Towards the miniaturization of core-shell cylindrical structures: fabrication and characterization of ferromagnetic core-shell micro- and nanowires

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“So many people enter and leave your life! Hundreds of thousands of people! You have to keep the door open so they can come in! But it also means you have to let them go!”

— Jonathan Safran Foer

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Abstract

The aim of the work reported in this thesis has been the development of a nanoparticle, which, due to its unique, optimized morphology, displays no magnetic stray fields. Since a similar configuration has been fabricated within the frames of this work on the microscale using core-shell microwires, the thesis focuses towards the miniaturization of ferromagnetic cylindrical core-shell nanostructures.

Here the design, fabrication, and investigation of ferromagnetic core-shell cylindrical structures at the micro- and nanoscale, consisting of two ferromagnetic phases separated by a non-ferromagnetic intermediate layer and predefined magnetic properties, is elucidated. The thesis consists of three parts: (i) the fabrication and investigation of core-shell structures, followed by (ii) the micromagnetic simulations of the magnetization reversal of core-shell nanowires, which suggest the optimal particle materials and dimensions to move towards their miniaturization, and, finally, (iii) the development and implementation of a novel fabrication method for short core-shell nanowires fabrication, with optimized control over the material selection and geometrical parameters of the constituents.

(i) Core-shell microwires with amorphous FeSiB and crystalline CoSiB cores and Co, CoNi, and FeNi external shells separated by a Pyrex layer, have been fabricated by the combined Ulitowski-Taylor, sputtering and electrodeposition technique. Moreover, a partially covered core-shell microwire has been fabricated and investigated for the first time. The effect of the external shell geometry (partial or full shell), thickness, and composition on the overall magnetic response of the system has been investigated at room temperature, as well as in the temperature range $T = 295 - 1200$ K. It has been shown that the external shell drastically modifies the magnetic behavior of the microwire, making it possible to tune the overall magnetic properties as desired via the magnetostatic and magnetoelastic coupling between the ferromagnetic core and shell. The influence of the temperature unwinds additionally magnetic phase transitions and structural transformations of the core and the shell independently, which does not leave the overall magnetic response unaffected. Moreover, exposure to high temperature induces irreversible changes of the magnetic properties of the core-shell microwires, due to modification of the material microstructure.

(ii) The magnetization reversal of a Co-Fe$_3$O$_4$ nanowire has been simulated using mumax$^3$, varying its core diameter, as well as the nanowire length, in order to provide a complete description of the system and to suggest the optimal particle composition and dimensions to obtain zero-remanence states at near-zero magnetic field. In such states, the magnetization of the core and shell have an anti-parallel alignment along their axis, resulting in a
particle with no stray field distribution. It has been shown that the influence of the length is irrelevant for thin nanowires (core diameters below 50 nm), while for longer nanowires, a 360° domain wall mediated remagnetization process takes place. A 360° domain wall is nucleated by the core in the external shell, and it remains stable and uninfluenced by the external field over a significant field range.

(iii) A novel multi-step approach for the fabrication of core-shell nanowires with several external shells, tunable geometrical parameters (nanometer precision), and a variety of possible materials for the constituents has been introduced and proved to be an efficient method for the production of Co-Fe$_3$O$_4$ core-shell nanowires. The approach is based on a combination of the ion-track template-method in electrochemistry, plasma etching, and molecular beam epitaxy. The structural and compositional characterization of single core-shell nanowires obtained by this method has been performed. Electron holography measurements have been used to visualize the magnetic stray field distribution of the fabricated Co-Fe$_3$O$_4$ single nanowire. This type of fabrication method has been reported for the first time, as well as the fabricated short bi-shell core-shell nanowires.
Kurzzusammenfassung


Darüber hinaus wird gezeigt, dass die Exposition bei hohen Temperaturen irreversible Veränderungen der magnetischen Eigenschaften der Kern-Schale-Mikrodrähte hervorruft, die auf eine Veränderung der Materialmikrostruktur zurückzuführen sind.

(ii) Die Magnetisierungsumkehr eines Co-Fe$_3$O$_4$-Nanodrahtes wurde mit mumax$^3$ simuliert unter Variation des Kerndurchmessers und der Nanodrahtlänge, was die Ermittlung einer optimalen Partikelkomposition und der Partikelabmessungen für die nachfolgende Synthese erlaubt. Es wurde eine Partikelkonstellation ohne Remanenz bei einer magnetischen Feldstärke nahe Null gefunden, bei dem die Magnetisierungsrichtung von Kern und Hülle antiparallel entlang der Längsachse des Drahtes ausgerichtet sind, was insgesamt zu einem Teilchen ohne Streufeldverteilung führt. Es konnte gezeigt werden, dass der Einfluss der Drahtlänge für dünne Nanodrähte mit einem Kerndurchmesser unterhalb von 50 nm vernachlässigbar ist. Für längere Nanodrähte wurde ein Ummagnetisierungsprozess gefunden, der durch eine 360° Domänenwand vermittelt wird. Die 360°-Domänenwand wird dabei durch den Kern in der äußeren Hülle erzeugt, und bleibt über einen signifikanten Feldabschnitt stabil und unbeeinflusst durch externe Magnetfelder.

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1.1 Objective of the Dissertation

"Nanotechnology is the idea that we can create devices and machines all the way down to the nanometer scale, which is a billionth of a meter, about half the width of a human DNA molecule."

— Paul McEuen

"Nanotechnology in medicine is going to have a major impact on the survival of the human race."

— Bernard Marcus

The magnetization reversal and its mechanism in magnetic micro- and nanostructures have been studied extensively, theoretically as well as experimentally, over the last years due to their great potential for innovative technological applications [1–8]. Nanostructures with cylindrical geometry, such as nanowires [9, 10], nanotubes [11, 12] and, recently, core-shell nanostructures [13] have gained an increasing scientific interest as they can be a potential substitute to spherical nanoparticles. However, in contrast to nanoparticles, nanowires provide more possibilities to tailor their magnetic response. For instance, their magnetic anisotropy, switching field, and remagnetization mechanism can be tailored over typically two orders of magnitude through a convenient selection of diameter and length. Moreover, in the case of core-shell nanowires, the presence of an additional ferromagnetic shell, separated from the core by a non-ferromagnetic material, provides a whole new range of possibilities to tailor the magnetic response of the nanowire. Additionally, core-shell nanowires have been shown to deliver active surfaces, flexibility, multifunctionality [14], and some fascinating topological effects emerge due to the curvature of the surface [15].

The working principle of most applications of nanoparticles is based on the possibility of non-invasively addressing those particles from a distance with a magnetic field, in order to control their position, to create forces, torques, to heat the nanoparticle, to create local magnetic fields, or to induce the desired magnetic state. There is a wide variety of applications, in which nanoparticles are used. The applications in biomedicine include magnetic resonance imaging contrast-enhancement agents...
targeted drug delivery [17, 18], magnetically induced hyperthermia [19–23],
cancer therapy via mechanical destruction of cellular matter [24–26], (biochemical) immunomagnetic cell separation [27–29], isolation and purification process of various biological molecules [30, 31], probing mechanical properties of individual cells and cellular components [32, 33], targeted activation of mechanosensitive ion channel signalling pathways and as carriers for targeted delivery of genes and drugs [34, 35]. On the other hand, nanoparticles have been suggested for the fabrication of sensors [36], magnetic memories devices [37], magnetic recording media [38] and microwave devices [39]. In most applications, a strong magnetization is required, which leads to the undesired agglomeration of the nanoparticles due to the magnetic dipolar interaction via their magnetic stray fields. This "side" effect is highly undesirable and especially dangerous in biomedical applications.

V. Novosad et al. [24] proposed a solution to the agglomeration problem based on magnetic vortex disks, which effectively have zero remanent magnetization and can be activated by a small external magnetic field. R. P. Cowburn et al. [40] proposed similar-sized disks consisting of several antiferromagnetically coupled films, stacked on top of each other, creating a synthetic antiferromagnetic (SAF) thin film. These magnetic disks are characterized by a zero magnetic moment at remanence, low susceptibility at low fields, and a large saturation magnetization created by the stacking of the basic coupled bilayer motif.

The aim of the investigation presented in this thesis has been the development of a nanoparticle, which, due to its unique, optimized morphology, displays no magnetic stray field distribution in small magnetic fields. The particle consists of two magnetic phases, a core and a shell, separated by a non-ferromagnetic intermediate layer. Such a coaxial nanostructure is designed to show an anti-parallel alignment of the magnetization along its axis, i.e., the stray field from the core and the shell compensate each other, causing a zero magnetic stray field at remanence in a zero or near-zero external magnetic field. In this way it is possible to avoid particle agglomeration, providing the stability of an assembly of particles in suspension or dispersed over a substrate.

In summary, the important properties of this type of magnetic nanostructures are:

1. zero remanence at zero or near-zero magnetic field, which will prevent the particles from agglomeration;
2. an abrupt switching to saturation magnetization at a certain value of the magnetic field $H_{sw}$, that can be predetermined and tuned in accordance with the desired application;
3. the possibility to tune the total magnetic moment of the structure without varying the remanent state;
4. a low susceptibility at low magnetic fields will prevent the effect of small magnetic fields on the agglomeration of nanostructures (such as the effect of the earths magnetic field $\sim 0.5$ Oe).
Since a similar configuration has been fabricated within the frames of this work for core-shell microwires, this thesis focuses towards the miniaturization of ferromagnetic cylindrical core-shell nanostructures. Here the design, fabrication, and investigation of ferromagnetic core-shell cylindrical structures at the micro- and nanoscale, consisting of two ferromagnetic phases separated by a non-ferromagnetic intermediate layer and with predefined magnetic properties, is elucidated. The magnetization reversal of a Co-Fe$_3$O$_4$ nanowire has been simulated using 	extsc{mumax}$^3$, varying its core diameter, as well as the nanowire length, in order to provide a complete description of the system and to suggest the optimal particle composition and dimensions. A state of zero-remanence at near-zero magnetic field has been found, in which the magnetization of the core and shell have an anti-parallel alignment along its axis, resulting in a particle with no stray field distribution. A novel multi-step approach for the fabrication of core-shell nanowires with several external shells, tunable geometrical parameters (nanometer precision), and a variety of possible materials has been introduced and proved to be an efficient method for the production of Co-Fe$_3$O$_4$ core-shell nanowires. The approach is based on a combination of the ion-track template-method in electrochemistry, plasma etching, and molecular beam epitaxy.

1.2 Outline of the Dissertation

This dissertation is organized in the following way: in chap. 2 a description of the fundamental micromagnetic energies, influencing the magnetic behavior of ferromagnets, in particular for the case of core-shell cylindrical structures, is discussed. In chap. 3, the experimental techniques used for the fabrication and characterization of core-shell micro- and nanowires are presented. First, a brief introduction to electrochemistry, its basic concepts, as well as the used electrodeposition cells, are discussed. After this, the working principle of the techniques, used for the structural and compositional characterization, i.e., a description of the working principles of scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), and electron energy loss spectroscopy (EELS), as well as for the magnetic characterization, i.e., electron holography (EH) for nanowires and vibrating sample magnetometry (VSM) for microwires, is described. The next three chapters are dedicated to the sample fabrication and the results of the investigation: (i) in chap. 4 the fabrication and characterization of coaxial microwires; (ii) in chap. 5 micromagnetic simulations of core-shell nanowires; and (iii) in chap. 6 the development of an approach for the fabrication of short
core-shell nanowires and their characterization.

Chap. 4 is an experimental chapter, in which a description of partially covered and fully covered coaxial microwires fabrication is given, followed by the description of their magnetic properties at room temperature (chap. 4.3.1) and in the high-temperature range, i.e., 295 – 1200 K (chap. 4.3.2), acquired by VSM.

Chap. 5 and chap. 6 are dedicated to core-shell nanowires. Chap. 5 is an entirely theoretical chapter, in which the results of micromagnetic simulations performed using mumax³ are presented. Here micromagnetic simulations are used as a tool to predict and tailor the magnetic behavior of the core-shell nanowires to determine the geometrical dimensions and materials that will be used for their posterior fabrication. Moreover, it is shown that a 360° domain wall can be induced by the core on the external shell of the coaxial nanowire.

In chap. 6, the 8-step approach for the fabrication of core-shell nanowires with several external shells, combining electrochemistry, plasma etching, and molecular beam epitaxy (MBE) is introduced. A detailed description of each step is provided. This method offers a unique possibility for the fabrication of ferromagnetic multishell nanowires and nanorods with selected dimensions and materials.

To close this work, I summarize in chap. 7 the main results presented in this thesis.
Micromagnetic energies and magnetic anisotropy

...one can still say that quantum mechanics is the key to understanding magnetism. When one enters the first room with this key there are unexpected rooms beyond, but it is always the master key that unlocks each door.

— J.H. Van Vleck

Nanomagnetism is the branch of magnetism (a field in physics), dedicated to the study of low-dimensional systems, nano- and microscale magnetic objects, for which at least one of the dimensions falls between 1 nm and 1 µm. Their magnetic behavior, magnetic ordering, and remagnetization mechanism may differ from the bulk. While at the atomic level, the magnetism and magnetic effects can be described by the overlap of electron wave functions, at the nanoscale the prediction of the magnetic behavior of the nanostructure becomes a challenge. The number of atoms in the nanostructure volume is high enough to neglect some quantum effects, giving the possibility to introduce micromagnetism as a fundamental tool, as an indispensable theory for the fundamental understanding and analysis of the nanostructure magnetic behavior. "Micromagnetism as a continuum theory closes the gap between quantum theory, dealing with atomic scales, and the Maxwell theory, dealing with macroscopic dimensions" [41].

Since the subject of the present thesis is the fabrication and investigation of core-shell micro- and nanowires with dimensions of the order 50 – 100 nm and 20 – 40 µm, respectively, it is necessary to first understand the micromagnetic energies and magnetic anisotropy governing their behavior. Some specific aspects of magnetization textures arising for cylindrical geometries will be outlined as well. I want to note that, for the simplicity of understanding, a revision of state of the art for each studied nanostructure as well the details on the magnetic state and remagnetization mechanism governing the respective structure, are made at the beginning of the respective chapter, in which they are addressed.

The most favorable state of a ferromagnetic material is determined by the different micromagnetic energy contributions. The equilibrium state of a ferromagnet is given
by the minimization of the total free energy, which is determined by the sum of the
different energy contributions:

\[ E_{\text{total}} = E_{\text{ex}} + E_{\text{mc}} + E_{\text{ms}} + E_{\text{me}} + E_z, \]  

(2.1)

where \( E_{\text{ex}}, E_{\text{mc}}, E_{\text{ms}} \) are the exchange, magnetocrystalline and magnetostatic
(demagnetizing) anisotropy energies, respectively; \( E_{\text{me}} \) is the magnetoelastic energy,
associated with the applied stresses and magnetostriction; \( E_z \) is the Zeeman energy
associated with the magnetic moment response to the applied external magnetic
field.

2.1 Zeeman energy

The Zeeman energy \( E_z \) is determined by the interaction between the magnetic
moments of the sample and the applied external magnetic field, and reflects the
influence of this field on the resulting magnetization. This energy is determined
as:

\[ E_z = -\mu_0 \int_V M H dV. \]  

(2.2)

Here the magnetization is defined like \( M = n \mu_m \) with \( n = N_{\text{at}} / V \), where \( \mu_m \) is the
magnetic moment per atom and \( N_{\text{at}} \) is the number of atoms. The detailed calculation
of the Zeeman energy can be found in [42]. The Zeeman energy has its minimum
when the magnetization is parallel to the external field and vice versa.

2.2 Exchange energy

The Heisenberg exchange interaction gives rise to the origin of ferromagnetism [43–
45]. It is a short-range interaction of quantum origin, resulting from the exchange
coupling between neighboring electrons with overlapping wave functions. For two
neighboring atoms \( i \) and \( j \), with spin angular momentum \( \vec{S}_i \), and \( \vec{S}_j \), the exchange
energy can be expressed as [46]:

\[ E_{\text{ex}} = -2J_{ij}\vec{S}_i\vec{S}_j, \]  

(2.3)

where \( J_{ij} \) is the exchange integral, which represents the coupling between the
two atomic moments of the atoms. The exchange energy is the energy difference
between a state with parallel and anti-parallel spin alignment. This energy has
its minimum value when \( \vec{S}_i \) and \( \vec{S}_j \) are parallel with \( J_{ij} > 0 \), i.e., for the case of a
ferromagnet, or antiparallel with $J_{ij} < 0$, i.e., for the case of an antiferromagnet. Extending eq. 2.3 to the first-order neighbors the exchange energy takes the form:

$$E_{ex} = -J \sum_{ij} \vec{S}_i \cdot \vec{S}_j = -JS^2 \sum_{ij} \cos \Phi_{ij} \approx \frac{JS^2}{2} \sum_{ij} \Phi_{ij}^2,$$

(2.4)

where $\Phi_{ij}$ is the angle between the neighboring spins. In a ferromagnetic material this angle is always very small $|\Phi_{ij}| \ll 1$. It is possible to make a first order approximation and remain with the term dependent on the material magnetization. From the other side, introducing the unit vectors $\hat{m}_i$ and $\hat{m}_j$ which make a small angle, the following approximation can be used:

$$|\Phi_{ij}| \approx |\hat{m}_i - \hat{m}_j| \approx |(r_i \nabla) \hat{m}|,$$

(2.5)

where $r_i$ is the vector which unites the magnetic moments $i$ and $j$. Finally the energy of the the whole material/particle with $N$ atoms, can be expressed by the equation:

$$E_{ex} = \frac{JS^2}{2} \sum_{i=1}^{N} \sum_{S_i} \left[(r_i \nabla) \hat{m}\right]^2.$$

(2.6)

Thereby, the first summation runs over all atoms in the particle, and the second summation takes the exchange interaction of first-order neighbors of the atom $i$ into account. Exchanging the summation over all atoms $i$ with the integral over the whole volume $V$, one obtains an alternative representation of the total exchange energy of the material:

$$E_{ex} = A \int \left[(\nabla m_x)^2 + (\nabla m_y)^2 + (\nabla m_z)^2\right] dV,$$

(2.7)

where $A$ is the exchange stiffness constant or exchange constant, which depends on the atomic magnetic moment, the exchange integral and the crystalline structure of the material. The exchange stiffness constant is a measure of the exchange interaction forces acting to maintain the magnetic moments of the atoms parallel aligned. For the nearest-neighbor interaction in a single-element system the exchange stiffness can be expressed as [47, 48]:

$$A = \frac{JS^2}{a} \approx \frac{J}{ag^2} \frac{\mu_S^2}{\mu_B^2},$$

(2.8)

where $S$ is the spin moment, $\mu_S$ the spin magnetic moment, $g$ the spectroscopic splitting factor, and $a$ the lattice constant.
2.3 Magnetic anisotropy

If only exchange energy would exist, which is isotropic and therefore independent of the spatial coordinate system, a ferromagnetic material would not have a directional dependence. However, in reality, the magnetization direction in a ferromagnet depends on the crystallographic directions, as well as on the sample shape, induced stresses, magnetostriction, and annealing [45]. In general, three anisotropies determine the orientation of the magnetization of the material: magnetocrystalline, magnetostatic (or shape), and magnetoelastic (or stress) anisotropies.

Magnetocrystalline anisotropy.
The spin-orbit interaction, which couples the spin to the lattice, gives rise to the magnetocrystalline anisotropy [44]. When a magnetic field is applied along a certain direction, the material saturates at a lower field compared to other directions. This is presented in Fig. 2.1 exemplarily for $Fe_{bcc}$, $Ni_{fcc}$ and $Co_{hcp}$. The directions determined by the crystal symmetry, along which the magnetization saturates at the lowest field are called easy magnetization directions, while the ones along which is the most difficult to magnetize the material and the highest magnetic field is required, are called hard magnetization directions. The intermediate, or medium magnetization direction is given for all the other crystallographic directions, where the magnetization is harder than for the easy, but easier than for the hard axis, yielding different intermediate magnetization curves between the two extreme cases [49].
The magnetocrystalline energy can be defined as the work done per unit volume by the magnetic field to magnetize a ferromagnetic material, which is stored in the crystal [45]:

$$E_{mc} = -\mu_0 \int_0^M \vec{H} \cdot d\vec{M}. \quad (2.9)$$

Experimentally the magnetocrystalline energy can be determined from the magnetization curve, by integrating the area of the $M(H)$ curve, for which the field has been applied along a selected crystallographic direction [45].

For cubic crystals (e.g. Fe and Ni), the magnetocrystalline energy can be expressed as a power series expansion of the directional cosines, $\alpha_1 = \cos a$, $\alpha_2 = \cos b$, $\alpha_3 = \cos c$ of the magnetization vector, i.e. the cosines of the angle $a$, $b$, and $c$ between the magnetization $\vec{M}$ and the principal axes $x$, $y$, and $z$ of the crystal, respectively [45]. Thus, the magnetocrystalline energy density for a cubic crystal, $E_{mc}^{cub}$, can be presented as:

$$E_{mc}^{cub} = K_0 + K_1 \left( \alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2 \right) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2 + \ldots, \quad (2.10)$$
where $K_0, K_1, K_2$ are the anisotropy coefficients (for more details see, e.g., [42, 45]). The higher-order terms are neglected, since they have a small contribution to $E^{\text{cub}}_{\text{mc}}$. In general, materials with a hexagonal crystalline structure (e.g. Co, cf. Fig. 2.1, right side) present the simplest case, since they have only one easy magnetization axis along their $c$ axis. The anisotropy in this case will be called *uniaxial anisotropy*. The magnetocrystalline energy can be expressed as a power series of the sines of the angle $\theta$ between the direction of magnetization and the $c$-axis. Thus, the magnetocrystalline energy density for a hexagonal crystal can be presented as:

$$E^{\text{uniaxial}}_{\text{mc}} = K_0 + K_u \sin^2 \theta + K_u^2 \sin^4 \theta + \ldots,$$

(2.11)

where $K_0, K_u, K_u^2$ are the uniaxial anisotropy coefficients. The higher-order terms can be neglected, since they have a small contribution to $E^{\text{uniaxial}}_{\text{mc}}$. 

