Organic spintronic devices utilizing spin-injection, spin-tunneling and spin-dependent transport

Ran Lin
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ORGANIC SPINTRONIC DEVICES UTILIZING SPIN-INJECTION, SPIN-TUNNELING AND SPIN-DEPENDENT TRANSPORT

by

Ran Lin

A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Physics in the Graduate College of The University of Iowa

December 2013

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To my parents Yi Lin and Lili Li, my wife Juan Chen, and my daughter Avery Muge Lin
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Spintronics, also known as spin electronics, or magnetoelectronics, refers to the study of the role that electron and (less frequently) nuclear spins play in solid state physics, and a group of devices that specifically exploit both the intrinsic spin of the electron and its associated magnetic moment, in addition to its fundamental electronic charge. As a principal type of spintronic device, a spin-valve is a device that uses ferromagnetic electrodes to polarize and analyze the electronic spins. The electrical resistance of the device depends sensitively on the relative magnetization of its two ferromagnetic electrodes, a phenomenon referred to as Giant Magnetoresistance (GMR). Having been successfully applied in the field of data storage, GMR also shows potential for future logic devices. Organic semiconductors possess many advantages in electronic device applications. Therefore, using organic semiconductors in spintronics is very interesting and promising, in part, because of their exceptionally long spin-decoherence times.

This thesis concerns itself with the scientific study of magnetic field and spin effects in organic spin valves (OSV) and organic light emitting diodes (OLED). Three projects were finished, achieving a better understanding of the transportation of charge and spin carriers inside organic films, and paving the way to enhancing the spin diffusion length and the organic magnetoresistance (OMAR) effect.

Firstly, C_{60} films were used as the spin-transport layer of OSV devices, because of its low hyperfine coupling and high mobility, which prior work suggested to be beneficial. Subsequently we studied the spin injection and transport properties by measuring the devices’ magnetoresistance (MR) response at various biasing voltages, V, temperatures, T and different C_{60} film thickness. But we do not observe a significantly increased spin-diffusion length compared to OSV devices based on other organic semiconductors. We propose conductivity mismatch as a likely cause of the loss of spin-valve signal with increasing C_{60} layer thickness.
There exists some disagreement in the scientific literature regarding whether OSV operate in the so-called tunneling regime or the so-called injection regime. To shed light on this question, we fabricated spin-valve devices made of organic semiconduc-
tor thin films of rubrene sandwiched between ferromagnetic cobalt and iron electrodes. Current-voltage (I-V) characteristics in Co/AlO_x/rubrene/Fe junctions with a rubrene layer thickness, \( d \), ranging from 5-50 nm, were measured, and we found two different modes of conductivity. The first mode, tunneling, occurs in relatively thin junctions, \( d < 15 \text{ nm} \), and decays exponentially with increasing rubrene thickness. We determined the tunneling decay length to be \( \approx 1 \text{ nm} \). The tunneling mode is also characterized by a weak temperature dependence and a nearly parabolic differential conductance. The second mode, injection followed by hopping, occurs in relatively thick devices, \( d \geq 15 \text{ nm} \), and can be identified by strongly temperature dependent, highly non-linear I-V traces that are similar to those commonly measured in organic injection devices such as OLEDs. We observed MR in devices with a rubrene thickness of 5 nm and 10 nm. Those devices are clearly in the tunneling regime. For the 15 nm device, for which the tunneling current is just barely measurable we could not observe MR.

In the third project, we show that the performance of both OMAR and OSV devices very sensitively depends on whether the metallic layers are deposited by thermal evaporation or electron-beam evaporation. A strongly reduced spin diffusion length and an enhanced OMAR response can be achieved in devices fabricated by electron-beam evaporation. Then we showed that the difference must be attributed to the generation of traps resulting from the exposure of the organic layer to X-ray bremsstrahlung that is generated during the e-beam evaporation process. We also used the thermally stimulated current technique (TSC) to characterize these traps.
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1.1 Introduction

As promising candidates for electronic devices, especially for optoelectronics devices, organic semiconductors (OSCs) possess advantages including high electrical and electroluminescent efficiency, chemical tuning of electronic functionality, easy structural modification, ability of mechanical flexibility, low production cost with relative ease of processing of the substrates and the compounds, and structural flexibility of the devices.

Figure 1.1: Organic light emitting diodes display products: (a) Sony XEL-1 11-Inch OLED Digital TV. (from http://store.sony.com) (b) Samsung Galaxy Tab™ 7.7 with AMOLED displays. (from http://www.samsung.com)
For the past few decades, research in OSCs has progressed impressively. Nowadays, high-efficiency, very bright and colorful thin displays based on organic light-emitting devices (OLEDs) have become available to consumers [1, 2, 3], see Fig. 1.1. There are also considerable improvements in organic field-effect transistors (OFETs) for use in low-cost electronics [4, 5, 6] and organic photovoltaic (OPV) devices for low-cost solar energy generation [7, 8], even in the use of organic electric memories for data-storage applications [9].

Recently, two new spintronic effects, namely the organic spin-valve (OSV) effect [10, 11, 12, 13] and organic magnetoresistance (OMAR) [14, 15, 16, 17, 18, 19, 20] have caught the attention of the spintronics community, who deal with utilizing the electron spin degree of freedom in electronic devices through a variety of spin-dependent phenomena.

OSVs are organic devices that use ferromagnetic metal (FM) electrodes as their spin carrier injectors and detectors. OMAR, on the other hand, is a low-field, room-temperature magnetoresistive effect in organic semiconductor devices with non-magnetic electrodes.

In this chapter, a brief review of $\pi$-conjugated organic semiconductors, spin diffusion mechanism and magnetoresistance effects will be given, followed by a short outline of this thesis at the end.

1.2 $\pi$-conjugated Organic Semiconductors

Based on their molecular weight, $\pi$-conjugated organic semiconductors are classified into two groups, small molecules and polymers. The common feature that both types have is a $\pi$-conjugated chemical structure that results in the delocalization of their highest energy electrons ($\pi$-electrons) over the entire extension of the $\pi$-conjugation. In general, organic semiconductor materials have an alternating sequence of single and double bonds along the backbone as shown in Fig. 1.2. The carbons in this sequence are $sp^2$
hybridized (σ bonds), which leaves one orbital p<sub>z</sub> perpendicular to the chemical bond direction, unhybridized. The electrons in these alternatively overlapping orbitals form a π-electron cloud, delocalized over the conjugation length. The σ bonds are the building blocks of the molecular skeleton and are thus responsible for the molecule’s integrity. π-conjugated organic materials are semiconductors, with filled bonding π-orbitals and unoccupied anti-bonding π<sup>*</sup>-orbitals. The π-orbitals form the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO), roughly equivalent to the inorganic semiconductor’s valence and conduction band edges, respectively. Most semiconductors have an energy gap between HOMO and LUMO that lies in the range 1.5-3eV, which makes them ideally suited for optoelectronic applications in the visible light range.
1.2.1 π-conjugated Small Molecules

Figure 1.3: Chemical structures of commonly used π-conjugated semiconductors. (a) Small molecular semiconductors. 8-hydroxy-quinoline aluminum (Alq₃) is used as an electron transport and emissive layer, Rubrene has been applied widely in organic light emitting diodes and field transistors, N,N'-diphenyl-N,N'-bis-(3-methylphenylene)-1,1'-diphenyl-4, 4'-diamine (TPD) is a hole transport material and 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) is an electron transport material. (b) Polymers normally used in organic light emitting diodes. The green fluorescent polymer poly(p-phenylene vinylene (PPV); the orange-red fluorescent MEH-PPV; the blue fluorescent Poly(dialkyfluorene)s (PFO); PEDOT:PSS mixing water solution widely used as hole-transporting layer; Polyacetylene (PA) is the first semiconductor polymer.

In π-conjugated small molecules, carbon atoms form larger molecules, typically with benzene rings as the basic unit, as shown in Fig. 1.2(b). The π-bonds become delocalized and form a π-system which often extends over the entire molecule. The gap between occupied and empty states in these π-systems becomes smaller with increasing delocalization, leading to absorption and fluorescence in the visible. These substances can be prepared as molecular single crystals. Due to the close coupling of the π-systems of
the molecules in these crystals, they show, in a purified form, remarkable transport properties, including band transport up to room temperature with mobility of 1-10cm²/Vs. Most of the molecules can also be easily evaporated to form polycrystalline (hopping transport with mobility typically around 10⁻³cm²/Vs at 300K) or amorphous (hopping with mobility typically around 10⁻⁵cm²/Vs at 300K) layers.

Small molecular-weight, organic compounds have been extensively investigated, see Fig. 1.3(a). Electroluminescence from OLEDs made from small molecules was first observed and extensively studied in the 1960s. In 1987, a research team in Kodak introduced a double layer OLED, which combined modern thin film deposition techniques with suitable materials and structure to give moderately low bias voltages and attractive electroluminescence efficiency [21]. Intense research in both academic and industry has yielded OLEDs with remarkable color fidelity, device efficiency, and operational stability.

1.2.2 Π-conjugated Polymers

A π-conjugated polymer is a carbon-based macromolecule through which the valence π-electrons are delocalized, and exhibits electronic properties that are quite different from those observed in inorganic metals or semiconductors. These unusual electronic properties may essentially be attributed to the fact that conjugated polymers are quasi-one dimensional systems, as shown in Fig. 1.2(c), owing to their strong intra-molecular but relatively weak inter-molecular interactions. The quantum mechanical wavefunction is therefore usually confined to a single chain. This quasi-one dimensionality results in weakly screened electron-electron interaction. Thus, electronic correlations are important in determining the character of the electronic states, and the neutral excited states are dominated by excitations. Another important factor in determining the character of the electronic states is that the electrons and lattice are strongly coupled. The effects of electron-lattice coupling are enhanced in low dimensions. Therefore charge carriers in these materials are positive and negative polarons, rather than holes and electrons.
Research into the electronic and optical properties of conjugated polymers began in the 1970’s after a number of seminal experimental achievements. First, the synthesis of polyacetylene [see Fig. 1.3(b)] thin films and the subsequent success in doping these polymers to create conducting polymers established the field of synthetic metals. Second, the synthesis of phenyl-based polymers (e.g. poly(para-phenylene-vinylene) or PPV, Fig. 1.3(b)) and discovery of electroluminescence under low voltages in these systems established the field of polymer optoelectronics. The discovery and development of conductive polymers was recognized by the award of the Nobel prize for chemistry in 2000 to Heeger, MacDiarmid and Shirakawa.

1.3 The Primary Excited Species in Organic Semiconductors

Two major excitations, namely charged and neutral excitations, are dominant in \( \Pi \)-conjugated Polymers (PCPs). Upon photoexcitation, neutral spinless excitations are photogenerated; consequently they may relax into charged excitations or other types of neutral excitations (i.e. spin triplets). Whereas upon electrical excitation only charged excitations are injected, these may recombine to form neutral excitations or other types of charged excitations.

1.3.1 Polaron

As the intermolecular (van der Waals) forces in organic materials are much weaker than the covalent and ionic bonds of inorganic crystals, organic materials are less rigid than inorganic substances. A propagating charge carrier is therefore able to locally distort its host material. The charge carrier combined with the accompanying deformation can be treated as a quasi-particle called a polaron. Polaron carries spin and is supposed to be the primary excitation upon electrical injection in the non degenerate ground state (NDGS) of PCPs. Polaron moves from chain to chain through hopping; also they are the major current carrier in device application. Upon collision, two oppositely charged
polarons can form a polaron pair if they are on adjacent chains or a triplet exciton or singlet exciton if they are within the exciton capture distance depending on their spin configuration. The relevant energy levels are shown in Fig. 1.4(a).

Polaron has two symmetrical, localized states in the energy gap. The lower energy level is derived from the ground state HOMO band, whereas the higher polaron level is derived from the ground state LUMO band. The polaron is charged with a negative charge ($P^-$) or a positive charge ($P^+$), has spin 1/2, and has two allowed below-gap optical transitions as shown in Fig. 1.4(a).

1.3.2 Bipolarons

A bipolaron is an excitation that combines two charged polarons on the same site. The bipolaron can be lower in energy than two separate polarons, because of attractive electron-phonon interactions. Just as in the case of the polaron, the bipolaron also
has two in-gap electronic states (Fig. 1.4). The bipolarons can be either empty \( BP^{2+} \) (doubly charged positively) or filled \( BP^{2-} \) (doubly charged negatively) [22]. Due to level symmetry, the bipolaron has only one allowed optical transition, compared to the two allowed optical transitions of the polaron, as shown in Fig. 1.4(b) [22]. Bipolarons are believed to become important at very high doping concentrations.

1.3.3 Polaron Pairs

Two oppositely charged polarons \((P^+ \text{ and } P^-)\) on two adjacent chains form a polaron pair (PP) species [23]. The PP binding energy is Coulombic. These species are actually the precursors to the formation of triplet and singlet excitons in OLEDs, and thus their associated physics is very important for device applications. In an electrically excited system, electrons and holes moving in different directions in the active polymer layer capture each other by a Coulombic interaction, and this forms the precursors of singlet or triplet excitons, which are intrachain species. In an optically excited system, the primary singlet excitons relax to the lowest singlet state that is the main source of luminescence, may produce triplet intrachain excitons by intersystem crossing, or may transfer an electron to the neighboring chain or the next conjugated segment of the same chain, to form a polaron pair (Fig. 1.4(c)).

