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Heterostructures of low dimensional materials for electronic, spintronic and sensor applications

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Heterostructures of low dimensional materials for electronic, spintronic and sensor applications

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Heterostructures of low dimensional materials for electronic, spintronic and sensor applications

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and in accordance with
the decision by the College of Deans.

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To my family

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Chapter 1: Introduction

Everyday life has been affected by the rapid progress in material science in recent decades. One of the most important examples includes advances in computing power. Nowadays, it plays a key role in many aspects of life. Yet, the demand continues for increasingly powerful, faster and miniaturized computing components. However, the well-known transistor elements, which are the central part of the today's computing devices, are increasingly difficult to manufacture due to downscaling limitations¹. Therefore, developing new structures with new functioning elements may help the development of future computing devices with high storage density.

Spintronic- and memristor-based devices are candidates, which possess the required characteristics for future electronics. As explained later in this introduction, suitably designed heterostructures of magnetic and nonmagnetic materials offer efficient control of the magnetization of magnetic materials, which is crucial for memory and computation. Also, memristors, which are heterostructures made of materials with different conductivities, are described and their functioning mechanisms are explained. This thesis illustrates the design and characterization of heterostructures of low dimensional materials for the applications mentioned above.

Heterostructures of different kinds of materials (any composition of magnetic, nonmagnetic, conductive, nonconductive, ...) benefit from the preservation of characteristics related to each element²⁻⁴ or showing additional characteristics related to the interface effects⁵⁻⁹. Heterostructures of low dimensional materials are one of the most important candidates for application in technological elements, like memories, sensors, and computing elements. In the following, we present spintronic and electronic applications of heterostructures related to the research done in this thesis. In addition, we explain heterostructures with respect to their sensor applications, which are also investigated in this thesis.

1.1 Spintronics

Spintronics, or spin electronics, refers to the study of the role played by the electron spin degree of freedom in solid state physics¹⁰. Spin transport in magnetic and nonmagnetic materials is one of the most attractive fields of research due to its potential application in electronic technology. Due to the discovery of giant magnetoresistance (GMR) effect in ferromagnetic/nonmagnetic (FM/NM) multilayer heterostructures, Albert Fert and Peter Grünberg jointly won the 2007 Nobel Prize in physics^{11,12}. After that, intense research in the field of spintronics, resulted in the emergence of magnetic random access memories, GMR based read-heads, and also magnetic sensors¹³. Heterostructures made of magnetic and nonmagnetic materials are suitably designed to make memory elements according to the spin degree of freedom in materials. This topic has recently developed with more attention on the spin-orbit torques (SOTs), which potentially opens avenues for fundamental studies and applications in future manufacturing. For example, the low energy consumption of controlling a magnetic state by SOTs resulted in much interest in SOT phenomenon in multilayer heterostructures in recent years^{14–18}.

Up until now, SOTs have originated from the spin Hall¹⁹ effect, and Rashba²⁰ and Dresselhaus²¹ spin-orbit coupling. These effects induce spin accumulation due to coupling between electron spin and orbital motion, which results in a torque on the magnetization of a neighbouring ferromagnet when a current of electrons is passing through the medium.

Figure 1-1: Illustration of the Mott-skew scattering. $-V$ is the speed of spin scattering centre and H is the magnetic field in the rest frame of the electron. Different scatterings for spin-up and spin-down electrons result when an electron scatters from a spin scattering centre. This mechanism is considered as extrinsic contributor to the spin Hall effect.

The origin of spin Hall effect is explained as following: different scatterings for spin-up and spin-down electrons result when an electron scatters from a spin scattering centre. To understand the effect we consider that the spin scattering centre approaches the electron with $-\mathbf{V}$. The spin scattering centre would have a magnetic field around it ($\mathbf{H}'$) due to the relative speed of electron to the spin scattering centre, as illustrated in Figure 1-1. The force acting on the spin of the electron is given by $\mathbf{F} = \nabla(\mathbf{s} \cdot \mathbf{H}')$, where $\mathbf{s}$ is the electron spin. When the spin up electron passes on the right side of the spin scattering centre, the spin direction and magnetic field would be parallel and the force deviates the electrons toward the increasing field, which is toward the left. When the electron passes on the left side, the magnetic field and spin directions are anti-parallel, and the force deviates the electron toward the weaker field, that is toward the left. Overall, an electron with up spin is scattered to the left and a down spin is scattered to the right²². This effect, also called Mott-skew scattering, was believed to be the major source of the spin Hall effect in early predictions²³. Briefly, this scattering can be understood as a spin dependent asymmetric scattering probability of an electron on an impurity due to the effective spin-orbit coupling. While this effect is understood as an extrinsic contributor to the SHE, there is an intrinsic origin known to be linked to the band structure, and the occurrence of band spin splitting by the spin orbit interaction at some high symmetry points near the Fermi level. Electrons experience an anomalous velocity perpendicular to the electric

Figure 1-2: Schematic of a ferromagnet/(heavy metal) heterostructure with spin orbit torque originating from the spin Hall effect. The spin current produced by the SHE in the heavy metal layer exerts a SOT on the ferromagnetic layer. Two types of torques can be produced according to the direction of the magnetic moment in the FM. They are field-like (FL) torque $\mathbf{T}_{FL} \sim \mathbf{m} \times \mathbf{y}$ and damping-like (DL) torque $\mathbf{T}_{DL} \sim \mathbf{m} \times (\mathbf{y} \times \mathbf{m})$, where $\mathbf{m}$ is the magnetization unit vector and $\mathbf{y}$ is the in-plane axis perpendicular to current flow direction $\mathbf{x}$.

field, related to the Berry's phase curvature²⁴.

In this context, heavy metals (HM), such as Pt and Ta, because they have large SOC²⁵, attracted special attention for their efficiency to produce SOTs through the spin Hall effect (SHE)^{26–30}. Figure 1-2 represents a schematic of what happens in a bilayer of HM/FM heterostructure when SHE exists. Spin current produced by the SHE in the NM layer exerts an SOT on the FM layer. Two types of torques can be produced depending on the direction of the magnetic moment in the FM. They are field-like (FL) torque $\mathbf{T}_{\text{FL}} \sim \mathbf{m} \times \mathbf{y}$ and damping-like (DL) torque $\mathbf{T}_{\text{DL}} \sim \mathbf{m} \times (\mathbf{y} \times \mathbf{m})$, where $\mathbf{m}$ is the magnetization unit vector and $\mathbf{y}$ is the in-plane axis perpendicular to current flow direction $\mathbf{x}$. The direction of the $\mathbf{T}_{\text{DL}}$ is opposite to the direction of the damping of the magnetization. The direction of the $\mathbf{T}_{\text{FL}}$ is tangent to the $\mathbf{T}_{\text{DL}}$ originating from the SHE in the adjacent HM layer. The magnitude of this $\mathbf{T}_{\text{DL}}$ depends on the transmission of spin current across the FM/HM interface^{31,32}. $\mathbf{T}_{\text{FL}}$ can originate from the Rashba-Edelstein Effect (REE) at the FM/HM interface due to the structural inversion asymmetry or from the spin current through HM via the SHE³³. When the magnetization lies in-the-plane of the bilayer sample, the action of $\mathbf{T}_{\text{FL}}$ is equivalent to an in-plane field $\mathbf{h}_{\text{FL}}$ parallel to $\mathbf{y}$, and that of $\mathbf{T}_{\text{DL}}$ establishes an out-of-plane field $\mathbf{h}_{\text{DL}} \sim \mathbf{m} \times \mathbf{y}$. Also, the presence of Oersted torque ($\mathbf{T}_{\text{Oe}}$) is due to the Oersted field generated from the charge current passing through the sample and is known as the main source for the $\mathbf{T}_{\text{FL}}$.

In this thesis, we focus on the evolution of the electric AC impedance of a ferromagnet due to the SOT originating from heavy metal and antiferromagnetic layers (Figure 1-2). By magnetoimpedance (MI) measurements at low frequencies ($\sim$ MHz), we probe SOT in IrMn/ferromagnetic-ribbon and Pt/ferromagnetic-ribbon heterostructures. In particular, we pay attention to two important cases of Pt, a well-known heavy metal for spintronic applications, and IrMn, a well-established antiferromagnet with strong exchange interaction with ferromagnets at room temperature. We chose these two cases due to their high SOC and capability to produce large SHE^{24,34–36}. Indeed, developing simple experiments at room temperature for the study of spintronic effects are valuable. The high permeability of thick, soft ferromagnetic ribbons at MHz frequency range makes it possible to detect spintronic effects by tuning the permeability.

1.2 Sensors

Magnetic sensors have inspired the research community not only because of their capacity for the detection of magnetic fields but also because of their suitability as detector of environmental elements such as biomaterials³⁷. Some magnetic sensors such as a superconducting quantum interference device (SQUID)³⁸ and GMR³⁹ sensors have been developed based on magnetic materials and have found practical applications including the detection of biological elements based on detection of magnetic fields arising from them. Although SQUID devices show very high sensitivity, they require cryogenic liquids to operate. GMR sensors perform at room temperature but show low sensitivity for detecting very weak magnetic fields.

The discovery of the MI effect⁴⁰ in soft ferromagnetic materials render them promising for the development of a generation of sensors for both magnetic field and environmental sensing applications. The basis for the sensitivity of this kind of sensor is the skin effect at high frequencies. The sensors based on the MI effect are promising for cost-effective and high sensitivity performance under ambient conditions^{41,42}. The MI effect is the change in electrical impedance as a function of external DC magnetic field⁴³. It is correlated with the skin depth (δ), $\delta = (\rho/\pi\mu f)^{1/2}$, of the high frequency (f) current and the magnetic permeability (μ) of a metallic ferromagnet with electric resistivity (ρ)⁴⁴. The MI response changes through the skin depth when an external magnetic field is applied. The origin of the high sensitivity of the MI sensor to external magnetic fields (H) is the high sensitivity of the permeability to the external magnetic fields in these sensors, which is in the order of pico-Tesla⁴⁵. Accordingly, these sensors can be used for detection of magnetic and nonmagnetic materials. An example is when biomaterials are attached to magnetic nanoparticles^{46–48}.

Both increasing the sensitivity of the MI sensor and modification of the surface of the sensor are desired for further enhancing their functionality. In this thesis, we use a coating of graphene-based materials on the surface of the MI sensor. The resulting heterostructures, made of the magnetic sensor and the coated layer, show enhanced sensitivity to external magnetic fields. Also, graphene based materials at the surface of the sensors assist biomaterials

detection. In our work, we benefit from (possibly) magnetic graphene too, which in addition to the surface modification for biomaterials, causes enhancement in the MI ratio and sensitivity due to its magnetic properties.

1.3 Electronics

Complementary metal–oxide–semiconductor (CMOS)-based technology for data processing is coming to the end of its lifecycle, on account of scaling limitations^{49–52}. Researchers in the field of electronics are searching the best architectures to increase the computing capabilities of devices. Among various elements, a great deal of attention is paid to memristors. These are devices with a simple two terminal structure, composed of a low conductivity material sandwiched between two conductive materials, and acting as a variable resistor suitable for data storage and processing^{6,53}. Different mechanisms in these devices lead to hysteretic

Figure 1-3: Schematic of memristivity mechanism in an electrochemical metallization memristor, Pt/SiO₂/Cu (Ref.⁵⁵). This memristor works based on the oxidation of Cu due to application of bias voltage and the transfer of Cu cations through the insulating layer followed by the reduction of Cu cations at the Pt electrode, which globally results in the formation of a metallic Cu filament. Also the reverse mechanism does occur by reversing the bias voltage and consequent rupture of the conductive Cu filament

current-voltage (I-V) behaviour. Electrochemical metallization memristors (ECM) and valence change memristors (VCM) are two important sets of memristors with promising characters. ECM memristors work based on oxidation of the active metal top electrode due to application of bias voltage and transfer of metal cations through the insulating layer and then reduction of the cations at an inert electrode, which results in the formation of a metallic filament. Also the reverse mechanism does occur when reversing the bias voltage and rupture of the conductive filament⁵⁴. An example of this kind of memristor is a Pt/SiO₂/Cu heterostructure with Cu and Pt as active and inert electrodes respectively and SiO₂ as the dielectric interlayer⁵⁵. The schematic of the ECM memristivity in this system can be seen in Figure 1-3, which depicts Cu moving under voltage bias and forming a conductive filament.

In the case of VCM memristors, by applying the bias or reverse bias voltage an oxygen deficient filament is created or ruptured. Also, switching in VCM memristors is believed to exist due to

Figure 1-4: Schematic of the valence change memristivity mechanism in a Pt/ZrO_x/Zr memristor⁵⁶. Memristivity in a Pt/ZrO_x/Zr structure is seen due to oxygen vacancy movements when applying a bias voltage. In this case, a conductive filament is formed by the atomic movements of the active medium itself.

oxygen anions/vacancy movement at the interfaces of the memristor electrodes and so modification of the Schottky barrier⁵⁴. For an example of VCM type memristivity see Figure 1-4, in which a schematic of VCM memristivity in a Pt/ZrO_x/Zr structure is seen, caused by oxygen vacancy movements when applying a bias voltage⁵⁶. Therefore, according to the kind and quality of the material used in a memristor structure, the ECM or VCM type of memristivity can dominate in the response of a memristor. The example of Ta₂O₅ used as an interlayer is reported in the literature⁵⁷.

In 1971, Leon Chua⁵⁸ theorized that memristor is the fourth fundamental element based on the symmetrical relationship between voltage (v), current (i), charge (q) and magnetic flux (Φ) (see Figure 1-5a). As can be seen in Figure 1-5a, the resistor establishes the relation between voltage and current ($dv=Rdi$), the inductor establishes the relation between current and flux ($d\Phi=Ldi$), the capacitor establishes the relation between voltage and charge ($dq=Cdv$), and the memristor establishes the relation between charge and flux ($d\Phi=Mdq$). In 2008, the first memristor device was realized in HP Labs⁶.

Figure 1-5b shows the hysteretic I-V curve observed from the fabricated memristor, which was a Pt/TiO_{2-x}/Pt three layer structure. The doping in the TiO₂ layer was performed by removing

Figure 1-5: a) fundamental two-terminal circuit elements: resistor, capacitor, inductor and memristor. the fourth fundamental element was suggested based on the symmetrical relationship between voltage (v), current (i), charge (q) and magnetic flux (Φ) b) An example of hysteretic I-V curve resulting from the sample presented in the inset.⁶

the negatively charged oxygen atoms from their position and creating positively charged oxygen vacancies in the crystallization stage over the length of the TiO_2 film. The mechanism of the hysteretic behaviour of the I-V curve was reported to be due to oxygen vacancy movement of the TiO_{2-x} thin layer over the length of the TiO_2 film by applying a bias voltage (see Figure 1-6).

Memristors are considered for industrial applications due to their low power consumption,⁵⁹ fast switching,⁶⁰ and high storage density⁶¹. Yet, applying new materials in memristor structures is required for achieving even better performance. Two-dimensional materials such as graphene and transition metal dichalcogenides with novel electronic properties^{62–65} are now considered for application in memristor structures with remarkable advantages like low power consumption and high stability^{66,67}. Therefore, developing new methods for fabrication of these materials with superior memristive behaviours is demanded.

In the research reported in this thesis, we worked on this issue and investigated memristive mechanisms with a focus on electrochemical redox reactions. Two separate samples composed of graphene oxide and oxidized MoS_2 layers in memristor structures were especially investigated. In addition, different semiconductive behaviours in MoS_2 , with different amounts of oxidation, were investigated for application in lateral heterostructures. No memristivity in lateral structures was seen but a rectified I-V curve was observed in this structure, which can be considered for electronic applications.

Figure 1-6: The mechanism of the hysteretic behaviour of the I-V curve in Figure 1-5 was reported to be due to oxygen vacancy movement in the TiO_{2-x} thin layer over the length of the TiO_2 film when applying a bias voltage. Because of their positive charge the oxygen vacancies can move towards negatively charged electrode under applied electric fields.

1.4 Outline of the thesis

Following this introduction chapter, the thesis is organized as follows:

Chapter 2 presents the experimental methods employed for structural characterization, electrical transport measurements, and material fabrication, which are common between the chapters.

Chapter 3 describes the magnetoimpedance response of thick magnetic ribbons when coated with Co and Ni nanolayers. We illustrate how surface modification of the ribbons by thin magnetic layers results in a higher MI response ratio. Magnetic exchange coupling between ribbon and thin layers with different thicknesses is discussed in the interpretation of the observed MI responses.

Chapter 4 is related to the MI response of thick magnetic ribbons when coated by nanometer thick Pt and IrMn layers. We discuss how spin-orbit torques originating from Pt and IrMn thin layers are detected via the MI effect. Also, the relation between exchange bias and spin-orbit torques is evidenced through the training effect (reduction of magnetic exchange coupling between a ferromagnet and an antiferromagnet by magnetic field sweeps) in the ribbon/IrMn sample.

Chapter 5 deals with a sensor application of magnetic ribbons based on the magnetoimpedance effect. The surface modification of the magnetic ribbons through graphene oxide coating for environmental sensor applications is presented in this chapter. We show that also the magnetic field sensitivity is improved by this modification.

Chapter 6 presents another surface modification of a magnetoimpedance based sensor. This chapter reports how a MI sensor with increased sensitivity can be realized via the application of a graphene/YIG composite on the surface. Also, the possibility of a magnetic proximity effect in graphene is discussed for a graphene/YIG sample and how it can increase the sensitivity of the sensor.

In **Chapter 7** we report on the fabrication of a semiconductive lateral heterostructure with rectified I-V curve using bipolar electrodeposition (BPE). In bipolar electrodeposition, it is

possible to deposit a layer with a gradient of composition along a conductive substrate. Different compositions of MoS₂, MoO₂ and MoO₃ result in different semiconductive characteristics.

In **Chapter 8** we describe the memristive behaviour of a MoS₂/MoO₂/MoO₃ composite material fabricated by electrodeposition and contacted with inert and active electrodes. Low threshold voltages of 0.1-0.2 V in the memristor were observed.

In **Chapter 9** a graphene oxide interlayer is used to observe the Ag⁺/Ag²⁺ electrochemical redox reactions in a memristor structure. We show that increasing the thickness of the electrolyte layer in a memristor prevents filament formation so that it can be used for the characterization of electrochemical reactions by observing current peaks in current-voltage (C-V) measurements of memristors.

In the final chapter (**Chapter 10**) an outlook of the thesis is presented.

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Chapter 2: Experimental methods

In this chapter, the fundamentals and details of experimental methods are presented. The following sections are related to the materials fabrication, structural characterizations and transport measurements of the fabricated samples.

2.1 Materials fabrication

In this section, the fabrication methods of the samples used in this thesis are presented. The melt spinning technique is described for fabrication of thick magnetic ribbons and electrodeposition technique for producing different magnetic and nonmagnetic layers. Also, preparation of graphene oxide is explained in this section.

2.1.1 Melt spinning

In **chapters 3-6** thick magnetic ribbons are used for magnetoimpedance (MI) measurements (see section 2.3.2 for MI measurement fundamental and details). Due to ease of manufacture, the melt spinning technique is the most widely used way of producing continuous and long magnetic metallic ribbons. Chen and Miller¹ designed a device for melt spinning containing a metallic wheel spinning at 300–1800 rpm. In this technique, a melted alloy is poured onto a rotating copper roller at high speed. During this process, an amorphous ribbon is formed. A schematic of this method is presented in Figure 2-1. The processing parameters widely influence the properties of ribbons.² The thickness and width of the ribbons are determined by the roller rotation speed and the casting speed of the melted alloy. Ribbons produced using this method typically have a width of 0.5 mm, a thickness of 20 μm , and are up to 100 m in length. Different kinds of magnetic materials such as Fe, Co, Ni, and their alloys can be produced using the melt spinning technique.

For this thesis, amorphous ribbons of nominal composition $\text{Co}_{68.15}\text{Fe}_{4.35}\text{Si}_{12.5}\text{B}_{15}$ (0.8 mm width, 40.0 mm length and about 28 μm thickness) were prepared by conventional melt spinning and used for the MI measurement experiments freely and without any substrate.

Figure 2-1: Schematic of the melt spinning method for producing amorphous ribbons. In this technique, a melted alloy is poured onto a rotating copper roller at high speed. During this process, an amorphous ribbon is formed.

2.1.2 Electrodeposition

Electrodeposition is used for the fabrication of thin layers of materials in **chapters 3, 5, 7 and 8**.

Figure 2-2: Schematic of an electrodeposition setup. By applying voltage between the platinized Si electrode (Anode, connected to positive voltage) and the substrate (cathode, connected to negative voltage), ionic elements in the solution can be coated onto the substrate. In this thesis we only use two electrodes without a reference electrode.

This method includes applying a voltage between two electrodes immersed in an ionic solution and coating of ionic elements on one of the electrodes, called substrate or working electrode. The other electrode is called a counter electrode. At the surface of the working electrode the following electrochemical reactions results in the formation of a layer:

where X can be an atom or a molecule. Electrodeposition has shown the capability of producing different kinds of metals, alloys, and semiconductor materials in the form of thin layers³⁻⁵. Faraday's law⁶ is used in electrodeposition to observe or control the growth rate of the electrodeposited layer. According to Faraday's law, the mass (m) of the electrodeposited material can be calculated by $m = \frac{QM}{Fz}$, where F is faraday constant, z is the valence number of the ion in the solution, Q is the total electric charge passed through the substrate during electrodeposition, and M is the molar weight of the electrodeposited material. Therefore, knowing the surface area of the electrodeposited substrate and the density of the layer, the thickness of the electrodeposited layer can be calculated. We use this method to estimate the thickness of Ni and Co thin layers in **chapter 3**.

The setup used in this thesis for electrodeposition experiments is made by a computer controlled current and voltage source. In electrodepositions of the layers (for different materials in all chapters), a two-electrode setup is used with 100 nm of platinized Si as the counter electrode, and the substrate (ribbon, Fluorine doped Tin oxide) as the working electrode. The electrodeposition was performed by immersing the electrodes in the respective electrodeposition solution and connecting them to the power source for a certain time. The solutions in which the electrodepositions were performed are explained in detail in each chapter. For the electrodeposition conditions, including applied voltage and currents, distance between electrodes, and thickness of the layers (growth rate) see the respective chapters. A schematic for the electrodeposition setup can be seen in Figure 2-2.

2.1.3 Graphene oxide synthesis

Graphene oxide (GO) was used for the experiments in **chapters 5 and 9**. In 1958, Hummers reported a new method for the synthesis of GO using KMnO_4 and NaNO_3 in concentrated H_2SO_4 ⁷. This method has been used extensively and has been modified by many researchers. In this thesis, GO was synthesized from natural graphite powder based on a modified Hummers method⁸. 0.5 g NaNO_3 , 3 g KMnO_4 and 0.5 g graphite powder were mixed with 23 ml H_2SO_4 solution (98 %). The mixture was stirred in a 35 °C oil bath for 24 h. Afterwards, 100 ml deionized (DI) water and 3 ml H_2O_2 (30 %) were slowly added to the mixture. The resulting mixture had a colour that gradually changed from dark brown to bright yellow during 15 min. The GO solution was then washed with HCl (10 vol %), H_2O_2 and DI water, respectively, by filtering it through vacuum filtration.

2.2 Materials characterization

Different methods of structural characterizations have been used throughout this thesis. This is used to better understand the origin of the observed phenomenon in each chapter related to the structure of the samples. Characterization techniques include X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Raman spectroscopy, Atomic force microscopy (AFM), and the resulting measurements for the materials will be explained in detail in the respective chapters.

2.3 Electrical characterization

In this section the fundamentals and experimental details for the electronic measurements are presented. I-V curves and MI measurements are used in this thesis and details are explained accordingly in the following sections.

2.3.1 I-V curve

For the memristive behaviour and rectified I-V characteristics of the samples in **chapters 7, 8 and 9**, I-V measurements were performed. I-V measurements are the main characterization for the memristors for both memristance quality and memristance mechanism studies^{9–11}. The qualities of a memristor are expressed by on/off ratio and set-reset voltages ($V_{\text{set}}-V_{\text{reset}}$). The set voltage is the voltage at which the resistance of the memristor changes from high to low and

Figure 2-3: Characteristics of a memristor behaviour observed in the I-V curve. The set voltage is related to the voltage at which the memristor switches to the low resistance state (on state) and the reset voltage is the voltage at which the resistance goes back to the high resistance state (off) state.

the reset voltage is the voltage at which the inverse mechanism occurs (Figure 2-3). The V/I ratio at each point of the I-V curve gives the resistance of the memristor at each point. Therefore, by measuring the I-V curve, quantities such as on/off ratio and set-reset voltages can be obtained.

For the I-V measurements a computer controlled source meter (Keithley 2450) was used in a two-probe mode at different voltage sweep rates (0.02-4 V/s). The sweep rate is an important parameter, which can change the measured parameters of the memristor. An image of this setup and the schematic of the measurement can be seen in Figure 2-4. Also, similar to electrochemical solutions, the memristor structure is considered as a solid based electrolyte and the electrochemical reactions at the interface of the metals and the solid electrolyte can be observed through I-V measurements^{12,13}. In this case in the I-V plot, some peaks do appear which show the occurrence of electrochemical reactions at specific voltages¹⁴, just like cyclic voltammetry of nonsolid systems. In **chapter 9**, I-V measurements have been used for measurement of Ag redox reactions in a GO based memristor.

