \textit{et al.} found a substantial room temperature MR (~ 30 %) in a lateral La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\)/T6/LSMO device, where T6 is sexithienyl and the gaps between two LSMO were ~ 140 nm\(^7\) (see Fig. 2.12 a & b). Although they did not find the standard spin-valve signal, the data suggested the possibility of injecting spin-polarized electrons into the organic semiconductor. Later on, clear spin-valve signals were observed by Xiong \textit{et al.}\(^7\). They reported negative MR ~ -40 % at 11 K in stacks of LSMO/Alq3 (120 nm)/Co, the MR vanished above 200 K (Fig. 2.12 c & d). Their results motivated considerable interest in organic spintronics, but, the weak temperature dependence of the \( I-V \) curves and the remarkable MRs at low bias voltage (down to ~2 mV), which are the features of direct tunneling, cast doubts on spin injection into the organic medium: whether the observed MRs
were due to spin injection into the organic layer or spin-conserving tunneling through the hot spots inside the thick junctions. To find out the detailed mechanisms of the spin injection, transport and relaxation inside the organic, a lot of work has been performed in this field. Making the spin-valve device with an organic spacer between two FM electrodes is the most convenient method. Despite all that, there are many obstacles both technical and in principle for organic materials: hot spots or pinholes can be easily generated in the fragile organic layer and organic materials are normally incompatible with a micro-fabrication process; the high resistance and low carrier mobility due to hopping conductivity in the disordered organic layer made the conductivity mismatch problem worse. It is well-known that interfaces are critical for injection of both charge and spin into the organic. However, the ill-defined interfaces between FM and OS result from physical and chemical problems, such as the penetration of the top FM into the soft organic layers and chemical interactions between them, which make the results poorly reproducible. In order to improve the quality of interfaces and enhance the injection efficiency, a number of recipes were developed by introducing a thin pre-injection layer between FM and OS, especially for the top interface where the FM is deposited: AlO\textsubscript{2}, MgO\textsuperscript{79} and LAO\textsuperscript{80} were chosen as efficient spin-conserving tunnel barriers, avoiding the possible interactions between FM and OS; LiF\textsuperscript{81}, Ca\textsuperscript{82}, Au\textsuperscript{83}, TPD\textsuperscript{84} and a self-assembled monolayers (SAM)\textsuperscript{83} were also used to decrease the injection barriers. Some special precautions were taken when depositing the FM electrodes onto OS, such as liquid nitrogen cooling, buffer layer assisted growth\textsuperscript{85} and indirectly deposition\textsuperscript{86}. Besides the widely-studied Alq\textsubscript{3}, a great number of other small molecules and polymers were tested, including rubrene, pentacene\textsuperscript{87}, CuPc\textsuperscript{88}, C\textsubscript{60}, P\textsubscript{3}HT\textsuperscript{89}, PTC\textsubscript{E}\textsuperscript{90} and P(NDI\textsubscript{2}OD-T\textsubscript{2})\textsuperscript{91} and so on. These OS show different properties (e.g. carrier mobility ranging from \(10^{4}\) to \(\sim 1\ \text{cm}^{2}\text{V}^{-1}\text{s}^{-1}\)) and stabilities. On the other hand, various FM electrodes were utilized ranging from the normal FM metals to LSMO and Fe\textsubscript{3}O\textsubscript{4}, which are oxide half metals, ideally with 100% spin polarization. A ferromagnetic OS, V(TCNE)\textsubscript{2}, was also
successfully applied for spin-valves with the a structure of LSMO/LAO/Rubrene(5 nm)/V(TCNE)\textsubscript{2}. With a few exceptant\textsuperscript{94}, sizable MRs at low temperature and even at room temperature have been widely reported, and people tended to believe that the spin injection was responsible for the observed spin-valve signals, conclusive evidences still missed.

These MRs were most commonly observed at relatively low bias voltages and the conductance of the devices showed weak temperature dependence, which seemed related to the direct tunneling mechanism rather than the spin injection into the organic and transport through it. It has been claimed that the weak temperature dependence of the conductance is because of the very low injection barriers\textsuperscript{95} but it is not proven. In a few experiments, a charge transport transition from the tunneling regime to the injection-limited hopping regime as the organic thickness increased was indeed reported and the small MR still persisted in the hopping regime\textsuperscript{96, 97, 98}. Epstein \textit{et al} claimed spin-conserving tunneling induced MRs in their LSMO/LAO/rubrene/Fe devices when the thickness of rubrene was \textasciitilde 5 nm, whereas the carrier injection and bulk transport in rubrene accounted for the GMR when the rubrene thickness were 20-30 nm (see Fig. 2.13). In the injection regime, clear MR was only observed when the bias voltage was large enough and the maximum MR was observed with a bias around +0.6 V at 10 K (for 20 nm rubrene)\textsuperscript{99}. These features were quite distinct from the direct tunneling behavior. Despite this, the possible involvement of tunneling MR was difficult to eliminate because of the relatively big size junctions\textsuperscript{100}, whereas at the same time Lin \textit{et al} reported MR only in the tunneling regime for stacks with slightly different structures, Co/AlO/rubrene/Fe\textsuperscript{101}. More definite evidence for spin injection was required: Dediu \textit{et al}. conducted a spin precession experiment on the LSMO/Alq\textsubscript{3}/AlO\textsubscript{x}/Co system to look for spin injection into Alq\textsubscript{3}. However, the expected Hanle effect wasn’t found, although there was clear MR\textsuperscript{102}, which casted further doubt on electrical spin injection into the organic.
Figure 2.13 Schematic illustration of tunneling vs carrier injection and transport in the rubrene layer. (a) When the thickness of rubrene is relatively thin, currents at low bias are provided by tunneling through the defect states in the energy gap. $\Delta E_1$ and $\Delta E_2$ describe the modification of the level alignment at the metal/OS interfaces due to dipolar barriers. (c) mechanism of the device operated at high bias: the thermionic field emission at the metal/OS interface controls the carrier injection into LUMO levels of OS layer. The temperature dependence of device resistances (b) and MRs (d), where the sample with 5 nm rubrene shows the standard direct tunneling behavior and the samples with thick rubrene display injection-limited transport behavior. Until now, in terms of spin precession, conclusive evidence for electrical spin injection into organics is still missing although clear MRs were observed in various spin-valves stacks made of different OSs and FM electrodes. On the other hand, successes in making spin-polarized organic light-emitting diode and the significance of the hyperfine interaction in
spins relaxation have strongly indicated the injection of spin-polarized current into these organic systems. Besides the ordinary MR and magneto-electroluminescence on the organic-based spin-valve devices, other experiments such as two-photon photo-emission, muon spin resonance and spin pump injection have provided pieces of evidence for the spin injection into organic systems under some special conditions (see Chapter 6 for details). However, the electrical spin injection and detection in the organic, a more accessible method, is still an open question.

On the other hand, the thin organic layers can certainly be used as tunnel barriers for TMR. Significant TMR, ~ 5%, was observed in the stacks of Co/AlOx/Alq3/NiFe at room temperature (8%-15% at 4.2 K). The hybrid tunnel barrier, AlOx (~ 0.6 nm)/Alq3 (1.5-3.7 nm), showed a reduced barrier height compared to the samples with Alq3. What's more important, the tunneling spin-polarization of the Co/Alq3/AlOx/Al structures was found ~ 27% at 0.4 K whereas it was down to ~ 6% for the stacks without AlOx as obtained from the Meservey-Tedrow measurement. These properties were ascribed to the minimized formation of an interfacial dipole layer between organic and metal electrode by depositing a thin AlOx layer between them. Similar results were found in the case of rubrene, where a spin flip length of around 13 nm in amorphous rubrene was calculated from the exponential fitting of the rubrene thickness dependence of tunneling spin polarization (rubrene, 0-15 nm) in the AlOx/rubrene-based junctions. This work suggested moderately spin-conserving transport in amorphous rubrene up to a thickness of 15 nm, where multi-step tunneling and even hopping characteristics emerged.

A quantitative multi-step tunneling model was proposed by Schoonus et al which revealed the intrinsic loss of MR at the onset of multiple-step tunneling in the organic layers, even without considering relaxation. Because of the different exponential thickness dependence, the conductance of two-step tunneling ($\propto e^{-\alpha d}$, where $\alpha$ is the extinction coefficient of the electron in the organic barrier) through localized states near the Fermi level of the electrodes overrides that of direct tunneling ($\propto e^{-2\alpha d}$) when the barrier thickness is
large enough. On the other hand, because the density of localized states is spin-independent
with the same maximum occupation number for spin up and spin down electrons, the TMR
of two-step tunneling is considerably lower than that of direct tunneling (see Fig. 2.14). The

![Diagram](image)

Figure 2.14 left panel: schematic diagram of two-step tunneling in FM/I/Alq₃/FM (top); the current
density $J$ and MR for two-step tunneling as a function of $d₁$ (bottom). Right panel: Alq₃ thickness
dependence of room temperature resistance (circles) and MR (squares) of the samples,
CoFeB/AlOₓ/Alq₃/Co, where the solid lines are fitted using the two-step tunneling model (solid line,
the basic model; dashed line, with hybridization at Alq₃/Co interface). The maximum TMR value of two-step tunneling is half that of direct tunneling (almost the same
as Eq. 2.22.3). Therefore, the TMR of the device dramatically decreases as two-step
tunneling starts to dominate the conductance. The total current is proportional to a weighted
superposition of the direct tunneling and two-step tunneling:

$$J \sim (1 - Nd)J_{\text{direct}} + N \int_{0}^{d} J_{\text{two-step}}(d_1) dd_1$$

(2.32)

Where $J_{\text{direct}} = e^{-2\alpha d}$, $J_{\text{two-step}} = (e^{2\alpha d_1} + e^{2\alpha(d-d_1)})^{-1}$, $N$ is the assumed linear
density of the homogeneous distribution of LS, \( d_i \) is the position of the localized state, \( d \) is Alq\(_3\) thickness (see the left panel of Fig. 2.14). The resistance and MR for various Alq\(_3\) thicknesses can be fitted by the formula above after taking into account the spin-dependent conductance and the electron extinction in AlO\(_x\) barrier.

![Diagram](image)

Figure 2.15 Spin of the injected electron from left electrode processes around the sum of the hyperfine field \( \overrightarrow{H}_{\text{hf}} \) and the applied magnetic field \( \overrightarrow{H}_{\text{a}} \) on a molecular site before tunneling to the right electrode. Different MR curves (%) are displayed for devices with 1 nm (b) and 4 nm (c) Alq\(_3\), where the direct tunneling and two-step tunneling dominated the conductance respectively. The left of (b) & (c) are experimental results and the right are the curves reproduced by considering the effect of randomly orientated hyperfine field.\(^{107}\)

An interesting aspect in the above CoFeB/AlO\(_x\)/Alq\(_3\)/Co stacks is the shape of the MR curves. The MR curves changed from the relatively instantaneous switching (Fig. 2.15b) to a symmetric positive (negative) contribution modified switching curve (Fig. 2.15c) for parallel (antiparallel) alignment as the direct tunneling changed to two-step tunneling. Considering spin precession at the molecular sites due to hyperfine coupling, the authors ascribed this behavior to the average effect of the randomly orientated hyperfine field\(^{107}\). The injected spins precess around the sum of the hyperfine field and the applied field with a canting angle, \( \theta \), and the modified two-step tunneling current is proportional to \( 1 + A_{\text{Rad}} \cos^2 \theta \), where the
sign $+(\rightarrow)$ corresponding to the parallel (antiparallel) alignment of two FM magnetizations $(A_{\text{AP}}) > 0$). In the case of $H_a << H_{hf}$, averaged over all occupied sites, these total sum of hyperfine fields will have a spherical distribution $(0 < \theta < 2\pi)$, which explains the increased (decreased) resistance for parallel (antiparallel) state.

Previous work in our group showed the possibility of using CoFeB/MgO as the spin injector. After patterning these stacks with a thin Alq$_3$ layer down to a $5 \times 5 \mu m^2$ junction size, a relatively high MR, $\sim 12\%$, at room temperature was found to be independent of the Alq$_3$ thickness (2-8 nm)$^{79}$. However, the following work on the hybrid AlO$_x$/Alq$_3$/AlO$_x$ based MTJs, where pinholes was excluded, only revealed a measurable MR with Alq$_3$ layer thinner than 3 nm at low temperature. This supports the speculation that the MR was due to multi-step tunneling$^{109}$.

### 2.2.3 Interface engineering

In contrast to making large-size junctions with sub-mm features without knowing the interface details, Barroud et al. fabricated small-size junctions (diameters $\sim 10$ nm) with a technique based on nano-indentation$^{110}$. It allows good characterization of the transport mechanism in local small areas, excluding possible of hot-spots. Unlike the negative MR reported in large-size junctions$^{85}$, a maximum $\sim 300\%$ positive MR was found for the small-size junctions of LSMO/Alq$_3$ (2 nm)/Co at 2 K, which is the highest MR reported so far in any organic-based spin-valve device. It is clear that the device was working in the direct tunneling regime and the unusual positive TMR was related to the spin-dependent hybridization of the Alq$_3$ with the LSMO. A model was proposed defining the effective spin-dependent interface to include the first molecular layer and considering the spin-dependent broadening of the molecule levels and the energy difference of these levels with respect to the Fermi level of the FM electrode. A striking point is that the effective tunneling spin polarization is inversely proportional to the weighted density of states in the FM in the strong
coupling regime, which explains the usual negative MR in the large LSMO/Alq$_3$/Co system, because of the dominant strong coupling; this suggested weak coupling in the small-size junctions for the positive TMR they observed.

![Figure 2.16 Schematic of the spin-filtering on the organic/FM interface. (a) when the magnetic metal (left) and the molecule (middle and right) are well separated, the overall DOS is simply the superposition of the individual DOS of the two spin components. When the molecule is brought into contact with metal (b & c) the DOS gets modified into two ways: the energy levels broaden and their position shifts in energy. The broadening and shifts can be spin-dependent and the positive (b) and negative (c) interface spin polarization are thereby possible depending on the details of coupling.]

To better understand the physics involved, it is helpful to consider what happens to the density of states (DOS) of a magnetic metal and an organic molecule as they are brought into contact (Fig. 2.16 from Ref. 111). When two systems are well-separated, the electronic structure of FM is characterized by a broad spin-split DOS corresponding to the majority and minority spin subbands, whereas that of the organic molecules is simply made of discrete molecular energy levels (in Fig. 2.16, only the HOMO is close enough to the electrode’s Fermi energy $E_f$). When the two materials are brought together the DOS of the molecule gets modified in two ways. First, the discrete molecular energy levels are broadened by coupling with the FM and exchanging electrons. The broadening depends on the degree of interaction
between the molecule and the electrodes, which is principally determined by their proximity and the symmetry of the molecular levels. Moreover, because the spin-up and spin-down bands of the FM are usually offset from each other in energy, the spin-up and spin-down energy levels in the molecule are broadened by different amounts (Fig. 2.16b). As a consequence, a special situation may arise where the broadened molecular orbital at $E_F$ presents an opposite spin-polarization to that of FM electrode. The interface states can dominate the conductance and lead to a negative MR. The second consequence of the interaction between the molecule and the electrode is that the molecules’ energy levels can be shifted. Again the shift can be spin-dependent, so that a particular spin-polarized molecular orbital can end up at $E_F$ and thus dominate the current as shown in Fig. 2.16c.

The hybrid FM/molecule interface properties, e.g. the resonance states and the effective tunneling spin polarization strongly depended on the coupling between the molecules and the FM electrodes. It would be most suitable to directly measure the spin-polarization of the current tunneling from a FM surface via a coupled single molecule by spin-polarized STM. It has been clearly shown from spin-polarized STM$^{112,113}$ that not only can the electron spin polarization from the FM/Molecule be opposite to that of FM substrate$^{114}$, but also different spin current polarizations are displayed in different regions of a single molecule. It was also found that the enhancement of spin polarization, a the spin-filter effect can be realized in the hybrid FM/organic interfaces$^{115,116}$. The exchange interaction between a FM substrate and transferred spin in the first layer of zinc methyl phenalenyl (ZMP) molecule together with a spin filter effect on the second ZMP layer was suggested as the reason for the spin-valve-like interface MR of Co/ZMP$^{117}$, which further enriched the possibility of manipulating of spin at the FM/organic interface.

2.3 Summary

Although considerable progress has been achieved in the field of organic spintronics (e.g. successful spin injection by two-photon photo-emission and spin pumping), the criteria for spin injection into organics are still under debate for the organic-based spin-valve devices.
Although MR was found in a vast amount of organic-based spin-valve systems, it has been mostly measured in the tunneling regime. The intrinsic hopping character is rarely displayed when non-vanishing MR is observed. Without unambiguous evidence, it is controversial to ascribe the MR to spin injection. In the most common vertical spin-valve devices, the ill-defined interfaces between the organic layers and FM electrodes and the fragile, unstable and disordered organic materials have hampered the development of this field. The magnetotransport measurement also has some limits for investigating the spins of organic systems, for example the carriers' mobilities in the devices are impossible to measure, even though it is vital for calculating the spin lifetime. Better-defined and better-reproducible organic systems, together with more effective methods for characterizing the spin properties, including spin lifetime, spin diffusion length, are urgently required. On the other hand, engineering the interface between FM and OSs has recently emerged as a promising direction for controlling the spin polarization and locally modifying the FM surfaces.

In this thesis, we will first present our various recipes for improving the performance of organic-based spin-valve devices (Chapter 3). hMTJ/MgO stacks were chosen as the spin injector for high efficiency. Liquid nitrogen cooling was used to mitigate the penetration of top FM electrodes into the organic layers. Small-size junctions were prepared as well as the ordinary large-size junction to avoid pinholes inside the organic materials. A set of work was shown in Chapter 4 for C$_{60}$-based spin-valve stacks, FM/I/OS/FM, fabricated with these recipes. A clear MR was only found in the tunneling regime for these different samples. For these devices with thin C$_{60}$ layer (< 15 nm), a multi-step tunneling model can quantitatively explain the temperature dependence of conductance and MR. Whereas for the thick C$_{60}$-based devices, VRH dominates the conductance and MR disappears.

In contemporary reports of three-terminal spin injection measurements in inorganic semiconductors, spin lifetime is evaluated, with only one interface between FM and NM required. This strategy is also potentially applicable for organic materials. We have thus performed a systematic study of the FM/I/NM structures to study the possibility of injection and detection of spin with only one FM electrode (Chapter 5). It turned out to be not the spin accumulation in the NM channel but the localized states inside the tunnel barrier that play
the main role in the observed Lorentzian-line-shape MR curves. Similar results were found for the organic-based three-terminal stacks; nevertheless, we have proposed some updated methods for studying of the intrinsic properties of certain organic materials (Chapter 6). Non-local spin-valve measurements were suggested for vertical organic-based stacks with a gap (10-100 nm). Inspired by the magnetic-field-modulated resonant tunneling model, we also put forward an idea for spin injection & detection through single molecules embedded within the tunnel barrier.
Bibliography


Chapter 3 Sample Fabrication and Characterization

3.1 Introduction

Fabrication of good samples is perhaps the most important step in experimental work. As we mentioned in previous chapters, for the fabrication of organic-based devices the main challenges lie in making well-defined thin films with perfect composition, crystal structure and high-quality interfaces. Unfortunately, most evaporated organic thin films are amorphous and the interfaces between the organic and metal electrodes are usually ill-defined. On the other hand, in our spin injection experiments, the normal FM metals (e.g. Co$_{50}$Fe$_{50}$ and Co$_{20}$Fe$_{40}$B$_{20}$) work very nicely with tunnel barriers. Therefore, we have focused on putting these two aspects together with various recipes.

Based on our existing UHV thermal evaporation system, Magnolia, for depositing organic materials and normal metals, we introduced liquid nitrogen cooling and electrical heating in order to obtain well-defined organic thin films. A new kind of shadow mask was designed to combine the MgO-based half magnetic tunnel junctions ($h$MTJs), prepared in the separate Shamrock magnetron sputtering system, with our UHV thermal evaporation system. Higher efficiency than for the AlO$_x$-based tunnel junctions was demonstrated. Besides the common large-size junctions we have developed a technique to make small-size sub-µm junctions based on UV and e-beam lithography and $h$MTJs with hybrid MgO/AlO$_x$ tunnel barriers. The samples are expected to work better than the large-size junctions in eliminating pinholes in the organic layer and clearly relating the transport mechanisms and magnetoresistance via a local measurement.

3.2 Facilities and materials in the experiments

3.2.1 Thin film deposition system
The UHV thermal evaporation system, Magnolia, was designed for making organic devices \textit{in situ} without breaking the vacuum; it is the main fabrication system used in our experiments. The chamber machined by Kurt J. Lesker Company is fully made of stainless steel with 27 CF flanges ranging from 2.75 inches to 12 inches. The main chamber is pumped by a Pfeiffer TMH 261 turbo molecular pump which has 250 l/s pumping speed with an Agilent SH-110 backing pump and a Perkin Elmer ion pump. A base pressure down to $\sim 1 \times 10^{-9}$ mbar can be achieved in this system. The most important parts of the system for our purposes include: five thermal evaporation sources for various metals and insulators (SiO, in our case), a triple source temperature-controlled organic molecular evaporation gun, a quartz crystal monitor (QCM) for detecting the thin film thickness, a retractable shadow masking system for making functional devices \textit{in situ}, a manually controlled shutter, a low angle ($\sim 5^\circ$)
Ar ion etching gun for \textit{in situ} thin film surface cleaning and a quick entry load-lock with a pressure down to $\sim 3 \times 10^{-7}$ mbar, which keeps the main chamber under UHV conditions when loading and unloading the wafers (see Fig. 3.1).

![Diagram of sample stage](image)

Figure 3.2 The sample stage inside the main chamber of Magnolia with heater and cooler. Left: the schematic drawing of the sample stage where the cartridge heater (red) and liquid nitrogen channel (green) are fed through a big copper block which is retractable and can touch and detach from the sample holder. Middle: the image of the stage when the copper block is closely touching the sample holder. Right: the 3-D design of the copper block with two parts screwed together for cartridge heaters and a copper tube channel.

For the organic devices and some other purposes, cooling and heating the substrate when depositing the materials is necessary\textsuperscript{2, 3, 4, 5}. We have therefore built and installed liquid nitrogen cooling and a cartridge heater on our sample stage (see Fig. 3.2). Without cooling and heating, the sample stage is rotatable for uniform deposition, whereas when heating or cooling the stage & sample we need to lower down a big copper block (diameter ($d$) $\sim$ 70 mm, height $\sim$ 100 mm) kept closely in touch with the back side of the sample holder, which does not rotate. Transferring the heat into or out of the stage is completed by cartridge heaters.
with an ac current power supply or flowing liquid nitrogen through a copper tube. By doing this, temperature of the sample can be changed from -197 °C to +350 °C during thin film deposition.

3.2.1.2 Shamrock magnetron sputtering system

Figure 3.3 Shamrock magnetron sputtering system. Top panel: a schematic drawing of the whole system (the top view). The pictures of chamber B, C and D are showing in the bottom panel from the front view.
The Shamrock magnetron sputtering system mainly consists of three interconnected chambers, A, B and D. The original part of the tool is chamber A, a process module (PM), which contains 6 DC magnetron sputtering guns for metal deposition. Chambers B and D are custom-designed chambers for the deposition of insulators, as well as metals under UHV conditions. Chamber B includes 6 DC guns for metal deposition and 2 RF guns for the deposition of insulators such as MgO, AlOx and SiO2. A heating capability up to 700 °C is available in this chamber. Chamber D includes a low pressure AJA magnetron sputtering gun which is mainly used for CoFeB deposition and four e-beam evaporation pockets which are applicable for MgO, Fe, Au and Cr deposition. Figure 3.3 shows the schematic layout of the whole sputtering system. The base pressures of chambers A, B and D are around $1 \times 10^{-7}$, $3 \times 10^{-8}$ and $1 \times 10^{-9}$ Torr respectively and they are separated from the transfer module (TM) by a slot valve. Each transfer module includes a computer-controlled robot to pick up the wafers from the load lock (cassette module (CM)) and transfer them to one of the deposition chambers. The thin film growth process in these chambers is basically computer controlled. Located in the class 10000 clean room at CRANN, this tool is currently used for depositing ultra-thin and uniform metal and insulator stacks. In our work, this magnetron sputtering system provides us full wafers of MgO-based MTJs: Ta(5)/Ru(30)/Ta(5)/NiFe(5)/IrMn(10)/CoFe(2.5)/Ru(0.9)/CoFeB(3)/MgO(2.75-3.25) (in the unit of nanometer), where CoFe, CoFeB and IrMn stand for Co$_{82}$Fe$_{18}$, Co$_{20}$Fe$_{60}$B$_{20}$, and Ir$_{46}$Mn$_{54}$ respectively. We also used the system for depositing the top electrodes or SiO$_2$ in the process of making small-size junctions prepared by UV lithography.

### 3.2.2 Organic materials in this thesis

Several vacuum-evaporable molecules were chosen for our spin injection experiments. Three of them, fullerene (C$_{60}$, purity $\sim$99.9%), Tris (8-hydroxiquinoline) Aluminum (Alq3, purity $\sim$99.9%) and pentacene (purity $\sim$ 99.9%) were purchased from the Sigma Aldrich company and were used in our work without further purification, whereas the spin cross-over (SCO) materials, Fe(phen)[H$_2$B(pz)$_2$)$_2$, (H$_2$B(pz)$_2$ = dihydrobis(pyrazolyl)borate, Phen = 1,10-
phenanthroline) were synthesized by Dr. Zhu in Prof. Wolfgang Schmitt's group from the School of Chemistry, Trinity College Dublin.

Figure 3.4 Structures of the molecules used in our experiments. (a) C_{60} (b) chemical formula and two geometrical isomers of Alq3 (c) Pentacene (d) Fe(phen)[H_{2}B(pz)_{2}].

3.2.2.1 Fullerene

The structure of the C_{60} molecule is like a truncated icosahedron with 60 vertices and 32 faces (20 hexagons and 12 pentagons, see Fig 3.4 a). C_{60} molecules are stable because of the sp^2-hybridized carbon atoms, yet, they are not totally unreactive because of bent sp^2 bonds
forming the closed sphere, which produces angular strain with higher energy than the case of flat graphene. For example, the characteristic reaction of fullerenes is electrophilic addition at 6, 6-double bonds, which reduces angular strain by changing sp²-hybridized carbons into sp³-hybridized ones. A C₆₀ molecule is a moderately effective electron acceptor that behaves like an electron-deficient alkene and readily reacts with electron-rich species, e.g. C₆₀ reaction with a strong organic donor molecule, TDAE, results in a compound that of ferromagnetic below 16 K. In C₆₀ crystals, the C₆₀ molecules bind together via van der Waals forces in a face-centered cubic (fcc) crystal structures. At low temperatures the individual molecules are locked against rotation in the crystal lattice. Upon heating, C₆₀ molecules start rotating and become completely orientationally disordered above ~260 K, which corresponds to a first-order phase transition. Crystals and thin films of pristine C₆₀ exhibit n-type semiconductor-like behavior; one of the highest electron mobilities, ~ 10 cm²V⁻¹s⁻¹, was found in C₆₀ single crystal ribbons. The band gap is about 2.3 eV (the mobility gap) but the optical absorption extends from the gap energy to the lower energy side (the optical gap, is ~1.6 eV) with the HOMO position of ~ -6.2 eV with respect to the vacuum level. Fcc C₆₀ crystals contain voids at the octahedral and tetrahedral sites which are sufficiently large (diameters ~0.6 nm and ~0.2 nm respectively) to accommodate impurity atoms. Alkali metal atoms can be doped into these voids, which significantly change the conductivity of C₆₀ from a semiconductor into a conductor or even a superconductor.