The polaron pair specie that is generated from a relaxed higher energy singlet has been dubbed geminate pair. The specie usually keeps the original spin 0 configuration. A nongeminate polaron pair, on the contrary is generated through recombination of polarons originated from different singlet excitons. The nongeminate polaron pair has a higher probability to be in the triplet configuration because of the degeneracy of the spin sublevels (triplet:singlet=3:1). Understanding the singlet and triplet polaron pair evolution under a magnetic field is the key to understanding the OMAR, as we will discuss in much detail later on.
1.3.4 Excitons

When a $\pi$-conjugated polymer absorbs a photon, it excites an electron from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) and forms a tightly bound electron-hole pair, namely an exciton. Recently Tong et al. studied the excited-state order and primary photoexcitations of the singlet manifold states in PCPs [24]. They concluded that a photo-generated-exciton may undergo several processes following photon absorption. It may recombine radiatively by emitting light [25], i.e. by photoluminescence (PL), which is the light source in OLEDs, or nonradiatively by emitting phonons. It may also be trapped at defect centers; undergo intersystem crossing (ISC) into a long-lived triplet state [26]; or dissociate into a polaron pair. The difference between the singlet and triplet exciton is the relative alignment of the electrons spins. Due to the rules of quantum mechanics, only one possible alignment is formed for the singlet and three states for the triplet. Radiative recombination from the excited singlet state, namely fluorescence, is usually fast with lifetime of about 100 picoseconds. Intersystem crossing from the singlet to the triplet manifolds is possible within about 10 ns, caused by a spin flip of one of the electrons involved in the exciton, due to spin-orbit coupling, hyperfine interaction, or the existence of radical impurities on the chains.

The radiative emission from the excited triplet state, namely phosphorescence (PH), is usually weaker in organic materials since the optical transition from the triplet lower state to the ground state is forbidden; however the transition may be possible when one of the electron spin flips due to the spin-orbit interaction. In $\pi$-conjugated polymers this interaction is usually weak, and therefore the optical transition of the triplet exciton is relatively long; in the millisecond range [26]. Fig. 1.5 shows the processes of photon absorption into the singlet manifold and radiative, non-radiative recombination, and the inter-system crossing to the triplet manifold.
1.4 Spintronics

Spintronics is a branch of electronics that takes full advantage of not only the charge, but also the spin of the electron. Spintronics encompasses different topics, and it involves the generation of a non-equilibrium spin polarization in various materials and devices, as well as its manipulation and detection. Among the most fascinating examples of spintronic applications are giant magnetoresistance (GMR, also referred to as spin-injection magnetoresistance) and tunneling magneto resistance (TMR). In both cases, a considerable variation of the electrical resistance can be achieved by switching the magnetization of the device's electrodes from parallel to antiparallel configuration. Recently, OSC have been considered as spintronic materials [10, 11, 12, 13]. A GMR effect has been detected [10], but there remains some controversy as to whether the effect
is due to tunneling or spin-injection. We will introduce a criterion for distinguishing between tunneling and injection conductivity necessary for properly analyzing organic spin-valve phenomena in the later chapters. Moreover, recently a surprisingly large intrinsic magnetoresistive effect called OMAR has been found in both polymers and small molecule organic semiconductors at relatively small applied magnetic fields and at room temperature [14, 15, 16, 18, 19, 20].

1.4.1 Giant Magnetoresistance

As the principal spintronic device, a spin-valve device consists, in its most basic form, of two ferromagnetic electrodes separated by a non-magnetic spacer layer. The two ferromagnetic electrodes are chosen to exhibit two distinct switching fields, and the device can be switched between a parallel and antiparallel magnetization configuration using an applied magnetic field, $B$. The significant difference in resistance between the two configurations is referred to as GMR [27, 28]. The overall resistance is relatively low for parallel alignment and relatively high for antiparallel alignment. In GMR devices, typically metallic spacer layers are used, and the spin-polarized current is injected into and transported through the spacer layer.

The phenomenon of GMR was discovered in 1988 and the Nobel Prize in Physics 2007 was awarded jointly to Albert Fert and Peter Grünberg "for the discovery of Giant Magnetoresistance". GMR also has been successfully applied in industry in the last decade, revolutionizing techniques for scanning data on hard disks.

1.4.2 Tunneling Magnetoresistance

If a thin layer of insulator is chosen as the spacer-layer instead of a metal, the corresponding effect is called TMR, because the spin-polarized carriers tunnel through the insulating layer.

The effect was originally discovered in 1975 by M. Jullière (University of Rennes,
France) in Fe/GeO/Co-junctions at 4.2 K. The relative change of resistance was around 14%, and did not attract much attention.[29] In 1991 T. Miyazaki (University Tohoku, Japan) found an effect of 2.7% at room temperature. Later, in 1994, Miyazaki found 18% in junctions of iron separated by an amorphous aluminum oxide insulator [30] and J. Moodera found 11.8% in junctions with electrodes of CoFe and Co [31]. The highest effects observed to date with aluminum oxide insulators are around 70% at room temperature.

Since the year 2000, tunnel barriers of crystalline magnesium oxide (MgO) have been under development. In 2001 Butler and Mathon independently made the theoretical prediction that using iron as the ferromagnet and MgO as the insulator, the tunnel magnetoresistance can reach several thousand percent [32, 33]. The same year, Bowen et al. were the first to report experiments showing a significant TMR in a MgO based magnetic tunnel junction [Fe/MgO/FeCo(001)] [34]. In 2004, Parkin and Yuasa were able to make Fe/MgO/Fe junctions that reach over 200% TMR at room temperature [35, 36]. In 2009, effects of up to 600% at room temperature and more than 1100% at 4.2 K were observed in junctions of CoFeB/MgO/CoFeB [37].

In industry, the read-heads of modern hard disk drives work on the basis of magnetic tunnel junctions. TMR, or more specifically the magnetic tunnel junction, is also the basis of Magnetic Random Access Memory (MRAM), a new type of non-volatile memory. The first generation technologies relied on creating cross-point magnetic fields on each bit to write the data on it, although this approach has a scaling limit at around 90-130 nm [38]. There are two second generation techniques currently being developed: Thermal Assisted Switching (TAS) and Spin Torque Transfer (STT) [38]. Magnetic tunnel junctions are also used for sensing applications.
1.4.3 Organic Magnetoresistance

In addition to the spin-valve effect, there exists another magnetoresistive effect that is particular to organic devices, the so-called Organic Magnetoresistive effect (OMAR). OMAR is a recently discovered, large (15% or more in some materials), low-field, room-temperature magnetoresistive effect in organic devices with nonmagnetic electrodes [14, 15, 16, 18, 19, 20]. Recently, an exceptionally large (>2000%), room-temperature, small-field (a few millitesla) OMAR effect in one-dimensional, nonmagnetic systems formed by molecular wires embedded in a zeolite host crystal was reported [39]. The observed super large OMAR effect in this one-dimensional device is believed to be a proof of the so-called "spin-blocked" mechanism [39, 40].

OMAR devices do not require ferromagnetic electrode materials resulting in a flexibility in material choice not achievable for other magnetoresistive devices. They can be manufactured cheaply on flexible substrates, and may also be transparent. The devices therefore hold promise for applications where large numbers of MR devices are needed, such as MRAM, potentially with optical readout if desired; and applications related to OLED display screens such as touch screens where the position of a magnetic stylus is detected.

1.5 Spin Relaxation

In a perfect OSV, the spin could be transported over an arbitrarily long distance. In reality however, this distance is limited by spin relaxation. In this section, we discuss the underlying mechanisms for spin relaxation in organic semiconductors, divided into spin-orbit coupling and hyperfine interaction. Both of them are expected to be small, but not completely negligible for most organic materials. Naber et al. summarized the spin relaxation mechanisms in inorganic and organic materials and more details about spin relaxation can be found in [41].
1.5.1 Spin-orbit Coupling

Spin-orbit coupling is a relativistic effect, describing the interaction between the electron’s spin and its orbital motion around an atomic nucleus. More generally, spin-orbit coupling occurs whenever a particle with non-zero spin moves in a region with a finite electric field. In the rest frame of a particle moving at a relativistic velocity, a static electric field Lorentz-transforms into a field with a finite magnetic component. Thus, although the spin degree of freedom only couples to a magnetic field, it is indirectly affected by an electric field via spin-orbit coupling. The electrical field can have various physical origins, such as the electric field of an atomic nucleus or the band structure of a solid. As spin-orbit coupling generally grows with atomic number $Z$ (it scales as $Z^4$ in the case of an hydrogen-like atom [42]), and organic materials consist mainly of low-$Z$ materials (in particular Carbon atom), spin-orbit coupling is usually small. Sulphur, Aluminum or platinum atoms could provide a considerable spin-orbit coupling, but these atoms normally play a marginal role in carrier transport in organic material. Depending on the exact band structure of the organic material, spin-orbit coupling is actually not always negligible.

1.5.2 Hyperfine Interaction

Another source for spin relaxation is the hyperfine interaction. It originates from the interaction of the electron spin with the nuclear spins of the host material, primarily emitted by the compounds hydrogen atoms. In general, the electron spin interacts with many, say $N$, nuclear spins. The electron-nuclear coupling Hamiltonian is then given by:

$$H_{hyp} = \sum_{i}^{N} A_i \vec{T}_i \cdot \vec{S}$$

(1.1)

Where $\vec{T}_i$ and $\vec{S}$ are the spin operator for nucleus i and electron spin, respectively, and $A_i$ the coupling strength between spin.
The nuclear spins affect the spin relaxation time by means of so-called electron-nuclear flip-flops. In addition, fluctuating nuclear spins also results in dephasing. For an electron spin interaction with N nuclear spins, the statistical fluctuation scales with $\frac{1}{\sqrt{N}}$. Hence the more delocalized the electron wave function is, the less the influence of the nuclei. The nuclear spins in organic materials are mainly originating from the isotopes $^1H \ (I = \frac{1}{2})$, $^{13}C \ (I = \frac{1}{2})$, and $^{14}N \ (I = 2)$. Despite the presence of nuclear spins, the hyperfine interaction in organic materials is usually weak. The reason is that for organic conductors often use is made of $\pi$-conjugated molecules with delocalized states that have practically no overlap with the C or H atoms, since the wavefunctions of the $\pi$-electrons mainly consist of $p_z$ orbitals, whose nodal plane coincides with the molecular plane. In chapter 3, we will discuss spin-valves based on fullerene $C_{60}$, which contains $^{13}C$ only, to achieve an even smaller hyperfine interaction.

1.6 Outline of this Thesis

The outline of this thesis is as follows.

In chapter 2, we discuss the structures and basic science of organic spin valve (OSV) and organic light emitting diode (OLED). We also briefly introduce most of the experimental techniques used in this thesis. In this chapter we present the different experiments performed for the study of organic spin valves in the first part, and the study of OMAR in the second part.

For spin valves, the spin-relaxation length is one of the most important figures of merit. The ideal would be an infinitely large spin-diffusion-length, because in this case the spin could be transported around inside, e.g., a logic circuit without any decay, but in reality various processes limit this length. Several works indicate [43, 44] that hyperfine coupling may be the most important of these limiting processes in OSCs. In order to potentially overcome the limitation on the spin-relaxation length in organic semiconductors caused by the hyperfine coupling, we fabricated spin-valves based on $C_{60}$
for which the hyperfine coupling is minute in chapter 3. However, our devices do not show a significantly larger spin-diffusion length. This suggests that either a mechanism other than hyperfine coupling causes the loss of spin-polarization, or that in thick devices an increasing conductivity mismatch [45] limits spin-injection.

There exists some uncertainty in the literature whether OSV work TMR or spin-injection GMR. In chapter 4, we introduce a criterion for distinguishing between tunneling and injection conductivity necessary for properly analyzing organic spin-valve phenomena. We measure current-voltage (I-V) characteristics in Co/AlO\textsubscript{x}/rubrene/Fe junctions with a rubrene layer thickness, \( d \), ranging from 5-50 nm. For \( d \leq 10 \) nm the I-V traces are typical of tunnel junctions. At \( d > 15 \) nm the tunneling current becomes negligibly small. At larger biases, however, a second type of conductivity sets in. In this regime, the I-V curves are strongly non-linear and temperature dependent. By comparing these to I-V curves measured in organic light-emitting diodes, we assign the latter mode to injection into the organic layer followed by hopping transport. We observe a spin-valve effect only in the tunneling regime.

In chapter 5, we report the effect of X-rays produced during electron beam deposition of metallic electrodes on the performance of organic spintronic devices. The X-rays generate traps with an activation energy of \( \approx 0.5eV \) in a commonly used organic. These traps lead to a dramatic decrease in spin-diffusion length in organic spin-valves. In OMAR devices, however, the traps strongly enhance magnetoresistance. We also discuss our observations in the frame work of currently existing theories.

The summary of this thesis is presented in Chapter 6.
CHAPTER 2
EXPERIMENTAL TECHNIQUES

This chapter briefly introduces most of experimental techniques used in this thesis. The different experiments performed for the study of organic spin valves (OSVs) will be presented in the first part, and the study of organic magnetoresistance (OMAR) in organic light emitting diodes (OLEDs) will be shown in the second part.

2.1 Organic Spin Valve Device

In this section we would like to introduce the OSV device structures, present our actual device fabrication and describe the experiments performed on these devices.

2.1.1 Organic Spin Valve Device Structure

![Figure 2.1: The organic spin valve device structure and measurement configurations.](image)

Our OSV devices have the vertical sandwich structure configuration, see Fig. 2.1. There are basically three layers involved: two ferromagnetic (FM) electrode films and
the organic semiconductor layer as the spacer. By engineering the two FM electrodes to have different coercive fields, their magnetization directions can have either a parallel or anti-parallel alignment configuration upon sweeping an external magnetic field. In our experiments, we used La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO), Cobalt, Iron as ferromagnetic electrodes. In some devices, we introduced a very thin oxide layer to improve the metal/organic interface.

2.1.1.1 Ferromagnetic Electrodes

![Crystal structure and energy diagram of LSMO](image)

Figure 2.2: Crystal structure and energy diagram of LSMO: (a) The basic perovskite structure, LSMO crystal structure. (b) The energy diagram at $T \ll T_C = 325$K (Mixed valence $Mn^{3+}(3d^4)$ and $Mn^{4+}(3d^3)$).

(from [46])

The special ferromagnetic electrode material we used, LSMO, is introduced first, because it is crucial for obtaining the OSV effects in our experiments. LSMO is a 'half-metal', which has been defined as a material that has propagating electron states at the Fermi energy only for one of the two possible spin projections. Its crystal structure and
energy diagram is shown in Fig. 2.2. LSMO is believed to be a half-metallic ferromagnetic that possesses near 100% spin polarization at low temperature.