Figure 2-4: a) The setup for I-V measurements and b) the schematic of the circuit with two probes attached to the sample for the measurements. In this setup a Keithley source meter measures the current and voltage with controlled scan rates via LabVIEW software.

For the electrical contacts to the samples and measuring I-V response, inert probes made of Au were directly put on memristor electrodes and in the case of lateral heterostructures (**chapter 7**) silver paste is used for electrical contacts. Also, no patterning on the samples is used in this thesis for the I-V measurements.

2.3.2 Magnetoimpedance measurements

Chapters 3-6 are based on MI measurements. First, an introduction to the MI effect and the equations of impedance are presented to see how external factors such as external magnetic field (H_{ext}) or spin-orbit torques (SOTs) can change the impedance. The measurement setup is then described.

When a sinusoidal current, $I = I_{ac} \sin(\omega t)$, passes through a uniform magnetic conductor, its impedance is given by the V_{ac}/I_{ac} ratio, where V_{ac} is the voltage measured between the ends of the conductor (Figure 2-5b)¹⁵. The impedance for a metallic ferromagnet with length L and cross section area A , assuming a linear approximation, can be expressed as the following:

$$Z = \frac{V_{ac}}{I_{ac}} = \frac{LE_z(s)}{A\langle j_z \rangle_A} = R_{dc} \frac{j_z(s)}{\langle j_z \rangle_A} \quad ,$$

where E_z and j_z are the longitudinal components of the electric field and the current density, respectively, and R_{dc} is the dc electrical resistance. S refers to the value at the surface, and $\langle \rangle_A$ is the average value over the cross-section A . The current density $j(r)$ in a conductor can generally be obtained in a continuous media within the framework of classical electrodynamics

Figure 2-5: Schematic of orientations of magnetic moments in a sample with transverse magnetic anisotropy (left) and the MI response change at different external magnetic field values (right, line to guide the eye). The peak appearing in this figure is related to the highest transverse permeability of the sample and occurs when a magnetic field with strength of H_k (anisotropy field) is applied to the sample in longitudinal direction.

for a magnetic material with the magnetization vector ($\vec{M}$) by solving simultaneously the reduced Maxwell equation:

$$\nabla^2 \vec{H} - \nabla(\nabla \cdot \vec{H}) = \frac{\mu_0}{\rho} \frac{\partial}{\partial t} (\vec{H} + \vec{M})$$

and the Landau–Lifshitz equation for the motion:

$$\frac{d\vec{M}}{dt} = -\gamma \vec{M} \times \vec{H}_{eff} + \frac{\alpha}{M_s} \vec{M} \times \frac{d\vec{M}}{dt} ,$$

where γ is the gyromagnetic ratio, M_s the saturation magnetization, $\vec{H}_{eff}$ the effective magnetic field, and α the damping parameter^{16,17}. One often assumes the material relationship between the induction and magnetic field is linear ($B = \mu H$ and μ is constant) and uses this relationship to solve the Maxwell equation while ignoring the Landau–Lifshitz equation of motion. The classical skin effect solution of the Maxwell equation is obtained when the calculated impedance of an infinite planar magnetic film is¹⁸:

$$Z = R_{dc} \cdot jka \coth(jka)$$

(Because of the similarity between $\coth(\dots)$ plot and the experimental MI plot, $\coth(\dots)$ function is used in Z equation) where $2a$ is the thickness of the ribbon, R_{dc} is the dc electrical resistance and $k = (1 + j)/\delta_m$ with imaginary unit j ; δ_m is the penetration depth in a magnetic

medium, with circumferential (perpendicular to the direction of the passing current) permeability (μ_T) for the case of a planar film:

$$\delta_m = \frac{c}{\sqrt{4\pi^2 f \sigma \mu_T}}$$

where σ the electrical conductivity, c the speed of light, and $f = \omega/2\pi$ the frequency of the ac current flowing along the sample. According to the equations of impedance and skin depth, MI can be understood as a consequence of the increase in the skin depth until it reaches the half thickness of the ribbon (a) through a decrease in the transverse permeability under an applied dc magnetic field. The effect of different applied external magnetic fields on the domain structure and the MI response of a ribbon with transverse magnetic anisotropy are illustrated in Figure 2-5. At $H_{\text{ext}} = H_k$ (anisotropy field), the magnetization has the highest transverse magnetic permeability and therefore the impedance is at its maximum according to the equation of impedance for a ribbon. Accordingly, other external factors such as SOTs can change the MI response of a magnetic film through changing the magnetization state of the sample and so the transverse magnetic permeability of the sample. In **Chapter 4**, the effects of SOTs on the MI response are investigated. As the magnitude of SOT is dependent on the passing current, therefore, by measuring impedance at different currents, different effects of SOT can be seen in the impedance of a magnetic sample.

To measure the MI response of the samples, an external magnetic field was applied along the

Figure 2-6: a) The setup for magnetoimpedance measurements and b) The schematic of the circuit. The oscilloscope measures the voltage drop across the sample at different applied magnetic fields. The current of the circuit is determined by measuring the voltage drop of a known resistance in the circuit.

ribbon axis. This magnetic field was produced by a solenoid (40 cm long), which can generate a magnetic field up to 120 Oe. The longitudinal direction of the samples was perpendicular to the Earth's magnetic field to minimize its effect on the MI response of samples. The impedance was measured by means of a four-point probe method. The ribbon is put into the circuit using silver paste to have minimum noise level. An AC current passed through the longitudinal direction of the ribbon (length= 4 cm) with different frequencies supplied by a function generator (GPS-2125). The current amplitude is controlled by the amplitude of the applied voltage. The current is determined by measuring the voltage across a known resistance in series with the sample. The impedance was evaluated by measuring the voltage and current across the sample using a digital oscilloscope (GPS-1102B). An image of the MI measurement setup and a schematic of the circuit are presented in Figure 2-6. The setup is controlled using LabVIEW software.

2.4 References

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Chapter 3: Magnetoimpedance Exchange Coupling*

Abstract

A systematic study of the effect of deposition of Co and Ni layers of various thicknesses on the magnetoimpedance response of a soft ferromagnetic amorphous ribbon ($\text{Co}_{68.15}\text{Fe}_{4.35}\text{Si}_{12.5}\text{B}_{15}$) was performed. The Co and Ni layers with thicknesses of 5, 10, 20 and 40 nm were grown on both sides of the amorphous ribbons by electrodeposition technique. Microstructures, determined by X-ray diffraction pattern and field emission scanning electron microscopy, showed a higher crystallinity of deposited Ni and the amorphous nature of deposited Co. Measurement of magnetic properties using vibrating sample magnetometry did not show significant differences between samples. This is attributed to the small contribution of such thin layers deposited on thick ribbons. However, the magnetoimpedance response dictates that magnetic coupling effects occurred at the interface of such bilayers, which is sensitive to the skin effect. The response of Co deposited ribbons showed magnetoimpedance hysteretic behaviour depending on the deposited layer thicknesses with an optimum response for the thickness of 20 nm. No hysteretic behaviour was measured for Ni deposited ribbons. This behaviour is explained according to the exchange coupling between the magnetization of electrodeposited layers and magnetic ribbons with respect to the different magnetic properties of Co and Ni at different thicknesses. The magnetoimpedance response of Ni and Co deposited ribbons enhanced significantly at low thicknesses relative to bare ribbon. By increasing the thickness of deposited layers, the magnetoimpedance response decreases considerably. The differences in magnetoimpedance ratios of Co and Ni deposited ribbons are explained in terms of exchange length, crystallinity and roughness of deposited layers. Our results could offer a simple way to achieve a higher magnetoimpedance response and explain the physical aspects of exchange coupling on the magnetoimpedance response, contributing to a better performance of magnetic field sensors.

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3.1 Introduction

With more than two decades of research history since its last revival^{1,2}, the magnetoimpedance (MI) effect is a classical electrodynamic phenomenon in magnetic metals. This effect measures electrical impedance changes as a function of external magnetic field. The MI is correlated with the skin depth (δ), $\delta = (\rho/\pi\mu f)^{1/2}$, of the high frequency f current and the magnetic permeability μ of a metallic ferromagnet with electric resistivity ρ ³. Magnetic permeability changes by applying an external field. This results in a new current skin depth and hence a change in the MI response. The MI response is interesting from a fundamental point of view in ferromagnetic metals and is also known to be promising for the development of high sensitivity magnetic field sensors⁴. The MI effect is studied in different soft magnetic materials such as ribbons, amorphous films, wires, and their nanocrystalline counterparts⁵⁻⁹. How the impedance of a ribbon changes with skin depth when passing a current is described in chapter 2.

At moderate frequencies ($f \sim 1$ MHz), the skin effect becomes a dominant contribution and the changes in the MI are caused by domain wall movement and magnetization rotation. At higher frequencies, the skin effect is very strong because the ac current is confined to the sheath of the ribbon. In this frequency range, the MI of the ribbon is very sensitive to its environmental condition¹⁰.

The magnetic properties of soft magnetic materials and the MI effect can be influenced by coating a magnetic or conducting layer on them. Some researchers recently reported that conductive or magnetic coating layers enhanced the MI ratio of an amorphous ribbon¹¹⁻¹⁷. They have discussed the MI response which was influenced by the surface structure and the interaction between the magnetic field and the surface domain structure. Controlled engineering of the surface of a soft ferromagnetic ribbon has been shown to enhance the MI effect and has practical applications in magnetic sensors. For example, researchers reported the enhanced MI response of an amorphous Co-based ribbon when coated with Cu¹² and Zinc oxides¹³, diamagnetic organic thin film¹⁴, Co¹⁵, Carbon nanotubes¹⁶ and CoFe₂O₄¹⁷. In the case of Co, the surfaces of the amorphous ribbon were coated with a 50 nm thick Co film using magnetron sputtering. They achieved the largest values of MI effect and field sensitivity in the

sample coated with Co on the free ribbon surface, which has a smaller surface roughness as compared to that coated with Co on the wheel-side ribbon surface with a larger surface roughness. Their results showed that this originates from a reduction in stray fields due to surface irregularities and the closure of magnetic flux paths, which is caused by the Co layer. Both contribute to enhance the MI effect in the Co-coated ribbons.

In this chapter, we report on the investigation of the MI effect in Co-based ($\text{Co}_{68.15}\text{Fe}_{4.35}\text{Si}_{12.5}\text{B}_{15}$) amorphous ribbons coated with various thicknesses of Ni and Co layers by electrodeposition. The applicability of this method has been proven for deposition of magnetic materials^{18–20}. To elucidate the influence of the deposited layer on the MI response of the ribbon, we performed a thorough study of the structure, magnetic properties, and MI effect. We observed that the MI response is strongly dependent on the thicknesses of the Ni and Co layers. The observation of a single peak and hysteretic behaviour of MI response for Co deposited ribbons is attributed to exchange coupling between magnetization of the ribbon and the Co layer. Such coupling is not significant for Ni deposited samples. Our results address for the first time the magnetic MI coupling effect between magnetic ribbons and Ni or Co magnetization with different thicknesses. This effect in addition to its fundamental interest, suggests a new method to improve MI response. Results are potentially useful for MI applications such as increasing the MI response and tuning a field dependent response for improved magnetic sensors.

3.2 Experimental Methods and Sample Fabrication

Amorphous ribbons of nominal composition $\text{Co}_{68.15}\text{Fe}_{4.35}\text{Si}_{12.5}\text{B}_{15}$ (0.8 mm width, 40.0 mm length and about 28 μm thickness) were prepared by a conventional melt spinning technique as explained in chapter 2. Electrodeposition of Ni and Co layers was done from aqueous solutions of 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.4 M boric acid (pH= 4) for Ni deposition and 0.1 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.4 M boric acid (pH= 4) for Co deposition. Such electrodepositions were done in a beaker at room temperature. Experiments were done at a constant current density of 0.36 mA/cm^2 , utilizing a computer controlled current source in a two-electrode configuration cell using ribbon as cathode and a 1×3 cm Platinum plate as anode. X-ray diffraction (XRD) was performed using a STADI STOE diffractometer with $\text{CuK}\alpha$ ($\lambda=1.54 \text{ \AA}$)

for the angle (2θ) range from 10–80° and X'pert software was used for analysing the data. Field emission scanning electron microscopy (FESEM) was performed on a VEGA TESCAN instrument to observe microstructural changes resulting from electrodeposition. The experimental details of the MI measurements are described in chapter 2. The applied current amplitude for the MI measurement is 30 mA. The oscilloscope measurement resolution gives a $\pm 6\%$ error in the observed MI ratio. Due to the fact that at H_{max} the skin depth is maximum and the Impedance saturates to a constant value, the MI ratio can be defined as

$$MI\% = \frac{Z(H) - Z(H_{max})}{Z(H_{max})} \times 100 \quad (3.2)$$

Where Z refers to the impedance as a function of external field, H , and H_{max} is the maximum field applied to the samples in the MI measurement. The longitudinal hysteresis loop of ribbons was measured using a vibrating sample magnetometer (Meghnatis Daghigh Kavir Co.) at room temperature.

3.3 Results and discussion

Figure 3-1: Schematic diagram of the deposition process of Ni and Co layers on ribbons. By applying a voltage between Pt and ribbon, Ni or Co ions move towards the ribbon and a layer of Ni or Co forms. The thickness of the coated layers is controlled by the electrodeposition time.

Faraday's law was applied to achieve the desired layer thicknesses (5, 10, 20, 40 nm) deposited on magnetic ribbons. A 7 cm long ribbon was immersed in an electrodeposition cell. A current density of 0.36 mA/cm^2 was applied between the cathode and the anode for different deposition times ranging from 6.5-54 s for Ni and Co layers. A schematic of the deposition process is presented in Figure 3-1. Ni and Co layers were deposited on both free sides of the

Figure 3-2: XRD pattern of the Ni and Co deposited ribbons (linear y-axis). For Ni deposited ribbons with thicknesses of 5 and 20 nm, the XRD patterns showed the crystalline structure of Ni along with the amorphous background of the ribbon. The Co showed no crystalline nature. Also, there is a broad peak at about $2\theta = 20-30^\circ$, indicating presence of small SiO_2 crystals in the ribbon²¹.

Figure 3-3: FESEM images of a) bare ribbon b) 20 nm Ni and c) 20 nm Co deposited on ribbons. The surface of deposited ribbons show higher smoothness. The Ni layer appears with some more white points, which show formation of crystals in this layer. The surface smoothness may affect the magnetoimpedance differently in these two samples.

ribbon. Oxidation of the surface of Ni and Co deposited layers occurs upon exposure to air after the deposition process. However, the interface between the ribbon and the thin layers should not have been affected by the oxidation as they represent the coupling effect. Figure 3-2 shows the XRD patterns of bare ribbon compared with that for 5 and 20 nm Ni and Co deposited layers on ribbon. The XRD pattern of the uncoated ribbon showed their amorphous nature except for a broad peak appearing at $\theta = 20\text{--}30^\circ$ which is related to the small SiO_2 crystals formed in the ribbon²¹. For Co deposited ribbons (5 and 20 nm), no peak in the XRD patterns was observed. This indicates that no crystallization occurred for 5 and 20 nm thick Co layers deposited on ribbons. A peak for 5 and 20 nm Ni deposited layer on ribbon measured at 44.47° related to the (111) plane of a fcc structure of Ni (JCPDS 001-1260). For Ni deposited ribbons with thicknesses of 5 and 20 nm, the XRD patterns showed the crystalline structure of Ni along with the amorphous background of the ribbon. A higher crystallinity was observed for the 20 nm thick layer deposited on ribbon while the 5 nm layer showed lower crystallinity.

Field emission scanning electron microscopy images of bare ribbon and 20 nm Ni and Co deposited on ribbons are presented in Figure 3-3 (a-c), respectively. In panel (a), for the surface of bare ribbon, surface fluctuations can be seen which represent a rough surface. In Figure 3-3 (b), an image of 20 nm Ni deposited on ribbon, reveals small crystals appearing with light colour

which show a considerable amount of Ni crystalline layer nucleated at the surface of the ribbon, as confirmed with XRD analysis. In Figure 3-3 (c), the image of 20 nm Co deposited on ribbon is smoother with smaller amount of crystals than those of bare ribbon and Ni deposited on ribbon. XRD showed no crystal phase of Co deposited layers. As known, the MI response is a surface dependent phenomenon so these results should be considered in the analysis of MI results.

To investigate the effect of deposition of Co and Ni layers on the magnetic properties of the ribbons, the magnetic hysteresis loops of the bare ribbons and ribbons where 40 nm Co and 40 nm Ni had been deposited were recorded at room temperature. Figure 3-4 shows the magnetic hysteresis loops of bare, and Co and Ni coated ribbons normalized to the saturation value ($M_{\text{normalized}}$). It can be seen that the loops are all thin and narrow, and magnetization saturated at low applied field, indicating their soft ferromagnetic characteristics. There is little difference between coated and uncoated ribbons. This is because the large volume of ribbon has the dominant contribution in measured magnetization of the samples. In fact, based on our analysis, there is no difference between samples in terms of their coercivity. There are indeed

Figure 3-4: Magnetic hysteresis loops of bare ribbons and of ribbons coated with 40 nm of Co or Ni. The inset is a zoom-in, which shows the higher saturation field for the Co-covered ribbon. This is due to the higher coercivity of Co with respect to that of Ni. The magnetic coercivity of Ni and Co may result in different coercivity for the magnetoimpedance response.

changes in magnetization in a small field interval, shown in the inset in Figure 3-4, suggesting that the Co coated sample has a higher saturation field than that of the other two samples. This confirms a strong coupling between the Co layer and the ribbon.

In order to understand the impact of Co and Ni deposition on the MI response of the ribbon, the magnetic field and frequency dependences of the MI ratio of all the samples were studied up to 120 Oe magnetic field strength at frequencies of 2.5, 5, 7.5, 10, 12.5 and 15 MHz. Figure 3-5 shows the MI response of a bare ribbon, a ribbon with a 20 nm Ni coating and a ribbon with a 20 nm Co coating, all measured at $f = 10$ MHz. In the MI plots, two main differences can be seen between Ni and Co coated ribbons. First, we see the hysteretic behaviour of a Co deposited ribbon in Figure 3-5, whereas for Ni deposited ones there is no hysteretic behaviour. The hysteretic behaviour of the MI response of the Co coated ribbon is related to the hysteretic behaviour of its surface longitudinal magnetization. The appearance of this longitudinal ferromagnetic behaviour is related to strong ferromagnetic coupling of the Co layer and the magnetic exchange between the magnetization of Co with the magnetization of the ribbon, as evidenced by the symmetry breaking MI profile thanks to the skin effect. The larger magnetization of the Co layer than that of the ribbon affects the MI response whereas this effect does not occur for Ni deposited ribbon because of the lower magnetization of the Ni layer compared to the ribbon (see Table 1). As the Co layer has stronger magnetization, it can affect the field dependent domain wall response with a large amount of magnetic coupling energy. A little more change in the magnetization response for the Co layer observed in Figure 3-4 confirms this argument. This does not occur for the Ni layer. The amorphous phase of the Co layer might have more random magnetization than that of Ni with better crystallinity, resulting in more irreversible magnetization of Co deposited samples.

Second, by sweeping the magnetic field from positive saturation to negative values, we observe an asymmetric single peak of MI for decreasing magnetic field that occurs in a nonzero applied magnetic field. This shows the effect of exchange coupling between the Co layer and the ribbon. These two properties can be created through magnetic exchange couplings such as ferromagnetic or spring exchange²¹. The resultant longitudinal magnetization of such a double layer with mentioned magnetic couplings can be seen in Figure 3-6. This figure shows the

evolution of the longitudinal component of magnetization with respect to the external applied magnetic field. As the magnetic moment of the Co layer is strongly coupled to that of the ribbon, the Co layer does not contribute much to the permeability value independently but determines the magnetization direction of the wholly coupled system. By moving from H_{Max} from right to left (stage (3) in Figure 3-6), according to the exchange interaction between the longitudinal remnant magnetization of the Co layer and the ribbon, at $H=0$ Oe, we observe a non-zero net magnetization and we do not have a MI ratio peak at $H=0$ Oe. The steps of Figure 3-6 are specified by numbers in Figure 3-5.

The exchange coupling comes from the following Equation²²:

$$H = -2 \sum_j J_{ij} M_i \cdot M_j \quad (3.3)$$

where H is the interacting Hamiltonian, M_1 and M_2 are magnetization of atoms in the ribbon and the Co layer on it and J is the exchange constant. Some researchers^{23,24} have seen such an exchange between a ribbon and Co crystals sitting on its surface formed during open air annealing. Also Y. Hun et al²⁵ have attributed the measured hysteresis in their MI plots of permalloy sputtered ribbons to the exchange interaction between the permalloy layer and a ribbon. Here, Ni has smaller magnetization than that of the ribbon, therefore there are neither changes in MI peak nor hysteretic effect and magnetization is mainly controlled by that of the ribbon.

Table 3-1: Magnetic moments (M) of Ni, Co and the ribbon²⁶.

<i>Material</i>	<i>M (emu/cm³)</i>
Ribbon	550
Ni	482
Co	1400

Figure 3-5: Hysteretic behaviour of MI response at $f= 10$ MHz. Arrows show direction of the magnetic field sweep. As the Co layer has stronger magnetization than the ribbon, it can affect the field dependent domain wall response with a large amount of magnetic coupling energy. Ni has a lower magnetization than the ribbon.

Figure 3-6: Schematic of the magnetization profile affected by exchange coupling between the longitudinal magnetization of the ribbon and that of Co layer at the skin depth.

Figure 3-7: a) The hysteretic behaviour at different thicknesses of Co. The maximum coercive MI response is related to the 20 nm Co deposited ribbon and b) the peak evolution of different thicknesses of Co layer (the presented error bar at each point is $\pm 6\%$). Evolution from double peak to single peak behaviour when going from the lowest thickness of 5 nm up to 20 nm is in good agreement with the observed hysteretic behaviour.

The MI ratio of 0, 5, 10, 20 and 40 nm Co deposited ribbons at $f = 10$ MHz are plotted in Figure 3-7(a). It can be seen that by increasing thickness of Co layer from 5 to 20 nm, the hysteretic behaviour increases. A further increase in thickness to 40 nm, causes the hysteretic behaviour to decrease. Such a decrease in coercivity of Co thin films by increasing thickness, is reported by many authors^{27–31}. Also, an increase in thickness reduces the strength of exchange interaction between deposited layers as the coupling is expected to obey $\frac{1}{t}$ behaviour (t is the thickness of deposited layer). Two parameters (thickness dependent exchange coupling strength and thickness dependent coercivity of the Co layer), result in a maximum coercive MI plot observed for the 20 nm Co deposited layer. Figure 3-7(b) shows the peak of MI profile for all thicknesses of Co deposited ribbons measured at $f = 10$ MHz. In this figure, we see a similar evolution from double peak to single peak behaviour from the lowest thickness of 5 nm up to 20 nm which is in good agreement with the observed hysteretic behaviour. The observed single- or double-peak behaviour is associated with the longitudinal or transverse magnetic anisotropy as a function of external field direction³². However, the single peak can be seen when the thickness is above 10 nm, indicating that the magnetic anisotropy of layers changes from a transverse to a longitudinal direction. This implies that for a layer thickness below 10 nm, the exchange

Figure 3-8: a, b) MI response for 20 nm Co deposited ribbon. These hysteretic and single peak behaviour is magnetization anisotropy alignment dependent. This shows that at all frequencies we have the same ratios for alignments of transverse and longitudinal permeability on the surface of this 20 nm Co deposited ribbon and the existence of strong exchange between 20 nm Co and the ribbon. We observe the same behaviour at lower frequencies with higher skin depth. The plots of different frequencies are presented in different panels for better visualization.

interaction is strong and deposited layers follow the magnetization direction of the ribbon, which is transverse.

In Figure 3-8 one can see the peak evaluation at different frequencies for a 20 nm thick Co deposited layer on ribbon, which shows no variation depending on frequency. Different frequencies mean different skin depths of the ribbon, a parameter that can affect MI response. As mentioned, these hysteretic and single peak behaviours are magnetization anisotropy alignment dependent. This shows that in all frequencies we have the same ratios for alignments of transverse and longitudinal permeability on the surface of this ribbon and the existence of strong exchange between 20 nm Co and the ribbon. We observe the same behaviour at lower frequencies with higher skin depth.

The maximum MI ratio of all Ni and Co deposited ribbons and the bare ribbon versus frequency are plotted in Figure 3-9, to better illustrate the effect of Ni and Co coatings. MI measurements

Figure 3-9: Maximum MI response for all a) Ni and b) Co deposited thicknesses versus frequency. For all investigated samples, with increasing frequency, the maximum MI ratio first increases, reaches a maximum at a particular frequency (10 MHz), and then decreases for higher frequencies (the presented error bar at each point is $\pm 6\%$). This trend can be interpreted by considering the relative contributions of domain wall motion and magnetization rotation to the transverse permeability and hence to the MI^{10} . The magnetoimpedance ratio decreases at high frequencies. This is due to the presence of eddy currents that cause damping of domain wall displacements and only rotation of magnetic moments takes place. Therefore, the transverse magnetic permeability decreases and results in the observed decrease in the MI ratio.

were done at different frequencies ranging from 2.5 to 15 MHz. It is noted in Figure 3-9 that for all investigated samples, with increasing frequency, the maximum MI ratio first increases, reaches a maximum at a particular frequency (10 MHz), and then decreases for higher frequencies (except for the 40 nm Ni deposited ribbon). It is believed the exception for the 40 nm Ni coated ribbon is resulted from the 12% uncertainty in the MI measurement due to oscilloscope resolution (error bar is shown in the figure). This trend can be interpreted by considering the relative contributions of domain wall motion and magnetization rotation to the transverse permeability and hence to the MI¹⁰. The magnetoimpedance ratio decreases at high frequencies. This is due to the presence of eddy currents that cause damping of domain wall displacements and only rotation of magnetic moments takes place. Therefore, the transverse magnetic permeability decreases and results in the observed decrease in the MI ratio^{6,10}.

