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# 7.1 Introduction

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Magnetism and spintronics has its origin in quantum mechanics, that is, the existence of electron spin and the Pauli exclusion principle. However, it is also associated with a variety of classical effects, arising from both short- and long-range interactions, and is widely associated with the materials microstructure or the morphological arrangements of phases, grains, or individual atoms themselves. Interaction among these different phases, grains, or individual atoms leads to the richness of properties encountered in magnetic and spintronic systems from which various useful and technological applications arise. These interactions also partly explain why the collective spin response of materials or heterostructures is complex and many fundamental questions remain unanswered. There are two distinct limits to magnetic behavior as a function of particle size and dimensionality - classical and nanomagnetism. At one end of the spectrum, the microstructure determines the hard and soft magnetic behavior of materials, whereas, at the other end, the decreasing length scales of magnetic particles, approaching the size of domain wall widths, that is, the nanostructures, lead to lateral confinement (shape and size) and interparticle exchange effects start to dominate, rendering classical descriptions grossly inadequate, until finally, at atomic dimensions guantum-mechanical tunneling effects predominate.

In order to fully understand the effect of dimensionality on magnetic behavior of a material, thorough investigation of its structural, magnetic, and transport properties as a function of particle size has been done. These investigations include nanoparticles (NPs), nanotubes (NTs), nanostructured (NS) films, or different thin film heterostructures and gave rise to the exciting new field of nanomagnetism and spintronics. The magnetic properties of these nanomaterials or heterostructures are rich in new phenomena and include recent highlights such as surface/interface anisotropy as well as frustration, proximity, and interface effects that lead to exchange bias in ferromagnet (FM)/antiferromagnet (AFM)

Hybrid Organic–Inorganic Interfaces: Towards Advanced Functional Materials, First Edition. Edited by Marie-Helene Delville and Andreas Taubert. © 2018 Wiley-VCH Verlag GmbH & Co. KGaA. Published 2018 by Wiley-VCH Verlag GmbH & Co. KGaA. bilayers and exchange spring (FM/FM bilayer) behavior. These magnetic properties are also dominated by the physical, chemical, and magnetic structure of their interfaces, and a large variety of appropriate methodologies have been used for studying them most effectively at relevant length scales. Understanding the origin of these phenomena is essential for controlling their properties at the atomic length scales. Exploring the fascinating physics of magnetic NP or nanostructures is of utmost importance for their incorporation to the future emerging technologies. Improvement in magnetic materials would lead to higher efficiency devices in electric power generation, conditioning, conversion, transportation, and other energy-related sectors in the future.

The emerging technology of spintronics, where, in addition to the electronic charge, electron spin also carries information, promises the future generation of electronics combining standard microelectronics with spin-dependent effects that arise from the interaction between spin of the carriers and the externally applied magnetic fields. The science of spintronics bridges the important knowledge gap in the field of information processing where the storage of information is predominantly based on magnetism and the information processing and related operations are mainly charge based. Spintronic components are more versatile, energy efficient, and faster than their traditional counterparts. Since the discovery of giant magnetoresistance (GMR) effect in 1988, the field of spintronics emerged rapidly as an extremely important branch of condensed matter physics. The interest is not only due to the immense technological potential of spintronic devices in memory and sensor application but also due to novel and fascinating spin physics of different materials for spin-polarized (SP) carrier injection and transport and multilayer device structures. Discovery of GMR led to the Nobel Prize in Physics in 2007 for A. Fert and P. Grunberg. Successful developments in spintronics include GMR in magnetic metal multilayers, spin valve devices, and tunneling magnetoresistance (TMR) in magnetic tunnel junctions (MTJs) that are intended primarily for applications in magnetic field sensing elements such as read heads and nonvolatile magnetic random access memories (MRAMs). Spin valve heads and nonvolatile MRAMs are already in market, and continuous research effort is on for improved data integration density and additional functionalities in them. Spin manipulation in semiconductors is also an attractive alternative for applications in the future generations of energy-efficient sensors, memory, and logic architectures.

Successful operation of spintronic components relies on efficient electrical injection without losing the spin information significantly in the process, transport, and sensing of magnetic moment associated with the spin of the charge carriers. Major challenges in the field of spintronics are addressed by experiment and theory pertaining to the optimization of electron spin injection, spin lifetimes, detection of spin coherence in nanoscale structures, transport of SP carriers across relevant length scales and heterointerfaces, and the manipulation of both electron and nuclear spins on sufficiently fast time scales. It is envisioned that the merging of electronics, photonics, and magnetics will ultimately lead to new spin-based multifunctional devices such as spin field-effect transistor (FET), spin light-emitting diode (LED), spin resonant tunneling device (RTD), optical switches operating at terahertz frequency, modulators, encoders, decoders,

and quantum bits for quantum computation and communication. The success of these ventures depends on a deeper understanding of fundamental spin interactions in solid-state materials as well as the roles of dimensionality and defects in modifying these dynamics. With proper understanding and control of the spin degree of freedom in semiconductors and ferromagnet-semiconducting heterostructures, potential for high-performance spintronic devices is excellent.

The research in this field so far clearly led to the conclusion that the future of spintronics depends mainly on the successful spin injection and manipulation in the multilayer devices and optimization of spin lifetimes in these structures. Hence, for obtaining multifunctional spintronic devices in the future, different materials suitable for efficient spin injection and spin transport need to be studied thoroughly. For spin injection purposes, inorganic metals and half-metals are very important as they have high net spin polarization and are able to inject SP carriers efficiently in a device depending on their matching of work functions and conductivity mismatch with different semiconducting materials that are suitable as spin transporting materials. In this respect organic semiconductors play a vital role. As the organic materials are mainly hydrocarbons, their spin-orbit interaction is significantly smaller compared with their inorganic counterparts that leads to longer spin diffusion time in them. Based on these aspects, hybrid inorganic-organic spintronic research has gained momentum in the last decade. One of the major drawbacks of spintronic components, identified so far, is their poor SP transport at room temperature that makes them unsuitable for practical applications. In order to address this challenge, the hybrid spintronics might rely on materials and components of further reduced dimensions, that is, one- and zero-dimensional objects. Spin dynamics of hybrid nanomaterials and nanostructures is therefore considered of utmost importance for future hybrid spintronic devices.

In recent years, organic semiconductor (OSC) small molecules, pi-conjugated polymers (PCP), graphene, and carbon NTs have gained considerable attention as promising spin transport materials. In his Nobel Lecture in December 2007, Fert [1] dedicated the later part of his lecture to "spintronics with semiconductors and molecular spintronics" where he underlined the importance of small molecules and polymers as alternative materials for spintronic applications. The first decade of the field of hybrid spintronics has been phenomenal where many breakthrough experiments have advanced the frontiers of our knowledge and conceptual understanding on spin-dependent phenomenon in organic semiconductor small molecules and polymers. On the one hand, we observed several exciting and promising results regarding the spin injection and transport (or tunneling) in organic spin valves and MTJs; however, at the same time, several technical challenges of device fabrication, reproducibility, and so on have also emerged. Also several experimental results challenged our present understanding of the subject and gave rise to strong debates and discussions on those issues among the scientists in the community. Several comprehensive review articles have covered the initial years of this field quite thoroughly. The current chapter will discuss some of the more recent findings focusing on breakthrough experiments and their theoretical understanding and the open questions in this field. The chapter is divided into sections covering spintronic devices consisting of sandwich structures of magnetic and nonmagnetic (NM) multilayers and single molecular devices and spin switching molecules and different preparation techniques of the organic thin films for spintronic components and their morphology-dependent spin properties. In general the aim is to provide the readers with an overview of the major findings in the field of hybrid spintronics and the future research directions.

## 7.2 Fundamentals of Spintronics

#### 7.2.1 Spin Injection, Transport, and Detection

Before going into the details on the fundamental physical processes of spintronics, let us first discuss, in short, about the basic structure of spin devices, that is, the spin valve geometry. Spin valve architectures where an NM metal or a semiconducting material is sandwiched between two ferromagnetic (FM) electrodes with different coercive fields,  $H_{C1}$  and  $H_{C2}$ , form the very basic architecture of spin-electronic devices (schematics in Figure 7.1). The role of the FM electrodes is to inject and detect SP carriers, whereas the NM spacer decouples the two FM electrodes in order to enable them to switch their magnetization direction when the external magnetic field is reversed. When a spin valve is placed in an external sweeping magnetic field, the magnetic moments of the two FM electrodes attain either parallel or antiparallel alignment depending on the coercive fields of the ferromagnets and also the applied magnetic field (H). When the applied magnetic field is in between the coercive fields of the electrodes  $(H_{C1} < H < H_{C2})$ , the two FM electrodes attain an antiparallel orientation, and when the applied field is higher than both the coercive fields,  $H > H_{C1}$  and  $H_{C2}$ , the two electrodes are in parallel orientation. The carriers entering the device through the FM electrode become SP and undergo spin-dependent scattering in the two electrodes. For parallel orientation of the FM electrodes, one of the carrier spins (up or down) can pass without suffering from scattering, whereas for antiparallel orientation, both spin orientations suffer from scattering. Scattering of both spin channels



**Figure 7.1** Schematic diagram of a spin valve architecture for parallel and antiparallel alignments of the two ferromagnetic electrodes showing spin-dependent scattering at the two electrodes.

for antiparallel orientation of the electrodes gives rise to a high resistance (OFF) state, while a low resistance (ON) state can be achieved for the parallel orientation of the electrodes. For an MTJ, the NM layer is generally an insulator with thickness >5 nm so that the SP carriers can quantum mechanically tunnel through the barrier.

The three most important aspects of spintronic devices are (i) injection of SP carriers from the first FM electrodes to the NM layer, (ii) transport of SP carriers in the NM layer either by drift and diffusion (for semiconductors) or by tunneling (for insulators), and (iii) detection of SP carriers at the second FM electrode. SP carriers can be generated in the spin transporting layer by electrical, optical, and other methods as described by Zutic *et al.* [2]. Electrical injection and detection of SP carriers are the methods of choice for solid-state device fabrication, as realized in spin valves showing GMR. In this chapter, we mostly discuss such devices.

#### 7.2.1.1 Spin Injection

Our understanding of SP carrier generation and transport in FM materials and systems was put forward by Sir Nevill Mott [3, 4]. He experimentally observed that the resistance of an FM metal alters in the presence of a magnetic field. He explained the phenomenon by considering that at sufficiently low temperatures (LT), magnon (quantum of a spin wave) scattering decreases sufficiently and electrons of majority and minority spins do not mix in the scattering process when their magnetic moments are parallel or antiparallel to the magnetization direction. The conductivity is then the sum of two independent and unequal parts for two different spin projections, that is, the currents in FM are SP. This model, called the two-current model, has been then thoroughly studied by Fert and Campbell [5]. The degree of SP carrier injection from the FM electrode to the NM region is the measure of electrical spin injection efficiency. A theory of spin injection across an FM/NM interface was first introduced by Aronov et al. [6], with subsequent studies on spin injection into a semiconductor [7]. Later, Johnson and Silsbee [8–10], van Son et al. [11], Valet and Fert [12], Hershfield and Zhao [13], and others also studied the electrical spin injection in detail. Rashba [14] explained spin injection as a steady-state flow of electrons along the x direction in a three-dimensional (3D) geometry consisting of a metallic ferromagnet (region x < 0) and an NM metal or semiconductor (region x > 0). The two regions form a contact at the interface x = 0. The degree of polarization in the current injected into the NM layer is measured by the relative magnitudes of three characteristic resistances: the contact resistance  $r_{\rm c}$  and the resistances of the NM and FM layers, represented by  $r_{\rm NM}$  and  $r_{\rm FM}$ , respectively. Each term gives the ratio of the spin diffusion length and the effective bulk conductivity in the corresponding region. Two limiting cases correspond to the transparent limit where  $r_c \rightarrow 0$ , and the low transmission limit where  $r_{\rm c} \gg r_{\rm NM}$ ,  $r_{\rm FM}$ . To summarize, efficient spin injection in a spintronic structure relies mainly on the factors like the spin polarization of the FM injector, the interfacial characteristics of the FM/NM junction, and the conductivity of the NM spacer.

#### 7.2.1.2 Spin Transport and Relaxation

Following successful injection, SP carriers travel through the NM spacer to reach the second FM electrode. During the transport process, these carriers undergo different scattering and relaxation mechanism and tend to lose their original spin direction. The main reasons for spin relaxation in solids are the spin–orbit coupling and hyperfine interactions.

*Spin–Orbit Coupling* The spin–orbit coupling is the interaction between the spin of an electron and its orbital motion around the nucleus. When an electron moves in a finite electric field of the nucleus, the spin–orbit coupling causes a shift in the atomic energy level of the electron due to the electromagnetic interaction between the spin of the electron and the electric field. In the rest frame of the electron, a magnetic field is created by the interaction of the angular momentum of the electron and the electric field of the nucleus.