The Curie temperature of the LSMO is about 325K and its magnetization is strongly temperature dependent. We note that unlike metallic FM films such as cobalt, iron, nickel or their alloys, the LSMO films are already stable against oxidation. In fact, our LSMO films have been cleaned and re-used many times without any apparent degradation. The LSMO substrate are provided by Prof. Y. Suzuki’s group at University of California at Berkeley and Stanford University.

With different coercive fields, cobalt and iron were also used as electrodes, but their spin polarizations are much lower, only 44% for iron and 34% for cobalt. (Spin Polarization of Electrons Tunneling from Films of Fe, Co, Ni, and Gd)

2.1.1.2 The Organic Semiconductor Materials

![Chemical structures of organic semiconductor materials](image)

Figure 2.3: The chemical structures of the small $\pi$-conjugated organic semiconductor, polymers and $C_{60}$ fullerene used as spacer layers in our OSV devices.
In our study, we have chosen small \(\pi\)-conjugated molecules and polymers to serve as an organic semiconductor spacer in OSV, because small molecules can be easily deposited, polymers can be easily made as solutions and spin-coated as thin films and integrated with a variety of metallic electrodes. Compared to the inorganic semiconductor materials, the organic semiconductor materials have several advantages for use in the spintronic devices: their ability to be economically processed in large areas, their compatibility with low-temperature processing, the tunability of their electronic properties, and the simplicity of thin-film device fabrication. The virtually limitless flexibility of synthetic organic chemistry allows the fabrication of \(\pi\)-conjugated organic semiconductor structures with a degree of control unattainable with the conventional inorganic semiconductors. In addition, the organic semiconductors have extremely weak spin-orbit interaction and weak hyperfine interaction [10, 11, 12, 13], so that the spin relaxation time is especially long. These properties make them ideal for spin-polarized electron injection and transport applications. In our experiments, we studied three different organic molecules and \(C_{60}\) as spacer layers in spin-valve devices. Their chemical molecular structures are shown in Fig. 2.3. The ones used most in our experiments were: (a) 8-hydroxy-quinoline aluminum (Alq3), most commonly used in organic light emitting diodes with green emission; (b) 5,6,11,12-tetr phenylnaphthacene (Rubrene), commonly used as hole transport layer in organic optoelectronic devices; and (c) \(C_{60}\), fullerene; due to its lack of hydrogen, \(C_{60}\) is not a typical organic semiconductor. \(C_{60}\) is supposed to be a good spin-valve spacer layer, because of its small hyperfine constant [47].

2.1.2 Device Fabrication

In this part, we introduce the OSV device fabrication. Though the possibility of magnetoresistance in OSV devices had been recognized, there are still difficulties related to the study of voltage, temperature and other physical properties of the OSV devices. These difficulties originate because OSV devices are sometimes not stable during the
measurement. The OSV devices are very sensitive to the FM interface contamination, the organic layer thickness and the organic purity. The device fabrication is essential to solve these problems.

2.1.2.1 Substrate Preparation

Spin-valve devices using LSMO as bottom electrodes were fabricated on SrTiO$_3$ (STO) (001) substrates and Si wafers covered with 300 nm of thermal oxide were diced into 12.5×9 mm pieces substrates for other spin-valve devices.

All substrates were washed in several solvents, deionized water, acetone, methanol, iso-propanol, using an ultrasonic cleaner and and finally cleaned in an oxygen plasma cleaner, and all cleaning steps were handled in a class 1000 clean-room.

2.1.2.2 Vacuum Electron-beam and Thermal Deposition Techniques

![Schematic drawings of vacuum e-beam and thermal evaporation setup](image)

Figure 2.4: Schematic drawings of vacuum e-beam and thermal evaporation setup: (a) Vacuum e-beam evaporation.(from Wikipedia.org) (b) Vacuum thermal evaporation.
We used the vacuum e-beam and thermal evaporation for fabricating the organic layer, the cobalt and Fe electrodes, thin oxide layer and aluminum protecting layer, as shown in Fig. 2.4.

The e-beam evaporation is a form of physical vapor deposition in which a target anode is bombarded with an electron beam given off by a charged tungsten filament under high vacuum. The electron beam causes atoms from the target to transform into the gaseous phase. The thermal evaporation deposition technique is based on heating until evaporation of the material to be deposited is possible. The material vapor finally condenses in the form of a thin film on the cold substrate surface. To avoid reaction between the vapor and atmosphere, low pressures are used, typically about $10^{-6}$ torr. At these low pressures, the mean free path of vapor atoms is the same order as the vacuum chamber dimensions, so these particles travel in straight lines from the evaporation source towards the substrate. This effect is called shadowing phenomenon, especially in those regions not directly accessible from the evaporation source (crucible). In chapter 5, we will discuss how the X-rays generated by e-beam evaporation affect organic spintronic devices.

In thermal evaporation the average energy of vapor atoms reaching the substrate surface is generally low (of the order of $kT$, i.e. tenths of meV). This affects seriously the morphology of the films, often resulting in a porous and poorly sticking material. Based on the above properties of the e-beam and thermal deposition, we used a shadow mask to form the pattern of the organic layer and FM electrodes. The layer thickness was measured by a vibrating crystal thickness monitor device, and independently confirmed outside the chamber by an optical thickness profilometer. It is noteworthy that the interface between the organic layer and top electrode layer is not very well defined or neat, because the high energy of metal vapor (evaporating temperature 1945°C) reaching the organic films enables the metal particles to penetrate somewhat deep (≈10nm) into the organic films. The 'ill-defined' thickness may be different for the various organic
molecules in this thesis.

2.1.3 Device Characterization

We used the magneto-optic Kerr effect to study the magnetization of the LSMO, Iron and cobalt electrodes. By measuring the current-voltage characteristics at various temperature, we studied the electron and hole charge tunneling through the spacer layer or injection from the electrode into organic film, and the transport inside the organic semiconductor layer. The most import measurement for the OSV is the magnetoresistance loop that shows the OSV device resistance at anti-parallel (AP) and parallel (P) configurations of the FM magnetization orientations. These techniques are explained below.

2.1.3.1 Magneto-optic Kerr Effect

In these experiments, magnetic characterization of the ferromagnetic electrodes is completed, e.g., by measuring of M(T,B) (M is the magnetization of the ferromagnetic electrodes, T is the temperature and B is the applied magnetic field). In our work a home-built magneto-optic Kerr effect (MOKE) system was used for measuring magnetization vs. field loops either at room temperature or in a variable-temperature cryostat from 10K-300K using fields up to ±0.1Tesla. The MOKE technique exploits the change in optical polarization of a laser light beam reflected from a magnetic material surface. A focused laser spot is reflected from the surface to be analyzed, and the change in polarization of the reflected light relative to the incident light is then analyzed. The change in polarization can either be a rotation about the polarization axis (Kerr rotation) or a change from linear to elliptical polarization (Kerr ellipticity) where the change in polarization is proportional to the magnetization of the surface being measured. The sampling depth of a MOKE experiment is governed by the penetration depth of the laser used; meaning that typically only layers within a few nms of the sample surface can be
measured.

As we will show in chapter 4, the MOKE data for the bottom Co electrode was measured directly on the electrode line of the device and reproduces the switching behavior of the lower electrode observed in the magnetoconductivity data quite well. The top Fe electrode interface is however optically inaccessible because the Si substrate is opaque at the HeNe laser wavelength. Instead, a Fe electrode line was deposited on top of a Si substrate, and the MOKE data was measured for the Fe-air interface.

2.1.3.2 Current-Voltage Characteristics in Organic Spin Valve

![Experimental Setup Diagram](image)

Figure 2.5: The experimental setup for the I-V characteristics and magnetoresistance measurement.

Our main experimental setup for measuring OSV magnetoresistance (MR) is shown
in Fig. 2.5. The OSV devices were mounted on the cold-finger of a close-cycle helium cryostat placed between the poles of an electromagnet. The Keithley 2400 source measurement unit may supply constant voltage for measuring the current across the device; or, alternatively supply constant current for measuring the voltage across the device. The device temperature is kept constant by a temperature controller of the cryostat, in the range from 10K to 300K. The magnetic field on the devices was measured by the Hall Effect sensor, which was placed to be near the devices. The magnetic field range was swept between ±1.5 Tesla. With this setup, we could measure the I-V characteristics, the device MR at different temperatures, at various magnetic fields. Also by analyzing the current-voltage relation and differential conductance vs. bias (dI/dV-V), the basic charge injection mechanism from the electrode to the organic layers, and the charge transport in the organic layer could be obtained.

2.1.3.3 Magnetoresistance in Organic Spin Valve

![Figure 2.6: Jullière model for tunneling magnetoresistance, where the tunneling current is proportional to density of state (DOS); during tunneling, the spin quantum number is conserved.](from wikipedia.org)
There are two important MR effects, TMR and GMR, discovered in OSVs. For TMR effect, assuming that the two FM electrodes are separated by an insulating layer with parallel magnetization orientations (Fig. 2.6 left), then due to the spin conservation, tunneling may only occur between bands of the same spin orientation in the two FM electrodes. This means tunneling from the spin-up band to the spin-up band; and complimentary from the spin-down band of one FM electrodes, to spin-down band of the other. Based on this tunneling model, the conductance for parallel magnetization $G_p$ is given by:

$$G_p = G_{↑↑} + G_{↑↓} \propto N_{↑}n_{↑} + n_{↓}n_{↓}$$

(2.1)

where $G_{↑↑} (G_{↓↓})$ is the conductance in up (down) spin channel and $N_{↑} (n_{↓})$ is the majority (minority) spin density of states at $E_f$. When the magnetization orientation is anti-parallel (Fig. 2.6 right), tunneling between the anti-parallel electrodes means tunneling from the majority to the minority band. The conductance for anti-parallel magnetization configuration $G_{ap}$ is:

$$G_{ap} = G_{↑↓} + G_{↓↑} \propto N_{↑}n_{↑} + N_{↓}n_{↓}$$

(2.2)

Thus the conductance is different for parallel and anti-parallel magnetization configurations; consequently the tunneling junction shows a pronounced magnetoresistance effect. This was dubbed tunnel magnetoresistance (TMR), which is defined (following the majority of workers) as the difference in conductance between parallel and anti-parallel magnetization configurations, normalized by the antiparallel conductance. For the general case with non-identical electrodes, the TMR can be calculated from (Eq. 2.1 and Eq. 2.2)

$$TMR = \frac{G_p - G_{ap}}{G_{ap}} = \frac{R_{ap} - R_p}{R_p} = \frac{2P_lP_r}{1 - P_lP_r}$$

(2.3)

where $P_l(P_r)$ is the spin polarization in the left (right) ferromagnetic electrode;
keeping in mind here that $P$ is not simply the difference in total density states at the Fermi level, but is still determined by the effective masses of different band electrons and interface bonding. The above theory is based on the tunneling junction.

MR effect also exists in the OSVs with thick organic spacer layers and other structures such as FM/normal metal/FM, which is defined as Giant magnetoresistance (GMR):

$$GMR = \frac{G_p - G_{ap}}{G_p} = \frac{R_{ap} - R_p}{R_{ap}} = \frac{2P_l P_r}{1 + P_l P_r}$$  \hspace{1cm} (2.4)

Recently, there has been increasing interest in using organic semiconductors (OSCs) for spintronics, motivated, in part, by their long spin relaxation times [41, 48]. GMR signals detected in such OSVs suggest successful spin-injection from FM into OSC spacer layers, demonstrating the possibility of implementing spintronic logic devices.

Apparently, in OSVs, both spin-injection, corresponding to GMR, and spin-tunneling, corresponding to TMR, are possible, and a criterion, will be shown in chapter 4, for a clear distinction between tunneling and injection is required for the proper analysis of spin-valve effects in organics.

### 2.2 Organic Light Emitting Diode

The simplest OLED device structure is shown in Fig. 2.7. It consists of a thin film of indium-tin-oxide, (ITO), coated onto the substrate, as the bottom electrode upon which the organic semiconductor thin film is deposited. Finally, the top electrode is conveniently formed by vacuum evaporation. ITO is a transparent metal that allows the light generated within the diode to leave the device. Diodes of this type can be readily fabricated by spin-coating of the semiconducting polymer, or evaporating the small molecular film, onto the ITO-coated glass.

The electrodes are chosen to facilitate charge injection; ITO has a relatively high work function and is therefore suitable for use as a hole-injecting electrode; low work
function metals such as Ca, Mg or Al are suitable for injection of electrons. Organic semiconductors have an energy gap between the bonding and antibonding $\pi$ and $\pi^*$ states, respectively, of between about 2 to 3eV, covering the whole visible spectrum. More recently, higher efficiencies have been reported for diodes using a layer of poly(dioxyethylene-thienylene) doped with polystyrene sulphonic acid (PEDOT:PSS) (shown in Fig. 1.3) between the ITO and the emissive polymer layers. The principal interest in the use of polymers lies in the possibility of low-cost manufacturing, using solution-processing of film-forming polymers, although low-cost processing techniques have recently been developed also for small molecules [49].

In parallel with these development and commercialization activities, much progress has been made in the understanding of the underlying science that controls the properties of OLEDs and the organic semiconductors used. However, in comparison with inorganic semiconductors, relatively little is known about the electronic properties of these materials; even the nature of the semiconductor excitations remains controversial [50].
2.2.1 Organic Light Emitting Diode Device Fabrication Process

![Schematic drawing of OLED/OMAR devices.](image)

We commercially purchased most of the organic semiconductors used in our study. The fabrication of the organic sandwich devices is started with a careful cleaning of the glass substrates coated with 40nm of ITO, purchased from Delta Technologies. For normal devices, we draw photoresist patterns on top of ITO, and for some special devices with extra thin electrodes, we apply photolithography for patterning. Then, tin etchant is used to etch the parts of ITO not covered by photoresist. The etched ITO coated glass slides are then cut into the desired substrate size, typically 9 × 12.5 mm². Mechanical rubbing with 2-propanol as the first cleaning step in order to remove any surface contamination and a sequence of 50°C ultrasonic baths in the following order: 2% detergent in de-ionized water, two baths in pure de-ionized water, acetone, methanol, and 2-propanol. Being dried with nitrogen, samples are cleaned one more time by oxygen plasma cleaning from any remaining organic dirt and solvents. The conducting polymer, PEDOT:PSS, purchased from H. C. Starck, is then passed through a 0.45µm PVDF filter and spin coated at 3000 rpm on top of the ITO in some devices to provide an efficient hole injecting electrode. All the following manufacturing steps are carried out in a nitrogen glove.
box. Samples are then baked at 100-150°C on a hot plate for 30 minutes to remove any residual water. The next step is to deposit the small molecular film by thermal evaporation with a 0.05nm/sec rate. Following this, the Ca cathode followed by a capping layer of Al are then deposited by thermal or electron beam evaporation, respectively, at a base pressure of $\approx 1 \times 10^{-6}$ mbar on top of the organic thin films through a shadow mask. The device area is $\approx 1 \text{ mm}^2$ for all devices. The general device structure used for our measurements was metal/organic semiconductor/metal (see Fig. 2.8).