**Magnetostatic anisotropy energy** or **Shape anisotropy energy**.

When a sample is magnetized, the material induces a magnetic field on itself, which has an opposite direction to the magnetization direction, named demagnetizing field, $H_d$. The demagnetizing field is determined by the sample shape as well as by the sample size. Consequently, during the magnetization of the sample, a work to overcome the influence of the demagnetizing field has to be done, named magnetostatic energy $E_{\text{ms}}$ (shape anisotropy energy, or demagnetizing anisotropy energy), expressed as [45, 50]:

$$E_{\text{ms}} = -\int M_s \mu_0 H_d \, dM.$$

(2.12)

The demagnetizing field can be expressed as:

$$H_d = -N_d \vec{M},$$

(2.13)
where $N_d$ is the demagnetizing factor, which depends on the sample shape. The demagnetizing factors for some simple shapes are listed in Tab. 2.1. To see the calculation of the demagnetizing factor in detail see [45]. Thus, the magnetostatic energy takes the form:

$$E_{ms} = -\int_0^{M_s} \mu_0 \vec{H}_d \, d\vec{M} = \int_0^{M_s} \mu_0 N_d \vec{M} \, d\vec{M} = \frac{1}{2} \mu_0 N_d M^2. \quad (2.14)$$

Since during the magnetization process of a sample its magnetic moments are the source of the demagnetizing field, as well as its object, the factor $1/2$ is used to eliminate the calculation the same magnetic moment twice (self-energy calculations).

### Tab. 2.1: Demagnetizing factors for simple geometries. Adapted from [51].

<table>
<thead>
<tr>
<th>Shape</th>
<th>Magnetization direction</th>
<th>$N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>any direction</td>
<td>1/3</td>
</tr>
<tr>
<td>Long needle</td>
<td>parallel to axis</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>perpendicular to axis</td>
<td>1/2</td>
</tr>
<tr>
<td>Thin film</td>
<td>in-plane</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>out-of-plane</td>
<td>1</td>
</tr>
<tr>
<td>General ellipsoid of revolution</td>
<td>$N_c = 1 - 2N_a$</td>
<td></td>
</tr>
</tbody>
</table>

With $N_c$ and $N_a$ being the demagnetization factors for the $c$ and $a$ axes.

The most energetically favorable state for a sample is the one in which its stray fields will be minimized. Thus, for thin films, this state takes place when the magnetization is in-plane, while for an ellipsoid it takes place when the magnetization is parallel to the ellipsoid symmetry axis (the same goes for cylinders).

Since in this work I fabricate and investigate short cylindrical microwires and nanowires (nanorods), a good approximation is the shape anisotropy equation for an ellipsoid from [52] and [43]:

$$E_{ms} = \frac{1}{2} \mu_0 M_S^2 V \left(1 + \frac{1 - ln[2\omega]}{\omega^2}\right), \quad (2.15)$$

where $\omega$ is the aspect ratio of the ellipsoid axes and $M_S$ is the saturation magnetization.

In this work I focus on multilayer systems, i.e., core-shell microwires and nanowire. The classic dipole-dipole energy between two magnetic moments $m_i$ and $m_j$
separated by a distance $r_{ij}$ is expressed by the equation:

$$E_{ij} = \frac{\mu_0}{4\pi} \frac{m_i m_j - 3(m_i \hat{n}_{ij})(m_j \hat{n}_{ij})}{r_{ij}^3},$$

(2.16)

where $\hat{n}_{ij}$ is the unitary vector, which unites both magnetic moments.

The magnetostatic energy between interacting magnetic systems with arbitrary geometry can be expressed analytically, based on the semi-classical approach introduced by Brown [53], by the equation:

$$E_{\text{mag}} = \sum_{i=1}^{N} E_{\text{dem}}(i) + \sum_{i=1}^{N-1} \sum_{J=i+1}^{N} E_{\text{int}}(i, j),$$

(2.17)

where the demagnetization energy of each system is

$$E_{\text{dem}}(i) = \frac{\mu_0}{2} \int M_i(r) \nabla U_{\text{dem},i}(r) dV,$$

(2.18)

and the magnetostatic interaction between them

$$E_{\text{ms}}(i, j) = \mu_0 \int M_i(r) \nabla U_{\text{dem},j}(r) dV.$$

(2.19)

**Domain formation**

In order to minimize the magnetostatic energy, the sample splits into magnetic domains, each of which has an opposite orientation of its magnetization [54]. In this way the magnetic charges generated by a certain domain will cancel out the magnetic charges generated by the adjacent domains, reducing the $E_{\text{dem}}$ [50, 55]. Fig. 2.2 shows a schematic representation of the domain formation.

The balance between the exchange energy and the demagnetization energy is responsible for the magnetic domain formation in a material. The formed domain structure, i.e., the size and shape of each domain, is determined by the magnetic parameters of the material (exchange constant, anisotropy constant, and saturation magnetization), the shape of the sample (demagnetizing factor), and the magnetic history of the material [56].

**Magnetoelastic anisotropy energy.**

The energy of a crystal, caused by the interaction between the magnetization of the material and the induced mechanical strain is called magnetoelastic energy (or magnetostriction) [45]. The magnetoelastic anisotropy reflects the influence of the variations of the distance between the atoms in the spin-orbit interaction. It has its origin in the coupling between the magnetostriction $\lambda_S$, and the stress induced on the material $\sigma$, and is described by the equation:

$$E_{\text{me}} = K_{\text{elast}} \int m_z^2 dV = \frac{3}{2} \lambda_S \sigma \sin^2 \theta,$$

(2.20)
Fig. 2.2: Schematic representation of the domain formation. From left to right: mono-domains, two-domains, 4-domains, and closed domains [57].

where $K_{\text{elast}}$ is the magnetoelastic anisotropy constant, which depends on the magnetostriction and the induced stresses, and $\theta$ presents the angle between the magnetization direction and the applied stress direction [45].
Magnetostriction is the fractional change in length of a ferromagnetic material under the effect of an applied magnetic field [58]. Since the magnetoelastic interaction is a long-range interaction, which arises as a result of the internal stresses induced (cf. chap. 4).

### 2.4 Magnetic interactions in multilayer systems with curved geometries

Generally, magnetic interactions are divided into two main groups: short-range interactions and long-range interactions. The following short range interactions can be distinguished:

1. tunneling exchange interaction, which is only relevant if the magnetic layers have a distance of a few nanometers between them [59];
2. direct exchange interaction, which takes place between ferromagnetic materials, which are in direct contact with each other [60];
3. indirect or Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interaction, which take place in ferromagnetic materials via conduction electrons in a dia- or paramagnetic intermediate medium [61, 62];
4. superexchange interactions, which takes place in ferromagnetic particles in an insulating matrix or in antiferromagnetic oxides.

All these interactions decrease as a function of the distance between the magnetic materials. For all the multilayer samples, investigated in this thesis, short-range
interactions are irrelevant, since the core and the shell are separated by a non-
ferromagnetic layer (several micrometers thick in the case of core-shell microwires,
and several nanometers in the case of core-shell nanowires). Thus, only the long-
range interactions will govern the magnetic behavior of the studied core-shell
systems, i.e., magnetostatic and magnetoelastic interactions, which have been
discussed in detail above.
The fabrication of the samples, presented in this thesis, is based on electrochemistry. The different electrochemical modes, used for the fabrication of ferromagnetic core-shell cylindrical structures at the micro- and nanoscale, consisting of two ferromagnetic phases separated by a non-ferromagnetic intermediate layer, are presented in this chapter. Thereby, the first part of the chapter is dedicated to electrochemistry as a tool for the electrodeposition of micro- and nanostructures (chap. 3.1), including the template electrodeposition of nanowires in chap. 3.1.1, the fundamentals of electrochemical deposition in chap. 3.1.2, and the used electrodeposition cells for galvanostatic and potentiostatic electrodeposition in chap. 3.1.3. The galvanostatic mode has been used during the fabrication of core-shell microwires to deposit the external ferromagnetic shell, while the potentiostatic mode has been used for the template-assisted fabrication of the core of the core-shell nanowires.

In the second part of the chapter, chap. 3.2, the structural and material characterization techniques are introduced and their working principle described.

3.1 Fabrication Techniques

3.1.1 Template electrodeposition of nanowires

Over the last 50 years, the interest in the fabrication of nanostructures has increased significantly. Initially, this interest was caused by two main reasons: first, the possibility of using the nanostructures as tools to study a wide range of phenomena [14, 15], and second, there is a wide variety of potential applications for nanostructures [1–8, 14, 16, 19–22].

One of the simplest nanostructures to consider is a nanowire. Several techniques are known for the fabrication of nanowires with small diameters (i.e., below 100 nm). The most well-known are lithographic methods, in which a thin film is patterned into the desired form [63–66], and template-based synthesis [67–69].

The nanowire synthesis is all about constraining the material growth material in two dimensions to a few nanometers and allowing its growth in the third dimension. An elegant way of achieving this constraint is using a template-based synthesis of nanomaterials [14, 67, 68]. Template-based synthesis of nanostructures is an elegant and precise approach to fabricate nanostructures, such as nanotubes and nanowires, which gives the possibility of tuning the size and length of the
nanostructures as desired via the suitable template thickness and pore size selection. As templates for template-based synthesis of nanostructures porous templates are used, which contain a large number of straight cylindrical holes with a narrow size distribution. According to the literature for most of the reported works, nuclear track-etched membranes are used as templates, i.e., mica films [70] and polycarbonate membranes (PC membranes) [67, 68], aluminum oxide membranes (AAO) [71, 72], nanochannel glass [73, 74] and mesoporous channel hosts [75–77]. Thereby, the most well-known and used are polycarbonate membranes and alumina oxide membranes, which are both commercially available [78, 79]. In this work, as a template for the fabrication of nanowires, PC membranes were selected. More details on the membrane itself and the reasons for selection will be given in chap. 6.2.1.

There is a wide variety of methods used for the growth of material from a solution inside of templates. Among these, the most well-known are electrochemical deposition [14, 67], electroless deposition [80, 81], electrophoretic deposition [82], polymerization reactions [83, 84], high-pressure injection of a melted material [85, 86], hydrothermal method [87, 88], metal amplification [89] and sol-gel [90, 91]. In this work, I focus on the electrochemical deposition of materials inside PC templates. Electrodeposition is a low cost and efficient method to produce nanostructures, with the possibility to tune the deposited material structural properties as well as its oxidation state and its length.

The electrochemical synthesis of nanowires inside templates as a method to fabricate single-metal nanowires was developed in 1970 by G. Possin [92]. He reported on the deposition of 400 Å thick nanowires inside of a track-etched 15 μm porous muscovite mica films by the method of P. B. Price and R. M. Walker [93], with a hole density of the order of 10^4/cm^2. Thereby the limit on the nanowire diameter was set not by the pore diameter, but by difficulties in the electrodeposition process. A big challenge was to minimize the diameter of the nanowires. After this, in 1983, W. O. William and N. Giordano [94] performed studies on the electrical conductivity of thin wires and refined Possin's technique to be able to produce smaller nanowires inside a mica film. William and Giordano developed a method to control the etching rate of the pores inside of the mica film, getting down to 80 Å in diameter with an etching rate of 0.16 Å/s at room temperature. The thickness of the mica film was 5 μm. The surface of the mica film was modified by a Cu wire, glued to each side of the mica film, to provide electrical contacts to the wires inside the pores and achieve a better growth of material. In this case, the nanowire's diameter was already determined by the pore diameter, not by difficulties in the electrodeposition process.

The conditions for the electrodeposition of nanowires with small dimensions are still a great challenge nowadays. The small pore diameter (and high aspect ratio of the pores) restrict the metal ions diffusion to the pore bottom during electrodeposition.
Besides, hydrogen reduction as a side product of the electrodeposition process results in bubbles, which obstruct the ion diffusion inside the pores. The viscosity and surface tension of the electrolyte is often an issue as well, since it can hinder the solution ions from reaching the bottom of the pores [95]. Thus, it is a technological challenge to synthesize nanowires with small diameters and length, i.e., with a small aspect ratio. Moreover, the coating of such nanowires with small aspect ratio with several shells presents a big difficulty [14]. Finding a solution to this problem and its implementation for coaxial nanorods fabrication has been one of the aims of this thesis.

### 3.1.2 Fundamentals of electrochemical deposition

The electrochemical synthesis of nanowires is a reduction-oxidation (redox) reaction, in which the ions from an electrolyte, i.e., an aqueous solution which contains metal ions, are reduced inside nanochannels under current on a conductive surface through the reversible chemical reaction of the type [67, 96]:

$$M_{aq}^{z+} + z \cdot e \leftrightarrow M_{solid}$$  \hspace{1cm} (3.1)

where $M_{aq}^{z+}$ is an ion with the charge $z+$. The term $M_{aq}^{z+}$ in (eq. 3.1) means that the metal ions in the electrolyte are charged positively, i.e., they are attracted to negatively charged surfaces. Electrons are provided from an external current source, inducing a potential. The chemical reaction, described by eq. 3.1, is characterized by an equilibrium potential, $E_{eq}$, at which the reaction is in equilibrium, and no material is deposited. For potentials below the equilibrium potential, the reaction taking place is a reduction: the positive ions bond with an electron from the negatively charged electrode, forming the growth of material. This process takes place on the surface of an electrode, called cathode or working electrode. For potentials above the equilibrium potential, an oxidation reaction takes place, leading to material dissolution. The oxidation reaction takes place on the anode or counter electrode. The anode is usually made from an inert material, which will not participate in the reaction, or from a material whose ions are already in the electrolyte, preventing possible contamination of the electrolyte.

The cathode and the anode are placed inside a solution named electrolyte. The electrolyte consists of a supporting electrolyte (a solution of not electroactive chemical species with a high ionic strength and conductivity) and the ions of the material desired for the deposition. In this work electrolytes on an aqueous basis will be used. In general, a third electrode is inserted during electrodeposition as a reference electrode, to ensure that the I vs. V response of the electrodeposition cell
will be measured only from the cathode.
As mentioned above, during electrodeposition, an electrical current is applied from an external source (a potentiostat) to form the potential difference between the cathode and the anode. This potential difference should provide energy, high enough to overcome the spontaneous tendency of the ions to remain as ions and start the reduction of material on the working electrode. The potentiostat controls the potential applied between the cathode and the reference electrode, ensuring that between the cathode and the anode, the required amount of current will be circulating. For more details see chap. 3.1.3.

Electrical double layer
When an electrode is placed inside an electrolyte (solid-liquid interface), a surface charge is created on the electrode surface, inducing an oppositely charged region in the adjacent electrolyte volume. This charge distribution on the solid-liquid interface is called electrical double layer (EDL) (see Fig. 3.1) [97]. There are several models to describe the EDL, which are well described in the literature, e.g. see for more detail [98, 99]). In Fig. 3.1 a schematics of the EDL is presented, according to the Gouy-Chapman-Stern model [67, 98]. Here, the EDL is divided into three layers: the inner Helmholtz plane (IHP), the outer Helmholtz plane (OHP), and the diffuse layer (DL).

![Schematics of the electrical double layer (EDL), according to the Gouy-Chapman-Stern model. The EDL is divided into the inner Helmholtz plane (IHP), the outer Helmholtz plane (OHP), and the diffuse layer (DL). Adapted from [99, 100].](image)

The area, close to the electrode surface, is called the inner Helmholtz plane, in which the not hydrated ions with the same charge, coions, are specifically adsorbed on the electrode surface. The bound hydrated and partially hydrated ions with an opposite
charge, counterions, remain at a certain distance, forming the Outer Helmholtz plane. The third layer is called the diffuse layer, which consists of mobile ions. Here, the ion concentration is equal to the ion concentration in the electrolyte volume. The EDL thickness depends on the ion electrolyte concentration, which has to be taken into account for electrodeposition in nanochannels. When the EDL has the same thickness as the diameter of the nanochannel, the local electrolyte distribution and velocity profiles can be influenced by the interaction with the EDL. Some problems may appear when the EDL thickness becomes bigger than the nanochannel diameter [101, 102], so the EDL from opposite walls will overlap causing a non-zero potential inside the pore (an increase of pore resistance and a decrease in electric conductance).

**Diffusion layer**

When a current is applied to the working electrode, the ion concentration on its surface decreases, generating an ion gradient in the volume of the electrolyte, close to this electrode. This area is called the diffusion layer, schematically shown in see Fig. 3.2.

![Fig. 3.2: Schematics of the diffusion layer, including the processes involved in an electrochemical reaction, i.e., diffusion, adsorption and electron transfer. Adapted from [67, 100].](image)

For the electrodeposition to take place, the ions from the electrolyte must reach the cathode surface, be adsorbed on it, and react with the cathode through a reaction of electron transfer. The material, ones reduced can be incorporated to the surface of the cathode or can be dissolved and diffused back to the electrolyte volume. Thus, there are two continuous and simultaneous processes involved in the electrodeposition, mass transport, and electron transport. The slower of these
processes will be the process that will limit the reaction. To be able to understand the reactions occurring during the electrodeposition process, it is necessary to first understand the reaction of electron transfer and the ion transport processes.

**Electron transfer**

When a metal is inserted in an electrolyte, containing the same ions as the introduced metal, the atoms on the metal surface hydrate and dissolve. In the same way, the ions from the solution are deposited on the metal surface. The potential for which the rate of these two reactions is the same is called equilibrium potential. The relation between the chemical species undergoing reduction/oxidation and the equilibrium potential is describe by the Nernst equation [99]:

$$E_{eq} = E^0 + \frac{RT}{nF} \ln \frac{a_O}{a_R},$$

(3.2)

where $E^0$ is the standard potential (equilibrium potential value, when all the reagents and products have the same activity equal to "1", $R$ is the gas constant (8.3145 $J\text{mol}^{-1} \text{K}^{-1}$), $T$ is the temperature, $n$ is the number of the transferred electrons, $F$ is the Faraday constant (96485.3 $C\text{mol}^{-1}$), $a_O$ and $a_R$ are the concentrations of the oxidized and reduced material, respectively. It is not possible to experimentally measure an absolute value of the potential, but a potential difference. That is why it is necessary to have a reliable reference electrode, towards which the potentials can be measured. Conventionally, as a reference potential $E^0 = 0.000 \text{V}$, the potential of the standard hydrogen electrode (SHE) is taken. The chemical species with positive values of $E_0$ are reduced more easily, while the ones with a negative $E_0$ value are oxidized.

**Hydrogen evolution reaction**

The hydrogen evolution reaction (HER) arises as a result of the reduction of protons or water at the electrode interface [103]. HER is one of the most important reactions in aqueous electrolytes, since it takes place simultaneously with the electrodeposition of metal for most of the deposition potentials. Consequently, HER reaction may have some negative effects on the electrodeposition process, lowering the efficiency of the reaction, or partially blocking the electrode surface with hydrogen $H_2$ bubbles resulting from the HER. Due to the extra amount of protons at the cathode surface some changes in the pH value of the electrolyte may be induced near it, which will affect the equilibrium potential of the HER [103].

HER can occur from the reduction of protons, as well as from the reduction of water molecules, which are its two sources. For the HER to take place the availability of free adsorption sites at the electrode surface for binding hydrogen is mandatory.
The reduction of protons takes place in the range of low overpotentials through a stepwise reaction [100, 104–106]:

\[
\begin{align*}
1. & \quad H^+ + e^- \rightarrow H_{ad}, \\
2a. & \quad H_{ad} + H_{ad} \rightarrow H_{2,ad}, \\
2b. & \quad H^+ + H_{ad} + e^- \rightarrow H_{2,ad}.
\end{align*}
\] (3.3)

During the first step (see eq. 3.3, 1.), named the **Volmer or discharge reaction**, the electrochemical reduction of aqueous protons \(H^+\) to atomic protons takes place, after which they get adsorbed on the cathode surface, \(H_{ad}\) [104, 105, 107]. During the second step, molecular hydrogen is formed as a result of a chemical (eq. 3.3, 2a) or electrochemical (eq. 3.3, 2b) reactions [103]. In the chemical reaction, named **Tafel or combination reaction**, two adsorbed atomic hydrogen diffuse through the cathode surface and combine to form molecular hydrogen \((H_2\) gas). In the electrochemical reaction, named the **Heyrovsky reaction**, a proton is reduced over an already adsorbed atomic hydrogen producing molecular hydrogen.

One of these reactions determines the HER rate [108]. If it is determined by the Volmer reaction, only a few \(H_{ad}\) will be desorbed on the cathode surface. If one of the second-step reactions is determining, then the cathode surface will be partially occupied by the \(H_{ad}\). As the overpotential increases, the reduction of water molecules starts to have importance. This can be expressed by the equation:

\[
3. H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-.
\] (3.4)

The potential, calculated by the Nernst equation, is the **equilibrium potential**. In order to get the desired reduction of material at an appropriate rate, its necessary to apply an additional potential called **overpotential**:

\[
\eta = E - E_{eq},
\] (3.5)

where \(E\) is the real electrode potential and \(E_{eq}\) is the equilibrium potential.

When a negative potential is applied, the energy of the electrons is increased, so they gain enough energy to be excited to the vacant states of the electrolyte ions. Therefore a flow of electrons from the electrode to the electrolyte will take place, generating a reduction current. The concentrations \(a_O\) and \(a_R\) will vary to satisfy the Nernst equation. The current, generated on the electrode after applying a potential can be described by the Butler-Volmer equation [99]:

\[
i = i_0(e^{\alpha_A f \eta} - e^{-\alpha_C f \eta}),
\] (3.6)

where \(\eta\) is the overpotential, \(\alpha_A\) and \(\alpha_C\) are the transfer coefficients for the anodic and cathodic reactions respectively, constants with values between 0 and 1 (usually estimated to be equal to 0.5) and \(f = nF/RT\). This equation describes the kinetics
of the reaction in a general way, taking away the restrictions of considering only equilibrium reactions [100].