The electrical field in this case arises from various physical origins, such as the electric field of an atomic nucleus or the band structure of a solid [15]. The spin–orbit coupling increases with increasing atomic number Z of the atom as  $Z^4$  in hydrogen-like atoms [16]. The general derivation of spin–orbit coupling from the Dirac equation for an electron of mass m and charge -e < 0 in an external electrical field  $E(r) = \nabla \varphi(r)$  gives the expression

$$H_{\rm SO} = \frac{e\hbar}{4m^2c^2}\hat{\sigma} \cdot [E(\vec{r}\times\vec{p})] \tag{7.1}$$

where  $\vec{p}$  is the momentum operator and  $\hat{\sigma}$  the Pauli spin matrices. Two main contributions to spin–orbit coupling in most inorganic solids are the Dresselhaus contribution and the Rashba contribution. The Dresselhaus contribution occurs in crystals with bulk inversion asymmetry, implying that there is a net electric field for certain crystal directions [17, 18]. The Rashba contribution appears in systems with net electric field due to structural inversion asymmetry [19, 20]. There are several spin–orbit coupling-related spin relaxation mechanisms in solids among which the three main mechanisms – that is, the Elliot–Yafet (EY), D'yakonov–Perel (DP), and Bir–Aronov–Pikus (BAP) mechanisms – are discussed here in details.

The EY mechanism [21] suggests that relaxation of conduction electron spins mainly occurs through momentum scattering (such as by phonons or impurities) if the lattice ions induce spin–orbit coupling on the electron wave function. Any momentum scattering event is associated with a finite probability of spin flip. The EY mechanism describes the spin relaxation time to be proportional to the momentum scattering time. Momentum scattering is generally associated with scattering due to defects or impurities at lower temperature and by phonons at higher temperature [2]. EY is normally a dominant mechanism in metallic solids; however, recent experimental results [22, 23] suggested that EY mechanism could be dominant in organic semiconductors (OSC) also.

The DP [18] mechanism arises in solids with no center of symmetry and is therefore directly related to the Dresselhaus contribution. In DP mechanism, spin dephasing mainly occurs as the electrons feel an effective magnetic field resulting from the spin–orbit interaction. This spin–orbit interaction changes in random directions every time the electron scatters to a different momentum state, resulting in a loss of initial spin memory. In the case of frequent scattering events, the spin relaxation slows down as the spin is unable to follow the rapidly changing internal magnetic field. Therefore, the spin relaxation time becomes inversely proportional to the scattering time.

BAP [24] mechanism is an effect of electron-hole (e–h) exchange interaction, playing a role only in systems where there is a large overlap between the electron and hole wave functions. This mechanism is important for p-doped semiconductors, in which spin relaxation of conduction electrons can proceed through scattering, accompanied by spin exchange with holes.

**Hyperfine Interaction** Hyperfine interaction is another major source of spin relaxation that originates from the interaction between a nucleus and its surrounding environment. The hyperfine interactions shift energy levels and lift the energy level degeneracy through the interaction between the electron spins and the nuclear spins. The electron–nuclear coupling Hamiltonian is given by

$$H_{\rm hyp} = \vec{S}. \sum_{i}^{N} A_{i} \vec{I}_{i}$$
(7.2)

where  $I_i$  is the spin operator for nucleus *i*, *S* is the electron spin, and  $A_i$  is the coupling strength between them. The nuclear spin can affect both spin relaxation times,  $T_1$ , and spin dephasing time,  $T_2$ . For an electron spin interacting with *N* nuclear spins, the statistical fluctuation varies as  $1/\sqrt{N}$  [25, 26]. Therefore more delocalized electron wave functions will influence the nuclei less.

#### 7.2.1.3 Spin Detection

Spin detection is the process of sensing the SP carriers reaching the second FM electrode with their original spin direction. For efficient collection of SP carriers traveling by either ballistic or tunneling transport through the NM spacer, a second FM electrode is needed. For efficient spin sensing, a well-defined interface between the NM spacer and the FM electrode plays an important role. Recent experiments [27] using Fe/GaAs Schottky tunnel barrier showed that both the magnitude and sign of the spin-detection sensitivity are widely tunable with voltage bias applied across the interface. Experiments and theory suggest that this tunability comes from the interplay between two physical processes, that is, the bias dependence of the tunneling spin polarization and the bias dependence of spin transport in the semiconductor that can enhance or suppress the spin-detection sensitivities.

#### 7.2.2 Giant and Tunneling Magnetoresistance

Thus the magnetoresistance (MR) arising from the resistance bistability due to sweeping magnetic field is referred to as giant magnetoresistance. In spin valves, the roles of the two FM electrodes are to inject and detect SP carriers, whereas the role of the NM spacer is to decouple the two ferromagnets so that they can switch their magnetic moments independently. At the same time, the spacer should allow the transport of SP carriers without too much scattering

for maximizing the device MR. The up and down spin carriers suffering a spin-dependent scattering in the two FM electrodes based on their parallel and antiparallel orientation leading to a high and low resistance state are shown schematically in Figure 7.1. Hence based on the applied magnetic field, electrical resistance of a spin valve device switches between high and low states, leading to GMR effect. GMR is defined as

$$GMR = \frac{R_{high} - R_{low}}{R_{low}} * 100\%$$
(7.3)

where the  $R_{high}$  and  $R_{low}$  are the high and low device resistance, respectively. In MTJ, a similar architecture is used; however the NM spacer in this case is a very thin layer of an insulating material (a few nanometers) called a barrier through which SP carriers can quantum mechanically tunnel from one electrode to the other. The resulting MR is termed as tunneling magnetoresistance. Although the physics of GMR and TMR was known since Sir Nevill Mott's theory of conduction of SP electrons and Julliere's experiment in the early 1970s, the field could not gain enough momentum due to the lack of technology essential for fabricating few nanometers thick continuous films with desired material properties. GMR was first reported in metallic multilayers of Fe and Cr in 1988 separately by Fert's group [28] and Gründberg's group [29], which subsequently led to the Nobel Prize in Spintronics in 2007. Tunneling devices were reported by Meservey and Tedrow already in 1971 [30], and TMR was first reported by Julliere in his seminal paper in 1975 showing TMR response in Fe/Ge (10-15 nm)/Co device based on the parallel or antiparallel alignment [31]. However, even after this promising finding, the field did not progress until the 1990s. In 1995, Moodera et al. [32] and Miyazaki and Tezuka [33] separately showed that the tunneling current between two FM films separated by ultrathin oxide layer strongly depends on an external magnetic field that aligns the spin orientation of the two FM electrodes, and subsequently research on MTJs became the most important branch of spintronics. The TMR is calculated similar as GMR as described in Eq. (7.1). In Julliere's formalism the TMR can be written as

$$TMR = \frac{2P_1 P_2}{1 - P_1 P_2}$$
(7.4)

In this formalism it was assumed that spin travels from one SP electrode to the other without any spin flip and  $P_1$  and  $P_2$  represent spin polarization of electrodes 1 and 2 where *P* is defined as

$$P = \frac{N(\uparrow) - N(\downarrow)}{N(\uparrow) + N(\downarrow)}$$
(7.5)

and  $N(\uparrow)$  and  $N(\downarrow)$  represent density of states at the Fermi level of the up ( $\uparrow$ ) and down ( $\downarrow$ ) spin carriers. Also TMR can be calculated using the expressions for tunneling currents in the parallel and antiparallel configuration of the devices using the following formula, where  $G_{\uparrow\uparrow}$  and  $G_{\uparrow\downarrow}$  are the junction conductance for the parallel and antiparallel configuration of the electrodes, respectively:

$$TMR = \frac{G_{\uparrow\uparrow} - G_{\uparrow\downarrow}}{G_{\uparrow\downarrow}}$$
(7.6)

However, it is important to note that in all these formulas, the effect of the electrodes has been taken into account only. In practice, the interface between the electrodes and the barrier is of utmost importance. Spin scattering, trapping, and filtering effects at the interfaces are significant in most practical devices and often determine the device properties.

The last one and half decade in the field of spintronics witnessed many fascinating materials, device architectures, and exciting new science, leading to physical miniaturization to an unprecedented level of computer memories. Introduction of semiconductors in the field of spintronics in the late 1990s and eventually introduction of organic semiconductors in the last decade have also substantially contributed to more fascinating results, advancing our fundamental understanding of spin injection and transport that could lead to versatile, multifunctional, and energy-efficient spintronic devices for future memory and logic operations.

# 7.3 Hybrid Organic–Inorganic Spin Valves and Magnetic Tunnel Junctions

#### 7.3.1 Hybrid Spin Valves

The field of organic-inorganic hybrid spintronics was pioneered by the report of SP injection and transport in OSC molecule sexythiophene  $(T_6)$  in 2002, where a spin diffusion length of 200 nm at room temperature was reported in a planar spin valve structure with La<sub>2/3</sub>Sr<sub>1/3</sub>MnO<sub>3</sub> (LSMO) as both spin-injecting and spin-detecting electrodes [34]. In 2004, Xiong et al. reported GMR response from a vertical spin valve structure using OSC tris-(8-hydroxyquinoline)aluminum  $(\mathrm{Alq}_{\scriptscriptstyle 2})$  as the spacer layer between FM electrodes LSMO and Co. At 11 K, a GMR response of 40% was reported in these devices [35]. However, it was found that in LSMO/Alq<sub>3</sub>/Co spin valve devices, the GMR response decayed monotonously with increasing temperature, leaving no MR response above 180 K. This loss of GMR response with increasing temperature was later found to be universal for different FM electrodes and different OSC spacers. The effect was initially dedicated to the loss of spin polarization at the FM electrodes, especially the half-metallic oxide LSMO with Curie temperature  $(T_c)$  of 350 K. However, in the next few years, several other groups reported MR response from organic spin valves even at room temperature although the effect was barely measurable. Wang et al. showed [36] by spin 1/2 photoluminescence-detected magnetic resonance (PLDMR) studies that the spin diffusion length ( $\lambda_s$ ) in OSC is largely temperature independent, and hence the observed decay of GMR response with increasing temperature of the hybrid spin valves appears mainly due to loss of spin polarization of the FM electrodes. It is important to mention here that the reported loss of GMR response with increasing temperature showed similar tendency in devices with low  $T_C$  half-metallic LSMO or high  $T_{\rm C}$  transition metal electrodes. It was found that LSMO on different oxide substrates, with varying strain states and hence different  $T_{\rm C}$ , exhibit similar decreasing tendency in GMR response when increasing the temperature [37]. Even devices based on La<sub>2/3</sub>Ca<sub>1/3</sub>MnO<sub>3</sub> (LCMO), another

half-metallic oxide with significantly reduced  $T_{\rm C}$  of ~250 K, also showed similar loss of GMR response with increasing temperature [38]. In 2009, Drew *et al.* [39] studied  $\lambda_{\rm S}$  of Alq<sub>3</sub> as a function of temperature in a spin valve structure by muon spin rotation technique and reported that  $\lambda_{\rm S}$  in Alq<sub>3</sub> decays sharply with increasing temperature. In 2012, similar temperature-dependent  $\lambda_{\rm S}$  is reported in regio-regular poly(3-hexylthiophene) (RRP3HT) although the decay of  $\lambda_{\rm S}$  with increasing temperature was not as sharp as in Alq<sub>3</sub> [40]. Also comparison with regio-random P3HT (RRaP3HT) showed, depending on the polymer structure and charge carrier mobility, that the relation of  $\lambda_{\rm S}$  versus temperature could be different (Figure 7.2). The more ordered RRP3HT showed longer  $\lambda_{\rm S}$  with lesser temperature dependence [41]. In 2009, Bobbert *et al.* [42] suggested a theory for spin diffusion in disordered OSCs based on incoherent hopping of charge carriers and coherent precession of its spin in the presence of a random hyperfine field and an externally applied magnetic field.