2.2.2 Organic Light Emitting Diode Device Characterization

![Diagram of OLED/OMAR device testing experiment.](image)

Figure 2.9: A schematic drawing of OLED/OMAR device testing experiment.

Fig. 2.9 shows a schematic drawing of OLED/OMAR device testing experimental setup. The samples are mounted on the cold finger of a closed-cycle helium cryostat purchased from Advanced Research System located between the poles of an electromagnet purchased from GMW. A Keithley 2400 source measure unit was used to perform
I-V and MR measurements.

2.2.2.1 Current-Voltage Characterization

The I-V curves for all operating OLEDs are non-linear, independent of the number and configuration of the organic layers. This nonlinear property is associated with several basic facts: first, the charge injection at the electrodes may be non ohmic; second, charge transport through the $\pi$-conjugated Polymer (PCP) layer under the influence of an external electric field is nonlinear. The models used in the literature for describing electron and hole injection from the metal electrode into organic media are the Fowler-Nordheim (FN) model of tunneling injection [51] and the Richardson-Schottky (RS) model of thermionic emission [52] over a barrier formed at the metal/organic interface. The charge transport mechanism in the organic layers under the electric field is mainly via hopping, which is limited by shallow and deep trapping, recombination, PCP morphology, temperature, etc. When the applied electric field is less than $10^4$V/cm and the injected current density is less than the intrinsic charge density, the current flow in the organic is limited by the Ohm’s law. When the applied electric field (biasing voltage) increases, then the injected current density becomes larger than the intrinsic charge density, under this conditions the injected carriers form the space charge layer near the organic/metal interface because of the small carrier mobility. The space charge enhances the internal electric field and the current flow is then governed by the space charge limited conduction (SCLC) mechanism described by the equation (Mott-Gurney law):

$$J = \frac{9\varepsilon\varepsilon_0\mu V^2}{8L^3}$$  \hspace{1cm} (2.5)

where $\varepsilon$ is the relative dielectric constant, $\varepsilon_0$ is the vacuum dielectric constant, $\mu$ is the carrier mobility, and L is the organic layer thickness. For the bipolar injecting device, such as OLED, and also considering electron and hole recombination, the SCLC
model is modified to be:

\[ J = \frac{3\varepsilon \varepsilon_0}{4} \left[ \frac{2\pi \mu_e \mu_h (\mu_e + \mu_h)}{\mu_r} \right]^{1/2} \left( \frac{V^2}{L^3} \right) \]  

(2.6)

where \( \mu_r \) is the recombination mobility [53, 54].

![Image of I-V and EL-V curves]

Figure 2.10: Typical I-V and EL-V curves measured of an OLED of the structure ITO/PEDOT:PSS/Alq3/Ca/Al.

The Fig. 2.10 shows the I-V and EL-V measurements of a typical OLED (ITO/PEDOT/Alq3/Ca/Al). Detail I-V curves in OLED analysis was discussed in [55].

2.2.2.2 Magnetic Field Effects in Organic Light Emitting Diode Devices

The magnetic field is measured using a GMW Hall effect teslameter, see Fig. 2.9. The magnetoresistance ratio, \( \Delta R/R \), is determined by measuring the change in current at a constant applied voltage (using Keithley sourcemeter unit) for different magnetic fields, \( B \).
\[
\frac{\Delta R}{R} \equiv \frac{R(B) - R(0)}{R(0)} = \frac{\frac{V_{\text{I}(B)}}{I(B)} - \frac{V_{\text{I}(0)}}{I(0)}}{\frac{V_{\text{I}(0)}}{I(0)}} \approx -\frac{\Delta I}{I} \tag{2.7}
\]

A temperature controller unit is also connected to the cryostat that allows measuring \(\Delta R/R\) at different temperatures. The electroluminescence of the devices is measured with a photomultiplier tube that is shielded from the magnetic field using high-saturation mu-shield foil.

2.2.2.3 Thermally Simulated Current Measurements

Thermally Simulated Current (TSC) \[56\] is the preferred method for studying traps, i.e. energy levels within the bandgap caused by the presence of other atoms or a structural defects, in OLEDs. In our TSC experiments, the devices were mounted inside a closed cycle He cryostat and cooled down to 20 K. Photocarriers were then generated using a 300 W Xenon lamp while the device was kept under a small electrical bias of \(V=0.2V\) ("load" voltage \[56\]). Some of the photogenerated carriers will get trapped, and the current produced by their thermal release is the quantity measured in TSC experiments. More specifically, the samples were heated at a constant rate of 15 K/minute and the thermally stimulated current was measured using a Keithly 6517A electrometer. All TSC experiments were carried out under a bias of \(V=-0.3V\), small enough not to cause a significant leakage current.

Peaks of thermally released current are the signature of thermal release from deep traps. And the trap depth can be determined by calculating the slope of the low temperature side of peak. Examples can be found in chapter 5.

2.2.3 Theoretical Models of Organic Magnetoresistance

In spite of the latest surge of interest in OMAR, its underlying mechanism is still hotly debated. Due to the weak magnetic field involved, it is widely believed that magnetic-conductance (MC) and magnetic-electroluminescence (MEL) originates from
the spin sublevel mixing via the hyperfine interaction (HFI), which is relatively small in π-conjugated organic semiconductors. However two competing basic models based on HFI have been proposed for explaining the spin-mixing process that causes OMAR \[15, 57, 58, 19, 59, 60, 61, 16, 17\]. These are the excitonic model, in which the magnetic field modulates the singlet and triplet interconversion, or triplet-exciton polaron quenching; and the bipolaron model. The exciton model is based on the spin dependent Coulombically bound polaron pair (PPs) formation from the oppositely injected P\(^+\) and P\(^-\) current in the devices; whereas the bipolaron model relies on the spin dependent formation of doubly charged excitations. We will introduce these models in the following sections.

2.2.3.1 Singlet-triplet Polaron Pair States and Their Mixing under an External Magnetic Field

MFE has been studied extensively in the field of photochemistry to explain the product yield changes that occur by applying a small magnetic field. There are two types of singlet-triplet conversions. For close polaron pairs, the singlet-triplet conversion is possible by involving heavy atom-centered such as chemical compounds with S and Ge. The S-T conversion is induced by the strong spin-orbit interaction of S and Ge. For the close pair involving light atom-center such as C, N, and O, no spin conversion occurs between the singlet and triplet states. Only in the separated pairs, the S-T conversion becomes possible through weak magnetic interaction as the Zeeman and hyperfine. Fig. 2.11 shows spins on separate molecules, each precessing about their individual hyperfine field. We will discuss the latter conversion mechanism in the following.

The spin Hamiltonian (H) of polaron pairs in organic molecules can be represented by the exchange (\(H_{ex}\)) and magnetic (\(H_{mag}\)) terms:

\[
H = H_{ex} + H_{mag}
\] (2.8)
Figure 2.11: Electron spins precess about the local hyperfine fields of Alq$_3$ molecules, which vary randomly in direction from molecule to molecule.

Where

\[ H_{ex} = -J(2\vec{S}_1 \cdot \vec{S}_2 + \frac{1}{2}) \]  

(2.9)

\[ H_{mag} = (g_1 \mu_B \vec{S}_1 \cdot \vec{B} + \sum_i A_i \vec{S}_1 \cdot \vec{I}_i) + (g_2 \mu_B \vec{S}_2 \cdot \vec{B} + \sum_k A_k \vec{S}_2 \cdot \vec{I}_k) \]  

(2.10)

Here, $\vec{S}_1$ and $\vec{S}_2$ represent the spin of the two polarons in the polaron pair; the $g_1$ and $g_2$ is the corresponding gyromagnetic, or g-factor; $J$ is the value of the exchange integral between the two polarons. $A_i$ and $A_k$ are the hyperfine coupling constants with nuclear spins ($I_i$ and $I_k$) in the polaron 1 and 2. The combination of two polarons with spin $S_1 = S_k = 1/2$ generates the singlet (S) and triplet ($T_n = \pm 1, 0$) states. From standard quantum mechanical calculations using Schrödinger representation wave functions of singlet $|S>$, $|T_n>$ and nuclear-spin $|\chi_n>$, it is straightforward to get the singlet
and triplet polaron pair energy levels:

\[ E(S) = \langle S | H_{ex} | S \rangle = J \]  

\[ E(T_n) = \langle T_n | H_{ex} | T_n \rangle = -J \]  

In the presence of the magnetic field, the various energy levels change as following:

\[ E(S) = \langle S, \chi_N | H_{ex} + H_{mag} | S, \chi_N \rangle = J \]  

\[ E(T_n) = \langle T_n, \chi_N | H_{ex} + H_{mag} | T_n, \chi_N \rangle = -J + n g \mu_B B + \frac{n}{2} \left( \sum_i A_i M_i + \sum_k A_k M_k \right) \]  

Here \( n = \pm 1, 0 \), \( M_i \) is the spin quantum number of nucleus \( i \), \( g = (g_1 + g_2)/2 \) and the level-crossing field \( B_{LC} = 2 |J(r_{LC})|/g \mu_B \). Fig. 2.12 shows the energy levels of the singlet and triplet polaron pairs as a function of distance, \( r \). When \( r \) is large enough, the triplet states and singlet state are almost degenerate with each other, because the strength of the exchange interaction strongly decreases with \( r \). When the energy separation between \( |T_n> \) and \( |S> \) becomes nearly zero, then the spin conversion between them occurs through the following off-diagonal elements:

\[ \langle T_0, \chi_N | H_{ex} + H_{mag} | S, \chi_N \rangle = \frac{1}{2} \Delta g \mu_B B + \left( \sum_i A_i M_i - \sum_k A_k M_k \right) \]  

\[ \langle T_{\pm 1}, \chi_N | H_{ex} + H_{mag} | S, \chi_N \rangle = \frac{\mp A_i}{2 \sqrt{2}} [I_i(I_i + 1) - M_i(M_i \mp 1)]^{1/2} \]  

here, \( \Delta g = g_1 - g_2 \). From the above Eq. 2.15 and 2.16, the S-T conversion of polaron pairs is influenced by the following terms: (a) the \( \Delta g \) mechanism through the Zeeman term which is characterized by \( \Delta g \mu_B B \); (b) the hyperfine interaction process
mechanism (HFI), that are characterized by the nuclear HFI constants $A_i$ and $A_k$; (c) the level crossing mechanism that is characterized by the exchange term $J$. The Fig. 2.13 summarizes the S-T conversion processes that are influenced by an external magnetic field, as well as the theoretical prediction of the magnetic effect. For the $\Delta g$ mechanism (a), there is no S-T conversion when $B=0$. When the field increases, S-T_0 conversion increases via the term $\Delta g \mu_B B$. However the MFE yield is proportional to $B^{1/2}$ [62, 63].

In the case of the hyperfine coupling mechanism (b) the S-T conversion at $B=0$ is induced between the singlet state and all three triplet sublevels through the HFI terms. At $B>0$, only S-T_0 conversion remains unchanged, while the S-T_{\pm1} conversion
rate decreases with increasing B. This decrease is saturated at high field that is larger than the HFI coupling constant. For the case of level crossing (c), no S-T conversion at B=0 because the exchange energy (2J) separates the singlet and triplet states as shown in Fig. 2.13. With B increasing level crossing occurs between S state and T_{-1} (or T_{+1}) sublevel at the level-crossing field (B_{LC}). The S-T conversion rate increases suddenly at the crossing field through the HFI term in equation 2.16.

2.2.3.2 Bipolaron Model

Based on the experimental results that the MR is also observed in the unipolar organic devices [64], in which only one type of charge carrier is injected into the device, i.e. either electrons or holes, the bipolaron model was proposed by P. A. Bobbert et
al. [17]. The bipolaron model was based on hopping of polarons and singlet bipolaron formation in the presence of the random hyperfine fields of hydrogen nuclei and an external magnetic field. In this model, the authors describe the magnetic field dependence of the bipolaron density. Monte Carlo simulations including on-site and longer-range Coulomb repulsion show how this leads to positive and negative OMAR. Depending on the branching ratio between bipolaron formation or dissociation and hopping rates, two different line shapes in excellent agreement with experiment are obtained.
3.1 Introduction

Recently, there has been increasing interest in using organic semiconductors for spintronics, partly because of their long spin relaxation times [41, 48]. The first demonstration of an organic spintronic device employed a planar structure of La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) electrodes separated by an ≈ 100 nm long channel of α-sexithiophene [11]. The first vertical organic spin valve device, which utilized LSMO and Co as the ferromagnetic layers and tris-(8-hydroxyquinoline) aluminum (Alq$_3$) as the organic semiconductor spacer, was demonstrated by Xiong et al. [10] and exhibited a clear spin-valve effect. The usefulness of spintronic devices for memory storage and logic operations is dependent upon the reliability of injecting and maintaining a spin polarized signal. Therefore the spin-injection efficiency and spin-diffusion length are amongst the most important parameters characterizing the performance of a spin-valve.

The spin diffusion length is determined by both the mobility of the carriers and the spin relaxation time. Whereas the long spin relaxation times [41, 48] in organics are promising, their weakness is a typically low mobility. Mobilities are often less than 0.1cm$^2$(Vs)$^{-1}$. Organic thin films consequently have a very large resistance, and therefore the conductivity mismatch problem, proposed as a principal obstacle to efficient spin-injection into semiconductors, may be particularly severe [45].