It is more common to use the limit form of this equation, named Tafel equation, which for high values of $\eta$, very negative potentials in cathodic reactions, takes the form:

$$\log|i| = \log|i_0| - \frac{\alpha n F}{2.3 R T} \eta. \quad (3.7)$$

And for very low values of $\eta$ the equation takes the form:

$$i = i_0 - \frac{n F}{R T} \eta. \quad (3.8)$$

Mass transport

In electrochemical systems, it is necessary to consider four types of mass transport [67, 99, 100]:

1. **Migration.** Migration is the movement of species with electrical charge due to an electrical potential gradient (Fig. 3.3, middle panel). In order to make this mechanism not relevant and negligible for the species involved in the reduction reaction and deposited on the substrate (the electroactive species), reagents are introduced in the electrolyte, which act as a support shielding the electrical field.

2. **Convection.** The convection is the movement of the species due to mechanical forces (Fig. 3.3, lower panel). It can be neglected in the case of an electrochemical reaction without stirring. If stirring is required, it is recommended to choose a system, in which the mass current can be defined.

The experiments addressed in this thesis were performed without mechanical agitation, but with the stirring provided by nitrogen bubbling.

3. **Diffusion.** Diffusion is the movement of the species due to a concentration gradient (Fig. 3.3, upper panel). When a reaction takes place on the cathode, the ion concentration on its surface decreases, becoming lower than the one in the electrolyte volume. As a consequence, an area in the electrolyte is created, in which the ion concentration varies. This area is called *diffusion layer*. In most of the experiments, the thickness of this layer increases with the time until it reaches a stationary value. Diffusion is the most important ion movement mechanism in the electrochemical processes, and it plays a significant role in the deposited material properties.

In the absence of migration and convection, the equations describing the mass transport are the Fick equations [99]. Assuming that the diffusion is linear, perpendicular to an infinite plane, from Fick’s second law, the mass transport can be described by:

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i. \quad (3.9)$$
The limiting current, which is by definition potential-independent, can be defined as:

\[ i_l = \frac{nFSDC}{\delta}, \]  

(3.10)

where \( S \) is the electrode area, \( D \) is the diffusion coefficient and \( \delta \) is the diffusion layer thickness. If the mass transfer is governed by diffusion, \( \delta = \sqrt{Dt\pi} \), the current will decrease over time, giving place to the Cottrell equation:

\[ i(t) = \frac{nFSDC}{\sqrt{Dt\pi}} = \frac{nFSD^{1/2}C}{\sqrt{t^{1/2}\pi^{1/2}}}. \]  

(3.11)

4. Adsorption. All the mechanisms taking place on the electrode surface affect the kinetics of the reaction as well, as it is the case of the species adsorption on the electrode surface. There are two different types of adsorption: the not specified adsorption, based on electrostatic forces, and the specified adsorption, based on a strong interaction between the electrode and the adsorbed species. Adsorption is a process, in which different species from the system compete with each other to occupy the free space on the surface. The adsorption plays an important role in the electrodeposition process when the adsorbate is the electroactive species, i.e., the one that exchanges electrons, or the end product. Moreover, the adsorption of
species that are not directly involved in the electron transfer play as well a crucial role, since it changes the reaction speed as well as the morphology of the end product. The adsorption of this type of species will decrease the redox reaction kinetics due to a reduction of the electrode area, and the electron transfer from the electroactive species must be performed at a higher distance. Nevertheless, in some cases, this adsorbed species may act as catalysts [100].

3.1.3 Electrodeposition cells for galvanostatic and potentiostatic electrodeposition

There are two modes of electrochemical deposition, namely galvanostatic and potentiostatic modes. During *galvanostatic electrodeposition*, the current density between the cathode and anode is maintained at a constant value. This deposition mode is the easiest one. Galvanostatic electrodeposition was used in this work to fabricate the external shell of the core-shell microwires (chap. 4).

During *potentiostatic electrodeposition*, the potential between the working electrode and the reference electrode is maintained at a constant value, and the current density between the cathode and anode is recorded as a function of time. This type of deposition was used in this work for the template-based fabrication of core-shell nanowires (chap. 6).

**Galvanostatic Electrodeposition**

During galvanostatic electrodeposition mode, a galvanostat will generate the current towards the working electrode, i.e., the sample. The disadvantage of this method is that the potential between the electrodes changes as the material is deposited on the cathode, and with it, the composition of the deposited material varies. That is why this method is suitable for short depositions, in order to provide the homogeneity of the deposited material. For galvanostatic electrodeposition, a two-electrode electrodeposition cell is used. This cell was designed and assembled specially for the electrodeposition of external shells on microwires in the group of M. Vazquez [109]. A schematic representation of the cell is shown in Fig. 3.4. The setup consists of a working electrode (here the microwire covered with a layer of Au) and a counter electrode (a Pt net, placed inside a supporting Teflon cylinder, surrounding the microwire). The geometry of the counter electrode has been chosen in such a way that the counter electrode is placed along the microwire, providing a homogeneous continuous growth of material around the microwire axis. A potentiostat-galvanostat Amel Instruments 2053 [110] was used to control the current density. The working and the counter electrodes are placed inside a Pyrex
beaker containing the electrolyte. The beaker plays the role of the electrolytic cell. The beaker volume can be varied depending on the amount of electrolyte required for the electrodeposition. The beaker is placed on a heater plate with a magnetic field, to provide magnetic stirring and temperature control.

![Schematic representation of the used two-electrode electrodeposition setup.](image)

**Fig. 3.4:** Schematic representation of the used two-electrode electrodeposition setup.

For the electrodeposition of the microwire external shell, three different Watts-type electrolytes were used: Co [111], Co$_{90}$Ni$_{10}$ and Fe$_{20}$Ni$_{80}$ [112, 113] electrolytes. **Co electrolyte:** CoSO$_4$·7H$_2$O (300 g/l), CoCl$_2$·6H$_2$O (45 g/l), H$_3$BO$_3$ (45 g/l) were prepared in distilled water. The pH of the electrolyte is adjusted to be equal to 4.3 with a 1 M potassium hydroxide solution (KOH). The electrolyte must be stirred for 1 h at \(T = 25 – 30 \degree C\). During the electrodeposition, the current density is kept on \(j = 12 \text{ mA/cm}^2\) at room temperature.

**Co$_{90}$Ni$_{10}$ electrolyte:** CoSO$_4$·7H$_2$O (150 g/l), NiSO$_4$·7H$_2$O (150 g/l), NiCl$_2$·6H$_2$O (22.5 g/l), CoCl$_2$·6H$_2$O (22.5 g/l), H$_3$BO$_3$ (45 g/l), prepared in distilled water. The electrolyte was stirred for 1 h at \(T = 35 – 40 \degree C\), and the pH was adjusted to be equal to 4.4 with a 1 M potassium hydroxide solution (KOH). These conditions were kept during the electrodeposition as well. The current density during deposition was kept on \(j = 12 \text{ mA/cm}^2\).

**Fe$_{20}$Ni$_{80}$ electrolyte:** FeSO$_4$·7H$_2$O (8 g/l), NiSO$_4$·6H$_2$O (125 g/l), NiCl$_2$·6H$_2$O (20 g/l), H$_3$BO$_3$ (40 g/l), C$_7$H$_5$NO$_3$S (6 g/l), prepared in distilled water. The pH of the electrolyte must be adjusted to be between 2 and 2.8 with 1 M potassium hydroxide solution (KOH). The electrolyte must be stirred for 1 h at \(T = 35 – 40 \degree C\). The electrodeposition is performed at \(T = 55 \degree C\). The current density during deposition was kept on \(j = 12 \text{ mA/cm}^2\).

In all the used electrolytes, boric acid, H$_3$BO$_3$, was used as a supporting electrolyte. Sulfuric acid, potassium hydroxide or sodium hydroxide were used to adjust the pH level of the electrolytes to the desired one.
Potentiostatic Electrodeposition

For the electrodeposition of nanowires, a homemade three-electrode electrodeposition setup was built. In Fig. 3.5 a schematic of the electrodeposition setup is shown. It consists of a working electrode, a reference electrode, and a counter (auxiliary) electrode. The voltage is applied between the working electrode and the counter electrode. In the case of a three-electrode electrodeposition setup, the use of a potentiostat is required to control the potential applied to a working electrode relative to the reference electrode, and to measure the current flowing between the working electrode (WE) and the counter electrode (CE). An Amel 2049 Potentiostat [114] have been used in this work. The voltage on the potentiostat is adjusted to maintain the targeted potential at the working electrode with respect to the reference electrode. The resulting current flowing to the working electrode is measured with the multimeter 2 (ammeter) and recalculated.

The working electrode was an Au film (thickness from 500 nm to 700 nm depending on the pore diameter) deposited on the surface of the polycarbonate membrane. The counter electrode was made out of a Pt wire in the shape of a net. The shape and size of the counter electrode in relation to the working electrode is an important criterion. The area of the counter electrode has to be comparable to the area of the working electrode and placed right above it, symmetrically and parallel, so that the potential and the current density over its surface are constant, and no gradient is generated. The most common reference electrodes are the Saturated Calomel Electrode (SCE) and Silver/Silver Chloride Electrode (Ag/AgCl) electrodes. The SCE electrodes consist of mercurous chloride (Hg$_2$Cl$_2$, calomel) in contact with mercury metal. To minimize the work with mercury-based equipment, an Ag/AgCl was selected for this work.

The electrodes are placed as close as possible to each other inside of the electrolyte, minimizing the solution resistance, without interfering with the current paths between them. It is important to place the reference electrode as close as possible to the working electrode, as the solution resistance between them could lead to an error in the measured potential between the working electrode and the reference electrode The potentiostat can electronically compensate the resistance between the working and the counter electrodes, but it is not able to do this for the resistance between the working and the reference electrodes. It is also necessary to take into account, that the reference electrode should not be kept inside of the electrolyte for a long time. After every deposition the reference electrode was taken out of the electrolyte, washed with milliQ water and kept inside of a saturated potassium chloride solution (KCl), i.e., a KCl solution between 3.5 M and 4.2 M. Otherwise, small amounts of the reference electrode components, such as Ag$^+$ may leak into the electrolyte, causing undesirable reactions. The inverse situation is also possible, when the ions from the electrolyte penetrate through the reference electrode capillary.
For the electrodepositions performed in this thesis (chap. 6), it was necessary that the oxygen dissolved in the electrolyte is removed from the cell. The oxygen is electrochemically active in the cathodic potential range, and reacts with the reduced material. This can lead to the electrodeposition of undesired metal oxides. To avoid this and remove the oxygen from the electrolyte, inert gas is used for deoxygenation. Here, the solution is rinsed with an abundant amount of Nitrogen for 10 minutes before the electrodeposition (for each 100 mL of electrolyte). After this, the cell is covered with Alumina foil, and a nitrogen flow at a low rate is maintained over the solution during the experiment, creating an inert gas "blanket" over it.

![Diagram](image)

**Fig. 3.5:** Schematic representation of the used home-built three-electrode electrodeposition setup.

### 3.1.4 Understanding Cyclic Voltammetry and Chronoamperometry

In this thesis, the properties of the deposited material are characterized and controlled using cyclic voltammetry and chronoamperometry. These techniques are electroactive species selective, high-sensitive, and provide quantitative as well as qualitative information about the redox process. Moreover, it is a cheap and portable technology.
Cyclic Voltammetry

Before proceeding with the electrodeposition of a material, it is necessary to learn how the ions of the material behave when a potential is applied. To start, the potential of the working electrode is changed with the time at a constant sweep rate, and the current flowing through the voltammetric cell is recorded. This type of measurement is called voltammetry. If the potential varies from $E_1$ to $E_2$ the voltammetry is called linear sweep voltammetry, while if the potential goes as well in the opposite direction back to $E_1$, then the voltammetry is called cyclic voltammetry. In the case of the cyclic voltammetry, it is possible to study not only the reduction on the cathode but as well the oxidation. The most amount of information is possible to get from the cyclic voltammetry. In Fig. 3.6, the schematics of typical graphs related to cyclic voltammetry are shown.

**Fig. 3.6:** A cyclovoltammogram for a reversible reaction. The triangular potential (upper panel), during which the cyclic voltammogram (lower panel) is recorded. $E_{pa}$ and $E_{pc}$ are the potentials at which the maximums of the current are registered for the anodic and cathodic reactions, respectively. Adapted from [99, 100, 115]
In Fig. 3.6 (upper panel) the potential variation is shown over time, a triangular potential, during which the cyclic voltammogram is recorded Fig. 3.6 (lower panel). The scan starts from the left, at $E_1$, where no current is flowing (point a). As the potential becomes more reductive, the current starts to flow, i.e., the oxidation of the ions starts (point b), reaching a maximum value (point c) at the potential $E_{pa}$. After the maximum, the current starts to decay, related to the lack of ions at the electrode surface due to limited time to refill the ions by diffusion from the bulk electrolyte, i.e., diffusion-limited current. (because the diffusion is not enough to compensate the ion consumption). The current decay follows the behavior predicted by the Cottrell equation (eq. 3.11). At point d, which corresponds to the potential $E_2$ the potential is reversed. The oxidation of ions continues until point e, i.e., the current remain anodic. At point e, the reduction of ions starts, reaching a maximum value at point f at a potential $E_{pc}$. After this, the current decrease again due to the fading of ions at the working electrode surface, ending at point g at a potential $E_1$. The low current value at this point is related to capacitive current.

In the case of a reversible redox system, the anodic and the cathodic current peaks are equal, shifting their positions as the reversibility reduces [99, 100, 115]. The mass transport during a cyclovoltammogram is governed by diffusion. The intensity of the peaks depends on the scan sweep rate [115]. For reversible reactions with a fast electron transfer, the intensity of the peak varies like the square root of the velocity. More details about the theory behind cyclovoltammetry and the different effects that can be observed can be found elsewhere [116, 117]. As an example, cyclic voltammetry is thoroughly described in chap. 6.2.3 for the deposition of Co nanowires.

**Chronoamperometry**

Chronoamperometry is a technique in which the current between the cathode and the anode is recorded as a function of the time at a fixed applied potential. The recorded curve is called potentiostatic curve.

During the experiment, the potential of the working electrode is changed from $E_1$, at which no deposition or dissolution of material occurs, to $E_2$, at which the redox reaction is so fast, that the concentration of electroactive species at the working electrode surface becomes very low, nearly zero. As a consequence, this sudden increase in the potential creates a gradient of the electrolyte concentration at the working electrode surface. If the electrolyte is not stirred, the mass transport of the electrodeposition process is controlled by diffusion. Under these conditions, a flux of electroactive species flows from the bulk electrolyte towards the working electrode, where the redox reaction quickly occurs. The electroactive species flux is proportional to the concentration gradient at the electrode surface. When the potential is changed from $E_1$ to $E_2$, the current value is very large. With the decrease
of the electroactive species due to the concentration gradient at the electrode surface, the diffusion-limited current decreases as well. At a planar electrode in an electrolyte with no stirring, i.e., the mass transport entirely controlled by diffusion, the recorded current is given by the Cottrell equation (eq. 3.11).

In Fig. 3.7 it is possible to see that the current decays like $t^{-1/2}$ (curve a). However,

![Graph](image)

**Fig. 3.7:** Chronoamperometry: potential-time waveform (upper panel), potentiostatic curves (lower panel). Adapted from [99, 100, 115]

when the potential $E_2$ is not high enough, the current will have the form of the curve c), since the concentration of electroactive species almost does not change at the working electrode surface. The system can be considered to be in a stationary state. For the intermediary case, the potentiostatic curve takes the shape of curve b), when the system is under mixed control. This means that the diffusion rate and the electron transfer are comparable. Chronoamperometry is usually used to study the electrodeposition mechanism.
3.1.5 Conclusions

Electrochemistry offers a variety of techniques, which allow the fabrication of novel micro- and nanomaterials in a controllable way. The nucleation and growth of the nanostructure are monitored in situ by current-time curves. A detailed analysis of these curves allows to determine the thickness of the deposited material, the deposition rate, as well as the modes of growth. Electrochemical deposition allows the deposition of a wide range of thicknesses, ranging from Angstroem to micrometer, and to tailor the deposited material properties through the adjustment of the solution concentration, pH, temperature, and deposition potential. Moreover, the advantages of electrodeposition are the reversibility of the electrodeposition reaction. It is possible to determine the thickness of the deposited material very precisely (down to 0.1 ML [118]), once it is dissolved in the same solution from which was deposited. The reversibility allows to dissolve the electrodeposited material and recover the substrate in the initial state (shown and explained in chap. 6.2.3 below). The co-deposition of two metals (formation of an alloy) and the deposition of several materials from one electrolyte (layer deposition) are also possible, but will not be discussed here. The investigation performed within this dissertation has been limited to the study of the magnetic and structural properties of coaxial nanowires of Co, CoO$_x$, and Fe, deposited inside a PC membrane.

3.2 Structural and material characterization techniques

3.2.1 Scanning electron microscopy

The scanning electron microscope (SEM) is a versatile tool that allows to get different information about the surface of the sample [119–121]. A simplified diagram of an SEM is represented in Fig. 3.8 and consists of a source of electrons, a column with electromagnetic lenses, an electron detector, a sample chamber, and a computer. The electrons are produced in the electron source (electron gun) at the top of the column and accelerated down the column. The electrons pass through a series of condenser lenses and apertures to generate a focused, high-energy electron beam, that will be focused on the sample surface. After the electron beam is focused, its position can be controlled by the deflection coils (or scanning coils) to scan the beam over the sample surface, obtaining information about a defined area of the sample surface. This type of microscopy is called scanning electron microscopy. As a
source of electrons in the SEM are commonly used:

- Tungsten filament, a tungsten wire with an inverted V-shape, 100 μm long (the most basic);
- Thermionic emission gun, a single-crystal of lanthanum hexaboride, LaB$_6$, or cerium hexaboride, CeB$_6$. This source has the highest brightness. Different thermionic sources show different performances;
- field emission gun, a tungsten wire with a sharp tip, 100 nm thickness or less. Advantages: thanks to the sharp tip, it’s possible to get a better focusing ability and emission.

When the high-energy electrons from the gun interact with the sample surface, secondary electrons, backscattered electrons, and characteristic X-rays are produced, coming from different penetration depths [124] (Fig. 3.9). The generated signals reveal information about the chemical composition of the sample, its crystalline structure, and surface topography. The penetration depth of the electron beam depends on the acceleration voltage and the density of the sample. Primarily, in the SEM are detected two types of electrons, secondary electrons (SE) and backscattered electrons (BSE), which are the most used to generate an SEM image.

The backscattered electrons are generated as a result of elastic interactions between the electrons from the electron beam with the atoms from the sample. The

![Fig. 3.8: Schematic representation of a scanning electron microscope. Adapted from [122] [123].](image)
Fig. 3.9: Schematic representation of the electron beam penetrating the sample and generated radiations. [123]

backscattered electrons have higher energy than secondary electrons, which can be understood due to the following analogy. Imagine a billiard game with a mixture of Snooker, English, American, and Russian billiard balls (different sizes). When the small balls (electrons) hit the bigger balls (atoms), the bigger balls scatter more small balls. The same happens with particles, a bigger particle will scatter more electrons back towards the detector, than small light particles, producing a higher signal, and therefore appearing brighter in the SEM image. The amount of electrons, backscattered to the detector, is proportional to the atomic number (Z number). Thus, giving information about the composition of the sample, due to different contrast from different materials. Furthermore, the backscattered electrons are useful for the investigation of the sample topography, and crystallography.

All the SEM images were acquired using an SEM LEO 1530 from the group of M. Farle [125], which is shown in Fig. 3.10.

Fig. 3.10: Picture of the used SEM LEO 1530 from the group of M. Farle [125].
3.2.2 Transmission electron microscopy

Nowadays, transmission electron microscopy (TEM) is one of the most efficient techniques for the characterization of nanomaterials, allowing structural analysis at the nanoscale through high-resolution (better than 0.2 nm) and high magnification imaging (up to 100 000 000 times) [126]. The investigated sample should be less than 100 nm thick [126, 127]. TEM provides structural information about the sample, through the investigation of periodic structures, like a crystalline structure, orientation of the crystallographic planes, using the diffraction of electrons (diffraction patterns), as well as chemical composition analysis from features down to a 1 nm size [126, 128–131].

![Schematic representation of a transmission electron microscope. Adapted from [132, 133].](image)

The electrons are created in the electron gun and accelerated towards the anode down the column with an acceleration voltage from 60 kV to 300 kV. Similar to the SEM, the electron beam is focused by a set of condenser lenses and apertures, that will focus the electron beam on the sample. As a result of the interaction with the sample, the incident electron wave changes its initial state because of elastic and inelastic scattering. The scattered electron wave, after passing through the sample, is focused by the objective lens system, amplified by magnifying lenses, and finally produce an image.
For the investigation of the fabricated samples two TEM were used: a Philips TEM CM-12 from the group of M. Farle (Fig. 3.12, left side) for pre-characterization of the samples [125], and a JEOL JEM-2200FS from ICAN CENIDE (Fig. 3.12, right side) for more detailed structural and elemental analysis [134]. TEM JEOL was used as well for mapping and EELS studies.

![Fig. 3.12: Pictures of the used TEMs. Left side: a TEM CM-12 from the group of M. Farle [125]. Right side: a JEOL JEM-2200FS TEM from ICAN CENIDE [135].](image)

### 3.2.3 Energy dispersive X-ray spectroscopy

*Energy dispersive X-ray spectroscopy* (EDX) can be used to get information about the chemical composition of the sample as well as their relative elemental quantity and the distribution of the elements in the sample (*mapping*).