3.2.2.2 Tris (8-hydroxiquinoline) Aluminum

Alq₃ is a coordination complex wherein the Al atom is bounded to three 8-hydroxyquinoline ligands, giving the chemical formula Al(C₉H₇NO)₃. HOMO and LUMO positions in Alq₃ are around -5.7 eV and -2.7 eV, respectively with respect to the vacuum level. Crystals and thin films of Alq₃ are usually classified as n-type organic semiconductors with low charge carrier mobility: ~10⁻⁵ cm²V⁻¹s⁻¹ for electrons. It is also conductive for holes with a mobility ~10⁻⁶ cm²V⁻¹s⁻¹. It is most commonly used in OLEDs as the electron transport/light emitting layer. There are two possible geometrical isomers for Alq₃: meridional (mer-Alq₃) and facial (fac-
Alq3. The latter is more insulating than the former due to the larger HOMO-LUMO gap\(^\text{14}\), which could influence the injection barrier and act as a trap for charge carriers\(^\text{15, 16}\). It is generally believed that the more stable isomer, mer-Alq3, is the dominant species in most cases such as thermally evaporated amorphous thin films\(^\text{17}\).

### 3.2.2.3 Pentacene

Pentacene, composed of five linearly-fused benzene rings (Fig. 3.4C), is one of the most thoroughly-investigated conjugated organic molecules due to its high hole mobility up to 5.5 cm\(^2\)V\(^{-1}\)s\(^{-1}\) in thin film transistors (TFTs) and \(\sim 35\) cm\(^2\)V\(^{-1}\)s\(^{-1}\) at room temperature for pentacene single crystals\(^\text{18}\). The pentacene thin films are relatively stable compared with C\(_{60}\) concerning their electrical properties in ambient condition, although it has been shown that some common gases such as O\(_2\) and H\(_2\)O affect the performance of organic devices\(^\text{19, 20}\). Besides, pentacene thin films with relatively high molecular ordering can be obtained by thermal evaporation on suitable dielectric surfaces\(^2, 21\). Hole injection from gold to pentacene is widely used in TFTs because of the matched energy diagram of the work function (-5.0 eV) and HOMO (-5.1 eV) for these two materials. However, the hole-injection barrier reaches 0.85 eV because of interface dipoles forming between gold and pentacene after contact\(^\text{22, 23}\).

### 3.2.2.4 SCO molecules

The complexes \([\text{Fe(H}_2\text{Bpz}_2)_2(L)](L = 2, 20\text{-bipyridine (bipy)} \text{ or } 1, 10\text{-phenanthroline (phen)})\]\(^\text{24}\) are currently used as the SCO materials deposited by the vacuum evaporation\(^\text{25, 26}\). In these compounds the iron (II) center is surrounded by bidentate ligands with the positive charge being compensated by two H\(_2\)Bpz\(_2\)-ligands (Fig. 3.4d). They change reversibly from a low-spin (\(S = 0\)) diamagnetic state, \(^5\text{T}_{2\text{g}}\), at low temperatures to a high-spin (\(S = 2\)) paramagnetic state, \(^1\text{A}_{1\text{g}}\), at temperatures higher than \(T_{\text{cr}} \sim 160\) K. It is also possible to optically switch into a metastable \(^5\text{T}_{2\text{g}}\) state below 50 K\(^\text{27, 28}\).

In our experiment, uniform thin films were obtained by heating the source materials up to the evaporation temperature while keeping the substrate rotating. For C\(_{60}\), Alq3, pentacene and Fe(H\(_2\)Bpz\(_2\))\(_2\)(L), the evaporation temperatures monitored with a K-type thermal couple are

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around 580 °C, 180 °C, 300 °C and 150 °C respectively and the deposited rates are around 0.01-0.03 nm/s. The film roughnesses are around 0.6-2 nm.

3.2.3 The R-T rig for magneto-transport measurements

The R-T rig is a purpose-built electrical measurement setup employed in our experiment for most $I-V$ ($dI/dV$) and magneto-transport measurements. Basically, this system provides us with a stage ($\leq 15 \times 15$ mm$^2$) with various controllable conditions: temperature, from 15 K and 300 K; magnetic field, from -180 mT to +180 mT; from ambient conditions to a vacuum environment ($\sim 10^{-4}$ torr). A cryostat system with the cryo con 34 controller is used to control the temperature and a closed-cycle liquid helium compressor is connected to the cryostat which can cool the cold head and the stage down to 15 K. A Kepco bipolar analogue power supply (10 A, 200 W) controls the current through an electromagnet. The resolution of the magnetic field is below 1 mT. With a Keithley 2400 source meter, it is possible to measure the $I-V$ characteristics of the samples with resistances up to hundreds of MΩ. Using the DC source meter together with a Keithley 2182 nanovolts meter, we are able to measure small resistances down to 2-5 μΩ (see the example in Fig. 6.9). Combining these two Keithley meters with two lock-in amplifiers (SR830), we can successfully measure the dynamic conductance and inelastic tunneling spectroscopy in our tunnel junctions.

Figure 3.5 The front view of the R-T rig
3.3 AlOₓ, MgO and hybrid MgO/AlOₓ tunnel barriers

As we have shown, spin-selective tunnel barriers are essential for spin injection into the semiconductor channel. We have first tested different recipes for preparing the AlOₓ and MgO tunnel barriers with the corresponding FM electrodes based on the previous work in our group (see Ref. 1). AlOₓ was prepared by a multistep oxidation process adapted from Dr. Tokuc’s recipes. After deposition of a bottom FM electrode, Co₅₀Fe₅₀ (6-10 nm), via a shadow mask in the UHV chamber, a very thin layer of Al (0.4-0.5 nm) was deposited onto these electrodes with the stage rotated without the shadow mask. The Al deposition rate is ~ 0.01 nm/s. It turns out that the thickness of this first Al layer is very important for obtaining high TMRs by this method. It should be thick enough to fully cover the bottom FM yet thin enough to be fully oxidized. The sample was then transferred to the load-lock, where the pressure was kept below 3×10⁻⁶ Torr before transfer. Pure oxygen gas flowed into the isolated load-lock until the pressure reached ~ 152 Torr, the Al thin film was thereby oxidized. The first time of oxidization is usually around 5-10 minutes to avoid over oxidization of the bottom CoFe electrode. After oxidization and pumping down the load lock, the sample was transferred back into the main chamber and the process repeated three more times to create a compact AlOₓ tunnel barrier. Normally, the corresponding oxidization times are fixed at 30 minutes. For standard AlOₓ-based MTJs (CoFe/AlOₓ/CoFe, 100 × 100 μm²) fabricated by this method, the TMRs were around 10-20% at room temperature (see Fig. 3.6).

We have a mature recipe in the Shamrock magnetron sputtering system to grow high-quality MgO-based MTJs with TMR ratios around 250 % at room temperature (see Fig. 3.6). It is thus desirable to use an MgO tunnel barrier for spin injection. The precursor work of Huseyin Tokuc revealed that it is actually feasible to grow the hMTJ stacks up to the MgO layer (~ 2.5 nm) and transfer them it into the organic UHV chamber for growing the rest of the stack (i.e. organic and top CoFe layers), even though the MgO was somewhat degraded by breaking the vacuum¹. Employing a lithography technique, the small-size junctions (with or without
an organic layer) had been made where the highest TMRs of full MTJs stacks (without the organic) was reasonably high, ~120% at room temperature. Stimulated by this achievement, we discarded the complicated lithographic process (see Fig. 3.9, which can be problematic after introducing an organic layer) and focused instead on making large-size junctions from MgO-based hMTJs by designing a new kind of shadow mask (see the chapter 3.4). The highest TMR in our full stacks, hMTJ/MgO/CoFe, is around 160% (Fig. 3.6 show the TMR of 100%), which is reasonable, and good enough to work on considering the large junction size (~200 x 400 µm² or even larger). Our process is described as follows.

1. The stacks of hMTJs, Ta(5)/Ru(30)/Ta(5)/NiFe(5)/IrMn(10)/CoFe(2.5)/Ru(0.9)/CoFeB(3)/MgO(2.75-3.25), were sputtered on 4" Si/SiO₂ (~ 500 nm) wafers in Shamrock. In this step, the quality of the MgO is the most important of all. These wafers were taken out from the sputtering system and transferred to another vacuum system for storage (10⁻⁵ -0.1 Torr, pumped down every week). Although, the MgO tunnel barriers were exposed to air in the transfer process, it was found that the MgO-based hMTJs continue working after keeping them in such a vacuum system more than a year (TMR ~ 40%).

2. Cut the 4" wafers into many pieces (~20 x 25 mm²) and anneal them in the vacuum furnace (≤ 1 x 10⁻⁶ Torr) at 350 °C under a magnetic field of 0.6 Tesla for 60 minutes. This is to activate the exchange bias, initiate the crystallization of the MgO barrier with bottom CoFeB, define the easy axis of the hMTJs and also to degass the absorbed molecules on the MgO surface.

3. After the annealing, transfer the sample into the Magnolia UHV evaporation chamber immediately after air exposure. Clean the top surface of the degraded MgO by low angle (~5°) Ar ion milling for 60-90 s (see the details in Ref. 1: beam voltage, 200 V; beam current, ~18 mA). Low angle milling reduces the beam current density and mildly remove the atoms on the surface. During this process, the sample is rotated and it should be at the center of the sample holder.
4. Do the deposition of the organic layer and the top electrode inside the UHV chamber to complete the device stack.

Figure 3.6 The standard \( I-V \) (a) \( dI/dV \) (b) and TMR (c & d) curves of our MTJs with different tunnel barriers prepared with shadow masks (excepting the MgO-based full MTJ stacks prepared by UV lithography, whose TMR ratio was multiplied by 0.5). The measurements were performed at room temperature and \( dI/dV \) was obtained by numerical differentiation of \( I-V \) curves. The inset of (b) show the results of BDR fitting of typical AlO\(_x\)'-based MTJ. The TMR curves of MTJs with hMTJ stacks are obviously different with the plain FM electrodes (CoFe/AlO\(_x\)'/CoFe, the green curve in (c)): the exchange bias cause the switch of bottom CoFeB at around 45 mT, where in the case of CoFe electrodes, the bottom FM switches at \( \sim 12 \) mT. The black and green arrows show the alignment states of the magnetic moments in top and bottom FM electrodes for hMTJ-based stacks and CoFe/AlO\(_x\)'/CoFe respectively.
Not only MgO tunnel barrier but also AlOx and hybrid MgO-AlOx and AlOx-AlOx' were tested for different purposes by a similar process, which all work better and more easily than the AlOx' alone. Here AlOx refers to the AlOx tunnel barrier prepared by sputtering (with the same hMTJ stacks) and AlOx' is the tunnel barrier prepared by multi-step oxidization of Al thin film in the UHV system (with CoFe electrodes). The room-temperature I-V and TMR curves of these MTJs with various tunnel barriers are displayed in Fig. 3.6. Usually, only the AlOx-based MTJs are well-fitted by the BDR tunneling model (see the inset of Fig. 3.6 b). The typical values for AlOx' tunnel barriers obtained from the fitting are: thickness, ~2 nm; average barrier height, 0.6-0.9 eV (the difference of the barrier heights for two FM electrodes is negligible). The clear asymmetry in the dI/dV curves of MgO-based MTJs (see Fig. 3.6 b) is mainly due to the different interfaces between MgO and the two FM electrodes.

3.4 Big-size devices made with a shadow mask

In situ manufacturing of large-size devices with a suitable shadow mask in the UHV chamber is the easiest way to make spin-valve stacks, where the cross configuration is widely used (see the top panel in Fig. 3.7). The hollow patterns in the shadow mask were chosen for subsequently depositing two CoFe rectangular strips onto the same position of the bare substrate, whereas the space-layer materials are sandwiched between them. As described above, the AlOx tunnel barriers were prepared after the bottom FM and before the top FM by four-step deposition and oxidization. The overlapping areas of these bottom and top electrodes define the junctions. If an organic material was introduced, the organic layer was deposited after AlOx. In some case, another AlOx layer was added between the organic and top FM. With our shadow mask, six junctions were produced in each batch and the junction areas were 100 x 100 and 100 x 200 μm². In our work on C₆₀-based spin-valves, AlOx tunnel barriers prepared by oxidization were employed.

We were not quite satisfied with the shadow mask method of making cross configuration devices for several reasons. Firstly, it is not compatible with the full wafers of MgO-based
Figure 3.7 Schematic diagram of the processes and the junctions produced with different shadow masks (left) and the top view of the samples (right). The junction sizes for the top and bottom one are usually $100 \times 100 \, \mu m^2$ and $400 \times 400 \, \mu m^2$.

$hMTJs$, which are more desirable for spin injection compared with the $AlO_x$-based junctions. Secondly, the $AlO_x$ tunnel barrier prepared by multi-step oxidization is not uniform especially at the edges of bottom $CoFe$ electrodes. This issue remains for a very thin organic layer (see Fig. 3.8). To avoid shorting problems, relatively thick $AlO_x$ prepared by the four-step method is required, which is the most tricky and time-consuming process in the experiment. We had designed a new shadow mask which is applicable for both $MgO$ and $AlO_x$ and the issue of a thinner space-layer at the edges of the bottom electrodes is avoided (see Fig. 3.8). In the new shadow mask, the bottom FM is deposited onto the whole wafer, while the patterned top electrodes are isolated from the bottom plane with the thick insulator ($SiO \geq 60 \, nm$) layers. The standard steps for the $MgO$-based spin-valves are listed as follows:

1. After the processes described before, i.e. annealing in the furnace where more than two wafers can be processed at the same time and $Ar$ ion milling in the UHV chamber (one wafer
at one time), the sample is carefully aligned with the shadow mask and the SiO layers are
deposited by two subsequent steps (35 nm + 25 nm) to avoid over baking the samples.
2. Retract the shadow mask, manually rotate the sample by 90° and keep it still. Slightly mill
the wafer again with Ar ions for about 6-9 seconds.
3. Organic layer deposition with the sample rotating (0.01-0.03 nm/s).
4. Realign the sample and shadow mask to have the proper patterns stretching across the gaps
(100-1000 μm) formed by SiO patterns and deposit the top electrode (e.g. CoFe 10 nm). If
liquid nitrogen cooling is needed, the sample holder should be contacted from the back side
with the copper block, where liquid nitrogen was flowing through a copper tube within it.
For the latest shadow mask we used, three different kinds of junctions, (e.g. the same bottom
JMTJ/MgO with different top CoFe, Au and organic/CoFe etc.) can be made in the same
batch and 27 devices are obtained, which allows us to perform a better control experiments

![Devices made with two different shadow masks. From left to right they are the optical
top and bottom panels respectively.](image)

Figure 3.8 Devices made with two different shadow masks. From left to right they are the optical
images, SEM pictures and schematic images of the cross sections of the junctions. The scale bars are
100 and 400 μm in the top and bottom panels respectively.

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with higher efficiency. In our experiment, this recipe with the new shadow masks indeed exhibited lots of advantages over the cross configuration, however, we should also notice possible problems in the samples prepared in this way. Firstly, there is more chance to form pinholes between top and bottom electrode through the relatively less dense SiO layer, especially if the wafers are not clean enough and one has to be careful when connecting the samples' top electrodes with the wires for measurement. Usually silver paint is used for connecting the thin silver conducting wires (diameter ~ 50 μm) to the top electrodes. Secondly, the diffusion of SiO on the top surface of hMTJ, can degrade the performance of the tunnel junction and the effective areas of the junctions may be considerable smaller than the size of the patterns in shadow mask. This is demonstrated by the fact that the highest TMRs were obtained from the samples with large gaps ≥ 400 μm and the R·A product of larger size samples are obviously smaller than for the small-size samples made under the same conditions. Therefore, avoiding over heating the sample by thermal radiation, decreasing the distance between shadow mask and sample surface and making relatively large size junctions are the ways to mitigate the issue. In fact, the quality of the MgO was sometimes so good (uniform and pinhole-free) that we can directly deposit the large patterns (≥ 800 × 800 μm²) onto the bottom plane of hMTJ stacks without the additional layer of SiO.
3.5 Small-size devices made by lithography processes

Because neither the ordinary FM metals nor the tunnel barriers nor the organic materials are readily compatible with the lithography processes, big-size junctions are normally produced in organic-based spin-valve structures. However, small-size junctions possess the advantages of avoiding pinholes, locally measuring the device MR\(^{30, 31}\), being able to access to the spinterface\(^{32, 33}\) with much higher resolution of tunneling spectroscopy for the organic species\(^{34}\). In view of the standard process of making micro-size MTJs, Szulczewski et al had employed such a patterning process to make small-size junctions ranging from 4 × 4 \(\mu m^2\) to 50 × 150 \(\mu m^2\) with integrated organic layer\(^{35, 36}\). It includes three steps of UV lithography, three steps of lift-off, two times of milling and two steps of insulation (see Fig. 3.9). It is very time-consuming with a low success rate because of the fragile and non-adhesive organic layer.

Figure 3.9 The conventional patterning process for making micro-size MTJs\(^1\).
It is necessary to find an easier way to make organic-based small-size junctions. In Ref. 37 and 38, a conductive AFM tip was employed to generate tiny pinholes (diameters: ~ tens to hundreds of nanometers) through the photo-resist down to the top surface of a bottom La$_2$/3Sr$_{1}$/3MnO$_3$ (LSMO) layer. The subsequent growth of an organic layer (e.g. Alq$_3$ and SAMs) and the top FM electrode defines the organic-based spin-valve device. It is a much easier way of making nano-size junctions. However, this method is suitable for making only a few samples at a time and is limited to very thin organic layers, otherwise the devices are too resistive to measure because of the small junction areas. Based on a similar idea, we have extended their scheme by developing an EBL-based method to make organic-based spin-valves with sizes range from tens of nanometers to hundreds of micrometers. What is more, many samples can be made in one run and the thickness of the embedded organic layer can range from a monolayer to tens of nanometers.

Without the air-stable LSMO electrodes, we have to adapt our tunnel barriers for lithography. Since MgO-based MTJs shows higher TMR than AlO$_x$-based MTJs while AlO$_x$ is more stable than MgO, AlO$_x$ covered MgO hybrid tunnel barrier were chosen for our EBL-compatible tunnel barriers. The standard full wafers of hMTJs stacks were sputtered with the hybrid tunnel barrier made of MgO (1.75)/AlO$_x$ (1.0). The hybrid tunnel barrier shows the best performances, while AlO$_x$ also works fine (see Fig. 3.12). After 350 °C annealing in vacuum as we mentioned above, the samples are ready for the patterning process. The details are explained below:

1. The first UV lithography step. Positive photoresist (Shipley S1813) was dropped onto the sample and spin coating at a speed of 3000 RPM to create a uniform layer of photoresist on the sample (thickness ~ 1.5 μm). The sample is then baked on a hot plate to evaporate the resist solvent. The hot surface of the hot plane is kept at 115 °C where the sample is heated for ~ 90 sec. After cooling down, the sample is transferred into the OAI mask aligner for exposure under the UV light (wavelength 365nm) for 6-9 sec. The
Figure 3.10 The process of making small-size junctions by UV and e-beam lithography

exposed regions of the resist become soluble in the photo-resist developer MF-319. The sample is thus immersed into that solvent to partly remove the photo-resist and transfer the patterns onto the sample. On gently agitating the sample in the developer solution for ~45 sec, the pattern should be clearly seen on the surface. Finally the sample is rinsed in deionized (DI) water and blow-dried with nitrogen gas (Fig. 3.10 a).

2. Ar plasma milling. These samples after UV lithography are placed in our Ar plasma milling machine, the Millatron, for selectively removal of the hMTJ stacks down to the Si/SiO₂ substrate which are uncovered by photo-resist. Usually, the angle between the Ar plasma beam and the sample surface is 75° and the power for generating the plasma is ~300 W. The etching process is monitored by an End Point Detector (EPD), which detects impinging atoms from the sample. The milling is stopped a couple of minutes after the final signal of tantalum atoms disappears. Sometimes some special precautions should be taken: stop the milling and rest for a while every ten minutes in order to cool down the wafer; a low angle milling, ~ 15°, for a relatively short time to remove the redeposited materials on the edges of resist. After milling, the samples were bathed ultrasonically in the hot resist remover 1165 (~ 80 °C) or hot acetone (≤60 °C) for ~ 20 mins. On rinsing the samples in fresh acetone and isopropanol alcohol (IPA) several
times, the photo-resist should be completely removed. The bottom electrodes with composition $h$MTJ/MgO/AlO$_x$ were defined on the samples (Fig. 3.10 b and c).

3. Electron beam lithography (EBL). Firstly, the samples are coated with a layer of PMMA A6 by spin coating (~ 3000 rpm) and baked at 180 °C for 2 mins. Re-cover them with a layer of MMA by spin coating at the speed of ~ 4000 rpm and do the following bake for ~ 5 mins. Hence, the e-beam resist is made of a PMMA/MMA bilayer, where the MMA is more sensitive than PMMA under the electron beam exposure. The thickness of the bilayer is ~ 400 nm. Special exposure doses were designed for the circular patterns: high dose (~ 200 $\mu$C/cm$^2$) in the middle to fully develop the resists and low dose (~ 65 $\mu$C/cm$^2$) at the periphery to selectively develop MMA. After developing with (MIBK/IPA (1:3)) for 30-45 s and rinsing in IPA, T-shape holes can be produced on the resist (i.e. tapered patterns from the top surface to the bottom and the patterns in MMA are much larger than these in PMMA). The T-shape holes are preferred because they are good for top contacts and excluding short circuits from the edges of the holes (see Fig. 3.10 d and the middle inset of Fig. 3.11).

4. Oxygen plasma cleaning. Before the plasma cleaning, many strips made of Teflon transparent tape are stuck onto the bilayer resist to partly cover the regions between the exposed patterns on the bottom electrodes. These tapes are sticking to the wafers until the end of the final deposition and will be removed to define the isolated top electrodes (see top inset of Fig. 3.11). After numerous tests with different recipes (Fig. 3.12a), we found that oxygen plasma cleaning for ~ 4 mins after the EBL process plays a crucial role for our present lithography conditions. These samples were cleaned in a plasma-generating machine, Diener PICO Barrel Asher, with a 200 W power supply and oxygen pressure of 0.3 mbar. In this step, the oxygen plasma not only removes the resist residues but more importantly restores the quality of the MgO/AlO$_x$ tunnel barriers. However, the
Figure 3.11 Optical images of the small sizes MTJs made by lithography. (a) Top views of one junction, where the vertical light-coffee bar is the top electrode; the narrow horizontal bar is the bottom electrode (hMTJ). There is a transparent PMMA/MMA resist layer (~400 nm) between them. As shown in the top inset a row of junctions (~10) are made on the one bottom hMTJ. (b), (c) and (d) show some representative junctions ranging from 0.2 \( \mu \text{m} \) to 10 \( \mu \text{m} \). The middle inset presents a schematic drawing of the cross section of a sample with an organic layer (the red region), which is not to scale with the real dimension.

Cleaning time depended on the thickness of resist residues and can’t be too long otherwise the top surface of CoFeB that underlies the tunnel barriers can be oxidized.
5. Top electrode deposition. After oxygen plasma cleaning, these stacks should be immediately loaded into the UHV organic evaporation chamber for the organic and top FM deposition (e.g. CoFe ~ 10 nm plus Au ~ 5 nm). Before top electrode deposition, Ar ion cleaning inside the UHV chamber can be used as usual (60-120 s) for further cleaning the tunnel barrier and slightly thinning the barrier for a smaller R·A product and higher TMR. However, it is not necessary to do this as shown in Fig. 12a that sizable TMRs up to ~40% can be obtained in the samples with only 4 mins oxygen plasma cleaning. It shows that our process is also applicable for the tiny junctions for which the low-angle Ar ion beam (~5°) is unable to clean the tunnel barriers at bottom of the holes. Assuming the junction areas are defined by the sizes of the holes on PMMA (thickness ~200 nm), we can see that the diameters of the holes in PMMA should be larger than ~2 μm = 200 / tan(5°) nm in order to clean the tunnel barriers at the bottom of the resist by the low-angle Ar ion beam. Although we did get the T-shape cross sections on the bilayer resist, because the depths of holes inside the resist are around 400 nm, the evaporated thin layers CoFe (10 nm)/ Au (5 nm), are not thick enough to be continuous at the inner walls of the holes. A thicker connection layer, Ta (5 nm)/Cu (100 nm)/Ru (5 nm), was sputtered in the Shamrock system after transferring the samples. Finally, the aforementioned tapes were removed and the top electrodes of each device are hence isolated from each other. From tens to hundreds of devices can be made in one run by our recipes (see Fig. 3.11 for top view the devices). The middle inset of Fig. 3.11 shows the schematic drawing of the cross-section of our small size junctions made by UV and e-beam lithography. During our tests, most of these devices (~ 80%) without organic showed reasonable TMR ratios at room temperature: with hybrid MgO/AlOₓ barriers, 30-50 %; with AlOₓ, 20-30 %. It indicates the good quality and reproducibility of the MgO/AlOₓ tunnel barriers after the patterning processes. We also tested our recipe with different junction sizes. For the AlOₓ-based MTJs with diameters of 0.2 μm, 2.4 μm and 12 μm, with the steps of oxygen
plasma and Ar ion cleaning (2 mins for each), the latter two show higher TMRs, which reveals the positive role of Ar ion cleaning. However, we stress here that the TMRs in our smallest junctions based on $h$MTJ/MgO/AlO$_x$ are much larger than those of LSMO-based devices at room temperature. It provides us with a good platform for studying the properties of small-molecules MTJs at room temperature.

Figure 3.12 The standard TMR curves at room temperature of small-size MTJs made by lithography. Left panel: MgO, AlO$_x$, and hybrid MgO/AlO$_x$ based small-size junctions ($d \sim 12 \, \mu\text{m}$) with different cleaning time (in units of minutes. O$_2$ denotes oxygen plasma; Ar denotes Ar ion). Right panel: AlO$_x$ based MTJs with different diameters ($O_2 \sim 2 + Ar \sim 2$).
Bibliography


C₆₀ molecules are composed purely of carbon atoms and the 99% abundant ¹²C isotopes have zero nuclear spin. The hyperfine fields are supposed to be very small in systems made of C₆₀ molecules. Therefore, the spin-life time in the C₆₀ system should be relatively long. Furthermore, one of the highest mobilities in n-type organic materials, up to ~ 11 cm²V⁻¹s⁻¹, was reported in crystalline C₆₀ ribbons¹. The long spin life time together with the high carrier mobility should lead to a long spin diffusion length in C₆₀ materials (crystals or thin films), which makes them of potential interest for spintronics. Furthermore, the C₆₀ system is well-known for its fascinating properties: C₆₀ thin films can be changed from semiconductor to highly metallic conductors and even become superconducting by doping². For the individual C₆₀ molecules, work based on STM or single molecule transistors have revealed a hybridization effect between the molecule and a FM substrate. The spin-polarized electron transfer from a cobalt substrate to C₆₀ induced a FM moment of 1.2 μB per C₆₀ molecule³. It was suggested to employ this effect for zero-voltage spin injection. As shown in Fig. 4.1, the spin polarized tunneling on the molecule-scale was studied with a lateral spin-valve configuration, FM/C₆₀/FM (FM are Ni or Co). Negative TMRs were frequently reported in different systems⁴,⁵,⁶. Kondo-assisted tunneling via C₆₀ molecules sandwiched between two FM nickel electrodes was measured, and the Kondo resonance occurred closer to the Fermi energy for the antiparallel FM electrodes configuration and enhanced the tunnel conductance leading to a negative value of magnetoresistance⁴. Fig.4.1 shows another mechanism that causes the negative TMRs in the Ni/C₆₀/Ni single molecule transistors. The spin-dependent hybridization between Ni 3d states and the LUMO of the C₆₀ molecule generated an antiferromagnetic configuration in the local density of states near the Fermi level, which inverses the tunneling conductance and gives rise to the negative TMR².
Figure 4.1 Left panel: Schematic of a Ni/C₆₀/Ni single molecule transistor and the TMR, from -10% (blue) to -80% (red), spectrum at 0.3 K as a function of source-drain bias voltage, $V_{SD}$ and gate voltage, $V_g$. Right panel: schematic representation of spin-resolved density of states and spin-dependent electron tunneling when the two Ni electrodes are in the parallel or the antiparallel configurations.

