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Hybrid organic spin valves

Popinciuc, Mihaita

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Introduction

1.1 Spintronics, a short introduction

Charge carriers, electrons and holes, have two fundamental properties, namely the charge and the spin, which are widely used in nowadays electronic devices. The charge defines the interaction with electric fields, whereas the spin (due to its magnetic moment) defines the interaction of the carrier with magnetic fields. Information technology based on boolean logic requires two states, a ”0” and a ”1” state which translateds into electronic devices into ”OFF” and ”ON” states (a high and a low resistance state). Using the charge property, the manipulation of these states (changing from ”OFF” into ”ON” and viceversa) can be done by electric fields, such as in a field effect transistor where the gate voltage controls the flow of current between the source and drain electrodes. The spin of the carriers is appealing to be used in electronic devices since, whenever measured in a certain direction, the spin can have only two states, simply defined as *spin up* and *spin down*. In addition to the manipulation of the carriers with electric fields, the interaction with magnetic fields allows for the manipulation of their spin state bringing additional functionality to a device. The field of electronics which uses the spin as the basic unit to transport and manipulate information is called *spintronics*.

Spintronic devices are most notably used as magnetic field sensors (for example the read-heads of hard-disks) and as magnetic random access memories. The functionality of these devices is derived from the following three major (spin related) effects: anisotropic magneto-resistance (AMR) [1], tunnel magneto-resistance (TMR) [2] and giant magneto-resistance (GMR) [3, 4], see [5] for a review. The resistance of a ferromagnetic wire depends on the relative orientation between the current flow and its magnetization direction, an effect known as AMR. This is a bulk effect and, historically, it was the first transport effect related to spin. Ferromagnet/tunnel barrier/ferromagnet layered structures show the TMR effect, that is the device resistance depends on the relative orientation of the magnetization of the ferromagnetic electrodes (parallel or antiparallel). This (interfacial) effect is explained by the fact that the two spin subbands in a ferromagnet are not equivalent. Under the assumption of spin and energy conservation in the tunneling process, in the antiparallel case the majority (minority) spins will have trouble to tunnel into the minority (majority) spins subband for positive (negative) bulk polarization ferromagnets. This causes the total resistance to be higher when the magnetization of the two ferromagnets are antiparallel compared with the parallel orientation. GMR was first observed in a Fe/Cr multilayered structure [3] as a dependency of the resistance on the orientation of the magnetization of the magnetic layers (parallel/antiparallel). The GMR effect is classified according to the direction of the current flow with respect to the multilayer interface: current in plane (CIP-GMR, used in most commercial applications) and current perpendicular to the plane (CPP-GMR) [5].

A *spin valve* is a device in which a non-magnetic material is placed between two ferromagnetic electrodes whose magnetization can be manipulated independently by applying an external magnetic field, for example. Typical device geometries are a layered (sandwich) or a lateral structure. The spin valve represents the simplest CPP-GMR structure and operates as follows. When a current is passed from a ferromagnet to a non-magnet, *spin accumulation* (non-equilibrium magnetization induced by the current) is created on both sides of the interface [6] which decays exponentially with the distance from the interface with a characteristic length: the *spin relaxation (flip) length.* If a second ferromagnetic electrode is placed within the spin flip length, and the magnetizations of the electrodes are oriented parallel, the device has lower resistance compared with antiparallel orientation because the induced magnetization (the spin accumulation) has the same orientation as the magnetization of the second ferromagnet and the spins are extracted more easily. The spin valve effect is of fundamental interest since the spins are transported in a non-magnetic medium, which allows studying the spin dynamics in the non-magnetic material. The functioning of a spin valve device is divided in three major processes: the injection, the transport and the detection of spins. The injection/detection of spins are similar and can be realized electrically or optically using circularly polarized light. In between the injection and detection the spin accumulation can be manipulated by inducing precession, for example. The first realization of the spin valve effect is due to Johnson and Silsbee in 1985 [7–9] who reported spin accumulation and precession in a single crystal aluminium (Al) slab up to temperatures of 77 K, followed by similar experiments in Au [10, 11]. In the past few years successful spin injection and precession was realized at room temperature in one and zero dimensional metallic lateral spin valve structures [12–16].