MI increases for 5 and 10 nm Ni deposited samples but decreases for the 20 and 40 nm ones. MI also increases for 5, 10 and 20 nm Co deposited samples and decreases for the 40 nm one. In Figure 3-10, the maximum of MI ratio for different thicknesses of Ni and Co layers at $f = 10$ MHz can be seen. A maximum MI ratio of ~315% is obtained for the sample with a 10 nm Ni layer and MI reaches the highest value of ~342% for a 5 nm Co layer deposited on ribbons. The increase in the MI response for magnetic layers deposited on ribbons has already been explained^{15,17,25}. It is due to modification of the ribbon surface and closure of magnetic flux paths of deposited ribbons with magnetic materials having low thicknesses and decreasing MI for higher thicknesses. In our samples, we see the same trend and the MI ratio for Ni and Co coated ribbons changes accordingly.

We will now discuss the physical aspects of thickness and the dependence of the MI response on roughness, crystallinity and exchange length of deposited layers. As the crystallinity of the Ni layer is more than the Co deposited one (according to XRD and FESEM) it is inferred that the formation of rigid random magnetic domains occurs at Ni layers. The MI ratio response of ribbon is sensitive to permeability. This possibly resulted in a decrease of permeability and consequently a lower MI response for Ni deposited ribbons compared to Co³³. The other reason for a relatively higher MI ratio for Co deposited ribbons can be due to the roughness¹⁵. From FESEM images, we concluded that decreasing the surface roughness of both Ni and Co

deposited ribbons causes the MI ratios to increase. According to images, the Co deposited ribbons have lower roughness than Ni. We can conclude that the Co layers cause a better magnetic closure flux path than Ni layers and hence higher MI response.

An increase or decrease in MI response is dependent on the thickness of electrodeposited layers through their exchange length of electrodeposited ribbons. Such layers can effectively improve the domain formation and surface anisotropy at the interface of a ribbon and Co or Ni thin layers. By increasing those thin layer thicknesses well above the exchange length, they realign the surface domain and make new anisotropy at the interface. We therefore speculate that, as the domain and anisotropy at the interface of a ribbon with those thin layers improves, due to interactions of domains at the surface with magnetization (with thickness not much above the exchange length) and hence transverse permeability increases accordingly. That effect is more pronounced when the interaction is stronger (based on Eq.3), i.e. the magnetic layer has larger magnetization. For example, we see an increase in MI for the Co thin layer compared to that structure coated with a Ni thin layer. Increasing the thickness of those coated

Figure 3-10: Maximum MI response vs thickness for Ni and Co deposited samples at $f = 10$ MHz (the presented error bar at each point is ± 6 %). As can be seen in Figure 3-10, the MI ratio for Ni is smaller than that for Co except at the thickness of 10 nm. At that point, the MI for a 10 nm Ni deposited layer (close to an exchange length for Ni of ~ 8.3 nm²⁵) is affected by increasing the transverse permeability whereas that for a 10 nm Co layer (about three times the exchange length of Co ~ 3.8 nm²⁵) the MI is affected by decreasing the transverse permeability.

layers to be higher than their exchange length cannot improve the transverse permeability at the interface as Co or Ni domains contribute to the interaction with their own magnetization strength and degrades the transverse permeability. In turn, a decrease in permeability results in decreasing MI response. This explanation can be demonstrated by comparing the MI ratio for 10 nm Co and Ni layers. As can be seen in Figure 3-10, the MI ratio for Ni is smaller than that for Co except at the thickness of 10 nm. At that point, the MI for a 10 nm Ni deposited layer (close to an exchange length for Ni of $\sim 8.3 \text{ nm}^{26}$) is affected by increasing the transverse permeability whereas that for a 10 nm Co layer (about three times the exchange length of Co $\sim 3.8 \text{ nm}^{26}$) was affected by decreasing the transverse permeability.

3.4 Conclusion

In this chapter, we showed that the magnetic exchange coupling between magnetization of deposited layers and a ribbon was not observable with VSM. In contrast, this effect became clear using the MI effect, which is sensitive to the surface skin effect. A change from the nominal two-peak behaviour of MI for a ribbon to a single asymmetric peak for Co deposited on a ribbon was observed due to strong exchange coupling. In contrast, we find that ribbons coated with Ni layers do not show significant changes. This is because the magnetic moment of Ni layers is smaller than that of the ribbon. An enhanced MI ratio was observed for ribbons due to the electrodeposition of Ni and Co layers. Our results show the advantage of electrodeposition as a method for fabrication of layers on both sides of a ribbon, controlling the double peak behaviour of MI response to a single and asymmetric one, probing magnetic coupling at the surface of ribbons and increasing the MI response using a simple and economic technique. More experimental studies such as deposition of other magnetic materials with different thicknesses on one or both sides of such ribbons and probing the ribbon surface by Magneto-Optical Kerr Effect are suggested to better understand the mechanisms of the MI coupling effect. Our results could be useful for the study of fundamental exchange coupling at the interface of MI elements and suggest the potential of a field dependent MI response for application as magnetic field sensors.

3.5 References

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Chapter 4: Independence of Exchange Bias from Spin-Orbit Torque*

Abstract

We investigated a possible correlation between spin orbit torque and exchange-bias in IrMn-layer/ferromagnetic-ribbon heterostructures by performing magnetoimpedance measurements. To study this correlation, we benefit from the exchange bias training effect probed by magnetoimpedance at room temperature. A damping-like spin-orbit torque is applied to the ferromagnetic ribbon layer by passing ac current through the antiferromagnetic IrMn, as observed by magnetoimpedance magnetic field and frequency sweeps. Furthermore, the magnitude of spin orbit torque was found to change significantly by field annealing, stemming from the presence of the magnetic spin Hall effect. Importantly, the magnitude of the spin orbit torque remained intact upon exchange-bias training and decreasing exchange-bias during alternative magnetic field sweep cycles. Our results pave the way to better elucidate the exchange bias effect, exchange bias training and the spin orbit torque, useful for future spintronic elements.

4.1 Introduction

Recently antiferromagnetic (AFM) materials have attracted great attention in the field of spintronics, due to their attractive features such as insensitivity to external magnetic fields, ultrafast dynamics and generation of large magneto-transport effects¹⁻³. The presence of prominent magneto-transport effects in AFM thin films has had significant impact in devices

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And:

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proposed for giant and anisotropic magnetoresistance^{4,5}, spin-orbit torque (SOT)⁶, direct and inverse spin Hall effect (SHE)^{7,8}, and current-induced domain wall motion⁹. Of the various AFM materials, noncollinear chiral ones are notable, due to their remarkable structural, magnetic, and electrotransport properties. A triangular spin configuration of AFM compounds gives rise to a large anomalous Hall effect (AHE)¹⁰, magneto-optical Kerr effect^{11,12} and SHE¹³. Both the AHE and SHE are favourite candidates to drive the magnetization dynamics of a ferromagnet in which spin currents can be used to manipulate magnetic moments. Because AFMs can have a large conventional SHE, they can thus exert a large magnitude SOT on an adjacent ferromagnet (FM). This has been confirmed by several experiments^{14–16}.

Very recently, a magnetic spin Hall effect (MSHE), has been proposed theoretically in noncollinear IrMn₃ AFM¹⁷ and experimentally observed in Mn₃Sn¹⁸. Although the MSHE was proposed in noncollinear AFM IrMn₃, the existence of the same property is expected in polycrystalline Ir₂₀Mn₈₀ (IrMn) given that it is formed by grains of IrMn₃^{19,20}. The MSHE is a transverse spin current, odd under reversal of magnetic moments, and has a distinct symmetry and origin from the conventional SHE. It is also expected that the transversal contribution of spin currents from MSHE in noncollinear AFMs can be greater than that originating from the conventional SHE¹⁷. The MSHE in noncollinear AFMs may open up new avenues in the understanding of SHE in AFMs.

On the other hand, the exchange-bias (EB) effect, known historically as a shift in the hysteresis loop (H_{EB}) of a ferromagnet arising from interfacial exchange coupling between adjacent FM and AFM layers^{21–23}, is an integral part of spintronic devices. This interfacial coupling has been studied intensively in the past two decades because of its applications in magnetic devices such as spin valve and magnetic random-access memory. Conventionally, the direction and strength of the EB is determined by an in-plane field applied during growth or field cooling below the ordering temperature of the AFM²⁴. Besides the hysteresis loop shift and coercivity enhancement, the EB phenomenon also exhibits asymmetry in the magnetization reversal process and training effect (TE)^{25–29}. The TE refers to the gradual and monotonous degradation of both H_{EB} and coercivity (H_C) to equilibrium values during consecutive hysteresis loop measurements after field growth or field cooling. It is generally accepted that the TE arises due

to irreversible changes in the magnetic microstructure of the AFM layer, as its spin texture rearranges with each magnetization reversal of the FM layer.

Therefore, in an FM/AFM structure, both SOT and EB effects coexist and affect the magneto transport. However, the contribution of interfacial exchange coupling to the amplitude of the SOT in the FM/AFM interface remains controversial. From this point of view, Tshitoyan *et al.*³⁰ have demonstrated that there is a direct link between the magnitude of the EB and spin torque efficiency. However, Saglam *et al.*³¹ have observed that the SOT is independent from the EB direction in a NiFe/IrMn bilayer. In addition, Zhang *et al.*¹³ found that there is no correlation between the in-plane EB and the magnitude of the spin Hall angle. With such diverse studies, finding a correlation between the EB strength and SOT remains under debate as one of the most important aspects in AFM spintronics.

In this chapter, we describe how we tried to uncover the presence of such a correlation using the MI effect in a high permeability FM/AFM bilayer. The heterostructure of interest was made of an amorphous FM $\text{Co}_{68.15}\text{Fe}_{4.35}\text{Si}_{12.5}\text{B}_{15}$ ribbon and a thin AFM layer of polycrystalline $\text{Ir}_{20}\text{Mn}_{80}$ (IrMn). In the MI effect, changes in the electrical impedance of a conducting FM with high transverse magnetic permeability (μ_t) in the presence of a static magnetic field can be monitored. By applying an external magnetic field, the skin depth ($\delta = (\rho/\pi\mu_t f)^{1/2}$) of applied ac current changes due to a change in the μ_t that alters the impedance (ρ is the electrical resistivity of the sample and f is the frequency of the passing current). Accordingly, the impedance of the FM ribbon is a function of frequency, driving current, and the external dc magnetic field (H) through μ_t and δ . Very recently we proposed that impedance spectroscopy can be used for detection of the SOT resulting from the SHE in Pt-layer/magnetic-ribbon heterostructures³². Furthermore, we showed that presence of a damping-like (DL) torque, arising from the Pt layer deposited on the FM, not only changes the MI response, but also tends to vary the transverse anisotropy of the magnetization. This was evidenced by impedance frequency shifts (see section 4.3.4).

In the study presented in this chapter, we observed the DL torque originating from an AFM IrMn deposited on a magnetic ribbon due to the conventional SHE and MSHE. In addition, in

order to investigate the correlation between the magnitude of the EB and SOT, we studied details of the EB and TE in our system. In fact, the MI effect probes the spin texture at the skin depth profile, which is less than 100 nm and close to the interface. Interestingly, the MI is used to observe both the EB and TE. It is also able to probe the SOT. Hence, by using MI spectroscopy, a correlation between the EB and SOT can be explored. Our results can be used for the development of simple methods for the study of fundamental and experimental spintronic phenomena.

4.2 Experimental details

Amorphous Co-based FM ribbons (0.8 mm width, 40.0 mm length and ~28 μm thickness) were prepared by a conventional melt-spinning technique. Before deposition of the IrMn layer, about 40 nm of the ribbons surface was etched via Ar plasma to have a clean and oxygen free surface. Immediately after that, the IrMn thin layer with thickness of 20 nm was deposited via sputtering on the surface of those ribbons in the presence of Ar with a pressure of 5 mTorr, base pressure better than 5×10^{-6} Torr and growth rate of 3 nm/minute (done by Azizmohseni, S.). In order to induce the EB, the as-deposited sample was subsequently annealed at 280 °C for 1 h under vacuum conditions (4×10^{-3} Torr) in the presence of an in-plane magnetic field and then cooled down to room temperature (done by Gharehbagh, J.). The applied magnetic field during the annealing and the cooling process was set to 230 Oe and applied in the longitudinal direction of the sample. Magnetic hysteresis loops were measured using the longitudinal magneto-optic Kerr effect (MOKE). For the MI measurements (done by Hajiali, M.R.), ribbons with preserved width and length was used. The MI measurements were performed following the explanations in chapter 2. The MI ratio is defined as $MI\% = \frac{Z(H) - Z(H_{max})}{Z(H_{max})} \times 100$; where Z refers to the impedance as a function of the external field H . The H_{max} is the maximum field applied to the samples during the MI measurement. All measurements were carried out at room temperature.

4.3 Results and discussion

4.3.1 Magneto-optical Kerr effect measurements

In order to examine the presence of the EB effect and occurrence of the TE in our sample, we first measured longitudinal MOKE hysteresis loop of FM/IrMn heterostructures. Figure 4-1 illustrates the consecutive longitudinal MOKE hysteresis loops (with magnetic field applied along the induced EB direction) with $n = 1, 2, 3$ and 4 (n = number of field sweep), for the magnetically annealed (280 °C/230 Oe) FM ribbon/IrMn sample. The inset of the figure shows the hysteresis loop for the FM ribbon that does not show any shift. As shown, the hysteresis loop for $n=1$ clearly exhibits the EB behaviour as a shift of the loop towards negative values, by $|H_{EB}| = 2.4$ Oe. During the consecutive M–H loop measurements, the TE was observed for the annealed IrMn/ ribbon sample. One can note that the substantial decrease in H_{EB} takes place only between the first two consecutive hysteresis loops. Also the shift is more prominent in the descending branch because in our measurement the loop starts at positive saturation.

4.3.2 Impedance measurements with magnetic field sweep

In the previous section we showed that the EB is present in our samples. Here, in order to elucidate the effect of the EB coupling on the MI effect, we carried out field sweep impedance

Figure 4-1: Successive longitudinal MOKE hysteresis loops of the magnetically annealed (280 °C /230 Oe) FM ribbon/IrMn (20 nm) heterostructure at room temperature. The inset displays the hysteresis loops for the FM ribbon that does not show any shift so that, for field annealed ribbon/IrMn heterostructures, the hysteresis loop clearly exhibits the EB effect by $|H_{EB}| = 2.4$ Oe. Also the hysteresis loop for $n=1$ clearly exhibits the TE between the first two consecutive hysteresis loops.

measurements. By applying an ac charge current with frequency $f=10$ MHz to the samples, we investigated how the impedance of the heterostructures changes as a function of the external magnetic field. So far, effect of the EB coupling strength on the MI was investigated theoretically and experimentally in different structures e.g. in thick FM ribbon/oxide layer³³ and also NiFe/FeMn³⁴ and NiFe/IrMn^{35,36} thin film multilayers. Due to presence of the EB in those systems, shifts were observed in both the hysteresis loop and the MI response, and the MI response showed an asymmetric magnetoimpedance (AMI). Generally, the MI as a function of the field has shown an asymmetric response against field polarities by applying additional bias field³⁷ or current³⁸, and EB³³. For a thick FM ribbon/oxide layer, the exchange interaction between the amorphous bulk and the surface crystalline regions leads to an effective unidirectional anisotropy, which is responsible for the AMI. For thin multilayers, the MI with significant EB effect was seen in the high frequency regime because of the low permeability of these layers at low frequency (MHz). However, there is no report on the presence of the EB in thick FM ribbon/AFM probed via the MI effect within the MHz frequency ranges.

Figure 4-2(a-b) and (c-d) show field sweep impedance measurements at a frequency of $f = 10$ MHz for a ribbon (as-cast and field annealed) and ribbon/IrMn heterostructures (as-deposited and field annealed) samples, respectively, with a current of $I = 66$ mA applied to the samples. Three main differences between the as-cast ribbon and the IrMn-deposited ribbons can be seen in MI plots.

Figure 4-2: Comparison of the MI response of the ribbon and the ribbon/IrMn samples at a frequency of $f = 10$ MHz and an applied current of $I = 66$ mA. The inset shows the MI response around zero magnetic fields. The decrease of MI response for IrMn-deposited samples is associated with a decrease of the transverse magnetic permeability, μ_t . Due to presence of the EB effect in the IrMn/ribbon interface, which pins the spins of the ribbon with additional anisotropy and reduces the μ_t , a decrease in MI ratio results. The numbers in the inset of panel (d) show the stages of magnetization reversal discussed in Figure 4-4.

i) MI% decreases from 265% for the as-cast ribbon to 259% for as-deposited ribbon/IrMn, and from 325% for the field annealed as-cast ribbon to 314% for the field annealed ribbon/IrMn samples. The decrease of MI response for IrMn-deposited samples is associated with a decrease of the transverse magnetic permeability, μ_t . Due to presence of the EB effect in the IrMn/ribbon interface, which pins spins of the ribbon with additional anisotropy and reduces the μ_t and thereby results in a decrease in MI ratio. Moreover, it can be seen in Figure 4-2(a) and (c) that the as-cast ribbon exhibits a double peak behaviour whereas the IrMn deposited ribbon shows a single peak one. This trend is also repeated for field annealed samples in which

their MI results are displayed in Figure 4-2(b) and (d). In general, the observed single or double-peak behaviour is associated with the longitudinal or transverse magnetic anisotropy with respect to the external field direction^{39,40}. Thus, we conclude that the IrMn layer changes the transverse magnetic anisotropy of the ribbon.

ii) We see a hysteretic MI behaviour for IrMn deposited samples (Figure 4-2(c-d)), contrary to that of as-cast ribbons. This potentially implies the presence of an antiferromagnetic coupling of the bias field with magnetization inside the amorphous phase⁴¹. Furthermore, in the previous chapter (also ref [42])⁴², it was shown that the hysteretic behaviour of the MI response of the ribbon depends on the strength of the magnetic exchange coupling in the bilayer. Accordingly, here in our sample (IrMn/ribbon), the exchange coupling at the interface between IrMn and the ribbon can cause the same effect and in turn the hysteretic behaviour of MI response can be observed.

iii) In ribbons coated with IrMn, by sweeping the magnetic field from positive to negative values (inset of Figure 4-2(d)), we observe an asymmetric single peak in the MI response with a nonzero H (2.4 Oe). The magnitude of this shift is similarly seen for the magnetization loop as an EB shift ($|H_{EB}| = 2.4$ Oe). It should be noted that the shift in MI curve occurs over the whole range of frequencies (1-20 MHz, not shown here). As mentioned before, an asymmetric MI

Figure 4-3: Schematic of the evolution of the spin configuration during external magnetic field (H) reversal from the opposite of exchange bias (H_{EB}) to its parallel direction in FM/AFM heterostructures in the skin depth (δ) region. The length of the black arrows shows the magnetic field strength. The interface of the FM ribbon in the skin depth region affected by the EB has a different FM property to the rest of it. In the region close to the interface spins are pinned stronger than in the volume underneath, i.e. the region close to the interface spins behaves as an exchange spring medium.

(AMI) response due to the presence of the EB³³ is interpreted as an exchange interaction between the amorphous bulk and the surface crystalline regions, forming an effective unidirectional anisotropy. Here, as represented in Figure 4-2 d, the exchange interaction between the IrMn and the surface of ribbon can lead to an effective unidirectional anisotropy which is responsible for the AMI.

We speculate that such a coupling mechanism with the observed AMI response is similar to those of soft/hard bilayer exchange spring magnets⁴³. The MI effect is mediated by the current skin depth with a thickness of approximately 100 nm. The interface of the FM ribbon in the skin depth region affected by the EB has a different FM property to the rest of it. In the region close to the interface spins are pinned stronger than in the volume underneath, i.e. the region close to the interface spins behaves as an exchange spring medium. A schematic of the spin configuration of ribbon/IrMn heterostructures at the interface with exchange coupling can be seen in Figure 4-3. This figure shows the evolution of spin configuration during external field (H) reversal from the opposite of EB induced field (H_{EB}) to its parallel orientation, in the skin depth (δ) region. Each step in Figure 4-3 is shown as panel numbers, referring to a corresponding reversal point addressed in the inset of Figure 4-2(d). By decreasing the external field H from positive saturation, from right to left, according to the exchange interaction between the spins of the IrMn layer and ribbon, the highest value of μ_t occurs in step 2 and MI has no peak at $H = 0$ Oe. When H is reversed, the spins of the FM ribbon completely switch. Due to the strength of the exchange interaction near the interface, the AFM spins are dragged along with FM spins and therefore create AFM exchange spring.

4.3.3 Training effect probed by MI

In section 4.3.1, using the longitudinal MOKE measurement, we showed that the TE occurs for the field annealed ribbon/IrMn samples. In this section, the TE is evaluated through the MI effect. Towards this, we have further examined successive field cycling while performing MI measurements for the same sample. Figure 4-4(a-d) shows consecutive MI curves for the mentioned samples at a frequency of $f = 10$ MHz, corresponding to first to fourth sequential MI measurements labelled by $n = 1$ to $n = 4$, respectively. We observe that by repeating the MI measurements continuously, the peaks which appear at positive and negative low magnetic

fields move towards $H = 0$ Oe. In addition, the asymmetric behaviour of the MI peaks disappears. This is obviously a consequence of the TE at the interface of the ribbon/IrMn. When the MI measurement is repeated continuously, the strength of exchange interaction decreases due to TE and finally the MI effect shows symmetric behaviour. Hence, the rearrangement of the magnetic moments of the AFM at the interface plays the main role in these observations. By further repeating the measurement, no additional changes appear in the MI plot. Using X-ray magnetic linear dichroism measurements, Dobrynin *et al.* have proposed that the AFM exchange spring is the origin of TE in the FM/AFM interface⁴⁴. According to the formation of AFM exchange in our sample, it is reasonable to consider the same origin for the occurrence of

Figure 4-4: The MI response of the field annealed ribbon/IrMn for 4 consecutive MI loops at $f = 10$ MHz. By repeating the MI measurements continuously ($n = 1$ to $n = 4$), the peak which appears at low magnetic fields moves towards $H = 0$ Oe. The MI response at $n=4$ increases in value with a symmetric and single peak behaviour. In fact by repeating the MI measurement and the consequent rearrangement of the magnetic moments based on the TE as the EB vanishes, unpinning occurs and results in an increased μ_t of the ribbon, which consequently causes the MI% to increase. Therefore, we can observe the TE evidenced by a peak shift and an increase in the MI%.

TE in the ribbon/IrMn samples.

As addressed in Figure 4-4, an abrupt decrease in the EB and the change in the AMI behaviour between the first and second cycles reveal that the TE is related to an athermal contribution, as previously seen in the hysteresis loop of longitudinal MOKE measurement (Figure 4-1). Hoffman predicted that athermal TE is due to the initial stabilization of a noncollinear arrangement of AFM sublattice spins after field cooling via a spin-flop like coupling mechanism at the interface²⁷. The rearrangement of AFM spins into a collinear style, after first field cycling, gives rise to an abrupt decrease in the H_{EB} .

It is worth mentioning that by repeating the measurement from the first to fourth cycle, the MI% increases as well. As mentioned before, the MI% is dominated by the strength of μ_t . By repeating the MI measurement and the consequent rearrangement of the magnetic moments based on the TE as the EB vanishes, unpinning occurs and results in an increased μ_t of the ribbon, which consequently causes the MI% to increase. Therefore, we can observe the TE

Figure 4-5: (a-c) Frequency sweep impedance measurement of the ribbon, ribbon/IrMn and the field annealed ribbon/IrMn. The ac current amplitudes (peak to peak) are (a) $I = 33$ mA, (b) $I = 66$ mA and (c) $I = 99$ mA to observe a higher frequency shift for higher driving currents. (d) Peak frequency obtained from (a)–(c) versus ac current amplitude, indicating the higher slope for the sample after annealing and no such shifts observed for the as-cast ribbon. (e) Schematic illustration of a ribbon/IrMn heterostructure. An in-plane charge current I_{ac} generates a perpendicular spin current, which in turn generates SOTs acting on FM moments. We should note here that this scenario happens in the skin depth δ of the ribbon.

evidenced by a peak shift and an increase in the MI% (here it is (52%)). We repeat the experiments for a field annealed ribbon without IrMn and we observe no variation in MI response, even by repetitive measurements.