For C₆₀ thin films incorporated into the spin valve structures, MRs were reported in many different systems made of different FM electrodes (and tunnel barriers) e.g. Co/AlOₓ, LSMO, and Fe₃O₄. However, we should note that the MRs were most likely only reported in the regime of tunneling (including multistep tunneling) where the C₆₀ was made of a very thin film (≤ 10 nm). As shown in Fig. 4.2, however, the spin-valve-like MRs, up to 7% were also reported in relatively thick C₆₀ films (up to 100 nm) in the structure of Fe₃O₄/AlOₓ/C₆₀/Co. The weak temperature dependence of their device resistances (Fig. 4.2 c) cast the doubt on the dominant transport mechanisms in the thick C₆₀ thin film. Whether it was spin-conserved hopping via the conductive states near Fermi level of the FM electrodes or tunneling through the FM pinholes in C₆₀, was not fully clarified. To summarize, no definitive evidence has so far shown of the injection of spin into the C₆₀
channel (more specifically to the HOMO or LUMO) although sizeable MRs were widely reported in the C\textsubscript{60}-based vertical spin-valves.

Figure 4.2 (a) TEM cross section of C\textsubscript{60}-based spin-valve structures, Fe\textsubscript{3}O\textsubscript{4}/AlO\textsubscript{x}/C\textsubscript{60}/Co/Al (scale bar, 100 nm); (b) MR with the bias voltage 30 mV at 150 K (c) the current-voltages curves for a device with 80 nm C\textsubscript{60} layer at different temperature (from 150 K to 300 K) (d) MR vs C\textsubscript{60} thickness measured at 150 K (red circles) and room temperature (black circles)."}

We started our work with the common case of large-size vertical junctions with a C\textsubscript{60} thin film between bottom CoFe/AlO\textsubscript{x} and top CoFe electrodes. The MR effect was only found in the tunneling regime. In order to improve the spin injection efficiency, MgO-based half MTJ stacks were employed for the C\textsubscript{60}-based vertical structures. We have further employed liquid nitrogen for cooling the samples during the top electrode deposition onto the “soft” organic thin film. We found that the issue of top electrode penetration into C\textsubscript{60} was thereby relieved. We have even developed a relatively simple technique in order to change from
large size junctions ($\sim 200 \times 400 \ \mu m^2$) to small size junctions ($\sim 10 \times 20 \ \mu m^2$) and thus reduce the number of possible pinholes inside the C$_{60}$, generated by the top electrodes. Strongly non-linear $I$-$V$ behavior was found for devices composed of $\sim 8$ nm C$_{60}$, which was showing a slightly non-linear behavior in the large size junctions. From all our work on C$_{60}$ thin film based spin-valve stacks made by different recipes, we confirmed that obvious MR can only be observed in the direct tunneling and multi-step tunneling regimes.

4.2 C$_{60}$-based vertical spin-valve

4.2.1 CoFe/AlO$_x$ as the spin injector

The Magnolia UHV organic chamber was employed for the deposition of stacks composed of organic layers, AlO$_x$ tunnel barriers and FM metals. For the AlO$_x$ tunnel barrier, a reliable recipe was developed by Huseyin Tokuc in our group (see chapter 3). The AlO$_x$ tunnel barriers were prepared on top of the bottom FM electrodes (i.e. CoFe) by oxidization of ultra-thin Al layers (thickness $\sim 4$ Å) in pure oxygen ($\sim 0.2$ atm) in four sequential steps: Al (4 Å, oxidization $\sim 5$ mins) + Al (4 Å, oxidization $\sim 30$ mins) + Al (4 Å, oxidization $\sim 30$ mins) + Al (4 Å, oxidization $\sim 30$ mins). Without organic materials, for the MTJs (junction areas $100 \times 100 \ \mu m^2$) of CoFe(6-10 nm)/AlO$_x$(2 nm)/CoFe(10-15 nm), the resistances are in the range of 200-1000 $\Omega$. Linear (or slightly non-linear) $I$-$V$ curves were usually found in a small voltage range ($\pm 0.1$ V), which is not enough to distinguish the good tunnel barriers. Their differential curves, $dI/dV$, are more useful as the smooth and regular parabolic $dI/dV$ indicated the good quality of the AlO$_x$. In our recipe, the highest TMR is $\sim 19$ % at room temperature and $\sim 46$ % at 20 K (see Fig. 3.6 in chapter 3). Although TMR of the devices increased more than two times when decreasing the temperature of the measuring stage from 300 K to 20 K, their zero bias resistance usually changed only a little (increased by 10 to 30 percent), which reflects the dominant direct tunneling behavior and the relatively low density of impurity states inside the AlO$_x$. For the $dI/dV$ curves at low temperature, it is worth mentioning that the dip in the voltage range near zero bias, well-known as the zero-bias anomaly (ZBA), is generally considered to be an indication of magnetic impurities.
inside the tunnel barriers. We found it commonly exists in almost all of our devices that show standard tunneling behavior, e.g. AlO\textsubscript{x}, MgO and AlO\textsubscript{x}/C\textsubscript{60} based MTJs. On the other hand, in organic spin-valves stacks, the ZBA was suggested to be an indication of FM particles diffused into the organic layer during deposition of the top electrodes\textsuperscript{10}. However, it is not easy to distinguish this possibility from the intrinsic properties of the AlO\textsubscript{x} tunnel barrier as similar behavior can be found in the systems with or without C\textsubscript{60} (see Fig. 4.5 a).

![Figure 4.3 AFM images of thin AlO\textsubscript{x} layer (~2 nm) on SiO\textsubscript{2} (a) and C\textsubscript{60} layer (~15 nm) on AlO\textsubscript{x}/SiO\textsubscript{2} (b).](image)

### 4.2.2 CoFe/AlO\textsubscript{x}/C\textsubscript{60}/CoFe spin valves

Based on the AlO\textsubscript{x} MTJ stacks, the C\textsubscript{60} thin layer was introduced by thermal evaporation of C\textsubscript{60} powders at ~580 °C at a deposition rate ≤ 0.02 nm/s before depositing the top FM electrode. The thickness of C\textsubscript{60} in our experiments was increased from 1 nm up to the point (~20 nm) where MR disappears entirely even at low temperatures, which roughly corresponds to the spin diffusion length in the C\textsubscript{60} thin film. The roughness of the C\textsubscript{60} thin film grown on AlO\textsubscript{x} was found to be below 1 nm (root mean square (RMS) ~ 0.6 nm, see the AFM and XRR measurements in C\textsubscript{60} thin film etc. in Figure 4.3 and 4.4). From the AFM images, we can see that the film was actually made of small domains (~10 nm), which are
supposed as crystallized structures. It is likely the $C_{60}$ thin films in our experiment are polycrystalline, in contrast to the amorphous structure in the more commonly studied organic Alq$_3$ although it is even smoother (see XRR in Figure 4.4). In each growth batch, six samples were obtained: half of them were deposited with $C_{60}$ (CoFe/AlO$_x$/C$_{60}$/CoFe), whereas half of them only included AlO$_x$ tunnel barriers as control samples. After deposition of the top FM electrodes, thin AlO$_x$ coating layers were deposited to protect the FM and $C_{60}$ from oxygen degradation.

Figure 4.4 XRR measurements (hollow patterns) and the corresponding fitting curves (solid lines) on $C_{60}$, Alq$_3$ thin films and bilayer and trilayer films, where the fitting parameters: thickness (roughness), of each layer are shown after the solid lines in the unit of Å. Alq$_3$ covered $C_{60}$ films show obvious improvement of the roughness compared with $C_{60}$ thin films, where the bilayer stack was employed to more accurately calibrate the $C_{60}$ thickness and also it may improve the $C_{60}$ performance in the devices stacks.
For the devices with 1 nm C₆₀, their (zero bias) resistances increased 5-10 times compared with the control samples without C₆₀ (Fig. 4.5 a & c). Standard tunneling behavior was displayed in these devices with C₆₀, nice parabolic dI/dV curves and weak temperature dependence of device resistances. Although a similar MR ratio (~ 44%) at 20 K was obtained for the devices with and without 1 nm C₆₀, a relatively steep decrease of MR in the temperature range of 30-50 K, was only observed in the case of the device with 1 nm C₆₀ (Fig. 4.6 b). Besides, we noted that there was an obvious increase of the switching field in the MR curves that related to the coercivity of FM electrodes and the switching fields also showed a steep decrease in the temperature range of 30-50 K which implies a close relation between the MRs and coercivity of FM electrodes (Fig. 4.6 a & b).

Figure 4.5 I-V and dI/dV curves of C₆₀-based large-size MTJs (100 x 100 µm²) with 0 nm (a), 1 nm (c), 5 nm (b) and 15 nm (d) of C₆₀ at low temperature and room temperature. Note that the low temperature data for the sample with 15 nm C₆₀ are multiplied by 30.
We believe the switching fields displayed on the MR curves on sweeping the magnetic field only reflect the properties of the FM domains involved in the spin injection. More specifically, the spin configurations at the interfaces of bottom CoFe/AlOx and top C60/CoFe determine the performance of the devices under the magnetic field. If we take the field where the device shows half of the maximum MR as the switching field of the corresponding FM interface (shown as the dashed lines in Fig. 4.6 a & c), the applied

Figure 4.6 (a) MR curves of the devices (100 × 100 μm²) with and without 1 nm C60 at ~ 19 K and 52 K. \( H_{c1} \) and \( H_{c2} \) are related to the small and large switching fields of the two FM electrodes in the device with 1 nm C60 and are marked by the dashed lines. (b) The temperature dependence of \( H_{c1} \) and \( H_{c2} \) obtained from the MR curves. (c) The effective coercivity of the devices with different organic thickness. The red dashed lines roughly mark the values of \( H_{c1} \) and \( H_{c2} \) in the case without the organic, where \( H_{c2} \) of the sample with only AlOx is obviously smaller than that of other samples is mainly because of the uniform and flat top CoFe electrode. (d) the temperature dependence of MR from direct measurements and calculations (described in the main text).
external magnetic field value can be thus roughly considered as the FM interface effective coercivity, $H_c$ (but not necessarily the coercivity of the FM electrode). Assuming both the coercivity and the interface spin polarization, $P$, of the FM electrodes scale with the surface magnetization, we have a qualitative relation that: $P \propto H_c$ and supposing this relation holds throughout the temperature range of our work, $P(T) \propto H_c(T)$.

From the Jullière formula, we can obtain a qualitative relation between the measured interface coercivity and MR: $MR(T) = \frac{2P^2(T_0)[H_c(T)/H_c(T_0)]}{1-P^2(T_0)[H_c(T)/H_c(T_0)]}$, where $T_0$ is the lowest temperature in our measurement and the corresponding $P(T_0)$ are calculated from the measured MR by the Jullière formula. As displayed in Fig. 4.6 d, this simple formula nicely reproduces the temperature dependence of MR of the AlO$_x$-based devices with and without 1 nm Ce$_6$. One may argue that the effective $P^2(T)$ of FM electrodes should be proportional to the product of $H_{c1}$ and $H_{c2}$ not to just one of them alone. A clue to the reason is the fact that the switching fields of two FM electrodes show almost the same temperature dependence for the case of AlO$_x$ tunnel barrier. We think the magnetic dipole interaction between two FM electrodes (for example due to the orange peel effect) through a thin insulating layer determines the switching fields of two coupled FM layers. Note that the coupling field strength of orange peel effect (related to the interface coercivity) is proportional to the product of saturation magnetization of two FM layers from Néel’s theory. It is expected that the temperature dependence of the coupled interface coercivity (i.e. switching fields) of FM electrodes should follow the same trend that actually relies on a composite effect of the interface magnetism being proportional to the product of them. Therefore, the effective interface tunneling $P^2(T)$ of two coupled FM electrodes (which is proportional to the product of interface spin polarization) only depends on $H_c(T)/H_c(T_0)$ for one of electrodes in the calculation. However, it is different for the case of introducing 1 nm Ce$_6$: the top interface of Ce$_6$/CoFe is supposed to be decoupled (or partly decoupled) from the bottom CoFe/AlO$_x$ interface. If for some reason, the polarization of the top interface changes much more rapidly than the bottom FM interface, we expected that the temperature dependence of spin polarization, $P^2(T)$ should follow the trend of the top FM
interface magnetism (i.e. $H_c(T)$), which explains the result of the device with 1nm C$_{60}$. From the AFM image of the C$_{60}$ thin film (Fig.4.3 b), we find the peak-to-valley distance in the thin film of C$_{60}$ can go up to 3 nm, which means that the nominal 1nm-C$_{60}$ can be discontinuous, the top interface of CoFe are discontinuous as well and in some regions there can be direct contact with AlO$_x$ (i.e. pinholes within the organic). One special possibility is that there are some regions of top CoFe at the C$_{60}$/CoFe interface made of small-size super paramagnetic nano-particles (< 10 nm), and the $T_b$ of them are around 20-50 K. We can expect a rapid decrease of $P(t)$ at these FM to paramagnetism transition temperatures.

Although the coercive field of the devices with organic layers is always larger than that of the AlO$_x$-barrier alone, the above modified Jullièere formula was found only to be applicable for the AlO$_x$ and AlO$_x$-C$_{60}$ tunnel barriers. For the two case of samples with lowest R·A, the direct tunneling and FM interfaces dominated the MRs (see Fig. 4.11a). When the devices resistances increase further as the organic layers become thicker (or homogeneous for the case of 1 nm Alq$_3$), we expected the transport properties inside the organic layer to determinate the device performance. As C$_{60}$ becomes thicker, the resistance of the device decreases with temperature more and more dramatically, as evidence of multi-step tunneling inside the C$_{60}$ layer. As described in chapter 2, the low bias conductance of the anti-parallel state of the devices can be fitted by the formula: $G_{AP} = G_{01} + G_2 T^{4.3} + G_3 T^{5.2}$, where $G_{01}$, $G_2$ and $G_3$ denote the conductance contributions from the tunneling via 0 (or one) localized
state (LS), two and three localized states respectively (see Fig. 4.7). The temperature dependent of these different power law was predicted by the theory\textsuperscript{14} and confirmed with experiments\textsuperscript{15,16}. We take the view that the localized states in our devices are provided by the Gaussian DOS of intermediate $C_{60}$-derived states, centered at the lowest unoccupied molecular orbital (LUMO) of $C_{60}$\textsuperscript{17}. It is found that the temperature dependence of $G_{AP}$ of the device with 5nm $C_{60}$ and 10 nm $C_{60}$ can be nicely fitted by the formula up to 2-LS and 3-LS respectively (Figure 4.8 a, b). After fitting, the contributions of each term at different temperature are plotted in Fig. 4.8 c, d. It is clear that as the temperature increases the contribution from multi-step tunneling can outweigh the direct tunneling (and two-step resonant tunneling) and dominant the conductance.

![Graph](image)

**Figure 4.8** Temperature dependence of the tunnel conductance in AP state for the samples with 5nm (a) and 10 nm C$_{60}$ (b). The corresponding relative contribution $W_N$ of different N-LS chains to the AP conductance are showing in (c) and (d).
According to the results from the references\(^\text{16}\), even for the spin-conserved multi-step tunneling, the TMR becomes considerable lower than direct tunneling:

\[
TMR_N = \frac{(1 + P)^{2(N+1)} + (1 - P)^{2(N+1)}}{2(1 - P^2) + 1}, \quad P = P_0(1 - \alpha T^{3/2})
\]

where \(P = \sqrt{P_1 P_2}\) is the assumed effective spin polarization for the two FM electrodes at various temperatures. \(P_0\) is the interface spin polarization at 0 K, \(\alpha\) is a material-dependent parameter related to the interfacial Curie temperature accounting for spin-wave excitations at the FM interfaces. \(N\) denotes the number of localized states which constitute the optimal path involved in the phonon-assisted tunneling process. It shows the \(TMR_N\) value of tunneling through \(N\)-LS is considerable smaller than the TMR due to direct tunneling. For example, for resonant tunneling through 1-LS, \(TMR_1\) is \(P^2/(1 - P^2)\) which is half of \(TMR_0\).

As mentioned above, for the samples with thicker \(C_60\) showing strong temperature dependence, the weighted contribution of multistep tunneling, \(W_N\), increase quickly with temperature, resulting in a rapid decrease of total TMR. The TMR temperature dependence can be calculated from the sum of \(TMR_N\) weighted by their fractional contributions \(W_N\):

\[
TMR(T) = \sum_N W_N TMR_N, \quad \text{where} \quad W_N = \frac{G_N^{AP}}{G^{AP}} \text{ was obtained from the fit of the } G^{AP} \text{ temperature dependence. Results are shown in Fig.4.9 b. For the devices with } 1 \text{ nm Alq}_3, 5 \text{ nm C}_{60} \text{ and } 10 \text{ nm C}_{60}, \text{ their } G^{AP} \text{ and TMR are fitted as typical cases. Most of the data points fall on the fitting curves which validates of the multistep tunneling model. Within this model, an unusual feature of the device can be explained. Usually } \Delta G(T) = G^{P}(T) - G^{AP}(T) \text{ should decrease with temperature because of the depolarization process in the FM characterized by } (1 - \alpha T^{3/2}). \text{ However, } \Delta G \text{ due to high order multistep tunneling is proportional to } T^{N-2(N+1)}, \text{ which may increase with temperature. This unique feature was observed in the sample with } 10 \text{ nm C}_{60}, \text{ where the phonon-assisted tunneling through a } 3\text{-LS chain plays a significant role in the conductance. As shown in Fig.4.9 a, } \Delta G \text{ are fitted by the formula below}\(^\text{16,18}\).}

\[
\Delta G(0,T) = G_0 \frac{C T}{\sin C T} TMR_{0(1)} + \sum_N G_N T^{N-2(N+1)} TMR_N
\]
where \( C = 1.387 \times 10^{-3} d / \sqrt{\phi} \) accounts for the thermal broadening of the electron Fermi distribution for modifying the elastic tunneling process \((N = 0\ and\ N = 1)\), \(d\) is the barrier width in nm and \(\phi\) is the barrier height in eV. For the above typical samples, the temperature dependence of \( \Delta G \) is reproduced by these fit parameters (Fig. 4.9): 1 nm Alq3, \(p_0 = 0.33, \alpha = 4 \times 10^{-5} K^{-1.5}, C = 0.0018 K^{-1.5};\) 5 nm C60, \(p_0 = 0.37, \alpha = 2.6 \times 10^{-5} K^{-1.5}, C = 0.0015 K^{-1};\) 10 nm C60, \(p_0 = 0.37, \alpha = 1.1 \times 10^{-5} K^{-1.5}, C = 0.0055 K^{-1}\). It is worth mentioning that for the elastic tunneling process, the combination of \(TMR_0\) and \(TMR_1\) are tuned to optimize the fits.

Compared with the parameters used for the samples with 5 nm C60, \(C\) is \(\sim 3.5\) times larger for 10 nm C60. If the relation, \(C \propto d\) holds for different C60 thickness, then the ill-defined C60 thickness should be around 3 nm (as \((10-3)/(5-3) = 3.5\)). It is consistent with the peak-to-valley distance we measured by AFM (see Fig. 4.3 b). The thickness dependent of \(\alpha\), which was also reported in the case of a single tunnel barrier\(^9\) is so far not well-understood. We suspect it is related to the properties of the interface between C60 and CoFe, and the sample with 10 nm C60 is thought to have better interface quality.

![Figure 4.9](image)

**Figure 4.9** (a) \( \Delta G \) vs \(T\) of the samples with different C60 thickness, nominally 5 nm (black square) and 10 nm (red dot). (b) TMR vs \(T\) of different samples.

For the samples with C60 \(\sim 15\) nm, strongly non-linear current-voltage curves were found. From low temperature to room temperature, the enhancements of resistances are normally in the range of ten (under high bias voltage) to a hundred times (under low bias voltage).
Under sufficiently large bias voltage ($|V| \geq 50$ mV), an obvious MR only can be found below ~180 K, where the curves are very noisy (Fig. 4.10). As the temperature increases, the simultaneous decrease of resistance and MR indicates a possible correlation between them. We believe the underlying transport mechanisms are responsible for this behavior. It is easier to show the transition of different transport mechanisms at the zero bias conductance, $G_0$. Below 150 K, $G_0$ can be fitted by a power-law with index up to 5. Above 175 K, the conductance increases dramatically. The temperature dependence of $G_0$ is nicely fitted by Mott’s variable-range hopping (VRH) model (see Fig. 4.10c):

Figure 4.10. MR curves of C$_{60}$-based devices with 15 nm C$_{60}$ thickness at different temperatures (a). The temperature dependence of resistance and MR of the sample with 15 nm C$_{60}$. The VRH fit of the devices with thicker C$_{60}$ layers (c) the temperature dependence of device conductivity (d) and bias voltage vs current density. The inset of (d) show the current-voltage curve from -2.5 V to +2 V at 15 K.
$G_{VRH} \propto \exp(-2\alpha \ell_{VRH}) = G_0 \exp[-(T^*/T)^{1/4}]$

where $\ell_{VRH}$ is the variable range hopping length, which increases with decreasing temperature as $T^{1/4}$ for 3-dimensional case, $\alpha$ is the localization length. The parameter $T^*$ scales with $\alpha$ and is obtained from the slope of $\ln G$ vs $T^{1/4}$. For the case of 15 nm C$_{60}$, $T^* \sim 4.08 \times 10^7$ K, which is significantly larger than the value ($\sim 4500$ K) reported in the case of rubrene-based tunnel junctions but smaller than the value of $1.24 \times 10^8$ K in the case of thick amorphous silicon barriers (30-150 nm). Compared with results in literature, the relatively large $T^*$ here is related to the tremendous temperature dependence in our sample, whereas the transition from inelastic multi-step tunneling to VRH as the amorphous layer became thicker is also consistent with case of amorphous silicon barriers. To understand the vanishing MR when the VRH start to play a role in the charge transport, one may extend the previous conclusion that the higher order of inelastic tunneling (i.e. hopping) excited by phonons leads to a large decrease of TMR. On the other hand, as the higher-order hopping channels ($N > 2$) dominate the conductance, the cross-over to VRH-like behavior emerges.

Figure 4.11 (a) Temperature dependence of $R_0A$ product of all the samples (the solid curvs are guide lines). (b) Thickness dependence of $R_0A$ product and MR of C$_{60}$-based stacks at low temperature, where the red solid curves are the filing results of $R_0A$ and MR.

Samples with 20 nm C$_{60}$ were also prepared. The VRH-like behavior was found in the sample even at low temperature. In the VRH model, the voltage dependence of current density at low temperature has a similar form as the temperature dependence of low bias...
conductance \( j_{E} \propto \exp(-2\alpha \ell_{VRH}) = j_{0}\exp[-(E^{*}/E)^{1/4}] \), where \( E = V/d \) is the electric field on the device. The line fitting of the \( \ln J \) vs \( E^{-1/4} \) data at a voltage range of +0.8 V to +2.5 V justifies the VRH transport mechanism in the samples with thicker \( C_{60} \). Again, we did not observe MR signal at any of the temperature or bias conditions. Therefore, for these vertical stacks, \( \text{CoFe/AlO}_{x}/C_{60}/\text{CoFe} \), only for the samples with thickness of \( C_{60} \) that below 20 nm showed clear MRs, where the charge transport in these sample are the range of direct tunneling and 1-D inelastic multi-step tunneling. Our results are in agreement with previous results on \( C_{60} \)-based spin valves\(^{16}\). According to the above analysis, we can fit the thickness dependence of \( R_{0}\cdot A \) and MR of \( C_{60} \)-based stacks at low temperature (Fig. 4.11b):

\[
R_{0}(t) = \frac{1}{1 + (1-Nd) \exp(-d_{0} - kd) + Nd \exp(-(d_{0} + kd)/2) + (Nd)^{2} \exp[-(d_{0} + kd)/3]}
\]

where the three terms of the denominator denote the direct, two-step and three-step tunneling conductances respectively, \( d_{0} \) sources from the contribution of \( \text{AlO}_{x} \) tunnel barrier, \( d \) is \( C_{60} \) thickness, \( N \) is the linear density of LSs (see Eq.(2.32)). The fitting result is shown in Fig. 4.11b. The corresponding TMR vs \( t \) is obtained by considering the different contribution of TMR in each term (see the red curve in Fig. 4.11b).

Because of the roughness of the \( C_{60} \) thin film there is inevitable penetration of the top CoFe into the \( C_{60} \) layer (~ 3 nm from the previous estimation). From the trend of TMR vs \( t \), we can roughly have a spin propagation length in \( C_{60} \) with the 10 nm range in agreement with a number of other reported results, however, we found that this character length is related to the cross-over transport mechanism from tunneling to hopping. One may still ask whether it is possible to improve the performance of the \( C_{60} \)-based devices as regards the ill-defined interfaces between \( C_{60} \) and the top FM. We have thereby performed another series of experiments on the \( C_{60} \)-based spin-valve structures as presented in the next part of this chapter.

### 4.3 MgO tunnel barrier for organic-based vertical stacks

In order to increase the spin injection efficiency, we have developed a recipe for using the MgO-based half MTJ stacks. In contrast to the highest TMR ~ 20% at room temperature
for AlOₓ-based MTJs, the highest TMR in the MgO-based MTJs is up to ~ 100% and should be conductive to the spin injection for organic materials. Similar to the process for making MgO-based full MTJs stacks in the sputtering and evaporation system, the C₆₀ thin films were introduced into these stacks before the evaporation of top FM (CoFe in most of our work). The cross-section of the sample is shown in Fig. 4.12 a. In following parts, we use hMTJ to denote the stacks of vertical stacks Ta (5)/Ru (30)/Ta (5)/NiFe(5)/IrMn (10)/CoFe (2.5)/Ru (0.9)/CoFeB (3). Fig.4.12 b, c and d show the results of the samples with 8 nm C₆₀, where s1 and s2 are typical samples of the same batch with relatively low and high

Figure 4.12 (a) Cross-section of hMTJ/MgO/organic/FM structures. (b) Current-voltage curves of s1 and s2 at room temperature. (c), typical MR curves for s1 and s2. (d) Bias dependence of R and MR for s2 at 19 K and 293 K.
resistance (~ 100 times different). It is clear that $s_2$ shows more features of multistep tunneling (nonlinear $I-V$ curves), whereas $s_1$ is direct-tunneling-like (linear $I-V$). The TMR $\sim 13\%$ in $s_1$ at room temperature implies a good efficiency of the $h$MTJ/MgO spin injector. Note that this value is slightly larger than the results shown in last part on the sample with 1 nm C$_{60}$. Compared with $s_1$, $s_2$ shows larger R:A and considerable smaller TMR ($\leq 3\%$), which are the consequences of multi-step tunneling. $s_2$ (8 nm C$_{60}$) shows a nominal R:A $\sim 10^{12}\Omega \cdot \mu m^2$, which is almost ten times larger than that of the CoFe/AlO$_x$/C$_{60}$ (15nm)/CoFe stacks shown in last part. However, the temperature dependence of device resistance for $s_2$ is not so notable. Because of the large R:A of $s_2$, a clear MR was observed only under the sufficient large bias ($|V| \geq 200$ mV) and MRs curves are relatively noisy (Fig. 4.12). Although a complete picture of the temperature dependence of the $R$ and MR is missing, the bias dependence at 19 K and 293 K provides some important information. A slight increase of the MR observed at 19 K reflected that under higher bias voltage, the N-LS that are responsible for the observed conductance are slightly different at low and high temperature. Both the $R$ and the MR of the sample show the asymmetry on the polarity of the bias, e.g. at the bias voltages of $+0.6V$ and $-0.6V$ the sample shows $R$ of $\sim 4$ M$\Omega$ and 1 M$\Omega$ and MR of 0.3% and 0.1% respectively.