From Monte Carlo simulations and an analysis of the waiting time distribution of the carriers, a weak temperature dependence, but a considerable magnetic field dependence of the  $\lambda_S$ , was predicted. It was shown that in the presence of hyperfine interaction, SP transport in OSC can get disrupted. One of the major sources of the hyperfine interaction is the hydrogen atoms of the hydrocarbons. The hyperfine fields could act as local random magnetic fields, and the SP carriers could start precessing around the random fields, losing their initial spin orientation. Therefore it was predicted that molecules without any hydrogen atoms such as fullerene molecules and graphene could be ideal for SP transport. Experimentally, hundreds of nanometers of  $\lambda_S$  in  $C_{60}$  molecules [43] and micrometers of  $\lambda_S$ in graphene have been obtained [44]. In subsequent years a considerable number of experimental investigations were carried out for achieving longer  $\lambda_S$  length from  $C_{60}$ -based devices. In 2011, Lin *et al.* [45] experimentally demonstrated hybrid spin valves based on  $C_{60}$  molecules, although the results failed to show any significantly improvement in  $\lambda_S$ . The explanations for the observations were



**Figure 7.2** (a) GMR response of a typical LSMO/RRP3HT/Co as a function of temperature measured with 100 nA current. (Majumdar and Majumdar 2012 [40]. Reproduced with permission of Elsevier.) (b) Spin diffusion length ( $\lambda_s$ ) of RRaP3HT and RRP3HT, calculated using the modified Júlliere formula, as a function of temperature. (Majumdar and Majumdar 2012 [41]. Reproduced with permission of Elsevier.)

the following: (i) a mechanism other than hyperfine coupling causes the loss of spin polarization, (ii) the observed MR is really due to TMR that would disappear for C<sub>60</sub> thicknesses beyond the tunneling range, or (iii) in thick devices an increasing conductivity mismatch limits efficient injection of SP carriers. Based on the device current-voltage characteristics and comparison of the electrodes' work function and the lowest unoccupied molecular orbital of  $C_{60}$ , it was proposed that the conductivity mismatch is a likely cause of the loss of spin valve signal with increasing C<sub>60</sub> layer thickness. Gobbi et al. [46] showed spin coherent transport in fullerenes at room temperature with > 5% MR at RT in relatively thick (>25 nm) fullerene-based spin valves. These experimental results were interpreted using a multistep tunneling model for both electronic and spin coherent transport. It was concluded that both the large MR values and relatively small applied bias dependence of MR are related to the robust intrinsic properties of fullerenes for spin transport. MR ratio of over 5% at room temperature in hybrid spin valve devices with  $C_{60}$  as the spacer layer was also reported by Zhang *et al.* [47]. Also, a large spin diffusion length of approximately 110 nm was found for the  $C_{60}$  layer at room temperature that is much higher compared with that observed for small molecule Alq<sub>3</sub> [39] or polymers [40, 41].

Recently, a report by Li et al. pointed out clear correlation between improved charge transport and better spin transport. In their spin valve devices with n-type semiconducting polymer P(NDI2OD-T2) with better charge carrier mobility, more than 3% MR at room temperature was reported [48]. Improvement of interface properties by insertion of a thin  $AlO_r$  layer at the Co/polymer interface together with optimal annealing of bottom LSMO electrode also improved the device response, and an MR ratio of 54% at LT was reported. A spin diffusion length of 64.5 nm, similar to that as RRP3HT, was reported for P(NDI2OD-T2); however the temperature dependence of  $\lambda_{S}$  was weaker. For improving the room temperature response from the spin valves, Sun et al. [49] employed another interesting way. Spin valves with an interlayer of barrier between the bottom FM electrode and spin-transporting layer of bathocuproine (BCP) were used where the barrier was either a leaky and a non-leaky  $AlO_x$ . The junctions formed by the non-leaky  $AlO_x$  layer formed a true inorganic tunneling device, with very high device resistance even at room temperature and a weak tunneling-like temperature dependence. In these junctions, 2% MR was only measured with ultrathin layers of BCP, as expected for tunneling transport. With increasing BCP thickness, the devices became extremely resistive, and above 10 nm, measurement of any clear MR signal was impossible. Instead, with leaky seed layers, a strong temperature dependence of the junction resistance was observed, and MR was measurable even for BCP layers up to 60 nm thick (Figure 7.3). These devices showed clear MR response for different thicknesses of the BCP layers (5, 10, 30, and 60 nm of BCP), and even for the 60 nm BCP film, the MR signal was clearly distinguishable. However, in thicker devices, the curves became noisy due to high junction resistance (in the giga-ohm range). A 7% MR value at ambient conditions was reported in these devices, and it was concluded that spin transport takes place in the molecular levels of BCP.



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**Figure 7.3** (a) Reference SV (without BCP) with non-leaky  $AIO_x$ , (b) 5 nm BCP SV with non-leaky  $AIO_x$ , (c) 5 nm BCP SV with leaky  $AIO_x$ , (d) 10 nm BCP SV with leaky  $AIO_x$ , (e) 30 nm BCP SV with leaky  $AIO_x$ , and (f) 60 nm BCP SV with leaky  $AIO_x$ . The blue and red lines represent the MR value corresponding to voltage sweep from negative to positive and back from positive to negative, respectively. (Sun *et al.* 2013 [49]. Reproduced with permission of Nature Publishing Group.)

#### 7.3.2 Hybrid Magnetic Tunnel Junctions

To avoid the challenges of achieving significant MR response near room temperature in thicker devices, efforts were made to achieve functional hybrid MTJs. However, achieving an organic-based MTJ without shorting is often tricky due to the well-known problem of top electrode penetration into the soft organic layer. The first MTJ using OSC Alq<sub>3</sub> was reported by Santos *et al.* [50] with a 6% positive TMR response at room temperature. Subsequently other OSC small molecules like rubrene [51] were used as the tunnel barriers in hybrid MTJs. Santos *et al.* [50] experimentally determined the spin polarization of Co, Fe, and permalloy (Py) electrodes through the junctions with Alq<sub>3</sub> barrier and an Al counter electrode using the Meservey–Tedrow technique [52]. A spin polarization (P) value of 27% was determined for the Co electrode and Al<sub>2</sub>O<sub>3</sub>/Alq<sub>3</sub> barrier. A P value of 30% for Fe and a P value of 38% for Py were determined. This measurement provided a direct evidence for the SP tunneling current from an FM to an OSC. However, the value of *P* reduced to only 6% for the junctions without any  $Al_2O_3$  barrier at the  $Al/Alq_3$  interface. For the junctions, with and without the  $Al_2O_3$  at the  $Al/Alq_3$  interface, a positive *P* value for Co, Fe, and Py electrodes was measured that justified the positive TMR values. This positive TMR is in contrast to the inverse GMR earlier observed by Xiong *et al.* [35] and others [53] in  $Alq_3$ -based spin valves. The authors noticed that the tunneling behavior observed in this study is similar to that for amorphous  $Al_2O_3$  and SrTiO<sub>3</sub> tunnel barriers [54], in which positively polarized itinerant *sp* electrons dominate spin transport [55].

In 2010, Barraud *et al.* [56] reported a nano-sized hybrid MTJ that exhibited a positive TMR response of up to 300% at 2 K (Figure 7.4). The nano-sized junctions were formed using contact atomic force microscopy tips to avoid the defect prone areas of the bottom LSMO and the  $Alq_3$  layer. The MTJs obtained in this way showed almost 65% device yield, among which 20% showed measurable MR from 10% to 300%. The authors also proposed a model for explaining the sign inversion of MR response called the spin-hybridization-induced polarized states (SHIPS) model.

SHIPS model explained the discrepancies of the signs of MR taking into account the spin injection into molecules and the other apparent discrepancies. Earlier negative MR in large-area junctions was explained using the Jullière model with LSMO as a spin analyzer with  $P_{\rm LSMO}/_{\rm Alq3}$ \* > 0 and  $P_{\rm Co}/_{\rm Alq3}$ \* < 0 at the Co/Alq<sub>3</sub> interface. However, SHIPS model proposed that, oppositely, a SHIPS inversion occurs in large-area junctions at the bottom LSMO/Alq<sub>3</sub> interface, leading to an effective  $P_{\rm LSMO}/_{\rm Alq3}$ \* < 0 while turning  $P_{\rm Co}/_{\rm Alq3}$ \* > 0. The positive sign of the  $P_{\rm Co}/{\rm Alq}_3$  indicates a weak coupling in the model that is supported by the direct measurement of  $P_{\rm Co}/{\rm Alq}_3$  > 0 [50] by the Meservey–Tedrow technique. Also insertion of an inorganic Al<sub>2</sub>O<sub>3</sub> spacer between Alq<sub>3</sub> and Co in an LSMO/Alq<sub>3</sub>/Co spin valve did not change the sign of the MR, whereas an



**Figure 7.4** (a) The device schematics of a La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>/Alq<sub>3</sub>/Co nanometric-size MTJ. The nanoindent in the Alq<sub>3</sub> layer is realized by a CT-AFM, allowing the control of the organic tunnel barrier thickness. This nanohole is then filled with cobalt, leading to the nanometric-size MTJ. (b) Magnetoresistance curve of the organic MTJ obtained at 2 K and -5 mV. The lower coercive field corresponds to the LSMO magnetic reversal and the higher coercive field to the Co magnetic switching. Inset: *I*(*V*) curves recorded at 2 K in the parallel (IPA) and antiparallel (IAP) magnetic configurations. (Barraud *et al.* 2010 [56]. Reproduced with permission of Nature Publishing Group.)

inversion is expected considering the commonly reported result of  $P_{Co}/_{A|2O3} > 0$ . Therefore  $P_{LSMO}/_{Alg3}^* < 0$  indicate a strong intermediate coupling in the SHIPS model in addition to disorder contribution. When the disorder contribution is distributed over space and energy, the model predicted that the inversion should not happen for all of the interfacial molecular states but only locally for the ones that are close enough to the Fermi level of the electrodes dominating the injection step. The local character of this SHIPS-induced bottom-interface inversion explains why the spin-polarized scanning tunneling microscopy (SP-STM)-like experiment, where a single outcome of the energetic disorder distribution is probed mainly at off-resonance condition, fails to see the sign inversion. SHIPS model clarified the results of Vinzelberg et al. [57], where negative MR on millimeter-wide LSMO/Alq<sub>3</sub>/Co spin valves changed to positive with changing bias voltages for a few samples. This inversion of MR sign as a function of bias was explained as a signature of spin-dependent resonant tunneling through localized states. For a single merged donor-acceptor state in resonance with the Fermi levels, the spin-dependent Breit-Wigner formula was used. The proposed SHIPS mechanism suggested that through modification of metal/molecule coupling, it is possible to tailor the properties of spintronic devices, ultimately controlling the spin injection sign and amplitude by an applied voltage. Use of self-assembled monolayers (SAMs) where it is possible to play with the anchoring groups and the backbone of the molecules is suggested as an interesting route that could bring new properties beyond the now recognized low cost, flexibility, and long spin lifetime interest, chemistry hardly available in conventional inorganic spintronics.

#### 7.3.3 Toward Single Molecular Devices

In recent times SP transport through single molecules has been visioned as the future of spintronics as it combines the goals of downscaling of electronic components (for lower power consumption with increasing speed and integration density) and increasing computational bandwidth by manipulating spin in addition to charge. With the recent promising discovery of formation of highly spin-polarized interface between a ferromagnet and the organic molecules, the idea of extreme downsizing of spin devices has gathered momentum. One such promising result is reported by Schmaus et al. [58] where SP transport was observed across a single NM hydrogen phthalocyanine molecule (H<sub>2</sub>Pc) with chemical formula  $C_{32}H_{18}N_8$  contacted by the FM tip (Figure 7.5). A 60% GMR response was measured by using SP-STM. This study identified that due to charge transfer toward the molecule and the hybridization of molecular orbitals near the Fermi level with bulk electronic states of the electrodes, transport across the molecule is nearly resonant in the minority channel. The results also verified that the organic molecules are able to sustain a large current density with substantial spin polarization, thus confirming the concept of single molecular spintronic devices.

A spin-dependent hybridization mechanism that can also dominate the MR in the TMR regime was also verified by *ab initio* theoretical analysis. Results by Raman *et al.* [59] showed that delocalized carbon-based radical species with

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**Figure 7.5** (a)  $H_2Pc$  molecules adsorbed on cobalt islands with different out-of-plane magnetic orientations. (a) Topographic image of  $H_2Pc$  molecules adsorbed onto two cobalt islands on the Cu(111) surface. Color code: measured dl/dV at -310 mV. The two island species can be distinguished by the magnetization parallel (in yellow) and antiparallel (in red) to the tip magnetization. (b) Typical dl/dV spectra taken on parallel and antiparallel oriented cobalt islands (marked by red and blue crosses in a) clearly reveal spin-polarized density of states below the Fermi edge. (c) Energy dependence of the optimistic TMR ratio calculated from the dl/dV spectra. The highest value is measured at approximately -350 meV and is used to distinguish between the magnetic orientations of the islands. (Schmaus *et al.* 2011 [58]. Reproduced with permission of Nature Publishing Group.)

unpaired spin, such as phenalenyl, could be very promising for the construction of quantum memory registers. These phenalenyl derivatives, formed by the fusion of three benzene rings, have considerable similarities with graphene fragments and belong to the class of open-shell systems. The spins of these molecules respond to external stimuli such as light and electric and magnetic fields opening up possibilities for performing single molecular spin memory and logic operations. A spin device based on such molecules as templates to engineer interfacial spin transfer resulting from hybridization and magnetic exchange interaction with the surface of a ferromagnet was fabricated, and the device reported an interfacial MR of more than 20% near room temperature. The report also confirmed that the formation of a nanoscale magnetic molecule with a well-defined magnetic hysteresis on FM surfaces that suggests the use of chemically tunable phenalenyl-based molecules is a viable and scalable platform for building molecular-scale quantum spin memory and processors at room temperature, opening up route for realizing future molecular quantum information processing systems.