4.3.4 Detection of spin orbit torque driven magnetoimpedance and independence of spin orbit torque from EB

In this section, we describe frequency sweep MI measurements carried out right after each cycle of MI measurement under magnetic field sweep. These measurements reveal two conclusions, which we will discuss separately.

i) Effect of SOT on MI due to SHE and MSHE: The results for frequency sweep MI measurements after three field sweeps are shown in Figure 4-5(a-c), for as-cast ribbon, ribbon/IrMn and field annealed ribbon/IrMn samples. Here, ac currents with different peak to peak amplitudes of $I = 33, 66$ and 99 mA were applied. It is noted that for all investigated samples, with increasing frequency, the maximum MI ratio first increases, reaches a maximum at a particular frequency, and then decreases in higher frequency ranges. The frequency dependent MI effect is explained upon considering a relative contribution of DW motion and moment rotation to the μ_t ^{45,46}. As the frequency increases, the contribution of DW motion is damped due to the presence of the eddy current and moment rotation becomes dominant. Also, this behaviour is interpreted by the change in the internal part of the ribbon inductance due to a change in permeability and eddy currents at different frequencies⁴⁵. Therefore, a peak in the impedance of the ribbon versus frequency can be observed.

As can be seen in Figure 4-5, the impedance peak frequency is shifted towards higher values, for either of IrMn coated samples with respect to the impedance of an as-cast ribbon. The peak frequency under applied ac current of 99 mA is 7 MHz for as-cast ribbon and shifts to 8.2 and 11 MHz for as deposited and field annealed samples, respectively. By increasing the amplitude of the ac current, we observe a systematic shift in the frequency of the impedance peak, as shown in Figure 4-5(d). This shift is higher for the sample after annealing and no such shifts are observed for the as-cast ribbon. This directly confirms the effect of SOT and its role in the impedance, which we will discuss in the following.

As shown schematically in Figure 4-5(e), in the presence of the IrMn layer, the oscillating electric current generates an oscillating spin current. This spin current flows into the adjacent FM layer and exerts two different types of oscillating SOTs; field-like (FL) torque $\mathbf{T}_{\text{FL}} \sim \mathbf{m} \times \mathbf{y}$ that is equivalent to an in-plane field $\mathbf{h}_{\text{FL}} \sim \mathbf{y}$ and DL torque $\mathbf{T}_{\text{DL}} \sim \mathbf{m} \times (\mathbf{y} \times \mathbf{m})$ that establishes an out-of-plane field $\mathbf{h}_{\text{DL}} \sim \mathbf{m} \times \mathbf{y}$, where $\mathbf{m}$ is the magnetization unit vector and $\mathbf{y}$ is the in-plane axis perpendicular to the current flow direction $\mathbf{x}$. The generated spin current and spin accumulation at the interface can result in various effects such as conventional SHE⁴⁷, MSHE and Rashba-Edelstein effect (REE). Generally, the REE and SHE are known as the origins of the $\mathbf{T}_{\text{FL}}$ and $\mathbf{T}_{\text{DL}}$. However, the $\mathbf{T}_{\text{FL}}$ is due to the REE revealed when an ultra-thin FM layer is adjacent to a heavy metals layer⁴⁸, and the $\mathbf{T}_{\text{FL}}$ is due to the SHE is very weak in metallic systems⁴⁹.

The $\mathbf{T}_{\text{FL}}$ due to SHE and REE is negligible in our studied structure because of the metallic nature of the ribbon/IrMn samples and the large thickness of the FM ribbon. We consider that the $\mathbf{T}_{\text{DL}}$ comes primarily from the SHE and MSHE in IrMn and $\mathbf{T}_{\text{FL}}$ comes from the Oersted torque ($\mathbf{T}_{\text{Oe}}$) due to the Oersted field. $\mathbf{T}_{\text{Oe}}$ is generated from the applied ac charge current that depends on the conductivity of each layer and skin depth δ .

The frequency shift in MI is more prominent in field annealed samples for two main reasons. One is the change in the IrMn resistivity and the other is the SOT efficiency. To see the effects of annealing on the electrical properties of the sample, we measured the resistance of our samples before and after annealing and no changes were observed. Hence, the only parameter is the SOT efficiency, which is directly related to the AFM domain structure and interface spin transparency. By field annealing of the sample, with field along the ribbon axis (x axis), one expects a reduction in spin transparency of the interface for longitudinal electric current which results in transverse spin polarization^{13,50}. This effect will cause a decrease in SOT and thus a smaller frequency shift in annealed samples. However, the presence of such a large frequency shift in annealed samples suggests another mechanism increases spin current and therefore the SOT. This can be explained by the presence of the MSHE in the heterostructure mediated by the IrMn layer. The polycrystalline Ir₂₀Mn₈₀ (IrMn) is formed by grains of IrMn₃^{19,20}, a noncollinear AFM that was recently predicted to show the MSHE¹⁷ (the excess of Mn that can exist in the layer has no effect on the SOT). It is important to note that generated spin current by MSHE is a

consequence of symmetry breaking caused by the noncollinear magnetic structure of IrMn₃ and is odd under time reversal. Hence, its polarization depends on the magnetic structure of IrMn. However, generated spin current by conventional SHE is even under time reversal and its polarization does not depend on the magnetic structure of IrMn. In Ref. 13, the effects of field annealing in (001)-oriented antiferromagnetic IrMn₃ thin films, coupled to ferromagnetic NiFe layers is investigated. The underlying mechanism is reported to be conventional SHE and is even under reversal of all magnetic moments and thus does not cancel out for random domain orientations. It can still depend on the magnetic order and thus can possibly lead to an increase in the SOT when the domains are oriented. In our sample, when annealing is carried out, applying an external magnetic field orients the direction of the magnetization of the ribbon. Hence, due to the presence of the exchange interaction across the AFM/FM interface, the magnetic configuration of the AFM will change¹³. Since the FM layer is magnetized in a unique direction, exchange coupling at the interface of FM and AFM layer forces the IrMn domains to follow a unique direction. The AFM domains were randomly oriented before annealing while after that, more AFM aligned domains are present. As mentioned previously, since the conventional SHE is even under time reversal symmetry, it is independent from AFM domain direction. Therefore, we expect that the spin current due to the SHE will not change upon annealing. However, the MSHE has a different polarization for a different AFM domain orientation because that is odd under time reversal symmetry. Before annealing, as the domain configuration of sample tends to be random, the resulting SOT will have lower impact. In contrast, after annealing, the spin polarization of the spin current from the MSHE has a preferential direction due to the unique domain orientation in IrMn. Since the odd spin currents can contribute to the SOT, the spin current from MSHE will exert a significant SOT on the FM layer. This together with the conventional SHE, results in a high frequency shift in MI.

ii) Independence of the SOT from the EB: Frequency sweep MI measurements show the same frequency dependency for all field sweep cycles (not shown) for ribbon/IrMn and the annealed one. Although, the longitudinal MOKE measurements from section 4.3.1 (Figure 4-1) indicate that there is no EB in the samples after field cycling three times, there is still a significant frequency shift in the MI measured (Figure 4-5). These two facts allow us to conclude the

independence of SOT from EB in our samples. In fact, the SOT depends on spin polarization of spin current from the MSHE which in noncollinear AFMs depends on the magnetic order direction. However, it does not depend on the strength of the EB which is the coupling of magnetic moments of the FM and AFM.

4.3.4 Detection of spin orbit torque by magnetoimpedance of ribbon when coated by Pt

Also, as a proof for the observed frequency shift of the impedance being from SOT, we also measured the frequency shift of the ribbon samples when coated with Pt thin films (thickness 10 and 20 nm). Frequency sweep impedance measurements against ac current with peak to peak amplitude of 33, 66 and 99 mA are shown in Figure 4-6 (a-c) for bare ribbons and ribbons covered with 10 and 20 nm Pt. It is clear from Figure 4-6 (a) that increasing the magnitude of the applied current for the bare ribbon does not affect the peak position of the impedance. Whereas for ribbons covered with 10 and 20 nm Pt, increasing the amplitude of the applied

Figure 4-6: Frequency sweep impedance measurement of (a) 0 nm, (b) 10 nm and (c) 20 nm Pt with different ac current peak to peak amplitude of 33, 66 and 99 mA with a higher frequency shift for higher driving currents. (d) Maximum frequency obtained from (a), (b) and (c) versus ac current amplitude indicating higher slope of increment for the ribbon coated with 20 nm Pt than for the ribbon coated with 10 nm Pt.

current results in a shift in the maximum impedance frequency. A comparison between the maximum impedance frequency shift and the applied current for all samples is shown in Figure 4-6 (d). As can be seen, the role of current for the thicker Pt coverage is more pronounced resulting in a larger frequency-current slope.

4.4 Conclusion

In summary, in this chapter, we described how we probed the exchange bias effect, the training effect and the presence of the spin-orbit torque through the magnetoimpedance effect in a ribbon/IrMn heterostructures. Using MI measurements with consecutive field sweep repetitions, we observed that training reduced the exchange bias field. The spin-orbit torque originating from the AFM IrMn in the mentioned heterostructure was observed as a shift in peak frequency of the MI effect, even by decreasing the exchange bias field using training. We conclude that the spin-orbit torque is independent from the exchange bias. Additionally, measurements on the field annealed samples showed higher spin-orbit torque efficiency due to the magnetic spin Hall effect and the well-defined spin polarization in the AFM layer. Our results can be used for the development of simple methods to study the fundamental magnetic effects for application in spintronic technologies.

4.6 References

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Chapter 5: Magnetoimpedance Sensor with Graphene

oxide*

Abstract

Graphene oxide layers have been shown to be fascinating elements for application in high performance sensors. They can be applied in multi-disciplinary designs based on surface selective sensing mechanisms. One immediate application of such surface sensitive elements is the implementation of graphene oxide layers in magnetoimpedance sensors to improve their multi-functionality. In this chapter, deposition of graphene oxide on the surface of Co-based amorphous ribbons ($\text{Co}_{68.15}\text{Fe}_{4.35}\text{Si}_{12.5}\text{B}_{15}$) is performed using an electrophoretic deposition method to evaluate the MI response. The magnetoimpedance ratio increased from 271% (bare ribbon) up to 281 % and 301 % when graphene oxide had been applied by electrophoretic deposition for 4 and 8 min, respectively. A similar experiment was carried out for a ribbon drop-coated with graphene oxide; in that case no enhancement in magnetoimpedance response was seen. Vertical growth of graphene oxide on the surface of the ribbon in electrophoretic deposition and drop-coated layers were observed by topographical measurements. We attribute the difference in magnetoimpedance response to the different surface bonding of GO to the ribbon and the consequent different quality of coatings. UV-visible absorption and Raman spectroscopies were used to study the nature of the graphene oxide. The high surface area of graphene oxide layers along with their biocompatibility and their anticorrosive properties opens pathways towards applications as surface selective and high sensitivity magnetoimpedance sensors.

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5.1 Introduction

The magnetoimpedance (MI) effect with a rich research history has gained much interest in the field of sensors because of its high sensitivity and low cost technological requirements^{1,2}. Fundamental aspects of the MI effect are explained in chapter 2. A fundamental interest in ferromagnetic metals and the development of high sensitivity magnetic field sensors has increased interest in the MI effect⁴. For dependence of impedance of a ribbon on skin depth see chapter 2. The electrical and magnetic environmental conditions would strongly affect the MI behaviour of a sensor⁵. Many researchers have recently reported observing MI response enhancement upon adding a coating of magnetic and nonmagnetic or conductive and insulating layers on the surface of soft magnetic materials^{6–12}. Some examples of dielectric materials are Zinc oxides⁸, Copper oxide⁷ diamagnetic organic thin film⁹ and CoFe_2O_4 ¹². The influence of surface structure on the magnetic field and surface domain structure and so tuning the MI response has been reported. Studies of conductive layers coated on the surface of MI sensors^{13,14} have discussed the impact of reducing irregularities and the closure of magnetic flux paths at the surface. Very recently we reported on the high sensitivity of the MI effect for a 10 nm thin Pt layer deposited on a magnetic ribbon due to a current-driven spin-torque effect¹⁵. The MI effect especially in the skin depth is sensitive to any small variations in the surface like the presence of magnetic particles¹⁶ or changes in the surface roughness^{17,18}. Annealing of ribbons to improve sensitivity to external magnetic field is another interesting subject discussed by many authors^{19–23}.

It is useful to be able to modify the surface of a sensor for its application in different environmental conditions and multi-sensing applications. Deposition of thin layers can adjust MI tenability that can be used in sensor design. One important candidate layer is the graphene (Gr) family of materials, frequently used in many devices and for many sensing applications. The properties of graphene, such as electrical, optical, mechanical and physiochemical, can change in response to environmental parameters^{24–26}. Thus, such two-dimensional materials with high surface to volume ratio have emerged as candidates for biosensing. There are few reports on the effect of the carbon family on the MI effect, namely nanotube¹¹ and Gr layer²⁷. A combination of the Gr sensing ability and the MI effect, offers an interesting avenue of study.

To achieve such a modified sensor, the method of fabrication can play a crucial role in the final results. The electrophoretic deposition (EPD) technique is an attractive approach for development of Gr based materials including graphene oxide (GO) films for a variety of applications²⁸. Its applicability for deposition of a wide range of materials, cost-effectiveness and simple equipment requirements are the advantages of the EPD method. The ability of being electrophoretically deposited, has made the use of GO possible in many advanced technological applications²⁹. The many interesting characteristics of GO have resulted in opportunities for the development of optical^{30,31}, electronic³² and sensor devices^{33,34}. In this chapter, we describe how we used the EPD method to deposit GO on the surface of Co-based magnetic ribbons ($\text{Co}_{68.15}\text{Fe}_{4.35}\text{Si}_{12.5}\text{B}_{15}$) of which we investigated the MI response. We used UV-Visible and Raman spectroscopy, atomic force microscope (AFM), field emission scanning electron microscopy (FESEM) and MI measurements to reveal the GO's role in the MI response. For the first time we reported the MI enhancement by application of GO layers on a soft ferromagnetic MI element. Drop coating of GO on the surface of the ribbon was examined and, unlike for ribbons on which GO was electrophoretically deposited, no enhancement was observed. Based on analysis of the surface of the GO-covered samples, the adhesion of GO layers on the ribbon has a dramatic impact on the MI response. We found that the EPD grown GO layer is formed vertically on top of the MI sensor element. The GO structure can act as an anticorrosive and particulate-like cover layer with high surface area. This technique can open the pathway for the use of MI surface sensitive elements in gas sensing and bio-detector devices.

5.2 Experimental

As explained in chapter 2, conventional melt-spinning technique was used to fabricate $\text{Co}_{68.15}\text{Fe}_{4.35}\text{Si}_{12.5}\text{B}_{15}$ magnetic ribbons with 0.8 mm width, 40.0 mm length and about 28 μm thickness. The alloys were prepared by arc melting under argon atmosphere. The surface speed of the copper wheel at the melt spinning stage was set to 40 m/s. X-ray diffraction (XRD) was performed using a STADI STOE diffractometer with $\text{CuK}\alpha$ ($\lambda=1.54 \text{ \AA}$) at angles (2θ) ranging from 10 to 80°. GO was synthesized from natural graphite powder using a modified Hummers method³⁵ and explained in the chapter 2 in detail. For the UV-Visible measurement and EPD, a

certain amount of GO was dispersed in DI water. UV–visible absorption spectra were collected using a PerkinElmer LAMBDA 20 UV–visible spectrometer (done by Sheykhifard, Z.). EPD of GO was done at room temperature in a beaker containing 0.1 mg/ml GO. Experiments were done at a constant applied voltage of 2 V, well under the reduction potential of GO²⁸, utilizing a computer controlled voltage source in a two electrode configuration cell. Ribbon with 5 cm length was set as anode and a 1×3 cm Platinum plate as cathode at a distance of 2 cm. Raman spectroscopy was performed using a Teksan (Takram P50C0R10) Raman microscope with wavelength and power incident laser light of 532 nm and 20 mW, respectively. AFM was performed using a Nanosurf atomic force microscope (done by Sheykhifard, Z.). FESEM of the samples was carried out using a MIRA3 TESCAN instrument. GO was drop coated on the ribbon from a 2 mg/ml solution at room temperature. The GO was dried in air overnight. The experimental details concerning the performance of MI measurements are explained in chapter 2. The oscilloscope measurement resolution gives a $\pm 6\%$ error in the observed MI ratio. The MI ratio can be defined as

$$MI\% = \frac{Z(H) - Z(H_{max})}{Z(H_{max})} \times 100 \quad (2)$$

where Z refers to the impedance as a function of external field (H) and H_{max} is the maximum field applied to the samples in the MI measurement.

5.3 Results and discussion

5.3.1 Ribbon and GO synthesis

The inset of Figure 5-1 shows the XRD pattern of the amorphous ribbon with an amorphous nature except for a broad peak at about $2\theta = 20\text{--}30^\circ$, indicating presence of small SiO_2 crystals in the ribbon³⁶. Prior to performing EPD of GO on the surface of ribbon samples, we tried UV-visible measurements to evaluate the nature of the prepared dispersion of GO through the Hummers method. For this purpose 0.02 mg/ml of GO dispersion in DI water prepared to be able to perform the measurement. The resulting UV-visible spectrometry is presented in Figure 5-1. The spectrum shows a main absorption maximum at 217 nm, which is due to the $\pi\text{--}\pi^*$ transition in the C-C aromatic rings. This peak shows a deviation from 300 nm, which could be due to some excess of oxygen bonding in the GO. Also there is a shoulder peak at 300 nm, which is attributed to $n\text{--}\pi^*$ transition of C-O bonds. The overall features of this spectrum and its adsorption peaks are identical to that of GO synthesized using a conventional Hummers method reported in literature^{37–39}. The prepared GO exhibited a brown colour, characteristic of GO dispersions in water,^{40,41} as can be seen in the inset of Figure 5-1.

Figure 5-1: UV-visible spectrum of GO prepared by the Hummers method (solution of the GO shows a brown colour). The inset shows the XRD pattern of the amorphous ribbon with a broad peak at about $2\theta = 20\text{--}30^\circ$, indicating the presence of small SiO_2 crystals in the ribbon³⁶. The overall features of this spectrum and its adsorption peaks are identical to that of GO synthesized using a conventional Hummers method reported in literature^{37–39}.

5.3.2 EPD of GO

For EPD of GO, 20 mg of GO was dispersed in 200 ml DI water and sonicated for about 1 h to obtain a homogenous dispersion that affects the deposition of GO on the surface of the ribbon. A schematic of the deposition process is depicted in Figure 5-2 (a). For all of the depositions, the wheel side of the ribbon was faced toward the Pt cathode. GO is negatively charged because of its oxygen functional groups and so anodic EPD was carried out⁴². In the process of EPD, GO flakes are deposited on both sides of the ribbon as it is conductive, free and uncovered in the deposition cell. By applying a constant voltage of 2 V, the current during the deposition was about 1.2 mA after a prime reduction (Figure 5-2 (b)). Two different deposition times of 4 and 8 minutes were used to deposit GO at the surface of the ribbons.

Figure 5-2: a) Schematic of EPD of GO on the surface of a ribbon (GO flakes are symbolized by blue sheets) and b) current and voltage during EPD. In the process of EPD, GO flakes are deposited on both sides of the ribbon as it is conductive, free and uncovered in the deposition cell. By applying a constant voltage of 2 V the current during the deposition was about 1.2 mA after a prime reduction. Two different deposition times of 4 and 8 minutes were used to deposit GO at the surface of the ribbons.

To describe the quality of the deposited GO layers we used Raman spectroscopy, the most reliable characterization technique for graphene-based materials^{43–45}. A Raman spectrum of a GO-coated ribbon is presented in Figure 5-3. Two distinctive peaks appear at 1359 and 1581 cm^{-1} , which correspond to the D and G bands²⁶. The G band represents the in-plane vibration mode of sp^2 hybridized carbon atoms (E_{2g}). The D band indicates structural defects (sp^3 -hybridized carbon) and disorder, and is associated with the interior phonon branches of the graphite Brillouin zone^{46,47}. Furthermore, the I_D/I_G ratio is commonly used to compare the degree of disorder and the crystallite size and also the degree of oxidation^{46,48,49}. The intensity ratio of I_D/I_G decreases as GO is converted to a graphene network because of the formation of the more extended sp^2 carbon network. As indicated in the figure, the ratio of I_D/I_G for the EPD GO layer on the ribbon is 0.98 which is similar to the I_D/I_G of GO reported by others⁵⁰.

Figure 5-3: Raman spectrum of 8 minutes GO deposited at the surface of the bare ribbon. As indicated in the figure, the ratio of I_D/I_G for the EPD GO layer on the ribbon is 0.98 which is similar to the I_D/I_G of GO reported by others. The G band originates from the in-plane vibration mode of sp^2 hybridized carbon atoms (E_{2g}); the D band indicates the presence of structural defects and disorder, and is associated with the interior phonon branches of the graphite Brillouin zone^{46,47}.

Figure 5-4: 2D and 3D AFM topographical images of a) bare ribbon, b) a ribbon on which GO was deposited for 4 min and c) a ribbon on which GO was deposited for 8 min. The mean roughness (R_a) determined for the bare ribbon and ribbon coated for 4 and 8 min were ~ 1 nm, ~ 10 nm and ~ 12 nm, respectively. The roughness may affect the magnetoimpedance ratio. A higher surface to volume ratio in the GO coated ribbons may also be useful for biosensor applications.

AFM was also used to further disclose the detailed structure of electrophoretically deposited GO. 2D and 3D topographical images of the surface of the bare ribbon and EPD GO deposited ribbon can be seen in Figure 5-4. These images reveal the higher surface roughness of the ribbons deposited with GO. There are many sharp edges appearing in the 3D topographical images of ribbon on which GO was deposited points to a vertical alignment of many GO flakes at the surface of the ribbon. This vertical growth can result in high surface area in the MI sensor, increasing its functionality when employed as gas- and bio-sensor. The mean roughness (R_a) determined for bare ribbon and 4 and 8 min deposited ribbon were ~ 1 nm, ~ 10 nm and ~ 12 nm, respectively. The thicknesses of the GO layers grown with 4 and 8 min EPD were evaluated from AFM measurements to be ~ 100 and ~ 150 nm, respectively. As the MI response of ribbons is highly sensitive to the surface morphological structures, these results should be considered in the analysis of MI results.

5.3.3 MI measurements

In order to understand the impact of EPD of GO on the MI response, magnetic field dependences of the MI ratio of the samples were measured. Measurements were carried out at different frequencies of 2.5, 5, 7.5, 10, 12.5 and 15 MHz, in the presence of an applied magnetic field (between 0 and 120 Oe). MI results for bare ribbon and 4 and 8 min deposited ribbon are presented in Figure 5-5. In panel (a) of Figure 5-5 we can see the field dependent MI ratio of bare ribbon versus frequency. There is a peak at low external applied magnetic fields because of transverse alignment of the magnetic anisotropy of the ribbon against the applied magnetic field direction⁵¹. This also happens at the ribbons coated with 4 (Figure 5-5 (a)) and 8 min (Figure 5-5 (b)) EPD GO. These indicate the existence of a transverse magnetic anisotropy component for the ribbon.

The MI ratio increases when increasing the frequency up to 10 MHz but then decreases upon further increases in frequency. Relative contributions of domain wall motion and magnetization rotation to the transverse permeability should be considered when interpreting this trend⁵². The reduction in MI ratio at high frequencies is due to the presence of eddy currents that cause damping of domain wall displacements and only rotation of magnetic moments takes place. In turn the transverse magnetic permeability diminishes, and the MI ratio decreases^{53,54}.

Figure 5-5: MI response of a) the bare ribbon, b) a ribbon on which GO was deposited for 4 min and c) a ribbon on which GO was deposited for 8 min. There is a peak at low external applied magnetic fields because of the transverse alignment of the magnetic anisotropy of the ribbon against the applied magnetic field direction. This also happens for the ribbons coated with 4 and 8 min EPD GO. These indicate the existence of a transverse magnetic anisotropy component for the ribbon.

The maximum of the MI ratio for the ribbons coated with GO for 4 and 8 min, at the frequency range of 5-15 MHz, are presented in Figure 5-6 (a). We observed that the maximum MI ratio of the ribbons on which GO was deposited has increased. This increase is larger for the longer deposition time. A comparison between the MI ratio of the samples at $f = 10$ MHz can be seen in the inset of Figure 5-6 (b). The MI ratios for the bare ribbon, and the ribbons coated for 4 and 8 min with GO were 271 %, 281 % and 306 %, respectively. The MI is a highly surface sensitive due to the low skin depth of the ribbon for such measured frequencies. As GO is a well-known

Figure 5-6: a) Maximum of MI ratio versus frequency of ribbons coated with GO electrophoretically and by drop coating ribbon; the presented error bar at each point is $\pm 6\%$. The MI ratio increases with increasing frequency up to 10 MHz but then decreases when the frequency is further increased. Relative contributions of domain wall motion and magnetization rotation to the transverse permeability should be considered in interpreting this trend. The reduction in MI ratio at high frequencies is due to the presence of eddy currents that cause damping of domain wall displacements and only rotation of magnetic moments takes place. In turn the transverse magnetic permeability diminishes, and the MI ratio decreases and b) MI response of the samples at $f = 10$ MHz (inset shows maximum of MI ratio for ribbons coated with GO electrophoretically deposited for 4 and 8 min).

dielectric material, we can conclude that there is no current passing through it and therefore no change in the skin depth of the ribbon does occur. There are many reports on the surface modification of magnetic amorphous ribbons by coating⁶⁻¹² or mechanical polishing⁵⁵. All reports correlated this phenomenon to the closure of magnetic flux paths and reduced surface roughness. Also some reports have used graphene based materials and reported better performance of their sensor materials^{11,56}. In the case of our samples, the layer cannot diminish the magnetic field passing through the surface because it has a paramagnetic character^{57,58}. Therefore, unlike in cases where magnetic materials are applied as coating^{13,14} and MI increased due to diminishing stray fields, here we can't propose such a possibility for the MI increase. During the sample preparation for the FESEM measurement, it was observed that the GO coated by EPD was much more stable than the GO coated by drop coating. This may be the result of oxygen removal from the surface of the ribbon during the EPD and therefore better bonding of GO to the ribbon. Therefore, as another possibility for the origin of MI increase in EPD coated GO sample we may consider the stress on the domain structure of the ribbon due to GO bonding to the ribbon and changing its magnetization dynamics⁵⁹.