4.4 Interface protection by liquid nitrogen cooling

Besides the FM and tunneling are important for spin injection, the interface between C$_{60}$ and the top FM also plays a key role for the MR measurement. In order to mitigate the issues related to the ill-defined C$_{60}$-FM interface and reduce the penetration of the top FM into C$_{60}$, we have introduced liquid nitrogen (LN) cooling during the deposition of the top FM. The details can be found in chapter 3. In the following, the terms of with/without LN-cooling refer whether LN-cooling is used when evaporating top FM onto the C$_{60}$ thin film. In order to compare with the previous results on the samples without LN-cooling, we have incorporated 8 nm C$_{60}$ into the MgO-based $h$MTJs. The results are shown in Fig. 4.13.
Figure 4.13 (a) Current-voltage curves of samples made with large size MgO-based hMTJs and 8 nm C₆₀. The sample without LN-cooling refers to the s2 in Fig. 4.12. The MR curves of representative samples with LN-cooling show relatively low (b) and high resistance (c). (d) The corresponding MR versus the bias voltage at low temperature of samples with and without LN-cooling.

Similarly, the samples prepared in the same batch showed a variation of resistance. Measurements on typical samples of relatively low resistance (LR) and high resistance (HR) are analyzed in the following. Compared with the samples without LN-cooling, obviously, the samples with LN-cooling exhibit a more dramatic temperature dependence, e.g. for the HR one, the resistance increased ~30 times from room temperature to low temperature. The straight-line-like curves in the logI-logV plot for these samples shows the power-law scaling of the current-voltage relation. The slopes for these samples are almost the same as the HR one: \( I \sim V^{1.5} \) at low temperature. This is considered as one of the universal features of hopping.
transport in organic materials\textsuperscript{21}, however, inelastic multistep tunneling could also be responsible for it. For the \textit{LR} sample, the sizeable of MR (\(\sim 17\%\) at the bias voltage of \(\sim +50\) mV) was observed both at room temperature and at low temperature although the resistance increased about \(6 \sim 8\) times. A striking feature emerged on the low-temperature MR curve is that the coercive field is greatly enhanced and the switching of the top CoFe seems quite slow. The round-shape of the MR curves could due to the ill-defined organic/FM interface as we discussed before. On the other hand, it was also ascribed to the precession of spins under the random hyperfine fields at the organic molecule sites. Unexpectedly, the \textit{HR}-sample showed even higher MR at room temperature (\(\sim 20\%\) at \(+100\) mV) with well-defined MR curves, although, a quite low MR \(\sim 6\%\) was observed at low temperature where the MR curves are noisy and fluctuated between two states. It is unclear why the MRs of these two samples show quite different temperature dependence. Similarly, the coercive field of the \textit{HR}-sample became significantly larger at low temperature than at room temperature. It seems unlikely the sample was degraded during the cooling down stage or measurement process because the \textit{I-V} curves measured were quite stable. Applying a suitable external magnetic field, we can keep the top and bottom FM electrodes of the sample in parallel and antiparallel configurations and the bias dependence of MR can be obtained from the \textit{I-V} curves at these states. The corresponding MR for \textit{HR} and \textit{LR} samples are shown in Fig. 4.13. Although the MR value is different for these two samples, a similar trend was found for both of them: the MR under negative bias decreased more quickly than that under positive bias. It is notably that the devices resistances are usually higher at negative bias voltage than positive bias voltage. A similar phenomenon was also reported in the Ref. 16, where the 1-LS for the two-step tunneling is believed to be shifted towards the \textit{Co}/FM interface that has a considerably larger roughness amplitude than the FM/AlO\textsubscript{x} interface. The local inhomogeneous magnetostatic field arising from the finite roughness of the FM electrode causes random precession of the spins\textsuperscript{22}, which is more serious for negative bias voltages.

100
Figure 4.14 (a) $I$-$V$ curves of the $C_{60}$-based spin-valves made by different recipes, where for the $h$MTJ-based $C_{60}$ stacks, LN-cooling was used. (b) Room temperature MRs of the MgO/AlO$_x$-based $h$MTJ with and without 10 nm $C_{60}$.

From the above results on the samples with LN cooling, it is found that the performance of the sample was indeed improved, e.g. the low bias MR $\sim$ 20% at room temperature and the more dramatic temperature dependence of junction resistance. The $HR$ sample prepared with LN-cooling with 8 nm $C_{60}$ actually displayed a behavior approach with that of the sample with 15 nm $C_{60}$ without LN-cooling (see Fig. 4.14 a). It is also in line with previous work that a sizeable MR can only be found in the direct tunneling and multi-step tunneling regime. On the other hand, the rough MR curves and the blurring of the coercive field of top FM electrodes at low temperature may still be indicative of the poor interface quality between $C_{60}$ and CoFe. As shown in Fig. 4.14 b, the complete magnetization reversal process of the top CoFe clearly composed of two steps implies two different FM domains. The small coercive field is equal to that of the large and smooth CoFe, whereas the larger coercive field is probably due to the reversal of nano-size CoFe (in the pinholes).

4.5 Small-size MTJs made by lithography

To continue our work on $C_{60}$-based spin-valve structure, we would like to see if we can prepare the devices with nice interfaces for spin injection and see whether MR of the $C_{60}$-
based spin-valve can be found in the charge hopping regime. Ideally, such useful interfaces require the smooth and abrupt structures between the organic and the top electrode. It is unlikely to realize it if the intrinsic roughness of C₆₀ can’t be improved even if the LN-cooling technique is used to preserve the organic layer from damage by the deposited atoms of the top electrode with high kinetic energy. It is demonstrated that even without any pinholes generated in the organic layer, the spin still suffers an additional random precession due to the inhomogeneous magnetostatic field resulting from the FM interface with finite roughness. The larger roughness of top FM is determined and limited by the roughness of C₆₀ layer. Such effects can be more serious for the thin layers because of the proximate distance and the magnitude of that stray field (up to tens of mT) is at least ten times larger than the hyperfine field inside the organic materials (~ mT).

An alternative method for avoiding the roughness and pinhole issue is to make small size junctions, where the local geometry could be much better. The group of Fert has developed a technique to make the tiny junctions (diameters ~ tens of nanometer) by indentation of AFM tips through the resist onto the top interface of LSMO and followed by deposition of the organic and top FM. The very thin organic layers such as Alq₃ and SAM are employed in their work. Huge MR signals, ~+300 % at 10 K for the LSMO/Alq₃/Co junction, were obtained in their samples, which are believed due to the hybridized Alq₃/LSMO interface properties, i.e. the spinterface properties. It is very likely that direct tunneling was dominating the charge transport in their devices and the question of whether the spin can hop in the organic layer is unresolved.

Here we have employed a technique based on the electron beam lithography (EBL) for making the small size junctions (sub-µm to tens of µm) with a relatively thin layer of C₆₀ (6 ~ 10 nm). The details of the process can be found in chapter 3. We aimed at observing spin transport by hopping in the organic layer.

4.5.1 Incorporation of small molecules within MgO/AlOₓ-based MTJs
In the work on $C_{60}$-based small size junctions, the diameters of 10 to 20 μm were tested with the $C_{60}$ layer from 6 to 10 nm. Normally, control samples without $C_{60}$ were prepared in the same batch by partly covering the wafers during the evaporation of $C_{60}$. We started the work on small-size junctions without LN-cooling. With 6 nm $C_{60}$ incorporated into the stacks, the device current-voltage curves are changed from the linear-like (no $C_{60}$) to nonlinear behavior and the resistance increased ~ 30 times, whereas the MRs are considerably decreased from ~ 28% to 3% (see Fig. 4.15 a and b). What is more serious, the devices with thin $C_{60}$ were not stable. The resistance changed after a short time and then the tiny MR disappeared. Such MR couldn’t be restored even at low temperature (Fig. 4.15 c, d). The sample also showed weak temperature dependence.

Figure 4.15 (a) current-voltage curves and the corresponding MRs (b) of the samples with and without $C_{60}$ prepared at the same batch. $I$-$V$ (c) and corresponding MR measurements (d) on the samples at room temperature and low temperature.
It is obvious that to make small-size (d ~ 10 μm) junctions alone is not enough to guarantee stable and reliable transport properties of C<sub>60</sub>-based devices. We have thereby combined LN-cooling with the small size junctions. The results are shown in Fig. 4.16. For the 10 nm-C<sub>60</sub> devices prepared with LN-cooling, compared with the large size junctions, the small size junctions clearly exhibited more features like strong non-linearity and bias polarity asymmetry, which reflect the properties of C<sub>60</sub> contacted with metal. Unlike the simple power-law scaling current-voltage relation, the sample showed linear two segments with different slopes in the log/I-logV plot (Fig. 4.16 b) at room temperature.

Figure 4.16 (a) Comparison of current-voltage curves at room temperature of LN-cooling samples with different sizes. (b) log-log plot of the I-V curves for the LN-cooled samples. (c) lnJ vs E<sup>1/4</sup> of the small size LN-cooled samples with different thickness. (d) MRs of the small-size samples with and without C<sub>60</sub>. All these results are measured at room temperature.
In order to show the feature of the 3-D VRH transport in these samples, the curves of $\ln J$ vs $E^{1/4}$ were plotted for the small size samples with 10 and 12 nm $C_{60}$. The linear fit at high bias voltage ($\geq 0.45$ V) manifests the transition from the injection-limited current regime to 3-D VRH, which is more evident for the sample with slightly thicker $C_{60}$. However, no clear MR was observed on these samples at any bias voltages.

4.6 Conclusions

We have performed a series of experiments on $C_{60}$-based vertical spin-valves stacks, and clear TMR was observed for the samples with relatively thin $C_{60}$ (1-15 nm). The temperature dependence of small-bias conductance of these devices supported the idea that direct tunneling and multistep tunneling are responsible for the charge transport in these samples with 'thin' and 'thick' effective $C_{60}$ layers, with the corresponding 'high' TMR with weak temperature dependence and 'low' TMR with strong temperature dependence. No obvious MR was found in the hopping transport regime in samples with thick $C_{60}$. Although we have improved the performance of the $C_{60}$-based devices by using MgO-based hMTJ stacks, LN-cooling and reducing the junction sizes, the same trend was qualitatively observed as the AlO$_x$-based spin-valves: the MR disappeared with the onset of electron hopping in the $C_{60}$ layer.

Our results question the possibility of spin injection into amorphous molecules systems. The crossover from (1D) inelastic multistep tunneling stimulated by phonon to the 3-D VRH occurs as the number of hopping/tunneling sites increases. As pointed out by Tran et al$^{16}$ that even without considering spin relaxation, when the number of inelastic tunneling steps increases in the amorphous organic channel, the spin resistance of the system will became too faint to see. It is similar to the conductivity mismatch problem in inorganic semiconductors. Only the first and the final tunneling between the localized states with adjacent FM electrodes has spin-dependent resistance, the ratio of which to the spin-independent resistance decrease quickly as the number of steps increases.
Bibliography


Chapter 5 Three-terminal Hanle measurements in vertical stacks

5.1 Background of three-terminal spin injection & detection and the MR effect

A method that combines a four-terminal nonlocal spin-valve (NLSV) with Hanle measurement was widely used in spin injection & transport experiments for a variety of materials, including Al\textsuperscript{1-3}, Ag\textsuperscript{4}, Si\textsuperscript{5-6}, GaAs\textsuperscript{7}, Graphene\textsuperscript{8}. As we showed in Chapter 2, tunnel barriers between FM electrodes and NM channel are normally introduced in order to circumvent the conductivity mismatch problem and increase the efficiency of spin injection & extraction (see Fig. 2.5). Great successes have been achieved with this method for determining the fundamental properties of potential materials for field of spintronics. However, there are some preconditions for its application: a good quality of FM/I/NM interfaces; a sub-micrometer (or even tens of nanometer) lateral distance between the two FM electrodes which necessitates electron beam lithography technique for preparing samples. For some materials, such as organics, these two requirements have so far been impossible to fulfill at the same time. Therefore, for organic materials, spin precession in a NLSV geometry has never been realized and measurement of the fundamental spin transport properties are still missing, although organics are supposed to possess an extremely long spin life time\textsuperscript{9}.

It has been demonstrated recently that a FM/I/NM structure alone can be used to inject and detect the spin accumulation in the NM underneath the FM, which is the so-called three-terminal spin injection detection\textsuperscript{10,11}. Without the necessity of making two FM electrodes with a nano-gap, the spin life time can be obtained by fitting the perpendicular magnetic field dependence of spin accumulation in the NM channel (\(\Delta \mu\) in Fig. 5.1). As long as the spin polarized current is injected into the NM channel, a spin accumulation will be built in the NM with an electrochemical potential differences between spin up and spin down: \(\Delta \mu = \mu^\uparrow - \mu^\downarrow\). Similar to the NLSV case, the spin imbalance in the NM channel can be detected
by a FM/1 contact by a voltage change, \( \Delta V = \gamma \Delta \mu / 2e \) (Eq. 2.9), where \( \gamma \) is tunnelling spin polarization of the tunnel barrier between NM and FM, and \( e \) is the electron charge. In the three-terminal geometry, the only FM electrode is considered as both the injector and detector that work independently.

Figure 5.1 The geometry and principle of three terminals spin injection & detection

Likewise, when a magnetic field is applied perpendicular to the electron spin orientation, the spins precess with the Larmor frequency (i.e. the Hanle effect). As a result, the net spin accumulation in the NM is reduced due to spin precession and dephasing. Accordingly, the magnitude of voltage detected between the terminals of FM/I and NM decreases with the field:

\[
\Delta V_{3T}(B_L) = \Delta V_{3T}(0)/\left[1+\left(\omega_L \tau_{sf}\right)^2\right]
\]

which can be obtained from Eq. 2.13 with \( L = 0 \). The spin life time is obtained from a Lorentzian fitting of the profile of voltage change under a scanning perpendicular magnetic field (or resistance change when a constant current is applied) (see Fig. 5.2). Compared with the four-terminal NLSV geometry, the three-terminal (3T) spin injection geometry has big advantages for sample fabrication and measurement (and is potentially applicable for organics). However, because of the proximity to a FM electrode, the spin accumulation and spin dynamics in the NM underneath the FM readily suffer the inhomogeneous magnetostatic field, \( B_{ms} \) arising from finite interface roughness\(^{12} \). In the case of Hanle measurement, in an addition to the external perpendicular magnetic field, the perpendicular component of the local \( B_{ms} \) also induces precession of spins in NM (Fig. 5.2 a). As calculated
Figure 5.2 The effect of inhomogeneous magnetostatic field on the spin accumulation\(^{12}\). (a) Spin precession under inhomogeneous the magnetostatic field arising from FM/I interface with a finite roughness. (b) three-terminal Hanle measurements on p-Si with different FM electrodes, where the larger magnetization in Fe (and larger inhomogeneous magnetostatic field) shows a larger line width. (c) Normalized Hanle (blue) and inverted Hanle (pink) curves for external applied magnetic field along the \(z\) or \(x\) axis, respectively, under the different magnetostatic fields that \(\mu_0\mu/4\pi = 2\, \text{T}\cdot\text{nm}^3\) (top panel) and \(10\, \text{T}\cdot\text{nm}^3\) (bottom panel), where \(\mu\) is magnetic dipole strength. The pure Lorentzian line shapes due to the intrinsic spin life time, \(\tau_s = 1\, \text{ns}\), are shown in green.\(^{12}\)

by Dash et al, the local \(B_{ms}\) can reduce the spin accumulation up to ten fold\(^{12}\). It broadens the standard Hanle curve and thereby leads to an apparent reduction of \(\tau_s\) (Fig. 5.2 b & c). On the other hand, if the external magnetic field is along the magnetization direction of the FM injector, the larger the external field the smaller is the perpendicular component of the local \(B_{ms}\). That is to say the spin precession due to \(B_{ms}\) is suppressed by increasing the external field along the easy axis of FM with enhanced spin accumulation, which is the so-call inverted Hanle effect.

Since the first demonstration of spin injection into silicon\(^{10}\) at room temperature, this method has been employed for many different nonmagnetic materials including GaAs\(^{13,14}\),
Si$^{15, 16}$, Ge$^{17}$ and graphene$^{18}$. However, two general features remain elusive in these experiments$^{19}$: the spin signals are several orders of magnitude larger than the predicted value, $R_s \sim \gamma^2 l_d/(A \sigma)$ (see Eq. 2.10, where $l_d$, $A$ and $\sigma$ are spin diffusion length, junction area and conductivity of NM material); the spin lifetimes are in a similar range for many different materials, e.g. spin lifetimes both in graphene and doped Si at room temperature are in the range from tens of to a few hundred picoseconds$^{20, 21}$. To interpret the discrepancies between spin injection theory and the experimental observation, Yang Song et al. suggested that a relatively large MR signal can be generated by resonant tunneling through the impurities with large on-site Coulomb interaction inside tunnel barriers of the FM/I/NM 3T structure (see the related part in Chapter 2)$^{22}$. Tunneling through resonant states can increase the conductance, however, because of the large on-site Coulomb energy ($U \gg k_B T$), only one electron with a certain spin direction is allowed to tunnel via a localized state at low bias voltage ($U \gg eV$). On the other side, the coupling between the localized states and the FM electrode is spin-dependent (as assumed in the Ref. 22) and the energy level of the localized states below Fermi level has more chance to be occupied by an electron whose spin direction is parallel to the majority spin direction in the FM than the minority spin direction. Thus, the resonant tunneling of majority spin electrons from FM to NM is impossible (direct tunneling is allowed), i.e. this channel is blocked. However, under a large out-of-plane magnetic field, the blockade is lifted due to depolarization of the impurity spin (Larmor precession). Taking account of molecular fields on the impurity sites arising from spin-spin interactions such as hyperfine and exchange interactions, they reproduced the AR and the sign dependence of the signal on magnetic field directions (i.e. the aforementioned Hanle and inverted Hanle effect) in experiments (see Fig. 2.10).

Yang’s model was supported by a subsequent experiment that a sizeable MR in FM/I/NM structures was only observed on the control samples with AlO$_3$ tunnel barriers where lots of impurities were deliberately generated$^{23}$. In the experiments, the NM/I/NM junctions also displayed a clear MR similar to FM/I/NM junctions under an in-plane magnetic field. To explain it, Yang’s model was extended to inelastic tunneling via at least two localized states of different types (type A and type B, for which the filling energy of the first and second electron is within the bias window respectively). One type of localized state plays the role
Figure 5.3 Schematics diagram and the experimental results for impurity-assisted MR. (a) because of the large on-site Coulomb repulsion, two-step tunneling via an A-B impurity chain is blocked when the electron spins of the lower levels in A and B are parallel. (b) The Pauli blockade is lifted when different magnetic fields in A and B randomize the correlated spin orientation of the chain. The in-plane (red) and out-of-plane (black) MRs obtained at NM/I/NM and NM/I/FM junctions are shown in (c) and (d) respectively. A steady-state solution for the dominant contribution can be obtained:

$$i_{AB}^L(\theta) \approx \frac{2e}{h} \left[ \frac{1}{\Gamma_L} + \frac{1}{\Gamma_R} + \frac{1}{\Gamma_L + \Gamma_R} + \frac{1}{\Gamma_{dd} \sin^2 \theta} \right]^{-1}$$

where $\Gamma_L(R)$ are impurity-lead coupling, and $\Gamma_{dd}$ is inter-impurity coupling. The magnetic field dependence is manifested via the angle $\theta = \theta_R - \theta_L$, which is determined by the sum of external field and the internal fields. When the external field is large enough, it is reasonable that $\theta = 0$ (as shown in Fig. 5.3 a, two-step tunneling is blocked) and without external field, $(\sin^2 \theta) \sim 1/2$ assuming an isotropic internal field (see Fig. 5.3 b, the blockade is lifted). Therefore, a modulation of current by external field (i.e. MR) is reproduced.
The model of magnetic-field-modulated resonant tunneling (and two-step inelastic tunneling) in FM/I/NM (and NM/I/NM) junctions has revealed a possible unexpected problem due to the tunnel barriers, which can explain the widely reported MR of Lorentzian line shape. It is helpful to compare this model with other related models and experimental results. Ephron et al observed a large MR at zero-bias voltage on NM/amorphous Si/NM junctions, where resonant tunneling dominated (Fig. 5.4)$^{24}$. Throughout the amorphous Si tunnel barriers, the localized states are distributed evenly and densely in space and in energy sufficiently close to the Fermi level. The localization of the wave functions of tunneling electrons within $\alpha^1$ ($\sim 0.7$ nm) of a resonant center leads to a Coulomb energy for the simultaneous resonant tunneling of two electrons via a single site, $U$, on the order of 100 meV. Therefore, the two resonant channels through a single site are general highly correlated; an electron tunneling through a particular localized state blocks resonant tunneling through the other state associated with the same site. A strong magnetic field ($B \gg k_B T/\mu_B$) lifts the degeneracy of the these two spin states and the correlations vanish as at most only one spin state associated with each site can contribute to the zero bias conductance at low temperature.

Figure 5.4 The normalized magnetic field dependence of the zero bias conductance of the sample Mo/amorphous Si (12 nm)/Mo and the comparison with a theoretical prediction, $F_\text{N}(x)$, which introduces the Coulomb correlation effect on resonant tunneling. The deviation ($\sim 20\%$) was ascribed to the Coulomb correlation effect on inelastic hopping.$^{24}$
It is well-known that many non-magnetic organic materials exhibit an intrinsic organic magnetoresistance (OMAR) (~ 10%) due to the spin-selective reactions between spin-carrying excitations. Kersten et al predicted that even larger MR can be realized in suitably synthesized doped conjugated polymers, where ionization of dopants create free charges that recombine at a rate governed by a competition between an applied magnetic field and random hyperfine fields. A spin-blocking effect occurs depending on the magnetic field (as shown in the left panel of Fig. 5.5) and a huge MR can be realized in doped polymers. The following experiment on one-dimensional molecular wires, DXP, embedded in a zeolite host crystal indeed found an exceptionally larger (> 2000%), room-temperature, small-field MR effect, which manifested the validity of this model (see Fig. 5.5). Spin-blockade applied for two electrons starting from a spin-triplet configuration. It can be lifted by spin relaxation with singlet character mixing. As shown in Fig. 5.5, for a molecular system, the random hyperfine interactions mix in singlet character, hence lifting the blockade at small external magnetic field, whereas the effective field due to hyperfine interactions, $B_{hf}$, is overshadowed by a larger external magnetic field so that spin blockade can’t be lifted. This process in organic molecules can occur at room temperature because of the strong wave function confinements, which results in a large energy spacing between the lowest singlet

Figure 5.5 Magnetic field dependence of spin blockade (left panel) and the experimental results on a molecule system of different forms (right panel).
and triplet states. It was predicted that this MR effect is relatively small in OSs exhibiting 3-D hopping conduction; however, confinement of the current path in one dimension could strongly increase the effect. The comparison measurements on thin film and 1-D wires of DXP confirmed the prediction as displayed in Fig. 5.5. It should be noted, however, that these experiments have not been independently reproduced by any other group. (In the process of examining this thesis, we noted that the Ref. 27 has been retracted because of inappropriate data handing. In spite of this, we still want to keep this paragraph in order to insist that a relatively large Lorentzian line shape MR effect\(^{25}\) (~10% or more\(^{26}\) can be generated in a total non-magnetic system because of certain spin-selective mechanism.)

Returning to the Lorentzian-line-shape MR (~ 0.1%) in the 3T FM/I/NM system, it is problematic to attribute such signals as the Hanle effect on the spin accumulation signals. In terms of a field-modulated spin blockade effect, a tiny contribution (~ 1%) from the resonant channel in conductance is able to explain the observed MR. It is difficult to interpret the relatively 'large' signals as the precession effect on spin accumulation and some modifications are required for this explanation. Tran et al suggested that the spin accumulation in the interface states localized between the tunnel junctions and NM semiconductors instead of in NM can greatly enhance the spin resistance\(^{29,30,31}\). Moreover, the inhomogeneous spin injection was thought to be responsible for the enhanced spin signal in some special experiments. Nevertheless, a ubiquitous picture and the dominant mechanisms to understand the Lorentzian-line-shape MRs in the 3T spin injection experiments are still under debate. Here, we present systematic work on FM/I/NM structures comprised of hMTJ/MgO with different nonmagnetic metals (Cu, Au and Al) in order to inject spin-polarized current into the NM metals via the 3T geometry. These NM metals are well-studied for their spin properties and can be thermally evaporated in our chamber. Besides these reasons, we chose these NM metals to avoid the complications (e.g. forming interface states) introduced by the Schottky barrier when using a NM semiconductor. Similar Hanle-like MR was found in these different materials, which scales with tunnel junction resistance. Apart from the Hanle-like MR under the perpendicular external magnetic field as usual, a specific MR was found in our devices when the external magnetic field is swept in plane because of the particular structure of bottom FM in our hMTJs. The
voltage bias and magnetic field angular dependence of MR (and TMR) were studied, and support the idea that a tunnel-barrier related effect rather than the spin accumulation in the NM plays the key role in determining the MR our 3T devices. Besides, the tunneling anisotropy of magneto-resistance (TAMR) in the hMTJ/I/NM can be excluded. Temperature dependence of transport properties indicates the increasing role of the multi-step tunneling process in the conductance of the tunnel junctions. Tunneling spectroscopy of these FM/I/NM stacks reflects the localized state due to defects or impurities involved in the tunneling process. On the other hand, it is very likely that the spin accumulation occurs in our hMTJ/I/NM stacks because the hMTJ/I/FM stacks prepared in the same batches clearly showed TMRs from 20% to 100%. It is thus necessary to find the possible effect of the spin accumulation (in NM) on these MRs we observed. We have also performed four-terminal NLSV measurements on these vertical stacks. The NLSV signals approximated to the FM injector were found to be significantly smaller than the Hanle-like MR, which is direct evidence to eliminate the role of spin accumulation on the MR. From these observations we conclude that the impurity-assisted MR accounts for the Hanle-like MR behavior.

5.2 Tunneling spectroscopy and experiment setup

Before presenting our experimental results, we would like to introduce some basic ideas about the tunneling spectroscopy, which is important in our work. As we have seen in Chapter 2, many different processes can occur in a tunnel junction according to energy of the tunneling electrons and properties of tunnel barriers. Under low bias voltage and low temperature, elastic tunneling processes (including direct and resonant tunneling) have the most probability to take place for the small energies above the Fermi level where tunneling electrons displaying a linear $I-V$ behavior.

Under higher bias, however, when the energy of a tunneling electron is equal to or higher than that of an excited state in the junction, crossing the barrier, the electron can induce an elementary excitation (e.g. phonon, magnon and even photon) in the path. It is the inelastic tunneling and the electron changes its energy and tunnels into a different state. In others
terms, the electron has more chance to tunnel as an additional conductance channel is available and the current increases (see Fig. 5.6). Because this current change is usually very small, it is more obvious to show it in the first and second derivatives of current-voltage curves, as illustrated in the middle of Fig. 5.6. In particular, the measurement technique for the second derivative is called inelastic electron tunneling spectroscopy (IETS).