# 7.4 Preparation Methods of Organic Semiconductor Thin Films for Spintronics

While the history of organic thin films can be dated back to about 2000 BC [60], the part of it related to the hybrid spintronics and spin crossover (SCO) materials

is less than two decades old. Although broad range of applications of OSC evolved since the 1990s in the form of organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaics, the organic spintronics has evolved as one of the hottest research topics since the evidence of spin transport in organic semiconductor sexithienyl ( $T_6$ ) material in 2002 [34]. Similarly to the  $T_6$  molecule, the spintronic properties have been also investigated for other oligomers such as metal chelates (Alq<sub>3</sub>), phthalocyanines (Pcs), and also acenes like tetracene, pentacene, and rubrene. The latter compound rubrene (tetraphenyltetracene) has been widely applied about three decades ago as a laser dye of excellent luminescence properties [61]. The renewal interest in it is due to the high carrier mobility in the range up to 20–40 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [62] among the aforementioned organic materials that are characterized by a similar molecule size (~1 nm) and can be fabricated by various growth techniques in either single crystal (SC), polycrystalline, or amorphous form.

#### 7.4.1 Single Crystals and Thin Film Fabrication

In understanding the spintronic functionality, the SC plays an important role because of the high material purity and degree of structural order that enable study of the charge transport mechanism at a level that is unattainable in polycrystalline materials. This becomes even more evident when processes such as charge separation and trapping and electron-hole recombination in spintronic devices are considered, which are entirely based on the properties of the organic semiconductor-metal interface. For example, usage of a SC p-type rubrene laminated on the fullerene derivative PCBM amorphous thin film on glass made possible the observation of effects characteristic for the PCBM-rubrene interface [63]. The photocurrent values in the visible region became greater by a factor of 300 compared with that of the bulk heterojunctions, and SC devices have been observed. The large photoresponse has been ascribed to improved charge transport and long exciton diffusion length due to the interface presence. It promotes polarization effect reducing the band gap and supports interfacial exciton separation to sufficiently distanced donor and acceptor layers, thus minimizing the electron-hole recombination. Similarly, Karak et al. studied the distribution of potentials at the rubrene-metal (Al) Schottky interface using the p-doped SC rubrene and clarified the effect due to insertion of an ultrathin LiF interlayer separating the rubrene and Al electrode in a model OFET device of lateral geometry on ITO [64]. At both the rubrene/Al and LiF/Al interfaces, the photo-potential was found to be equal to the built-in potential. While in the case of rubrene/Al it corresponded to the work function difference between Al and ITO, a substantial increase of this potential and reduction of the Al work function have been concluded as an effect of the LiF spacer insertion.

The previous examples not only confirm the importance of studies with the use of SC but also contribute to the knowledge applied in the area of organic electronic devices. On the other hand, the already mentioned properties of SC also prescribe research direction and goals to attain for their polycrystalline counterparts that are preferred in the industrial-scale applications. Despite appreciable results collected so far, the obvious size limitation of devices based on SC hinders substantially their application potential. This and other practical issues such as cost-effective manufacturing of flexible devices make thin polycrystalline films of OS materials preferable from the point of view of industrial-scale fabrication.

On the other hand, the carrier mobility values reported for rubrene thin films are much smaller in comparison with those of SC and can differ by several orders of magnitude (between  $\sim 10^{-5}$  and  $10^{-1}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) in dependence on preparation method [65], crystallinity, and structure as observed for other acenes like pentacene [66].

It is worth mentioning that a research route for high-performance organic thin films was proposed in an earlier milestone work reported by Garnier *et al.* [67]. That study showed in thiophene oligomers that relatively large mobilities in polycrystalline organic semiconductors are possible. Moreover, it indicated that a long-range molecular ordering and close-packed structure represent the two important conditions for increase of the carrier mobility and the performance improvement of the organic thin film devices.

Regarding OSC device fabrication, the main concerns are related to materials and morphology of the spin-transferring organic component and inorganic ferromagnetic spin-injecting electrode, which determine the hetero-interfacial properties, and both have a critical effect on the device performance as mentioned earlier in this review and other works [68]. It is also in agreement with the conclusion of a paper from the area of the SCO materials published recently, which points out material functionalities strongly dependent on the presence and content ratio of the solid amorphous and crystalline phases [69]. In particular, the experimental results convince that formation of different structures such as crystalline and/or polymorphs resulting from the applied preparation method can also be influenced by additional processing of the underlying surfaces prior to deposition of the organic material and application of intermediate layers supporting adhesion and nucleation such as various SAMs and also annealing of the grown OS structures [70].

After more than a decade of research, a substantial number of results and different aspects of the OSC materials are comprehensively discussed in review papers [71–74]. A summary on spin valve materials investigated so far is given in the paper of Devkota *et al.* [71], while functionalities in relation to materials and their fabrication are discussed by Sun *et al.* [72] and are also thoroughly analyzed for SCO complexes in review works [73, 74]. However, reviews devoted to the fabrication aspect of organic spintronics are missing in the literature, which seems somehow surprising, because it refers to the most critical factor of the application route.

The thin organic films for spintronic applications can be fabricated by means of various well-established techniques in dependence on the material to be deposited, substrate selected for interface formation and requirements for the film and interface quality. In the following, advances in preparation and fabrication of the OS materials are discussed and as far as possible with focus on the already mentioned semiconductor rubrene not only for consistence but also because of two other reasons. First, this compound can be considered as sufficiently representative at least for the entire class of intensively studied

oligomer materials. Second, the high value of carrier mobility makes rubrene very attractive for researchers and stimulates investigation of various fabrication concepts either already applied or applicable to other OS materials as well, which in turn ensures a more general approach in reviewing the fabrication techniques. Moreover, the approach also takes into account that in numerous works devoted to growth of the rubrene thin films on various substrates, the presence of amorphous films with spherulitic structures is reported. This undesirable growth effect originates in the rubrene molecular conformation characterized by the phenyl rings twisted in respect to the tetracene backbone, thus causing non-planarity of the molecule, which in turn hinders the growth of crystalline film [75].

#### 7.4.2 Fabrication from Solutions

The large class of fabrication techniques based on the use of liquid solutions includes the well-established ones such as dip coating, drop casting, and spin coating and also a variety of their modifications as discussed in Section 7.6 devoted to SCO materials in this chapter. These techniques belong to the relatively simple and most broadly applied, despite problems with fabrication of the agglomerate-free films of controlled thickness in particular on larger-area or rough surface substrates. Here, the Langmuir–Blodgett dip coating using SAMs represents an exception because of the film thickness control possible at the molecular level, which is crucial, for example, for studying the interface effect on the OS device performance as shown for the metal–organic–metal sandwich structure [76].

In the area of solution-processing fabrication schemes, the incorporation of a glass-inducing diluent (5,12-diphenylanthracene) that enables controlled crystallization from an initial vitreous state of the organic semiconductor was the principal difference from preceding works as reported in [77]. The vitrifying diluent was applied in order to prevent crystallization on casting from solution, while various crystallization routes following casting and drying were possible by establishing the phase behavior of the semiconductor and the vitrifying agent mixture. A nearly temperature-independent mobility value of up to  $0.7 \,\mathrm{cm}^2 \,\mathrm{V}^{-1} \,\mathrm{s}^{-1}$  obtained from OFET measurements confirmed the high crystalline quality of rubrene films obtained from this solution-based fabrication.

More recently, fabrication of the rubrene thin films via site-specific nucleation followed by growth of rubrene nanocrystals on the pre-patterned Ag electrodes has been reported [78]. The films were obtained in the reduction process of the cationic rubrene precursor by atomic Ag and resulted in neutral molecules with a concentration above the nucleation threshold. For OFET device based on polycrystalline rubrene films composed of triclinic nanocrystals obtained in that way, the mobility values of  $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  were observed.

The use of various solutions for fabrication of the crystalline films of rubrene has been reported by Matsukawa *et al.* [79]. In attempts to produce rubrene-based OFETs showing high carrier mobility, use has been made of the fact that rubrene solubility depends on the presence of aromatic rings and chloro groups rather than on the solvent polarity, and therefore the 1,2-dichloroethane

(DCE), aromatic (toluene, *p*-xylene), and aniline solvents were selected for the study. For rubrene SC (size up to ~1 mm) grown from *p*-xylene and aniline solvents, the absence of solvent content was confirmed by NMR. So triclinic crystallites characterized by stepwise flat surfaces as well as needlelike ones were observed. The model OFET devices based on the flat-faceted crystals with graphite electrodes and insulating parylene layer revealed carrier mobilities up to 1.6 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Also, the same author with colleagues [80] reported another experiment where single rubrene crystals were grown by using the solution-slow cooling technique with 1-propanol solvent. The growth resulted in two polymorphs of rubrene, one characterized by thin hexagonal platelets (size < 300 µm) of orthorhombic structure and the other needlelike triclinic, as concluded from XRD data. OFET devices assembled with these hexagonal and triclinic crystals revealed observably different mobilities of 1.6 and 0.1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively.

#### 7.4.3 Vacuum Deposition Methods

Methods of thermal evaporation and deposition in vacuum (VTE) involve purely physical processes such as the high temperature evaporation followed by condensation or plasma sputtering by means of the RF and microwave discharges. These methods make use of the fact that most of the organic molecules of interest for spintronics can be evaporated by heating to moderate temperatures close to their sublimation point (490–590 K). The evaporation proceeds without decomposition of the molecular structure, as shown, for example, for  $T_6$ , Alq<sub>3</sub>, and pentacene [34, 81, 82].

Properties of VTE-deposited pentacene thin films were investigated in dependence on substrate temperature by Salih *et al.* [83]. From X-ray diffraction and electrical conductivity measurements, it has been concluded that substrate heating from ~303 to 403 K led to increased film densities and molecular ordering accompanied by a slight decrease of the film roughness (~ 30 nm). Also higher mobilities of  $10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in comparison with values observed for room temperature substrates were obtained for OFET devices fabricated with these pentacene films (average thickness of ~100 nm). This has been ascribed to slower crystallization at higher substrate temperatures, resulting in large crystallites that in turn improved the charge transport across grain boundaries.

Thermally evaporated SC and multilayer (40 nm thick) rubrene films deposited on Au and also on glass at growth rates below 1 nm min<sup>-1</sup> using Knudsen cell operated at temperatures between 480 and 550 K were investigated in detail by Kafer *et al.* [75]. With the use of the X-ray absorption fine structure spectroscopy (NEXAFS), the authors observed that the C1s NEXAFS spectra of rubrene recorded for thick multilayer films closely correspond with those obtained for SC.

The posttreatment of thermally evaporated rubrene thin film, that is, the amorphous to crystalline phase transformation by means of an abrupt heating, was proposed for the improvement of the film morphology by Lee *et al.* [84]. The short-term process (duration  $\sim 1$  min) in which the substrate with deposit has been kept on a hot plate at about 445 K in the inert N<sub>2</sub> ambient resulted in continuous rubrene thin film comprising large single-crystalline grains of average

size of 80 µm. OFET devices based on such films revealed carrier mobility as high as  $1.21 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . While results reported for this simple approach are surprisingly good, the attempts of other groups to reproduce the effect were not satisfying enough, as stated by Qian, Wang, and Yan in a more recent paper [85]. Instead, these authors propose fabrication of a high quality thin rubrene films by means of the weak epitaxy method. The reported OFET device showing mobility up to  $1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  is prepared on ITO-coated glass in a multistep process. First, silicon nitride is sputtered on ITO and subsequently covered by a spin-coated benzocyclobutenone (BCBO) film, both forming dielectric layer that is then coated with the 8 nm thick layer of *para*-hexaphenyl (*p*-6P). The rodlike molecules of the latter ensure epitaxial growth of the island-like rubrene crystals (size about 2 µm) of well-fused boundaries as confirmed by AFM and XRD inspection, and the SAED pattern indicates that crystal planes of rubrene and *p*-6P crystals are perpendicular.

More recently, the photoluminescence (PL) enhancement of rubrene by means of the localized surface plasmon resonance was reported for a thin (50 nm) rubrene film covering the layer of Ag NPs obtained by RF sputtering on Si substrate [86] The film was grown by VTE at low deposition rate of 0.6 nm min<sup>-1</sup> and onto substrate preheated to 350 K in order to ensure polycrystalline structure. The revealed PL intensity around 560 nm that was larger by a nearly one order of magnitude compared with that of rubrene film without Ag layer has been ascribed to the spectral overlap of the Au NP resonant absorption and rubrene emission. These results indicate that tuning of the plasmonic resonance for optimum luminescence enhancement by selection of the NP size and packing density is possible as well.

#### 7.4.3.1 Hot Wall Epitaxy

Advantages of the organic material deposition under conditions close to thermodynamic equilibrium can be exploited by using the hot wall epitaxy method. Typically, the growth reactor consists of a vertical cylinder (quartz) closed on top by the substrate and heated by three separately controlled toroidal ovens. The bottom, middle, and upper ovens heat the target and control the growth rate, control the temperature of the wall between the target and substrate, and heat the substrate to influence the growth process, respectively. Using this method with the target and wall temperatures both kept at about 508 K, variable substrate temperature (344-393 K), and growth time up to 3 h, the thin rubrene films were deposited on muscovite (mica) substrates, and the film morphology and crystallographic properties were characterized by transmission electron microscopy [87]. It has been observed that the initially formed amorphous droplets merge together in partially crystalline open networks and finally result in the formation of spherulites and a variety of crystalline morphologies. Among them, platelet and needlelike crystals were assigned to the orthorhombic phase of rubrene with the [301] and [110] zone axes, respectively.