The EDX setup is usually integrated into a TEM, STEM or SEM. As mentioned above, high energy electrons are accelerated towards the sample. There is a probability that the incident electron inelastically interacts with an electron residing at lower energy levels of a sample atom transferring its energy, so both electrons have enough energy to scatter and leave the atom. This means the atom has now a vacancy in one of the electronic shells, and the atom is ionized. As a result, an electron from a higher energy level occupy the lower energy level and minimize its energy, releasing the energy difference in the form of X-ray radiation. An energy-dispersive spectrometer measures the number and energy of this X-rays radiation, registering a spectrum in which is shown the relative abundance of the X-rays versus their energy. Auger electrons are created instead of X-rays, when the energy difference between
the higher and lower energy levels is transferred to the neighboring electrons from a further outer shell, giving them enough energy to leave the atom, and can be used for Auger electron spectroscopy (which will not be discussed within the frames of this work).

The emitted X-rays are a characteristic of the energy difference between the two shells of a specific element, allowing an element specific analysis of the sample composition. It is possible to determine not only the elemental composition of a selected area on the sample but to determine the distribution of the elements along one chosen line (line scan) or a chosen area (mapping).

3.2.4 Electron energy loss spectroscopy

To determine the oxidation states of the fabricated nanowires electron energy loss spectroscopy (EELS) was used. EELS uses the energy distribution of high energy electrons (60 – 300 keV) after passing through a thin sample to give information about the atomic structure and chemical properties of a sample [136].

The electrons interact with the atoms of the sample as they pass through the sample. These interactions can be elastic or inelastic. The transmitted electrons are deflected by a magnetic prism at the end of the TEM column (Fig. 3.13) according to their energy and recorded by a CCD camera giving the EELS spectrum, an energy-loss spectrum presenting the amount of lost energy vs. the number of electrons that lost that specific amount of energy [137, 138].

In this thesis, a TEM JEOL JEM-2200FS [135] was used (Fig. 3.11, right side). In difference to EDX, which is so often used for chemical composition analysis in TEM as well as in SEM, EELS offers not only information about the chemical compositions but also about the sample thickness, electronic structure, oxidation state, etc. [138]. More information about the EELS spectrum and its analysis will be given in (chap. 6.3.2), in which EELS was used as a tool for the determination of the oxidation state of the different parts of the coaxial nanowires.
3.3 Magnetic characterization

3.3.1 Vibrating sample magnetometry

*Vibrating sample magnetometry (VSM)* was used to study the magnetic properties of the coaxial microwires. The broad measurement capability, the possibility of measuring bulk samples disregardless of their shape, the fast measurement speed and its high sensitivity \((5 \cdot 10^{-6} \text{ emu})\) makes the VSM a powerful tool for the measurements of the magnetic properties of materials \([139]\). The VSM allows to determine the magnetic moment of a sample as a function of the magnetic field at a constant temperature (Hysteresis loops) or as a function of temperature at a constant magnetic field. From hysteresis loops is possible to derive such information about the sample as the saturation magnetization, remanent magnetization, coercivity, and transition temperatures from the temperature measurements.

Fig. 3.14 presents a schematic representation of a VSM. The working principle is based on the Faradays law, according to which an electromotive force (EMF) is generated in a coil, when there is a change in magnetic flux through this coil. The sample is fixed on a quardz rod and introduced between the electromagnet coils. When a constant uniform magnetic field is applied, the sample is vibrated along the z axis, inducing a change in magnetic flux in the pick-up...
3.3.2 Off-axis electron holography

To image the stray field distribution of one single coaxial nanorod electron holography was used. Off-axis electron holography [141] is one of the most powerful techniques, which allows to image magnetic and electric stray fields of samples with nanometer spatial resolution. Moreover, is the only technique that enables the direct access to the phase shift of the electron wave after passing through the investigated sample. The phase shift is extracted from an interference fringe pattern, the hologram, which is created as the result of the interference of the object electron wave and the reference electron wave. The phase shift between the object and the reference electron waves gives to the fringes a periodicity. The phase shift is sensitive to variations in magnetic and electrostatic potentials, which allows to use the technique to get quantitative information about magnetic and electric fields of a sample. The intensity and contrast of the hologram depend on the amplitude and stability of the object electron wave [142, 143], i.e., a stable, high brightness, highly coherent electron source is required. In Fig. 3.15 a schematic representation of the typical TEM geometry for off-axis electron holography TEM mode is presented.
To record a hologram the sample region of interest is inserted in such a way, that it will cover half of the field of view. A biprism [145], which is typically a thin (diameter <1 µm) Au-coated quartz fiber or Pt wire, is used to create the overlap of the specimen electron wave (object wave), which has passed through the sample and the reference electron waves, creating an interference pattern [146–148]. This is possible, when a positive voltage is applied to the biprism, allowing it to act as a prism in optics, tilting the specimen wave "with respect" to the reference wave. If the electron source is coherent, an interference fringe pattern is formed, a hologram, in addition to a bright-field image of the sample. The respective position of the fringes and their intensity gives information about the phase shift and the amplitude of the specimen wave, available after a phase reconstruction process [143]. For the study of magnetic samples the process changes a little, since the magnetic state of the sample shall not be perturbated from the objective lens [131, 149]. Once the objective lens is off, providing magnetic-free conditions for the sample, a Lorenz lens is used to operate the microscope at high magnification. The objective lens can be used to apply an external magnetic field to the sample, exciting it to pre-calibrated values and tilting the sample.
Core-shell microwires

While the scope of this thesis mainly focuses on the fabrication and characterization of novel coaxial multilayer nanowires, this chapter has been dedicated to their predecessors, core-shell microwires. This type of systems has been investigated during the last two decades, and here I will focus on the magnetic response and the fundamental interactions governing this type of core-shell structures.

The chapter starts with chap. 4.1, an introduction to microwires and their outstanding magnetic properties and technological applications, based on a study of the existing literature on the topic, forming the current state of the art for single and bi-phase microwires.

Chap. 4.2 describes the methods, which I used for the fabrication of core-shell microwires, elucidating the possible ways of tuning the geometrical parameters and the composition of the core and shell. Here I introduce as well the partially covered microwires, which I fabricated for the very first time within the frames of this thesis.

Chap. 4.3 is dedicated to the investigation of the static magnetic properties of the fabricated microwires, carried out at room temperature (chap. 4.3.1) and in the temperature range from $T = 295\,\text{K}$ to $T = 1200\,\text{K}$ (chap. 4.3.2). Furthermore, the effect of the microwires geometry (partial or full shell), its thickness, and composition of the external shell on the magnetic properties of the multilayer system will be described. This part of the work aims to understand the magnetostatic and magnetoelastic interactions, which give rise to the outstanding magnetic properties of multilayer microwires.

The chapter ends with a summary of the experimentally achieved results as well as some concluding remarks and conclusions in chap. 4.4.
4.1 Introduction to core-shell microwires

Ferromagnetic amorphous materials are of big technological interest because of their exceptional magnetic behavior, which makes them suitable as sensing elements in numerous devices [150] and interesting for the study of fundamental micromagnetic problems (e.g., magnetization reversal modes [151]). The absence of crystallinity, i.e., their intrinsic atomic disorder, gives place to such fascinating magnetic effects, like single domain wall (DW) propagation, large Barkhausen discontinuity, giant magnetoimpedance (GMI) effect, almost non-hysteretic behavior, very high permeability and stress impedance [152].

The development of new magnetic materials with optimized, tunable/adjustable to the application properties is crucial for the evolution of technology and the development of new generation sensing devices. In 2004 the group of M. Vazquez purposed to deposit a ferromagnetic film on the amorphous microwires surface to obtain multifunctional materials with tunable magnetic properties for sensing technologies. It has been found that the external layer drastically modifies the magnetic behavior of the wire, making it possible to tune the magnetic properties as desired via the magnetostatic and magnetoelastic coupling between these two magnetic phases [153]. This type of multilayer microwires are usually named magnetically bi-phase microwires.

Multilayer microwires can be initially classified in two main groups: the ones with two magnetic layers in direct contact with each other (based on amorphous microwires with diameters about 100 – 120 µm, prepared by rapid quenching into rotating water (water-quenched amorphous microwires [154]) and the ones with two magnetic layers separated by a nonmagnetic spacer (based on amorphous glass-coated microwires with diameters from 2 µm to 20 µm, prepared by quenching and drawing technique [155]).

In this thesis, the focus has been kept on multilayer microwires with an insulating coating separating the two magnetic phases (see Fig. 4.1), i.e., microwires based on amorphous glass-coated microwires. Such microwires have several advantages: (i) it is possible to achieve smaller core diameter, (ii) they are more convenient for applications due to the insulation between the metallic layers and (iii) they display more interesting magnetic properties in terms of inter-layer magnetic coupling [14, 153].

Glass-coated amorphous microwires show typically small diameters (down to 1 µm) and the intermediate Pyrex glass microtube serves as a protection [150, 156], from corrosion and electrical viewpoints [152, 155]. In addition, the Pyrex glass separates the core from the shell, avoiding the exchange bias effect, which is observed in the case of water-quenched amorphous microwires, in such way that the interaction between the core and the shell becomes only magnetostatic and magnetoelastic.
Amorphous glass-coated microwires

Amorphous microwires were developed in 1924 by G. F. Taylor [157] and improved in 1960 by Ulitovsky [158], now glass-coated amorphous microwires (GCMWs), giving birth to the fabrication technique that is used till nowadays. The first study of their magnetic properties was published by L. Kraus et al. [159] and afterwards, amorphous microwires have been widely studied by J. Torrejon et al. [160].

Due to the absence of crystallinity (no magnetocrystalline anisotropy), their magnetic properties are defined by shape and magnetoelastic anisotropy. The latter is determined by the stresses of different origin induced during the fabrication process [161, 162]: (i) stress due to the drawing of the metal, (ii) stress due to the solidification process, and (iii) stress due to the difference in thermal expansion coefficients of the glass and the metal. The induced stress depends on the Pyrex thickness. The total internal stress couples with the magnetostriction determining the strength of the magnetoelastic anisotropy that governs the magnetic behavior of amorphous glass-coated microwires [163, 164].

Depending on the magnetostriction constant $\lambda_S$ value glass-coated amorphous microwires are divided into three groups:

1. **microwires with positive magnetostriction** $\lambda_S$, that is the case of FeSiB alloys. The domain structure of these microwires have a combined domain structure: the central part of the wire along its axis consists of a large single domain, covered by a radial domain structure pointing in and out the core domain [165, 166] like it is shown in **Fig. 4.2** (upper panel). On the ends of the microwire, small closure domains are generated to decrease the stray field [150]. The remagnetization process occurs in a single switching event between two stable remanent states with opposite axial magnetization, a large Barkhausen jump, via the depinning of a domain wall from the closure domain at one end, and its subsequent propagation along the whole microwire. This unique domain structure and magnetization process makes FeSiB microwires an ideal material to study fundamental micromagnetic processes, such as domain wall propagation even on big distances up to several meters [155, 167, 168].

**Fig. 4.1**: Schematics of a typical core-shell microwire and its constituent layers, respectively indicated on the SEM image of an FeSiB/CoNi microwire.
Fe-based microwires, $\lambda_s > 0$

CoFe-based microwires, $\lambda_s = 0$

Co-based microwires, $\lambda_s < 0$

**Fig. 4.2:** Schematic representation of the domain wall of glass-coated microwires with positive (upper panel), negative near vanishing (middle panel) and negative (bottom panel) magnetostriction constant with their correspondent hysteresis loops. Adapted from [166, 169].

The axial remagnetization process through a single large Barkhausen jump gives the hysteresis loop a perfect rectangular shape, so the magnetization can have only two values, positive or negative saturation magnetization, $\pm M_S$, making them interesting for such technological applications, as memory units for magnetic labels, e.g., [170], as well as for magnetoelastic based sensor applications based on the large magnetostriction constant [167].

2. *microwires with negative vanishing* $\lambda_s$, that is the case of FeCoSiB alloys. Their domain structure is combined as well: an axial domain along the center of the microwire is surrounded by circular domains [171, 172], shown in Fig. 4.2 (middle panel). The remagnetization process is determined by wall displacement in the internal region and by the rotation of the magnetic moments within the circular domains, always maintaining a small magnetized region along the microwire axis to reduce the exchange energy.
This type of wires are characterized by a reduced hysteresis loop with small coercivity and high initial permeability. Such a large initial permeability is very sensitive to external conditions, such as temperature, magnetic field, and mechanical stress. This sensitivity makes CoFeSiB wires very interesting for the development of miniaturized sensible sensors, especially for magnetic field sensors based on the giant magnetoimpedance (GMI) effect [173], which is one of the most perspective and widely investigated applications of GCMWs. Moreover, some theoretical investigations have been performed on the domain wall propagation in such wires [174].

3. **microwires with relatively high negative $\lambda_S$, which is the case of CoSiB alloys.** Their domain structure consists of circular domains, encircling the internal core of the microwire, see Fig. 4.2 (lower panel) [175]. The magnetization process in such microwires occurs via the reversible rotation of magnetic moments inside the circular domains. The magnetization of these microwires is proportional to the applied field, and the hysteresis loop is unhysteretic, making this type of wires interesting for the miniaturization of sensors and transformers [155, 167].

The above mentioned exceptional magnetic behavior (e.g., Barkhausen jump, nearly non-hysteretic behavior, GMI effect) make amorphous microwires suitable as sensing elements in diverse devices. For this reason, their magnetic properties have been extensively investigated. Over the years, many applications of GCMWs have been proposed and patented. Some of them are based on the magnetic bistability of FeSiB microwires, like the position sensor, the magnetic bar code reader [176, 177] or the position and velocity sensors, patented by M. Vazquez et al. [152, 176]. Some of them are based on the magnetoelastic behavior of magnetostrictive microwires, such as torsion sensors [176], or magnetoelastic pen for signature identification [178, 179], based on the fact that the stress, induced during writing in the sensing element of the pen, cause a series of voltage peaks which is unique for each person. Some of them use the GMI effect of microwires with vanishing magnetostriction for the detection of changes in different environments [180], such as the pressure/flux sensor [181], in which the stresses induced on a microwire by an airflow induce a change in the GMI properties of the materials, which can be directly related to the external stresses or the viscosity of the medium. The most significant industrial application of GCMWs was developed by the company Aichi Steel in the field of magnetic sensors [182], which are used in mobile phones from the brand Sharp. This company fabricates chips based on CMOS technology, in which is used the magnetoimpedance effect of CoFe microwires [183].

The study of amorphous microwires has been restricted mostly to the temperature range of their technological applications, which is around room temperatures. There are several works performed in the low temperature range [184–186] and the high temperature range in attempt to fully interpret the mechanism of magnetization reversal of these microwires. The influence of thermal treatment on the magnetic behavior of GCMWs has been studied in regard to domain wall velocity.
[187], magnetic hardening [188] and controlling the Curie temperature [189]. It has been established that thermal treatment at moderated temperatures results in the relaxation of stresses induced during fabrication. Thermal annealing at a temperature above the alloy crystallization temperatures results in the formation of nano- or microsized crystal phases or the crystallization of the whole amorphous material, which destroys the soft magnetic behavior [152, 162, 190]. In subsection chap. 4.3.2 some of this behavior have been observed during the investigation of core-shell microwires magnetic properties at high temperatures, up to 1200 K.

**Bi-phase microwires- State of the art**

In amorphous microwires the magnetization process is defined by shape anisotropy and by the magnetoelastic anisotropy, originating from the magnetoelastic coupling between magnetostriction inside the magnetic core and the stresses induced during fabrication by the glass layer (or by temperature) [162, 191]. In multilayer microwires the magnetostatic coupling between the magnetic core and shell, which radically modifies the magnetic behavior of the whole system, has to be taken into account, making it possible to control the overall magnetic response. The possibility of achieving such a "controllable" system is very attractive for the potential use in sensing technology [162, 192–194]. For example, the sensitive quick-response thermal sensors [150] are based on the magnetoelastic coupling (magnetoelastic behavior) in bi-phase microwires, i.e., the mechanical stresses induced by the shell. The asymmetric magnetoimpedance, arising from the magnetostatic coupling between the magnetic core and the shell, is used in magnetic field sensing (using the field created by the hard magnetic phase as an additional DC field). This properties make multilayer microwires suitable for a wide range of applications, such as microactuators [195], biomedical applications [196], stress or temperature [192], orthogonal flux-gates [197, 198]. More details about the applications of multilayer microwires can be found elsewhere, [14, 160].

The first attempts to fabricate multilayer microwires were made in 1991 by Rauscher and Radeloff [199] using mm-sized amorphous a soft NiFe based core (0.2 mm) and a hard CrCoFe shell, were was established that the magnetization state of the shell determines the switching behavior of the multilayer influencing the bistable magnetic behavior of the core. In a similar way, as an attempt to influence the magnetoimpedance properties, CoP [200, 201], CoFeNi [202] in 2000, and CoNi, NiFe [203] in 2005 alloys were electrochemically deposited on Cu or Cu-based microwires. Finally, multilayer microwires similar to the ones fabricated and investigated in this thesis were fabricated by a combination of quenching and drawing, sputtering, and electrodeposition techniques in 2004 by Pirote in the group of M. Vazquez [153]. The multilayer microwire consisted of two metallic ferromagnetic layers separated by an intermediate insulating layer. Pirote showed the influence of each of the steps on the magnetic response. The sputtering of an Au or Ti nanolayer on the GCMW
surface, which serve as an electrode for the subsequent electrodeposition of the ferromagnetic layer, impressively modifies the magnetic behavior of the CoFeNi-based microwire, changing the wires anisotropy from circular to axial, which is ascribed to the induced on the core compressive stresses. In his next works, Pirota studied further the modifications induced by the sputtering and electroplating of shells [204].

The magnetostatic and magnetoelastic coupling between the soft core and the hard shell was described and confirmed experimentally by Torrejon et al. [113, 205, 206] and later on described theoretically by J. Escrig [207] in 2007. Torrejon focused his thesis work on multilayer microwires with a magnetically soft CoFe core with a CoNi hard shell [113], in which the magnetostatic and magnetoelastic coupling arising from the hard phase dictates the behavior of the soft phase. This results in a shifting of the hysteresis loops making the remagnetization process asymmetric [208]. This shifting or bias field [207] acts similarly to the antiferromagnetic-like coupling in exchanged biased AFM/FM thin films. This magnetostatic bias effect appears as a result of the influence of a non-homogeneous magnetic field originated by the hard shell on the soft inner core. The magnetic coupling depends on the microwires geometric characteristics, such as length and thickness of each phase, making possible the tailoring of their magnetic response. J. Escrig continued the study of this magnetostatic biasing effect in terms of the microwire geometry [207].

G. Infante investigated the influence of magnetically hard (CoNi) and soft (FeNi) shells on the magnetic bistability of Fe-based microwires, varying as well the shell thickness [209]. Continuing their work, R. El Kammouni investigated the magnetic properties of multilayer microwires at low and microwave frequencies [112, 210]. The magnetic properties have been investigated as a function of temperature as well up to 1173 K by R. El Kammouni et al. [112, 210, 211] and up to 1200 K by myself, I. Iglesias et al. [212, 213].

Aim of the investigation
The aim of this work has been to further explore the ways to control and manipulate the magnetic response of multilayer microwires. Even though substantial attention has been drawn to the remagnetization process of core-shell microwires and the magnetic interactions between their constituents, this study provides novel results not only for the influence of the shell thickness and composition on the multilayer magnetic response but of its geometry (its continuousness) as well. For this purpose, a new type of core-shell microwires with the shell covering only one half of the wire along its axis, forming a half-tube, has been introduced within the frames of this work for the very first time. They have been named partially covered microwires. Their fabrication has served as a basis for the magnetostrictive-based micromanipulator, developed by M. Vazquez et al. [214]. The working mechanism of such a micromanipulator is based on the effect of materials with magnetostriction.
coefficients of opposite signs under an applied magnetic field. The materials of
the core and the shell have been selected in such a way that the core and the
shell have opposite magnetostriction coefficients. Thus, when a magnetic field is
applied the core and the shell react in an opposite way: when the shell contracts
the core expands, making the microwire bend in one direction; when the field is
reversed, it bends in the opposite direction, providing the opportunity to manipulate
objects, e.g., under a microscope. It is necessary to emphasize, that even though the
magnetostrictive effect is small in magnitude, it is possible to see under an optical
microscope the deflection of the microwire under an applied magnetic field [214].
Moreover, the application of this novel type of core-shell microwires can be extended
to the use of their surface properties and the possibilities arising from the microwires
having half conductor and half insulator surface. Hence, the investigation of their
magnetic properties is of great importance for further technological applications,
which can exploit the versatile properties provided by this novel system.
In this thesis, the investigation of the magnetic properties has been performed
at room temperature as well as in the high-temperature range, which has been
not so widely investigated so far. The high-temperature measurements provide
information about the magnetic phase transitions and structural transformation of
the investigated core-shell microwires.
Further, the influence of temperature on the magnetic phase transitions and
structural transformation of core-shell microwires has been investigated not only as
a function of their shell composition and thickness but of their shell geometry as
well. A comparative analysis of the magnetic behavior of fully and partially covered
core-shell microwires has been performed.
4.2 Fabrication of core-shell microwires

The core-shell microwires investigated in this thesis consist of two ferromagnetic concentric layers separated by an insulating layer, see Fig. 4.3. The fabrication of core-shell microwires is a multi-step process, developed and optimized in the group of M. Vazquez, which combines different techniques:
(i) *quenching and drawing technique* for the fabrication of the amorphous glass-coated microwire for the core surrounded by the non-conductive intermediate layer;
(ii) *sputtering* for the deposition of a noble metal 20 – 30 nm layer serving as an electrode for the shell deposition;
(iii) *electrodeposition* for the external shell fabrication.