Elastic tunneling
\[ eV < hv \]

Inelastic tunneling
\[ eV > hv \]

\[ \sigma_e \]

\[ \sigma_i \]

\[ G = \frac{dI}{dV} \]

\[ dG/dV = \frac{d^2I}{dV^2} \]

Figure 5.6 Schematic diagrams of elastic and inelastic tunneling (left) and the corresponding \( I-V, \) \( dI/dV \) and \( d^2I/dV^2 \) curves (middle). Right panel: the interaction between a tunneling electron and a molecule with an electric dipole, where the upper part displays the forces on the molecule from the tunneling electron at three different positions, suggesting a mechanism whereby the vibrations of a molecule are excited and the bottom shows the dimensions defined for describing the molecule's dipole field.\textsuperscript{32}

As a new spectroscopic technique developed by Jaklevic and Lambe\textsuperscript{33} in 1966, IETS was firstly used to probe the vibrational modes of molecules which were embedded in a M/I/M' tunneling junction near the oxide-metal interface. They observed some small peaks in the second derivative of the \( I-V \) curves at the voltages that corresponding to the energy of the characteristic vibrational modes of the molecules. It was then explained as tunneling electrons interacting with the dipole field from the molecules and exciting them from the
ground state to the $m$-th vibrational state giving up energy $\hbar \omega_m$. From Fermi's Golden rule, the inelastic tunneling transition rate can be written as:

$$\sigma_{l\rightarrow r} = \frac{2\pi}{\hbar} |\phi_r| U_{dp}(z) \phi_r|^2 \delta(E_l - E_r - \hbar \omega)$$

where $\phi_{l(r)}$ denotes the electron wave function in left (right) electrode. $U_{dp}(z) = 2e\rho_z/(z + r_\perp)^{3/2}$ is the electric potential of dipole field (where $z$ and $r_\perp$ are shown in Fig. 5.5). Within the WKB approximation, the transfer matrix element and finally the current and hence $d^2I/dV^2$ can be obtained:

$$I(V) = N_f N_G \int \sum_m |< m | P_z | 0 >|^2 \int_{-\infty}^{\infty} f(E) f(E + eV - \hbar \omega_m) dE$$

$$d^2I/dV^2 = N_f N_G [4\pi me / \hbar^2 \Phi \ln(t/r_\rho)] \sum_m |< m | P_z | 0 >|^2 \delta(eV - \hbar \omega_m) \quad (5.3)$$

Where $N_f$ is the number of final states, $N$ is molecules number, $\Phi = U_{dp} - E_k$, $E_K$ being the kinetic energy of the electron perpendicular to the barrier. $G_0$ is the elastic conductivity. $|< m | P_z | 0 >|^2$ is the dipole matrix element for a vibrational transition. It is clear that each vibrational mode generates a peak at $eV = \hbar \omega_m$, whose line-width is strongly dependent on the temperature.

In infrared absorption the same dipole matrix element is involved so that all the infrared-active (IR) modes should also be observed in IETS spectra. Although not all molecules have permanent dipole moments, all of them do have polarizability, which is a quantity that related to the induced dipole moment under an electric field. Therefore, polarizability components interact with the longitudinal electric field of a tunneling electron in the same manner, by means of induced dipole moments. Similarly, they interact with the transverse electric field of electromagnetic radiation in Raman spectroscopy. Therefore, the tunneling electron is capable of stimulating Raman-active vibrational modes as well. On the other side, IETS has many advantages over IR and Raman measurements: ultra-high sensitivity so that less than $10^{13}$ molecules are required to provide a spectrum (note that IETS of a
single molecule can be detected in STM\textsuperscript{36}); overtone and combination bands are exceptionally weak, which make it is easier to identify the fundamentals in IETS than in IR or Raman. Optically forbidden transitions may be observed as strong bands. Moreover, its resolution can be better than 5 cm\textsuperscript{-1} and it has a broad spectral range, 50 to above 19000 cm\textsuperscript{-1}. Therefore, it has been successfully applied to problems in surface chemistry and catalysis, electronic spectroscopy and electronic orbital mediated tunneling (OMT)\textsuperscript{35}.

Analogous to tunneling electrons exciting a molecular vibration mode, the vibration modes of the tunnel barrier and the electrodes lattice (phonon) can be excited as well, provided the tunneling electron has sufficient energy. In the case of magnetic tunnel junctions, the excitation of magnons in the ferromagnetic electrode by hot electrons was found to be mainly responsible for the decrease of TMR with temperature as shown in Chapter 2\textsuperscript{38}. IETS serves as a well-established method to characterize the tunneling process for non-magnetic or magnetic tunnel junctions. It can in principle reveal all inelastic processes where the tunneling electrons are involved. For the MTJs, it is possible to excite and identify phonons in the tunnel barrier and the electrodes as well as magnons in magnetic materials. Another prominent feature in IET spectra of MTJs is the zero bias anomaly (ZBA), which shows up in \(dI/dV\) characteristics as a sharp dip at zero bias. The origin of ZBA has been generally considered as the magnetic impurities in tunnel barrier\textsuperscript{39,40,41}. Fig. 5.7 shows the IETS in

![IETS of CoFeB/MgO/CoFeB tunnel junctions](image)

Figure 5.7 Representative IETS of CoFeB/MgO/CoFeB tunnel junctions\textsuperscript{37}. ZB, M, P and C correspond to the zero bias anomaly, magnon in CoFeB, Mg-O phonon and coherent tunneling respectively.
MgO-based MTJs. The Mg-O phonon frequency is 651 cm$^{-1}$ in bulk single crystals, which corresponds to the peak at $\sim$ 80.7 meV. The magnon excitations, in the range of 30-60 meV, tend to change their intensities and positions according to magnetization configurations of the electrodes. More specifically, for the IETS of CoFeB/MgO/CoFeB tunnel junctions with high TMRs, the structures at bias voltages above 200 mV have been ascribed to the coherent tunneling process.

Apart from the excitation states of tunnel barriers and electrode interfaces, the traps and the impurities inside the tunnel barriers can affect the tunneling process as well. The tunneling electron can be assisted or trapped by the traps. The trap-assisted tunneling is defined as a two-step tunneling process: an electron can tunnel into a localized trap in the dielectric and then tunnel out to the other side. This two-step tunneling process provides additional conducting channels. On the other hand the electrons can be captured by the traps inside the barrier, which then reduce the conductance channel. As a result, the trap features either a "peak-followed-by-valley" or "valley-followed-by-peak" in the IETS corresponding to the trap assisted tunneling or charge trapping respectively as shown in Figure 5.8.

The tunneling electron loses energy after an inelastic interaction and its subsequent tunneling probability is reduced because of the increased extinction coefficient in the barrier. As a result, the intensity of the peak in the IETS spectrum due to an inelastic interaction event near the interface where electrons are being injected into the barrier will be smaller.
than the peak due to a similar event near the opposite interface. In other words, IETS preferentially probes sites near the positively biased electrode.

As a characterization method, the resolution of IETS is crucial for detecting small signals, which are limited by experimental conditions\(^4\). Inherently, the thermal broadening of a sharp peak is \(\sim 5.4 \frac{k_B T}{k_B T}\). More precisely, \(d^2I/dV^2\) is a convolution product of the spectral weight function with the thermal function \(\chi(E)\). Another broadening is induced by the measurement itself. Due to the finite modulation amplitude \(dV\) a peak is broadened over the range of the modulation \((-\delta V \text{ to } +\delta V)\). The half-width of this function is \(\sim 1.22 \frac{e\delta V}{dV}\). The modulation amplitude can be modified in order to achieve optimum resolution. To get peaks that are limited only by the thermal smearing, the ac voltage modulation should satisfy: \(1.22 \frac{e\delta V}{dV} \ll 5.4 \frac{k_B T}{k_B T} \approx (0.468 \text{ meV}) T\).

In our experiments, the bias voltage is always defined with respect to the top electrode. Thus, positive bias results in electrons tunneling into the top electrode and the IETS is sensitive to the interface between MgO and top (FM or NM) electrodes. A constant current source (from Keithley 2400) provides the bias voltage (they are measured using a Keithley 2182 on the samples) to which a modulation of ac current with the frequency of 781.5 Hz \(-1234.5\) Hz is added from the internal oscillator of a Stanford SR830 DSP Lock-In Amplifier. The corresponding effective ac voltage on the samples is kept at around 2mV, which is smaller than the thermal smearing. Two SR830 Lock-In Amplifies were used to record the first and second harmonic voltages across the samples. Therefore, \(I-V\), \(dI/dV\) and \(d^2I/dV^2\) curves are measured simultaneously in our experiments. Magneto-transport measurements below 0.18 tesla were performed on a home-made stage, R-T Rig, equipped with an electromagnet and a liquid-helium-flow cryostat. The high-field measurements were executed on a PPMS system (at low temperature) or with a rotating permanent magnet, Multi-Mag (up to 2 T at room temperature). The magnetic field can be deployed along the in-plane and out-of-plane directions with respect to the thin films.

Because of the symmetry-based spin filtering effect, the CFB/MgO combination was chosen in our experiment to be an efficient spin injector. Typical hMTJ/MgO stacks were used as before. The samples were prepared in the same process as described in Chapter 3. The easy
axis is set by annealing in the magnetic field (~ 0.6 T at 350 °C) which is referred as x-axis (see Fig. 5.9). After transferring into the Magnolia UHV thermal evaporation system, Ar ion milling was implemented to remove the poor quality MgO top layers and adsorbed impurities (e.g. water, CO₂ molecules). The milling time was changed from 50 s to 100 s to obtain a set of tunnel barriers with resistance-area (RA) products ranging from 10⁵ to 10¹¹ Ω·µm². By using a shadow mask, the junctions are defined by the gaps between the thick SiO insulators (~ 68 nm) and different top FM and NM electrodes (10 ~ 30 nm) were normally deposited in the same batch so that finally 27 devices can be completed. Fig. 5.9 shows a schematic illustration of our devices. Fig. 5.9b is top view of the real devices which includes CoFe, Au and Al top electrodes on top of hMTJ. The red dashed rectangle regions show the FM/I/NM junctions, whose areas are 200 × 400 µm² (or 400 × 400 µm²). For the NLSV configuration, by using another pattern on the shadow mask we deposited the second
FM electrodes on top of the NM, which enables us to locally detect the nonlocal spin signal underneath FM/I interface (see Fig. 5.18).

As control samples, usually nine full MTJs (hMTJ/MgO/CoFe) were prepared in the each batch, which served as the reference samples to demonstrate the functionality of hMTJ/MgO stacks for spin injection and also to reveal the properties of hMTJ/MgO. Usually the full

![Figure 5.10 TMR (left) and IETS (right) of hMTJ/MgO/CoFe at low temperature.](image)

MTJs exhibit TMR ratios from 20 % to 100 % at RT depending on MgO thickness and milling time. Figure 5.10 shows the sample with MgO ~ 3nm milled for 50 s. Its effective MgO thickness is relatively large with RA product around $3 \times 10^9 \, \Omega \, \mu m^2$, and the TMR at low temperature is only around ~36 %, which is relatively low. The MTJ stacks were also used for IETS measurement. Comparing our results with reported data, we confirmed the quality of our measurement. We can identify the prominent peak around zero bias, which is the ZBA especially for the case of negative bias (~ -10 mV). Note the big difference between the parallel (P) and anti-parallel (AP) configurations at the bias of +20 mV, the peaks with shoulders might be the superposition of ZBA and magnon excitations. The bump around 75 mV is attributed to the MgO phonon. Because of the relatively low TMR ratio, coherent tunneling is not expected. Hence, the slight bump around +200 mV on the slope background may be due to the impurities in MgO tunnel barriers. From the results of TMR and IETS in the full MTJ stacks, we conclude that the hMTJ stacks and the IETS measurement are
working properly. We employed the same method to investigate the $h$MTJ/MgO/NM stacks in our spin injection experiment as we shall demonstrate in the next parts of this chapter.

5.3 Three-terminals spin injection on $h$MTJ/MgO/NM

5.3.1 Magneto-transport measurements on $h$MTJ/MgO/NM

![Fig. 5.11](image)

Figure 5.11 The normalized MR from the control samples made of FM/(Ta)/I/NM stacks. As an example, MR of $h$MTJ/MgO/Cu are fitted with a Lorentzian function (red curve) in (a). The inset of (b) shows the $\Delta R$ obtained from Lorentzian fitting with a parabolic background.

Fig. 5.11 displays the low temperature magneto-transport measurements on these control devices under a perpendicular magnetic field (i.e. along $z$-axis). The clear switch of $h$MTJ/MgO/CoFe stacks (TMR, $\sim$25% in Fig. 5.11a) when scanning the field suggest that the $h$MTJ/MgO stacks should serve as good spin injectors for these NM materials. The top CoFe was switched under the out-of-plane magnetic field at $\sim$ +100 mT, which is likely due to a slight oblique angle ($\sim$10°) between the magnetic field and the perpendicular axis of the plane. For these $h$MTJ/MgO/NM (Cu, Au and Al etc.) stacks, similar MR curves were found in almost all the samples prepared both in this same batch and different batches as long as the bias voltage is large enough. These curves can be nicely fitted with a Lorentzian function plus a quadratic background as shown in inset of Fig. 5.11b. In our experiment, $\Delta R/R(0)$, the change of resistance under the perpendicular magnetic field over the resistance without magnetic field, i.e. the MR is around 0.1-1 %. In order to exclude the possible artifacts from the fabrication procedure (e.g. the leakage through the SiO layer) or some other non-spin-
related effects, we also prepared a bottom stack with Ta (2 nm) inserted between CFB and MgO for complete suppression of spin injection similar to the work in Ref. 10. For CFB/Ta/MgO/CoFe stacks, no TMR was found (data not shown) and for CFB/Ta/MgO/Au no MRs was found in the same condition (below 0.001% as shown in Fig. 5.11b). From the control experiments, we can at least relate the MR to the magnetism of the bottom FM electrodes although it is not clear that whether the MR is related to spin injection.

Figure 5.12 (a): the $\Delta R\cdot A$ product vs tunnel barrier $R\cdot A$ product for different hMTJ/MgO/NM under perpendicular magnetic field and in low temperature. (b): the FWHM of these MR curves vs tunnel barrier $R\cdot A$ product.

In the literature, such Lorentzian-line-shape MR is usually ascribed to the Hanle effect of the spin accumulation in the NM. The spin accumulation is supposed to decrease as the perpendicular magnetic field increases because of the precession and dephasing of spin polarized current in NM materials. In order to make a reasonable comparison among our samples and also with the other reported results, the magnitude of the MR (i.e. $\Delta R$) and the FWHM of the MR profiles were obtained from the Lorentzian fitting as depicted in the inset of Fig.5.11b. When MRs are small or when the bottom FM axis is tilted out of plane under a magnetic field larger than 0.4 tesla, the quadratic backgrounds were normally included. From the viewpoint of spin injection theory, the intrinsic spin resistance in the NM materials is independent of the tunnel barrier $R\cdot A$ as long as the $R\cdot A$ is large enough to overcome the resistance mismatch problem in the spin injection (see Eq. 2.10). In the case of spin injection
into in NM metals, $R \cdot A \sim 10 \, \Omega \, \mu m^2$ is large enough for high spin injection efficiency and the corresponding spin resistance, $\Delta R_s / A$, due to spin accumulation should be in the range of $\gamma \rho / \rho_{st} \sim 0.1 \, \Omega \, \mu m^2$. We have prepared a set of devices with the junction $R \cdot A$ range from $10^3$ to $10^{11} \Omega \, \mu m^2$ for different top NM electrodes. The summary of our results is shown in Fig. 5.12. It is found even the lowest $\Delta R \cdot A$ (~$1 \, \Omega \, \mu m^2$) is much larger than the expected value. A power law scaling relation between $\Delta R \cdot A$ and $R \cdot A$ can be found, with an exponent factor of 1.22 ($\pm 0.06$), which is very close to the reported result in Ref. 23. This feature remains incomprehensible in many different systems as we mentioned above. On the other hand, there is no obvious trend in FWHMs was found for different NMs (Fig.5.12b). FWHMs observed in different NM are in the range of 150-350 mT. If calculating the $\tau_s$ from the FWHM of MR curves by using $\tau_s = 2h/\mu_B B_{FWHM}$ for Al, Au, Cu materials in our experiment, the values of $\tau_s$ are around 30-80 ps, which is not consistent with the NLSV results from literatures: ~3 ps for Au$^{46}$ and ~100 ps for Al$^{47}$. However, our result is comparable with the reported results of three-terminal spin injection experiment in NM metals$^{48}$ (e.g. Au and Al) and even semiconductors, where amorphous Al$_2$O$_3$ or high crystal quality MgO$^{49}$ were employed.

Besides the perpendicular MR described above, the change of junctions resistances are more prominent when the magnetic field is applied in plane. Fig. 5.13 a & b show the MRs of the representative result on $h$MTJ/MgO/Au (referred as S1 in the following parts) at 300 K (bias voltage ~ $+0.5 \, V$ and nominal $R \cdot A \sim 1.4 \, G\Omega \, \mu m^2$) when the in plane magnetic field is parallel (x-axis) and perpendicular (y-axis) to the easy axis of the hMTJ. When the magnetic field is large enough, the resistance of the device is increasing with the magnitude of parallel field. The $\Delta R$ is largest when the field is along the easy axis. At 10 K, $\Delta R \sim 120 \, \Omega$ with the field up to 1 T, which is about two times larger than the Hanle-like MR under the field perpendicular to the plane. The main features of our results are consistent with the literature result, where the positive Lorentzian-line-shape peak (in the perpendicular case) is explained as 'Hanle effect' and the negative 'background' MR (in the parallel case) is described by 'inverted Hanle effect'. In the context of spin injection, such MR behavior is described as below. For a real device, a certain roughness of the FM thin film is inevitable, which generates an inhomogeneous magnetostatic field, $B_{ms}$. Because of the proximity to a
Figure 5.13 the room temperature MR and TMR of S1 and S2 respectively, under the magnetic fields along x-axis (a) and y-axis (b) respectively. The red dashed lines mark structures in TMR and MR curves. The calculated results of MR and TMR of 1/2MTJ/I/NM (black) and full MTJs (green) respectively with the in-plane magnetic field along x-axis and y-axis are displayed in (c) and (d) respectively. (e) and (f) show the magnetization reversal processes of CoFe free layer (black), CoFeB (red) and exchange-bias CoFe (blue). Note that the structures in (a) and (b) are reproduced in (c) and (d) respectively.
FM interface, spin accumulation in the NM readily suffers from the inhomogeneous magnetostatic field. The perpendicular component of the local magnetostatic field also induces spin precession in the NM and reduces the amount of spin accumulation. It thus produces a broadening in the standard Hanle curve. On the other hand, if the external magnetic field is applied along the magnetization direction of the FM injector, spin precession due to $B_{\text{ms}}$ is depressed with increasing the in-plane external magnetic field. As a result, an increasing spin accumulation (i.e. MR) can be found, which explains the increase of MR in a parallel magnetic field. Although, it is difficult to ascribe the unexpected ‘huge’ MRs found in these three-terminal devices to the spin accumulation in the NM, we may adapt this viewpoint to interpret our results by considering the projection of the net magnetic field at local positions along the spin direction of tunneling electron: the larger the magnetic field component perpendicular to the spin direction, the smaller is the MR; the larger the component parallel to spin direction, the larger is the MR. It is just a phenomenological picture and is straightforwardly applicable for the case that the spin injector is made of a simple FM electrode where the tunneling spin direction is clear upon different external magnetic field. However, the synthetic artificial ferrimagnet (SAF, \textit{i.e.} CoFe2.5/Ru0.9/CoFeB3) structures in our hMTJ stacks made some differences.

It is noticeable that in Fig. 5.13a that there are four distinct ‘peak’ structures sitting at around -220 mT, -30 mT, +130 and +260 mT for S1, whereas the full MTJ stacks S2 prepared on the same hMTJ shows an ordinary high resistance plateau around -25 mT and a small ‘bump’ around +200 mT. Except for the large negative background, such structured in-plane MR has never been reported in plain three-terminal FM/I/NM stacks. One may speculate that this specific behavior is related to the SAF structures in our hMTJ. We can relate these four ‘peaks’ to the magnetization reversal process of the SAF after carefully comparing the MRs of hMTJ/MgO/NM devices (S1) with the TMR of hMTJ/MgO/CoFe (i.e. S2 in the later part). As a reference, the TMR curves of S2 prepared in the same run are useful for us to find information about the angle, $\theta$, between the bottom FM (CoFeB) and the top FM (CoFe). Due to Juliere formula, the change of conductance, $\Delta G$, during magnetic switching in a MTJ is proportional to $\cos \theta$, i.e. $\Delta G \propto P_1P_2\cos \theta$, where $P_1$ and $P_2$ are spin polarization of
bottom and top FM. We found the TMR curve in Fig. 5.13a is readily understood by considering the spin flop phenomenon induced by the SAF structure\(^5\).

In our SAF structure with an antiferromagnet, IrMn10/CoFe2.5/Ru0.9/CoFeB3, there is an RKKY interlayer exchange coupling between CoFeB and CoFe through an ultrathin Ru layer. For 0.9 nm Ru, it is antiferromagnetic coupling, \(J_2\). Besides, the CoFe2.5 is exchange biased by an adjacent antiferromagnetic layer (IrMn), \(J_3\). In the case of a full MTJs made of hMTJ/MgO/CoFe, there is also an interlayer coupling between the free layer of CoFe and CoFeB, \(J_1\). Taking into account of above exchange energy, demagnetization energy and anisotropy of these FM layers, we can treat the reversal process of FM layers by Stoner-Wohlfarth model\(^5\):

\[
E_{\text{tot}} = K_u t_1 \sin^2 \theta_1 - M_1 H \cos(\alpha - \theta_1) - J_1 \cos(\theta_1 - \theta_1) + K_u t_1 \sin^2 \theta_1 + M_1 H \cos(\alpha - \theta_1) - J_2 \cos(\theta_1 - \theta_2) + K_u t_2 \sin^2 \theta_2 + M_2 H \cos(\alpha - \theta_2) - J_3 \cos(\beta - \theta_2) \quad (5.4)
\]

where \(K_u\) is the anisotropy energy for each magnetic layer (1 and 2 refer to CoFe free layer, CoFeB and exchange biased CoFe), \(M\) is their magnetic moment, \(\theta\) is the angle between the magnetic moment and the easy axis, \(\alpha\) and \(\beta\) are the directions of external field and exchange bias relative to their easy axes, respectively. Minimizing the system’s total energy, we can find the rotation angle for each FM layer under different external field fields with different directions. Below, the parameters in this formula are selected carefully in order to firstly reproduce the TMR switching behavior, and then we use related parameters to mimic the hMTJ switching (without the first three terms in formula (5.4)). Fig.5.13e shows the angular variation of FM electrodes (\(\theta_1, \theta_1\) and \(\theta_2\)) in S2 as a function of magnetic field along the easy axis (\(\alpha = 0, \beta \sim 8^\circ\)) calculated from formula (5.4). The reversal of free layer CoFe is trivial in that it almost follows the external field; however, the reverse process of CoFeB is more meaningful. Clearly, a spin flop occurred and the corresponding TMR ratio can be obtained from the angles we get. Increasing the external field from -400 mT to -25 mT causes the slowly rotation of CoFeB from parallel (\(\theta = 0^\circ\)) to antiparallel (\(\theta = 180^\circ\)) to the field and the corresponding TMR from low resistance to high resistance. Because of the antiferromagnetic coupling with the underlying CoFe through the 0.9 nm Ru layer, the magnetic moment of CoFeB rotates away from \(\theta = 0^\circ\) with small angle (~25° at room
temperature) and back to zero again when the field increases from ~ +130 mT to +300 mT. It leads to a small plateau of TMR around +200 mT. On the other hand, from the MR curve of S1, we can find these two peaks on both positive and negative sides of the loop corresponding to the onset and the end of the rotation in the CoFeB layer. With the reverse details of CoFeB versus the magnetic field, the MR behavior can be understood by applying the tentative summary we made above: device resistance is proportional to magnitude of the external magnetic field component parallel to carrier's magnetic moment and inversely proportional to the magnitude of perpendicular component. Denoting $\theta$ the angle between the magnetic moment of CoFeB (which determines the spin of tunneling electrons) and the external magnetic field, we can write a simple formula: $\Delta R \propto c_1 B \cos^2 \theta - c_2 B \sin^2 \theta$. In this formula $c_1$ and $c_2$ are the fitting parameters from the data. Using the $\theta$ obtained from formula (5.4) and optimizing $c_1$ and $c_2$, we can nicely reproduce the $\Delta R$ we measured (see Fig. 5.13c). Especially, the four 'peaks' are explained, consistent with the negative background MR. As a result, the apparently complicated in-plane MR found in our devices is in principle compatible with standard results found in literature. It is further supported by the devices' MRs under an in-plane magnetic field perpendicular to the easy axis (i.e. along y-axis). Fig. 5.13b shows the room temperature MR and TMR together for S1 and S2 respectively. Only one symmetric 'peak' around zero field together with linear-like negative 'background' was found for S1. Similarly, it can be understood from the formula of $\Delta R$. To calculate the $\theta$ during scanning an in-plane field along hard axis, the same exchange and anisotropy energies in formula (5.4) are used ($\alpha = 90^\circ$), and the results are shown in Fig. 5.13f. When the in-plane field is small enough, the CoFeB electrode keeps its magnetic moment along the easy axis and being perpendicular to the external magnetic field hence a peak-like structure is produced. As the external field keeps increasing, the magnetic moment of CoFeB gradually rotates towards the field direction and it is finally almost in line with the field. Field dependences of TMR and MR are reproduced by using the same formulas we introduced above, and plotted in Fig. 5.13d.

In order to obtain a full picture of the dependences of MRs on the magnitude and directions of external magnetic field, we have performed angular-dependence measurements on the two typical samples. S1 was scanned from in plane (along the easy axis) to out of plane
under two different fields of 0.6 T and 2 T (bias voltage fixed at +0.5V). There are two main differences for these two fields: a larger change of MR for 0.6 T; a minimum of MR around the perpendicular direction (90°) for 0.6 T field whereas a local maximum for the 2 T field (Fig. 5.14 a). Both of the data sets can be fitted by the \( \cos^2\theta ' \) dependence except around the regions where the field is perpendicular to the plane, where \( \theta ' \) is the angle between magnetic field and the easy axis direction of the JnhMTJ. Obviously, the deviation between the magnetic moment and the easy axis of CoFeB is largest when \( \theta ' = 90^\circ \) especially for the case of larger

![Figure 5.14 a](image1.png) ![Figure 5.14 b](image2.png) ![Figure 5.14 c](image3.png) ![Figure 5.14 d](image4.png)

Figure 5.14 (a) Angular dependence of MRs of S1 at 10 K (bias ~ +0.5 V) and their \( \cos^2\theta ' \) and \( \cos^3\theta ' \) fittings. (b) Calculated results of the angles of CoFe free layer (\( \theta_i \)) and CoFeB (\( \theta_l \)) vs the rotating magnetic field. (c) Angular dependence of TMR of S2 with two different scanning fields at 10 K. (d) Polar plot of \( R \) vs \( \theta ' \) (S1) at different bias voltages under a magnetic field of 2 T. \( \theta ' \) is the angle between the applied magnetic field and the easy axis of S1 or S2.

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applied field. We calculated the real angle between the field and magnetic moment direction of CoFeB, $\theta$, from minimizing the total magnetic energy in formula (5.4) with the largest anisotropy energies. As displayed in Fig. 5.14a (the red and magenta curves), the fits are improved by replacing $\theta'$ by $\theta$. $\Delta R$ follows the $\cos^2\theta$ dependence and the local minimum or maximum of MR around $\theta' = 90^\circ$ result from the magnetic field dependence of $\theta$ (Fig. 5.14 b). Note that the relationship of $\Delta R \propto \cos^2\theta$ is actually the same as the relationship $\Delta R \propto c_1B\cos^2\theta - c_2B\sin^2\theta$ because of $\sin^2\theta = 1 - \cos^2\theta$. It is worth mentioning that the same relationship was also reported in the case of FM/MgO/Si (or Ge)\(^{52}\). In terms of spin injection, it was explained that the injected spin signal is proportional to $\cos\theta$ and to detect it another factor of $\cos\theta$ is multiplied. Consequently, $\Delta \theta$ is proportional to $\cos^2\theta$.