Kafer and Witte [88] observed that a highly oriented crystalline rubrene film on  $SiO_2$  and Au [111] substrates can be obtained by epitaxial growth, whereas thermal vacuum evaporation–deposition (VTE, also known as organic molecular beam deposition-OMBD) at elevated temperatures results in prevailingly amorphous layers or polycrystalline dendritic networks. This substantial difference in the film structure quality accompanied by enhanced thermal and chemical stability in the case of hot wall epitaxy has been ascribed to the conformational change of rubrene molecules with a loss of chirality upon crystallization and to diffusion effect due to high temperature and large vapor pressure applied.

#### 7.4.3.2 Physical Vapor Transport

The application of a seeded physical vapor transport (PVT), known also as the modified Lely method, has been reported mainly for the fabrication of the OS SC devices. Compared with hot wall epitaxy, the PVT is performed in a horizon-tally aligned heated tube (furnace) where both the temperature gradient along the tube axis and gas flow rate control the growth. For the PVT growth of rubrene crystals, the vapor transport is ensured by a low flow rate stream (obviously below  $1 \, l \, min^{-1}$ ) of an inert gas such as Ar or N<sub>2</sub>, and temperatures up to about 590 K are applied as reported by Pinto *et al.* [89] and Karak *et al.* [64]. It has been demonstrated also that using PVT deposition setup, the relatively long (up to 1.5 cm), almost needlelike rubrene SC can be grown directly from the powder sample in the furnace hot region. Such an approach, however, resulted in a rather disordered collection of crystals regarding both the size and growth direction that has been observed for evaporation temperature and N<sub>2</sub> gas flow rate of 600 K and 100 cm<sup>3</sup> min<sup>-1</sup>, respectively [90].

#### 7.4.3.3 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is obviously considered as not advisable for organic materials, since the laser pulse power required to ablate and deposit the organic target can cause breaking of molecular bonds. Nevertheless, the ongoing development and improvements of laser-based deposition systems open new research possibilities interesting from the point of view of organic thin film fabrication. Details regarding the PLD development, the state of the art, and discussion of possible applications can be found in the work of Greer [91, 92]. Till recently, fabrication of thin organic films by means of PLD has been considered as alternative, solvent-free physical vapor deposition technique. Successful applications of PLD were reported for a variety of materials of interest for organic spintronics, including rubrene, pentacene, Alq<sub>3</sub>, and anthracene, despite known constraints regarding mainly the material (molecular mass, vapor pressure) and thermal properties.

The PLD deposition of organic molecules requires a careful selection of the process parameters as concluded from marked differences in the properties of anthracene films deposited at different laser fluencies [93]. For films of a thickness up to 115 nm, fluence values close to and above 75 mJ cm<sup>-2</sup> resulted in poor quality films, and instantaneously the threshold for significant material removal has been observed. While electro-optical performance of the PLD-fabricated devices was found to be strongly dependent on the laser fluence applied, no significant differences were observed between their *I*–*V* characteristics compared with devices consisting of the spin-coated and vapor-deposited layers. Also XRD and Raman studies performed for PLD-deposited thin films of organic

materials including  $Alq_3$  confirm the film properties very close to those of target materials [94].

Properties of pentacene thin films fabricated by means of the PLD and VTE techniques have been compared and discussed by Salih *et al.* [83] with the effect of substrate (Si or glass) temperature taken into account. In both cases the films deposited around 403 K showed an improvement of the film morphology and decrease in surface roughness compared with films prepared on room temperature substrates, and this has been ascribed to the presence of larger crystals in the film resulting from smaller growth rates. However, a substantial difference has been observed between mobility values obtained for OFET devices with films produced by VTE ( $10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) and PLD ( $3 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), which was explained by a higher degree of molecular ordering in the latter case.

In the area of inorganic-organic complex materials, the results obtained for PLD growth of ferromagnetic half-metallic manganite La1-r Srr,MnO3 (LSMO) thin films are reported, and dependence of the film characteristics on PLD growth parameters is discussed with a broader context of literature data taken into account by Majumdar and van Dijken [95, 96]. These authors point out that PLD technique made possible engineering of the spintronic material properties and is anticipated to contribute substantially to the fabrication of the complex interface materials. Their fabrication using the same method such as PLD to deposit consecutively both the complex metal oxides and soft organic materials without breaking the vacuum can provide a way to atomically clean device interfaces and simplify the device production. Also, the control over PLD process parameters is expected to result in a variety of structure modifications and functionalities. Attempts to follow this concept have been performed in frames of the COST Action MP1202 HINT and collaboration between groups from Aalto University (Finland) and the Szewalski Institute, PAS (Poland). First, the preparation and properties of thin films of the organic semiconductor rubrene were studied. Films fabricated by PLD in vacuum from hardened pellets using pulsed laser at 1064 nm and energy fluence around  $0.2 \,\text{J}\,\text{cm}^{-2}$  were examined using surface inspection (AFM, profilometry), and also absorption, Raman, and XRR spectra were recorded [97]. For the reference rubrene samples on SiO<sub>2</sub> glass, the AFM data revealed continuous 5-7 nm thick films (see Figure 7.6, inset). The prevailingly amorphous structure was concluded from Raman spectra showing a broadband around 1370 cm<sup>-1</sup> and signatures of both tetracene and phenyl bands in agreement with XRD data. In the next step, for PLD-deposited rubrene films on LSMO, the interface properties of this hybrid organic-inorganic spintronic system were investigated and characterized [65] (for results see Section 7.5.2 of this chapter). These recent examples of the PLD fabrication of spintronic materials indicate that the application area and limits of this versatile technique are still unexplored.)

#### 7.4.3.4 Matrix-Assisted Pulsed Laser Evaporation

Among fabrication methods reported for OS materials, the matrix-assisted pulsed laser evaporation (MAPLE) is the one only that has been discussed in several comprehensive review works such as those of Pique *et al.* [98], which discussed the preparation of organic thin films of functional polymers, various carbohydrate, and biological materials (glucose, sucrose, and dextran) and also the fabrication of NPs [99]. Principles of the MAPLE operation together with



**Figure 7.6** Raman spectrum of the PLD-deposited 7 nm thick rubrene film showing a broadband around 1360 cm<sup>-1</sup> characteristic for amorphous phase with superimposed weaker signatures corresponding to vibrational bands of the crystalline content. (Adopted from Ref. [97], SPIE.)

application conditions and description of the commercially available equipment and also last developments such as devices ensuring resonant infrared ablation with the use of tunable laser sources (RIR-PLD, RIR-MAPLE) are discussed in the paper of Greer [91, 92]. Compared with MAPLE with use of the fixed wavelength lasers, the RIR modification is based on the use of the infrared laser sources (including free electron laser) tuned for match with the absorption corresponding to molecular bond in the solvent but not in the organic material. Advances and progress in MAPLE applications for deposition of organic, biological, and NP thin films are discussed in a review paper by Caricato and Luches [100]. Also, a detailed description of the MAPLE technique and deposition mechanism and discussion of the application capacity including fabrication of sensor materials, organic electronic devices, drug delivery systems, and medical coatings and implants can be found in a recent work of Shepard and Priestley [101]. The MAPLE transfer of polymer from the water, isopropanol, acetone, and toluene ice matrices has been studied in detail by observation of the deposition rates [96, 101-103]. In the case of the toluene and acetone matrices, the contamination of deposits has been ascribed to small molecular photofragments and carbon produced by laser-induced reactions.

With use of the MAPLE technique, a glassy polymer films (poly(methyl methacrylate) (PMMA)) of enhanced thermal and kinetic stability compared with bulk material were successfully produced [96, 101–103]. From AFM and scanning electronic microscopy (SEM) data of the film surface, a clear evidence of the NS morphology has been derived, which indicated that this is the reason for the observed unique properties of the films.

Among other MAPLE applications, the use of a target obtained by means of the RIR-MAPLE for ablative production of colloidal rubrene NPs has been reported [96, 101–103]. The laser ablation of such target immersed in water resulted in the dispersion of a highly crystalline spherical and nearly unidimensional rubrene

NPs of average size of  $75 \pm 5$  nm. Recently, the MAPLE fabrication of rubrene thin films has been investigated at the Szewalski Institute, PAS (Gdańsk), with results of the previous PLD study taken into account. Films were deposited from 0.5 wt% rubrene solution in 1,1-dichloroethane (DCE) using 1064 nm pulsed laser at fluencies from the range of 0.2 to  $4.7 \text{ J cm}^{-2}$ . The presence of a mixed crystalline–amorphous films characterized by a significant increase of the crystalline content compared with those fabricated by PLD has been concluded from Raman spectra and results of the surface inspection shown in Figure 7.7.



**Figure 7.7** Rubrene thin films deposited by MAPLE from solution in 1.1-DCE on Si substrate. (a) Stack-plotted Raman spectra recorded at three surface spots of the 120 nm thick film obtained from 0.5 wt% solution at laser fluence of 3.6 J cm<sup>-2</sup> (18 000 pulses) reveal presence of crystalline phase characterized by closely packed columnar crystals (inset). (b) Optical microscope view of the film sample produced from 0.35 wt% solution at 4.7 J cm<sup>-2</sup> (left) and SEM image (right) showing crystallites embedded in amorphous rubrene matrix.

The presence of crystallites that reveal differences in the size, shape, and orientation and degree of the dendritic growth observed in the films (Figure 7.7b) in dependence on the deposition conditions indicates that their optimal selection needs to be found in order to fabricate homogeneous polycrystalline films with minimized content of the amorphous phase.

A modification of the MAPLE technique, that is, emulsion-based RIR-MAPLE, based on the use of emulsified target material being a mixture (emulsion) of organic material dissolved in appropriate solvent and water has been proposed by Stiff-Roberts and coworkers in 2008 [104]. The approach was intended for deposition of organic thin films with application potential in the production of heterojunction solar cells. Recent results obtained by the same group with use of this technique indicate that not only the organic thin film growth but also the film structure (morphology, surface roughness) directly depends on the composition of the emulsion [105]. It is also shown that the detrimental nanoscale aggregation and clustering of particles that is frequently observed for composite organic films fabricated by other techniques can be minimized in the case of the emulsion-based approach by a sequential deposition with use of the multicomponent sectioned targets.

#### 7.4.4 Nanoparticles and Nanofibers

Attempts in NP fabrication of the organic molecular materials (ONPs) and SCO complexes contribute markedly to the fast-growing area of organic spintronics because of the already mentioned unique thermophysical and optoelectronic properties evidenced for nanoscale materials and the broad range of possible applications. Both the SCO and OS devices are known for performance critically dependent on the film structure and crystallinity of the material, and in both cases the use of NPs represents a qualitatively new factor. For consistency, methods of the chemical synthesis of SCO nanomaterials and their properties are discussed in Part 6.3. Regarding organic spintronics, a growing expectation can be observed that NP materials could close the qualitative gap between the SC and polycrystalline structures where properties of the latter (e.g., charge carrier mobility) are still on the level that hinders application. A short review on fabrication techniques of ONPs such as re-precipitation and pulsed laser ablation in liquids (LAL) and also related citations can be found in the work of Kostler *et al.* [106]. This group proposes the fabrication of ONPs from their concentrated liquid dispersion by direct condensation of an organic compound in the liquid. The method represents a combination of the physical vapor deposition (thermal evaporation (VTE)) widely used for crystal and thin film growth, with vapor direct cooling and condensation. For some typical OS acene materials such as tetracene, pentacene, and rubrene, the NPs were produced by means of the proposed approach using THF and 0-dichlorobenzene as solvents and have been characterized by AFM and SEM imaging and absorbance and PL spectra as well. Peaks observed typically in the absorption of tetracene and pentacene NPs revealed substantial red shifts (about 50 and 80 nm, respectively) compared with solutions and a presence of the Davydov peak due to band splitting, while a small red shift ( $\sim$ 5 nm) between solution and crystal and also

absence of the Davydov splitting were observed for rubrene particles. In the latter case the weak intermolecular interactions hinder the long-range order in rubrene NPs, and the effect shows similarity with that observed as growth of the prevailingly amorphous thin films of rubrene. It is also worth mentioning the fabrication of rubrene nanofibers by means of electrospinning of the rubrene solution in CHCl<sub>3</sub> (chloroform) with 0.33 wt% admixture of polyethylene oxide as reported by Dhakal *et al.* [107]. For 600 nm thick electrospun fibers obtained with optimized process parameters, the presence of a mixed amorphous and crystalline phase of rubrene has been concluded from the Raman and PL spectra.

The fabrication techniques of organic spintronic materials described earlier are listed in Table 7.1. In consistent with text, the selection of data refers to rubrene. These are given for thin films and SC as well, as both structural forms make the understanding of the performance and limitations of organic spintronic devices possible and anticipate properties promising for future applications.