All the microwires, presented in this chapter, were fabricated using the equipment at the Institute of Materials Science of Madrid, CSIC [215].

![Fig. 4.3: Schematics of the fabrication process of fully covered and partially covered microwires, which includes the following steps: (1) glass-coated microwire fabrication, (2) Au electrode deposition, (3) deposition of the external ferromagnetic shell fully (3a) and partially (3b).](image)

The most important geometrical parameters needed to describe the core-shell microwires, are introduced in Fig. 4.4: $d$ is the diameter of the metallic core, $D$ is the total diameter of the metallic core together with the glass coating, $t_{Au}$ is the gold layer thickness, $t_{shell}$ corresponds to the thickness of the external electrodeposited shell and $l$ represents the microwire length.
4.2.1 Fabrication of Fe\textsubscript{79}Si\textsubscript{10}B\textsubscript{8}C\textsubscript{3} and Co\textsubscript{59.2}Fe\textsubscript{14.8}Si\textsubscript{10.2}B\textsubscript{15.9} glass-coated microwires

The amorphous glass-coated microwires, used for the fabrication of core-shell microwires, have been fabricated by A. Jimenez in the group of M. Vazquez [109] by the quenching and drawing technique based on the works of Ulitovsky and Taylor [168]. Using this technique made it possible to fabricate microwires with a diameter of the metallic core ranging from 1 to 30\,$\mu\text{m}$, and a thickness of the glass shell from 2 to 12\,$\mu\text{m}$. The microwires can be 10\,$\text{th}$ to 100\,$\text{ths}$ of kilometers long, which presents a great interest for technological applications. The modified Ulitovsky-Taylor technique allows to obtain the desired magnetic properties, through a suitable composition selection of the initial alloy for the microwires, as well as their geometric dimensions, such as the diameter of the metallic core and thickness of the glass, through a fine-tuning of the fabrication parameters [168].

This technique aims to cool down the material so fast that its constituent atoms will not be able to reorganize in a crystalline structure, which corresponds to the position with minimal energy, creating an amorphous material. To get such an atomic “order”, it is necessary to achieve a cooling speed of $10^{10}$ K/s, which is not possible to achieve nowadays experimentally. In order to reduce the cooling speed up to $10^6$ K/s, a small amount of semiconductors (Si, B, P) is added to the desired alloy of transition metals (Co, Fe, Ni). In some cases [162, 216], to the alloy are added other elements to enhance its magnetic and mechanic properties (Cr, Mn, Al, Cu, Nb) [168]. The last will not be discussed in this work.

A schematics of the process is depicted in Fig. 4.5. Before starting the quenching and drawing, it is necessary to prepare a pellet of the alloy, which will be used for the core microwire. For the work presented in this thesis were used Fe, Si, B, and C to prepare an Fe\textsubscript{79}Si\textsubscript{10}B\textsubscript{8}C\textsubscript{3} alloy and Co, Fe, Si, and B to prepare Co\textsubscript{59.2}Fe\textsubscript{14.8}Si\textsubscript{10.2}B\textsubscript{15.9}. The desired elements are melted into a pellet in an electric Arc furnace MAM-1 from the company Edmund Burde, which is placed inside of a glass tube. In this work...
the glass tube is made out of low-thermal-expansion borosilicate glass, trademarked as Pyrex. The Pyrex tube with the pellet at the bottom is fixed in the setup in such way that the tip of the glass tube with the pellet is inside a high-induction coil. The high-induction coil is used to heat the pellet inside the Pyrex tube up to its melting point around 1200 °C to 1300 °C. The Pyrex melts at lower temperatures than the metal, specifically at 820 °C, forming a glass capillary, which is filled afterwards with the molten alloy, resulting in the microwire with a metallic core coated by a Pyrex shell. The melted Pyrex with the molten metal is drawn from the bottom of the Pyrex tube through a cooling water source down to a rotating coil at the bottom of the equipment, which picks up the solidified glass-coated microwire. The thickness of the metal core and glass coating can be controlled by varying the distance between the metal alloy and the high-induction coil, the pick-up coil rotation speed, and the vacuum inside the glass tube. The temperature and the cooling rate of the molten metal determines the amorphous state, i.e., the amorphicity, of the obtained core.

For the aims of the current thesis, I chose the following two soft magnetic alloys for the inner wire:

1. \( \text{Fe}_{79}\text{Si}_{10}\text{B}_8\text{C}_3 \) with a diameter of the metallic core, \( d = 20 \mu m \), and a total diameter, \( D = 30 \mu m \). The material has a positive magnetostriction constant close to \( \lambda = 3.2 \cdot 10^{-6} \) (for \( \text{Fe}_{77.5}\text{Si}_{7.7}\text{B}_{15} \) from [217]) and an axial magnetoelastic anisotropy;

2. \( \text{Co}_{59.2}\text{Fe}_{14.8}\text{Si}_{10.2}\text{B}_{15.9} \) with \( d = 10.2 \mu m \) and \( D = 20.6 \mu m \) and a very small magnetostriction constant, \( \lambda = -2 \cdot 10^{-6} \), [217] and circular magnetoelastic anisotropy.
For simplicity, I will refer to $\text{Fe}_{70}\text{Si}_{10}\text{B}_{8}C_{3}$ and $\text{Co}_{59.2}\text{Fe}_{14.8}\text{Si}_{10.2}\text{B}_{15.9}$ as FeSiB and CoFeSiB, respectively.

### 4.2.2 Galvanostatic electrodeposition of Co, Co$_{95}\text{Ni}_{5}$ and Fe$_{50}\text{Ni}_{50}$ external shells

Once the amorphous core is obtained, I proceed with the fabrication of core-shell microwires, with different external shell compositions, and thicknesses. Additionally, I fabricated for the very first time core-shell nanowires with the external shell partially deposited along the microwires axis.

**Working electrode sputtering**

An intermediate step is required before a homogeneous deposition of an external layer employing electrochemistry is possible. For the electrodeposition to take place, a conducting surface is required to play the role of a working electrode, on which the material will be grown (see chap. 3.1.2). Several tens of nanometers are enough. Titanium (Ti), gold (Au), and silver (Ag) are suitable materials to play the role of a working electrode. Taking into account all the criteria, gold is the most attractive material for this purpose, due to its non-reactivity (does not oxidize easily) and high conductivity, and has been the one selected for this work. In order to enhance the adhesion of the Au to the Pyrex surface a 5 nm layer of Ti was initially sputtered.

*Fig. 4.6:* Schematics (left) and a picture (right) of the Rotary Pumped Coater Q150R Plus used for the deposition of nanolayers of gold and titanium. The schematics have been adapted from [218].

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52 Chapter 4 Core-shell microwires
A 30 nm layer of Au was deposited on each side of the microwires Pyrex surface using a Q150R Plus Rotary Pumped Coater from Quorum [218], shown schematically and as a picture in Fig. 4.6. The sputtering has been performed under a 10^{-1} mbar pressure with a plasma current of 40 µA. The sputtering time was 30 min for each side of the microwire, which under the named conditions deposit a 30 nm Au layer. The thickness of the Au layer, as well as its homogeneity, was checked using a Scanning electron microscopy after the sputtering.

**External shell deposition**

As mentioned in the previous subsection, through the suitable combination of the core-shell materials it is possible to tune the magnetic behavior of the multilayers. For the purposes of this work, the following core-shell configurations have been selected:

1. soft/medium hard: Fe_{79}Si_{10}B_{8}C_{3} and Co_{59.2}Fe_{14.8}Si_{10.2}B_{15.9} cores with a Co_{95}Ni_{5} shell;
2. soft/hard: Fe_{79}Si_{10}B_{8}C_{3} and Co_{59.2}Fe_{14.8}Si_{10.2}B_{15.9} cores with a Co shell;
3. soft/soft: Fe_{79}Si_{10}B_{8}C_{3} and Co_{59.2}Fe_{14.8}Si_{10.2}B_{15.9} cores with a Fe_{50}Ni_{50} shell;

For each of this sample compositions I fabricated both type of shell configurations, i.e., fully and partially covering the microwire surface. More specific details of the geometrical parameters of the samples are listed in the next section in Tab. 4.1.

The amorphous core exhibit soft magnetic behavior with positive magnetostriction constant in the case of the FeSiB microwire and near-zero magnetostriction, in the case of the CoFeSiB microwire. The electrodeposited external shells are polycrystalline in character and have soft (FeNi), medium-hard (CoNi) and hard (Co) magnetic behavior.

The external shell electrodeposition was performed in a home-made electrodeposition setup, specially designed for the microwires particular geometry [153] using the galvanostatic electrodeposition method described in chap. 3.1.2. The Au layer was used as the working electrode (cathode), in which the material grows, and a Pt mesh with in form of a tube as counter electrode (anode). For the electrodeposition of the microwire external shell, three different Watts-type electrolytes were used to deposit Co [14, 219], Co_{90}Ni_{10} and Fe_{20}Ni_{80} [14, 113, 169] with hard, relatively hard and soft magnetic behavior, respectively.

**Co electrolyte:** CoSO_{4}·7H_{2}O (300 g/l), CoCl_{2}·6H_{2}O (45 g/l), H_{3}BO_{3} (45 g/l) were prepared in distilled water. The pH of the electrolyte is adjusted to be equal to 4.3 with a 1 M potassium hydroxide solution (KOH). The electrolyte must be stirred for 1 h at \( T = 25 - 30 \) °C. During the electrodeposition, the current density is kept on \( j = 12 \) mA/cm^2 at room temperature.
Co_{90}Ni_{10} electrolyte: CoSO₄·7H₂O (150 g/l), NiSO₄·7H₂O (150 g/l), NiCl₂·6H₂O (22.5 g/l), CoCl₂·6H₂O (22.5 g/l), H₃BO₃ (45 g/l), prepared in distilled water. The electrolyte was stirred for 1 h at $T = 35 - 40^\circ$C, and the pH was adjusted to be equal to 4.4 with a 1 M potassium hydroxide solution (KOH). These conditions were kept during the electrodeposition as well. The current density during deposition was kept on $j = 12$ mA/cm².

Fe_{20}Ni_{80} electrolyte: FeSO₄·7H₂O (8 g/l), NiSO₄·6H₂O (125 g/l), NiCl₂·6H₂O (20 g/l), H₃BO₃ (40 g/l), C₇H₅NO₃S (6 g/l), prepared in distilled water. The pH of the electrolyte must be adjusted to be between 2 and 2.8 with 1 M potassium hydroxide solution (KOH). The electrolyte must be stirred for 1 h at $T = 35 - 40^\circ$C. The electrodeposition is performed at $T = 55^\circ$C. The current density during deposition was kept on $j = 12$ mA/cm².

In all the used electrolytes, boric acid, H₃BO₃, was used as a supporting electrolyte. Sulfuric acid, potassium hydroxide or sodium hydroxide were used to adjust the pH level of the electrolytes to the desired one.

While the thickness of the deposited layer depends on the deposition time and the current density, the composition of the alloys (the relative amount of its constituent) varies with the current density during the electrodeposition [204]. To achieve a homogeneous deposition of the desired material composition, the current density has to be constantly monitored during the process and kept at the mentioned values for each of the electrolytes. The current during the electrodeposition was calculated using the equation:

$$I = j \cdot 2\pi \cdot \left(\frac{D}{2}\right) \cdot l,$$

(4.1)

where $j$ is the current density, $D$ the total diameter of the glass-coated microwire, $l$ the length of the glass-coated microwire. For FeSiB microwires $I = 0.197$ mA, for CoFeSiB $I = 0.206$ mA. The thickness is proportional to the deposition time as well as to the current density during deposition.

Since the aim of this work has been to study the magnetic properties of multilayer microwires as a function of the external shell thickness, an important point was the ability to make the electrodeposition controllable, i.e., to define the deposited external shell thickness with at least micrometer precision. For this purpose, the growth rate curves were plotted for each of the deposited materials (see Fig. 4.7). After each electrodeposition, the thickness, as well as composition of the grown layers, has been determined with an SEM-EDX, and plotted as a function of the correspondent deposition time. After checking the reproducibility of the results and fixing the current density, the growth rate curves allow to determine the thicknesses of the external shell analytically.
4.2.3 Structural and compositional characterization

The pre-characterization of the fabricated multilayer microwires has been performed using an optical microscope directly after each step of the process: the Au layer homogeneity to provide a homogeneous deposition of the subsequent ferromagnetic shell, and for an evaluation of the deposit presence, its homogeneity and a rough estimation of the thickness.

A qualitative and quantitative analysis of the morphology and composition of the different layers of the multilayer microwires has been posteriorly investigated using a Field Emission Scanning Electron (FE-SEM) with Energy Dispersive X-Ray Spectroscopy (SEM-EDX) in the ICMM-CSIC laboratory of microscopy [220]. It was possible to estimate the thickness of each of the layers and the core diameter imaging the cross-section of the sample on a special holder. As an example, the SEM images for each of the deposited external shells materials, Co, Co$_{95}$Ni$_5$ and Fe$_{50}$Ni$_{50}$, with the same Fe$_{79}$B$_8$Si$_{10}$C$_8$ core are presented in Fig. 4.8. It is possible to see the differences in the shell structure depending on their material composition.

In Fig. 4.9 an image of a partially core-shell microwires is presented, in which the shell has been deposited on the half of the microwire surface along its axis. In the image it is possible to see that the external shell has well defined sharp edges and covers the microwire tip as well.
The atomic composition of each of the multilayer systems has been analyzed by EDX. The composition and dimensions of amorphous microwires, used as the core, were previously determined by A. Jimenez [168]. An exemplary EDX spectra for three different deposited external shells is presented in Fig. 4.10.

The presence of such elements as S, K, Na, O, and Al is ascribed to the impurities obtained during electrodeposition from the electrolyte. Signals from Au and SiO$_2$ are detected due to the nanometer working electrode layer and the glass coating. Cu and C are ascribed to the sample holder and Kapton tape for the fixing of the microwires, respectively.

Tab. 4.1 and Tab. 4.2 present the correspondent elemental composition of the microwires used for the investigation in this thesis, as well as the thickness of the external shell, determined analytical from the electrodeposition rates. Were, as defined in figure Fig. 4.4, $d$ is the diameter of the metallic core, and $D$ is the total diameter of the metallic core together with the Pyrex coating.
Fig. 4.10: EDX spectra for the electrodeposited Co$_{95}$Ni$_5$, Co$_{90}$Ni$_{10}$ and Fe$_{70}$Ni$_{30}$ external shells to determine their material composition.

### 4.3 Magnetic properties of single core-shell microwires

Even though substantial attention has been drawn to the remagnetization process of core-shell microwires and the magnetic interactions between their layer constituents, the study presented in this thesis complements and deepens, with empirical analysis, the existing research, providing results not only for the influence of the shell thickness and composition, but of its geometry (i.e., shell continuousness) as well. For this purpose, a new type of core-shell microwires with the shell covering only one half of the wire along its axis, forming a half-tube, has been introduced within the frames of this work. They have been named *partially covered microwires*. Moreover, the investigation of the magnetic properties has been performed at room temperature as well as in the high-temperature range, which has not been widely
Tab. 4.1: List of all fabricated core-shell microwires with a fully deposited external shells and their respective thicknesses.

<table>
<thead>
<tr>
<th>Core material</th>
<th>Shell thickness [µm]</th>
<th>Core material</th>
<th>Shell thickness [µm]</th>
</tr>
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<tbody>
<tr>
<td>Fe₇₉B₈Si₁₀C₈</td>
<td>Co₀₅Ni₅, Co, Fe₅₀Ni₅₀</td>
<td>Fe₇₇,₅Si₇,₅B₁₅</td>
<td>Co₀₅Ni₅, Co, Fe₅₀Ni₅₀</td>
</tr>
<tr>
<td>d = 20 µm</td>
<td>0.5  2.0  1.0</td>
<td>d = 10.2 µm</td>
<td>0.5  2.0  0.5</td>
</tr>
<tr>
<td>D = 30 µm</td>
<td>1.0  3.0  3.5</td>
<td>D = 20.6 µm</td>
<td>1.0  3.5  0.7</td>
</tr>
<tr>
<td></td>
<td>2.0  4.0  3.7</td>
<td></td>
<td>2.0  4.0  1.5</td>
</tr>
<tr>
<td></td>
<td>2.5  5.0  4.0</td>
<td></td>
<td>2.5  5.0  3.5</td>
</tr>
<tr>
<td></td>
<td>3.0  10.0 5.0</td>
<td></td>
<td>3.0  7.0  4.0</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td></td>
<td>4.0</td>
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<td></td>
<td>4.2</td>
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<td></td>
<td>9.5</td>
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<td>6.0</td>
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<td></td>
<td></td>
<td></td>
<td>7.0</td>
</tr>
</tbody>
</table>

Tab. 4.2: List of all fabricated core-shell microwires with a partially deposited external shells and their respective thicknesses.

<table>
<thead>
<tr>
<th>Core material</th>
<th>Shell thickness [µm]</th>
<th>Core material</th>
<th>Shell thickness [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₇₉B₈Si₁₀C₈</td>
<td>Co₀₅Ni₅, Co, Fe₅₀Ni₅₀</td>
<td>Fe₇₇,₅Si₇,₅B₁₅</td>
<td>Co₀₅Ni₅, Co, Fe₅₀Ni₅₀</td>
</tr>
<tr>
<td>d = 20 µm</td>
<td>0.5  2.0  0.5</td>
<td>d = 10.2 µm</td>
<td>1.0  2.0  1.0</td>
</tr>
<tr>
<td>D = 30 µm</td>
<td>1.0  3.0  4.0</td>
<td>D = 20.6 µm</td>
<td>2.0  3.5  1.5</td>
</tr>
<tr>
<td></td>
<td>2.5  4.0  4.0</td>
<td></td>
<td>3.0  4.0  2.0</td>
</tr>
<tr>
<td></td>
<td>3.0  5.0  3.5</td>
<td></td>
<td>4.2  5.0  3.5</td>
</tr>
<tr>
<td></td>
<td>4.0  7.0  4.5</td>
<td></td>
<td>4.5  7.0  4.5</td>
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<td></td>
<td>4.2</td>
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<tr>
<td></td>
<td>9.5</td>
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</tbody>
</table>

investigated so far.
The overall magnetic behavior of core-shell microwires is determined by the magnetic properties of its constituents, as well as by the strength and the nature of the interactions between the core and the shell. Exchange interactions are irrelevant since the core and the shell are separated by a micrometer thick Pyrex layer, leaving the long-range interactions, magnetoelastic and magnetostatic, to govern the magnetic behavior of the investigated core-shell systems. The magnetoelastic coupling arises from the stresses induced by the external shell deposition. The magnetostatic coupling results from the interaction between core and shell, particularly if, for example, the shell is magnetically much harder than the core: the stray field of the harder phase magnetically biases the softer phase. Although the
magnetic behavior of the core-shell is determined mostly by the alloy composition of its constituents, their properties can be tailored through the variation of the distance between the core and shell, as well as geometry modification, including the shell continuousness.

Studying complex composite materials, such as multilayer microwires, it is possible to get information on the magnetic properties of the whole system as well as the contribution of the constituent magnetic phases for separated. The magnetization reversal of core-shell microwires occurs typically in two-steps: the first step is ascribed to the remagnetization of the soft magnetic phase, which occurs at low magnetic fields, while the second one is ascribed to the remagnetization of the hard magnetic phase, which occurs at higher magnetic fields.

4.3.1 Magnetic characterization at room temperature

Each one of the intermediate non-magnetic layers, the gold conductive layer and the Pyrex layer, influences significantly the magnetic response of the multilayer [221]. The influence of the conductive Au layer, deposited on the Pyrex for the subsequent electrodeposition of the ferromagnetic external shell, has been described in [152]. The compressive stresses, induced by only several tenths of nanometers of Au, change the shape of the hysteresis loop. The influence of the Pyrex thickness has been investigated in [112, 206]. It has been established that the increase of the Pyrex thickness leads to a reduction of the axial susceptibility due to the increase of circular anisotropy as a result of the internal stress induced by the Pyrex. These internal stresses arise as a result of the different thermal expansion coefficient of the core and the Pyrex coating and are strongly dependent on the Pyrex thickness [222] and the Pyrex to core ratio. This induced stresses can lead to significant changes in the magnetoelastic energy and even cause a change of the magnetostriction constant when the Pyrex thickness increases [223].

Even though coating, i.e., Au and Pyrex, has a strong influence on the magnetic behavior of the whole system, in this work, only the influence of the ferromagnetic shell on the multilayer microwire properties is investigated. In this regard, two types of studies have been performed:

1. influence of the external shell composition with different magnetic character and its thickness on the magnetic properties of the core (in chap. 4.3.1.1);
2. influence of the external shell continuousness on the magnetic behavior of the core-shell system (in chap. 4.3.1.2).

The measurement of the magnetic moment as a function of the magnetic field have been performed at room temperature under normal atmosphere conditions using a 7400 Series VSM from Lake Shore (cf. chap. 3.3.1) in the Laboratory of Novel
Magnetic Materials in Kaliningrad, LNMM. The samples were fixed on a 740934 Fiberglass sample holder \[224\] using a BF-6 glue \[225\]. The sample length has been selected to be 4 mm.

For the simplicity of understanding, the results of the investigation have been grouped into two main sections, according to their core composition: the ones with an FeSiB core and those with a CoFeSiB core.