However, we would like to stress that the aforementioned two puzzling problems remain unsolved in that work. This angular dependence of $\Delta \theta$ is also different at different bias voltages (Fig. 5.14d) under a 2 T magnetic field. For the smaller positive bias (+0.2V) and negative bias (-0.5V), the resistance of S1 is largest when $\theta' = 90^\circ$ which contradicts the case of large positive bias. It is related to the bias dependent of MRs as we will see later. A useful comparison is the angular dependence of the TMR in S2, from which we can obtain the angle between the bottom CoFeB and the top CoFe and verify the validity of the angles we calculated. At +0.5 V, a small TMR (~3%, see Fig. 5.16f) remains and a clear angle dependent is only observable under the 0.6 T field rotation. Making use of the relation that $\Delta G \propto P_1P_2\cos\theta$, we found that the angle between bottom CoFeB and the top CoFe is about $95^\circ$, when the 0.6 T field is applied perpendicular to the plane. On the contrary, under a rotating magnetic field of 2 T the resistance change is almost negligible in the MTJ. The $\Delta R/R$ in S2 is ~ 0.03%, which is ten times smaller than the MR level in S1 under the same condition. Moreover, S2 shows lowest resistance when the misalignment angle between CoFeB and CoFe is largest (~17° obtained from the angle dependence of TMR at +10 mV), which contradicts the TMR behavior (see Fig. 5.14c). It seems that the TMR is suppressed in S2 for some reasons under the magnetic field of 2 T at 10 K at the high bias voltage (+0.5V). A mechanism other than ordinary TMR takes the lead, which accounts for the decrease of resistance when the bottom FM is largely tilted out of the plane.
For the MR behavior of the $h$MTJ/I/NM stacks under different fields, a relatively large bias voltage is applied. Two different MRs were observed when the field is in parallel and perpendicular to the easy axis of $h$MTJ. An important question arising is whether the behavior originates from the same mechanism or different mechanisms, although it was described by a unified formula. Another investigation is to check the bias and temperature dependences. Firstly, we have measured the MRs along these typical directions applying different bias voltages. It appears that the polarities and magnitudes of the bias voltages remarkably change the MR of FM/I/NM stacks. Fig. 5.15 shows the example of another $h$MTJ/MgO/Au stack (S1', which is prepared in the same batch of S1 with double the junction area) at low temperature (10 K). In case of sweeping magnetic field along easy axis, a dramatic change emerged around one of the switching points of $h$MTJ (~ +25 mT): the MR developed slowly from a 'dip' to a 'platform' and finally a 'peak' when increasing the bias voltage from +21 mV to +336 mV. There are two obvious peaks at high bias voltage together with a big negative MR 'background' (four peaks are visible at room temperature because the negative background is relatively weak there). However, only one peak shows a clear transition from a 'dip' to a 'peak' when increasing the bias voltage. Similar behavior was also found for negative biases although it shows smaller changes. In case of sweeping the field perpendicular to the plane (Fig. 5.15b), MR changed from a simple quadratic background (no dip) to the 'peak' as the positive bias is increased. As depicted in the inset of Fig. 5.15d, we have displayed the in plane MRs magnitudes of the 'peak' around -25 mT and of the negative 'background' (up to 0.6 T) separately to check the synchronism between them. The 'peak' and negative 'background' in the in-plane MRs actually scale with each other. Further exhibiting the bias dependent of in plane MRs with the perpendicular Hanle-like MR, a similar trend was found for them: a certain critical voltage ($|V| \geq 60$ mV) for the onset of MR; the maximum magnitude of $\Delta R$ at $\sim + 0.7$ V (whereas $\Delta R/R$ keeps increasing up to +1V); larger $\Delta R$ for the positive bias voltage (Fig. 5.15d). Therefore, it is very likely that the same underlying mechanism is responsible for the high bias MR no matter which direction of the magnetic field. We found that the quadratic background MR (in both parallel and perpendicular cases) is universal and shows no clear bias dependence in the range of small bias (except for different polarity), which is in contrast with the MR behavior at large
bias. It is thereby obvious to distinguish this quadratic background at low bias with the high bias MR from their bias dependences. However, it is not straightforward to make a judgment about the ‘dip’ which evolved into a ‘peak’ in the in-plane MR. As shown in the inset of Fig. 5.15c, the small-bias MR under the fields parallel to the easy axis can be nicely fitted with a Lorentzian peak and a parabolic background. The height of the ‘dips’ also show a clear bias dependence (with a maximum around +70 mV, see Fig. 5.15c), which indicates a possible correction between the ‘dip’ and ‘peak’.

Figure 5.15 Bias dependence of MR for hMTJ/MgO/Au stacks (S1’) at low temperature in the case of magnetic field parallel (a) and perpendicular (b) to the easy axis. The bias dependence of $\Delta R$ of hMTJ/MgO/Au under small and high voltage range are shown in (c) and (d) respectively. In (c) the heights of the peaks attained by the Lorentzian fitting of the ‘dips’ (as demonstrated in the inset) are shown with blue squares and the background (up to 0.18 T) with black squares. Inset of (d) shows the different components of the in-plane $\Delta R$ plotted in (d). The Hanle-like MRs (under perpendicular field), $-\Delta R/R$, are plotted with blue hollow squares.
As temperature increased, the magnitude of MRs under high bias rapidly decreased. An example of the temperature dependence of high bias MRs is shown in Fig. 5.16a. During measurement, different fixed current biases were chosen at different temperatures to maintain the desired voltages over the samples. The meanings of the terms for different MR components in Fig. 5.16a are the same as Fig. 5.15. Different scale factors multiplied for the in-plane MRs are used in order to clearly show the data in one plot. The dip-like MR at +25 mV was obtained from the fitting as we mentioned above. In the case of scanning the field along the easy axis, a field up to +0.6 T was applied for high-bias MR, whereas it was +0.2 T for the small-bias MR. Similar trends of temperature dependence of MR was found for the perpendicular and in-plane MR with a bias of ~+250 mV. It is worth mentioning that the magnitude of the dip-like MR at +25 mV also decreased quickly as temperature increased and finally became too faint to see above 200 K. However, the quadratic background MR at small bias (e.g. +25 mV) shows temperature-independent behavior (data not shown). Actually, the temperature dependence of $\Delta R$ can be fitted by the Arrhenius law that, $\Delta R \propto 1 - \exp(-E_a/k_BT)$, where, $E_a$, is the activation energy for a certain mechanism. $E_a$ is found ~2.6 meV and 3.5-5.2 meV for the MRs at +25 mV and +250 mV respectively. Similar temperature dependence was reported in Ref.25, where the MRs were observed on the junctions with defective AlOx tunnel barriers formed by insufficient oxygen oxidization of Al thin films no matter whether FM electrodes were used. For the stacks of FM (or NM')/AlOx/NM with tunnel barriers oxidized by oxygen plasma, no such MR was found. Adapted from Song Yang’s model22, an impurity-assisted tunneling MR effect was suggested23 for understanding the Hanle-like MRs in their defective-AlOx-based tunnel junctions. These works presented a possible mechanism rather than spin injection and accumulation. We will next analyze results of transport measurements on our $h$MTJ/I/NM stacks and the control samples to reveal the possible roles of resonant tunneling or inelastic tunneling in the MRs we observed.

Temperature dependence of the zero bias conductance ($G_0$) is a first characterization of the tunneling process involved in our sample. Fig. 5.16b shows that $G_0$ of S1' only increased about ~19 % from 2 K to 300 K, which implies the dominant mechanism in this device is
Figure 5.16 Temperature dependence of MRs (a & b) and differential conductance (c & d) under different biases. (a & b) and (c & d) are corresponding to hMTJ/MgO/Au stacks (S1) of and full MTJ stacks (S2) respectively, where the dashed lines are guiding lines and the solid lines are fitting curves. (e) Shows the fitting of $G_0$ vs T by the magnon model (fitting_1) and multi-step tunneling model (fitting_2), whereas (f) displays bias dependence of TMR at room temperature (red) and low temperature (black).
direct tunneling or resonant tunneling. As introduced in Chapter 2.1.3.1, \( G(0, T) = G(0,0)CT/\sin(CT) \) accounts for the temperature dependence of zero bias conductance of elastic tunneling whereas \( G'(0, T) = G_0 + G_2T^{1.333} \) describes the phonon-assisted inelastic tunneling through two localized states (LS)\(^53\). We found that none of them can perfectly reproduce the \( G(0, T) \) measured. Therefore, we made a combination of these two contributions:

\[
G(0, T) = G(0,0)[CT/\sin(CT)](1+ G_2T^{1.333})
\]

where the first is due to the thermal smear and the term proportional to \( T^{1.333} \) originates from the inelastic tunneling. We have a better fitting then and \( C = 2.62 \times 10^{-3} \) was obtained from it (shown in Fig. 5.16b). Since \( C = 1.387 \times 10^4 d/\sqrt{\Theta} \) and 3.5 eV is usually chosen for \( \Theta \), the corresponding thickness of MgO, \( d \), is \( \sim 3.5 \text{nm} \). Besides, we find that about half of the increased conductance from 2 K to 300 K can be ascribed to the inelastic tunneling via two LSs in tunnel barrier. High bias voltages bring more LSs into the energy window of tunneling electrons thereby much larger contributions stemming from the inelastic tunneling is expected. Unfortunately, there is no such a formula that fits of the conductance at a finite bias voltage (i.e. eV is larger than \( k_B T \)), in which we are interested because a certain bias critical voltage exists for observing the MR behavior as we mentioned before. However, we can still spot the increase of the non-linear change in the conductance at larger bias as the temperature rise: as Fig. 5.16b shows, the conductance measured at +250 mV and +350 mV overtakes lower-bias conductance at 150-300 K. Compared with the strongly nonlinear behavior of inelastic tunneling conductance, the conductance from direct and resonant tunneling are temperature-independent and bias-independent, supposing a uniform energy level distribution in the tunnel barrier. The fact that all the conductance curves show very little change below 50 K indicates that most of the conductance is contributed by elastic tunneling processes below that temperature. However, it is so far unclear whether the small MRs observed in our conditions at low temperature and high bias voltage, are related to an
inelastic process. On the contrary, dominant inelastic tunneling conductance was found in the FM/AlOx/NM system.

Similar analysis can be made on the hMTJ/MgO/CoFe, which directly reflects the spin-related tunneling behavior of the tunnel barriers. We have first tested the magnon-excitation model by fitting TMR at zero bias. We first fit \( G_p(T,0) \) and \( G_{ap}(T,0) \) together with the formula (2.24):

\[
G_r(T,0) = G_r(0,0) \frac{CT}{\sin CT} \left[ 1 + \xi^2 \frac{2SQ}{E_m} k_B T \ln \left( \frac{k_B T}{E_c} \right) \right], \quad \xi = \frac{\xi_{g=1/2}}{1, g=1/2,3/2,5/2,7/2}
\]

(5.5)

with the parameters: \( \xi \equiv G_{ap}(0,0)/G_p(0,0) \approx 0.77, E_m = 121 \text{ meV}, S = \frac{3}{2}, \) after optimizing the fittings we have: \( C = 0.00198 \text{ K}^{-1}; Q = 0.0618 \) and \( E_c^p = 0.1055 \text{ meV}, E_c^{AP} = 0.115 \text{ meV}. \) It is notable that all these values fall in reasonable ranges, which manifests the reliability of the fitting process. The fitting results shown in Fig. 5.16e display a small deviation in \( G_{ap}(T,0) \) fitting between 10 to 75 K. However, if we display \( \Delta G(T,0) \) together with the fitting results, a distinct deviation (the blue curve shown in Fig. 5.16c) emerges and the maximum of \( \Delta G \) around 50 K is also missing. As a result, the fitted TMR(0) is larger than the measured value when temperature is below 50 K yet a little bit smaller when temperature is higher than 50 K. It is doubtful that the magnon excitation model can describe the transport features of our MTJs samples.

We then try to fit our data with the spin-polarized inelastic hopping model. Firstly, \( G_{ap}(0, T) \) was fitted with elastic and inelastic tunneling via two LSs: \( G_{ap}(0, T) = G_0 + G_2 T^{4.33} \) (for our sample, \( N = 2 \) is good enough for the maximum number of localized states in a tunnel chain). We can see that one-third of the conductance at 300 K is contributed by the multi-step tunneling. \( \Delta G(T,0) \) was next fitted the formulas (see formulas (2.22)) below:

\[
\Delta G(0,T) = G_0 \frac{CT}{\sin CT} TMR_{0(1)} + G_2 T^{4/3} TMR_2
\]

\[
TMR_\infty = \frac{(1 + P)^{2(N+1)}}{2(1 - P^2)^{2(N+1)}} - 1, \quad P = p_0 (1 - \alpha T^{3/2})
\]

(5.6)
where $P$ denotes the average spin polarization of the MTJ. The first term of the $\Delta G$ stems from direct tunneling ($N = 0$) and resonant tunneling ($N = 1$). We actually didn’t separate them and fit the two contributions together as an average result. The second term accounts for the inelastic hopping via two LSs. In our MTJs, the top FM electrode, Co$_{50}$Fe$_{50}$ is also different from the bottom FM electrode, Co$_{20}$Fe$_{60}$B$_{20}$, however, we chose an average spin polarization for them. TMR (0, 0) = 29.4 % was obtained from the extrapolation of TMR, thus we have $P_0 \equiv 0.36$. Using $C$ and $\alpha$ as the fitting parameters, we attained the result as shown in Fig. 5.16c (the red curves). The TMR$_A$ was calculated from $TMR(0,T) = \sum_N W_N(T)TMR_n(T)$, $W_N = G_N^{AP}/G_N^{AP}$ and was plotted as well in Fig. 5.16c.

We can see that it is better than the first fitting based on a magnon model and the trend of $\Delta G$ is now appearing in the new fitting. In the fitting, $C = 0.00169$, $\alpha = 1.878 \times 10^{-4}$ were obtained. The corresponding MgO thickness is thus $\sim 2.3$ nm, which is very believable. Meanwhile, it seems that the value of $\alpha$ in our fitting is larger than the reported value (0.14 - 6.8$\times 10^{-5}$). We think it is consistent with the relatively poor performance of our MTJs in TMR ($\leq 30\%$ at 10 K) as $\alpha$ characterizes the decrease in spin polarization with temperature. Considering the fabrication process, we believe that the quality of MgO and the top interfaces between MgO and CoFe are not as good as the samples prepared in situ and without air exposure, and a strong reduction of polarization with temperature, i.e. larger $\alpha$, is expected. Therefore, spin-conserving inelastic hopping can explain the zero bias behavior very well.

We should bear in mind that the Hanle-like MR in the hMTJ/I/NM stacks takes place at high voltage bias. It would be helpful if we could obtain information about the tunnel barrier in that region. Although, it is not easy to quantitatively fit the results, some important points can be obtained qualitatively. As Fig. 5.16d shown, there are mainly three unusual features in the temperature dependence of TMR. First, the TMRs at bias voltages below 0.25 V ($|V| < 0.25$ V) firstly increase with temperature until they reach a maximum around 50 K and
then decrease up to 300 K. The slight increase of TMR is perhaps partly related to the increase of $\Delta G$ from 10 K to 100 K, which is more prominent for higher bias (data not shown). Analogous to $\Delta G$ at zero bias, the increase of $\Delta G$ at a finite voltage may be explained as the increased contribution the spin polarized inelastic hopping, if the extrapolation of zero bias conductance is acceptable. However, the increase of TMR is not explainable from the multi-step tunneling picture as TMR decrease with the number of tunneling steps. Alternately, it may indicate that the TMR at 10 K is suppressed compared with 50 K for some reason. Secondly, the TMR curves show an asymmetrical bias dependence and it decreases faster at positive bias than at negative bias, especially when the temperature is lower (see Fig. 5.16f). It is probably because many more LSs are well-aligned under positive voltage bias and contribute to the inelastic tunneling. Thirdly, the corresponding voltages of the highest TMRs are shifted from $\sim$ -25 mV to $\sim$ -100 mV when the temperature rises from 10 K to 300 K respectively. It implies a large asymmetry of the tunnel barrier. From the BDR fitting at room temperature$^{56}$, we have some information about the tunnel barrier in S2: $d \sim 9.6 \, \text{Å}$, $\varphi \sim -1.01 \, \text{eV}$, $\Delta \varphi \sim 0.42 \, \text{eV}$ (averaged from P and AP configurations). The big asymmetry may be due to contamination of the top interface during fabrication, e.g. organic and SiO molecules. Interface contamination is definitely detrimental for observing higher TMR, yet its role on the Hanle-like MR signal is unclear. Nevertheless, we have found the existence of phonon-assisted multi-step tunneling through LSs or impurities in the full MTJs stacks which can explain the temperature and bias dependence of $\Delta G$ and TMR. However, we stress that the majority of the conductance in our samples is provided by the elastic tunneling especially at low temperature, which is in contrast to the work in Ref. 23, where they claimed that the phonon-assisted multi-step tunneling through impurities dominate the conductance. It is, therefore, vital to find the roles played by the elastic (resonant) and inelastic tunneling in the Hanle-like MR. Tunneling spectroscopy measurements serve as an effective tool to distinguish them.
5.3.2 Tunneling spectroscopy of hMTJ/MgO/Au

Tunneling spectroscopy measurement is a useful method to look into the microscopic tunneling process concerning the phonons and localized states or defects in the tunnel barrier. In order to find the roles of elastic and inelastic tunneling processes in the Hanle-like MR, we have performed tunneling spectroscopy measurements in a series of different magnetic fields: parallel and perpendicular to the thin-film plane in the range of +173 mT. The representative $dI/dV$ and $d^2I/dV^2$ curves measured at 20 K in our stacks of hMTJ/MgO/NM are shown in the inset of Fig. 5.17a. The $dI/dV$ curves look plain and structure-less. Perhaps the most obvious feature for them is that the curves are quite different under positive and negative bias. The differential conductance grows regularly under negative bias but changes slowly from zero to +200 mV (some samples even show decreased differential conductance in this range and have a minimum at ~+160 mV). This asymmetry is probably related the large barrier asymmetry $\Delta \phi$ with two different electrodes and one interface may have some contamination\textsuperscript{46}. We think it is more likely to be related to the band structure of the CoFeB electrode as reported in the case of CoFeB/MgO/W junctions\textsuperscript{57,58}. In order to compare the first derivative and second derivative of $I-V$ with the MR, Fig. 5.17 b, c and d show 2D-contour plots of all the data after subtracting the data measured at -110 mT for clarity (however, the spectroscopy in range of +25 mV were not well-measured). With field scanning along easy axis, as shown in Fig. 5.17 b, the $dV/dI$ precisely reproduced the trend of the in-plane MR as we have seen (Fig. 5.15a): a small peak in the field range of -100 ~ +50 mT with a local maximum resistance around ~+25 mT; dynamic resistance increases as the in-plane field rises outside the above range; larger dynamic $\Delta R$ for positive biases; threshold for observing clear MRs at +0.1V. Fig. 5.17d shows the results measured under perpendicular fields. Although the signal is a little noisy, we can still identify the maximum dynamic resistance around zero field and minimum at largest field, which is found in perpendicular MR as well (see Fig. 5.11). Fig. 5.17a shows the $d^2I/dV^2$ curves at in-plane magnetic fields of -100 mT and +173 mT that correspond to the minimum and maximum resistance in the scanned field range. The positive and negative bias dependence of the $d^2I/dV^2$ curves are divided by $dI/dV$ and plotted together for better
comparison. These curves show the peaks at the same positions which confirms the validity of IETS measurement (almost the same peak positions for positive and negative bias as well). They are nearly identical with each other below ~100 mV, however, the one measured at -100 mT starts to exceed the other measured at +173 mT when the biases are larger than ~100 mV. In the \( \frac{d^2I}{dV^2} \) curves we can firstly recognize the ZBA near zero bias. The shoulder close to it (~25 mV) is attributed to the magnon in CoFeB which is more obvious.

Figure 5.17 Tunneling spectroscopy of hMTJ/MgO/Au at 20 K (S1). (a) \( \frac{d^2I}{dV^2} \) curves (divided by \( \frac{dI}{dV} \)) under in-plane magnetic fields of -100 mT (black and green) and +173 mT (red and blue), where inset shows the full plot of typical \( \frac{dI}{dV} \) and \( \frac{d^2I}{dV^2} \). Contour plot of \( \frac{dI}{dV} \) (b) and \( \frac{d^2I}{dV^2} \) (c) under various bias voltages and in-plane magnetic fields. (d) Contour plot of \( \frac{dV}{dI} \) under perpendicular fields.
when the electrons tunnel into CoFeB (corresponding to negative bias). The peaks around 60 mV and 80 mV are identified as the Mg-O phonons. Obviously, there are a series of peak positions above 100 mV up to the maximum voltage applied, 120, 180, 220 and 265 mV in the negative bias (-IETS(-V) curves) although they are not so prominent in positive bias (IETS(V) curves). The phonons of gold and possibly SiO can be excluded as responsible for them as they are < 5 mV and around 145-155 mV respectively. Because the top surfaces of MgO barriers were exposed to atmosphere, these peaks are presumably related to the degradation of the tunnel barrier. An inverted magnetic field dependence of $d^2I/dV^2$ with that of resistance can be roughly identified: minima of $d^2I/dV^2$ around +25 mT and +173 mT and the larger differences of $d^2I/dV^2$ under different magnetic fields for the negative biases compared with positive biases. The field dependence of $d^2I/dV^2$ can be understood from the relation that, $d^2I/dV^2 = -(dV/dF)/(dV/dF)^3$, where $d^2V/dF^2$ and $dV/dF$ but not $d^2I/dV^2$ are measured directly in our experiments. We can roughly estimate the change of $d^2I/dV^2$ under different magnetic fields:

$$\Delta(d^2I/dV^2)/(d^2I/dV^2) \approx \Delta(dV/dF)/(d^2V/dF^2) - 3\Delta(dV/dF)/(dV/dI)$$

and almost equal contributions from the terms of $\Delta(d^2V/dF^2)$ and $\Delta(dV/dF)$ are found. A slightly different result was reported in 3T devices made of CoFe/SiO2/Si, where $\Delta R$ in their device was believed to be almost all generated from magnetic-field-induced changes of the IETS, with contributions of inelastic tunneling. For the case of applying a perpendicular field, we couldn’t find a clear trend in the $d^2V/dF^2$ contour. Because of the synchronism of the in-plane MR and the Hanle-like MR we showed above, we think it is because the small changes of the signals are masked by the relatively large noise level. It is possible for the same reason we could find the ‘dip’ structure in case of small bias when applying an in-plane magnetic field. Nevertheless, it is now clear that the inelastic processes above a bias voltage of ~+100 mV contribute to the Hanle-like MR although we haven’t identified the source of the IETS modes.

5.3.3 Non-local spin-valve signals on the hMTJ/MgO/NM stacks
Although the expected spin signals due to spin accumulation are much smaller than the Hanle-like MR in the FM/I/NM devices, the real magnitude of spin accumulation in proximity to the FM/I injector hasn’t been measured in a reliable way. In principle, the spin accumulation in the NM 10-30 nm underneath the FM/I interface should be detected by the second FM' nearby. We have prepared four-terminal NLSV devices in the context of the vertical 3T FM/I/NM devices. As depicted in Fig. 5.18 a & b, the procedure of making the four-terminal NLSV devices is similar to that of three-terminal devices excepting the additional deposition of SiO and CoFe (~ 10 nm) on top of hMTJ/MgO/NM. The deposited second SiO and CoFe patterns were rotated 90° with respect to NM pattern by using a shadow mask. Effective NM/FM' junction areas are about 100×100 μm² which is much smaller than the FM/I/NM junction areas (e.g. 400×400 μm²). There are two possible measurement geometries: current flows between hMTJ/MgO/NM with voltage detected between NM/CoFe and current flows between CoFe/NM with voltage detected between NM/MgO/Cu (see Fig. 5.18a). In the stacks of hMTJ/MgO/Au/CoFe, no NLSV signals larger than 50 μΩ (the noise level) were detected for these samples that exhibited Hanle-like MR (Fig. 5.19a). However, a portion of hMTJ/MgO/Au (or Cu)/CoFe stacks showed clear NLSV signals as presented in the range of mΩ in Fig. 5.19. Usually different MRs were obtained for these biases with different polarities. In the literature, the NLSV measurements were generally performed in a lateral structure with hundred-nanometer gaps between injector and detector where the spins transport in the diffusion regime. Our measurement is perhaps the first vertical NLSV measurement approximate to the FM/I

Figure 5.18 Cross-section view (a) schematic drawing (b) and the real top view (c) of a vertical NLSV device made of hMTJ/MgO/Au/CoFe stacks.
injector with a distance of tens of nm between the spin injector and detector. According to the lateral NLSV measurements from the literature, Al, Au and Cu show different spin resistances in the range of Ω, mΩ and tens of mΩ respectively mainly because of the longer spin life time in lighter metals. In our best results of vertical NLSV measurements, the spin resistances for Cu and Al are around mΩ and nearly 10 mΩ which are roughly consistent with the trend for them in literatures. While, the reasons for the much smaller nonlocal spin resistance can be understood from the formula we showed before (see Eq. 2.10): \[ R_s = \gamma^2 l_0 \exp(-L/l_0)/(\sigma_{NM} A_{NM}). \] Although, \( L (\sim 20 \text{ nm}) \) here is much less than \( l_0 \) it only gives a finite enhancement for spin resistance. On the other hand, the spin current cross section areas (\( \geq 400 \times 0.02 \ \mu\text{m}^2 \)) in our vertical geometry are 2-3 orders of magnitudes larger than

![Figure 5.19 NLSV measurements on hMTJ/MgO/Au/CoFe (a) and hMTJ/MgO/Al/CoFe (b) stacks at low temperature (~ 20 K), where different measuring configurations were used. The bias (c) and temperature (d) dependence of NLSV in hMTJ/MgO/Al/CoFe, where the Hanle effect was tested at room temperature under a perpendicular magnetic field (blue and dark green).](image-url)
that of lateral geometry. Besides, spin detection by transparent contact between NM and CoFe is normally less efficient than the spin-selective tunneling contact. Therefore the spin resistance measured here should be at least two orders of magnitude smaller than that of lateral NLSV. We also tried to measure the Hanle effect in the vertical NLSV measurements under a perpendicular magnetic field. However, we didn’t succeed in observing it for some reasons (Fig. 5.19d). It is presumably ascribed to the short spin transport time from injector to detector which is much less than the spin lifetime. Despite all this, we should notice that the maximal NLSV resistance in our system is ~10 mΩ which stems directly from the spin accumulation in the NM channel in proximity to the FM/I injector. Because of the transparent contact between NM and FM, it is possible to obtain a NLSV resistance in the range of tens to hundreds of mΩ with an I/FM spin detector. Even so, it is still much smaller than the MR we have seen before in the 3T geometry (from Ω to hundreds of Ω). Therefore, the NLSV measurement on the vertical stack serves as direct evidence to eliminate the possibilities that spin accumulation in NM is responsible for the large Hanle-like MR and it further questions the possibility of locally detecting the spin procession effect. In other words, such a large MR must have another origin.