It is easy to observe that some of the reported fabrication techniques of polycrystalline and SC OS materials include the pre- and posttreatments (substrate preheating, film annealing, ambient gas selection), adlayers (e.g., SAMs), and also combined approaches. This trend seems to follow consistently the research route proposed already in 1993 by Garnier *et al.* [67]. Nevertheless, the appreciable contribution of this development, availability, and usage of various fabrication techniques to the huge research advance can be also validated by a simple observation of the carrier mobility values reported over the last two decades as it is shown in Figure 7.8 for the rubrene-based OS devices.

The data indicate that values close to  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  are reported for solutionbased fabrication during the last decade. This range of carrier mobility represents



**Figure 7.8** Values of the carrier mobility reported for rubrene-based OS devices obtained by various fabrication techniques over the last two decades; data extracted from Table 7.1 refer to polycrystalline (squares) and single crystal (circles) materials, and these grown from solutions are highlighted (oval marks).

Deposition/	Add process	Substrate	Resulting	material	Carrier mobility	References
fabrication method			Structure	Thickness/crystal (particle) size/roughness	cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	
Aromatic solvents			Single crystals (SC)	Bulky, size about 200 µm	0.75	[79]
From 1-propanol solution			SC platelets, orthorhombic + needlelike triclinic	Size ~300 µm	1.6 0.1	[80]
Dip casting, supersaturated solution	Film (5,12-dipheny lanthracene)	Glass	Glassy or polycrystalline orthorhombic needles		$0.1 - \le 0.7$	[77]
Reaction of rubrene perchlorate in solution		Patterned Au electrode	Polycrystalline (nanocrystals)	Crystal size 60–70 nm	0.02	[78]
Electrospinning			Fibers, mixed amorphous/crystalline	Thickness 600 nm		[107]
Hot wall epitaxy	Substrate preheated 344–393 K	Mica (muscovite)	Mixed amorphous (spherulites)/crystalline (needles and platelets)			[87]
Weak epitaxy growth	p-6P add layer	SiO <sub>2</sub>	Crystalline	$Crystalline domains \sim 2\mu m$	1–1.3	[85]
						(Continued)

Table 7.1 Rubrene-based spintronic materials: Exemplary data on fabrication techniques and results reported.

(Continuea)

Deposition/	Add process	Substrate	Resulting	y material	Carrier mobility	References
fabrication method			Structure	Thickness/crystal (particle) size/roughness	cm² V <sup>-1</sup> s <sup>-1</sup> )	
VTE	L-B DPPC pre- deposit. + post -annealing	Si	polycrystalline, interconnected platelets	−/~20 nm/1.5 nm	$0.85 \pm 0.18$	[70]
VTE	Substrate preheating	Glass or Si	Polycrystalline	100 nm/-/29 nm	10-4	[83]
VTE	Post-proc. abrupt heating		Polycrystalline, needlelike and platelets	Crystals > 80 μm	$1.03 \pm 0.11$	[84]
VTE		Au film on PDMS	SC		20	[62]
PLD		Glass or Si	Polycrystalline	30  nm/-0.4-5  nm	$3 \times 10^{-2}$	[83]
PLD	Substrate preheating	LSMO on STO/glass	Amorphous, small amount of cryst. phase	8 nm/-/1.2 nm	10 <sup>-6</sup>	[65]
PVT		Rubrene powder	SC, needlelike	$-/2-4  \mu m/-$	1.2	[06]
PVT	Predeposit. spin-coat. PCBM		SC	200–800 nm thick		[89]

Table 7.1 (Continued)

the technologically accepted level that – in the meantime – is also attained by using the continuously developed fabrication techniques based on physical vapor deposition. Among them, promising results are reported for vacuum thermal evaporation, vapor transport, and epitaxial growth of the polycrystalline films, which are of particular importance for OS applications, and it is expected also that the use of laser-based fabrication can unveil new potential in this area. The example of rubrene indicates that this could make closing the relatively large gap between the mobility values obtained in devices based on the use of high purity SC with adlayers and values reported for polycrystalline films recently possible.

#### 7.4.5 Morphology-Dependent Spin Transport Properties

As morphology of the organic thin films strongly affects the charge transport properties through it, spin transport in thicker spin valve devices also crucially depends on morphology. Based on the preparation techniques and post-annealing conditions of the organic thin films, an amorphous, semicrystalline, or single-crystalline thin films can be obtained, as discussed earlier, and moving from amorphous to crystalline phases would result in higher spin transport efficiency together with better charge carrier mobility. This prediction is based on the fact that in crystalline materials, there would be much less grain boundaries and other structural defects where SP carriers would suffer from scattering and trapping and would lose their spin memory. Also with higher mobility OSC, the SP carriers have to spend less time inside the OSC, and hence the probability of their spin relaxation would be minimized. Mooser et al. reported a direct scaling of the MR response with respect to the bulk mobility of the charge carriers in OSC TIPS pentacene thin films [108]. In a recent report Miller et al. [109] studied the role of spin-dependent processes on conductivity of polyfluorene (PFO) thin films by electrically detected magnetic resonance (EDMR) spectroscopy. PFO, with two distinct intrachain morphologies of an amorphous (glassy) phase and an ordered ( $\beta$ ) phase, demonstrated that conformational disorder can influence the observed EDMR signals, including the sign of the current changes on resonance as well as the magnitudes of local hyperfine fields and charge carrier spin-orbit interactions. In both morphologies, the presence of at least two different spin-dependent recombination processes was observed. At 293 and 10 K, the dominant process was polaron-pair recombination through weakly spin-spin coupled intermediate charge carrier pair states, while at LT an additional signature of spin-dependent charge transport through the interaction of polarons was observed. This additional contribution could arise due to increased triplet lifetimes at lower temperatures.

In a recent study Sun *et al.* [110] reported the morphology dependence of spin valve response on an n-type semiconductor-fluorinated copper phthalocyanine ( $F_{16}$ CuPc)-based spin valves. By using an LT deposition method, they regulated the morphology of the  $F_{16}$ CuPc thin films and tested the spin properties of  $F_{16}$ CuPc with the films grown at room temperature. For the LT films with the very smooth amorphous films (~0.2 nm root mean square roughness), a considerable MR (>4%) and a very long spin diffusion length (up to 180 nm) have

been reported at room temperature. Another important aspect of rough organic film is having a poorly defined organic/FM top interface that can promote additional spin scattering, which was experimentally observed by Liu *et al.* [111]. Therefore both for thicker and thinner devices where SP carriers travel by hopping or tunneling respectively, a smooth film with good crystalline property is an essential condition for high performance spintronic devices.

## 7.5 Inorganic Ferromagnet–Organic Interface

## 7.5.1 Interface Spin Polarization

Interfaces between different materials are the fertile new ground for many unexpected and technologically important phenomenon due to reconstruction of charge, spin, and orbital states. These reconstructions often lead to novel features often missing in individual components. Recent years saw a particular surge of interest on the hybrid organic/FM interface where a strongly spin-polarized interface termed as *spinterface* is experimentally realized [112, 113]. Results showed that adsorption of organic molecules on an FM surface leads to bonding-specific electronic coupling affecting the magnitude and sign of the spin polarization at the hybrid interface. Due to the adsorption of the molecules, a chemical reaction takes place between the FM surface and the organic layer forming a hetero-interface with completely different features compared with the individual thin film surfaces. Reports so far showed clear indication toward promising effects occurring at such interfaces that can be used for improved spintronic components. This section of the chapter will discuss the recent research results of such interfaces. Since the FM/organic interface determines both the charge and spin injection/detection, the performance of the devices is critically dependent on such interfaces. The present chapter reviews different techniques used for experimentally measuring interface spin polarization including X-ray magnetic circular dichroism (XMCD), spin-polarized photoemission spectroscopy (SPPES), spin-polarized metastable de-excitation spectroscopy (SPMDS), SPSTM, two-photon photoemission, and so on.

#### 7.5.1.1 Energy Level Alignment of FM Electrode/OSC

The interface energy level alignment between the metallic or metal-oxide electrode and OSC plays a vital role in organic electronic devices. Estimation of injection barrier height is possible from the measured energy level alignment of the individual materials, and therefore it can be predicted whether an interface energetically favors the injection of electrons or holes into an electronic device. However, an important point to consider is that the energy level at an interface is often different from that on the vacuum level, preventing us from predicting the device performance accurately. Therefore in order to clarify the device performance comprehensively, a thorough knowledge of the interface energy band structure is important. Zhan and Fahlman [114] have shown that based on the device fabrication process, there are direct or indirect contact formations between the FM and the organic layers (Figure 7.9). Indirect contacts are formed

**Figure 7.9** Schematic illustrations of the interactions between the metal d-band and the HOMO and LUMO of the organic molecule: (a) original molecular states, (b) formation of the broadened molecular states by the interaction with the broad continuum of the metal sp-bands, and (c) formation of the bonding and antibonding states by the interaction with the metal d-band states. (Reproduced from Zhan and Fahlman 2012 [114]. Reproduced with permission of John Wiley & Sons.)



between the OSC and the FM electrode when the individual layers are deposited under ambient conditions, causing a native oxide and/or hydrocarbon surface layer on the FMs. Another possibility is when a tunnel barrier is intentionally inserted between the organic and the FM layer. In organic spin valve devices, barriers such as Al<sub>2</sub>O<sub>3</sub> or LiF are the most commonly used ones. These native or engineered barrier layers isolate the FM metal or metal-oxide surfaces from the organic layers, preventing any chemical bond formation between the OSC and the FM. Under these circumstances, spin polarization of  $\pi$ -conjugated orbitals of the OSC does not interact with the SP d-bands of the FM, at least not through any direct exchange interaction of wave functions across the interface. Indirect contacts can, however, strongly modify the work function of the FM electrodes due to the so-called pushback effect [115] even when barrier layer is an insulator and has no intrinsic dipole (e.g., hydrocarbon contamination). Therefore the work functions of atomically clean FM surfaces are inadequate to estimate the real energy level alignment. When the barrier layer (natural or engineered) is within tunneling limit, SP charge carriers can tunnel from the FM into the OSC (or vice versa), and the energy level alignment at the interface depends on the position of the Fermi level of the (modified) FM surface. Also it depends on the energies that correspond to the ionization potential, the electron affinity (hole and electron polaron formation energies) of the OSC molecules at the interface, the intermolecular and intramolecular ordering of the molecules at the interface, and the electrostatic interaction with the substrate. The energy needed to create a hole (or electron) in a particular molecular orbital of an OSC molecule is determined by its interface properties. The energy mismatch between the modified surface of the FM electrode and OSC layer can introduce an intermolecular order very different from that in the bulk of the OSC film. Depending on the local intermolecular order, the ionization potential energies can vary even up to 1 eV. However, it is important to note here that large variations in local intermolecular order could lead to a wide distribution of polaron energies manifesting in a modification of the injection and multistep hopping process. This could enable low bias injection and transport even when the polaron energies of the majority intermolecular order distributions are far from the Fermi level of the spin valve device. In a direct contact, chemical interaction between metal surface and some

specific atoms of the OSC leads to the reconstruction of molecular structure through covalent bonding to the surface, thus creating a hybrid interfaces states, which has been discussed previously. Here we discuss a few experimental methods and results to characterize such hybrid interface states.

#### 7.5.1.2 Hybrid Spinterface Characterization Techniques and Results

Although the name "spinterface" appeared recently, the high spin polarization at an FM/organic interface was reported already in 2002 by Suzuki et al. using the SPMDS studies [116, 117]. These works demonstrated the electronic structure and spin asymmetry of metal (Mn, Fe, Cu, and Mg) phthalocyanine molecules (Pcs) and metal-free Pc thin films of 1-monolayer (ML) thickness on a Fe (100) substrate. The sign of the spin asymmetry of these interfaces was found positive on Fe (100), which according to the SPMDS convention signifies negative spin polarization. Therefore, it was concluded that the spin polarization of both metal and metal-free phthalocyanines is antiparallel to Fe (100) substrate. The surface density of states (SDOS) of the Pcs was almost identical for different central metal ions, leading to the conclusion that the Pc electronic structure is insensitive to the variation of the central metal atoms. However, the SPMDS measurements exhibited noticeable differences in the spin asymmetry signal among different Pcs, which were explained from the viewpoint of the electronic structures of the Pcs. This difference in the spin asymmetry irrespective of non-changing SDOS indicated an important role of the central metal atoms for determining the spin polarization. Structural analysis using low-energy ion scattering spectroscopy revealed that Cu-phthalocyanine (CuPc) molecules adsorb on the Fe (100) surface with their planes parallel to the surface when the film thickness is one monolayer. With increasing film thickness, the films start to become disordered, which was also supported from the SPMDS spectra for the CuPc films.