4.3.1.1 Influence of the shell composition and thickness

Core-shell microwires with FeSiB core

Core-shell microwires consisting of an amorphous magnetically soft FeSiB core and three different ferromagnetic polycrystalline shells composition has been studied:

1. soft/hard: \(\text{Fe}_{79}\text{Si}_{10}\text{B}_{8}\text{C}_{3}\) core with a Co shell in Fig. 4.12 (upper panel), further called FeSiB/Co;
2. soft/medium hard: \(\text{Fe}_{79}\text{Si}_{10}\text{B}_{8}\text{C}_{3}\) core with a Co\(_{95}\)Ni\(_{5}\) shell in Fig. 4.12 (middle panel), further called FeSiB/CoNi;
3. soft/soft: \(\text{Fe}_{79}\text{Si}_{10}\text{B}_{8}\text{C}_{3}\) core with a Fe\(_{50}\)Ni\(_{50}\) shell in Fig. 4.12 (bottom panel), further called FeSiB/FeNi.

Information about the whole studied thickness range of the external shells can be found in Tab. 4.1 for each shell composition. Nevertheless, for simplicity, in Fig. 4.12 the hysteresis loops only for selected shell thicknesses with the most significant magnetic behavior are shown.

Before starting the analysis of the core-shell microwires magnetic properties as a whole, the magnetic behavior of only the FeSiB core has been investigated (see Fig. 4.11). The magnetization reversal of FeSiB core occurs through a single switching event between two stable remanent states (a single large Barkhausen jump), via the depinning of a domain wall from the closure domain at one end and its subsequent propagation along the whole microwire. Such bistable behavior is typical for microwires with high positive magnetostriction and gives the hysteresis loop the observed rectangular shape. The amorphous Fe-based soft core shows a low coercivity value, \(H_c \approx 5\) Oe. The susceptibility of high-magnetostrictive Fe-based alloys (\(\lambda_S \approx 10^{-5}\)) is very sensitive to external tensions, i.e. the external shell deposition can significantly modify the magnetic behavior of the core.

In Fig. 4.12 the hysteresis loops for the core-shell microwires with an FeSiB core and Co (upper panel), CoNi (middle panel) and FeNi (bottom panel) external shells are presented. As typical for bi-phase systems, two steps are visible in the
hysteresis loops. The observed hysteresis loops present some common features, based on which a common behavior can be described. The hysteresis loops for these core-shell microwires can be divided into two groups, according to the influence exerted by their shell thickness on the overall remagnetization process: the first group includes core-shell microwires with shell thicknesses below $t_{\text{crit}}$, while the second group includes core-shell microwires with shell thicknesses above $t_{\text{crit}}$.

For the first group, at small thicknesses of the external shell, the two-step behavior typical for multilayer microwires is observed as the magnetic field is reversed from $+1$ kOe to $-1$ kOe. The first step occurs at low magnetic field, and it corresponds to the magnetically soft bistable FeSiB core, reflecting the domain wall propagation in a single step through a Barkhausen jump. The second step occurs at higher fields corresponds to the magnetically harder external shells. The shells are polycrystalline due to the fabrication method, hence present a multidomain structure. The remagnetization process occurs through the rotation of the magnetization and domain wall propagation. They are characterized by an open hysteresis loop with a high coercivity and an inclined shape. More details can be found in [113].

It is necessary to emphasize that the step associated with the bistable FeSiB core becomes less abrupt and sloped as the external shell thickness increases. The presence of an external ferromagnetic shell affects the core magnetic bistability. The magnetoelastic anisotropy, arising from the internal stresses induced by the shell $\sigma_{\text{shell}}$, deteriorates the bistable behavior of the FeSiB core and finally destroys it shortly before $t_{\text{crit}}$ is reached.

For the second group, at thicknesses above critical, $t_{\text{crit}}$, the first step corresponding to the core starts to get less visible, until at some point completely disappears, and the hysteresis loops reflect the remagnetization process of the external shell. This is related to the magnetic coupling induced during the deposition of the external shell [113]. The increase of the external shell incite an increment of the coercivity $H_c$, and the magnetic moment $M$ (Fig. 4.13). The peculiarities of the different shell composition will be described in more detail for Co, CoNi and FeNi shells for...
**Fig. 4.12:** Hysteresis loops for core-shell microwires with selected shell thicknesses at room temperature: FeSiB/Co- upper panel, FeSiB/CoNi- middle panel, and FeSiB/FeNi- bottom panel. To be noted, in the lower panel the scale is smaller (±100 Oe), which evidence the overall magnetically softer character of the FeNi shell in comparison with Co and CoNi shells.

Separated.

**Co shell:** For core-shell FeSiB/Co microwires with the increasing of the Co shell thickness, the bistable behavior of the core its overtaken by the hard shell due to the increase of the magnetic volume of the hard Co shell. Nevertheless, it is still possible to see the core influence in the whole studied thickness diapason, at 10 µm. The evolution of $H_c$ and $M$ follows a linear-like behavior in the studied thicknesses diapason.
CoNi shell: For FeSiB/CoNi the external shell influence is more significant than in the previous case, showing already at $t_{\text{crit}} = 2 \mu m$ a strong influence on the systems hysteresis loops shape. Even though CoNi is magnetically less hard than Co, it is possible to see, that the microwire magnetic behavior is influenced mostly by the CoNi shell already at $t_{\text{crit}} = 4 \mu m$. The two-step behavior is no longer visible. The hysteresis loop reflects the magnetization reversal of the CoNi shell, with its typical open inclined hysteresis loop with a high coercivity [113].

The evolution of the coercivity, $H_c$, shows (Fig. 4.13), for $t_{\text{CoNi}}$, that below $t_{\text{crit}}$ $H_c$ increases with the thickness, and it is determined by the combination of core and shell coercivities, while for thicknesses above 4 $\mu m$ the overall $H_c$ decreases and its determined by the CoNi shell magnetic behavior.

FeNi shell: In the case of FeSiB/FeNi, the FeNi shell exerts a strong influence on the magnetic behavior of the multilayer. Even though the FeNi shell has a soft character as well as the FeSiB core, it seems that it is magnetically harder than that of the FeSiB core. The core influence is overcome and completely blurred at 5 $\mu m$, showing the remagnetization only of the external shell.

The evolution of the coercivity is shown in Fig. 4.13 and it increases with the shell thickness. The magnetic moment follows a linear-like dependence as the shell
thickness increases, as it is shown in Fig. 4.13. For shell thicknesses below 4 µm is in agreement with the theoretical calculations performed in [113].

**Multilayers with CoFeSiB core**

The study of core-shell microwires has been extended to microwire systems with a magnetic behavior, completely different from the bistable-based one. Here, CoFeSiB glass-coated microwires were fabricated with reduced quenching rate so that the microstructure is no more fully amorphous, and results in a relatively hard magnetic behavior as can be observed in Fig. 4.14.

Core-shell microwires consisting of a CoFeSiB core and three different ferromagnetic polycrystalline shells composition have been studied:

1. hard/hard: Co<sub>59.2</sub>Fe<sub>14.8</sub>Si<sub>10.2</sub>B<sub>15.9</sub> core with a Co shell, further called CoFeSiB/Co (Fig. 4.15 upper panel);
2. hard/medium hard: Co<sub>59.2</sub>Fe<sub>14.8</sub>Si<sub>10.2</sub>B<sub>15.9</sub> core with a Co<sub>95</sub>Ni<sub>5</sub> shell, further called CoFeSiB/CoNi (Fig. 4.15 middle panel);
3. hard/soft: Co<sub>59.2</sub>Fe<sub>14.8</sub>Si<sub>10.2</sub>B<sub>15.9</sub> core with a Fe<sub>50</sub>Ni<sub>50</sub> shell, further called CoFeSiB/FeNi (Fig. 4.15 bottom panel);

Information about the whole studied thickness range of the external shells can be found in Tab. 4.1 for each shell composition. Nevertheless, for the simplicity of understanding, in Fig. 4.15 only the hysteresis loops for selected shell thicknesses with the most significant magnetic behavior have been selected.

![Figure 4.14](image.png)

**Fig. 4.14:** Hysteresis loops for the crystalline CoFeSiB microwire at room temperature.

Once again the investigation of the core-shell microwires magnetic properties has been started with the analysis of the magnetic behavior of the CoFeSiB core. Fig. 4.14 shows the hysteresis loop for the crystalline CoFeSiB microwire, which has been used as the core for the studied bi-phase microwires, at room temperature. For CoFeSiB microwires with negative magnetostriction a non-hysteretic behavior is typical. Nevertheless, Fig. 4.14 shows that the hysteresis loop for CoFeSiB microwire
exhibit a high coercivity value, $H_c = 211$ Oe, evidencing a remagnetization process occurring primarily via irreversible processes, likely through the domain wall propagation in its internal part (cf. chap. 4.1).

**Fig. 4.15:** Hysteresis loops for core-shell microwires with selected shell thicknesses at room temperature: hard/hard CoFeSiB/Co- upper panel, hard/medium hard CoFeSiB/CoNi- middle panel, and hard/soft CoFeSiB/FeNi- bottom panel.

Core-shell microwires with a CoFeSiB core exhibit a two-step hysteresis loop (Fig. 4.15), characterizing its bi-phase magnetic behavior, like in the case of FeSiB core. Nevertheless, in this case, the remagnetization mechanism of the core-shell system occurs in a different way, than it has been observed before. The first step on the hysteresis loop at low field and corresponds to the remagnetization of the external ferromagnetic shell, the second one at higher fields corresponds to the remagnetization process of the CoFeSiB core. Moreover, the influence of the external shell on the magnetic properties of the
whole system will depend on its composition. For each of the shell materials, the magnetic behavior is modified differently. In Fig. 4.16 is presented the evolution of the $H_c$ with the shell thickness.

**Co shell:** For CoFeSiB/Co (Fig. 4.15, upper panel) with small shell thicknesses it is hard to see the typical two-step behavior on the hysteresis loop. For Co shell thicknesses below $t = 3 \mu m$ the observed magnetic behavior is mostly the one corresponding to the CoFeSiB core, the hysteresis loops shape is practically indistinguishable from the one of the single CoFeSiB core. Which serve as a proof of the hard magnetic character of the core. Moreover, the fact that it is not possible to distinguish the two-step remagnetization process indicates that the external Co shell is hard as well.

For Co thicknesses above $t_{Co} = 3 \mu m$ the two-step behavior ascribed to the two magnetic phases is clearly distinguishable. the influence of the shell increases with the thickness until at thicknesses above $t_{crit} = 6 \mu m$ it is no longer possible to distinguish the influence of the core.

The coercivity $H_c$ decreases with the external shell thickness, while the saturation magnetization $M_s$ increases (Fig. 4.16).

**CoNi shell:** In the case of the CoNi shell (Fig. 4.15, middle panel), already at small CoNi shell thicknesses, $t_{CoNi} = 0.5 \mu m$ the influence of the external shell is significant, a well defined two-step behavior is visible, which remains until $t_{crit}$ is reached. When the shell thickness reaches $t_{crit} = 4 \mu m$ the hysteresis loop reflects solarly the remagnetization process of the CoNi shell. The coercivity $H_c$ decreases

---

**Fig. 4.16:** Left side: Evolution of the coercivity of the shell (solid line) and CoFeSiB core (dotted line) as a function of the external shell thickness for CoFeSiB/Co, CoFeSiB/CoNi, and CoFeSiB/FeNi. Right side: evolution of the magnetic moment at saturation field as a function of the external shell thickness for CoFeSiB/Co, CoFeSiB/CoNi, and CoFeSiB/FeNi.
with the external shell thickness until $t_{\text{crit}}$ (Fig. 4.16). Once $t_{\text{crit}}$ is reached a sudden increase in $H_c$ is observed, after which $H_c$ remains constant for higher thicknesses (up to 9.5 µm within the frames of this work). Such behavior of the $H_c$ results from the remagnetization process determined fully by the external polycrystalline shell. The magnetic moment at saturation field (Fig. 4.16, right side) follows a linear-like behavior, showing an increase when the external shell thickness is increased.

FeNi shell: For CoFeSiB/FeNi (Fig. 4.15, bottom panel), like in the case of a CoNi shell, the influence of the shell is very strong already at small FeNi shell thicknesses, $t_{\text{FeNi}} = 0.2$ µm. The first step, ascribed to the external shell, gets more pronounced and abrupt as its thickness increases, while the second step ascribed to the remagnetization of the CoFeSiB core gets smaller. In this case, the external shell has a soft magnetic character, so the signal of the core remains for all the studied thicknesses, $t_{\text{crit}}$ has not been reached.

The coercivity $H_c$ decreases with the external shell thickness in all the studied thickness diapason. $M_s$ follows a linear-like behavior, increasing with the external shell thickness.

### 4.3.1.2 Influence of the external shell geometry

Once it is clear how the electrodeposition of an external ferromagnetic shell modifies the magnetic response of the whole core-shell system, this study can be extended to the analysis of the influence of the shell continuousness, weather it is homogeneously deposited around the microwires surface forming a tube (fully covered microwires), or it covers only one half of the wire along its axis, forming a half-tube (partially covered microwires).

I successfully fabricated partially covered microwires for the first time within the frames of this thesis in the ICMM/CSIC in Madrid. Their fabrication has served as a basis for the magnetostrictive-based micromanipulator, developed by M. Vazquez et al. [214]. It is necessary to emphasize, that even though the magnetostrictive effect is small in magnitude, it is possible to see under an optical microscope the deflection of the microwire under an applied magnetic field [214].

In order to understand how the shell continuousness influences the magnetic response of the core-shell, a comparative analysis of the hysteresis loops for fully and partially covered microwires has been performed, from which the differences in the remagnetization process can be derived for same shell thicknesses and compositions.

For simplicity, the results of this investigation have been divided into two groups as in the previous subsection: the investigation of core-shell microwires with a magnetically soft bistable FeSiB core and the ones with magnetically hard CoFeSiB core. Information about the studied fully and partially covered microwires can be
Core-shell microwires with an FeSiB core.

In Fig. 4.17 the normalized hysteresis loops for fully and partially covered core-shell microwires with a CoNi external shell, measured at room temperature, are presented. The shell thicknesses were selected to be 1 µm, 2.5 µm and 4 µm for both, partial and full covered shells. As has been previously stated, for fully covered FeSiB/CoNi microwires (Fig. 4.17 left), the CoNi external shell significantly modifies the magnetic behavior of the core-shell, displaying already at $t_{\text{CoNi}} = 1$ µm two well-defined steps in the hysteresis loop, defining the presence of two magnetic phases, the core and the shell. The first step is observed at a low field value and corresponds to the remagnetization of the FeSiB core conserving the abrupt bistable character, while the second step takes place at a higher field value and corresponds to the remagnetization process of the magnetically harder external shell.

![Fig. 4.17: Hysteresis loops for FeSiB/CoNi core-shell microwires with the external shell fully (left side) and partially (right side) electrodeposited onto the core surface along its axis. Full and partial shells have been selected to have same thicknesses. The measurements have been performed at room temperature.](image)

The magnetic fractional volume associated with the shell increases with the thickness, which is reflected in the second step on the hysteresis loop until it overtakes the magnetic behavior of the multilayer completely, and the hysteresis loop reflects entirely the remagnetization process of the external shell (blue line in Fig. 4.17, $t_{\text{crit}} = 4$ µm). The open inclined hysteresis loop with a high coercivity is characteristic for the remagnetization process of CoNi shells. The magnetic bistability in core-shell microwires is very sensitive to each small mod-
ifcation in the geometry of the external shell. Every small geometry modification induces changes not only in the magnetostatic coupling between the core and shell, but it changes the stresses induced by the shell on the ferromagnetic core, thereby modifying the magnetoelastic interaction. The intensity of these couplings can be tailored in such a manner to achieve the desired magnetic response.

When the external shell is deposited only on one half of the microwire surface along its axis, asymmetric stresses are induced on the core, which influences the magnetoelastic interaction noticeably. In Fig. 4.17 (right) are presented the hysteresis loops for microwires with a partial shell, but with the same thickness and composition as for the full shell in Fig. 4.17 (left). The two-step behavior is well defined for all the investigated shell thicknesses.

![Non-normalized and normalized hysteresis loops](image)

**Fig. 4.18:** Non-normalized (left side) and normalized (right side) hysteresis loops for FeSiB/CoNi core-shell microwires with a 4 µm external shell fully and partially electrodedeposited onto the core surface along its axis. The measurements has been performed at room temperature.

The magnetization reversal mechanism is found to be the same as in the case of a fully covered core-shell: the first step at a low magnetic field value is ascribed to the remagnetization of the bistable FeSiB core, while the second step at a higher magnetic field value is ascribed to the remagnetization of the magnetically harder polycrystalline shell. However, in this case, there is no critical thickness, above which the magnetic response of the core-shell is entirely dictated by the shell. Even though the shell thickness is the same for a full and partial shell, their fractional volume is different, i.e., two times smaller for the partial shell. The magnetic signal from the partial shell is not enough to overcome the magnetic signal from the FeSiB core. Instead, at 4 µm (the critical thickness for fully FeSiB/CoNi), the first step on the hysteresis loop, ascribed to the bistable core remagnetization, becomes less abrupt and sloped as the external shell thickness increases. I want to point out, once the external shell is deposited the magnetic behavior of the core is no longer
bistable. This happens, because the magnetoelastic anisotropy, arising from the internal stresses induced by the shell $\sigma_{\text{shell}}$, deteriorates the bistable behavior of the FeSiB core.

The step ascribed to the external shell remagnetization gets more pronounced with the shell thickness, which evidences the increase of its magnetic volume. It is remarkable, that for partially covered microwires there is a near-zero remanence state at near-zero magnetic field, which is not achievable for fully covered core-shells, because of the critical length effect, after which the remagnetization is defined solely by its shell (blue line in Fig. 4.17 right, $l_{\text{CoNi}} = 4 \mu m$).

In Fig. 4.18 the not-normalized (left) and the normalized (right) hysteresis loops for FeSiB/CoNi core-shell microwires with a 4 $\mu$m thick full (blue line) and partial shell (red line) are presented. The full shell contributes to a higher magnetic moment than the partial one, as could be expected since the magnetic volume of the shell is two times smaller for a partial shell.

**Core-shell microwires with an CoFeSiB core.**

In the case of CoFeSiB, the difference between partial and full shells is not so significant, as in the FeSiB core case. As for fully covered microwires, the remagnetization mechanism for CoSiB-based core-shell microwires occurs in two steps: first occurs the remagnetization of the external shell followed by the remagnetization of the core. In the case of CoFeSiB core the changes to the magnetic behavior of the core-shell induced by the shell geometry are in this case relatively small, compared to those presented for magnetically soft FeSiB core, due to the magnetically hard character of the crystalline CoFeSiB.

![Hysteresis loops for CoFeSiB/CoNi core-shell microwires](image)

**Fig. 4.19:** Hysteresis loops for CoFeSiB/CoNi core-shell microwires with the external shell fully (left side) and partially (right side) electrodeposited onto the core surface along its axis. Full and partial shells have been selected to have same thicknesses.
Fig. 4.19 (left) presents the hysteresis loops for bi-phase microwires with CoFeSiB core and a CoNi shell, fully (left) and a partially (right) with 4 µm, and 4.5 µm shell thicknesses. This shell thickness corresponds to the CoNi critical thickness in the case of fully coated microwires (cf. chap. 4.3.1.1), so the hysteresis loop shows mostly the remagnetization of the external shell.

In the case of a partial shell, the two steps are still distinguishable Fig. 4.19 (left) at 4 µm, the shell remagnetizes first followed by the remagnetization of the core at higher fields. The effect of the shell continuousness for a core, magnetically harder as its shell, is not so radical, as in the case of a magnetically bistable soft core.

Fig. 4.20: Non-normalized (left side) and normalized (right side) hysteresis loops for CoFeSiB/CoNi core-shell microwires with a 4 µm external shell fully and partially electrodeposited onto the core surface along its axis. The effect of the shell geometry is in this case relatively smaller, due to the magnetically hard character of the crystalline CoFeSiB.

Fig. 4.20 shows the not-normalized (left) and the normalized (right) hysteresis loops for CoFeSiB/CoNi core-shell microwires with a 4 µm thick full (blue line) and partial shell (red line). The magnetic moment of fully covered bi-phase microwires is significantly bigger than the magnetic moments of partially covered bi-phase microwires with the same shell thicknesses, like in the previous case.

4.3.2 Magnetic characterization in the temperature range 295-1200 K

The study of the magnetic properties of fully and partially covered core-shell microwires can be extended to high temperatures, specifically, the temperature range $T = 295 – 1200 \text{ K}$, in order to investigate the influence of temperature on the mag-
netic phase transitions and structural transformations which undergo the core-shell microwires as a function of their shell composition and thickness, as well as their shell geometry. As has been mentioned in chap. 4.1, only a few studies have enlightened the magnetic behavior of multilayer microwires at above-room temperatures. The high-temperature measurements provide information about the magnetic phase transitions and structural transformations of the investigated core-shell microwires. To be noted, exposure to high temperatures may result in an irreversible modification of the material microstructure, depending on the exposure time and temperature. Which leads to significant changes in their magnetic properties. Some of these changes can be tracked in the heating-cooling curves, as well as in the hysteresis loops before heating, during heating, and after cooling. Moreover, with the increase of the temperature the external ferromagnetic shells together with the Pyrex induce additional stresses onto the core.

The thermomagnetic analysis has been performed within the temperature range from \( T = 295 \text{ K} \) to \( T = 1200 \text{ K} \) in Argon atmosphere in a near saturation magnetic field, \( H = 1 \text{ kOe} \), using a 7400 Series VSM from Lake Shore with a 74034 high temperature oven [226]. I carried out the VSM measurements in the Laboratory of Novel Magnetic Materials [227]. The heating rate was kept at \( 3 \text{ K/min} \) with an average time of measurement at each temperature of \( 5 \text{ min} \). The samples were fixed on a 740931 Quartz L-shaped sample holder [228] using a Thermeez ceramic putty from Cotronics [229]. The sample length has been selected to be \( 4 \text{ mm} \). Once again, for the simplicity of understanding, the results of the investigation have been aggregated according to the core composition, FeSiB and CoFeSiB respectively.