To indicate the role of the EPD method in the observed results we did MI experiments for ribbons drop coated with GO. We did not see any enhancements in the MI response in that case. We can mention the good surface coverage and strong bonding of GO on the surface of the ribbon using EPD^{60,61} and its effective impact on the closure of magnetic flux paths and induced stress on its surface. Several experiments were carried out to confirm the repeatability of these results.

Finally, we used FESEM microscopic images to better illustrate the microscopic origin of this effect. Images of ribbons EPD-coated with GO for 8 min and drop coated with GO layers are presented in Figure 5-7. As it can be seen, the electrophoretically coated GO layer (Figure 5-7 (a)) has a significantly smoother surface than the drop coated one (Figure 5-7 (b)). The well-ordered structure of GO flakes deposited by the EPD method has resulted in higher compactness and so a better surface coverage of the ribbon. Due to its anticorrosion properties^{62–64}, our results suggest that GO can be used for better performance and higher stability of MI sensors in different physical/chemical environmental conditions. Also, our results can open a pathway towards the development of GO based gas sensors. Even though the drop coated sample reduces the MI response, it can still be used as a higher vertical alignment of

Figure 5-7: FESEM images of ribbons coated with GO by a) 8 min EPD and b) drop coating. As can be seen, the electrophoretically coated GO layer has a significantly smoother surface than the drop coated one. The well-ordered structure of GO flakes deposited by the EPD method has resulted in higher compactness and so a better surface coverage of the ribbon.

surface features for sensing applications.

5.4 Conclusion

In conclusion, we believe that GO coated by electrophoretic deposition on the ribbons that are the active element of a magnetoimpedance-based sensor, allows for enhanced sensor functionality. The many interesting properties of GO such as being anticorrosive, biocompatible and having a high surface area, can open pathways towards the development of MI based sensors. We employed UV-visible and Raman spectroscopy, as well as AFM and FESEM measurements to determine the quality of the GO starting material and of the coated layer on the surface of a magnetic ribbon. The surface coverage and vertical alignment of the GO flakes have shown significant impact on the sensing response thus opening pathways for many applications.

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Chapter 6: Magnetoimpedance sensor based yttrium iron garnet particles coated with graphene*

Abstract

Graphene when combined with magnetic materials opens new possibilities for applications in electronic and sensor devices. In this chapter, we report on the synthesis of composites of graphene and yttrium iron garnet magnetic nanoparticle and on their magnetic properties. Two sets of samples with different yttrium iron garnet particle size were synthesized. The samples with smaller particles have higher saturation magnetization with super paramagnetic character. Microscopic analyses show that fine magnetic nanoparticles distributed uniformly on the graphene nanoplatelets. We propose that such magnetic layers can be used to shield the stray field generated on the surface of magnetic sensors and play a role as a magnetic lens to prevent the field emanating outside the body of a magnetic specimen. The (graphene nanoplatelets)/(yttrium iron garnet) composites were coated on a magnetic ribbon and proposed for application in magnetoimpedance sensors. We demonstrate that such planar magnetic flakes significantly enhance the magnetoimpedance response against external applied magnetic field. We discuss two possible scenarios for the interpretation of the results: (i) proximity induced magnetism in graphene and (ii) superparamagnetic characteristics of the sample with smaller particles. The suggested application can be further developed towards bio-sensing and magnetic shielding in different magnetic sensors and devices.

6.1 Introduction

Proximity-induced magnetism (PIM) is a process where a non-magnetic material acquires magnetization due to coupling with a magnetic film¹. The first report on magnetic proximity was in 1969 in superconductors². It was found that the superconducting transition temperature

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in a Pb/Pd/Fe structure decreased with decreasing thickness of Pd, indicating that the Pd layer became magnetized in contact with the Fe layer. Later, it was shown that Fe and Co ferromagnetic materials can induce magnetization into 4d and 5d elements such as Pd and Pt³⁻⁶. Very recently, groundbreaking work has revived the debate for applying wider windows of materials presenting PIM. It was observed that a graphene (Gr) layer transferred onto an insulating yttrium iron garnet (YIG) magnetic thin film exhibits a magnetic signature in the Hall effect measurement⁷. The striking observation is that the non-magnetic Gr layer becomes magnetized when in contact with a magnetic YIG thin film, formed as a YIG/Gr bilayer⁷. This observation has led to research interest in uncovering the PIM in two-dimensional materials⁸⁻²⁰.

Several studies suggest that the interface between the ferromagnetic and non-magnetic materials is a key point to observe the PIM²¹⁻²⁴. Not only has attention focused on thin film structures; but also on Gr plates that acquire ferromagnetism in the proximity of magnetic nanoparticles²⁵. However, the subject is in its infancy and requires further study. For example, the effect of magnetic nanoparticles size and distribution on the magnetization of such compositions has yet to be determined. In this chapter we describe a study where we combined Gr with YIG nanoparticles and also discuss the possible PIM in the Gr based on the results obtained when changing the YIG nanoparticle size. The planar shape of Gr with high surface to volume ratio, when decorated with magnetized nanoparticles, can be applied as magnetic shielding to absorb undesired magnetic field in different devices such as sensors. It is necessary to mention that such magnetic nanoparticles cover only a small portion of the Gr platelets' surface. Hence, together with other well-known Gr functionalities, magnetic Gr could be applied in biosensors and many other magnetic functional elements.

Here, we explain how we introduced a useful technological application of such magnetic graphene nanoplatelets. The magnetic property of such planar magnetic plates was employed to improve the sensing of the magnetoimpedance (MI) effect through their magnetic shielding ability. High sensitivity and facile technological requirements have resulted in the MI effect creating a fertile research field^{26,27}. As described in previous chapters, MI depends on frequency (f), electric resistivity (ρ) and s transverse magnetic permeability (μ_t)²⁸. The fundamental properties of ferromagnetic metals in the form of a wire, a ribbon or a thin film²⁹⁻³² and the

development of highly sensitive magnetic field sensors has increased interest in the MI effect^{29,30,33}. The electrical and magnetic environmental conditions profoundly affect MI behaviour. This phenomenon has two prospective applications, one is related to improving the magnetic field sensor performance, and the other to the environmental sensing ability. There are reports of magnetic field sensitivity enhancement by coating layers with different magnetization and conductivities on the surface of MI sensors^{32,33-38}. These layers can change the MI response mainly due to closure of the magnetic flux path at the surface of the MI elements.

Interestingly, the MI element maintains its surface sensitivity to probe the spin-orbit torque as the thin skin depth is sensitive to any changes at the surface.^{39,40} This was observed as a change in the MI response upon deposition of thin non-magnetic Pt³⁹, IrMn⁴⁰ layer or coating of vertically-oriented graphene oxide nanostructures³² on the ribbon surface.

Gr-based materials play an essential role in environmental detection owing to their stability in different conditions^{41,42}. Due to the uniform distribution of YIG nanoparticles on the surface of Gr, a completely magnetized plane is obtained here. Such a magnetized plane can be mounted on the surface of MI ribbon sensors. One can speculate that the MI sensor is affected by the magnetization of these planes, as a thick layer coated on the ribbon that acts as a shielding medium. Such a shielding layer prevents magnetic flux leakage from the ribbon surface. The presented application shows that Gr when composited with magnetic nanoparticles can be important for magnetic field shielding applications.

6.2 Experimental

6.2.1 Materials and characterization

For the study described in this chapter, Gr (N002-PDR, xy dimensions of about 7μm, thickness 50-100nm) was supplied by Angstrom Materials Inc. Ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), yttrium nitrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), citric acid, ethylene glycol, dimethylformamide were all from Merck (99.9% pure) to prepare YIG magnetic nanoparticles. Transmission electron microscopy (TEM) was carried out with a LEO 906, Zeiss, 100KV, Germany. A high-resolution JEOL 2800 S/TEM system was used for performing transmission electron microscopy (HRTEM). X-ray diffraction

(XRD) was performed using a STADI STOE diffractometer with $\text{CuK}\alpha$ ($\lambda=1.54 \text{ \AA}$) at angles (2θ) ranging from 10 to 80° .

6.2.2 Preparation of yttrium iron garnet magnetic nanoparticles

Following our previous work on the preparation of magnetic nanoparticles⁴³⁻⁴⁷, YIG particles were synthesized by citrate nitrate and modified co-precipitation methods, as two different sets of samples. The YIG sample prepared by citrate nitrate method is called YIG-1 and that prepared by modified co-precipitation method is called YIG-2. For the citrate nitrate synthesis, we dissolved the required amount of the metal nitrates in the stoichiometric ratio of Y: Fe = 3:5 in distilled water. Citric acid was then added into the prepared aqueous solution to pH=1. The solution was heated to dry and then annealed in ambient air at a temperature of 800°C with a heating rate of $10^\circ\text{C}/\text{min}$ for 2 h. For the synthesis of YIG magnetic nanoparticles by modified co-precipitation method, we mixed the required amount of Y and Fe nitrates in the stoichiometric ratio of Y: Fe = 3:5 in dimethylformamide to form a metal-organic solution. Ethylene glycol was then added into the prepared metal-organic solution. A small amount of ammonia was added to the solution to adjust the pH value to about 10.5. During the procedure, the precipitate was continuously stirred using a magnetic agitator. Then the precipitate was collected and washed with distilled water and ethanol. The obtained precipitate was dissolved in distilled water with a small amount of citric acid to reach pH=2. Finally, the solution precursor was heated to dry and annealed to 700°C for 2 h. Details of the modified co-precipitation method are well-discussed in our recent work⁴⁶.

6.2.3 Preparing graphene on yttrium iron garnet

YIG powder from each set of samples described above were added to 35 ml ethanol followed by probe sonication for 30 min. Then Gr was added to the mixture followed by additional sonication for 30 min; the weight ratio of Gr to YIG is chosen as 1:0.5. After the ultrasonic treatment, the solution was heated inside an oven at 75°C for 12 h to dry the sample (done by Hosseinzadeh, S.).

6.2.4 Magnetoimpedance setup

The conventional melt-spinning technique (explained in chapter 2) was used to fabricate $\text{Co}_{68.15}\text{Fe}_{4.35}\text{Si}_{12.5}\text{B}_{15}$ magnetic ribbons with 0.8 mm width, 40.0 mm length and about 28 μm thickness. The impedance measurement was done using the four-point probe method. The details of the MI measurement setup are presented in chapter 2. An ac current with a constant amplitude of 30 mA was applied for the MI measurements. The oscilloscope measurement resolution gives a $\pm 6\%$ error in the observed MI ratio.

6.3 Results and discussion

6.3.1 Characteristics of yttrium iron garnet

Figure 6-1 shows TEM images of YIG particles prepared by citrate nitrate, YIG-1, and modified co-precipitation, YIG-2, methods. It can be seen in Figure 6-1a that the YIG-1 particles are aggregated and exhibit irregular shapes. Figure 6-1b illustrates TEM images of YIG-2 particles, showing a moderate particle clustering. In the recently published work,⁴⁶ dynamic light

Figure 6-1: a) TEM image of YIG particles prepared by the citrate nitrate method, YIG-1. The particles are aggregated and exhibit irregular shapes. b) TEM of YIG particles synthesized by modified co-precipitation method, YIG-2, showing moderate clustering of particles and some small aggregation. From dynamic light scattering measurement, a size distribution from 6 to 26 nm with a maximum at 17 nm was deduced for the YIG-2 particles while for the YIG-1 particles a much larger size (>100 nm) was found, which may be due to larger aggregation on this sample.⁴⁶

scattering has been used to gain size distribution of the particles. A size distribution from 6 to 26 nm with a maximum at 17 nm is observed for the YIG-1 particles, while for the YIG-2 particles a much larger size is observed (>100 nm) which may be due to larger aggregation in this sample.

Figure 6-2a shows the XRD pattern of YIG prepared samples at room temperature. YIG-1 and YIG-2 samples contain YIG phase having main diffraction peaks of (400), (420), (422), (444), (640) and (642) (JCPDS card no. 43-0507) and no trace of intermediate phases. From the Scherer's equation, the mean crystallite sizes of YIG-1 and YIG-2 samples were estimated to be about 38 and 17 nm, respectively. Also, the XRD peaks are very sharp which may be due to presence of some big crystal sizes in the sample.

Figure 6-2b shows the room temperature magnetization loop measured by vibrating-sample magnetometer (VSM) for both samples. The saturation magnetization (M_s) of YIG-1 and YIG-2 samples is seen to be ~23.23 emu/g. The coercivity (H_c) and remanent magnetization (M_r) of

Figure 6-2: a) XRD patterns of the YIG samples prepared via citrate nitrate, YIG-1, and modified co-precipitation, YIG-2, methods. The peaks indicate formation of the YIG phase (JCPDS card no. 43-0507). The mean crystallite sizes of YIG-1 and YIG-2 were estimated to be about 38 and 17 nm, respectively. b) The VSM hysteresis loops of the same samples (inset shows their coercivity). The saturation magnetization of YIG-1 and YIG-2 samples is seen to be ~23.23 emu/g. The coercivity (H_c) and remanent magnetization (M_r) of YIG-1 sample are 30.2 Oe, and 9.94 emu/g and those of YIG-2 sample are 30.1 Oe and 4.52 emu/g, respectively.

YIG-1 sample are 30.2 Oe, and 9.94 emu/g and those of YIG-2 sample are 30.1 Oe and 4.52 emu/g, respectively.

6.3.2 Characteristics of graphene nanoparticle-yttrium iron garnet composites

Figure 6-3a, b shows the TEM and HR-TEM of the Gr decorated with two different YIG samples (Gr/YIG-1 and Gr/YIG-2). As can be seen, the flake-like shapes of Gr are observed to be embedded with YIG particles. A good distribution of YIG particles can be seen in contact with the Gr in Gr/YIG-2 sample, and there is a significant portion of the YIG attached to the surface of the Gr contrary to Gr/YIG-1 sample. It is important to note that higher uniformity can be effective on the observed MI results and magnetic field shielding. Figure 6-3c and Figure 6-3d show a selected area electron diffraction (SAED) pattern and the lattice fringe of the Gr/YIG-2 sample. The SAED shows two diffraction rings with d-spacing of 0.34 nm ($2\theta = 26^\circ$) and 0.21 nm ($2\theta = 44^\circ$) that are characteristic of Gr (002) and (010) spacing⁴⁹, whereas the XRD result confirms its graphite nature. The distinct bright diffraction spots of YIG are also observed in this SAED pattern⁷. The fringe spacing is measured to be 0.27 nm which corresponds to the (420) crystallographic plane of the YIG⁷ and another d-spacing obtained from the lattice fringe was 0.34 nm which was consistent with the d-spacing value of (002) crystallographic planes of the Gr. The element distribution of the Gr/YIG-2 was analysed by EDS over the inset (rectangular region) of Figure 6-3b. The obtained distributions of different elements are shown in Figure 6-3e, which indicates the present of Y, Fe, and O on the surface of the Gr and the structural stability of the YIG particles was further confirmed.

XRD patterns of Gr and Gr/YIG-2 are presented in Figure 6-4a. The (002) plane at $2\theta = 25^\circ$ attributed to Gr and the main peaks of YIG particles are observed too. Also, the XRD profile of

Figure 6-3: TEM images of the Gr/YIG composite with YIG prepared via a) citrate-nitrate, Gr/YIG-1, and b) modified co-precipitation, Gr/YIG-2, methods. In both cases, the flake-like shapes of Gr are observed to be embedded with YIG particles uniformly. C) selected area electron diffraction and d) lattice fringes of the Gr/YIG-2 sample. e) Corresponding element mapping images of an arbitrary point of the Gr/YIG-2 composite.

the Gr/YIG indicates the formation of composites having main diffraction YIG peaks of (400), (420), (422), (444), (640) and (642) which can be indexed to JCPDS card no. 43-0507 properly dispersed in Gr matrix. The other less noticeable peak of the Gr around $2\theta = 42^\circ$ is interrelated to the (100)/(101) plane. It is worth mentioning that the peaks related to YIG on Gr have lower intensity which might indicate that less large YIG particles are attach to the Gr.

Figure 6-4b shows the hysteresis loops recorded at room temperature for both samples prepared by the citrate nitrate and the modified co-precipitation methods. The M_s of samples prepared with a mass ratio of 1:0.5 for the Gr/YIG-1 and Gr/YIG-2 are 2.25 emu/g and 7.26 emu/g, respectively. The magnetic properties of compositions can be tuned by making changes in the proportion of the YIG to Gr owing to the fact that magnetization may decrease by addition of the Gr, as a non-magnetic portion³⁸.

Two possible mechanisms can be considered in interpretation of the observed differences in VSM results: (i) firstly, due to better distribution of the smaller YIG particles on the surface of Gr a better proximity is gained. Therefore, PIM does occur in the sample with smaller YIG particles and results in a higher magnetization. (ii) Secondly, mainly smaller YIG particles can attach to

Figure 6-4: a) XRD pattern of the Gr and Gr/YIG-2 sample (broad peak between 20-30 degrees is related to Gr and b) the VSM hysteresis loops of Gr/YIG samples (inset shows the zoom-in of the plot at the origin). The composite sample with smaller YIG particles (Gr/YIG-2) shows super paramagnetic properties, which is more desired for MI sensor applications due to the higher permeability.

the Gr. Therefore, in the case of smaller YIG particles, a higher weight ratio of YIG can be obtained and result in higher magnetization of this sample. Also, the composite sample with smaller YIG particles shows super paramagnetic properties, which is more desired for MI sensor applications due to the higher permeability.

6.3.3 Magnetoimpedance sensing of the graphene-yttrium iron garnet composites

To understand the impact of Gr/YIG on the MI response of a ribbon, the MI effect was measured at different frequencies of 2.5, 5, 7.5, 10, 12.5, and 15 MHz. The magnetic field was applied up to 120 Oe during the MI measurements. The MI ratio can be defined as

$$MI\% = \frac{Z(H) - Z(H_{max})}{Z(H_{max})} \times 100 \quad (2)$$

Figure 6-5: Magnetoimpedance response of a) bare ribbon and ribbons drop coated by b) Gr-YIG-1 and c) Gr-YIG-1; d) the maximum in MI% for all three samples at all frequencies (the presented error bar at each point is $\pm 6\%$). The MI ratio increases by increasing the frequency up to 10 MHz and then decreases by further increasing the frequency. The reduction of the MI ratio at high frequencies is due to the presence of eddy currents that causes damping of domain wall displacements and only rotation of magnetic moments takes place. In turn, the transverse magnetic permeability diminishes and the MI ratio decreases.

where Z refers to the impedance as a function of an external field (H) and $H_{\max}$ is the maximum field applied to the samples in the MI measurement. MI response for the bare ribbon and the ribbons drop coated by Gr/YIG-1 and Gr/YIG-2 are presented in Figure 6-5. Field dependent MI ratio of the bare ribbon at different frequencies can be seen in the panel (a) of Figure 6-5. There is a peak at low external applied magnetic fields ($|H| \approx 2$ Oe) at both directions of applied magnetic field (to better see the peak, see Figure 6-6a for a zoom in picture) because of transverse alignment of magnetic anisotropy of the ribbon against applied magnetic field

direction⁵⁰. Also, this peak appears for the ribbon samples drop coated by the Gr/YIG composite. This means that the coating did not change the transverse anisotropy of the ribbon.

The maximum MI ratio occurs at a frequency of 10 MHz. Relative contributions of domain wall motion and magnetization rotation to the transverse permeability should be considered in interpreting this trend²⁹. The MI ratio increases by increasing the frequency up to 10 MHz and then decreases by further increasing the frequency. The reduction of MI ratio at high frequencies is due to the presence of eddy currents that causes damping of domain wall displacements and only rotation of magnetic moments takes place. In turn, the transverse magnetic permeability diminishes and the MI ratio decreases^{29,51}. The maximum in MI ratio for a bare ribbon and ribbons coated with Gr/YIG composites in the frequency range 2.5-15 MHz are presented in Figure 6-5d. We observed that the increase in the maximum MI ratio for the ribbons covered by Gr/YIG-2 is more pronounced than that of the ribbons covered with Gr/YIG-1.

A comparison between the MI ratio of the samples at $f = 15$ MHz can be seen in Figure 6-6a. The MI ratio for the ribbons with and without Gr/YIG coating are 254 % (bare), 278 % (Ribbon with

Figure 6-6: a) Magnetoimpedance ratio of the Gr/YIG samples at $f = 15$ MHz versus frequency. b) Maximum in MI response and field sensitivity of the samples at $f = 15$ MHz (the presented error bar at each point is ± 6 % and the sensitivity error bar is 0.2 Oe^{-1}). A reduction of the fringe fields of the ribbon surface by coating with the Gr/YIG composite causes a significant increase in the MI%. This is more pronounced for the Gr/YIG-2 composite, which due to its higher magnetization and permeability is able to significantly reduce the stray field at the ribbon surface.

Gr/YIG-1), and 296 % (Ribbon with Gr/YIG-2), respectively. It is worth mentioning that the maximum MI% for Gr/YIG-2 coated ribbon appears at 12.5 MHz. As discussed before, the reduction of MI% at high frequencies is due to the presence of eddy currents that cause damping of domain wall displacements and hence a reduction of the μ_r . The impedance for the bare ribbon and the ribbon coated by the Gr/YIG-1 composite at $H=0$ Oe and $f=15$ MHz is about $14.1 \pm 0.1 \Omega$. While for the ribbon coated with the Gr/YIG-2 composite, the impedance is about $13.7 \pm 0.1 \Omega$. In turn, a reduction of the MI ratio occurs at high frequencies (lower skin depth and higher current density). Other reports on the surface modification of magnetic ribbons by coating with various materials^{35,36,38,39,52} report the enhancement of MI to the point of closure of the magnetic flux path and reduction in surface roughness stray field.

Based on the two aforementioned reasons for the difference in the VSM results of the two samples the following phenomena can happen in the MI response enhancement. In the case of the PIM in the Gr we have a fully magnetized plane, which covers large part of the ribbon surface and therefore the MI increases more in the case of the sample with smaller YIG particles. In the case we assume that Gr is not magnetized and only YIG particles play the main role, we should refer to the higher permeability of the sample with smaller YIG particles, which is more desired for MI ratio enhancement.

The MI field sensitivity can be defined as $\eta = d(\Delta Z/Z(\%))/d(H)$. As can be seen in Figure 6-6b, the sensitivity is increased in the presence of the composite layer on the ribbon due to the same reasons explained above. In the following, we describe using a MI sensor as a probe for detection of a possible PIM in a Gr composite containing YIG particles.

6.3.4 Magnetoimpedance-based detection of proximity-induced magnetism in graphene nanoplates

The MI is a surface sensitive effect due to the small skin depth of the ribbon. This property is key to the high surface functionality of MI sensors. Figure 6-7 shows a schematic of the structural conditions of the MI sensor coated with Gr/YIG composites. There are random fringe fields that emanate from the surface of amorphous ribbons, which is more pronounced before

saturation. As schematically presented in Figure 6-7a, stray magnetic flux is diminished in a Gr/YIG-2 composite layer because their whole plane is magnetized. The attenuation of the flux density of the ribbon results from a shielding effect of the ferromagnetic Gr/YIG composite, which acts as a magnetic short circuit and drives the flux lines directly in the plane. In Figure 6-7b, a weaker magnetized composite layer on the surface of the ribbon can not shield all of the magnetic field components of the surface ribbon. Both types of Gr/YIG composites play this role, and their MI is enhanced compared to the bare ribbon, while the planar Gr/YIG-2 magnetized sample has a more pronounced impact. In the case of PIM in the sample with higher MI ratio, the MI sensor acted as a PIM detection probe.

In comparison to methods like X-ray magnetic circular dichroism, magneto-optical Kerr effect, anomalous Hall effect,⁵³ which provide more direct proof of the magnetic proximity effect, our method presents an alternative measurement tool, which can be applied if calibrated properly.

Figure 6-7: Schematic of the structure of the surface coverage of the MI sensor and the closure of the magnetic flux path when the ribbon is coated with a) Gr/YIG-2 and b) Gr/YIG-1. In the case of ribbon coated with Gr/YIG-2, the undesired surface magnetic flux is suppressed more because the whole surface plane is magnetized. Both types of Gr/YIG composites play this role, and the MI is enhanced compared to the bare ribbon but for a) the impact is more pronounced.