More recently, Djeghloul et al. [118] reported a highly efficient spinterface of phthalocyanine molecules on a Co SC surface. Spin-polarized direct and inverse photoemission (SPPES) experiments conducted at room temperature at this interface revealed a high degree of spin polarization. The measured magnetic moment on the nitrogen p orbitals of the molecules supported with an ab initio calculation confirmed highly spin-polarized charge conduction across the interface due to differing spinterface formation mechanisms. Based on the previous results, they proposed a recipe to engineer simple organic-inorganic hybrid interfaces with remarkable spintronic properties, sustainable well above room temperature. Using spin-resolved photoelectron spectroscopy and *ab* initio calculations, Lach et al. [119] also reported possible injection channels in metal phthalocyanines (MPc) (Figure 7.10). Based on the changing central metal atom of an MPc, it was shown that selective hybrid interface states at the Fermi level of an FM-OSC hybrid junction can be formed. Gruber et al. [120] explicitly demonstrated the role of magnetization of an FM layer (Co) in promoting and controlling the magnetization of molecular layers (MnPc) across a noble metal layer (Cu). The underlying FM promotes magnetic moments on the molecular sites through adsorption-induced electronic hybridization via the spin polarization of quantum well states within the noble metal layer.



**Figure 7.10** Magnetic coupling of FePc and CoPc to Co where the magnetization density is dominated by the iron and cobalt central atom at the molecular side in an out-of-plane geometry. Note the spin polarization present on carbon and nitrogen atoms of the phenyl rings, which is created through interaction with the spin-polarized Co-d states of the substrate. (Lach *et al.* 2012 [119]. Reproduced with permission of John Wiley & Sons.)

At the same time, the molecular magnetic moments are aligned by the resulting interlayer exchange. The sign and amplitude of spin polarization was shown to be controllable by nanoscale engineering of the spacer thickness. When the FM surface was coated with a graphene layer, the magnetic coupling became weaker, leading to a less robust SP interface.

Spin-resolved real-time pump-probe two-photon photoemission experiment (2PPE) together with femtosecond spin dynamics studies by Steil *et al.* [121] confirmed that the prototypical interface between cobalt and metal-organic molecule  $Alq_3$  can exhibit highly efficient spin filtering properties. The microscopic origin of spin filtering was verified with an optically generated transient spin polarization in a well-defined hybrid interface state followed by 2PPE measurements. The electrons were found to be trapped at the interface in a spin-dependent manner for a surprisingly long time of the order of 0.5–1 ps. This leads to the conclusion that electrons get trapped in hybrid interface states by spin-dependent confining potentials, resulting in spin filtering hybrid interfaces between FM metal and OSc.

XMCD measurement also provided direct evidence for the spin polarization of Alq<sub>3</sub> sub-monolayers on Fe surfaces [122]. Hybridization and exchange coupling between  $\pi$ -conjugated orbitals in Alq<sub>3</sub> and the 3d orbitals of Fe substrate were confirmed from the measurements. More recent XMCD measurements including C *K*-edge on C<sub>60</sub>/Fe interfaces showed mixture of C<sub>60</sub>  $\pi/\pi^*$  orbitals at the FM metal–organic interfaces [123]. A few other reports on the spin-polarized ultraviolet photoemission spectroscopy (SPUPS) focusing mainly on MPc/FM metal interfaces [124, 125] also directly demonstrated the formation of hybrid interface states induced by chemisorption of CuPc, CoPc, and FePc molecules at the Co surface. Among these three interfaces, CuPc/Co interface showed the strongest spin polarization directly at the Fermi level.

All these results mentioned previously discussed mainly the spin polarization properties at the interface between OSCs and FM transition metals. However it is expected that at the interfaces between OSC and the complex metal oxides such

as LSMO or LCMO, even more versatile properties might arise due to reconstruction of charge, spin, and orbital states at the interface of a complex oxide with another oxide or an organic material that can pave the way for many fascinating properties absent in the individual materials. A recent report by Grisolia *et al.* [126] experimentally demonstrated that reconstruction of charges at oxide interfaces can be engineered for novel phases at the interface that could enhance the device responses and control them more accurately.

#### 7.5.2 Interface Magnetism

Previously, XMCD measurements confirmed that adsorption of 1 ML of Mn phthalocyanine (MnPc) molecules decreases the magnetic moment of Co from 1.73 to 1.67 $\mu_{\rm B}$  (supplementary information of Ref. [118]). On-site local magnetization density maps also confirmed a strong AFM coupling between Co and C benzene sites that leads to a reduction of the total magnetic moment of Co by  $0.22\mu_{\rm B}$  for all C atoms [118]. Iacovita *et al.* [127], however, have shown FM interactions at the CoPc/Co nano-islands with a hybridization between Co 3d and N 2p states, resulting in a reduced magnetic moment of  $0.7\mu_{\rm B}$ . Several other groups [128, 129] also reported a change in the Co 3d electronic distribution due to chemisorption and subsequently hybridization with phthalocyanine molecules, leading to a suppressed magnetic moment of CoPc on Co or Fe substrates. Combined X-ray absorption spectroscopy (XAS) and XMCD study on sub-monolayer (ML)  $C_{60}/Fe_3O_4(001)$  interface showed reduction in ratio of  $Fe^{3+}/Fe^{2+}$  due to electron donation by the C<sub>60</sub> molecules [130]. Also hybridization of  $C_{60}$  molecules and Fe(001) surface leads to significant magnetic polarization of  $C_{60} \pi^*$ -derived orbitals [131].

The modified magnetic property at the FM half-metallic oxide LSMO and two OSCs cobalt phthalocyanine (CoPc) [132] and rubrene [65] interface is reported recently using bulk magnetic measurements (SQUID). A detailed X-ray photoemission spectroscopy (XPS) measurement indicated chemical reaction between the LSMO and the organic layers, resulting in a modified band diagram of the half-metallic oxide. For both OSCs, increase of FM properties both in terms of increased saturation moment  $(M_s)$  and Curie temperatures  $(T_c)$  were reported. From XPS, a modified core-level spectrum of Sr and Mn of LSMO surface in contact with rubrene or CoPc was confirmed. These modified core-level spectra do not return to their original states even after washing the OSCs away indicating chemisorption of the OSC molecules on the half-metallic oxide LSMO surface, causing interface hybridization between  $\pi$ -orbitals of OSCs and d electrons of LSMO. By modifying the interface with annealing treatments and insertion of additional dielectric layer of AlO<sub>r</sub>, the interface magnetism can be tuned significantly (Figure 7.11) [65]. Also, it was noted that after removal of OSC rubrene molecules, the improvement in FM property of LSMO surface remained although the  $M_{\rm S}$  value decreased compared with the 7 nm rubrene-coated LSMO. This is indicative of the fact that there are two contributions present simultaneously: (i) the rubrene molecule is chemically absorbed on the LSMO surface and changes its electronic and magnetic properties permanently, and (ii) in close contact with FM LSMO, a magnetic moment



**Figure 7.11** (a) Schematic diagram of the architectures of the grown multilayers with LSMO crystal structure and chemical structure of the rubrene molecule. (b) Field-cooled (FC) magnetization as a function of temperature together with the first derivative of magnetization (c) for pure LSMO and the LSMO coated with rubrene as grown (sample A), surface treated (sample B), and one with an AlO<sub>x</sub> layer in between (sample C)). (Majumdar *et al.* 2015 [65]. Reproduced with permission of ACS.)

is induced in OSC rubrene molecules that increases the  $M_{\rm S}$  of the LSMO coated with rubrene. After removal of the rubrene layer from the LSMO surface, the effect at the modified interface can be seen more clearly. It is calculated that the  $M_{\rm S}$  of LSMO is increased by  $0.592\mu_{\rm B}$ /formula unit (f.u.) because of rubrene coating. The important point to consider here is that the change in  $M_{\rm S}$  took place for a 20 nm thick LSMO film, while the main change takes place in the top 1 nm layer (~2 – 3 unit cells) of the LSMO (in contact with rubrene molecules). Considering the change in magnetization in the first 1 nm thickness of the film,  $M_{\rm S}$  was calculated to be 11.84 $\mu_{\rm B}$ /f.u. that leads to an impressive improvement of over 230% in surface magnetization of LSMO.

Morley *et al.* [133] also reported similar modified interface magnetic properties at the interface between  $Alq_3$  and two different magnetic electrodes NiFe and

CoFe by using XPS, Kelvin probe, and magneto-optic Kerr effect (MOKE) magnetometry. The surface magnetization of the transition metal electrodes, studied using MOKE magnetometry, showed that the surface magnetization of the NiFe electrode changed with the Alq<sub>3</sub> layer on top, which was considered to be due to the Alq<sub>3</sub> chemisorption onto the NiFe electrode altering the electronic states at the interface. The XPS spectra and MOKE data confirmed strong bonding between Alq<sub>3</sub> and the surface of the transition metal electrodes. This bonding was attributed to chemisorptions of the Alq<sub>3</sub> onto the metal surface, as traces of Alq<sub>3</sub> were seen by XPS on the surface after washing, in line with previous reports of chemisorption [65, 133]. The authors concluded that this chemisorption changes the surface magnetization and the spin polarization of the magnetic electrodes.

In this respect it is important to point out that the relationship between increased ferromagnetism and increased spin polarization at the FM/organic interface is not very straightforward as increased magnetic moment can also arise from trapped electrons, whereas only itinerant electrons contribute to spin polarization. Recent SPMDS measurements at the LSMO/graphene-indicated spin polarization at the interface improve compared with bare LSMO films [134]. Alteration of nature and the orientations of the molecules can affect the interface hybridization, leading to a promising way of designing SP interfaces that would control molecular spin state in the first molecular level next to the FM and is a step forward toward single-molecule spintronic component. Another important aspect of ultimate miniaturization of spintronics to single molecular level is to employ the SCO molecules where the molecules, without any contact with FM electrodes, can switch from low spin (LS) to high spin (HS) states and vice versa when subjected to external stimulus like temperature, pressure, optical excitation, and so on. The vast and very interesting field of SCO nanomaterials is discussed in the following section of the chapter.

## 7.6 Spin Crossover Nanomaterials

Among the family of switchable molecular materials, bistable molecular complexes exhibiting SCO present a wide range of assets and are therefore the topic of numerous investigations. SCO discovery dates back to 1931 when Cambi *et al.* recognized an anomalous thermomagnetic behavior in Fe<sup>III</sup> dithiocarbamate complexes, which they could not ascribed to classic antiferromagnetic interactions [135]. Much later, the phenomenon could be identified in several  $3d^4-3d^7$  transition metal ions in octahedral surroundings [136] and comprehensively investigated for a large number of Fe<sup>II</sup> complexes since the 1960s [136a, 137], mostly due to the development of <sup>57</sup>Fe Mössbauer spectroscopy [138]. In a typical Fe<sup>II</sup> SCO material, a reversible intraionic electron transfer from a LS ( $^{1}A_{1g}$ ) state to a thermally populated paramagnetic HS ( $^{5}T_{2g}$ ) state is recognized as an entropy-driven process, which can be addressed thermally, by external pressure, optically, and even electrically, yielding spectroscopic, optical, magnetic, and dielectric readout signals [139]. In the solid state, the presence of short- and long-range interactions mediated by phonons, solvent, and/or anion occupancy

in the crystal lattice can drastically affect the cooperative elastic communication among iron centers, thereby modifying their magnetic response [136]. In the 1990s, Kahn *et al.* recognized SCO compounds for their potential use in display devices and data binary recording because of their abrupt spin transitions (ST) with a large hysteresis width (>50 K), accompanied by an easily detectable optical response, together with a very good stability [140]. Later, such materials were proposed as pressure and optical sensors [141], for example, for the cold channel control for food and drugs [142] or for aeronautic applications [143], or as THz photonic filters [144].

Micro- and nanofabrication technologies have undergone revolutionized sophistication. Intensified activities surged in NP synthesis, thin film processing, and micro/nano-patterning for the design of SCO-based spintronic and nanoelectronic devices [73, 145-148]. For this purpose, a race between different research groups for the miniaturization of SCO particles has recently been launched [149–154]. In addition, thin films [155, 156], gels [157, 158], nanocomposites [159-161], liquid crystals [162], monoliths [163], patterned nanostructures [156, 164], and hybrid SCO nanomaterials made of SiO<sub>2</sub> [154], polystyrene [165a], PMMA [165b], and a biomembrane [166], to name a few examples, were successfully prepared. Yet, Monte Carlo simulations for cubic or spherical NPs [167] as well as practical sense predict a lowering of cooperative effects upon size reduction. Indeed, as much as the size decreases, the number of active sites is less, and therefore the SCO transition is observed more gradually, sometimes in an incomplete fashion. This is exemplified, for instance, for the 3D SCO material  $Fe(pyrazine)[Pt(CN)_4]$  [151a,b], which is known to display a hysteretic SCO behavior centered at room temperature. Compared with the bulk material, nanocrystals prepared by the reverse micelle method of size down to  $61 \text{ nm} \times 61 \text{ nm} \times 21 \text{ nm}$  show a gradual and incomplete yet still hysteretic ST shifted downward around 260 K (Figure 7.12) [151a]. When the size decreases



**Figure 7.12** Temperature dependence of magnetic properties of Fe(pyrazine)[Pt(CN)<sub>4</sub>] prepared under different crystal size. (Boldog *et al.* 2008 [151a]. Reproduced with permission of John Wiley & Sons.)

further below 12 nm, hysteresis even disappears but surprisingly reappears for 2 nm NPs [151d]. This reentrance phenomenon that has been recently theoretically predicted [151e] is very promising regarding the potential use of hysteretic NPs into devices, for example, for quantum computing.