5.3.4 Discussion

From all these experiments, we’d now like to draw some overall conclusions. First of all, the spin accumulation in NM metals of FM/I/NM configurations can be ruled out as the reason for the Hanle-like MR. Note that a certain magnitude of MR (ΔR/R ~ 1% or higher) was also reported in some special FM/I/NM stacks, for example the crystalline layer structures of GaAsMn/AlOx/Au\(^{62}\) and Co/Al\(_2\)O\(_3\)/Al & Au\(^{63, 64}\). This kind of behavior is explained as tunneling anisotropic magneto-resistance (TAMR) resulted from anisotropy of the density of states at the Fermi surface due to spin-orbital interaction in FM electrodes. As for the Hanle-like MR in our \(h\)MTJ/MgO/NM stacks, a simple relationship between resistance change and magnetic field that \(ΔR \propto c_1 B\cos^2 θ - c_2 B\sin^2 θ\) was obtained, which predicts MR of the single domain FM electrode, for example, ΔR keeps increasing with B even θ ≡ 0. Besides, the angular dependence of MR only shows nearly two-fold symmetry (Fig. 5.14) which is also different from the good crystalline samples showing
TAMR. More importantly, the Lorentzian-line-shape MR is unexplainable by the TAMR mechanism. This eliminates the possibility of TAMR. We note that the Lorentzian-shape MR and the angle-dependence of $\Delta R \propto \cos^2 \theta$ were found in a purely organic system\textsuperscript{65}, where the magnetic field modulated spin-spin interaction was suggested as the governing there. We have shown in the first part of this chapter that the spin-blockade and coulomb blockade mechanisms were also proposed as an explanation\textsuperscript{26}. It is very similar to the case of NM/I/NM system reported in Ref. 22, which prompt us to believe a similar mechanism is responsible for FM/I/NM.

Figure 5.20 (a) High field MR of ST with bias voltages $\pm 0.5$V at 2 K; (b), high field MR (parallel and perpendicular to the easy axis) of SI with bias voltage -0.5V at 10 K. The red dashed lines mark the clear ‘peak’ structures in the MR curves.

We tend to accept the impurity-assisted tunneling magneto-resistance mechanism. The magnetic field dependence of $dI/dV$ and $d^2I/dV^2$ reproducing the trend of the typical in-plane MRs behavior demonstrated the important roles played by the elastic and inelastic tunneling process. Because of the large junction areas, the special resonant states and inelastic channels may not be clearly identifiable\textsuperscript{56}. Some other evidences can be found in the control samples of full MTJs which have the same hMTJ/MgO structure. As we have shown, it is necessary to introduce spin-conserved inelastic hopping via two localized states inside the tunnel barrier to explain the increase of $\Delta G$ even for the case of zero-bias conductance. A more important role played by inelastic process for relatively higher bias voltage is expected. For the increase of TMR from 50 K to 100 K in the MTJ stacks, we presume that Coulomb
blockade is responsible for the suppression of TMR at low temperature (< 50 K) whereas the blockade is lifted at high temperature, TMR increases a little bit and reaches the maximum at a slightly higher temperature (~50 K). For the FM/I/NM stacks the evidence for Coulomb blockade can found in the measurement of high field MR (Fig. 5.20). Even under a large field up to 5 T the in-plane MR is still not saturated. It follows the prediction of high-field MR in NM/I/NM junction because of the on-site Coulomb energy on the localized stats as we introduced in the first part of this chapter. Within this mechanism, the universal-like small parabolic MR at small biases in relatively low magnetic field can be interpreted as the first order approximation of the MR at high field. It seems that two mechanisms based on large on-site coulomb energy are needed for the full picture. In the case of relatively low magnetic field, the spin blockade is lifted by the precession of the spins under an effective field that has large enough perpendicular components, for the case of large magnetic field, the Coulomb correlation (larger conductance) is suppressed by the large Zeeman energy. It is probably because of impurities or LSs inside the barriers involved in the tunneling that the small ‘dip’ in plane MR was found. It is also responsible for the sign reversal of dynamic MR (dV/dI vs B) at +0.5V and 10 K in hMTJ/MgO/CoFe (not shown but a similar trend can be seen in Fig. 5.16f).

One remaining question is that since, as temperature increases, more and more conductance channels are contributed by inelastic processes, which is the main sources of the Hanle-like MR as we assumed, then why does such MR at higher bias decrease monotonically? Without a quantitative calculation we can only consider that the on-site Coulomb interaction is the most important factor which decreases as temperature rises because of the thermal activation of nearby localized states. Another explanation may ascribe such MR mainly to the field-modulated elastic resonant tunneling, whose conductance remains unchanged or falls as temperature rises. Together with the thermal activation of on-site Coulomb energy, resonant tunneling explains the monotonic decrease of MR. According to this picture, the voltage for maximum MR found in our sample, ~ 0.7 V, corresponds to the highest density of resonant states at that site ~0.35 eV below the Fermi energy of CoFeB electrode.
Considering the sample preparation process, where the MgO was exposed to the air and annealed at 350 °C under high vacuum (~ 10^{-7} mbar), we think that oxygen vacancies ($V_o$) are most likely generated in our samples and responsible for resonant tunneling or inelastic hopping. It is reported that a luminescence peak around 2.3-2.4 eV is ascribed to the $F^+$ center in MgO and we actually found a small photoluminescence (PL) peak around 2.43 eV in our devices (Fig. 5.21). It supports the existence of $V_o$ in our MgO tunnel barriers.

![Fig. 5.21 Room temperature photoluminescence measured on the range of bared MgO (blue) and SiO (black) regions at hMTJ/MgO/Au stacks.](image)

What's more, for the stacks of hMTJ/MgO, with 3nm-thicknesses MgO changed to ~2 nm after Ar ion milling. After top electrode deposition, $R \cdot A$ of the final devices were often around $10^7$-$10^9 \, \Omega \cdot \mu \text{m}^2$, which is ten to hundred times larger than the full-stack samples made in situ in the magnetron sputtering system. For these full MTJs, the samples completed in two systems showed much lower TMRs (20-100 %) than that of the samples in situ sputtered (180-250 %). It was reported that $V_o$ in the MgO barriers of epitaxial Fe/MgO/Fe MTJs leads to higher junctions resistance, lower TMR and increased bias and temperature dependence because of symmetry-breaking scattering and the resultant incoherent tunneling. This is consistent with our results. Therefore, we tend to believe that $V_o$ are the main defects of our MgO tunnel barriers. Note that Hanle-like MR was reported in MgO,
AlO\textsubscript{x} and SiO\textsubscript{2}-based three-terminal tunneling devices; we think \( V_0 \) and its complexes must play a universal role in all these systems.

### 5.4 Further work to support our conclusions

We have shown the connection between resonant tunneling and inelastic hopping in our MgO tunnel barrier with the Hanle-like MRs and we tentatively related the impurities and localized states to \( V_0 \) and its complexes in MgO. Then the important question is how to find definite evidence for our conclusions. According to the fabrication process, we planned to do two more pieces of work:

1. A series of \( h \text{MTJ}/\text{MgO/NM} \) control samples with different MgO. The first one is to prepare the full stacks of \( h \text{MTJ}/\text{MgO/NM} \) in our magnetron sputtering system which should have the best-quality MgO. We expect that the Hanle-like MR should be much smaller in this case. For those samples with MgO exposed to the air, the annealing time in vacuum furnace at 350 °C should change the density of defects, \( V_0 \), inside MgO. We expect to see the control of the magnitude of MR with the density of localized states. In-depth x-ray photoemission spectroscopy may provide a more accurate detection of the impurities.

2. Our sample size is too large (400 × 400 \( \mu \text{m}^2 \)) to identify the possible localized resonant states inside the barrier, thus, we have also planned to make small junctions of samples which displayed the Hanle-like MRs. Based on the technique we introduced in Chapter 3, it is possible to prepare tunneling junction down to sub-\( \mu \text{m} \) size. With the small size junctions, upon performing the tunneling spectroscopy measurement, we expect to see discrete LSs in the \( dI/dV \) curves as in Ref. 66.
Bibliography


Chapter 6 Spin lifetime in organic-based spin valves

6.1 Introduction

The spin lifetimes in organic systems are believed to be quite long\(^1\) because of the weak spin-orbital interactions. Spin-relaxation times of localized spins in organic materials in excess of 10 \(\mu\)s were obtained by resonance techniques\(^1\). However, to the best of our knowledge, the spin lifetime of spin-polarized mobile electrons hasn't been directly measured so far. Since the first introduction of organic materials on spintronics\(^2\), the topic of organic spintronics has progressed impressively over the past decades. Although most of the works were focusing on the organic-based spin-valve (or MTJ) structures and MR were reported for a great number of systems, there are still some basic questions confusing the scientific community. The most important of all the questions is whether the observed MR is because of spin injection into the organic semiconductor (OS) or it is due to spin-conserving tunneling through the organic barriers (by single step or multi-step tunneling). In some special cases of organic systems, the phenomena of OMAR also contributed to the MR results.

In order to directly inject spins into the NM materials and detect the spin accumulation and relaxation, there are plenty of methods successfully used in inorganic systems including magneto-optical effects, lateral NLSV measurement and spin pumping. Unfortunately, most of them aren't applicable for organic systems because of the weak spin-orbit coupling and the incompatibility of organic materials with micro-fabrication processes. MR measurement in a spin-valve configuration is perhaps the most accessible method to investigate the spin properties in NM materials, and it has been widely applied for organics up to now. In this context, the spin diffusion length can be obtained by changing the channel length of organic layer, \(d\), and measuring the corresponding MR from the modified Juliere formula\(^3\): \(\text{MR} = 2P_1P_2e^{-d/\ell_{st}}/(1 - P_1P_2e^{-d/\ell_{st}})\). The spin lifetime is then calculated from the spin
diffusion length by the relationship: \( \tau_{sf} = l_{sf}^2 / D \), where \( D \) is the diffusion constant. In spite of this, the spin diffusion length, \( l_{sf} \), in organic hasn't been unambiguously measured for the vertical spin-valve geometry because of some technical obstacles, for example the penetration of top FM electrode into the organic, which often makes the channel length impossible to determine. It is also difficult to distinguish between the spin injection efficiency across the interface and spin transport in the organic material itself from this experiment.

Figure 6.1 Left panel: illustration of the principle in spin-resolved two-photon photoemission (SR-2PPE) experiment for spin injection and transport in a Co/CuPc heterojunction. Right panel: representation of the quantities \( N_i = N_{up} + N_{down} \) that are used to extract the inelastic mean free path \( \lambda_{inel} \) and the quasi-elastic spin-flip length \( \lambda_{qsf} \) of electrons in CuPc orbitals lying \((1.8 \pm 0.1)\) eV above the LUMO onset, where \( N_{up} \) and \( N_{down} \) denote the number of photoemitted electron with spin parallel and antiparallel to the magnetization direction of Co substrate respectively.

Cinchetti et al first made a direct experimental observation of high spin injection efficiency across a prototypical interface, Co/CuPc, and also directly measured the inelastic mean free path and the spin-flip length within CuPc. As illustrated in Fig. 6.1, the proper photon energy of the pulsed laser source was chosen such that a photoelectron can be emitted only if it absorbs two photons. The first photon creates the spin-polarized hot electrons in Co,
some of them diffuse across the Co/CuPc interface and inject into the unoccupied states of CuPc lying above the lowest unoccupied molecular orbital (LUMO) onset, where they absorb a second photon and are photoemitted. Because the probing depth of photoemission determined by the inelastic mean free path of optically excited electron in CuPc is ~ 1 nm, only the electrons that absorb the second photon within 1 nm of the top surface of CuPc can be detected. Among them, are the spin-polarized electrons excited from Co. The energy and spin of photoemitted electrons for varied CuPc coverage were measured and compared with those obtained from bare Co substrates. Information about spin injection efficiency at the Co/CuPc interface and the microscopic spin-flip mechanisms were acquired. For the spin-polarized hot electrons injected from Co into CuPc unoccupied molecular orbitals lying 1.8 ± 0.1 eV above the LUMO onset, a spin injection efficiency of around 85% (normalized by the spin polarization of Co) at room temperature was found. The quasi-elastic spin-flip length of these electrons given by \( \lambda_{el,flip} = 2 \lambda_e \lambda_s / (\lambda_e - \lambda_s) \) = 12.6 ± 3.4 nm was obtained. For the electrons with lower injection energies (0.5-1.3 eV above LUMO onset), the estimated quasi-elastic spin-flip length is even longer: \( \lambda_{el,flip} \approx 35 ± 16 \) nm. This work actually demonstrated the high efficiency of spin injection into OSC under ideal condition of well-defined, high quality FM/OSC interfaces. It is also notable that, the injected electron energy is 1-3 eV higher than the Fermi energy, which is out of thermal equilibrium and the conductivity mismatch problem was avoided there (see Chapter 2). Real organic devices differ in their interface qualities and working conditions. Work to demonstrate spin injection in a real and fully-functional organic device is required as well.

Almost at the same time, Drew et al measured the spin polarization of current-injected electrons within a realistic organic spin valve applied with the depth-resolved technique of low energy muon spin rotation (LE-\( \mu \)SR)
. Their vertical device was composed of NiFe(17)/LiF(1.9)/Alq3(200)/TPD(50)/FeCo(17) (unit, nanometer and TPD is N, N'-Diphenyl-N-N'-bis(3-methyl-phenyl)-1,1'-biphenyl-1-4, 40-diamine). Spin polarized electrons were injected from the top NiFe into the organic layer and thus generate a local magnetization that adds to the dipolar stray field from the FM layers. On the other hand, the \( \mu \)SR line shape of implanted muons is sensitive to the local magnetic field where they stop inside the organic. Measuring the \( \mu \)SR lineshape at different implantation energy, a
depth-resolved profile of the local magnetization and hence the diffusion length was obtained. Comparing the temperature dependence of MRs from the macroscopic measurement and the spin diffusion lengths obtained from the above microscopic techniques, they clearly showed a qualitative agreement between them. Therefore, the spin diffusion length in Alq3 was found to be \(~31 \pm 3\) nm at 10 K and fell to \(~10\) nm at room temperature, which is in the same range as the result measured by SR-2PPE.

Although the above work promisingly presented the feasibility and high efficiency of spin injection into organic material, these techniques are rather complicated and not easily accessible. In order to further clarify the disputes over spin injection and extend the work for the possible applications in spintronics, a widely applicable technique for a vast amount of tests is required for different OSCs. Analogous to the counterpart inorganic semiconductors, the Hanle effect that detects the precession of spin polarized electrons in the organic channel is not only considered as convincing proof of spin injection but also provides a method to definitely measure the spin lifetime in the organic material. Hanle measurement itself is relatively easier and can be in principle performed on the vertical spin valve devices by applying an external magnetic field perpendicular to the magnetization direction of spin injector.

A few groups have performed the Hanle measurement on their devices which clearly show spin-valves-like MR signals. However, there is no successful experiment so far in vertical spin-valves and the spin-life time inside the organic-based devices (either single molecule or organic thin film) has thus never been successfully measured directly. Dediu et al investigated the Hanle effect on an organic device (Fig. 6.2) that consists in a LSMO(20)/Alq3(200)/AIOx(2.5)/Co(20) stack (junction area: \(~1\) mm\(^2\)) at 100 K, which has been extensively studied and its properties are well known\(^6\). Keeping the magnetization of two FM electrodes almost in plane, they carefully swept the external magnetic field along various angles to the plane (\(\theta = 0^\circ, 45^\circ, 60^\circ\) and \(90^\circ\), the case of \(0^\circ\) and \(90^\circ\) are shown in Fig. 6.2). Excepting resistance switching due to the electrodes magnetization switching, no dependence of MR on \(\theta\) and field magnitude clearly showed the absence of Hanle effect in
their devices. They tentatively ascribed it to the exceptionally high mobility (~30 cm²V⁻¹s⁻¹) conductive path in the Alq₃, although there is no good evidence for this viewpoint.

Figure 6.2 Left: schematic drawing of the organic spin-valve devices for the (oblique) Hanle measurement. Right: resistance in the parallel (P) and antiparallel (AP) state of the device, with the magnetic field perpendicular to the plane (θ = 90°). The top left inset shows the typical MR (~ -18%) when the field is applied in the plane of the device, while the inset to the top right shows the complete MR for the perpendicular case. The linear behavior at high field is due to the out-of-plane tilt of the FM electrode's magnetization.⁶ All measurements were taken at 100 K.

Besides the small molecules Alq₃ with low mobility (~10⁻⁵ cm²V⁻¹s⁻¹), the high-mobility n-type organic semiconductor PTCDI-C₆F₇ was also tested by Schmidt et al for the Hanle effect and it was again missing, although the MR did exist⁷. On the contrary, they believed that the absence of Hanle-type effects indicate that the MR is not based on the injection of spin-polarized electrons into the organic semiconductor but rather on tunneling through pinholes superimposed on tunneling anisotropic magnetoresistance. They suggested that even for the organic samples with clear spin-valve signatures, similar to the Hanle precession in inorganic spin valves, control experiments should be established which can be used to confirm or disprove the electrical detection of injected spin-polarized carriers.

On the other hand, Kawasugi et al. have fabricated lateral spin-valves consisting of doped conducting polymer poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) and Ni₈₀Fe₂₀ narrow line (width: 530 nm) electrodes⁸. A NLSV signal was
expected, which serves as important evidence for spin injection and the parasitic effects from the organic itself or from the FM electrode can be excluded. However, they couldn’t observe any spin signals, and the main reason could be that the channel length (~530 nm) is much larger than the spin diffusion length in PEDOT:PSS.

To understanding the widely observed MR in organic-based spin-valves along with unsuccessful detection of the Hanle effect, Yu et al suggested a fascinating explanation. It is well-known that in organics, carriers are localized polarons and charge transport is via polaron hopping. Spin transport, however, can utilize the exchange coupling between localized polarons, which can be much faster than polaron hopping and rapidly increases with the carrier density. Consequently, a much stronger magnetic field than estimated from the carrier mobility is required to modify spin polarization and observe the Hanle effect. He also claimed the exchange-induced spin transport can greatly mitigate the conductivity mismatch between FM and OSC, enabling spin injection into organics. The latest experiment has recently shown indirect evidence for this exchange-mediated mechanism in Alq3.

Because of the limited success in electrical spin injection and detection experiments in organic materials, some groups turned to the ferromagnetic resonance spin pumping technique for dynamical injection of pure spin currents into organics and detect the spin signal by inversed spin Hall effect (ISHE). This technique has some big advantages over the spin-valve measurement: free from the conductivity mismatch problem for spin injection and no need for growing high-quality tunnel barriers; amplitudes of spin currents are several orders of magnitude larger than the spin currents obtained by electrical spin injection through a tunnel barrier. Ando et al first applied this technique to pump spin current from a magnetic insulator, Y3Fe5O12 into the solution-processed conducting polymer, PEDOT:PSS (80 nm) (left panel of Fig. 6.3). A large spin accumulation was thus produced in the PEDOT: PSS layer because of the exceptional long spin life time. Spin accumulation
Figure 6.3 (a) Schematic illustration of spin pumping in PEDOT:PSS/Y₃Fe₂O₁₂ structures. \( M(t) \), \( E_{\text{ISHE}} \), \( j \), and \( \sigma \) denote the dynamical magnetization, electric field due to the spin-charge conversion, spin current and the spin-polarization vector of the spin current respectively. (b) Magnetic field \( (H) \) dependence of the FMR signal \( dI/dH \) and the electromotive force \( V \) for the PEDOT:PSS/Y₃Fe₂O₁₂ film at 20 mW microwave excitation, where \( I \) is the microwave absorption intensity. (c) Spin pump geometry (upper) for Ni₈₀Fe₂₀(10)/PBTTT(60)/Pt(7) trilayer and the principle for Hanle precession (bottom). (d) Angular dependence of \( V_{\text{ISHE}} \), where solid circles are experimental data and solid curves are fitting results using various spin relaxation times, \( \tau_s \), from 1 ps (orange) to 1 \( \mu \)s (red).

and the resultant spin current were converted into electric voltage, \( V_{\text{ISHE}} \), for detection via the inverse spin Hall effect in PEDOT:PSS. From the film thickness dependence of \( V_{\text{ISHE}} \), the spin diffusion length was estimated as 22-31nm and the spin relaxation time 5-11 \( \mu \)s in PEDOT: PSS (based on the diffusion coefficient \( D = 8 \times 10^7 \text{ cm}^2\text{s}^{-1} \)). Watanabe et al further extended this technique for studying the undoped semiconducting conjugated polymer, PETTT, which has high in-plane field effect mobility up to \( \sim 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) (right panel of Fig. 6.3). A thin layer Pt adjacent to PETTT was used to convert the spin current transmitted.
from PETTT into electric voltage via ISHE. They demonstrated that pure spin currents can be carried by the localized spin -1/2 polarons inside PETTT over a distance that is over hundreds of nanometers (153 ± 32 nm) long. Evidence of Hanle precession in PETTT from angular dependence of $V_{ISHE}$ was claimed (Fig. 6.3d), however, it is still in controversial. Again calculated from $\tau_{sf} = l_{sf}^2 / D$, the spin life time extracted was up to 20 ms at 200 K. Note that the precision of $\tau_{sf}$ in their work relies on the reliability of $l_{sf}$ and the diffusion constant $D$ (provided spin currents are transported by diffusion), which actually haven’t been confirmed experimentally. Kimata et al conducted a comprehensive study on the spin transport by means of spin pumping, electron paramagnetic resonance and charge transport using a highly-doped PEDOT:PSS for obtaining $l_{sf}$, $\tau_{sf}$ and $D$ respectively. From their work, $\tau_{sf}$ was determined in the range of 5-100 ns at room temperature (~ 1 µs at 9 K) which is much shorter than the value we mentioned above.

To conclude our introduction to spin injection into organics and measuring the spin lifetime, some important progress has been achieved recently especially for the spin pump technique. It has been successfully demonstrated by several different groups that pure spin current can be injected into the organic system and transport in it over lengths of 10-100 nm before relaxation, although the details of spin transport and relaxation are not fully understood. Even so, the topic of organic spintronics is still in its infancy: the precise values of the spin lifetimes in the prototypical organic materials are missing, the standard Hanle effect and generally accessible methods are required, and the propagation of the transported carriers must be officially detected.

6.2 Three-terminal spin injection geometry for organics

Since the first reports of spin injection into silicon and detection of spin precession in it at room temperature by means of a three-terminal configuration (FM/I/NM), this method appeared as a simpler and well-reproduced way for electric-spin injection and detection. It has been performed on many different NM systems, e.g. Si, Ge, GaAs, graphene etc., where
the Lorentzian-line-shape MR was widely reported and ascribed to the Hanle effect the injected spin in the NM. However the source of the relatively large MR and the ‘spin-life time’ obtained by this method is controversial. We have tested the case of hMTJ/MgO/NM (Al, Au and Cu etc.) and we tend to believe the Hanle-like MRs are mainly generated by field-modulated resonant or inelastic tunneling processes in the defective tunnel barriers, rather than the intrinsic spin resistances in NM layer due to spin accumulation (see the NLSV measurement in last chapter). The former increases with the tunnel barrier resistance, whereas the latter is proportional to the ρl_s/A, where ρ is the resistivity of NM material and l_s is the spin diffusion length. Note that the resistivity of semiconductors are 10^2-10^8 times larger than metals together with 10^1-10^3 times their spin diffusion length, we expect the spin resistance of semiconductors to be 10^2-10^7 times larger than the nonmagnetic metals. That is to say, it is possible to detect the spin current in semiconductor with the three-terminal method because the intrinsic spin resistance of NM here may exceed the extrinsic MR signals from the tunnel barrier. It was actually found in some special cases of GaAs^17 and graphene^18 that the results of three-terminal spin injection are consistent with the results of four-terminal NLSV.

Therefore, we have performed a series of experiments with different organic-incorporated hMTJ/MgO/NM stacks as we did before in the organic-based spin-valve stacks (Fig. 6.4a). The processes were similar to that of making organic-based spin-valves shown in chapter 3. After the deposition of SiO layer, a thin layer of organic material (normally ≤ 10 nm) was evaporated onto the top surface of the MgO (1/3 of the samples are not covered to make hMTJ/MgO/NM (or FM) reference samples) and then the top electrodes were deposited. Both FM and NM top electrodes are deposited in the same batch for comparison. Because p-type organic semiconductors are usually more stable than n-type, gold electrodes with pentacene (PEN)^19, 20 are normally chosen in the hole-injection experiment, and the measurements on hMTJ/MgO/PEN/Au stack were first tested.
As shown in Fig. 6.4b, compared with hMTJ/MgO/Au prepared in the same batch, hMTJ/MgO/PEN (~10 nm)/Au (denoted as PEN/Au) stacks show resistances ~10^4 times larger. It means that the PEN layer was well-protected during the deposition of Au by thermal evaporation. On the contrary, compared with the case of depositing CoFe and Al top electrodes (denoted as PEN/CoFe and PEN/Al), PEN/Au shows smaller resistance but stronger bias and temperature dependence, which indicates that contacting PEN with Au indeed reduces the contact resistance effectively. For PEN/CoFe and PEN/Al, their zero bias conductance increased only a few times (CoFe, ~2 times; Al, 4 times) from 17 K to 300 K, whereas zero bias conductance of PEN/Au increased about ~40 times. At first sight, from the temperature dependence of zero bias conductance, the main conductance mechanisms in PEN/Au are identified as multi-step tunneling or hopping while the direct tunneling dominate the conductance in the junctions of PEN/CoFe and PEN/Al at small bias.

It is worth mentioning that different differential conductance curves often correspond to different magneto-transport results. Fig. 6.5 a & b show the typical cases of PEN/Au and PEN/Al. A clear Hanle-like MR under the perpendicular magnetic field (for NM top electrodes) or TMR curve (for FM top electrodes) was only found on the samples which show a smooth and stable $dI/dF$ curves. For the samples that display a noisy and unstable $dI/dV$ curve, there is no chance to see any meaningful and reproducible MR. The quality of the $I$-$V$ and $dI/dV$ curves actually serves as a simple criterion for observation of Hanle-like MR. For the PEN/Au sample that shows Lorentzian-line-shape MR behavior, the saturation
junction resistance under perpendicular magnetic field and the corresponding $\Delta R$ were obtained from the Lorentzian fitting as we did in last chapter (Fig. 6.5c shows the bias dependence at 17 K). When positive bias increased from $\sim 0.25$ V to 1.2 V, the junction resistance decreased quickly and the $\Delta R$ also decreased except from $+0.25$ to 0.33 V, while the MR kept increasing until reaching a maximum around 0.7-1 V and decreasing from there. It is slightly different from the case of hMTJ/MgO/Au (see the inset of Fig. 6.5 d). As we mentioned before, the multi-step tunneling or hopping via the PEN molecules are the main

Figure 6.5 $dI/dV$ (a) and MR curves under the perpendicular magnetic field (b) for the typical PEN/Au (black curve) and PEN/Al (blue curve). (c) bias dependence of minima resistance from the Lorentzian fitting of Hanle-like MR curves and $\Delta R$ and $MR = \Delta R/R$ for PEN/Au at 17 K. (d) bias dependence of conductance for PEN/Au (red) and hMTJ/MgO/Au (black) at low temperature ($\sim 20$ K). Inset of (d) shows the bias dependence of resistance minima (from the Lorentzian fitting), $\Delta R$ and MR for hMTJ/MgO/Au.
source of conductance in PEN/Au, however, a minor conductance contribution from direct tunneling between Au and \(hMTJ/MgO\) due to pinholes in PEN cannot be excluded in our large size junctions. To account for the drop of MR between 0.7 V to 1 V in PEN/Au, we can consider a general case of two parallel channels where the total junction conductance is the sum of direct tunneling conductance, \(\sigma_d\) and hopping (or multistep tunneling) conductance, \(\sigma_h\): \(\sigma = \sigma_d + \sigma_h\) and the corresponding \(R^{-1} = R_d^{-1} + R_h^{-1}\). Hence we have: 

\[
\frac{\delta R_t}{R_t} = \left( \frac{R_{h}}{R_{h} + R_{d}} \right) \frac{\delta R_d}{R_d} + \left( \frac{R_{d}}{R_{h} + R_{d}} \right) \frac{\delta R_h}{R_h},
\]

where \(\frac{\delta R_t}{R_t}, \frac{\delta R_d}{R_d}\) and \(\frac{\delta R_h}{R_h}\) represent the MRs of the junction, direct tunneling channel and hopping channel respectively.