6.4 Conclusion

In summary, we have observed a MI enhancement when coating the ribbon that acts as active element in a MI sensor with a composite made of graphene and magnetic nanoparticles. A smaller size of the magnetic nanoparticles resulted in a higher MI enhancement. Smaller particles can show superparamagnetic properties and be more effective on the MI response through their high permeability. It is also possible that a proximity-induced magnetism occurs in the composite sample and since smaller YIG particles make better contact and are better distributed on the graphene, the effect is stronger in this case. This should result in magnetized graphene, which can shield the magnetic flux at the surface of the MI element. The results of the MI measurements reveal a significant improvement in sensing performance and promise application in high sensitive magnetic field sensors.

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Chapter 7: MoS₂ based materials with rectified I-V behaviour*

Abstract

Unidirectional current flow is at the heart of modern electronics, which has been conceived by making p-n junctions or Schottky barriers between different kinds of materials. Within such elements, however, synthesis of thin film lateral heterostructures has so far remained challenging. In this chapter we report on a one-step simple synthesis of lateral heterostructures that are p-type at one side and n-type at the other using bipolar electrodeposition; specifically Molybdenum oxide and sulfides with gradients of oxygen and sulfur were deposited on a metallic substrate and a lateral heterostructure was achieved with electrical properties that change from p- to n-type semiconductor by moving in the plane of the layer. This effect is observed due to an increase in MoO₂ and reduction of MoS_x from one side of the structure to the other side. Finally, when the layer was transferred onto a dielectric substrate, the current-voltage (I-V) characteristic of the layer was found to show a rectifying behaviour with a low threshold of 0.45 V and a rectification of about 10 at relatively low applied voltages.

7.1 Introduction

Semiconducting lateral heterostructure thin films, one of the most important electronic elements in modern technology, have been intensively investigated in the last few years due to their wide applications in rectifiers, photodetectors and field effect transistors.¹⁻⁶ Between the various methods of fabricating semiconducting lateral heterostructures, chemical vapor deposition (CVD) has been the most common and practical method because of its success in producing semiconductor materials such as transition metal dichalcogenide.⁷⁻¹¹ The drawbacks of CVD preparation of lateral heterostructures include, in most cases, two-step growth and

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reliance on complicated CVD instrument designs at relatively high working temperatures. Other methods include selective chemical,^{12–15} thermal¹⁶ or plasma¹⁷ treatments have successfully produced lateral p-n junctions from one specified kind of material. These methods rely on multistep fabrication processes with limited applicability for different kinds of materials. Furthermore, the small size of the lateral heterostructures fabricated via the above-mentioned methods hinders successful device fabrication.^{10,18} Therefore, the field is open for the development of methods for semiconductive lateral heterostructure growth.

Here, we report a simple one-step fabrication of semiconductive lateral heterojunctions using bipolar electrodeposition (BPE) technique. BPE involves placing a metallic electrode, called a bipolar electrode, in an electrolyte solution with an electric field applied to the solution. The electric field is produced using two feeder electrodes connected to an external power supply, which in turn causes an Ohmic drop in the solution. Therefore, an interfacial potential polarization appears between the metallic substrate and the solution that can promote electrochemical reactions at the edges of the bipolar electrode.^{19–21} The BPE has shown its capability for designing of chemical composition gradients over conductive substrates.^{22–28} In fact, due to applications of new materials and structures in modern technology, BPE has seen a renewal and offers many opportunities in materials science. Gradient composition polymers and metallic heterostructures are examples of bipolarly prepared materials.^{22–24} Even semiconductors have been successfully deposited using BPE.²⁵ Some other examples include fabrication of Schottky contact of semiconductor to metal,²⁶ fabrication of MoWS_x with gradients of Mo and W ($\text{Mo}_x\text{W}_{1-x}\text{S}_2$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_3$) for catalytic activities (hydrogen evolution)²⁷ and also fabrication of materials without gradient (MoS_x) for hydrogen evolution reaction application.²⁸

In this chapter, for the first time, we suggest BPE for producing semiconductive lateral heterostructures with rectified current-voltage (I-V) characteristics. Our method involves fast growth of gradients of molybdenum sulfides and oxides along a conductive substrate, by changing both oxygen and sulfur content, using very low-cost equipment at room temperature. Type I and type II band alignments between the semiconductive lateral heterostructures were found to be formed and the band gap energy resulted modulated along the gradient of the

composition. Because of the vast number of groups of materials capable of being fabricated via electrodeposition, it is concluded that BPE can open a pathway towards the development of lateral semiconductive heterojunctions with a high diversity of materials.

7.2 Results and Discussion

Figure 7-1a represents a schematic of the BPE setup used for the research reported in this chapter. A steel electrode with length, width and height of 30, 15 and 0.5 mm is put at the bottom of a petri dish as the bipolar electrode. Two platinized silicon pieces with a width of 10 mm are used to produce a gradient of electrochemical potential. A solution containing MoS_4^{2-} ions is used to carry out the BPE experiments. For preparation of the solution, similarly to our previous work²⁹, we used an aqueous bath containing 0.39 M $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and 0.88 M $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ with pH adjusted to 7 by addition of sulfuric acid. Fresh solutions were used in the bipolar electrodeposition of the heterostructures. Solutions containing MoS_4^{2-} have usually been used in electrodeposition of MoS_2 but result in oxidized molybdenum. The applied voltage during the electrodeposition is the parameter, which controls the percentage of oxygen and sulfur in the final product.^[24,25] Therefore, because the steel substrate is aligned with the gradient of electrochemical potential, it experiences different electrochemical applied voltages on different points of its surface. The BPE performed during 60 s by applying 10 V to the platinized electrodes. A simulation profile of the potential distribution in the steel is depicted in Figure 7-1b when a potential difference of 10 V is applied between the two platinized electrodes at a distance of ~3 cm. Therefore, we expect different compositions of the deposited layer by moving from the edge of the steel substrate towards its centre. Figure 7-1d represents the Raman scattering of 6 different points (named p1, p2, p3, p4, p5, p6) along the gradient of applied potential. Figure 7-1c is the optical microscopic image of the sample and the points where Raman was measured. The Raman spectrum of the p1 and p2 points indicate formation of MoS_x with two broad peaks at about 298 cm^{-1} (Mo–S vibration mode) and 446 cm^{-1} (Mo–S–Mo vibration mode).^{31,32} By moving towards p6, peaks related to MoS_2 , MoO_2 and MoO_3 appear in the spectrum. In p3, p4, p5 and p6 there is a peak at 404 cm^{-1} related to MoS_2 (A_{1g} vibration mode).^{33,34} The low intensity of this peak is due to the lower Raman intensity of molybdenum sulfide compared to molybdenum oxides. Also the peaks at 722 cm^{-1} (metallic MoO_2), 354 cm^{-1}

Figure 7-1: a) Schematic of the BPE condition, by increasing the voltage on the surface of the bipolar electrode higher sulfur reduction can occur; b) the simulation of the potential distribution over the bipolar electrode; c) the optical microscopic image of the fabricated heterostructure by BPE shows a colour evolution when moving from p1 to p6. This results from an evolution in thickness and composition of the layer (the scale bar shows 4 mm). d) The Raman scattering of 6 different points in the layer, marked in panel c, indicates that at higher electrochemical voltages, more sulfur reduction occurs and the oxygen content increases in the structure.

(A_g (O-Mo) vibration mode) and 483 cm^{-1} (metallic MoO_2) indicate that MoO_2 is formed at points p3, p4, p5 and p6.³⁵ A peak related to MoO_3 (A_{1g} vibration mode) appears with highest intensity at 821 cm^{-1} at points p5 and p6.³⁶ The similarity of the Raman spectra for p1 to p2, p3 to p4 and p5 to p6 indicates that lateral heterostructures with widths for each compound in the order of millimeters are formed.

Finally, the Raman scattering at 6 different points indicates that at higher electrochemical voltages, more sulfur reduction occurs and the oxygen content increases in the structure. In addition, we note that the higher electrochemical potential applied at one side (p1) of the steel substrate results in higher current density used for the growth. Therefore, the thickness of the layer increases by moving from p1 to p6. This is confirmed by the fact that the optical microscopy image shows a colour evolution from p1 to p6. In electrodeposition, no distinct threshold can be determined for electrochemical reactions, and hence it can be concluded that there is no sharp interface formed in the lateral heterostructures. This characteristic may be considered as a drawback of the BPE fabrication of lateral heterostructures, as sharp interfaces are desirable for sensitive photodetectors.³⁷

For a better understanding of the mechanism of growth at different points of the layer, we performed electrodeposition on the steel substrates using different applied voltages of 1 and 3 V with a 1×2 cm steel as cathode and a 1×2 cm platinized silicon as anode, and probed the corresponding Raman scattering response (see Figure 7-2). To see the electrochemical reactions occurring in the cell at different applied voltages we measured the C-V curves; Figure 7-2a

Figure 7-2: a) C-V curve during electrodeposition in a cell with steel as cathode and Pt as anode. The peak appearing at about 1.5 V is related to the reduction of MoS_4^{2-} . Therefore the layer resulting from electrodeposition at voltages lower than 1.5 V must have a high sulfur content. The increase in the current by sweeping the voltage to higher voltage regions is related to the replacement of sulfur by oxygen, which consumes more electrons and so results in higher electrical current. (b) Raman scattering of the layers electrodeposited at 1 and 3 V and of the heterostructure at points p1 and p4. The observed similarities between the Raman spectra support the growth mechanism of lateral heterostructures by BPE and confirm the relation between voltage and composition.

shows an example of such a C-V measured at a scan rate of 10 mV/s. The peak appearing at about 1.5 V is related to the reduction of MoS_4^{2-} . Therefore the layer resulting from electrodeposition at voltages lower than 1.5 V must have a high sulfur content. The increase in the current by sweeping the voltage to higher voltage regions is related to the replacement of sulfur by oxygen, which consumes more electrons and hence results in higher electrical current. Figure 7-2b compares the Raman spectra for layers electrodeposited on steel substrate at applied voltages 1 and 3 V with those collected at points p1 and p4 of the heterostructure. One observes that the spectrum of the layer electrodeposited at 1 V is similar to that of p1 and that of the layer electrodeposited at 3 V is similar to that of p4. This finding supports the growth mechanism for the lateral heterostructures by BPE and confirms the relation between voltage and composition.

scanning electron microscopy (SEM) images of the lateral heterostructures coated on the steel substrate, taken with a MIRA TESCAN instrument (MIRA2 TESCAN), are presented in Figure 7-3(a-h). There are many rolled up flakes at the outer most part of the lateral heterostructure, which increase when approaching p6. We suggest that these rolled up flakes are related to

Figure 7-3: SEM images of the lateral heterostructures when moving from point p6 to p1 (a-h). There are many rolled up flakes at the outermost part of the lateral heterostructure, which increase when approaching p6. These rolled up flakes are most probably related to oxygenated compounds. Also, upon inspection of panel f it can be seen that the interfaces are not very sharp and the morphology changes gradually.

oxygenated compounds. It has been reported previously that rolled up MoS_2 can be fabricated by reduction of sulfur.³⁸ The surface of the heterostructures becomes smoother when moving towards p1. Also, upon inspection of panel f it can be seen that the interfaces are not very sharp and the morphology changes gradually.

We repeated the experiments for a FTO coated glass substrate and Raman spectra again showed the same trend in oxygen and sulfur evolution. The optical microscope image and a Raman spectrum of the layer coated on FTO can be seen in Figure 7-4. Two different points, p1 and p2, were chosen to examine Raman characteristics (Figure 7-4a). At p1 of the FTO sample, the presence of MoS_2 , MoO_2 and MoO_3 was observed. Measurements at p2 show the formation of pure MoO_3 (Figure 7-4b). Raman spectra of the substrate are also shown in the plot. The cracks appearing in the optical microscopic image were also observed in our previous work when using FTO as substrate in electrodeposition from solution.²⁹

To study the electronic properties of different points of the sample, such as the energy gap and the band alignments, scanning tunneling spectroscopy (STS) was used. Scanning tunneling

Figure 7-4: a) Optical microscopy image of the heterostructure coated onto FTO (the scale bar shows 0.5 mm). Similar cracks were also observed in our previous work when using FTO as substrate in electrodeposition from solution.²⁹ b) Raman spectra of different points of the heterostructure on FTO (the points are indicated in panel a). At p1 the presence of MoS_2 , MoO_2 and MoO_3 was observed. Measurements at p2 show the formation of pure MoO_3 .

spectroscopy (STS) measurements were performed using a NAMA SS2 scanning tunneling microscope (STM) (done by Hosseini, S. A.). An error of 0.1 eV for the obtained band gaps is determined for this device by multiple measurements. In this method, the ground is connected to the steel substrate and a STM tip approaches the point under it and collects the tunneling current (Figure 7-5a). Assuming that the density of states of the approaching tip is constant, the tunneling current is evaluated by summing over all relevant states:

$$I \propto \int_0^{eV} \rho_s(E_F - eV + \varepsilon) d\varepsilon$$

where ρ_s represents the density of states (DOS) of the sample, E_F the energy at the Fermi level, eV the voltage applied to the tip and ε energy parameter with finite value. Differentiation dI/dV determines the energy dependence of density of states:

$$\frac{dI}{dV} \propto \rho_s(E_F - eV)$$

The normalized dI/dV by I/V can give the DOS at the measured point. Therefore, for discussing

Figure 7-5: a) Schematic of the STS measurement of different points of the heterostructure. In this method, the ground is connected to the steel substrate and a STM tip approaches the point under it and collects the tunneling current. b) STS spectrum at different points with the band gaps indicated by the red and green markers. c) Band gap energies at the different locations. In the heterostructures produced it is possible to see p-n and n-n lateral contacts. The error bar for E_g is 0.1 eV.

energy gaps at different points, the DOS (normalized dI/dV by I/V) for points p2 to p6 is presented in Figure 7-5b. From the DOS plot, we could locate conduction band (CB) and valence band (VB) edges where the current starts to increase. The band gap, valence band and conduction band energies (E_g , E_v , and E_c) are presented in Table 8.1. The edges were obtained with respect to the Fermi energy (E_F) of the respective point, which is considered to be aligned to 0 V. The E_g of all the points is plotted in Figure 7-5c, which shows that E_g becomes smaller when moving from p2 to p6. At p2 MoS_x shows a p-type semiconductor nature ($E_g = 2.8$ eV), since the VB edge was closer to its Fermi energy. Points p3 and p4 with the $\text{MoS}_2/\text{MoO}_2$ show n-type semiconductor characteristics with $E_g = 2.65$ eV and 2.3 eV, respectively, with the CB edge observed closer to the Fermi energy. At p5 and p6, n-type semiconductor behaviour is observed, with reduced E_g of 1.65 eV and 1.50 eV, respectively. This decrease in the E_g can be a result of the increase in MoO_2 metal^{39–41}. In the heterostructures produced it is possible to see p-n and n-n lateral contacts. This high tunability of the conductivity of the layer fabricated by BPE is an advantage worth developing in further experiments through controlling applied voltage, distance and size of the electrodes as these parameters have been known to be highly influential in the growth process.⁴²

Table 7-1. Energy of the gap (E_g), valence (E_v), and conduction (E_c) bands of different points of the heterostructure.

Points	E_v (eV)	E_c (eV)	E_g (eV)	Type
p2	1.2	1.6	2.8	p-type semiconductor
p3	1.25	1.4	2.65	p-type semiconductor
p4	1.2	1.1	2.3	n-type semiconductor
p5	0.85	0.8	1.65	n-type semiconductor
p6	1	0.5	1.50	n-type semiconductor

Figure 7-6: a) a heterostructure which was grown on a Pt substrate was used for the I-V measurements. The I-V curve of the transferred heterostructure (the inset shows the transfer steps) and b) the band alignments related to different points along the gradient of composition. In type I band alignment, the band gap of one of the semiconductor with smaller gap is under the band gap of other semiconductor. In type II band alignment, the conduction band of the semiconductor with smaller band gap material might lie above that of the larger band gap material, or its valence band might lie below that of the larger gap material. This infers that the rectifying characteristic appeared as a result of the heterojunctions between different parts of the layer itself. It is not possible to determine the contribution of each interface in the resulting rectified I-V curve.

Tunneling current and correspondingly the DOS determined through STS can be utilized as a powerful method to determine band edges and types of band alignments in lateral heterostructures.^{43,44} Using the band energies presented in Table 1, the band alignments corresponding to the points p2 to p6 are plotted in Figure 7-6b. This plot shows that band alignments of type I and type II are possible in the heterostructure. In type I band alignment, the band gap of the semiconductor with smaller gap is under the band gap of another semiconductor. In type II band alignment, the conduction band of the semiconductor with smaller band gap material might lie above that of the larger band gap material, or its valence band might lie below that of the larger gap material. Type II band alignment is observed between p2 and p3 and type I band alignment is formed between other points, e.g. p1 and p2, etc. Therefore, rectification is expected to be observed in the I-V characterization of the lateral heterostructure.

Figure 7-7: I-V curve of the lateral heterostructure; a rectifying behavior can clearly be discerned - the threshold voltage is found to be about 0.45 V. Inset shows the current log-scale presentation.

For the I-V measurements of grown heterostructure by BPE we used a Pt substrate because of the easy separation of the heterostructure from the Pt substrate. The I-V plot of the transferred lateral heterostructure is presented in Figure 7-6a. For I-V measurements, the layer was separated from the substrate using a procedure similar to the scotch tape method. Here we put a tape (Scotch® Magic™) in touch with the grown layer and pressed it gently onto the layer for about 30 s, then we peeled the tape off slowly (in ~10 s). The layer attached to the tape was used directly for the I-V measurement because separation from the tape would have damaged the layer. Also, for the I-V measurements of the transferred lateral heterojunction, a Keithley source (model 2450) was used in two-probe mode. The I-V plot shows a rectifying behaviour with a ratio of about 10 at relatively low voltage limit of -0.6 to +0.6 V. The characteristic curve exhibits a good rectification response, with a threshold voltage of about 0.45 V under forward bias (Figure 7-7). This rectifying behaviour raises a question about the nature of the contacts and their effect on the resulting I-V curve (silver paste was used as electrical contacts). In order to address this, we should mention the direction of applied voltage (inset of Figure 7-6a) when measuring the I-V curve and the direction of the rectification. This infers that the rectifying characteristic in Figure 7-6a appeared truly as a result of the heterojunctions between different

parts of the layer itself. In addition, we cannot determine the contribution of each interface in the resulting rectified I-V curve. The threshold voltage of the I-V curve of the lateral heterostructure was found to be about 0.45 V (Figure 7-7). The inset in this figure shows the log scale plot of the I-V curve.

7.3 Conclusion

In summary, bipolar electrodeposition was successfully applied for fabrication of lateral heterostructures made of molybdenum sulfides and oxides with rectifying I-V curve characteristics. Scanning tunnelling spectroscopy showed that the band gap decreases with increasing the oxygenated elements and reducing of sulfidic elements. Semiconductive lateral p-n and n-n junctions with band alignments of type I and type II were formed in the heterostructure. A rectification of 10 was observed at low voltage limits with a threshold of 0.45 V in the I-V curve. We performed similar experiments on platinum, aluminium, graphite and gold substrates and similar results were observed (not shown). It is worth mentioning, that the Raman spectra confirm that this method can be applied for the fabrication of lateral multi-junctions that are attractive from both fundamental and technological perspectives.⁴⁵ Because of the applicability of the electrodeposition technique to a large number of metallic and semiconductive materials, BPE of metallic and semiconductive lateral heterostructures could potentially open a pathway to fabrication of future electronic devices.

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Chapter 8: MoS₂ based materials for memristor

applications*

Abstract

Simple fabrication of materials with superior memristive behaviour is a key aspect of developing functional memristor devices. Partially oxidized MoS₂ thin layers have been one of the most attractive candidates due to their promising memristive characteristics. However, their fabrication involves complicated multi-step methods. Here, we fabricated a thin film composed of MoS₂, MoO₂ and MoO₃ elements with distinguishable memristive behaviour through electrodeposition. Both electrochemical metallization and valence change memristive responses were observed with different top electrodes. When an active Ag top electrode was used, the device showed electrochemical metallization memristive behaviour with low threshold voltages of ~ 0.1 - 0.2 V and an on/off ratio of ~ 200 . Different valence change memristive behaviours at different voltage sweep intervals were observed when inert Au was used as the top electrode. The results indicate that the memristive behaviour originates from the composite nature of the MoS₂-MoO₂-MoO₃ layer. Annealing MoS₂-MoO₂-MoO₃ composite layers in Ar and air, produced pure phases of MoS₂ and MoO₃, respectively, which did not show memristive behaviour. This simple one-step synthesis of MoS₂-MoO₂-MoO₃ composite layers at room temperature with the possibility for upscaling production may pave the way for the development of functional memristors.

8.1 Introduction

Memristors are one of the most promising candidates for next-generation nonvolatile memories and neuromorphic computing due to their high scalability,¹ low power consumption,² fast switching,³ and high storage density.⁴ Two classes of memristors, *i.e.* electrochemical

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metallization memristors (ECM) and valence change memristors (VCM), with simple metal/insulator/metal (MIM) structures show particular promise. ECM memristors work based on the oxidation of an active metal top electrode upon application of a bias voltage and transfer of metal cations through an insulating layer and then reduction of the cations at an inert electrode, which results in formation of a metallic filament. The reverse mechanism does occur by reversing the bias voltage and rupture of the conductive filament.⁵ In the case of VCM memristors, by applying the bias or reverse bias voltage, an oxygen deficient filament is created or ruptured. Also, switching in VCM memristors is believed to exist due to oxygen anions/vacancy movement at the interfaces of the memristor electrodes and consequent modification of the Schottky barrier.⁵ Therefore, depending on the type and quality of the different layers of a memristor, a different type of memristivity, ECM or VCM, is determined. It is well known that defects in memristors play a crucial role in making different memristance mechanisms possible in a material.⁶ Composite materials can be designed to contain a high number of defects and may be used in memristive devices. In this chapter we report on a study where we investigated both ECM and VCM memristivity in a composite active layer when the top electrode was changed.

Molybdenum disulfide (MoS_2) as a transition metal dichalcogenide has attracted tremendous attention because its sizable bandgap that changes from indirect to direct when go from bulk to single layer. MoS_2 allows for applications such as transistors, photodetectors and electroluminescent devices based on a active sheet that is only 3 atoms thick.⁷⁻¹⁰ Memristive behaviour of MoS_2 specially has been understood in different structures when used as the active layer. The memristive effect due to the boundary defects of single layer MoS_2 and its gate voltage tenability has been reported in literature.^{11,12} Also, ECM memristivity of MoS_2 microspheres when Ag is used as a top electrode¹³ and migration of defect sites in MoS_2 nanospheres have been observed.¹⁴ Furthermore, memristive behaviour of few layers of MoS_2 through modulation of the metal/ MoS_2 Schottky contact by vacancy movements has been investigated in a lateral structure.¹⁵ Most recently, ECM memristivity of a double layer MoS_2 using Cu as the top electrode in a vertical structure has been reported with low programming voltages of 0.1-0.2 V.¹⁶ Also, there are some reports on the memristive response when MoS_2 is

accompanied by some other materials as the active layer.^{17–20} When partially oxidized, MoS₂ is of significance due to its superior memristive characteristics and MoO_x/MoS₂ heterostructures have been proposed as a superior candidate for printable electronics with low programming voltages (0.1–0.2 V).²¹ In another report, D. Son *et al.*²² demonstrated VCM filament formation and Schottky contact tuning for a memristor with MoS₂-MoO_x heterostructure as the active layer with high on/off ratio ($\sim 10^6$). M. Wang *et al.* fabricated a MoS₂-xO_x thin layer sandwiched between two graphene electrodes and observed memristivity stability up to 340 °C via oxygen and sulfur movements under bias voltage. Therefore, it would be valuable to go further and fabricate a vertical memristor structure with oxidized MoS₂ as the active layer with new methods that yield structures and compositions with better functionalities and remove limitations for real device fabrication. In the case of oxidized MoS₂, explained in the works cited above, up to now a rather cumbersome protocol was applied where the layers were successfully fabricated via exfoliation, coating and post annealing steps in a vertical structure. Here, we present the fabrication of a thin MoS₂-MoO₂-MoO₃ (MoSO) composite active layer using a simple, low cost, one step electrodeposition method, which preserves promising memristive characteristics of low switching voltages (0.1–0.2 V) with relatively high on/off ratio ($>10^2$). Both ECM and VCM memristivities were investigated when different active or inert top electrodes were used. Room temperature fabrication with a possibility of scaling up makes the results presented in this chapter valuable for the development of memristors at large scales.

8.2 Results and discussion

Device Fabrication and Characterization. Memristor structures composed of FTO/MoSO/(top electrode) layers with fluorine-doped tin oxide (FTO) as bottom electrode were fabricated on a transparent glass substrate. The MoSO layer was electrodeposited for 30 s on FTO at room temperature. Electrodeposition of MoSO was done in a two-electrode cell by applying a constant voltage of 2.5 V between a 2×3 cm² platinized silicon wafer and the FTO substrate. The distance between the electrodes was 2 cm. Details of the solution preparation are presented in chapter 7.