Yet, a different behavior was observed for surfactant-coated NPs of the triazole-based 1D SCO polymers  $[Fe(NH_2trz)_3]Br_2 \cdot 3H_2O$  (NH<sub>2</sub>trz = 4-amino-1, 2,4-triazole), the abruptness of the ST, and the hysteresis width diminish as the particle size decreases with minimal displacement of the transition temperature in the heating mode,  $T_{1/2}^{\dagger}$  [152a–c].

An intriguing example was given by the 1D chain coordination polymer  $[Fe(Htrz)_2trz]BF_4$  (Htrz = 4H-1,2,4-triazole, trz = 1,2,4-triazolato), which was communicated to feature an exception to this trend [150a,b]. Indeed, while the bulk material displays a hysteretic ST above room temperature, no change of magnetic properties was observed when studying NPs in the solid state for particles as small as ~10 nm. This behavior most presumably calls for an aggregation of particles in the solid state. Recent investigation of NPs of the same system in solution showed the expected hysteresis decreases, translating a decrease of cooperative effects, with size reduction [150c, 161]. Similar observations were recently done on the monohydrate [Fe(Htrz)\_2trz]BF\_4·H\_2O [168, 169].

#### 7.6.1 Spin Crossover Thin Films

The Langmuir–Blodgett technique applied to an amphiphilic Fe<sup>II</sup> trisubstituted 1,10-phen compound provided the first SCO thin films whose spin switching properties were studied by variable temperature IR spectroscopy on CaF<sub>2</sub> slides [170a]. A more exhaustive investigation was done by Delhaes et al. [170c] on an amphiphilic mononuclear Fe<sup>II</sup> complex with substituted bipyridine ligands thanks to variable temperature IR spectroscopy. Langmuir-Blodgett films presenting spin state photoswitching properties at helium temperature were also reported [170] as well as thermally induced SCO around temperature [170]. Recently Matsuda and Tajima [170d] reported a study on thin film of an  $Fe^{II}$ 2,6-di(pyrazolyl)pyridine mononuclear complex obtained by spin coating on a glass substrate and used absorption spectroscopy and electrical resistance change to investigate the SCO behavior of the film. The reported film thickness was 30 nm and AFM confirmed the smoothness of the film. Another example of spin coating was realized by Naik et al. on a mononuclear Fe<sup>II</sup> complex [Fe(3-bromo-1,10-phenanthroline)<sub>2</sub>(NCS)<sub>2</sub>]·0.5MeOH exhibiting a gradual incomplete SCO behavior on cooling [171]. This compound was selected as suitable candidate to study the effect of alteration of particle size and shape on SCO properties. This compound is soluble in common solvents (MeOH, CHCl<sub>3</sub>) and is air/moisture stable, and its SCO properties are known in bulk sample [172]. The films were spin coated on both quartz substrate and silicon wafers with different spinning speed from a saturated solution of CH<sub>2</sub>Cl<sub>2</sub> and MeOH mixture. The color of the obtained film was pale pink. Raman spectroscopy was used as a prime tool to identify the compound, focusing on the major band located near 2061 cm<sup>-1</sup> associated with the C–N stretching mode of the isothiocyanato ligand [173]. This signal was slightly shifted to higher frequency compared with the bulk sample  $(2054 \text{ cm}^{-1})$  as expected for the LS [173].

<sup>57</sup>Fe Mössbauer spectroscopy was rarely used to investigate thin films probably due to the low amount of sample deposition, which necessary implies a long acquisition time, and weak signals. Therefore, the sample amount was increased by performing multiple coating steps to improve signal/noise ratio. Although no signals could be observed by X-ray powder diffraction due to low sample deposition and loss of crystallinity, UV-Vis optical spectra in absorbance mode gave bands that are comparable with that of bulk sample, thus confirming the identity of the complex upon film formation. Mössbauer spectroscopy recorded in transmission mode for the thin film of [Fe(3-bromo-1,10-phenanthroline)2(NCS)2].0.5MeOH at room temperature shows a LS signal with isomer shift  $\delta_{\rm LS} = 0.24(1) \,\rm mm\,s^{-1}$ . Since the same signal was detected for the bulk compound, no appreciable change in the electronic distribution around each individual iron atom was observed. The thin film however does not reveal any HS quadrupole doublet as found for the bulk material, thus demonstrating the effect of texture modification on increasing the ligand field strength. Morphology analysis by scanning electron micrographs shows a drastic reduction in particle size and deformation in shape compared with the bulk sample. Nearly spherical particles of 200-500 nm diameter were obtained, and further reduction in size down to 50-120 nm was obtained with increase in spin coating speed. Other surfaces were also used for deposition, for example, highly oriented pyrolytic graphite (HOPG) [174]. More recently deposition by sublimation under high vacuum [175-178] or layer-by-layer epitaxial growth techniques was employed [156, 179–181].

Recently, a bio-inspired approach was introduced to produce bio-inorganic thin films and in fine NPs of a SCO complex [166]. For this purpose, the model SCO complex  $[Fe(ptz)_6](BF_4)_2$  (ptz = 1-propyl-tetrazole) was selected due to its well-known thermo- and photochromic properties [136c] as well as its ability to crystallize at ambient conditions. Three methods were followed using a solution of the complex precursor in MeOH: (i) seeding of the crystals on the biomembrane, (ii) dip coating, and (iii) capillary deposition. Among the various available biomembranes, credentials of onion (Allium cepa) skin are well recognized [182, 183]. Indeed, this low-cost membrane is widely available, biodegradable, and thermally stable, up to  $\sim 200$  °C, which was precisely followed using thermogravimetry. Most importantly, its regular structuration observed by SEM featuring square shape cells of dimensions  $330 \,\mu\text{m} \times 93 \,\mu\text{m}$  can not only reduce the size of the deposited particles but also serve as a support to produce a SCO thin film. Accordingly, the size of the deposited crystals ranges from nano- to micrometers and can be controlled depending on nucleation and growth rate, as shown by SEM, which also revealed morphogenesis. Indeed,  $2 \mu m$  particles of  $[Fe(ptz)_6](BF_4)_2$  could be deposited by seeding after only 20 h. By lowering seeding time, it was possible to reduce the size of the particles down to 40–60 nm. After having checked that the deposited particles correspond to the targeted iron complex as deduced by EDX, X-ray diffraction, and Raman



**Figure 7.13** (a) UV–Vis spectra showing the SCO behavior of the biomembrane. (b) LS state of the  $[Fe(ptz)_{6}](BF_{4})_{2}$  complex identified by <sup>57</sup>Fe Mössbauer spectroscopy.

spectroscopy, the SCO properties of the hybrid thin film were confirmed by both UV–Vis spectrophotometry and Mössbauer spectroscopy (Figure 7.13).

The hybrid interface nature is of high interest given the complexity of the biomembrane featuring a phospholipid bilayer combined with a variety of proteins, carbohydrates, and other organics, embedded in a fluid mosaic arrangement [183b, 184]. Practically, the sugar chain layer of the cell membrane, cellulose, and glucoproteins of the cell wall contain abundant functional groups that are assumed to play a role in the formation of NPs [183b] and may offer variety of nucleation sites for controlled crystal growth. Interestingly, a high percentage of potassium was detected by EDX measurements on nucleated microcrystals. Since this element was not used at any stage of the synthesis of the complex, it is assumed to originate from the membrane because abundant potassium is present in *A. cepa* [185]. <sup>57</sup>Fe Mössbauer spectroscopy allowed distinguishing two anchoring sites of the SCO complex on the biosurface [166b].

Microcontact printing ( $\mu$ CP) has emerged as a powerful replication technique in recent years [186]. It uses patterned elastomer as the mold to generate or transfer the pattern of a given model. Since microprocessor devices are produced from silicon, patterning on/of silicon is of high significance although patterning complex electronic circuit or materials of interest on bendable plastic substrate is the claim of today's electronic commerce [187]. Patterning organic or inorganic switchable materials is also important in the frame of molecular electronic devices [146]. In this context, the SCO complex-loaded biomembranes with [Fe(ptz)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> were used as natural stencil, and the patterns in the form of either nanocrystals or thin films were successfully transferred to Si wafer (or glasses) by conformal contact with the Si wafer to yield to nanodots of 30–55 nm (Figure 7.14). This transfer method opens novel perspectives to study NPs away from their natural confinement and directly on selected supports. Regular micro- and nanometer-sized patterns containing bistable nanodots (30 nm) of Fe(pyrazine)[Pt(CN)<sub>4</sub>] have been fabricated by Molnár *et al.* using a



Figure 7.14 Microcontact printing of the SCO complex [Fe(ptz)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub>.

combination of lift-off and multilayer sequential assembly methods [179]. The question of the characterization of the SCO properties of such dots remains open due to the unavailability to record the SCO properties of such low magnetization particles.

This new concept in SCO research provides an opportunity for investigating properties of materials in their unnatural habitat, whose origin is a biosurface. It could in principle be applied to other types of complexes with diverse functionalities.

#### 7.6.1.1 Spin Crossover Hybrids

A strategy to prepare a hybrid SCO material consists of inserting a guest magnetic molecule into a given matrix. The first developments in this direction were achieved by encapsulation of two classic mononuclear Fe and Co complexes, namely,  $[Fe(2-pic)_3]^{2+}$  (2-pic = 2-picolylamine) and  $[Co(bipy)_3]^{2+}$ (bipy = 2, 2'-bipyridine), into Y-zeolite supercage using the ship-in-a-bottle approach [188, 189]. Other hosts were later used to welcome Fe<sup>III</sup> SCO complexes such as montmorillonite [190] or MPS<sub>3</sub> layered magnet [191]. In these cases, matrices isolate SCO particles, thereby lowering cooperative effects. Recent examples focus on the inclusion of SCO complex into MCM-41 mesoporous matrix [161] and metal-organic frameworks [192, 193]. The choice of the matrix is to consider with care because it should be transparent, diamagnetic, and compatible in size to host suitable guests and preferably provide a good mechanical protection. The 1D coordination polymer  $[Fe(Htrz)_2trz]BF_4$  has been selected as a suitable guest for the production of hybrid materials. This material bears exceptional SCO characteristics featuring a sharp ST well above room temperature, with a reproducible hysteresis loop associated with a drastic color change [194]. Last but not the least, it does not contain any water molecules that are known to give rise to unstable hysteresis loops due to solvent release [140b, 195]. This material was successfully inserted into a mesoporous silica monolith [163], graphene [196] and silica-gold nanocomposites [197], and other silica assemblies for fluorescence applications [154, 198]. Interestingly, MCM-41 was found to loosely surround the embedded 1D SCO coordination polymer [Fe(Htrz)<sub>2</sub>trz]BF<sub>4</sub> as concluded by Mössbauer spectroscopy, which shows identical isomer shift and quadrupole splitting as for the bulk sample [161]. As a result of a pressure and crystal size effects (2 nm nanocrystals being identified), a shift as well as a decrease of the hysteresis width was observed while the sample maintained its thermochromic properties.

# 7.7 Conclusion and Future Perspective

After a decade of intensive research efforts, the field of hybrid spintronics is in a very interesting state where rapid development is expected toward the single molecular and two-dimensional spintronic components with the newly emerging ideas of SP interfaces and SCO materials. To achieve this goal, material scientists still need to overcome major challenges like yield, reproducibility, sizable room temperature operations, and so on. Some promising new ideas pointed toward utilization of the optical control of spin flipping of charge carriers in conjugated polymers for spintronic devices [199]. On the basis of the dynamics of polaron relaxation in conjugated polymers, it is theoretically found that the spin of an injected electron, which converts to a negative polaron in a conjugated polymer, is reversed by photoexcitation. This effect of photoinduced spin flipping in polymers could be used to design a device of an optically controlled spin valve. Here the spin flipping being driven by the electric dipole transition rather than the magnetic dipole transition could lead to much higher efficiency. Also Velev et al. [200] theoretically predicted that using organic ferroelectric PVDF in a MTJ structure such as Co/PVDF/O/Co (0001) with asymmetric interfaces, both TMR and tunneling electroresistance (TER) can be obtained, giving rise to four-state memory devices that could be extremely interesting. Also inclusion of spin switching molecules in present-day components could open up a vast range of possibilities for designing new functionalities for improved spintronic devices with optimized performance in the near future.

## List of Abbreviations

AFM	antiferromagnet
BAP	Bir–Aronov–Pikus
DP	D'yakonov–Perel
EY	Elliot–Yafet
FM	ferromagnetic
GMR	giant magnetoresistance
FET	field-effect transistor
LED	light-emitting diode
MRAMs	magnetic random access memories
MTJ	magnetic tunnel junctions
NM	nonmagnetic
OSC	organic semiconductor
PCP	pi-conjugated polymers
PLD	pulsed laser deposition
RTD	resonant tunneling device
TMR	tunneling magnetoresistance

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