Integrating semiconductors into spintronic devices is appealing due long spin relaxation times [17, 18], good optical properties, amplification abilities which could give rise to novel devices with improved functionalities [19–23], visions for the future including quantum computing. When using semiconductors and ferromagnetic metals for building a spin valve, the resistivity of the semiconductor (which is spin independent) is orders of magnitude higher than that of the metal (which is spin dependent) and dominates the total resistance of the device. This leads to the vanishing of the spin signal, i.e. there is no measurable difference in device resistance between the parallel and antiparallel orientation of the magnetization of the ferromagnetic electrodes. This is known as the conductivity mismatch problem [24]. In order to overcome this problem, one needs to match (to a certain extent) the spin dependent part of the device resistance with the spin independent part. This can be offered by the natural Schottky barrier (if it exists and provided that the spins are not mixed at the interface), by the insertion of a tunnel barrier or by the use of ferromagnetic semiconductors [24, 25]. Efficient electrical spin injection in semiconductors was reported, for the first time, by Fiederling *et al.* [26] and Ohno *et al.* [27] in 1999 . They used ferromagnetic semiconductors to inject spins in GaAs/AlGaAs light-emitting diodes, the induced spin polarization being probed by the circular polarization of the emitted light. Since then, numerous efforts were made towards the realization of efficient spin injection in semiconductors, out of which only a few unambiguously demonstrated the effect, see [28] for a review. Only recently, all electrical spin injection/detection and precession was reported in Fe/GaAs heterostructures [29].

The use of organic semiconductors for spintronic applications promises cheap fabrication (by spin coating, low temperature processing) and compatibility with plastic (bendable) substrates. Moreover, chemistry (functionalization) is envisioned to play an important role in tailoring the properties of organic materials in order to improve their performance in electrical devices. Organic spin valve effects were reported for carbon nanotubes [30–34]. Spin polarized transport in thin films of organic materials were reported by Dediu *et al.* [35], in sexithienyl (T_6) and more convincingly by Xiong *et al.* [36] in 8-hydroxy-quinoline aluminium (Alq_3). Yet, organic spintronics is a field still in its infancy (see [37] for a recent overview) and one faces the problem of choosing the (right) materials. Building organic spin valves is of general interest and a multitude of materials could be used, therefore, before we present the layout of this thesis we explain the choice of pentacene, Co and aluminum oxide (AlOx)[1] as a tunnel barrier for realizing hybrid organic spin valve devices.

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[1] Throughout this thesis the aluminum oxide is termed as AlOx, see *Section 3.3.2* for details.

1.2 Why pentacene, Co and AlOx?

Why pentacene?

The spin flip length is the most relevant parameter when dealing with spin valve devices. If it is long enough (at least a few hundreds of nanometers), devices may be fabricated using current technologies without too much trouble. The spin flip length (λ_{sf}) is related to the diffusion constant (D) and the spin relaxation time (τ_{sf}) by $\lambda_{sf} = \sqrt{D\tau_{sf}}$. Since the diffusion constant is proportional to the mobility (μ) of the carriers [38], it follows that $\lambda_{sf} \propto \sqrt{\mu}$, i.e., the higher the mobility of the carriers the longer the spin can travel. This is the reason why pentacene was chosen: it has one of the highest mobilities among the organic semiconductors, ranging form several cm^2/Vs in thin film devices [39] up to tens of cm^2/Vs in pure single crystal devices [40, 41]. Recently [42], we have shown record mobilities of 15-40 cm^2/Vs in high purity pentacene single crystal field effect transistors that use pentacenequinone as the gate oxide [41, 42]. The spin relaxation time is mainly determined by the spin orbit interaction which in turn is proportional to Z^4 [37], where Z represents the atomic number. It is believed that organic semiconductors, mostly consisting of light carbon atoms, have a long spin relaxation time.

Why Co?

In view of the conductivity mismatch problem a good candidate for the ferromagnetic injector/detector would be a ferromagnetic semiconductor. However, in spite of the advantage of a higher resistivity, these materials have Curie temperatures below room temperature [43–45] and besides that, with our current laboratory facilities, they could not be made readily available. For these reasons we chose as ferromagnet one of the $3d$ transition metals, namely Co. Co has a Curie temperature of 1388 K [46], a characteristic which makes it also useful for room temperatures applications.