The thickness of the MoSO layer was found to be proportional to the electrodeposition time. For evaluation of the thickness dependence of the MoSO layer with respect to electrodeposition time we determined the thickness from profilometry data acquired with a Tencor D100; KLA Tencor profilometer (done by Azizmohseni, A.). In Figure 8-1 we can see the profile of such a measurement and the sharp edge of the MoSO layer, which was used for measuring the thickness. This result demonstrates the formation of a uniform MoSO layer on the surface of FTO. In Table 1 we see the measured thicknesses of MoSO layers deposited in 15, 60, 120 and 300 s versus deposition time. This data and their linear fit show uniform growth rate of ~ 0.83 nm/s. The thickness of the MoSO layer used in the experiments described below was about 25 nm.

Table 1: Thicknesses of MoSO layers at different deposition times.

Deposition time (s)	Thickness (nm)
0	0
15	12
60	50
120	101
300	250

Figure 8-1: a) Profilometry of a MoSO layer deposited in 120 s; the inset shows the thicknesses measured from profilometry data (dots) for different deposition times and their linear fit (red line) which gives a growth rate 0.83 nm/s. For the experiments described in this chapter a layer with a thickness of about 25 nm was used.

UV-visible (UV-vis) absorption of the MoSO layer (Figure 8-2a) proves the high transparency of the prepared layer in the range 360-1100 cm^{-1} , essential for application in transparent electronics, and a broad peak at about 731 cm^{-1} . The inset of Figure 8-2a displays an image of the transparent MoSO layer with Al as top electrode (circular with 1 mm diameter), deposited on its surface by physical vapour deposition. The field emission scanning electron microscopy (FESEM) image of the surface of electrodeposited MoSO layer, presented in Figure 8-2b, shows that the surface is smooth and without voids. FESEM of the samples was carried out using a MIRA3 TESCAN instrument. Preserving uniformity at very low thickness is crucial for developing memristor devices. This characteristic of the electrodeposited layer indicates that the applied

Figure 8-2: Characterization of the MoSO layer. a) UV-vis absorption spectrum of the MoSO layer, which documents high transparency. The inset shows the layer with Al as top electrode (circular, with 1 mm diameter). b) The FESEM image of the MoSO surface shows no voids and a granular appearance (scale bar corresponds to 500 nm). c) The Raman spectrum exhibits peaks related to MoS_2 , MoO_2 and MoO_3 . The X-ray photoelectron spectra of the d) Mo3d/S2s and e) S2p core level regions can be fitted (coloured lines) to deduce the relative molar content of MoS_2 , MoO_2 , and MoO_3 .

growth method is suitable for the fabrication of large scale devices.

Figure 8-2c presents the Raman spectrum of the MoSO layer where peaks related to MoS₂, MoO₂ and MoO₃ appear. Raman spectroscopy was performed using a Teksan (Takram P50COR10) Raman microscope spectrometer with wavelength and power incident laser light of 532 nm and 20 mW, respectively. There is a peak at 404 cm⁻¹ that is related to the A_{1g} vibration mode of MoS₂.^{23,24} In general, the Raman peak intensity of molybdenum sulfide is lower relative to molybdenum oxides. Also, the peaks at 367 cm⁻¹ (A_g-δ(O-Mo) vibration mode), 465 cm⁻¹ (B_{1g}-ν(OMo₃) vibration mode), and 489 cm⁻¹ (metallic MoO₂) indicate formation of MoO₂ in the layer.²⁵ Peaks related to MoO₃ also appear in the spectrum, the most intense one at 821 cm⁻¹ being related to the A_{1g} vibration mode.²⁶

X-ray photoelectron spectroscopy (XPS) was used in order to understand the chemical composition of the MoSO layer (Figure 8-2(d,e)). XPS data was obtained using a ESCA/AES system (CHA, Specs model EA10 plus) equipped with a hemispherical analyser. XPSPEAK software was used for analysing the XPS peaks. The C1s line of adventitious carbon at a binding energy of 284.8 eV was employed as reference for the binding energies of all peaks. The profile of the peaks was taken as a convolution of Gaussian and Lorentzian functions. The fitting results are depicted in Figure 8-2(d, e). The spectral region shown in Figure 8-2d contains both the Mo3d and the S2s core level signals and can be fitted with three Mo3d doublets and one singlet peak (S2s). The S2p core level spectrum is shown in Figure 8-2e in which one doublet is observed. Table 2 represents the data related to the position of the fitted peaks. We see Mo3d_{3/2} and Mo3d_{5/2} peaks related to the MoS₂, MoO₂, and MoO₃ phases at the presented energies. From the area of the various components in the Mo3d core level region the relative molar contents can be determined. We found a relative molar content of 54 % of MoS₂, 15 % of MoO₂, and 31 % of MoO₃ in the layer.

Table 2: Peak positions of XPS data.

material	Peak positions in binding energy (eV)			
	Mo3d _{3/2}	Mo3d _{5/2}	S2p _{1/2}	S2p _{3/2}
MoS ₂	231.3	229.5	162.2	160.8
MoO ₂	232.0	230.2	-	
MoO ₃	234.6	232.8	-	

Memristive characterization. Figure 8-3a shows the current-voltage (I-V) characteristics of the FTO/MoSO₂/Al device. A bias voltage was applied to the top Al electrode, while the bottom FTO electrode was grounded (for details see chapter 2). I-V hysteresis loops were obtained by performing 4 voltage sweep cycles -2.00 V→0.00 V→2.00 V→0.00 V→-2.00 V. The obtained curves correspond to typical bipolar resistive switching memory behaviour. The fourth cycle sweep is plotted with semi-log scale in Figure 8-3b. By sweeping voltage from -2.00 V up to 1.15 V the device is in its high resistance state (off). After that, the current sharply increases from 2.66×10^{-6} A to 7.70×10^{-5} A and the device goes into the low resistance state (on). Therefore, the corresponding voltage to the resistance state changes from off to on, called set voltage (V_{set}) or threshold voltage (V_{th}), is 1.15 V. In memory, this phenomenon is also referred to as “programming” process (set) and the reverse process, on to off state, is named “erasing” (reset). During the reverse voltage sweep, even when the voltage enters the negative range, the device is still in the on state. When the voltage exceeds the negative reset value of 0.45 V, the state of the device is quickly switched from on to off. The off state is well maintained up to -2.00 V. Therefore, the fabricated device represents bipolar resistive switching behaviour with an on/off current ratio of about 50.

To know the memristive mechanism in the FTO/MoSO/Al device, the I-V curve in the positive region of Figure 8-3b is plotted on the logarithmic scale. Slopes calculated in the logarithmic scale plots have no units. The slope of the I-V curve in the on state was calculated to be 1.00, which shows that the device has ohmic conduction characteristics in this region. According to the nature of the fabricated layers, it can be anticipated that the ohmic conduction behaviour is due to the existence of Al filaments, which are formed during the set process and act as conductive channels in the MoSO layer. The other evidence for Al filament formation is the reduction of the set voltage during repetitive voltage cycling as can be seen in Figure 8-3a, which is due to (more) Al aggregates remaining in the MoSO layer after completing each cycle. There are two different regions in the off state with different slopes. This behaviour is

Figure 8-3: Memristive characterization of the device made of the MoSO layer with Al and Ag top electrodes. a,d) The I-V curve of the sample for the first 4 cycles with the bias voltage applied to the top electrode. An evidence for Al filament formation is the reduction of set voltage during the repetitive voltage cycles. b,e) The semi-log scale plot of the 4th cycle showing on/off ratios of 50 and 200 for Al and Ag top electrodes, respectively. c,f) log-log scale plot of the 4th cycle when Al and Ag are used as top electrodes, respectively. The observed slopes are interpreted using the trap-controlled space-charge-limited current (SCLC) model. Slopes calculated in the logarithmic scale plots have no units. The I-V curve slope in the on state is 1.00, which shows that the device has ohmic conduction characteristics in this region. The ohmic conduction behaviour is due to the existence of Al filaments, which are formed during the set process and act as conductive channels in the MoSO layer.

interpreted using the trap-controlled space-charge-limited current (SCLC) model.^{27,28} Typically, SCLC consists of an ohmic current region ($I \propto V$) and a Child's square law region ($I \propto V^2$), which are dominated by the thermally generated charges and the trapped charges injected from the electrodes, respectively. Here the slope of 1.14 corresponds to the ohmic current region while the slope of 1.63 characterizes the Child's square law region. Thereafter, the current sharply increases when the applied voltage approaches the SET value, where the conduction paths are formed.

It should be noted that the changes of interfacial contact barrier or defects under external bias or illumination may also contribute to the resistance of the device and hence to the observed slopes in the plot.^{29,30} The experiment and analysis was performed for a device with Ag as the top electrode. Figure 8-3(d,e,f) presents the same plots as those discussed before for the device with an Al top electrode. The same trend for reduction of V_{set} in repetitive voltage sweep cycles is observed also in this case. Given the similar resistive switching behaviour and the diffusive nature of Al and Ag in these memristors, the mechanism for the device with the Ag top electrode is concluded to be filament formation and disruption of the MoSO layer. But there are some important differences in memristive character of these two samples. When using Ag as top electrode, the on/off current ratio increased to 200 and the threshold voltage for set and reset decreased to ~ 0.20 V and ~ 0.10 V, respectively. This enhancement could be related to the low reduction and oxidation reaction voltages of Ag/Ag^+ .^{31,32} The I-V slopes in different regions when Ag is used as the top electrode are shown in Figure 8-3f. These results could be important in the development of memristors with low threshold voltages.

A totally different memristive behaviour is observed when Au is used as top electrode; Figure 8-4 represents the I-V curves for this case. Since Au is inert and has a relatively high ionic radius, which hinders its diffusion in the MoSO, the atomic mobility in the medium decreases³³ and filament formation does not occur. Figure 8-4a shows a voltage sweep in the range -20.0 to +20.0 V with scan rate of $v = 2.0$ V/s that exhibits a pinched hysteretic behaviour with a non-zero crossing voltage bias. The slight shift of the curve crossing from the origin is caused by capacitive contributions. Similar results have been observed in a Pt/SrTiO₃/Pt system.³⁴ Two different conductive states can be attributed to the on and off states, derived from the slopes at the pinch. The derived slopes show an on/off ratio of about $\frac{0.68}{0.12} = 5.6$ in this plot. From the composition of the layer, one expects the presence of sulfur and oxygen vacancies, which give rise to memristivity when Au is used as top electrode. At a higher scan rate of $v = 4.0$ V/s the hysteretic I-V plot does not show a pinched character anymore (Figure 8-4b). This behaviour can be the result of differences in electric field response of different ionic elements present in the MoSO layer. Some elements contributing in the memristivity of lower frequencies might not be able to respond at higher frequencies. At the much lower voltage range from -0.5 to +0.5 V, the sample shows a not pinched hysteretic behaviour, as seen in Figure 8-4c). Although the scan rate this case is much lower than 2.0 V/s, the device shows a non-pinched behaviour. In this

Figure 8-4. Memristive behaviour of the device with Au as the top electrode. a,b) the I-V curve between -20.0 to +20.0 V at two scan rates of 2 and 4 V/s, respectively and c) the I-V curve of the sample between -0.5 to +0.5 and scan rate of 0.1 V/s. The slight shift of the curve from crossing the origin is caused by capacitive contributions. At a higher scan rate of 4.0 V/s the hysteretic I-V plot does not show a pinched character. This behaviour can be the result of differences in electric field response of different ionic elements present in the sample. Some elements contributing in the memristivity of lower frequencies might not be able to respond at higher frequencies.

case, we should mention the effect of the electric field strength on the movement of the different ionic elements in a memristor. The difference in ionic mobility of S and O ions might explain the non-pinned plot.

These examples demonstrate that the MoSO composite layer shows promising characteristics for use as both ECM and VCM memristivity if the suitable top electrode is chosen. Some reports have investigated different vacancy designs and observed different memristivity responses.³⁵ Different relative compositions of MoS₂, MoO₂ and MoO₃ might result in different memristivities. We showed that in the case of the ECM memristivity of the device, there was no effect observed ascribable to VCM memristivity. This can be understood as due to the low working voltage of the ECM memristor and the much lower current densities observed in the VCM memristor relative to ECM memristors. In terms of the origin of the memristivity from oxygen vacancy movements in a molybdenum oxide medium, we refer to the very low oxygen vacancy mobility observed in such a system by D. Kalaev *et al.*³⁶

For a better understanding of the origin of memristivity in these devices, we annealed the MoSO layer in two different ambient conditions, in air and in a Ar gas flow. Figure 8-5a shows the Raman spectrum for both samples annealed in air and Ar gas flow. Pure phases of MoS₂ and MoO₃ are identified for the samples annealed in Ar and air, respectively. The major peak at 404 cm⁻¹ and the shoulder at about 380 in the sample annealed in Ar flow shows formation of

Figure 8-5: Effect of annealing on the structure and memristivity of the MoSO layer. a) Raman shift of the MoSO layer annealed in air and Ar flow, b) the I-V behaviour of the layer with Ag as top electrode with no hysteretic behaviour and c) the colour change of the samples due to annealing.

MoS₂.³⁷ The pattern for the sample annealed at air with the main peak at 808 cm⁻¹ shows formation of a pure α -MoO₃ phase.^{38,39} Also, optical images of the samples indicate different colours of white and grey for samples annealed in air and Ar, respectively (Figure 8-5c).

After annealing, the Ag top electrode was applied to perform I-V measurements; the resulting I-V curves are presented in Figure 8-5b. The MoS₂ sample shows a rectified I-V curve due to the Schottky contact between the FTO and MoS₂. The MoO₃ sample presents dielectric characteristics and no current passes through it. As can be seen, no hysteretic behaviour is observed in the plots in the range from -1.0 to +1.0 V for the annealed samples with pure phases while, as discussed above, for the as-cast MoSO layer in low voltage range from -0.2 to 0.2 V, ECM memristivity was observed and for sweeps from -0.5 to +0.5 V, VCM memristivity was seen. We therefore conclude that the individual phases separately cannot be at the origin of memristivity in the MoSO layer. Tsuruoka *et al.*⁴⁰ reported an increased redox reaction voltage for a Ag top electrode when the density of the interlayer was increased. In the case of our experiments, one can expect such an effect because annealing resulted in just one compound and in general composites have a higher porosity than single compound structures. This could explain why the ECM memristivity vanished with annealing. To explain why also the VCM memristory behaviour is no longer observed after annealing, we need to consider the disappearance of the O and S vacancies as the symmetries of the structure in the annealed single element layers does not allow for them to exist. In addition, structural disorder in general leads to facilitation of vacancy migration in the structure.⁴¹ Most recently, R. Schmitt *et al.* reported on the effect of amorphous structure on the memristivity of LaFeO₃ and found that when the amorphous phase is removed, the memristivity vanishes.⁴² In summary, the lower density, the vacancies or other effects that vanished upon annealing, all originate from the composite nature of the electrodeposited MoSO layer. The results presented in this chapter lead to the suggestion that samples with different relative compositions in the layer⁴³ need to be prepared with different electrodeposition conditions and their ECM and VCM memristivities investigated to better understand the origin of the memristivity and to find the optimum memristor.

8.3 Conclusions

A simple electrodeposition method was used for the fabrication of MoSO thin layers with promising memristive behaviour at low voltages. Both ECM and VCM memristive behaviours deriving from the composite nature of the fabricated layer can be observed with different top electrodes. The possibility of producing a vast number of composite materials using this approach opens the way for further research in this field. The prospect of using the method for scalable production makes it attractive for industrial application.

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Chapter 9: Facilitating the measurement of electrochemical reactions in memristors*

Abstract

Redox reactions at the interface of a metal/electrolyte system are the basis of electrochemical metallization memristors that can be understood through cyclic voltammetry (C-V). However, voltage limitation during C-V measurements that prevents the resistance switching has hampered full understanding of the redox reactions. We apply a thick ($\approx 20\ \mu\text{m}$) graphene oxide (GO) electrolyte layer in a memristor structure and show that all redox reactions can be determined through C-V measurements without resistance switching by sweeping the voltage up to high values. We are able to reveal details of the Ag redox reactions (Ag^{2+}/Ag) utilizing a GO thick layer as the solid electrolyte in a Pt/GO/Ag cell structure. The results are fundamentally valuable for designing methods to uncover memristive mechanisms of memristors.

9.1 Introduction

Memristors are the most promising candidates for future non-volatile memory devices due to their low power consumption, excellent scalability, simple device structure, fast switching, and high storage density. They also show potential for fabricating multistate memories.^{1,2} Electrochemical metallization (ECM) memristors are a set of resistive random access memories that work based on redox reactions and ion migration in a solid electrolyte.³⁻⁶ The structure of a ECM memristor includes an inert electrode (usually Pt, TiN or W), an ion conducting solid electrolyte (oxide, chalcogenide and sulfide films) and an active electrode (usually Cu or Ag).⁷⁻⁹ The mechanism of resistive switching in ECM systems is well understood: under the oxidation of an active electrode, mobile ions migrate in the solid electrolyte and their reduction at an inert

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electrode finally results in the formation of a conductive filament between the two electrodes. Rupture and formation of this conductive filament under bias voltage determines resistance switching.^{10–12} Therefore Redox reactions at the interface of a solid electrolyte and metal electrodes play a vital role in ECMs. Electrochemistry at the nanoscale has inspired research towards understanding the mechanisms involved in the resistance switching of memristors.¹³ In the last few years electrochemical measurement methods such as cyclic voltammetry (C-V), chronoamperometry, pulsed techniques and steady-state measurements have been used to study redox reactions occurring in solid electrolytes to reveal resistance switching mechanisms.^{14,15} C-V curves can be used to understand the nature of redox reactions at the interfaces of active electrodes and solid electrolytes, as recently demonstrated to reveal redox reactions in Cu/SiO₂/Pt cell^{16,17} and Cu diffusion into SiO₂. Another study in a Cu,Ag/Ta₂O₅/Pt cell² has shown that using C-V curves reveals the effect of density on diffusion and filament growth of Ag and Cu. Also the effects originating from environmental conditions, such as moisture in the air, can be revealed using C-V curves.^{10,12,18,19} Ag is the most promising candidate for use in ECM cells because of its high ion mobility and desirable electrochemical properties. Because of this, Ag is extensively studied using C-V curves to reveal the nature of its redox reactions in memristors. However the C-V study of Ag redox reactions has been limited by the electronic leakage current in thin films that masks the ionic currents and C-V peaks.

Usually there is a voltage limit in the C-V curve study to prevent switching of the resistance – in other words, only a voltage lower than the switching voltage should be applied. This prevented for example, Tuhro *et al.*² from observing the redox reaction of Ag^{z+}/Ag for $z > 1$ and they could only present the Ag⁺/Ag redox reaction as they could not increase the applied voltage. In fact, at higher voltages the system switches and so one cannot measure the redox reaction current peaks. In addition, during repetitive voltage cycling, the filament grows and the switching finally occurs. Hence, finding a method to prevent the switching of the resistance is desirable in order to understand all Ag redox reactions involved in an ECM memristor.

Here, we use a thick layer of graphene oxide (GO) as the solid electrolyte in a Pt/GO/Ag cell to prevent switching of the cell resistance during C-V curve measurements even at high applied bias voltages. An Ag active electrode is used and its redox reactions up to 5 V are discussed. In

addition, we use C-V curves to study redox reactions of Ag at the interface with GO and consequent diffusion of Ag ions. Results are useful to better comprehend memristors at the nanoscale.²⁰

9.2 Experimental section

GO was prepared using the conventional Hummers method²⁰ as detailed in Chapter 2. A platinized Si/SiO₂ substrate was used to drop-cast GO on its surface. The Pt layer was sputter-deposited using a 99.99% pure Pt target in Ar gas under 5 mTorr pressure with a base pressure better than 5×10^{-8} Torr and a growth rate of 3 nm min⁻¹. GO was drop-cast onto the Pt layer from a 10 mg ml⁻¹ solution to obtain a thick GO layer. The GO was dried in air for three days. Silver paste containing silver nanoparticles was used to form the active top electrode with a surface area of about 0.25 mm² on the GO layer. Therefore the final structure is Si/SiO₂/Pt/GO/Ag. Before electrical measurements, the sample was exposed to ambient air. The GO solution was distilled to 0.2 mg ml⁻¹ and the UV-Visible spectrum was taken using a PerkinElmer LAMBDA 20 UV-visible spectrometer in the range 190-700 nm. Raman spectroscopy was performed on the GO layer using a Teksan (Takram P50C0R10) Raman microscope spectrometer with a wavelength of 532 nm and an incident power of the laser light of 20 mW. Field emission scanning electron microscopy (FESEM) of the sample was performed with a MIRA3 TESCAN instrument. A Keithley 2450 source was used for electrical measurements of the cell with triangular voltage sweeps in two probe mode. All electrical measurements were performed at room temperature in ambient air.

9.3 Results and discussion

Figure 9-1 a shows the UV-visible and Raman spectra of GO. The UV-Visible spectrum in Figure 9.1(a) shows a main absorption peak at 217 nm, due to the π - π^* transition in the regions where the sp² bonding is not interrupted by functional groups. A shoulder at 300 nm is attributed to the n- π^* transition of C-O bonds. The spectrum is identical to that reported in literature of GO synthesized using the conventional Hummers method.²¹⁻²³ The GO was brown in colour (characteristics of GO dispersions in water^{24,25}) as can be seen in the inset of Figure 9-1a. For characteristics of drop-cast GO layers, the Raman spectrum²⁶⁻²⁸ of deposited GO layer is shown

Figure 9-1: (a) UV-visible spectrum of GO (identical to spectra of GO prepared by Hummers method reported in the literature) and in the inset a photograph of GO in water; (b) Raman spectrum of GO and in the inset cross sectional FESEM images of the GO layer in which the thickness of the layer can be estimated to be about 20 μm . The Raman peaks appearing at 1359 and 1581 cm^{-1} correspond to the D and G bands.²⁹

in Figure 9-1b. Peaks appearing at 1359 and 1581 cm^{-1} correspond to the D and G bands.²⁹ As indicated in the Figure, the intensity ratio I_D/I_G for the drop coated GO layer on the ribbon is 0.96, which is similar to the I_D/I_G of GO reported by others.³⁰ Cross sectional FESEM images of the GO layer can be seen in the inset of Figure 9-1b; here the thickness of the layer can be estimated to be about 20 μm , which is much thicker than in previously reported memristor structures.³¹

The C-V curve for the prepared Pt/GO/Ag cell is depicted in Figure 9-2. The sweep rate of the voltage in this measurement is 20 mV s^{-1} . As the current is dependent on the area of the Ag active electrode, current density is plotted. The peaks in this curve indicate the redox reactions occurring in the system. As the Pt electrode is inactive, these redox reactions are considered to be related to the silver electrode. In this measurement and other C-V curves, data are gathered after the first cycle. By starting the sweep from -5.00 V, the first peak is measured at $V = 1.23$ V (marked $j_{p,ox1}$ ($\text{Ag} \rightarrow \text{Ag}^+$) in the figure) and the second peak is measured at $V = 1.85$ V (marked $j_{p,ox2}$ ($\text{Ag}^+ \rightarrow \text{Ag}^{2+}$) in the figure). The error of the peak positions is negligible (0.02 V). Because there is no standard reference electrode in the experiments, it is not possible to exactly assign

the observed peaks to a specific redox reaction but we use the proportion of the energies of the reactions in discussing the nature of the peaks. The standard potentials for Ag^+/Ag and $\text{Ag}^{2+}/\text{Ag}^+$ redox reactions in aqueous solutions are 0.80 and 1.98 V.³² According to the lower energy of the Ag^+/Ag oxidation reaction than the higher orders of oxidation for Ag, we can conclude that the peak at 1.23 V is related to Ag^+/Ag oxidation. Subsequently, the peak at 1.85 V is attributed to the higher oxidation level of Ag ($\text{Ag}^{2+}/\text{Ag}^+$). By increasing the applied voltage up to 5 V, there are no other peaks observed in the current.

By applying a voltage to the system, Ag ions diffuse into the GO layer and form aggregates of Ag. When using thin layers of solid electrolytes, these ions can shape filaments, which connect the metallic electrodes and cause resistance switching to occur.^{33,34} This phenomenon is the basis of electrochemical metallization memristors. In the study of memristors using C-V curves, switching can complicate the measurement because it causes an intense current increase, much higher than the measured currents. To prevent this switching during the C-V measurement, we applied a limitation on the maximum voltage allowed during the voltage

Figure 9-2: Cyclic voltammetry of the Pt/GO/Ag cell collected at a sweep rate of 20 mV s^{-1} . The voltage bias is applied to the Ag top electrode. Redox reaction peaks are specified in the figure. The standard potentials for Ag^+/Ag and $\text{Ag}^{2+}/\text{Ag}^+$ redox reactions in aqueous solutions are 0.8 and 1.98 V.³² Given the lower energy of the Ag^+/Ag oxidation reaction as compared to higher orders of oxidation for Ag, we can conclude that the peak at 1.23 V is related to Ag^+/Ag oxidation. The peak at 1.85 V is attributed to the higher oxidation level of Ag ($\text{Ag}^{2+}/\text{Ag}^+$).

sweep.² This results in a loss of information on the chemical reactions that occur above the switching voltage. Previous studies have claimed that a full interpretation of redox reactions is not possible because of high diffusion and consequent switching at low voltages.^{2,19} However, due to the wide application and importance of Ag in ECM memristors, it is worth trying to facilitate the study of the redox reactions. Thickening the solid electrolyte prevents formation of filaments and hence switching. The GO layer used in this work is thick enough (20 μm) to enable voltage sweeps to much higher values than the redox potentials of Ag without resistance switching. This technique allows to use the C-V curves to analyse the electrochemical reactions that occur at higher voltages and how they affect the memristor function.