Spin relaxation times depend predominantly upon two mechanisms: spin-orbit coupling and hyperfine interaction. Spin-orbit coupling results from a particle’s spin coupling to a magnetic field or, if we change reference frames, moving through an electric field. In organic semiconductors, spin-orbit coupling is usually weaker than the hyperfine coupling and therefore not the dominant spin-relaxation mechanism. This was most clearly demonstrated by studies of the organic magnetoresistive effect [18, 19, 15, 65].
Figure 3.1: Transport of charge carrier through a chain of Alq₃ molecules. The red arrow depicts the carrier’s spin, the blue arrows are the local hyperfine fields. The hyperfine coupling leads to spin-randomization, because the electron spin precesses about local hyperfine fields.

(and refs. therein).

Indeed, a theory for spin-diffusion in disordered organic semiconductor devices based on hyperfine coupling was recently developed [43]. The importance of hyperfine coupling on the spin-diffusion length in organic spin-valves was experimentally verified in a recent work that demonstrated enhanced spin-diffusion lengths in deuterated compounds [44]. Because spin precesses about local hyperfine fields, originally polarized spin is randomized by the hyperfine coupling, as shown in Fig. 3.1.

Fullerene C₆₀ is one of the most interesting organic materials and has been studied intensively because of its versatile functions, for instance, its superconductivity [66] and n-type field-effect transistor (FET) operation [67, 68, 69]. Its electron mobility (greater than 0.1 cm²/Vs) is much larger than most organic materials [67, 68]. Due to the small natural abundance of ¹³C (1.1%) and its small hyperfine coupling constant
(0.06G) [47], the hyperfine interaction in fullerene $C_{60}$ is much smaller than other organic semiconductor materials. The injection of spin polarized electrons from ferromagnetic metal into $C_{60}$ has been proved [70, 71]. The extraordinarily long spin coherence time in $C_{60}$ solid at room temperature [69] implies that the room temperature $C_{60}$ spin valve could be obtained. All these render the fullerene $C_{60}$ as an excellent candidate for spin valve devices.

Therefore we fabricated spin-valves using a $C_{60}$ film as the spacer layer to potentially overcome the limitations imposed by hyperfine coupling.

### 3.2 Device Fabrication and Measurements

Our devices were fabricated on SrTiO$_3$ (STO) (001) substrates. On these substrates, 1 mm wide, 60 nm thick LSMO films were fabricated by pulsed laser deposition through a shadow mask. The LSMO deposition was performed with a KrF excimer laser (248 nm) in 320 mTorr $O_2$ at 700 $C$ with a laser fluence of 1-1.5 $J/cm^2$, followed by post-growth cooling in 300 Torr $O_2$. The LSMO covered substrates were washed in several solvents using an ultrasonic cleaner and handled in a class 1000 clean-room. As the organic semiconductor spacer layer, a $C_{60}$ layer was fabricated by thermal evaporation in high vacuum at a rate of 0.1 nm/s. Then a 0.5 mm wide, 15 nm thick Co top electrode covered by 30 nm of Al was deposited by electron beam evaporation at a rate of 0.1nm/s. All fabrication steps involving the organic layer and the top electrode were performed inside a glove-box or inside the glove-box-integrated vacuum evaporation chamber. The device structure is shown schematically in Fig. 3.2. The substrates were then mounted inside a closed-cycle He cryostat located between the poles of an electromagnet.

Current-voltage (I-V) and magnetoresistance (MR) measurements were performed using a Keithley 2400 source measure unit, with the positive pole connected to the LSMO electrode. Two or four point measurements were performed depending on the relative size of the junction and electrode resistance. Fig. 3.2 shows the experimental setup for
Figure 3.2: Structure of LSMO/$C_{60}$/Co spin-valve and diagram of the 4-point measurement.
Figure 3.3: Schematic band diagram of the LSMO/$C_{60}$/Co spin-valve showing the Fermi levels and the work functions of the two FM electrodes, LSMO and Co, respectively, and the HOMO and LUMO levels of $C_{60}$. The diagram is meant to be qualitative, as it neglects any interface dipoles and other effects that modify the band diagram in real devices. The inset shows the chemical structure of $C_{60}$.

a four point measurement. The molecular structure of $C_{60}$ is shown in Fig. 3.3 together with the energetic location of its highest occupied and lowest unoccupied molecular orbitals, HOMO and LUMO, respectively. For comparison, the workfunctions of LSMO and Co are also shown [10].

3.3 Magnetoresistance of Fullerene Spin-valve Devices

Fig. 3.4, inset, shows a magnetoresistance trace, $\Delta R/R$, measured in a LSMO/$C_{60}$ (40 nm)/Co spin-valve at 15K. The figure shows that sizeable magnetoresistance can be achieved in these devices. The main panel of this figure shows that the magnitude of the MR signal decreases with increasing temperature, in agreement with results reported by
Figure 3.4: Temperature dependence of the magnetoresistance, $\Delta R/R$, measured in a LSMO/$C_{60}$ (40nm)/Co spin-valve. The inset shows the $\Delta R/R$ at 15K.
others for organic spin-valves using LSMO [72]. The temperature dependence is believed to reflect a loss in spin-injection efficiency from the LSMO [73].

Fig. 3.5 shows $\Delta R/R$ traces measured in a LSMO/$C_{60}$ (40 nm)/Co spin-valve at 15 K. The figure shows that the magnitude of the MR signal decreases with increasing bias voltage, in agreement with results reported by others for organic spin-valves using LSMO [10]. The origin of this voltage dependence is, to the best of our knowledge, not yet sufficiently understood. It is phenomenologically very similar to the voltage dependence in tunnel junctions, where large applied voltage biases lead to the excitation of magnons and phonons in the ferromagnetic contacts that reduce the spin-valve effect [74, 75].
Fig. 3.6 shows magnetoresistance, $\Delta R/R$ curves, measured in a LSMO/$C_{60}$/Co spin-valve for three different organic layer thicknesses at 100K. For the thinnest spacer layer thickness, a MR signal of up to 13% is achieved. However, the figure shows that the MR signal decreases rapidly with increasing layer thickness. Similar thickness dependencies are also obtained for other temperatures (data not shown).

3.4 Discussion of Unexpectedly Short Spin-diffusion Length

Our data therefore indicate that the spin-diffusion length is only several tens of nanometers, in rough agreement with results from organic spin-valves based on other organic materials [11, 10, 76]. It therefore appears that the strong reduction of the
hyperfine coupling, which was the primary motivation for our work, did not lead to a significant improvement of the spin-diffusion length. The implication of our experiments therefore appears to be that mechanisms other than hyperfine coupling, such as spin-orbit coupling, are also important in determining the spin-diffusion length. There are however, other possible explanations for this observation.

A second possible interpretation is that spin-tunneling rather than spin-injection is active in our spin-valves, and the decrease in spin-valve signal merely reflects the diminishing of the tunneling component to the device current with increasing layer thickness. Indeed, the inset of Fig. 3.6 shows that the conductivity is very strongly thickness dependent, suggesting tunneling conduction. In the next section we will take a closer look at the I-V traces for different thicknesses and temperatures to more carefully analyze the mode of conduction. A third possible explanation of the decay of the spin-valve effect with increasing $C_{60}$ layer thickness is the increasing conductivity mismatch with increasing semiconductor layer thickness. Once more, a careful analysis of the I-V is required to explore the validity of this possibility.

3.5 Current-Voltage Characteristics of Fullerene Spin-valve Devices

Several recent works have described experimental criteria for distinguishing between tunneling and spin-injection, or more generally, to assess the relative magnitude of injection and semiconductor bulk resistivity in organic spin-valves. Whereas details can be found in Refs. [76, 77], the proposed criteria examine the behavior of the devices’ I-V curves. If spin-injection occurs, the I-V traces should be strongly temperature dependent, and because organic films typically possess electric-field dependent mobilities, these I-V curves are also expected to be highly non-linear. In contrast, tunneling I-V curves are known to be only weakly temperature dependent and to exhibit parabolic differential conductance traces. In addition, tunneling conductivity should exhibit an
Figure 3.7: The temperature dependent I-V curves: a) Current-voltage I-V traces at different temperatures for LSMO/$C_{60}$/Co devices with 25nm thick $C_{60}$ layer. Inset: Their differential conductance traces at different temperatures. b) Current-voltage I-V traces at different temperatures for LSMO/$C_{60}$/Co devices with 40nm thick $C_{60}$ layer.

To further examine whether tunneling or injection occurs in our devices, we report the temperature dependent I-V curves for our devices in Fig. 3.7. Fig. 3.7 a) shows the temperature dependent I-V curves for a relatively thin device ($C_{60}$ layer thickness of 25nm). It is shown that the I-V curves are largely temperature independent, and the inset shows that the dependence of the differential conductance on the voltage is near exponential dependence on layer thickness at constant electric field, whereas the same dependence is much weaker for ordinary hopping transport.
parabolic, indicative of tunneling. Tunneling here could either refer to tunneling through the whole organic layer, or a dominance of the interface resistance due to tunneling of the carriers into the organic over the transport resistance within the organic layer. We note that if tunneling indeed occurs through a 25nm thick layer, it cannot be direct tunneling. Multistep tunneling is a possibility, which would take advantage of some sort of states far inside the gap as a stepping stone. [78] The behavior of the I-V curves shown in Fig. 3.7 b) for a thicker device (40 nm) is however strikingly different. The I-V curves have now become strongly temperature dependent, and, at low temperatures, strongly non-linear. In the light of two recent works, these kinds of I-V curves, together with the observation of sizeable GMR (Fig. 3.6) are indicative of spin-injection.

Nevertheless, Fig. 3.6 shows that the GMR quickly decays with increasing thickness, and becomes unobservable for thicknesses of greater than 100 nm. This spin-diffusion length is not significantly larger than that observed in spin-valves based on organic semiconductors other than $C_{60}$. Our observation is contrary to our expectation that the spin-diffusion length in $C_{60}$ should be much larger than in organic semiconductors that exhibit much stronger hyperfine coupling.

3.6 Scenarios to Explain Unexpectedly Short Spin Diffusion Length

We can think of three different scenarios that could explain this result.

a) a mechanism other than hyperfine coupling is the dominant spin-relaxation mechanism in organic semiconductors. Spin-orbit coupling is a possibility. Indeed, the relevant spin-orbit coupling matrix element for $C_{60}$ was recently estimated to be $\approx 10\mu\text{eV}$ [79, 80], i.e. about ten times as strong as typical hyperfine values in organic semiconductors [14]. However, Rybicki et al. [81] recently pointed out that time-reversal symmetry of the spin-orbit coupling Hamiltonian prevents electron spin-precession about the effective magnetic field produced by the orbital motion. This is a consequence of Kramers
degeneracy. To avoid possible misunderstandings we point out that the treatment by Rybicki et al. is valid for stationary electron wave functions. In band transport systems that support itinerant Bloch-type electron wave functions, spin-precession due to spin-orbit coupling is possible in crystals that lack inversion symmetry. This is the so-called Dyakonov-Perel \cite{82} mechanism. We do not believe that this mechanism applies to organic hopping systems. The dominant importance of hyperfine coupling to the spin-physics in organics has also been amply demonstrated \cite{43, 44, 17}. For example, a recent work examined the spin-diffusion length in organic spin-valves in deuterated and undeuterated compounds, and clearly demonstrated a significantly larger spin-diffusion length in deuterated materials, where the hyperfine coupling is weaker \cite{44}. Nevertheless this possibility can not be excluded.

b) TMR is the cause of the observed spin-valve effect, and the decay of spin-valve signal is simply a consequence of the diminishing contribution of tunneling current to the device current with increasing thickness. This explanation is unlikely, because we have shown above that the I-V curves of a 40nm device are typical of injection, but still a sizable MR is observed. A possible contribution due to tunneling, which would exhibit parabolic and temperature independent differential conductance traces is negligibly small (see Fig. 3.7). We also note that an examination of the relative positions of the Fermi energies in the electrode and $C_{60}$ layers suggest that the barrier for electron injection into $C_{60}$ should be relatively small. Indeed, $C_{60}$, with its relatively low lying LUMO \cite{83}, is well known as an organic material with very favorable conditions for electron injection and transport \cite{84}.

c) Layers with increasing thickness lead to a larger and larger conductivity mismatch, reducing the spin-valve signal for large layer thickness. In this scenario, the I-V curves for small $C_{60}$ layer thickness look like tunneling I-V curves because the interface resistance due to tunnel injection outweighs the transport resistance through the organic
layer. With increasing layer thickness, however, the bulk resistance grows, finally out-
weighing the tunnel interface resistance, resulting in I-V curves typical of bulk-limited
transport in organic semiconductors. As the bulk resistance starts to dominate the inter-
face resistance, the conductivity mismatch becomes applicable, resulting in diminishing
spin-valve signal.

At present, scenario c) seems the most likely to us, e.g. because of the relatively
close alignment of the $C_{60}$ LUMO with the electrodes’ work function, although further
study is clearly necessary. For example, from a series of measurements with increasing
organic layer thickness, one could separate contribution due to interface resistance and
bulk resistance, and correlate this with the measured spin-valve signal. Careful device
modeling should accompany such an endeavor.

3.7 Conclusions and Future Outlook

Motivated by recent work that suggests that the spin-transport length in organic
semiconductors is limited by hyperfine coupling, we fabricated organic spin-valves based
on $C_{60}$. In our experiments, however, we do not observe a significantly increased spin-
diffusion length. We discussed three possible explanations for this observation: a) A
mechanism other than hyperfine coupling causes the loss of spin-polarization; b) In
thick devices an increasing conductivity mismatch limits spin-injection; c) The observed
magnetoresistance is really due to tunneling magnetoresistance which would disappear
for $C_{60}$ thicknesses beyond the tunneling range. Based on an analysis of the devices’
current-voltage curves, and expectations resulting from the close match of the electrodes’
work function with the lowest unoccupied molecular orbital of $C_{60}$, we propose the
conductivity mismatch as a likely cause of the loss of spin-valve signal with increasing
$C_{60}$ layer thickness.