Why Co/AlOx?

We will show in *Chapter 4* that a significant hole injection barrier exists at the clean Co/pentacene interface, a barrier which could allow for an efficient injection of spins. However, due to the conductivity mismatch problem, it is not clear if efficient detection can be realized. For this reason the insertion of a tunnel barrier in between Co and pentacene may be necessary and we chose aluminium oxide (AlOx) as the tunnel barrier material. AlOx was used because of its interfacial properties with Co: small metallurgical width (sharp interface), stable Co/AlOx interface (CoOx/Al interface is not energetically favorable) and thin natural oxide thickness. Recently, the use of AlOx tunnel barriers enabled us to observe spin transport in graphene (a single layer of carbon atoms) based spin valves [47], whereas when using clean contact Co/graphene no spin signal was observed.

1.3 This thesis

This thesis aims to advance the knowledge of spin injection/transport in pentacene by means of contacting it with Co or Co/AlOx electrodes. In view of the conductivity mismatch problem, knowledge of the interfacial electronic structure (barrier heights, chemistry) is crucial for the design and operation of hybrid Co and pentacene based organic spin valves. Understanding Co/pentacene and Co/AlOx/pentacene interfaces is equally important for the field of organic semiconductor devices, not only for the particular field of organic spintronics.

In *Chapter 2* we review some theoretical aspects related to electrical spin injection/detection and photoelectron spectroscopy, aspects which we find relevant for understanding the rest of this thesis. Successful realization of organic semiconductor spin valves requires overcoming the conductivity mismatch problem: that is the spin injector/detector resistance (the spin dependent resistance) should be matched with the spin independent resistance of the semiconducting layer. Photoelectron spectroscopy is introduced as a tool for investigating the interfacial properties (carrier injection barriers, interfacial chemical reactions, band bending) at hybrid metal-organic or metal-oxide-organic interfaces.

Chapter 3 presents experimental details of the material deposition, the fabrication technologies used to build the spin valve devices (optical and electron beam lithography) and the electrical and photoelectron spectroscopy characterization setups. The magnetic properties of Co electrodes and the properties of Co/AlOx interface are demonstrated by experiments.

In *Chapter 4* the energy level alignment symmetry at Co/pentacene interfaces is investigated. Both, pentacene deposited on Co and Co deposited on pentacene interfaces were studied by X-ray and ultraviolet photoelectron spectroscopy experiments (XPS and UPS). The surface sensitivity of the UPS enables the sampling of the electrostatic potential within pentacene as a function of its thickness atop of a Co thin film and provides insight in the energy level alignment mechanism at the interface and far from it. Moreover, a widely used spin valve geometry is a stacked one in which the transport medium for spins is sandwiched between two ferromagnetic electrodes. Since the deposition of metals on organics may be accompanied by significant diffusion of the metal atoms into the open organic matrix, the resulted interface is ill defined and very different from the sharp interface in which the organic is deposited on the metal. Therefore, it is of interest to study both interfaces and we will show that they provide complementary information on the interaction between Co and pentacene.

XPS and UPS studies of the energy level alignment and electronic structure at Co/AlOx/pentacene interfaces as a function of the aluminium oxide (AlOx) tunnel barrier thickness and the oxidation state of Co are presented in *Chapter 5*. The energy level alignment is consistent with band bending in the AlOx layer and the formation of an interfacial dipole at the Co/AlOx interface, its magnitude being determined by the oxidation of Co and the thickness of the tunnel barrier. The hole injection barrier varies with the thickness of the tunnel barrier and the oxidation of Co at a fixed thickness of the AlOx layer. This enables tuning the performance of pentacene based spin valves by controlling the thickness of the tunnel barrier.

In *Chapter 6* we present electrical measurements of pentacene spin valve devices with clean Co contacts and pentacene field effect devices with Co/AlOx source-drain electrodes. Current-voltage measurements were performed for different device configurations: Co/pentacene clean contact devices in lateral and vertical geometries. Field effect devices employing Co/AlOx electrodes were fabricated in order to allow for tuning of the resistances of the spin valve circuit. The electrical measurements are in qualitative agreement with the photoelectron spectroscopy experiments. Magnetoresistance measurements were performed in a few cases at room temperature. Except for the vertical structures, no magnetoresistance signal was observed.

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