By sweeping back the voltage Ag^+ and Ag^{2+} ions in the cell experience a reduction reaction. Consequently, by continuing to sweep the voltage towards minus voltages, two reduction current peaks are observed at -1.12 V ($j_{p,\text{red}2} (\text{Ag}^{2+} \rightarrow \text{Ag}^+)$) and -1.85 V ($j_{p,\text{red}1} (\text{Ag}^+ \rightarrow \text{Ag})$). The peak at -1.12 V is attributed to the energetically favourable reduction of Ag^{2+} to Ag^+ . The peak at -1.85 V is attributed to the reduction of Ag^+ to Ag. There are no more peaks upon sweeping the voltage down to -5.00 V. The high symmetry observed in the C-V curve can be an indication of the unchanged condition for the reduction and oxidation reaction experienced by Ag thanks to the thick GO which prevents the Ag ions from reaching the Pt layer. It is worth mentioning that there might be other types of oxidation and reduction reactions contributing to the C-V curve, especially near the measured double peaks.³⁵ Further investigation of these reactions needs additional experiments.

Figure 9-3: (a) The C-V curve for two different sweep rates of 20 and 100 mV s⁻¹ and (b) calculated charge concentration, C_{ion} and D at the two frequency sweeps. As expected, like standard redox systems, by increasing the sweep rate from 20 to 100 mV s⁻¹ both reduction and oxidation current peaks become larger and the position of them shifts towards the higher voltage side. By increasing v , there is less time for Ag to be oxidized and so the ion concentration decreases. Moreover, the ion-ion interaction reduces by decreasing C_{ion} and in turn, diffusion of Ag ions in GO occurs more easily and results in increasing D . Calculated diffusion coefficients are about 10⁻⁶ to 10⁻⁷ cm² s⁻¹.

Figure 9-3 shows the typical C-V curves for a Ag/Go/Pt cell measured at different sweep rates. As expected for standard redox systems, when increasing the sweep rate from 20 to 100 mV s⁻¹ both reduction and oxidation current peaks become larger and their position shifts towards higher voltages. This indicates that an inhibited charge transfer controlled electrode reaction

takes place at the interface of the active Ag electrode and the GO solid electrolyte.³² In the case of an inhibited charge transfer at room temperature, the reduction current density can be estimated from the Randles–Sevick equation:³⁵

$$j_{p,red} = 2.99 \cdot 10^5 \cdot z^{3/2} \cdot c_{ion} \cdot \sqrt{\alpha D v} \quad (1)$$

where D is the diffusion coefficient in $\text{cm}^2 \text{s}^{-1}$, c_{ion} the concentration in mol cm^{-3} , z the number of electrons transferred in the redox reactions, α the charge transfer coefficient ($\alpha = 0.5$) and v the sweep rate in V s^{-1} . Using the data shown in Figure 9-3a, we calculated the diffusion coefficient of Ag in GO at the two sweep rates of 20 and 100 mV s^{-1} (inset of Figure 9-3b). For simplicity, we take into account the first reduction peaks that appear in the plots with $z = 1$. We use the geometry of the cell ($500 \times 500 \times 20 \text{ }\mu\text{m}$) and C-V plots at the oxidation region to calculate the ion concentrations (Figure 9-3b). Similar to other works^{2,16} for diffusion of Ag in SiO_2 and Ta_2O_5 , we observe an increase of D when increasing the sweep rate of the voltage. In the inset of Figure 9-3b it Also can be seen that the increase of v causes the c_{ion} to decrease. These two effects show that the GO acts as a concentrated solution and the ion-ion interaction at the interface of Ag and GO is responsible for the decrease in diffusion of Ag. By increasing v , there is less time for Ag to be oxidized and so the ion concentration decreases. Moreover, the ion-ion interaction reduces by decreasing c_{ion} and, hence diffusion of Ag ions in GO occurs more easily and results in increasing D . Calculated diffusion coefficients are about 10^{-6} to $10^{-7} \text{ cm}^2 \text{s}^{-1}$. We could not find any similar system in previous reports to compare with our results. These values are much higher than those obtained for diffusion of Ag in SiO_2 or Ta_2O_5 .^{2,16} We note that, one should pay attention to the high porosity of GO and to the much higher surface area of the interface between Ag and GO. This high surface area can cause some deviations in the calculated D using the Randles–Sevick equation.

Recently much attention has been paid to the reactions occurring at the interfaces of layers in these systems.^{12,36} For an extended discussion on the effects of moisture on redox peaks see ref. 19. For example the reduction of water at the interface of a Pt counter electrode with solid electrolyte has been considered as follows:^{10,12,37}

Figure 9-4: Repetitive voltage cycling at $v = 100 \text{ mV s}^{-1}$ results in gradually increased current. At the same time, the voltages at which the current peaks appear do not vary. This is because of the unchanged origin of the peaks during different cycles of voltage sweep. By repeating the voltage cycling, a higher amount of Ag penetrates inside the GO layer and so the surface area increases. Therefore, higher current yields can be observed at the same applied voltage.

In the case of our sample, the absorption of water is possible and so its reduction at the Pt electrode can also contribute to the resulting currents in C-V curve. For further explanation of the contributions of different redox reactions in the resulting C-V curves we use repetitive cycling of the voltage and measuring current. Figure 9-4 represents 22 cycles of the C-V measurement at the sweep rate of 100 mV s^{-1} . By increasing the number of cycles, the redox reaction current increases; at the same time, the voltages at which the current peaks appear do not vary. This is because of the unchanged origin of the peaks during different cycles of voltage sweep. By repeating the voltage cycling, a higher amount of Ag penetrates inside the GO layer and so the surface area increases. Therefore, higher current yields can be observed at the same applied voltage. This behaviour benefits from the high diffusion coefficient of Ag and indicates that the role of Ag ions is significant in the resulting current peaks in C-V curves.

Also there are some previous works mentioning the domination of oxygen vacancies in the resistance switching of GO in addition to the electrochemical metallization process.³⁸ However, the overall behaviour of our system, including the aforementioned variations occurring under different voltage sweeps, multi-peak C-V curve, variation in C-V curve under repetitive cycling of the voltage, and non-crossing currents in C-V plots, all together resemble effects originating from Ag redox reactions in the electrochemical cell.

9.4 Conclusion

In summary a thick layer of GO was used in a Pt/GO/Ag solid electrolyte cell to hamper filament formation between Pt and Ag electrodes even at high bias voltages. Therefore, we could follow all possible electrochemical redox reactions happening at the interface of GO and Ag up to 5.00 volts without switching of the resistance. Using this method, we observed second-order oxidation of Ag at GO. These results are valuable from a fundamental point of view and contribute towards a better understanding the ECM memristors.

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Chapter 10: Conclusions and outlook

In **chapters 3 and 4** it was shown that the magnetic exchange coupling in magnetic ribbons when coated with ferromagnetic and antiferromagnetic thin layers can drive the magnetoimpedance effect. The effect of the exchange coupling on the magnetoimpedance response is high enough to promote magnetic field sensitivity. In the presence of such a coupling, the magnetoimpedance exhibits a single peak behaviour against the applied field and shows a higher magnetoimpedance ratio. Of the two metals studied, the Co layer was found to display a higher exchange coupling with the ribbon than the Ni one. Therefore, higher ratios with more coercive response can be obtained with the Co electrodeposited layer. These results originate from the higher magnetization of Co in comparison to Ni. Also, electrodeposition was presented as a simple one-step method for coating both sides of the ribbon to achieve highest effectiveness on the magnetoimpedance response. It was observed that different thicknesses of electrodeposited layers result in different MI ratio. For the Ni coated ribbon, the maximum of MI ratio was achieved for a Ni layer thickness of 20 nm and for the case of Co the maximum MI ratio was achieved for a coating thickness of 10 nm. This observation is the result of different magnetic exchange lengths of Ni and Co materials.

In the case of ribbons coated with an antiferromagnetic IrMn layer (**chapter 4**), a training effect was observed. Performing several consecutive MI measurements, the exchange coupling between IrMn and the ribbon decreased and the MI ratio increased as a result. Besides, in each measurement of the magnetoimpedance response, effects of the spin-orbit torques were observable in the magnetoimpedance response. These two observations led us to conclude that the exchange coupling is independent from the spin-orbit torques. In **chapter 4**, we also showed that the spin-orbit torques result in a single peak behaviour of the magnetoimpedance response as well as in a frequency shift of the impedance when the applied ac current is increased. In addition to the antiferromagnetic IrMn, coating with a Pt layer also resulted in a frequency shift of the impedance and in single peak behaviour of the MI response, which further supports that the observations originate from spin-orbit torque.

Besides these fundamental studies through the magnetoimpedance effect, **chapters 5 and 6** were related to the magnetoimpedance sensor modifications by coating graphene-based materials on the surface of the magnetic ribbon. In **chapter 5** we showed that when the ribbons were coated by graphene oxide (GO) flakes through electrophoretic deposition, the magnetoimpedance ratio increased; this in combination with some other characteristics of GO, like anticorrosion and biocompatibility, can further increase the functionality of the sensor for application in different environments. The role of electrophoretic deposition is crucial in the observed enhancement because drop casting of GO on the ribbon did not result in MI enhancement. In **chapter 6**, hybrid samples of graphene and yttrium iron garnet (YIG) nanoparticles were synthesized and coated on the surface of the sensor. Also this coating led to a modification of the magnetoimpedance ratio and the sample with smaller YIG nanoparticles resulted in a higher magnetoimpedance ratio. This result might be due to the higher super paramagnetic properties of the smaller YIG nanoparticles because the super paramagnets have higher permeability. Moreover, this result led to the conclusion that magnetic proximity effects in graphene might be the cause of the magnetoimpedance modification.

In the next three chapters, the electronic behaviour of different heterostructures was investigated. **Chapter 7** presents the fabrication of lateral heterostructures of semiconductive materials through a one-step simple method. Bipolar electrodeposition resulted in a coating with gradient of composition in the structure, going from molybdenum oxide and to molybdenum sulfide and mixed phases in between. The fact that different electrochemical potentials can give different compositions from a single solution makes fabrication of the lateral heterostructure possible. Type I and Type II band alignments were formed between different parts of the heterostructure. The layer showed rectified I-V behaviour with an on/off ratio of 10 and a threshold voltage of 0.45 V. In **chapter 8**, the memristive behaviour of a composite thin film made of MoS_2 , MoO_2 , and MoO_3 was described. The layer showed low threshold voltages of about 0.1-0.2 V with relatively high on/off ratio of about 200. This result confirmed the advantages of the simple fabrication method of the composite layer via electrodeposition. Also, the results showed that the composite nature of thin films can be important for observation of memristive properties. In **chapter 9**, a simple method for the study of electrochemical reactions

in redox based memristors was reported. By thickening the solid electrolyte layer, filament formation does not occur and the range of current remains limited. Therefore, by sweeping to higher voltages in C-V measurements of the memristor one can observe more peaks related to redox reactions. In this chapter how this effect can be exploited to reveal second order Ag redox reaction peaks in the C-V curve.

In the magnetoimpedance response of the magnetic ribbons when coated with high spin-orbit coupling metals, the spin-orbit torque drives the magnetization dynamics and therefore the magnetoimpedance response. It would be desirable to derive theoretically the effect of the spin-orbit torque on the magnetization dynamics as well as on the skin depth of a magnetic conductor and therefore establish the foundations of a new spin Hall angle detection mechanism based on the magnetoimpedance effect. In chapter 4, we reported a measured impedance change when changing the driving current. This effect could be exploited to realize a high resolution spin Hall angle detector.

As suggested, the magnetoimpedance sensor when coated with graphene-based materials can be modified for detection of biomaterials. For further research it is suggested to bring such sensors to a higher level of technological readiness. MI sensors may be used in liquid electrolytes containing biomaterials. By attachment of biomaterials to the graphene-based materials, the MI response may change.

Since a vast variety of materials can be fabricated via electrodeposition, the results of chapter 7 suggest that bipolar electrodeposition can be used to realize lateral heterojunctions with highly diverse materials. Electrodeposition method is suitable for the fabrication of both metallic and semiconducting materials. Therefore, solutions which both metals and semiconductors can be electrodeposited from and bipolar electrodeposition can hence serve for the fabrication of lateral Schottky heterostructures.

For improving the memristive characteristics of $\text{MoS}_2\text{-MoO}_2\text{-MoO}_3$ composite materials (MoSO) it should be explored whether different relative content of these 3 elements can be achieved by changing the voltage of the electrodeposition. Also, the thickness of the layer is an important parameter, which can change the characteristics of the memristor and should be considered in

the future research. These materials have shown a great potential for use as memristor at high temperatures¹ and their full potential should be tested further. For a better understanding of the underlying mechanism of the memristivity it is also important to use *in-situ* structural characterization methods with high spatial resolution. Using flexible top and bottom electrodes in the memristor structure, *i.e.* graphene, such MoS₂-MoO₂-MoO₃ composite layers can also be investigated for transparent and flexible electronics.

The final future direction stemming from this thesis are heterostructures of magnetic and nonmagnetic materials, where the nonmagnetic material shows memristive properties. The combination of these materials has led to new concepts and designs in the field of magnetism and made it possible to efficiently control the magnetism by electric fields.²⁻⁸ As an example, composite MoSO showed memristive behaviour and can be coated on conductive magnetic thin films. A next step could be to use a gate voltage on a ferromagnet/MoSO heterostructure that can lead to a change in stoichiometry of MoSO at the interface due to memristive properties of MoSO. In turn, a change in the magnetic properties of the magnetic thin layers may be observed due to different interface quality. For example, higher or lower spin-orbit coupling structures at the interface may tune the magnetic anisotropy of magnetic materials. This way it may be possible to control magnetic anisotropy by an electric field. This also is a useful method to study effects of interface composition on the magnetic properties in a single sample instead of making several samples with different compositions. It is also suggested to use memristive materials on the surface of a MI sensor in order to investigate the above mentioned phenomena.

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Summary

Heterostructures can possess integrated properties of their individual ingredients with superior functionalities. This advantage makes heterostructures suitable candidates for use in advanced technological elements and devices. In the research subject of this thesis we investigated the novel characteristics of heterostructures for application in spintronics, sensors and electronic elements. The major part of the thesis is focused on electronic and spintronic devices, which were most investigated in recent years for their capability to overcome the limitations of CMOS-based computing technology. For the future computing developments, it is needed to design new structures with new functionality to overcome these limitations, *i.e.* high energy consumption.

In fact, spin-based device architectures promise a wide range of opportunities. They show energy-efficiency, lack of Joule heating losses, feasible scaling down to nanometer size, ultrafast memory operation and ease of integration with data storage systems.

Also, new designs of materials in the field of electronics have resulted in the fabrication of functional elements for data storage and processing. In addition to the advantages of spintronics elements, memristors are fully controlled by electric fields and hence have low energy consumptions. Therefore, also memristors have been intensely investigated in the last decade.

In the research projects reported in chapters 3 and 4 we focus on the spintronic properties of heterostructures of magnetic and nonmagnetic materials through studying the magnetoimpedance (MI) effect. In chapter 3 illustrate how we found the relation between the MI response and the magnetic exchange coupling between materials. Coercivity and single or double peak behaviour of the MI response determines the quality of the exchange interaction. In the study described in chapter 4 we probed the effects originating from the spin-orbit torques (SOTs) in addition to the magnetic exchange coupling between the materials in the heterostructure. Frequency shift behaviour and single peak behaviour of the MI response was

used to show the SOT in the sample. By placing heavy metals in the proximity of magnetic materials, we developed a new method for fundamental studies of SOTs in spintronic systems. Investigating the nature of the SOT is crucial for development of fully electric field controlled spintronic memory devices.

Chapters 7-9 are related to the heterostructures, which were fabricated for electronic devices. In chapter 7 we report on a lateral heterostructure of semiconductive materials fabricated with a simple and cost effective method. Bipolar electrodeposition was used for deposition of a layer with gradient of molybdenum sulfide and oxides on a conductive substrate. This heterostructure showed a rectified I-V curve with a low threshold voltage of 0.45 V, which demonstrates that bipolar electrodeposition is functional for producing lateral heterostructures with tuneable electronic properties.

Chapters 8 and 9 are devoted to memristors in the field of electronics. In chapter 8 we describe how a memristor with promising characteristics were fabricated by electrodeposition, a method that offers the possibility for scaling up. The memristor showed a threshold voltage of 0.1-0.2 V and an on/off ratio of ≈ 200 . High efficiency memristors have low voltage thresholds and high on/off ratios; these characteristics were observed in the MoS₂ described here and identify it a suitable candidate for use in future memristors.

In chapter 9 a simple method was presented for a better study of the memristivity mechanism in heterostructures. Reaching conditions in which electrochemical reactions can take place in a memristor structure is important for the study and development of memristors. In this chapter we show how a thick electrolyte layer in a memristor structure was used to prevent filament formation when performing CV measurements. Filament formation during a CV measurement prevents electrochemical reactions from occurring in the system. In the study described in chapter 9, redox reactions of Ag were observed when a thick graphene oxide layer was used as the solid electrolyte layer. This method can be employed to study memristors that work based on electrochemical redox reactions. By suppressing filament formation during the CV measurement, one can better see the electrochemical reactions that occur when high bias voltages are applied to the memristor.

In addition to the electronic and spintronic properties of heterostructures, sensor characteristics of some elements were explored in the studies described in chapters 5 and 6. The base for the sensitivity of the devices was the magnetoimpedance effect. MI sensors are mainly used for the detection of magnetic fields but they have been exploited for the detection of substances in the environment. The high sensitivity of the MI effect to the surface conditions of the sensor can be used for biosensing and detecting magnetic materials in the environment. In the study detailed in chapter 5, the surface of a MI sensor was coated with graphene oxide and the MI ratio was found to have increased. Coating of the surface of a MI sensor with a biocompatible material like graphene oxide also prepares it for use as biosensor. Electrophoretic deposition, the method for coating the surface of the ribbon at the core of the MI sensor, can be used for developments of the MI sensors at the future. The project detailed in chapter 6 concerned an MI sensor coated with a composite material consisting of graphene nanoplatelets and yttrium iron garnet nanoparticles. This time in addition to the advantage of the modification of the surface of the MI ribbon with a graphene-based material, a magnetic material is also included to increase the MI ratio and sensitivity and the MI ratio was found to have increased from 271 % up to 301 %. The results of this study can be used for the detection of magnetic nanoparticles in the environment.

Samenvatting

Heterostructuren kunnen geïntegreerde eigenschappen van hun individuele componenten bezitten en daarmee superieure functionaliteiten tonen. Dit voordeel maakt heterostructuren geschikte kandidaten voor gebruik in geavanceerde technologische elementen en apparaten. In dit proefschrift hebben we nieuwe kenmerken van heterostructuren onderzocht met toepassingen in sensors, spintronische- en elektronische elementen. Het grootste deel van het proefschrift is gericht op de elektronische en spintronische elementen die de afgelopen jaren het meest zijn onderzocht op hun vermogen om de beperkingen van CMOS computertechnologie te overwinnen. Voor de toekomstige computerontwikkelingen is het nodig om nieuwe structuren met nieuwe functionaliteit te ontwerpen om zo beperkingen, zoals een hoog energieverbruik, te overwinnen.

Op spin gebaseerde apparaat architecturen beloven een breed scala aan mogelijkheden. Ze tonen energie efficiëntie, geen Joule warmte verliezen, haalbare verkleining tot nanometer schaal, ultrasnelle werking als geheugen en eenvoudige integratie met gegevens opslagsystemen.

Ook hebben nieuwe ontwerpen van materialen op het gebied van elektronica geresulteerd in de fabricage van functionele elementen voor gegevensopslag en gegevensverwerking. Naast de voordelen van de spintronica-elementen worden memristors volledig bestuurd door elektrische velden en hebben daardoor een laag energieverbruik. Daarom zijn memristors het afgelopen decennium intensief onderzocht.

Het onderzoek gepresenteerd in dit proefschrift zet deze inspanningen voort. In de hoofdstukken 3 en 4 richtte we ons op de spintronica van heterostructuren in magnetische en niet-magnetische materialen door het magnetische impedantie (MI) effect. In hoofdstuk 3 vonden we de relatie tussen de MI-respons en de magnetische uitwisselingsinteractie tussen materialen. Coerciviteit en enkel of dubbel piekgedrag van de MI-respons bepalen de kwaliteit van de uitwisselingsinteractie. In hoofdstuk 4 hebben we naast de magnetische uitwisselingsinteractie tussen de materialen in de heterostructuur ook de effecten onderzocht

die voortkomen uit de spin-baan-momenten (SOT's). Frequentieverschuivingen en enkelvoudig piekgedrag van de MI-respons worden gebruikt om de SOT in het monster aan te tonen. Door zware metalen te gebruiken in de nabijheid van magnetische materialen hebben we een nieuwe methode ontwikkeld voor fundamentele studies van SOT's in spintronische systemen. Het onderzoeken van de aard van de SOT is cruciaal voor de ontwikkeling van een spintronische elementen voor geheugenopslag die volledig door een elektrisch veld kunnen worden bestuurd.

De hoofdstukken 7-9 hebben betrekking op de heterostructuren die zijn gemaakt voor de studie van elektronische eigenschappen. In hoofdstuk 7 rapporteren wij een laterale heterostructuur van halfgeleidende materialen die is vervaardigd met een eenvoudige en kost effectieve methode. Door middel van bipolaire elektrodepositie op een geleidend substraat groeiden wij een laag met een gradiënt van alleen molybdeensulfide tot alleen molybdeenoxide met een gemengde compositie in het midden. Deze heterostructuur heeft een gerectificeerde I-V-curve met een lage drempelspanning van 0,45 V, wat aantoont dat bipolaire elektrodepositie geschikt is voor het produceren van laterale elektronische heterostructuren.

Hoofdstuk 8 en 9 hebben betrekking op memristors voor toepassing in volgende generatie elektronica. In hoofdstuk 8 beschrijven we een memristor met veelbelovende karakteristieken en met mogelijkheid tot opschaling. De met elektrodepositie gemaakte memristor vertoonde een drempelspanning van ongeveer 0,1-0,2 V en een aan/uit verhouding van ongeveer 200. Memristors met een lage spanningsdrempels en een hoge aan/uit verhouding hebben een hoog rendement. In dit proefschrift zijn deze kenmerken waargenomen in een op MoS₂ gebaseerd materiaal wat het een geschikte kandidaat is voor gebruik in toekomstige memristors.

In hoofdstuk 9 werd een eenvoudige methode gerapporteerd om het mechanisme van de memristiviteit in heterostructuren beter te bestuderen. Het realiseren van de elektrochemische reacties in een memristor structuur is belangrijk voor de studie en ontwikkeling van de memristors. In dit hoofdstuk werd een dikke elektrolyt laag in een memristor structuur gebruikt om formatie van een filament te voorkomen bij het uitvoeren van CV-metingen van de memristor. Vorming van een filament tijdens een CV-meting voorkomt elektrochemische reacties in het systeem. Door de techniek die in dit proefschrift wordt gebruikt, vormt zich geen

filament tijdens de CV-meting en daardoor zijn de elektrochemische reacties, die optreden bij hoge spanningen op de memristor, beter te zien. In dit hoofdstuk werden redoxreacties van Ag waargenomen wanneer een dikke grafeenoxide (GO) laag als elektrolyt laag werd gebruikt. Deze methode kan worden gebruikt voor het bestuderen van memristors die werken op basis van elektrochemische redoxreacties.

Naast de studies van elektronische en spintronische eigenschappen van heterostructuren, werden sensorische eigenschappen van sommige elementen onderzocht in de hoofdstukken 5 en 6. De basis voor de gevoeligheid in deze sensoren was het MI-effect. MI-sensoren worden voornamelijk gebruikt voor de detectie van magnetische velden maar ook voor het detecteren van materialen in de omgeving van de sensor. De hoge gevoeligheid van het MI-effect voor de oppervlaktetoestand van de sensor maakt het geschikt voor gebruik als biosensor en voor detecteren van magnetische materialen in de omgeving. In hoofdstuk 5 was het oppervlak van de MI-sensor gecoat met GO wat leidde tot een verhoging van de MI-verhouding. Het coaten van het oppervlak van een MI-sensor met een biocompatibel materiaal zoals GO maakt het geschikt voor gebruik als biosensor. De methode voor het coaten van GO op het oppervlak van het lint in de kern van de MI-sensor, waarbij gebruik wordt gemaakt van Elektroforese, is een methode die kan worden gebruikt voor toekomstige ontwikkelingen van de MI-sensoren. In hoofdstuk 6 werd de MI-sensor gecoat met Gr/YIG samengesteld materiaal. Naast het voordeel van de modificatie van het oppervlak van het lint met een op Gr gebaseerde materiaal, wordt het ook gecoat met een magnetisch materiaal dat de MI-verhouding en gevoeligheid van de sensor verhoogt. De MI-verhouding steeg van 271% naar 301%. De resultaten van dit hoofdstuk kunnen worden gebruikt voor de detectie van magnetische nanodeeltjes.

Curriculum Vitae

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