Although we did not observe a significantly increased spin diffusion length in $C_{60}$
spin-valve devices, but it does not mean that fullerene materials are not good candidates
for spintronics applications. For example, carbon nanotubes and graphene, both of which have even higher mobility with weak hyperfine interaction strength, should be excellent ones for spin-valve devices. For carbon nanotube spin-valve devices, placement of carbon nanotubes with high density and excellent selectivity is the prerequisite of the applications. Based on the chemical self-assembly method recently developed [85], we developed a new method using potassium salt to remove excess anionic surfactant easier and more efficiently, and improved the placement of carbon nanotubes with higher density and selectivity, shown in the Fig. 3.8 (paper in preparation in collaboration with IBM Research).

Besides, we recently found that X-ray exposure generated by the e-beam evaporation system may affect organic films, introducing traps, decreasing their mobility, and limiting the spin-diffusion length. Therefore, using a modified fabrication procedure based solely on thermal evaporation may lead to improved devices.

Figure 3.8: Selective placement of carbon nanotubes on substrates. (The potassium salt method applied.)
CHAPTER 4
DISTINGUISHING BETWEEN TUNNELING AND INJECTION
REGIMES OF ORGANIC SPIN-VALVE DEVICES

4.1 Introduction

The first demonstration of an organic spintronic device employed a planar structure of \( \text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3 \) (LSMO) electrodes separated by an \( \approx 100 \) nm long channel of \( \alpha \)-sexithiophene [11]. The first vertical organic spin valve device, which utilized LSMO and Co as the ferromagnetic layers, was demonstrated by Xiong et al. [10] and exhibited a clear spin-valve effect. The relatively thick spacer-layers employed in Ref. [10] (>100 nm) suggest that spin-injection into the organic layer (rather than tunneling through it) must have occurred. However, these devices display a surprisingly low resistance at low-bias (<100 mV), weakly temperature-dependent current-voltage (I-V) curves and approximately parabolic differential conductance traces. All of these properties are characteristic of tunneling, and are uncharacteristic of organic semiconductor devices that function by carrier injection and hopping transport (cf. organic light-emitting diodes OLEDs [86]), as we will show below. Recently, TMR using the organic semiconductor rubrene was demonstrated with tunneling distances as long as 15 nm [87].

Apparently both spin-injection and spin-tunneling are possible, and a criterion for a clear distinction between tunneling and injection is required for the proper analysis of spin-valve effects in organics. Since tunneling is expected to dominate in thin junctions, but decays exponentially with increasing thickness [32], there will be a critical thickness beyond which tunneling is improbable, and injection will become the dominant mode of conductivity. In our experiments we looked for and identified this transition between the two modes of conductivity. A similar strategy was recently employed in LSMO/rubrene/Fe devices [76].

The distinction between tunneling and spin-injection is crucially important for
possible semiconductor spintronics applications: only if the spin gets injected into the semiconductor (i.e. its wavefunction is entirely contained within the semiconductor) is the effective manipulation of its spin-state, necessary for logic gates [88, 89], possible. We note that in inorganic semiconductor spintronics identification of spin-injection is possible using spin-orbit-coupling-based methods and Hanle effect measurements. In organic semiconductors, however, the minuteness of spin-orbit-coupling [81] makes such measurements extremely difficult [90]. Furthermore, the very slow carrier drift velocity requires very small Hanle magnetic fields. The presence of hyperfine fields [43] will mask the Hanle effect. We note that two methods for detecting spin-injection in organics have recently been demonstrated [91, 92] using two-photon photoemission and low-energy muon spin rotation, respectively. However, these are very complex experiments that are not widely available.

4.2 Device Fabrication and Measurements

Our devices were fabricated on Si wafers covered with 300 nm of thermal oxide. The wafers were diced into 12.5×9 mm pieces, washed in several solvents and finally cleaned in an oxygen plasma-cleaner. All these steps were performed in a class 1000 clean-room. A 15 nm thick Co electrode was deposited by electron-beam evaporation through a shadow mask in high-vacuum at a rate of 0.1nm/s and covered by a 2.5 nm thick Al layer, also deposited by electron-beam (e-beam) evaporation. The Al layer was then oxidized ex-situ in an oxygen plasma. The Al layer thickness and plasma oxidation time were chosen to yield a maximum room-temperature TMR signal of ≈ 8-10% in a Co/Al-oxide/Fe device. The purpose of the Al-oxide (AlO) layer is to crucially improve the film quality of the organic film that will be grown on top of it, because we found, in agreement with earlier work [93, 94, 95, 87], that organics grow more uniformly and with a smoother surface on oxides than on metals. The rubrene spacer layer was grown by thermal evaporation in high-vacuum at a rate of 0.1nm/s. All fabrication steps involving
the organic layer were performed inside a glove-box or inside the glove-box-integrated vacuum evaporation chamber. Finally a 15 nm thick Fe top electrode covered by 15 nm of Al was deposited by electron beam evaporation at a rate of 0.1 nm/s. The RMS roughness of the individual layers was measured using atomic force microscopy (AFM) in unfinished devices as follows: Co: \( \approx 300 \) pm, rubrene at 10 nm: \( \approx 600 \) pm. 12 devices of an area of 130x130 \( \mu \)m were fabricated on each substrate. The substrates were then mounted inside a closed-cycle He cryostat located between the poles of an electromagnet. I-V and magnetoresistance (MR) measurements were performed using a Keithley 2400 source measure unit, with the positive pole connected to the Co electrode. The I-V curves reported here were typically obtained by measuring \( \approx 5 \) devices on a substrate and averaging the corresponding data. This resulted in low noise traces that can be numerically differentiated resulting in differential conductance traces. The reported MR traces are for individual junctions.

For comparison, we also fabricated a rubrene device using electrode materials commonly employed for fabricating OLEDs, specifically poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT) spin-coated on top of an Indium-Tin-Oxide (ITO) covered glass slide as the bottom electrode, and Ca covered by Al as the top electrode. Otherwise the fabrication procedures for the rubrene organic light emitting diode (OLED) follow that of the ferromagnetic junctions described above. The device area was \( \approx 750 \times 750 \) \( \mu \)m, the rubrene layer thickness was 20 nm.

Magneto-optic Kerr effect (MOKE) measurements were performed at various temperatures using a focused HeNe laser beam. Changes in beam polarization were detected by measuring the intensity reflected off the sample located between two crossed polarizers as a function of \( B \). A Si detector and a lock-in amplifier (together with an optical chopper) were used for measuring the light intensity. The MOKE data for the bottom Co electrode was measured directly on the electrode line of the device, whereas the MOKE data for the top Fe electrode was measured on an electrode line deposited on top of
a 10nm rubrene film. In the latter measurement, the Fe/rubrene interface is optically inaccessible, and the Fe/air interface was measured instead.

### 4.3 Two Different Types of Current-voltage Characteristics

Fig. 4.1 a) and b) shows measured I-V traces in devices with two different rubrene thicknesses, 10nm and 20nm, respectively, at various temperatures ranging from room-temperature to \( \approx 13K \). Fig. 4.2 a) and b) shows room-temperature I-V data of devices with several different rubrene thicknesses, \( d \), this time plotted as differential conductance versus the (average) electric field. The electric field was determined by dividing the voltage by the sum thickness of the AlO and rubrene films. We note that a typical resistance measured in our Co/AlO/Fe devices is less than 1 k\( \Omega \), whereas the typical resistance in even our thinnest rubrene devices is on the order of 100 k\( \Omega \) at comparable bias suggesting that our rubrene layers are near-pin-hole-free. Comparison of the data shown in Figs. 4.1 a) and 4.2 a) with that shown in Figs. 4.1 b) and 4.2 b) makes it clear that there exist two entirely different modes of conductivity in our devices. The mode shown in Figs. 4.1 a) and 4.2 a) displays weak temperature dependence and near-parabolic differential conductance traces typical of tunneling conduction and occurs in devices with thickness \( d \leq 15nm \). Our data agrees with data published for similar TMR devices with similar thicknesses by the MIT group [87]. The tunneling nature of this mode is confirmed by plotting the junction current measured at a bias voltage of 0.5 V vs. \( d \). As expected for tunneling the dependence is exponential, from a fit to the dependence \( \ln(I) \propto -d/d_0 \) we obtain a tunneling decay length, \( d_0 \approx 1 \text{ nm} \), i.e. the length at which the conductivity has dropped to \( 1/e \) times the value of the Co/AlO/Fe "0 nm" device (to avoid confusion, we emphasize that \( d \) is the thickness of the rubrene layer alone, not including the AlO layer).

The mode shown in Figs. 4.1 b) and 4.2 b), on the contrary, is strongly temperature dependent, and the IV-curves are typical of those commonly measured in OLEDs:
Figure 4.1: Current-voltage (I-V) characteristics of Co/AlO/rubrene/Fe junctions at different temperatures. a) Device with rubrene thickness of 10nm. Note that the IV curves for 100K, 200K and 300K are almost overlapping. b) Device with rubrene thickness of 20nm. c) I-V characteristics of a PEDOT/rubrene (20nm)/Ca OLED at different temperatures.
Figure 4.2: Differential conductance versus average electric field of Co/AlO/rubrene/Fe junctions at room temperatures for different rubrene thicknesses, $d$. a) $d=5$, 10, and 15nm. b) $d=15$ and 20nm. Notice that the data in both panels are plotted on two different y-scales, left and right y-axis. The corresponding y-axis is assigned using an arrow. Inset: Natural logarithm of the tunneling current $I$ measured in $A$ at a bias voltage of 0.5V versus $d$. The 0 nm data refers to a Co/AlO/Fe junction. The line is a fit to an exponential.
They possess an onset voltage below which hardly any current flows, and above which the current increases in a highly non-linear fashion. The similarity to OLEDs is clearly demonstrated by comparison with Fig. 4.1 c) which depicts data measured in a rubrene OLED. Both Fig. 4.1 b) and c) show a very similar functional dependence between current and voltage, as well as a characteristic temperature dependence where, with decreasing temperature, larger and larger biases are required to obtain a certain conductivity. Since current conduction in OLEDs is well-known to occur by carrier-injection followed by carrier hopping [96], we assign the second mode observed in our ferromagnet/organic semiconductor/ferromagnet junctions to carrier injection/hopping.

OLED I-V curves are commonly explained by either a space-charge limited current model [96] or modeled by Monte Carlo simulations considering (nearest neighbor) hopping in a disordered density of states [97]. In both models, the high non-linearity is caused by a distribution of deep traps. Fig. 4.2 a) shows that the tunneling current is barely detectable for the 15 nm device (note that the data are plotted on two different y-scales, left and right y-axis), and shows the beginning of the injection mode at a bias of \( \approx 75 \text{ mV/nm} \). The 15nm data is replotted in Fig. 4.2 b) on a larger y-scale to demonstrate the dominance and high non-linearity of the injection mode at larger biases. Fig. 4.2 b) also shows the differential conductance of a much thicker device \( (d=50 \text{ nm}) \) demonstrating injecting behavior.

In a recent work, Yoo et al. [76] performed a study of LSMO/rubrene/Fe junctions. They identified two modes of conductivity: tunneling and a mode they called phonon-assisted field emission. In the latter mode carriers are injected into the organic layer even at low bias, resulting in I-V curves that look similar to the tunneling case. This mode of injection is different from the injection mode we found in this work, for which the conductivity at low bias is negligible. Injection due to field emission at low bias can occur only as a temperature activated process because the carriers must overcome a significant energy offset between electrode workfunction and unoccupied energy levels.
Figure 4.3: Magnetococonductivity traces measured in a Co/AlO/rubrene(5nm)/Fe device (thin lines) and a Co/AlO/rubrene(10nm)/Fe device (thick lines), at a bias of 0.2 V, at room temperature (panel a) and 100K (panel b).

in the organic. As a result this injection mode is highly temperature dependent, but even at room temperature the electrode injection resistance is quite large and the device conductivity is injection limited. We do not observe this mode in our experiments, where the I-V exhibit a direct transition from tunneling to OLED-like, i.e. bulk-limited, hopping conductivity (see section 4.5).
4.4 Magnetoresistance

Fig. 4.3 shows magnetoconductivity traces, $\Delta I/I \equiv \frac{I(B) - I(B_{\text{max}})}{I(B_{\text{max}})}$ measured in two devices, one with $d = 5 \text{ nm}$ (thin lines) and the other with $d = 10 \text{ nm}$ (thick lines) at two different temperatures, 300K and 100K (panels a) and b), respectively. $B_{\text{max}}$ is the maximum reported field in the respective graphs, and corresponds to a parallel orientation of the two electrodes. At 100K both devices show a maximum MR ratio of 5-6% which shows that spin polarized tunneling can occur over lengths $\geq 10\text{nm}$. Our observation is consistent with results obtained by the MIT group for rubrene [87]. For the 10nm device a similar MR ratio is also achieved at room-temperature, whereas the MR ratio for the 5nm device is significantly smaller than its 100K value. This possibly indicates a competing pin-hole transport mechanism active at room-temperature in the very thin junction. We note that we found a device to device variation of $\approx 1\%$ absolute in MR, but somewhat larger than that for the 5 nm devices at room temperature. The figures also demonstrate that the coercive field of the electrodes increases significantly with decreasing temperature. Such behavior was also previously observed in organic spin-valves [10] and may indicate pinning of domains on the organic semiconductor surface.