The contributions of \(\frac{\delta R_d}{R_d}\) and \(\frac{\delta R_h}{R_h}\) to the total MR depend on the weight of the conductance in each channel. For PEN/Au, the junction conductance increased about 33 times from +0.25 V to +1.0 V (~ 83 times to 1.2 V), while for the sample without PEN, its conductance increased merely about 3 times from +0.25 V to 1 V (from the results in last chapter). It suggests relatively weak bias dependence of direct tunneling conductance, whereas the conductance of multi-step tunneling or hopping strongly increases with bias. We can consider an extra case for making the direct tunneling the dominant conductance for bias lower than 0.4 V, and \(\frac{\delta R_t}{R_t} \approx \frac{\delta R_d}{R_d} \sim 0.4\%\) as \(R_h \gg R_d\). However, as the bias increased above 1 V the hopping conductance starts to dominate and it becomes at least ~ 10 times larger than direct tunneling conductance (i.e. \(R_h \sim 0.1R_d\)), thus we have \(\frac{\delta R_t}{R_t} \approx 0.09 \frac{\delta R_d}{R_d} + 0.91 \frac{\delta R_h}{R_h}\). Because \(\frac{\delta R_t}{R_t} \approx 0.1 \frac{\delta R_d}{R_d} + 0.9 \frac{\delta R_h}{R_h} \sim 0.8\%\) at 1 V in the experiment, we have \(\frac{\delta R_h}{R_h} \sim 0.8\%\) at 1 V and it slowly decreases as bias increases further. We have thus demonstrated that a similar size of Hanle-like MR exists in the system with multi-step tunneling or hopping via the localized states of the organic molecules, which is an extension of the results we observed in last chapter.

Besides PEN, we also observed the Hanle-like MRs in the devices incorporating with other organic materials. A special case are the iron-based organic compound, spin-cross-over materials (SCO) which were also chosen as the organic medium in order to explore the
possible role of magnetic ions in spin-related tunneling or hopping. However, very similar Hanle-like MR was observed in all these organic-based junctions. The magnitude and FWHM of MR signals were found in accordance with our hMTJ/MgO/NM stacks, although the signal/noise ratios are sometimes much lower in some samples. The tunnel barrier $R \cdot A$ dependence of $\Delta R \cdot A$ for two organic materials (PEN and spin-cross-over materials) are fitted on almost the same line of that of nonmagnetic Al, Au and Cu with slope ~ 1.2 (see Fig. 6.6a). The FWHM of Hanle-like MR curves also fall in the same range for different materials (Fig. 6.6b). Again, the Hanle-like MR in these junctions isn’t due to the spin accumulation in the thin organic layers and hopping via these organic molecules is believed to contribute to the observed MR. Therefore, the spin lifetime obtained by this method is unreliable.

It is very likely the pinholes commonly exist in the organic thin layers for samples with the top electrode deposited at room temperature. Penetration of the top electrodes into the organic is a serious issue for organic devices, especially for direct deposition of CoFe onto the organic (mainly because of the high evaporation temperature required: $\geq$ 1500 °C).

![Figure 6.6 3T 'Hanle' measurement on hMTJ/MgO/organic and NM metals. The $R \cdot A$ dependence of $\Delta R \cdot A$ (a) and FWHM (b) in organic and NM metals are showing a similar trend (the dashed line in the left panel is the linear fitting of the samples with organic materials).](image)

As Figure 6.7 shows, for the samples with ~10 nm of PEN, the junction resistance increased $\sim 5 \times 10^5$ times but the TMR values ($\sim 13.3\%$) are even larger than that of the control sample
without PEN (~5%). The coercivity of the CoFe top electrode in PEN/CoFe junctions also significantly increases which is actually evidence for very small FM particles found in many organic-based MTJs in our work (see chapter 4). Compared with the resistance at room temperature, the low-temperature resistance increase is merely ~ 1.5 times, therefore direct tunneling due to the CoFe pinholes is confirmed. We also checked the Hanle effect in these

Figure 6.7 (a) MRs of hMTJ/MgO/PEN/CoFe (black) and hMTJ/MgO/PEN/CoFe (blue) at room temperature. (b) MR of hMTJ/MgO/PEN/CoFe under perpendicular magnetic field at low temperature (~ 20 K). Current-voltage curves (c) and MR (d) of the stacks composed of hMTJ/MgO/C60 8nm and CoFe or Au top electrodes, where LN cooling was used when depositing the top electrodes.

organic-based MTJs by measuring the junction resistance under perpendicular field, and no evidence for spin precession was found. In Fig. 6.7b the resistance changed because of the magnetization angles between hMTJ and top CoFe were changed when the magnetic field was swept under a slightly tilted angle normal to the device plane.
To avoid the top electrode penetration problem, we tried to cool the thin organic film with liquid nitrogen (LN) when depositing the top electrodes. Representative results are shown in the figure below. C\textsubscript{60} was selected in this work because of its relative stable and robust under top metal deposition\cite{1}, which is reflected by its relatively high evaporation temperature (\geq 500 °C). We find that the contributions of multistep tunneling and hopping are increased, estimated from the fact that the junction resistances increased 5-10 times as temperature decreased from room temperature to 20 K (Fig. 6.7 c, d). TMR (~ 15%) was found for the junctions with CoFe top electrodes and the in-plane version of the Hanle-like MR showed up in C\textsubscript{60}/Au stacks when the bias voltage is large enough. However, the interface is poor, and possibly reddened with pinholes because of which a larger switching field is needed (up to 150 mT) for complete parallel alignment of CoFe with bottom hMTJ stacks. It is a sign of small FM particles as we stressed in chapter 4. It is thus difficult to distinguish between hopping and the direct tunneling and a quantitative identification of each contribution is missing.

6.3 Detection of the NLSV signals in organic-based vertical stacks

In spite of the technical simplicity in the three-terminal spin injection geometry, its validity has not been verified without doubt. We failed to measure spin lifetime in the organic by this method. In the context of electrical spin injection and detection, the four-terminal NLSV measurement has been proven as the credible method. Compared with lateral spin-valve geometry device, the vertical spin-valve geometry possesses the merit of easily producing a nano-gap space between two FM electrodes, which is a crucial precondition for detecting the injected spin current in a system where the injected spin only diffuses tens of nanometers. We consider here the possibility of injecting the spin polarized current into the NM channel but only detecting the pure spin current by the non-local spin valve signals in our vertical stacks as shown below (Fig. 6.8).
The MgO-based /\textit{h}MTJ was used as the spin injector, and in principle the spin-polarized current can be injected from CoFeB/MgO into the organic channels effectively. Since the conductivity of organic layers is usually quite low, another counter electrode is required to extract the injected current. After this thin NM counter-electrode, the second FM layer is deposited on top of it as the spin detector. Introducing this additional layer of very thin metal (or graphene) between organic and top FM is perhaps vital for detecting the spin-injection signal for several reasons:

1. The injected spin-polarized current is separated into mainly the charge current flowing away from the NM layer and the pure spin current detected by the FM adjacent to the NM with a relatively high signal-to-noise ratio (because of the low resistance); The possible intrinsic OMAR signals from organic channel can be excluded as well.

2. Electrons transported through a very thin layer of metal e.g. Al and Au or graphene, may lose the spin polarization very little, but the total current injection can be greatly enhanced because of the short channel length (~ tens of nm) and large contact area and the lower contact resistance (as the case of PEN/Au interface);

3. It is relatively easier to fabricate flat and smooth interfaces between organic and top electrode which is made of a low melting point metal e.g. Al. This NM layer (or graphene) can prevent the penetration of FM into the organic channel as well.
4. The thin metal layer, Al etc., can protect organic from atmospheric degradation.

It is also flexible to adapt this method for different materials, e.g. for the spin injector of LSMO, the tunnel barrier is not necessary and it is also compatible with ambient conditions; for the organic channel that is made of a highly conductive polymer, e.g. PEDOT:PSS, the top NM can be removed as well. As far as we know, this is actually the first suggestion to measure the NLSV signal in organic system with a transport distance around 10 nm without any lithography technique, which circumvents the very basic limitations for many lithography-incompatible organic materials.

In order to verify the feasibility of this idea in our system, we did a simplified experiment on Al-based vertical junctions as depicted in Fig. 6.9. Firstly a wafer was fully sputtered with a smooth and uniform NM trilayer, Ta5/Cu40/Pt5, in our Shamrock magnetron-sputtering system. This is to avoid the AMR effect from the CoFe layer deposited subsequently in our Magnolia thermal-evaporation system by reducing its contribution in the total bottom electrode conductance. A thin film of CoFe (~6 nm) was deposited onto the whole wafer. All the other structures were completed in the Magnolia system with the help of a shadow mask. An insulator layer of SiO (≥ 60nm) was deposited with the first shadow mask pattern to partly cover the bottom electrode, and the Al electrode strip bars (thickness ~20 nm) were deposited as the spin transport channel. The second shadow mask pattern at an angle rotation of 90° the the first one was used to deposit the second SiO layer to fully cover the edges of the wider Al bars (width ~ 400 μm). Finally the top electrodes, CoFe’ (~10nm), were deposited by another 90° angle rotated shadow mask to contact the Al in the gaps (~100 μm) of the second SiO layer. Cross section and 3D schematic illusion of these devices are shown in the top panels of Fig. 6.9. With this structure, three-terminal local MR measurement and four-terminal nonlocal MR measurement can be performed on one sample as shown in Fig. 6.9a (at 20 K). Firstly, the AMRs of FM electrodes were identified in local MR measurement. For the top CoFe’ the resistance is ~ 3 KΩ from two terminal $I-V$ measurements and its MR is directly measured by sweeping an in-plane external magnetic field perpendicular to the longitudinal direction of the CoFe’ stripes. However, the tiny contribution of bottom FM in the bottom electrode conductance masks the direct AMR
effect from CoFe'. Instead, its AMR effect was obtained from the three-terminal local measurement of the control sample without the top CoFe' (R \approx 60 \, \text{m} \Omega). The coercivity of CoFe and CoFe' was thus found to be around 1 mT and 10 mT respectively (Fig. 6.9c). We have detected a negative MR (\Delta R \leq 10 \, \mu \Omega) in the four-terminal nonlocal MR measurement with a DC current +50 mA flowing between CoFe and one end of the Al bar. As depicted in Fig. 6.9, plateaus around 1 to 10 mT correspond to the antiparallel alignment of the magnetizations of top CoFe' and bottom CoFe. Its background is a little large (~ 175 m\Omega), which is perhaps due to a part of the current actually flowing through CoFe' and building a
voltage between CoFe’ and the second terminal of Al. For the local MR measurement on the same sample, a positive MR was detected ($\Delta R \sim 15 \, \mu \Omega$), however, its switching field is larger than that of the nonlocal MR and very close to the coercivity of the top CoFe’. It is likely due to the admixture of AMR in both top and bottom FM electrodes. The MRs under ‘perpendicular’ magnetic field was also measured. However, the Hanle effect is not expected here as the transport time ($\sim 10$ fs) from injector to the detector is far shorter than the spin life time ($\sim 100$ ps). A similar negative MR was found in the nonlocal MR measurement under a ‘perpendicular’ magnetic field. Larger switching field of -2 mT and -30 mT was detected, which corresponds to the $20^\circ$ tilt angle between the normal direction of the plane and the magnetic field.

Let’s see if we take the $\Delta R$ in the nonlocal measurement as the non-local spin valve signal whether its value is reasonable. Again the formula $R_s = \gamma I_s \exp(-L/\ell_d) / (\sigma_{Al} A)$ can be used for a qualitative estimate. For Al at 20 K we use the parameters $\ell_d = 1 \, \mu m$, $L = 0.02 \, \mu m$ and $\sigma_{Al} \sim 4 \times 10^7 \, \Omega^{-1} \, m^{-1}$ and the channel area $A \sim 400 \times 0.02 \, \mu m^2$. We find that if $R_s \sim 10 \, \mu \Omega$, the corresponding spin injection efficiency at the CoFe/Al interface is about $\gamma \sim 6\%$, which is a little bit lower for a transparent contact, but certainly reasonable. Compared with the spin resistance in the four-terminal nanostructure of lateral FM/AlOx/Al/AlOx/FM’ (maximum $R_s \sim 1 \, \Omega$ in Ref. 22), the spin resistance in our vertical large size junctions is lower by 5 orders of magnitude. There are two main reasons: the channel width $\sim 400 \, \mu m$ ($\sim 1000$ times larger than that of Al nanowires) and the lower spin injection efficiency $P^2 \sim 3.6 \times 10^{-3}$ (10-100 times smaller than the best tunnel barrier). Obviously introducing AlOx tunnel barriers of good quality between the Al and CoFe’ should enhance the spin signal. There is also a side conclusion from the 3T & 4T spin injection measurement. We find that even without a tunnel barrier and the possible impurity-assisted tunneling MR effect, the spin accumulation in the NM channel still can’t be detected by the local geometry (three-terminal spin injection), i.e. one FM electrode working as both injector and detector is not actually realized.

Furthermore, to detect the spin current in OSC channels within our devices the most serious problem is the large background resistance, which would mask any small spin signals below
its noise level. Ideally the background resistance should be much smaller than the channel spin resistances to effectively show the spin-related signals. However, the possible currents flowing from FM generated a large voltage background in our two terminals nonlocal detectors. Inserting a thin tunnel barrier between NM channel and top FM can isolate the detector more effective from the charge current in the NM channel than increasing NM thickness (which presents the case of a bipolar spin transistor\(^{23,24}\)) and thus reduces the background. Moreover, as we pointed out above, the spin detection efficiency can be also enhanced by good tunnel barriers. To reduce the background further, the bottom FM electrodes should be made as small strips by shadow mask not as a whole wafer because there are possible short circuits existing in the SiO isolation layer between the top FM' and bottom FM in our present devices. We definitely need to redesign a shadow mask and introduce a tunnel barrier between NM channel and FM if we want to continue this work with organic layers.

In the NLSV geometry, it actually detects the small voltage signals from spin accumulation (as \(R_s = \frac{\Delta V_s}{I}\)). It is notable that this effect is inversely proportional to the NM channel area which means such signals in the large-size junctions (sub-millimeter width) are generally several orders of magnitude smaller than that of small areas junctions (sub-micrometer size). A more feasible strategy for our big size junctions is perhaps to detect the spin-related current signal (rather than the voltage signals) in the NM channel, which increases with the junction area. Apart from the plain MR measurement, a hot electron magnetic transistor can be produced in the vertical planar stacks\(^{25}\). As we mentioned in Chapter 2, Appelbaum et al have successfully demonstrated that spin-polarized ballistic hot electrons can be injected into the conduction band of a single-crystal undoped Si and coherently transported in such a channel over ~ 350 \(\mu\)m at room temperature with a spin life time ~73 ns\(^{26}\), which advances this topic with a big step. In their device only the electrons with high enough energy can pass through the second Schottky barrier (~ 0.8 eV between Cu and n-Si) and the scatter out possibility of these hot electrons by a second FM detector depends on the angle between the directions of hot-electron spin and the FM magnetization (NiFe in Fig. 6.10). A small perpendicular magnetic field can induce an obvious rotation of the electron spin orientation after traveling through a relatively long Si channel and the oscillation of the currents were
Figure 6.10 Left panel: schematic band diagram of a four-terminal (two for tunnel junction and two for FM semiconductor-metal-semiconductor detection) ballistic hot electron injection and detection device with a thick Si transport layer 350 μm. Right panel: graphite crystal, a possible prototypical π-conjugated system for spin injection and detection. Actually there have been few attempts to implement this method for organic systems. There are certainly many obstacles: technical incompatibility; the unknown Schottky contact barriers between the organic layer and metal electrodes; poor conductivity and low mobility for most of amorphous organic semiconductors. Considering the reliable fabrication process and the quality for organic materials, we think some special organic single crystals can be used as the prototype systems to investigate the spin injection and transport in these van der Waals crystals. For instance, electron & spin transport along the c-axis direction of a thin graphene crystal (due to the overlap of p̂-orbitals of the carbon atoms in adjacent graphene layers), high mobility C₆₀ and rubrene (single) crystal thin film are possible prototypes.
6.4 Spin injection beyond the diffusive regime

Throughout the topic of spin injection into organic systems, most interests has been focused on the systems composed of a great many molecules in disordered or ordered structures, where the charge & spin are transported by hopping or diffusion. In this regime, conclusive evidence for spin injection into the organic and the spin precession process haven't been clearly captured. Referring to spin injection into organic systems, it means that the carriers should be transported in the Lowest Unoccupied Molecular Orbital (LUMO) energy levels or Highest Occupied Molecular Orbital (HOMO) of the organic system, not by tunneling through the very thin organic layer. It is also different from the interface properties due to the hybridization between the FM and the molecules or layer forming the spinterface (see Chapter 2), where a sizable or even enhanced MR can be obtained. Turning from the thin film or bulk system to the basic units, the single molecules, we will find that even for single molecules spin injection and precession haven't been demonstrated, although it is easier to realize it in some special case (e.g. spin-polarized STM) than the complicated systems made of many of them. In this part, we tried to extend our work from organic thin films to the individual molecules. We propose a possible scheme to inject the spin-polarized current into isolated single molecules and estimate the condition for distinctly showing the spin injection and precession and hence measuring the spin lifetime in single molecules.

Inspired by the resonant tunneling magneto-resistance effect in the FM/I/NM or even NM/I/NM structures, we think the local defects or impurities in a tunnel barrier can be replaced by the small molecules, e.g. C₆₀ molecule (Fig. 6.11). We expect to observe spin-polarized resonant tunneling through single molecule embedded in the tunnel barrier, which works like a quantum dot (QD). A suitable tunnel barrier is one of the most important factors. It should be of good quality with high spin injection efficiency and low density of localized states. The tunnel barrier should be thick enough otherwise the direct tunneling will dominate the conductance, however, it should not be so thick that the inelastic processes and multi-step tunneling can exceed the resonant tunneling. The molecules should sit in the
Figure 6.11 Illustration of injecting spin into a single molecule and detecting the spin lifetime on it by resonant tunneling via the LUMO of a C$_{60}$ molecule embedded in a tunnel barrier.

Besides, the HOMO or LUMO of the molecules should be not too far from the Fermi level of the FM electrodes, otherwise, a large bias voltage is required to align the nearby energy level of molecule with Fermi level of the FM, which is usually detrimental for high spin injection efficiency. In order to clearly display the resonant tunneling with spin-polarized current, small-size junctions (diameter ≤ 0.5 µm) are preferred for detecting the signals from individual molecules because very few molecules are involved in the junctions and we suppose that each individual molecule gives roughly the same signal. Tunneling spectroscopy can be used to identify the energy levels of molecules and the role in spin relaxation. If we want to measure the spin lifetime directly from the Hanle effect, an additional condition must be satisfied. Roughly speaking, the dwell time of the spin carrier in an embedded QD relies on the coupling between two electrodes (which is inversely proportional to the resistances between the molecule and the electrodes$^{31}$). Therefore, these couplings and the corresponding resistance should be suitable to make the spin dwell time on molecules in the range of the spin lifetime (~ ns to µs). It is perhaps the trickiest part in the experiment. However, we noted that the spin lifetime in the QDs are not necessary obtained from the Hanle effect. The bias dependent TMR measurements can be used to
deduce the spin lifetime in the QDs in the regime of Coulomb Blockade\textsuperscript{32}. (Note that the results (spin lifetime) in Ref. 32 are surprisingly large).

We have started our work with AlO\textsubscript{x}-based hMTJs and the highly symmetrical C\textsubscript{60} molecules were used as the QDs. Firstly of all, the typical hMTJ stacks up to AlO\textsubscript{x} (2.5 nm) was tested for the quality of the tunnel barrier after exposure to atmosphere. Through a similar process with MgO-based hMTJ, the full MTJ stacks fabricated in two systems show TMR ratios up to 60\%, which is not bad as the starting point. Next we prolonged the Ar ion milling time of AlO\textsubscript{x} in the organic UHV evaporation system and performed two or three rounds of deposition and oxidization of the very thin Al layers (~0.4nm) (see the description in Chapter 3). Finally the full MTJs stacks were made and the quality of the hybrid AlO\textsubscript{x}/AlO\textsubscript{x}' barrier was tested (where AlO\textsubscript{x} and AlO\textsubscript{x}' refer to the barrier made by sputtering AlO\textsubscript{x} and oxidizing Al respectively). The TMR ratios up to ~20% at room temperature were generally obtained, which is reasonable because the best TMR from the AlO\textsubscript{x}'-based MTJs is below 20\% at room temperature (see Chapter 3).

After verifying the validity of those two kinds of AlO\textsubscript{x} tunnel barriers, we introduced a sub-monolayer of C\textsubscript{60} between these two AlO\textsubscript{x} tunnel barriers (the control samples without C\textsubscript{60} were prepared at the same time). The tentative results are shown in Fig. 6.12. At room temperature, the sample with nominal 0.8 nm of C\textsubscript{60} shows resistances about 10 times larger than the one without C\textsubscript{60}, however, the TMR ratio only slightly decreased (7\% and 5\% for the samples without and with C\textsubscript{60} at the bias voltage +50 mV). The d//d\textit{V} curve of the sample with C\textsubscript{60} shows a clear deviation from symmetric parabolic behavior, which indicates indirect tunneling behavior. Because of the large junction area, most of the d//d\textit{V} curves are featureless, from which the existence of resonant tunneling via C\textsubscript{60} can’t be verified. However, some samples showed signs of resonant tunneling. For the sample hMTJ/AlO\textsubscript{x}/C\textsubscript{60} 0.8 nm/AlO\textsubscript{x}'/CoFe, its TMR changed from positive to negative when the bias goes from zero to below -0.4V, which was reported as the result of resonant tunneling\textsuperscript{33}. A few samples showed peak structures in the d//d\textit{V} curve although those were not well-reproducible (Fig. 6.12c with Alq\textsubscript{3} inside). Nevertheless, further detailed measurements are
Figure 6.12 (a) $I$-$V$ and $dI/dV$ curves of hMTJ/AIO$_x$/C$_{60}$ (0.8 nm)/AIO$_x$/CoFe (b) the TMRs of the two samples at the bias voltage of $+50$ mV. (c) $I$-$V$ and $dI/dV$ curves of hMTJ/AIO$_x$/CoFe, where some structures emerge in the $dI/dV$ curves. (d) The bias dependent of TMR in a C$_{60}$ imbedded tunnel junction.

required to prove the resonant tunneling via C$_{60}$ molecules. We have planned to shrink down the sizes of the samples by lithography in order to have a better resolution of resonant tunneling and the inelastic tunneling spectroscopy on these samples. We should mention that under present conditions the $RA$ product of the tunnel barrier is too large ($\geq 10^{11}$ ohm$\cdot$µm$^2$) to make small size junction. Therefore, before minimizing the sizes, optimization of the tunnel barrier thickness in order to obtain the best TMR signal is needed. On the other hand, making FM/I/C$_{60}$/I/NM is also in our list for further experiments into the role of resonant tunneling in the Hanle-like MR, we mentioned above. The ultimate objective is to prove spin injection, and obtain the spin life time for the individual molecules.
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Chapter 7 Conclusions and future work

7.1 Conclusions

In order to inject the spins into thin films of C$_{60}$ and PEN etc., two different schemes were investigated. In the context of organic-based spin valves, i.e. the FM/I/OS/FM's stacks, we have tested the spin injectors with AlO$_x$ and MgO tunnel barriers in order to enhance the spin injection efficiency. The techniques of liquid nitrogen cooling and making small-size junctions were developed to prepare well-defined OS/FM' interfaces and avoid pinholes in the organic layers. However, even with liquid nitrogen cooling, penetration of the top FM' electrode into organic layers appears to be inevitable, especially for large-size junctions. Nevertheless, we can still draw some qualitative conclusions. MR was only found in the tunneling regime, which includes direct tunneling and multi-step tunneling. The number of localized states (LS) for multi-step tunneling increases with the thicknesses of the C$_{60}$ layer and it starts to dominate the spin valves' conductance as indicated by the strong bias voltage and temperature dependence of the conductance. At the same time, MR dramatically decreases with thickness. When VRH emerged in the devices, MR disappeared completely. Our results cast doubt on the possibility of injecting spin-polarized currents into the disordered organic systems. The main obstacles for spin injection into organics are the ill-defined OS/FM interface and large resistance mismatch.

For the second scheme, three-terminal spin injection, only one FM/I/NM interface is important, and such interface can be well-defined even for the organic-based NM materials. However, as an initial test, in the case of non-magnetic metals, Au, Al and Cu, we found that within this method, what is actually measured is the MR effect resulting from impurities or localized states inside the MgO tunnel barrier. Introducing non-local spin-valve measurements, we eliminated the role of spin accumulation in the NM; from the angular dependence of MR, we excluded the TAMR effect in the FM/I/NM stacks, as well. We believe that the LSs inside the tunnel barriers are responsible for the Hanle-like MR as supported by the temperature dependence of MR and field dependent inelastic electron tunneling spectrum. We tentatively associated the LSs with the oxygen vacancies inside the
defective oxides tunnel barriers. This work reveals an extrinsic source of Hanle-like MR in a FM/I/NM structure, which can mask the intrinsic Hanle effect on spin signals.

Because of the possible high spin resistance in the organic materials, intrinsic spin signals due to spin accumulation in organics may exceed the extrinsic tunneling MR signals from the tunnel barrier when the spin injector of FM/I is utilized. We have thus introduced various organic layers in the three-terminal spin injection experiment. However, similar results were found for organics as for NM metals. The spin lifetimes (below 100 ps) of these organics obtained by this method is actually not credible. It is likely that this method still suffer from the problems above: the ill-defined OS/FM interface and large resistance mismatch. Based on our existing results, we proposed two improved methods to inject the spins and measure the spin lifetime in some prototype organic structures: four-terminal NLSV measurement on stacks of FM/I/OS/NM/FM and spin injection into individual molecules via resonant tunneling in a structure of FM/I/C_{60} QDs/I/FM.

### 7.2 Future work

Making well-defined interfaces is a key step in developing and studying organic-based spintronics devices, not only for intrinsic spin transport in organics, but also for the organic-modified FM interface, the spinterface. We are specifically interested in electric spin injection and detection in organic systems, and the proposed future work is based on our existing results and line of thought.

Organic thin films are perhaps the most common and easily accessible system for spin injection & detection, however, their soft, fragile, high-resistance and disordered nature is not good for neat and tidy work. Experiments are poorly-reproduced and there is a lack of conclusive results and convincing evidence for electronic spin injection transport and detection. We would rather turn to some ‘simpler’ prototype systems for the spin-transport in organic structures. As we mentioned in Charter 6, graphite layers, for example HOPG with thickness of 10-100 nm, provides us an ideal prototype system. It is a π-conjugated system in out-of-plane direction (van der Waals bonded) and is also stable, conductive and compatible with the lithography processes. We may actually view it as a single crystal of
layered graphene ‘molecules’, and the spin lifetime and spin diffusion length in its out-of-plane direction should be the upper limit for all organics. Furthermore, we can easily mimic the effect of disorder, which is the realistic case for most organics, in this system, by doping. The vertical NLSV configuration is perhaps the most effective way of studying the intrinsic spin properties in such system.

We are also interested in another extreme condition, the spin injection & detection in single molecules such as C_{60}. It is accessible in the FM/I/QDs/I/FM (or NM) structure based on our recipes of making small-size junctions. Resonant tunneling and IETS will be used to relate the energy levels (or local excitations) of the molecules to their (spin-related) transport properties. Hanle effect is also expected under some special conditions and it should help to determine the spin lifetime within individual molecules.

Bibliography