Core-shell microwires with an FeSiB core.

Multilayer microwires composed by an Fe-based magnetically soft core and three different ferromagnetic shells with hard, medium-hard and soft magnetic behaviors are studied in this subsection. The thickness of each shell has been varied as well. The following core-shell microwires configurations have been studied (presented in Fig. 4.25):

1. soft/hard: \( \text{Fe}_{79}\text{Si}_{10}\text{B}_{8}\text{C}_{3} \) core with a Co shell in Fig. 4.25 upper panel, further called FeSiB/Co;
2. soft/medium hard: \( \text{Fe}_{79}\text{Si}_{10}\text{B}_{8}\text{C}_{3} \) core with a \( \text{Co}_{95}\text{Ni}_{5} \) shell in Fig. 4.25 middle panel, further called FeSiB/CoNi;
3. soft/soft: \( \text{Fe}_{79}\text{Si}_{10}\text{B}_{8}\text{C}_{3} \) core with a \( \text{Fe}_{50}\text{Ni}_{50} \) shell in Fig. 4.25 bottom panel, further called FeSiB/FeNi;

Information about the whole studied thickness diapason of the external shells and their geometrical parameters can be found in Tab. 4.1 for each shell composition. Nevertheless, for the simplicity of understanding, the hysteresis loops only for selected shell thicknesses with the most significant magnetic behavior have been presented in Fig. 4.12.
To provide a deeper understanding of the presented results on multilayer microwires, the temperature dependence of the magnetic moment for the FeSiB core solely has been analysed at first (Fig. 4.21). FeSiB magnetic moment at room temperature has a value of $M = 20 \cdot 10^{-7}$ A m$^2$ and it decreases with the temperature to a value of $M = 8 \cdot 10^{-7}$ A m$^2$ at $T = 757$ K, and remains almost constant until $T = 780$ K, after which increases again when the crystallization temperature of the amorphous FeSiB core is reached. The Curie temperature of the Fe-based amorphous microwire has been determined by the minimum of $dM/dT$ method, and has been evaluated to be $T_{C, Fe} = 622$ K, relatively similar to the reported $T_{C, Fe} = 698$ K [112], $T_{C, Fe} = 706$ K [209, 230] for GCMWs and $T_{C, Fe} = 688$ K [167] for ribbons. A further increase of the temperature leads to a sudden magnetic hardening, an increase of the magnetic moment, reaching a value of $M = 10.4 \cdot 10^{-7}$ A m$^2$, as a consequence of the formation of an $\alpha$-Fe(Si) phase and Fe-boride grains [231] at $T_{cryst, Fe} = 808$ K amorphous FeSiB crystallization temperature (similar to $T_{cryst, Fe} = 806$ K [230], $T_{cryst, Fe} = 798$ K [112]). After this the magnetic moment decreases until reaching its minimum, $M = 0.33 \cdot 10^{-7}$ A m$^2$, at $T = 1003$ K and remains vanishing constant till the end of the studied temperature range, $T = 1200$ K is reached. The crystallized $\alpha$-Fe(Si) phase Curie temperature has been evaluated to be $T_{C, \alpha-Fe} = 925$ K, which is as well in agreement with literature ($T_{C, \alpha-Fe} = 918$ K from [112, 167], and $T_{C, \alpha-Fe} = 974$ K from [232]).

In Fig. 4.22 the temperature dependences of the magnetic moment for FeSiB/Co (upper panel), FeSiB/CoNi (middle panel) and FeSiB/FeNi (bottom panel) are presented.

![Fig. 4.21: Temperature dependence of the magnetic moment for the amorphous FeSiB core. Vertical lines denote the Curie temperature of the amorphous and crystalline phases.](image)

Once a polycrystalline ferromagnetic shell is electrodeposited onto the FeSiB core surface, the magnetic moment of the whole core-shell system increases proportion-
Fig. 4.22: Temperature dependence of the magnetic moment for core shell microwires consisting of an FeSiB core and a Co (upper panel), CoNi (middle panel) and FeNi (bottom panel) with selected shell thicknesses. Vertical lines denote the Curie temperature of the amorphous and crystalline phases of the core and Curie temperature of the FeNi shell.

ally to the shell thickness and its magnetic moment, but the M vs. T curve shape is not strongly modified, i.e., the magnetic contribution of the core predominates (prevails) the overall behavior of the multilayer. The Curie temperature of the amorphous core, $T_{c,Fe} = 622$ K, and the crystallized core, $T_{c,α−Fe} = 925$ K, remain unchanged, regardless of outer shell composition and thickness, as well as the crystallization temperature of the amorphous core, $T_{cryst,Fe} = 808$ K. Regarding the external shell, the Curie temperature of polycrystalline Co ($T_{C,Co} = 1404$ K, [233]) and CoNi ($T_{C,CoNi} = 1348$ K, [234], [167]) external shells has not been reached in the studied temperature range at the highest temperature value, $T_{max} = 1200$ K. In the case of an FeNi external shell, Fig. 4.24 (bottom panel), in addition to the Curie temperature of the core in the amorphous and crystalline
state, it is possible to identify the Curie temperature of the FeNi outer shell. FeNi undergoes a magnetic phase transition at $T_{C,FeNi} = 823\,\text{K}$, which has been found to be its Curie temperature (relatively similar to the reported $T_{C,FeNi} = 874\,\text{K}$ in [112] [235], and $T_{C,FeNi} = 837\,\text{K}$ in [167]) after the crystallization temperature of FeSiB has been reached at $T_{\text{cryst,Fe}} = 808\,\text{K}$. With the further increase of the temperature, the presence of the paramagnetic FeNi shell attenuates the magnetic response of the crystalline $\alpha$-Fe phase, leading to a reduction of the core-shell microwire overall magnetization. The temperature evolution of the magnetic signal has a more abrupt character and a linear-like slope, reaching a value of $M = 0.6 \times 10^{-7}\,\text{A}\,\text{m}^{-2}$ at $T_{C,FeNi} = 949\,\text{K}$ and remains nearly constant till $T_{C,FeNi} = 1200\,\text{K}$.

Another peculiarity of FeSiB/FeNi microwires is the fact that when the external shell thickness reaches $t_{\text{crit}} = 4\,\mu\text{m}$ (Fig. 4.22, green line), the magnetic behavior of the system is identified completely by the FeNi shell. This matches the results, obtained for FeSiB/FeNi at room temperature, described in chap. 4.3.1, Fig. 4.12. Nonetheless, once $T_{C,FeNi} = 823\,\text{K}$ is overcome, the magnetic behavior of the core-shell microwires is identified by the magnetic behavior of the core once again. I want to note, that the critical value of the shell thickness, $t_{\text{crit}}$, after which the magnetic behavior of the system is determined by its external shell solely, has not been observed for the studied thicknesses of Co and CoNi external shells. This contradicts the results obtained in Fig. 4.12.

Core-shell microwires with a CoFeSiB core.

Multilayer microwires composed by an CoFeSiB magnetically hard core and 3 different ferromagnetic shells with hard, medium-hard and soft magnetic behaviors are studied in this subsection. The thickness of each shell has been varied as well. The following core-shell microwires configuration with a CoFeSiB core have been studied (presented in Fig. 4.24):

1. hard/hard: $\text{Co}_{59.2}\text{Fe}_{14.8}\text{Si}_{10.2}\text{B}_{15.9}$ core with a Co shell, further called CoFeSiB/Co (Fig. 4.24 upper panel);
2. hard/medium hard: $\text{Co}_{59.2}\text{Fe}_{14.8}\text{Si}_{10.2}\text{B}_{15.9}$ core with a Co$_{95}$Ni$_5$ shell, further called CoFeSiB/CoNi (Fig. 4.24 middle panel);
3. hard/soft: $\text{Co}_{59.2}\text{Fe}_{14.8}\text{Si}_{10.2}\text{B}_{15.9}$ core with a Fe$_{50}$Ni$_{50}$ shell, further called CoFeSiB/FeNi (Fig. 4.24 bottom panel);

Each shell has been investigated as a function of the external shell thickness. The fabricated and investigated thicknesses are presented in Tab. 4.1 for each of the shells.

Once again, the temperature dependence of the magnetic moment for the CoFeSiB core is first considered Fig. 4.23. The magnetic moment at room temperature has
a value of $M = 11.57 \cdot 10^{-7}$ A m$^2$, and it decreases with the temperature to a value of $6 \cdot 10^{-7}$, at $T = 805$ K. The Curie temperature of CoFeSiB amorphous microwire was found to be $T_{C,Co} = 645$ K, (which is in agreement with literature $T_{C,Fe} = 688$ K [167], $T_{C,Co} = 650$ K [112], $T_{C,Co} = 661$ K [236], $T_{C,Co} = 686$ K [230], $T_{C,Co} = 691$ K [237]). With a further increase of the temperature, a slight increase of magnetic moment is observed, which is ascribed to the crystallization process of CoFeSiB. The crystallization process of CoFeSiB alloys occurs in two stages according to literature: at $T_{cryst-1,Co} = 852$ K, and $T_{cryst-2,Co} = 893$ K. In Fig. 4.23 is possible to distinguish the first crystallization temperature of the CoFeSiB amorphous core at $T_{cryst-1,Co} = 857$ K ($T_{cryst-1,Co} = 840$ K [238], $T_{cryst-1,Co} = 842$ K [211]), during which Co$_3$B and Co$_5$Si$_2$ phases and a very small amount of pure Co are formed [239]. During the second crystallization temperature at $T_{cryst-2,Co} = 893$ K, Co$_2$B, Co$_2$Si and a small amount of Co are formed [239]. However, the second crystallization temperature has not been clearly observed in the measured curve, since this phase is not clearly defined magnetically (its residual magnetic moment and/or the applied field has is insufficient to get a significant magnetic response). The Curie temperature of the crystallized Co phase has been estimated to be $T_{C,crystCo} = 1002$ K.

The formation of Co$_3$B and Co$_5$Si$_2$ and pure Co phases $T_{cryst-1,Co} = 857$ K, leads to a sudden magnetic hardening with an increase of the magnetization, reaching a value of $M = 6.5 \cdot 10^{-7}$ A m$^2$, which rapidly decreases its value with the further increase of temperature until reaching a value of $M = 6.5 \cdot 1.2^{-7}$ A m$^2$ at $T = 1033$ K. After which it slowly decreases until reaching a value of $M = 0.6 \cdot 10^{-7}$ A m$^2$ at $T = 1200$ K. In Fig. 4.24 the temperature dependences of the magnetic moment is presented for CoFeSiB/Co (upper panel), CoFeSiB/CoNi (middle panel) and CoFeSiB/FeNi (bottom panel).

After the polycrystalline ferromagnetic shell electrodeposition onto the CoFeSiB core surface, the overall magnetic moment increases proportionally to the shell thickness,
Fig. 4.24: Temperature dependence of the magnetic moment for core shell microwires consisting of an CoFeSiB core and a Co (upper panel), CoNi (middle panel) and FeNi (bottom panel) with selected shell thicknesses. Vertical lines denote the Curie temperature of the amorphous and crystalline phases of the core and Curie temperature of the FeNi shell.

but the M vs. T curve shape is not strongly modified. The overall behavior of the core-shell system is dominated by the magnetic contribution of the core for all the studied thicknesses of Co and CoNi shells. In the case of an FeNi shell, the behavior is different. The Curie temperature of the CoFeSiB core, amorphous at $T_{C,Co} = 645$ K, and crystallized at $T_{C,crystCo} = 1002$ K, as well as the crystallization temperature of the CoFeSiB core $T_{cryst−1,Co} = 857$ K, remain unchanged, regardless of outer shell composition and thickness. For Co and CoNi shells $t_{crit}$ has not been reached within the studied diapason of thicknesses, i.e., for the magnetic behavior of the core-shell is governed by the core for all studied Co and CoNi shell thicknesses. The Curie temperature of polycrystalline Co ($T_{C,Co} = 1404$ K, [233]) and CoNi ($T_{C,CoNi} = 1348$ K, [167]) external shells has not been reached in the studied tem-
temperature range.

In the case of an FeNi external shell, Fig. 4.24 (bottom panel), like it has been mentioned above, in addition to the Curie temperature of the core in the amorphous and crystalline state, it is possible to identify the Curie temperature of the FeNi outer shell. FeNi undergoes a magnetic phase transition at $T_{C,FeNi} = 823$ K, ($T_{C,FeNi} = 837$ K in [167]). When the external shell thickness reaches a value of $t_{crit} = 4 \mu m$ (green line), the magnetic behavior of the system is identified by the FeNi shell. Nonetheless, once $T_{C,FeNi} = 823$ K is overcome, the magnetic behavior of the core-shell microwires is identified by the magnetic behavior of the core solely and the M vs. T curve coincides with one of the CoFeSiB curve.

**Figure 4.25:** Temperature dependence of the magnetic moment for core-shell microwires with the external shell fully and partially electrodeposited onto the core surface along its axis: FeSiB/CoNi with a 2.5 $\mu m$ shell thickness (upper panel) and FeSiB/CoNi with a 1.0 $\mu m$ shell thickness (bottom panel). Vertical lines denote the Curie temperature of the amorphous and crystalline phases of the core and Curie temperature for the FeNi shell.

In Fig. 4.25, the temperature dependences of the magnetic moment for fully and partially covered bi-phase microwires are shown for selected samples, specifically FeSiB/CoNi with $t_{CoNi} = 2.5 \mu m$ (upper panel) and FeSiB/FeNi with $t_{FeNi} = 1 \mu m$. 

**Partially and fully covered core-shell microwires**
(lower panel). As in the case of fully covered bi-phase microwires, the contribution of the core remains after external shell electrodeposition, and becomes less visible with the shell thickness increment. The Curie temperatures of the amorphous core and shell remain unchanged, $T_{C,Fe} = 622$ K and $T_{C,FeNi} = 823$ K respectively, as well as the amorphous core crystallization temperature, $T_{cryst,Fe} = 808$ K, with the respective Curie temperature of the crystallized $\alpha$-Fe(Si) phase, $T_{C,\alpha-Fe} = 925$ K.

A relevant change in the magnetic moment value of the whole bi-phase system is observed in the case of partially covered microwires compared to fully. Since the external shell is electrodeposited along the wire axis only partially, the fractional volume of magnetic material is twice smaller for partially covered microwires. Nevertheless, an increase of the magnetic moment is observed for the microwires with a partial shell with the same shell thickness. Thus, in the case of FeSiB/CoNi with $2.5 \mu$m shell thickness (Fig. 4.25, upper panel) the magnetic moment at room temperature for the fully covered microwire is found to be $M = 27 \cdot 10^{-7}$ Am$^2$, while for the partially covered microwire $M = 30 \cdot 10^{-7}$ Am$^2$. This difference of $M = 3 \cdot 10^{-7}$ Am$^2$ in the magnetic moment value persists over the studied temperature range, till $T_{max} = 1200$ K. In a similar manner, in the case of FeSiB/FeNi with $1 \mu$m shell thickness (Fig. 4.25, lower panel) the magnetic moment at room temperature for the fully covered microwire is found to be $M = 25 \cdot 10^{-7}$ Am$^2$, while for the partially covered microwire $M = 31 \cdot 10^{-7}$ Am$^2$. In this case the difference in the magnetic moment value persists until the Curie temperature of the FeNi shell is reached at $T_{C,FeNi} = 823$ K. The magnetic moment of the glass-coated FeSiB microwire at room temperature has a value of $M = 20 \cdot 10^{-7}$ Am$^2$. 

4.3 Magnetic properties of single core-shell microwires
4.4 Conclusions

I successfully fabricated core-shell nanowires with several shell compositions (Co, CoNi and FeNi) and thicknesses up to 10 µm (see Tab. 4.1 and Tab. 4.2), in order to investigate the influence of shell thickness and composition on the core-shell magnetic response. Additionally, to study the influence of the external shell continuousness on the magnetic properties of the whole system, I deposited the external shell partially along the microwires symmetry axis. Partially covered microwires have been successfully fabricated and investigated for the first time. The obtained results have been used for a patent [214].

The magnetic properties have been investigated at room temperature as well as in the high-temperature diapason, 295 – 1200 K, providing information about the magnetic phase transitions and structural transformation of core-shell microwires. Here the main conclusions, obtained during the performed investigation, are summarized.

1. Influence of shell composition and thickness on the magnetic properties of the core-shell microwires.

The remagnetization mechanism for core-shell microwires based on FeSiB and CoFeSiB cores is distinct. For core-shell microwires with an FeSiB soft magnetic core has been determined, that:

- Core-shell microwires present a magnetization process with a typical two steps behavior: the first step occurs at low magnetic field, and it corresponds to the magnetically soft bistable FeSiB core, the second step occurs at higher fields and corresponds to the magnetically harder external shells.
- Even though the magnetically hardest shell (Co) is expected to exert the strongest effect on the magnetic properties of the multilayer, it has been observed, that the soft FeNi shell has the strongest observed influence.
- The existence of a critical thickness, \( t_{\text{crit}} \) at which the hysteresis loop reflects the remagnetization process of the external shell, has been observed.
- The coercivity, \( H_c \), increases with the shell thickness, and it is determined by the combination of the core and shell coercivities, for thicknesses below \( t_{\text{crit}} \), and by the shell magnetic behavior for thicknesses above \( t_{\text{crit}} \).
- The saturation magnetization, \( M_s \), increases with the shell thickness having a linear-like behavior until \( t_{\text{crit}} \), having a substantial increase after that since the magnetic behavior is represented by the CoNi shell.
For core-shell microwires with a magnetically hard CoFeSiB core has been determined, that:

- The CoFeSiB core hysteresis loop exhibits an open hysteretic behavior with a high coercivity value, \( H_c = 211 \text{ Oe} \), while typically for CoFeSiB amorphous microwires with negative magnetostriction a non-hysteretic behavior is expected.
- Core-shell microwires present a typical two steps behavior: the first step occurs at low magnetic field, and it corresponds to the magnetically soft bistable FeSiB core, the second step occurs at higher fields and corresponds to the magnetically harder external shells.
- Like in the case of FeSiB, the strongest effect on the magnetic properties of the multilayer is exerted by the soft FeNi shell.
- The existence of a critical thickness, \( t_{crit} \), at which the hysteresis loop reflects the remagnetization process of the external shell, has been observed.
- The coercivity, \( H_c \), decreases with the shell thickness increase, and it is determined by the combination of the core and shell coercivities, for thicknesses below \( t_{crit} \), and by the shell magnetic behavior for thicknesses above \( t_{crit} \).
- The saturation magnetization, \( M_s \), increases with the shell thickness having a linear-like behavior.

2. Influence of shell continuosnes on the magnetic properties of the core-shell microwires.

- The two-step remagnetization behavior is well defined for all the investigated shell thicknesses, and the magnetization reversal mechanism has been found to be the same as in the case of a fully covered core-shell with the same composition.
- The magnetization of fully covered bi-phase microwires is significantly bigger than the magnetic moments of partially covered bi-phase microwires with the same external shell thicknesses.
- No critical thickness of the external shell, \( t_{crit} \), has been observed, i.e., for all the investigated thickness diapason, the remagnetization process is determined by both, the core and shell, and has a two-step behavior.
- The magnetic bistability deteriorates as the external shell thickness increases, but it is not fully destroyed in the studied thicknesses diapason.
- A near-zero remanence state at near-zero magnetic field is achievable (not possible in the case of fully covered core-shells, because of the critical length effect).

3. Influence of the temperature on the magnetic properties of the core-shell microwires. Thermomagnetic analysis of the core-shell microwires provides information about the magnetic phase transitions and structural transformations. It has been determined that:

- The Curie temperature of the FeSiB amorphous and crystalline phases has been found at \( T_{C,Fe} = 622 \text{ K} \) and \( T_{C,α-Fe} = 925 \text{ K} \), respectively.
- FeSiB amorphous microwire undergoes a structural transformation at $T_{\text{cryst},Fe} = 808$ K, formation of an $\alpha$-Fe(Si) phase and Fe-boride grains, which leads to magnetic hardening.

- The Curie temperature of the CoFeSiB amorphous and crystalline phases has been found at $T_{C,Co} = 645$ K and $T_{C,\text{cryst}Co} = 1002$ K, respectively.

- The crystallization of CoFeSiB alloys occurs in two stages, at $T_{\text{cryst}_{-1},Co} = 857$ K with the formation of Co$_3$B, Co$_5$Si$_2$ phases and a very small amount of pure Co, and at $T_{\text{cryst}_{-2},Co} = 893$ K with the formation of Co$_2$B, Co$_2$Si phases and a small amount of Co.

- The magnetic phase transitions and structural transformations of the core are still distinguishable when a shell is deposited until its $t_{\text{crit}}$ is reached, at which the temperature dependence of the magnetic moment corresponds to its shell.

- The magnetization of the core-shell microwires is proportional to their shell thicknesses.

- The Curie temperature of Co and CoNi external shells has not been reached in the studied temperature diapason, while the Curie temperature of the FeNi shell has been estimated at $T_{C,FeNi} = 837$ K.