Fig. 4.4 shows a comparison between the magnetoconductivity data for the 10nm rubrene device and MOKE data for the ferromagnetic electrodes. The comparison is shown for room-temperature in panel a) and for 100 K in panel b). The MOKE data for the bottom Co electrode was measured directly on the electrode line of the device and reproduces the switching behavior of the lower electrode observed in the magnetoconductivity data quite well. The top Fe electrode interface with rubrene is however optically inaccessible because the Si substrate is opaque at the HeNe laser wavelength. Instead, a Fe electrode line was deposited on top of a rubrene-covered Si substrate, and the MOKE data was measured for the Fe-air interface. Although the MOKE data for the Fe electrode agrees reasonably well with the magnetoconductivity data, and accurately
Figure 4.4: Comparison between magnetoconductivity traces measured at a bias of 0.2 V in a Co/AlO/rubrene(10nm)/Fe device (thin lines) and magneto-optic Kerr effect traces (thick lines), at room temperature (panel a) and 100K (panel b). For the MOKE data, the inner loop is for the Co bottom electrode, and the outer loop for the Fe top electrode.
reproduces the temperature dependence of the switching field, the MOKE data exhibits a much sharper switching behavior than that observed in the magnetoconductivity data. This discrepancy may be due to the fact, as described above, that we cannot measure the rubrene/Fe interface directly. At present we do not have a firm explanation for the rather rounded switching of the top Fe electrode observed in the magnetoconductivity data, but it could be due to imperfections in the rubrene/Fe interface. We will address this issue in our future work. For the 15 nm device the tunneling current has become very small even at larger biases (see Fig. 4.2 a)), and no MR (with roughly 0.1% accuracy) could be detected. We have similarly been unable to detect any MR for thicker devices (at the necessarily larger biases required for measurable conductivity). The absence of TMR at these larger biases is not unexpected since we found, in agreement with other works on tunneling junctions [87], that the MR ratio decreases significantly with increasing bias voltage. In addition, no MR was detected at biases leading to injection conductivity.

4.5 Discussion of Two Different Modes of Conductivity

Our results yield a value of $\approx 1$ nm for the tunnel decay length in rubrene (see Fig. 4.2, inset). A measurable tunneling conductivity through the organic semiconductor layer is limited to devices of $\approx 15$ nm thickness or thinner. Reports of giant magnetoresistance (GMR) effects in organic spin-valves with a thickness in excess of 100 nm [10, 98, 99] clearly seem beyond the tunneling range. Tunneling scenarios in such thick devices would only be plausible if there existed locally thin regions in the organic layer (i.e. the film quality is poor or effects occurring at sharp edges of devices), or if the effective barrier height for tunneling through the organic were exceptionally low. The latter scenario is highly unlikely, though: $d_0$ is proportional to the square root of the barrier height, and a ten-fold larger $d_0$ would require a tunnel barrier 100-fold smaller
than in our devices.

If one rejects tunneling through the thick organic layer as a possibility for the spin valves reported in Refs. [10, 98, 99], then an alternate explanation is required for their I-V curves which are clearly characteristic of tunneling, and not injection, devices. This is possible modeling the devices as a series of (at least) two resistors. One corresponds to the resistance to carrier injection from the electrodes into the organics. Another represents the resistance to the transport of the carrier/spin through the organic. In OLEDs efficient hole- and electron-injection electrodes are employed (such as PEDOT and Ca, as in the case of the OLED data we report here) resulting in small injection resistance and bulk-limited devices. However, in devices using LSMO, Co or Fe the injection resistance will be much larger than in OLEDs, since these materials are much less efficient injectors due to their unfavorable work functions. Assuming that the devices in Refs. [10, 98, 99] are (tunneling) injection limited rather than bulk-limited, their I-V curves would mimic tunneling even though carriers get injected into the organic.

Such a scenario could also explain the recent observation of injection-GMR in LSMO/rubrene/Fe junctions in the regime of phonon-assisted field emission [76]. In these devices conduction is still injection-limited. Because the spin-dependent injection resistance is much greater than the spin-independent bulk resistance the possible conductivity mismatch problem is overcome [100, 101]. We note however that we did not observe this scenario in our study using Co and Fe as the electrode materials: For thin devices we observed tunneling through the devices, as evidenced by the exponential decay of the current with increasing layer thickness. In our devices with \( d \geq 15 \) nm, however, the I-V curves are like those of typical OLEDs and therefore typical of bulk-limited devices. In bulk limited devices the resistance of the organic semiconductor outweighs the injection resistance, and the conductivity mismatch may apply. This could explain the absence of injection GMR in our devices. We note that whereas the conductivity mismatch problem is well established for inorganic semiconductor spintronics, the situation is much less
understood in organic spintronics. Nevertheless, significant progress in the modeling of organic spintronics devices has been made (Refs. [102, 103, 48] and references therein). Schoonus et al. [78] recently demonstrated a loss of spin-valve signal as the mode of conductivity changes from singlestep to multistep tunneling in CoFeB/Al$_2$O$_3$Alq$_3$/Co devices. This shows that additional mechanisms of loss of spin-polarization are active once spins get injected into the organic and may provide another reason for the absence of spin-valve signal in the injection devices we studied.

4.6 Summary and Future Work

Two different modes of conductivity in Co/AlO/rubrene/Fe junctions have been clearly demonstrated. The first mode, tunneling, occurs in relatively thin junctions, $d < 15$ nm, and decays exponentially with increasing rubrene thickness. We determined the tunneling decay length to be $\approx 1$ nm. The tunneling mode is also characterized by a weak temperature dependence and a nearly parabolic differential conductance. The second mode, injection followed by hopping, occurs in relatively thick devices, $d \geq 15$ nm, and can be identified by strongly temperature dependent, highly non-linear I-V traces that are similar to those commonly measured in OLEDs. We observed MR in devices with a rubrene thickness of 5 nm and 10 nm. Those devices are clearly in the tunneling regime. For the 15 nm device, for which the tunneling current is just barely measurable we could not observe magnetoresistance. GMR could also not be detected in the injection regime (for $d \geq 15$ nm). The conductivity mismatch problem provides a possible explanation for the absence of magnetoresistance in this regime.

Recently, we found that X-ray exposure generated by e-beam evaporation system may affect organic films, introducing traps, decreasing their mobility, and limiting the spin-diffusion length. Therefore, interesting future work could include a study of how trap-generation affects the transition thickness between the tunneling and injection regimes.
There has been much interest in the detection of spin-injection in OSCs for the purposes of developing spintronic logic devices. Therefore, carefully distinguishing between tunneling and injection is important for properly analyzing spin-valve phenomena in organic semiconductor devices, in particular for proving spin-injection.
5.1 Introduction

It has been found that hyperfine interaction is important for current theories of both organic magnetoresistance (OMAR) and organic spin-valve, the two most studied effects of organic spintronic devices. The hyperfine interaction can be viewed as the precession of the electronic spin about the local hyperfine field, which is a quasi-static magnetic field that varies randomly in direction from molecule to molecule, as shown in Fig. 3.1.

Although the exact mechanism behind OMAR is still debated, there exists some agreement that the hydrogen hyperfine fields are involved, influencing spin-dependent reactions between paramagnetic species (polarons, triplet excitons) [61, 65, 17]. At the same time, hyperfine interaction is important also for spin valves: as the initially spin-polarized carriers diffuse through the device along different paths, the different local hyperfine-induced precessions they experience will lead to a dephasing and loss of spin polarization. Indeed, a successful theory of spin diffusion in organic semiconductors has been formulated along these lines [43].

Although hyperfine interaction lies at the heart of both the current theories of OMAR and organic spin-valves, they depend on the hyperfine strength in a completely opposite way. Whereas hyperfine interaction causes the OMAR effect, and therefore the effect increases with increasing hyperfine strength, strong hyperfine fields cause spin-randomization and therefore reduce the observed spin-valve effect. Indeed, it has remained a significant mystery why then large OMAR and long spin-diffusion length are observed in organic devices using the same organic semiconductor, namely tris(8-hydroxyquinolinato) aluminium (Alq$_3$) [10, 104]. Here we will show that the conditions
for large OMAR and large giant magnetoresistance effect, respectively, are indeed complimentary to each other, and, in particular, that they depend on the trap concentration in opposite ways.

The motivation for this project is developed from an intriguing set of observations that we have made while working on organic spintronic devices over the years. We found that the performance of both OMAR and spin-valve devices very sensitively depends on whether the metallic layers are deposited by thermal evaporation or electron-beam evaporation. We will show that this behavior results from the generation of traps through the exposure of the organic layer to x-ray bremsstrahlung that is generated during the electron-beam (e-beam) evaporation process. Our analysis of the role played by traps in organic spintronic devices will allow us to shed light on the physics of these devices, and indicate the possibility of using ”trap engineering” to optimize the performance of organic magnetosensors.

5.2 Effects on Organic Spin Valve Devices

5.2.1 Device Structures

Our spin-valve devices were fabricated on SrTiO$_3$ (STO) (001) substrates. On these substrates, a 1-mm wide, 100-nm thick LSMO film was fabricated by pulsed laser deposition through a shadow mask. The LSMO deposition was performed with a KrF excimer laser (248 nm) in 320 mTorr $O_2$ at 700°C with a laser fluence of 1-1.5 $Jcm^{-2}$, followed by postgrowth cooling in 300 Torr $O_2$. The LSMO covered substrates were washed in several solvents using an ultrasonic cleaner and handled in a class 1000 cleanroom. As the organic semiconductor spacer layer, the Alq$_3$ layer was fabricated by thermal evaporation in a vacuum of $10^{-6}$ mbar at a rate of 0.1 $nms^{-1}$. The Fe top electrodes were deposited by thermal evaporation. For comparison, a second group of otherwise identical devices was fabricated, this time using e-beam evaporation for the
Figure 5.1: Spin-valve effects for pristine and X-ray exposed devices: a) Thickness dependence of the magnitude of the observed spin-valve response at 12K, both for a pristine device (scatter plots with square symbol) and an X-ray exposed device (scatter plots with triangle symbol, 20 mins exposure time). From this data the spin-diffusion length can be extracted. b) Voltage dependence of the observed spin-valve response at 12K. c) Temperature dependence of the magnitude of the observed spin-valve response. d) Magnetoresistance traces at 12 K for the pristine device.

Fe top electrode. The device area was approximately 1 mm$^2$. 
5.2.2 Difference in Magnetoresistance and Current-Voltage Characteristics of Organic Spin Valve Devices Caused by X-ray Exposure

Figure 5.1 shows the observed spin-valve response, both for a pristine device (scatter plots with square symbol) and an x-ray exposed device (scatter plots with triangle symbol, 20 mins exposure time). Figure 5.1(a) shows that the pristine and irradiated (20-minute) devices exhibit a spin-diffusion length at 12 K of $\approx 40$ nm and $\approx 7$ nm, respectively. This demonstrates that the spin-diffusion length in organic spin valves is very sensitive to the presence of traps. The remaining panels of Fig. 5.1 show additional data measured in the spin valves for completeness. The voltage dependence and temperature dependence we observe agree well with those observed by others, and we refer to the literature for a discussion of these dependencies [10]. Fig. 5.2 shows measured I-V traces for the pristine (thick lines) and irradiated (thin lines) devices at 12K with three different Alq$_3$ thicknesses, 5nm(a), 20 nm(b), and 60 nm (c). The three panels show that the irradiated devices are dramatically more resistive and have I-V traces that are more non-linear. Further studies are required to uncover the nature of this dramatic change, but it is possible that it is related to bistability effects recently reported in organic spin valves. Dediu and co-workers [105] suggested a mechanism for this bistability based on charge storage in deep traps. Our experiments may support this model, and provide a simple technique to quantitatively relate bistability and trap concentration in future work.

5.2.3 Discussion of the Reduction in Spin-diffusion Length

Let us now turn to the discussion of the experimental findings, starting with the reduction in spin-diffusion length. For the purpose of this discussion, we will compare this experimental observation with the expectations that arise from current theories of
Figure 5.2: Current-voltage (IV) characteristics for LSMO/Alq₃/Co organic spin-valves with three different organic layer thickness shown for both the pristine devices and X-ray exposed devices.
the spin-diffusion length in organic devices. To the best of our knowledge, two different such theories have been developed in detail so far. Chronologically the first theory [43] is based on hyperfine interaction. As the carrier moves through the organic film, it will precess about the random local hyperfine fields, and carriers taking different paths through the film will dephase unpredictably. Bobbert et al. [43] have reported a detailed numerical Monte-Carlo simulation of hyperfine-induced spin-randomization as a function of various device and material parameters. These simulations showed, that in a certain limit, the spin-diffusion length, $l_s$, can be written as

$$ l_s = \frac{r^2}{2a}, \quad (5.1) $$

where $a$ is the intermolecular distance, and $r$ is the ratio of the spin-precession period to the average time the carrier spends on each site. We do not claim that we are in the limit where Eq. 5.1 holds strictly, but for a qualitative analysis this formula should be sufficient. It certainly captures the main idea of the hyperfine-limited spin-diffusion length, because the larger $r$, the faster the carrier moves and the less time there is for the hyperfine interaction to reorient the spin. Since traps slow down carrier motion, our experimental observation that the spin-diffusion length decreases is certainly in line with the hyperfine model.

The second model for the spin-diffusion length was proposed by Yu [106] and is based on spin-orbit coupling. Yu gave the following expression:

$$ l_s = \frac{a}{4\gamma}, \quad (5.2) $$

where $\gamma$ is a measure of the molecule-internal spin-orbit coupling strength. In this model the spin-diffusion length does not depend on mobility or the time the carrier spends on a site, but only on the number of hops the carrier makes [106]. Therefore this model appears to be incompatible with our experimental results.
5.2.4 Conclusion and Future Outlook

In summary, we demonstrated that X rays produced during e-beam evaporation strongly reduce spin diffusion length. Therefore, appears that studies, reported in the literature, of the spin-diffusion length in devices fabricated by e-beam evaporation (e.g. [76, 77]) may have to be carefully reevaluated. The reduced spin-diffusion length upon X-ray irradiation is not too surprising. However, next we will show that it can also have a positive effect in organic spintronic devices, specifically in OMAR devices. The second part of this chapter was completed in close collaboration with James Rybicki, a former PhD student in our lab.

5.3 Effects on Organic Light Emitting Diode Devices

5.3.1 Device Fabrication and Measurements

The structure of our OMAR devices is largely identical to that of organic light emitting diodes (OLED). Our devices were fabricated on glass substrates, coated with 40 nm of indium tin oxide (ITO) and a \(\approx 100\) nm thick layer of the conducting polymer Poly (3,4-ethylenedioxythiophene)-poly (styrene-sulfonate) (PEDOT). All subsequent manufacturing steps were carried out in a deposition chamber located inside a nitrogen glovebox. Next, the organic layer Alq3 (70 to 100 nm) followed by the top electrode calcium (20 nm), and a capping layer of aluminum (40 nm) were deposited by thermal evaporation.

Current-voltage (I-V), electroluminescence quantum efficiency, \(\eta_{EL}\) and magneto-conductivity (MC) experiments were performed on these devices. To study the effect of the electron beam’s radiation, as it would have occurred if the metallic layers of the devices had been fabricated by e-beam evaporation, the devices were then returned into the deposition chamber, the electron beam (4.5 keV) was then turned on and directed onto a Au target for a time of up to 25 mins. We choose a beam current of \(\approx 40\) mA, a
value typically used for Al evaporation, but insufficient for evaporation of the Au target. After this exposure, we again performed I-V, electroluminescence quantum efficiency and magnetoconductivity experiments on these devices.

Therefore, our procedure allows us to make accurate comparisons between pristine and radiation exposed devices. We emphasize that in our radiation treatment neither the e-beam nor any evaporated metal hits the OMAR device, rather the effects we report below must be due to a secondary radiation (which we will identify as bremsstrahlung).

5.3.2 Difference in Current-Voltage Characteristics, Quantum Efficiency, Organic Magnetoresistance of Organic Light Emitting Diode Devices Caused by X-ray Exposure

Fig. 5.3 (a) shows I-V measurements for Alq₃ OLED/OMAR devices irradiated for 0, 10, and 25 minutes at an e-beam current of 40 mA and an accelerating voltage of 4.5 kV. The onset voltage increases significantly with exposure time, the increase being approximately proportional to the exposure time. The larger electric fields that are required in the irradiated devices to drive a significant current are indicative of the presence of increased disorder within the irradiated Alq₃ film. Fig. 5.3 b) shows that irradiation also leads to a significant reduction in the electroluminescence quantum efficiency, \( \eta_{EL} \).

Fig. 5.4 a) shows magnetoconductance traces for the pristine as well as X-ray exposed devices. The pristine device demonstrated only a small OMAR effect, with a maximum change in conductance of approximately 0.5 %, whereas this value increased to 7.7 % and 15.5 % for the ”10 minute” and ”25 minute” devices, respectively (even longer exposure times lead to unstable devices). All OMAR traces shown are for the bias voltage that gives the largest magnetoconductance (see Fig. 5.4 b and c).

Comparing Fig. 5.4 a) with the corresponding I-V and electroluminescence data in Fig. 5.3 a) and b) we arrive at the initially somewhat surprising conclusion that the
Figure 5.3: The effect of X-ray irradiation on a) current-voltage characteristics and b) electroluminescence quantum efficiency, for PEDOT/Alq₃ (100 nm)/Ca devices with 25 minutes, 10 minutes, and zero minutes of exposure time.
Figure 5.4: OMAR effects for pristine and X-ray exposed devices: a) Magnetococonductance traces for the pristine and X-ray exposed PEDOT/ Alq₃(70 nm)/Ca devices, respectively. b) Dependence of the measured OMAR effect on the voltage for several different temperatures for x-ray irradiated (25 mins) device c) Dependence of the measured OMAR effect on the voltage for several different temperatures for pristine device.
devices work best as OMAR devices, when they show the poorest performances as light emitting diodes and are the most resistive. However, our results are in agreement with recent reports [107, 108] that demonstrated that the production of traps through ”device conditioning” leads to an increase in magnetoconductance.

5.3.3 Confirmation of X-ray Damage to Organic Light Emitting Diode Devices

To determine the nature of this secondary radiation we inserted Al shields of different thickness between the device and the Au target. The shields were implemented by thermally evaporating an additional Al layer onto the finished device.

It is widely known that bremsstrahlung is produced during e-beam evaporation: as the accelerated e-beam hits the metal target the electrons experience a sudden deceleration, and photons are emitted over a wide spectrum. We propose that it is the bremsstrahlung that leads to the irradiation effects we observe. We now confirm that soft-X-ray photons are the cause of the irradiation effects, rather than heat radiation or visible/UV radiation that are also generated during metal evaporation.

To answer this question we take advantage of the fact that photons can be shielded using metal layers, and the thickness of the required shield is related to the photon wavelength through the so-called skin-depth. We chose to use Al as the shield, since its transmission coefficient is well documented in the available literature over a wide frequency range [109]. Guided by initial experiments, we selected three different Al shield thickness for more detailed measurements: 100nm, 200nm and 300nm. Fig. 5.5 shows a 100 nm thick Al shield does not lead to efficient protection from the radiation, as the I-V curve is similar to the unshielded device. However, a 200 nm shield provides effective protection, and increasing the shield thickness to 300nm only leads to a small shift in the I-V characteristics. According to Ref. [109] the skin depth in Al equals 200nm for a photon energy of 0.4 keV, or 3nm wavelength. Of course this number is a kind of
Figure 5.5: Demonstration that the device can be effectively shielded from the radiation damage using a relatively thick layer of Al.
average, since the bremsstrahlung has a broad spectrum and the spectral efficiency curve for the irradiation damage is not known. Nevertheless, the number appears reasonable for a 4.5 keV bremsstrahlung spectrum that is produced by our e-beam evaporator, and confirms that the damage is caused by soft-X-ray photons.

5.3.4 Determination of Trap Depth and Density

Initially one would hope that the generated defects can be detected and characterized directly by infrared (IR) or Raman spectroscopy. However, as was found to be the case also in temporal degradation induced defects in OLEDs [110], their density is too small, and we did not succeed to detect their spectral signatures using common spectroscopies, including infrared FTIR, Raman and photoluminescence optical spectroscopy and XPS. Nevertheless, we have succeeded in making the traps visible using the TSC technique, which is well suited for the investigation of traps. The TSC experimental setup was introduced in chapter 2.

Fig. 5.6 shows the measured TSC traces for the pristine device, and the device after exposure to 3 and 20 minutes of x-ray radiation. In this figure we report the TSC spectrum as an Arrhenius plot, which aids the identification of the relevant excitation energies. The TSC spectrum of the pristine device, consisting of a broad peak, agrees well with that reported by other groups [111, 56]. We note that the steep increase in signal at high temperatures is caused by leakage current, and is not related to stimulated current. In the irradiated samples, the most obvious change is that the broad peak decreases in magnitude. In addition, a sharp feature appears in the irradiated devices at large temperatures (see inset to Fig. 5.6 for a zoomed view). Since this sharp feature is entirely absent in the pristine device, it is clear that it is the signature of thermal release from deep traps that are generated by the X-ray irradiation. Indeed, the low temperature side of this peak coincides well with a straight line (dotted lines in the figure), and the incline of the line yields a trap depth of approximately 0.5 eV. The depth of these traps
Figure 5.6: Measured TSC traces for the pristine device, and the device after exposure of 3 minutes and 20 minutes of x-ray radiation. Dotted lines are interpolations, strong oscillations, which were removed from the data, occurred in this temperature region because of instabilities in the temperature controller. Inset: feature of the trace related to deep traps generated by X-ray irradiation.
should be compared to the width of the Gaussian density of hopping sites, which is usually believed to be between 50 and 100 meV [97]. Therefore, these are deep traps.

Having determined the depth of the traps that result from X-ray irradiation, it remains to determine their density. To the best of our knowledge, the density of traps cannot be directly determined from the TSC spectrum. However, integrating the stimulated current over time we obtain the amount of charge released from the traps. Integrating under the sharp feature, we obtain the following value for the number of occupied deep traps: $10^{-7}$ traps per Alq$_3$ molecule. Whereas this obviously gives a lower limit to the number of traps, there need not be a simple relationship between the number of occupied traps and the number of available traps, since the number of occupied traps will likely be limited by carrier recombination or electrostatic repulsion between the trapped carriers. Despite the integral under the sharp feature being equal for the 3 min and 20 min device, it is clear that TSC spectrum of the 20 min device is significantly more different from the pristine device than the 3 min one: in the 20 min spectrum the deep trap spike accounts for a much greater fraction of the TSC spectrum. Indeed, since we know that the number of generated traps is a relatively small fraction of the number of molecules (otherwise they would show up in IR and Raman spectra), it would be highly implausible that any kind of saturation in the trap generation rate should occur; therefore the number of traps must be proportional to the exposure time. However, we do not know of any simple and reliable way to extract the trap density in a quantitative way from the TSC spectra.

5.3.5 Discussion of Enhanced Organic Magnetoresistance by Traps and Low Mobility

The exact mechanism behind OMAR is currently not known with certainty. Several different models have been proposed [15, 57, 58, 19, 59, 60, 61, 16, 17]. However, all these models share a common basis: spin-dependent reactions that occur in paramagnetic
pairs. The hyperfine interaction leads to a spin-mixing between singlet and triplet pairs. The potency of this mixing depends critically on the ratio $r$, which we introduced above. The potency is maximum if $r$ is small (the so-called slow hopping regime) [17]. If $r$ is large, however, then the local spin projection is not a good quantum number, and any spin-dependence in the pair reaction rates is weakened as the spin-state is smeared out, so to speak, and hyperfine-induced spin-mixing becomes irrelevant. Therefore it can readily be understood that the magnitude of OMAR increases as the hopping motion is slowed by the presence of traps. This mechanism applies equally to all mechanisms for OMAR which rely on hyperfine-induced singlet-triplet mixing. Specific to the bipolaron model [17] is another enhancement mechanism. The bipolaron mechanism is based on the formation of a doubly occupied molecular site. Such a doubly occupied site is however a high-energy state, since two carriers on the same site will strongly repel each other by the Coulomb force, and its formation is therefore suppressed by the corresponding Boltzmann factor. If, however, the already occupied site is a deep trap state, i.e. very low in energy, the negative energy of the trap can compensate the positive on-site repulsion, and bipolaron formation becomes much more probable. Recently, there is another "spin-flip" model [40] showing that "spin-blocked" pathways could be opened up by faster spin-flip transitions to become viable conduction channels, producing magnetoresistance (MR). The "spin-blocked" mechanism makes the MR sensitive to the ratio of the carrier hopping time to the hyperfine-induced carrier spin precession time. At the same time, traps generated by X-ray exposure definitely make the average carrier hopping time much longer and enhance the OMAR. This model was proved by a recently reported extraordinarily huge OMAR effect [39].

5.3.6 Summary and Future Outlook

We found that the deep traps generated by the X-ray irradiation can be observed using thermally stimulated current measurements, and possess an activation energy of
≈ 0.5eV, and traps lead to an enhanced OMAR response.

Our finding suggests an interesting research program: careful control of the density and activation energy of the traps, as it could be achieved by thermal co-deposition of two different small molecule organic semiconductors or mixing solutions of two different polymers together, may lead to highly sensitive organic magneto-sensors.
CHAPTER 6
SUMMARY

The thesis presents several experimental results and accompanying theoretical analysis in the field of organic semiconductor spintronics and magnetoelectronics. The goal of these works is to further the understanding of how charge carriers, and more specifically spin-carriers, are injected into the device as well as transported through it. More specifically, our goal is to enhance the spin-diffusion length and the size of the intrinsic organic magnetoresistance (OMAR).

Motivated by recent work which suggests that the spin-transport length in organic semiconductors is limited by hyperfine coupling, we fabricated organic spin-valves based on fullerene $C_{60}$. Fullerene, because it consists entirely of carbon atoms, has a much smaller hyperfine coupling than hydrocarbon materials. In our experiments, however, we do not observe a significantly increased spin-diffusion length. We discussed three possible explanations for this observation: a) A mechanism other than hyperfine coupling causes the loss of spin-polarization; b) In thick devices an increasing conductivity mismatch limits spin-injection; c) The observed magnetoresistance is really due to tunneling magnetoresistance which would disappear for $C_{60}$ thicknesses beyond the tunneling range. Based on an analysis of the devices’ current-voltage curves, and expectations resulting from the close match of the electrodes’ work function with the lowest unoccupied molecular orbital of $C_{60}$, we propose the conductivity mismatch as a likely cause of the loss of spin-valve signal with increasing $C_{60}$ layer thickness. Although we did not observe a significantly increased spin diffusion length in $C_{60}$ spin-valve devices, this does not imply that fullerene-like materials are not good candidates for spintronics applications. For example, carbon nanotubes and graphene, both of which have even higher mobility with weak hyperfine interaction, should be excellent choices for spin-valve devices. For carbon nanotube spin-valve devices, placement of carbon nanotubes
with high density and excellent selectivity is a prerequisite for applications. Based on the chemical self-assembly method, we developed a new method applying potassium salt to remove excess anionic surfactant easier and more efficiently, and improve the placement of carbon nanotubes with higher density and selectivity.

There exists some disagreement in the literature on whether organic spin-valves work by carrier-tunneling or injection. We examined this issue. We demonstrated two different modes of conductivity in Co/AlO$_x$/rubrene/Fe junctions. The first mode, tunneling, occurs in relatively thin junctions, $d < 15$ nm, and decays exponentially with increasing rubrene thickness. We determined the tunneling decay length to be $\approx 1$ nm. The tunneling mode is also characterized by a weak temperature dependence and a nearly parabolic differential conductance. The second mode, injection followed by hopping, occurs in relatively thick devices, $d \geq 15$ nm, and can be identified by strongly temperature dependent, highly non-linear I-V traces that are similar to those commonly measured in organic light emitting diodes. We observed magnetoeresistance in devices with a rubrene thickness of 5 nm and 10 nm. Those devices are clearly in the tunneling regime. For the 15 nm device, for which the tunneling current is just barely measurable we could not observe magnetoeresistance. Giant magnetoeresistance could also not be detected in the injection regime (for $d \geq 15$ nm). The conductivity mismatch problem provides a possible explanation for the absence of magnetoresistance in this regime.

In the third project, we reported that X-rays produced during electron beam deposition of metallic electrodes drastically change the performance of organic spintronic devices. The X-rays generate traps with an activation energy of $\approx 0.5$ eV in a commonly used organic. These traps lead to a dramatic decrease in spin-diffusion length in organic spin-valves, at the same time, the traps strongly enhance magnetoeresistance in OMAR devices.

We hope that the conclusions drawn in this thesis will lead to improved spin-diffusion lengths and better performance of organic spintronic devices. This may enable
the design of spintronic logic devices, even optical control ones. Our result that X-ray irradiation leads to enhance OMAR response, may lead to highly sensitive organic magneto-sensors.
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