- Exposure to high temperature induces irreversible changes in the magnetic properties of the core-shell microwires, due to modification of the material microstructure.
Micromagnetic modelling of Co-Fe$_3$O$_4$ core-shell cylindrical nanowires

An accurate prediction of the magnetic behavior of nanomagnetic systems and its understanding is crucial for the discovery of new phenomena and the development of novel applications, as well as for the fabrication of nanosystems with predefined magnetic properties. Micromagnetic simulations give the possibility to predict the properties of the desired nanosystem based on selection of materials and geometrical parameters prior to the experiment, which may be otherwise expensive, time-consuming, or even impossible to perform experimentally. In the current chapter, the magnetization reversal process of magnetic core-shell nanowires has been investigated using a micromagnetic simulation tool, mumax$^3$. The chapter starts in chap. 5.1 with an introduction to nanowires with their possible applications and current problems, followed by a description of the magnetic states and remagnetization process in nanowires, giving an insight into the magnetic reversal modes, i.e., which type of domain wall is nucleated under which conditions in nanowires and nanotubes. After this, remagnetization through a 360° domain wall is introduced and its importance for technological applications is highlighted. In chap. 5.2 an introduction to magnetization dynamics simulation and an overview of available micromagnetic simulation software are given, followed by the description of the simulation process using mumax$^3$. In chap. 5.3 the results of the micromagnetic simulations are presented, starting with the description of the simulation model (chap. 5.3.1). The simulation results for an individual Co-Fe$_3$O$_4$ core-shell nanowire, performed systematically increasing its core diameter, are shown in chap. 5.3.2. This reveals the effect of the magnetostatic interaction between the core and the shell and has been done with the aim of achieving a geometrical parameter configuration (a core-shell configuration), for which the nanowire has no stray field distribution, which can be used to avoid particle agglomeration during applications. In chap. 5.3.3, a way of self-nucleation of a 360° domain wall in the external shell of the core-shell nanowire by its core is shown. This investigation has resulted in a patent [240]. This chapter ends with a summary of the achieved results and highlights their future perspectives in chap. 5.4.
5.1 Introduction to ferromagnetic nanowires and motivation

As it has been described in chap. 1, the magnetization reversal process and its mechanism in magnetic nano- and microstructures have been extensively investigated, theoretically as well as experimentally, over the last years due to their great potential for innovative technological applications [1–8]. In most applications, a strong magnetization is required, which leads to the undesired agglomeration of the nanoparticles due to the magnetic dipolar interaction via their magnetic stray fields. This "side" effect is highly undesirable and especially dangerous in bioapplications. The aim of the investigation presented in this chapter has been the development of a nanoparticle, which, due to its unique, optimized morphology displays no magnetic stray field distribution. The particle consists of two magnetic phases, a core and a shell, separated by a non-ferromagnetic intermediate nanolayer. Such coaxial nanostructure is designed to show an anti-parallel alignment of the magnetization along its axis, causing a zero magnetic stray field at remanence in a zero or near-zero external magnetic field. Thus, the stray field from the core and the shell compensate each other. In this way it is possible to avoid particle agglomeration, providing the stability of an assembly of particles in suspension or dispersed over a substrate. Hence, very important properties of this type of magnetic nanostructures are:

1. zero remanence at near-zero magnetic field, that prevents particles from agglomeration;
2. an abrupt switching to saturation magnetization at a certain value of the magnetic field $H_{\text{sw}}$, that can be predetermined and tuned in accordance with the desired application;
3. the possibility of the tuning of the total magnetic moment of the structure without varying the remanent state;
4. a low susceptibility at low magnetic fields will prevent the effect of small magnetic fields on the agglomeration of nanostructures (such as the effect of Earth's magnetic field $\sim 0.5$ Oe).

In order to get an estimation of the selection of the materials and the geometrical parameters, which will lead to the described magnetic behavior of the core-shell nanowire, a series of micromagnetic simulations have been performed prior to the fabrication (cf. chap. 6).

Magnetic states and remagnetization process in nanowires

There are several reports in literature dedicated to the characterization of the magnetization process in nanowires and the domain wall nucleation, stabilization and
control [241–244]. At the macro- and mesoscale (conventional magnetism), the remagnetization occurs through the creation of regions in the material in thermodynamic equilibrium, in which all the magnetic moments are (or tend to be) aligned in the direction, determined by the minimization of energy. On the other hand, at the nanoscale due to surface curvatures, confinement effects, and special geometrical configurations, such as additional coating shells and diameter modulations, some novel non-trivial topological structures and fascinating effects are expected to arise [15].

According to experimental results [245], the magnetization reversal does not occur uniformly in a submicrometer-sized system, even in the case when it is mostly uniformly-magnetized at rest, but through such processes as the nucleation of small reverse domains and their expansion through domain wall motion [246]. The domain walls in nanowires are naturally nucleated at their ends. Here the demagnetizing field has the highest values (this position is the locus of magnetic charges [247]), and acts together with the external field to rotate the magnetic moments [248], i.e., end domain formation.

The remagnetization of a nanowire is influenced by its material and dimensions. The material properties are influenced by the fabrication technique, which may result in induced stresses, modifying the magnetic interactions, and magnetic ordering. The dimensions of the nanowire, i.e., the finite-size effect, may induce faster magnetization thermal decay. However, in electrodeposited nanowires, which is the technique used for the sample fabrication (cf. chap. 6), it is possible to disregard this effects since they are particularly resistant against strain and finite-size effects.

Depending on the nanowire material properties and dimensions, either a transverse or vortex-like domain wall can be nucleated (Fig. 5.1) [241–243, 250, 251]. For nanowires with small diameters, below 30 nm to 50 nm, a transverse domain wall is nucleated (Fig. 5.1 left side), while for larger diameters a vortex-like domain wall takes place (Fig. 5.1 right side) (cf. chap. 5.3.2).

A vortex-like domain wall (Fig. 5.1 right side) consists of magnetic moments curling around the nanowire axis. This domain wall is invariant upon the azimuthal rotation, $m_\phi$. Since the magnetization is slightly tilted outwards by the head-to-head positive charge of the domain wall, the radial component, $m_\rho$, is weak. Consequently, according to this boundary conditions, the magnetization must be undefined at the very center (the core), since it can be neither in the axial, nor transverse directions. This peculiarity has the name Bloch point, and its the only singularity predicted in micromagnetism [252]. This is the only possible topological defect in ferromagnetic materials, as a result of which the magnetization vanishes [244, 253]. In vortex structures, the chirality is defined by the relative orientation between its azimuthal component and the core direction, while the polarity is indicated by the
Fig. 5.1: Simulated micromagnetic structure of domain walls in permalloy nanowires: left side - a transverse domain, middle side - an asymmetric transverse domain wall and right side - a vortex (Bloch point) domain wall. The cross-section insets indicate the inner magnetic configuration of the domain walls at the marked positions. The diameter range was $10^{-100}$ nm, and the length was fixed on $2\mu$m. Information about the used material parameters and more details can be found in [249].

core direction. Vortex domain walls have been experimentally observed in permalloy nanowires with a 85 nm diameter using XMCD-PEEM [254]. In contrary to nanowires, in the case of nanotubes, a different type of domain wall is obtained under the same boundary conditions due to a different topology, which is often named vortex domain wall for nanotubes. The difference between the vortex domain wall in nanowires and the one in nanotubes is that for nanotubes, due to their hollow nature, there is no Bloch point [255]. For diameters between the transverse and vortex domain walls, close to the transition between them, a third type of metastable domain wall is possible, which presents characteristics of both domain walls, named asymmetric transverse domain wall (Fig. 5.1 middle side) [244, 256].

It should be noted, that more exotic magnetization configurations, such as the hedgehog point [257], helical domain walls [258] (formed when two vortices with opposite chiralities meet in the encountering position), skyrmion tubes [257] (induced by the nanowire curvature in the absence of Dzyaloshinski-Moriya interactions in the absence of antisymmetric exchange) have been reported in the literature as well. For more details see references.

**Domain wall propagation.**
The domain wall motion can be controlled by various methods, including external magnetic field [259–262], spin-polarized current [263], spin waves and tempera-
ture gradients [264]. The propagation of the domain walls driven by an applied magnetic field in nanowires occurs without the existence of a drop in domain wall propagation velocity at the so-called Walker Breakdown field, which is one of their most fascinating peculiarities. In nanostripes, the domain wall velocity under an applied magnetic field its first increasing and suddenly decays at the Walker breakdown field.

**Domain wall pinning.**

For many of the applications, the stabilization and manipulation of domain walls in nanowires, in particular, the precise control of the domain wall position along the nanowire length is of great importance, especially for racetrack memory applications [265]. There is a variety of ways to achieve the domain wall positioning (its pinning) through the creation of potential wells and barriers (pinning sites), on which the domain wall may get pinned. The strategies to create this pinning sites can be intrinsic, via geometrical (defects, diameter modulations, constrictions) and material (layers) modifications, as well as extrinsic, via the creation of local stray fields, form surrounding nanostructures [266] or local thermal gradients [266, 267]. The domain wall pinning and the depinning depends on the domain wall type as well as on its chirality, which has been experimentally observed for nanostripes [264].

**360° domain wall nucleation**

Over the last decade, the interest in the study of formation mechanism, control, and stability of 360° domain walls has increased due to their potential applications, such as domain wall memory, logic devices, and more. 360° domain walls can be stable over a range of fields and at remanence. X. Zhu and J. Zhu [268] have proposed a 360° domain wall for use in magnetic random access memories, in which a ferromagnetic ring is switched between two vortex states, each of which contains a 360° domain wall, switching between two "twisted" states, by a small circumferential field. Hertel et al. [269] found that it can be possible to use a 360° domain wall as a phase shifter for spin waves interference devices since the spin waves can be phase-shifted by 180° when they pass through a 360° domain wall (this was shown as a result of micromagnetic simulations on a ferromagnetic stripe). 360° domain walls can be used for spin waves generation and multiplication. Hermsdoerfer et al. [270] showed by micromagnetic simulations that 360° domain walls can act as spin-wave frequency doubler (the spin waves are emitted with a double frequency of their own resonance frequency). However up to now, the usual way to create 360° domain walls has been by successive injection of two transverse 180° domain walls with opposite orientation. This was shown theoretically as well as experimentally for different geometries: ferromagnetic stripes [269, 271, 272], films [273], rings [274–276], nanowires [277], magnetic tunnel junctions [278]. In this I present a way of self-nucleation of a 360° domain wall in the external
shell of a core-shell nanowire by its core. The natural creation of such domain wall in stripes and nanowires has been a challenge so far, theoretically as a result of micromagnetic simulations, as well as in the experiment. Moreover, I show as well, that the nucleated 360° domain wall dwell in a metastable state, protected by the magnetostatic coupling between the core and the shell, i.e., it remains stable and uninfluenced by the external field over a significant field diapason. Such a self-stabilizing, self-nucleated 360° domain wall is very perspective for applications in magnetic data storage and processing, especially in race-track memory, since it provides a solution to the instability problem of magnetic domain walls against stray fields. This investigation has resulted in a US patent "Tubular nanosized magnetic wires with a 360° magnetic domain walls", released on April 7, 2020 [240].

5.2 Basic principles of micromagnetic simulations

An accurate prediction of the magnetic behavior of nanomagnetic systems and its understanding is crucial for the discovery of new phenomena and the development of novel applications, as well as for the fabrication of nanosystems with predefined magnetic properties. Micromagnetic simulation is a tool that can provide such information, serving as a bridge between theory and experiments. The most important reasons to perform micromagnetic simulations according to [279, 280] are:

- to confirm or interpret experimental results,
- to test or optimize a device design,
- to predict new phenomena,
- to validate (approximate) analytical theories.

5.2.1 Magnetization dynamics: Landau-Lifschitz-Gilbert Equation

To simulate the magnetization dynamics of a nanostructure it is necessary to solve the Landau-Lifschitz-Gilbert (LLG) equation using numerical methods to minimize the free magnetic energy [279, 281–283]. The LLG equation describes the time evolution of the magnetization $\vec{M}$ under a local effective field $\vec{H}_{\text{eff}}$:

$$\frac{\partial \vec{M}(\vec{r}, t)}{\partial t} = -\frac{\gamma_0}{1 + \alpha^2} \left( \vec{M} \times \vec{H}_{\text{eff}} + \alpha \cdot \vec{M} \times (\vec{M} \times \vec{H}_{\text{eff}}) \right), \quad (5.1)$$

Chapter 5  Micromagnetic modelling of Co-Fe$_3$O$_4$ core-shell cylindrical nanowires
where $\gamma_0$ is the gyromagnetic ratio (is defined positive), $\alpha$ is the Gilbert damping parameter, and $\vec{H}_{\text{eff}}$ is the effective field. Taking into account only the interactions which I use in my simulations, the effective field $\vec{H}_{\text{eff}}$ can be defined as:

$$
\vec{H}_{\text{eff}} = \vec{H}_{\text{ext}} + \vec{H}_{\text{Demagnetization}} + \vec{H}_{\text{Exchange}}.
$$

(5.2)

Fig. 5.2: Schematic representation of the terms in the LLG equation for a single magnetic moment. Adapted from [284].

Fig. 5.2 displays a schematic representation of the LLG equation. The first term on the right side in eq. 5.1 is the gyromagnetic torque term, which promotes a uniform precession of the magnetization around the effective field. The second term in eq. 5.1, the phenomenological damping torque, makes it possible to reach the equilibrium state by a reduction of the radius of the magnetization precession around the effective field. Once the equilibrium state is reached, the magnetization is parallel with the effective field, since it has released its kinetic energy by the damping losses. Eq. 5.1 takes the form:

$$
\vec{M} \times \vec{H}_{\text{eff}} = 0.
$$

(5.3)

This equation is known as the equilibrium condition of the LLG equation. Additional torques, for example the spin transfer torques, can take into account the interaction of the magnetization with spin-polarized currents [281, 285]. These, however, are not important for this thesis. Furthermore, it should be noted that eq. 5.1 is only valid when:

1. the magnetization is a continuous function of the position $\vec{M} = \vec{M}(r)$,
2. The magnetization modulus is constant in every point and equal to the saturation magnetization, $|\vec{M}| = M_s$. 

5.2 Basic principles of micromagnetic simulations
5.2.2 Micromagnetic simulation software: mumax

Micromagnetic simulations are based on solving the LLG equation. In order to solve the LLG equation numerically, the continuum theory is approximated as a discrete problem [279, 286]. Two main discretization methods are used in micromagnetic simulations: finite difference (FD) method [287], in which the system is divided in orthorhombic cells, and the finite element (FE) method [286], in which the system is divided in tetrahedral cells [246]. Even though the finite difference method is faster, and usually more suitable for larger simulation grids, it relies on scrupulous interpolation schemes and error estimation, and a fast Fourier transform for the simulation of dipolar fields can be used, an artificial roughness its created when curved surfaces are described [288]. To reduce discretization artifacts, the finite element method is used for curved geometries. It does not use the fast Fourier transform for dipolar fields computation, leading to a larger computational time.

There is a variety of micromagnetic simulation software packages, used to solve the LLG equation, within which the most widely used are OOMMF [289], mumax\(^3\) [281, 290], magnum.fd [291], \(\mu\)MAg [292], FeelLGood [293] and others. The micromagnetic simulations performed in this thesis were made using mumax\(^3\) software. mumax\(^3\) is a GPU-accelerated micromagnetic software package, written in Go programming language [294] in connection with Nvidias CUDA Toolkit [295], which numerically solves the LLG differential equations to calculate the magnetization dynamics in a simulated sample system using the "finite difference in time domain" method, discretizing the magnetization into a mesh of orthorhombic cells. Thanks to the use of a GPU, a Graphics Processing Unit, this software can perform large scale micromagnetic simulations with high throughput performance. The GPU give the advantage of accelerating the micromagnetic simulations, due to its potential to make parallel calculations.

The aim of the simulations is to minimize the total energy, that is usually subdivided in a mesh of cubes, called unit cell, with lateral sizes preferable lower than the characteristic exchange length \(l_{ex} = (2A/\mu_0 M_s^2)^{1/2}\), of the simulated magnetic material (e.g., shown in [296]). The simulation starts from an initial magnetization state that can be stimulated with an external magnetic field. Generally, such initial magnetization conditions do not represent the magnetic state with minimum energy, so the simulation runs iteratively to minimize the energy until a given convergence criteria is satisfied. This could be either a maximum numbers of iterations or a certain minimum value, which is reached by the the variation of the system magnetization over time. The final magnetic configuration is considered the equilibrium state for a given external magnetic field. The solution of the eq. 5.1 allows calculating the magnetization direction distribution through the dynamic evolution of the system. However, if one is only interested in determining the magnetization distribution at equilibrium, i.e., static method, it is sufficient to solve the equilibrium eq. 5.3.
mumax$^3$ has been used within the frames of this work in a Windows-based computer with Nvidia GPUs GeForce GTX 1080 with 8 Gb of RAM memory. According to [281], mumax$^3$ its able to fit up to 16 million cells in 2 Gb GPU RAM. It is necessary to emphasize that mumax$^3$ has a user-friendly interface and a simpler programming language than the rest of the simulation software. Moreover, mumax$^3$ has a large community of users, which maintains it constantly and actively developing. The processing of the micromagnetic simulation results has been realized in various ways: the "OVF" data format [289] (for magnetic textures imaging) has been visualized with the 3D rendering software MuView [297], while the data analysis and graph plotting has been carried out using Origin [298].

5.2.3 Magnetic hysteresis simulation

The following factors influence the hysteretic effects [299] (Tab. 5.1). The intrinsic factors are related to atomistic electronic properties, while the extrinsic factors are related to microstructural issues [300].

<table>
<thead>
<tr>
<th><strong>Sources of hysteretic effects</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Extrinsic sources</strong></td>
</tr>
<tr>
<td>Microstructure</td>
</tr>
<tr>
<td>• Grain size</td>
</tr>
<tr>
<td>• Phase coexistence,</td>
</tr>
<tr>
<td>boundary movement</td>
</tr>
<tr>
<td>• Stress at interface</td>
</tr>
<tr>
<td>• Defects, twinning,</td>
</tr>
<tr>
<td>• Phase purity</td>
</tr>
<tr>
<td>• Finite size effects</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Time-dependence</td>
</tr>
<tr>
<td>• Kinetics of the transition</td>
</tr>
<tr>
<td>under magnetic-field sweeping</td>
</tr>
</tbody>
</table>

To achieve an accurate simulation the exchange stiffness, saturation magnetization and anisotropies must be known [301]. Nevertheless, often the results of a simulation diverge (sometimes dramatically) from the experimental observations due to missguidance or omission of such information as specific granular distribution, interface stresses, dislocations, local defects, proportion of crystalline phases in the simulation parameters. Such a detailed experimental description of the material microstructure is often not available.
5.3 Magnetization reversal of Co-Fe$_3$O$_4$ core-shell nanorods

In this section, the results of the micromagnetic simulations will be presented. An estimation of the material combination and geometrical parameters for a core-shell coaxial nanowire will be given as well, taking into account the predefined magnetic properties, i.e., zero-remanence state at near-zero magnetic field, the biological limitations on the size and material of the particle. It is shown, that the magnetostatic coupling between the ferromagnetic core and the shell, as well as the core thickness and length, defines the magnetization reversal mechanism of the core-shell nanowire.

5.3.1 Simulation model description

The geometry of the simulated nanowire is presented in Fig. 5.3. This coaxial nanosstructure consists of a ferromagnetic core and shell separated by a non-ferromagnetic material. The separation between the ferromagnetic layers leads to the absence of an exchange bias interaction. Consequently, the core-shell nanostructure is governed by magnetostatic and magnetoelastic interactions.

![Schematic representation of the simulated coaxial nanorod with the core diameter, $d_{\text{core}}$, shell thickness, $t_{\text{shell}}$, spacer thickness, $t_{sp}$, and $l$- the core-shell length.](image)

**Fig. 5.3:** Schematic representation of the simulated coaxial nanorod with the core diameter, $d_{\text{core}}$, shell thickness, $t_{\text{shell}}$, spacer thickness, $t_{sp}$, and $l$- the core-shell length.
The material choice is ascribed to the magnetic signal to biocompatibility and cytotoxicity ratio. For the core Co with a polycrystalline structure with an hcp phase with uniaxial magnetocrystalline anisotropy has been considered, according to studies performed on Co nanowires \([241, 250, 302, 303]\). For the shell Fe\(_3\)O\(_4\) with a polycrystalline structure with a bcc phase with cubic anisotropy has been selected. The material parameters has been taken from experimentally investigated Fe\(_3\)O\(_4\) nanotubes, obtained by ALD \([304, 305]\). The material parameters used in the simulations are presented in Tab. 5.2. The choice of Co is due to its high saturation magnetization. While Co is known for its high cytotoxicity, Fe\(_3\)O\(_4\) is one of the most biocompatible materials widely used in biomedical applications. The Fe\(_3\)O\(_4\) shell is designed to cover the Co surface, shielding the body from the damaging Co effect.

**Tab. 5.2:** Material parameters values used in the micromagnetic simulations. From left to right the columns are: saturation magnetization, exchange stiffness, magnetocrystalline anisotropy constant and anisotropy type.

<table>
<thead>
<tr>
<th>Material parameters used for the simulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core material</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>Fe(_3)O(_4)</td>
</tr>
<tr>
<td>Co</td>
</tr>
</tbody>
</table>

The particle size is determined by the biological limit and penetration into the cell, limiting the particle size to be below 200 nm \([306]\). The elongated morphology is selected to achieve a higher torque, and a bigger surface area to functionalize.

The diameter of the nanorod, the Co core, \(d_{\text{core}}\), in the simulation has been increased from 10 nm to 50 nm with a step of 10 nm, while the external shell, \(t_{\text{shell}}\), and spacer, \(t_{sp}\), thicknesses has been kept constant for all the performed simulations, \(t_{\text{shell}} = 10\) nm and \(t_{sp} = 10\) nm. The separation between the two ferromagnetic phases must be higher that the exchange length to avoid exchange effects. The total length of the nanorod was set to 100 nm in chap. 5.3.2 and increased to 160 nm in chap. 5.3.3. For the simulations, a cell size of \(1.5 \times 1.5 \times 2.8\) nm\(^3\) was selected, which is small enough to model the complex structure with cells smaller than the exchange length of the ferromagnetic materials, \(\lambda_{\text{ex}} = \sqrt{(2A/\mu_0 M_s^2)}\).
5.3.2 Core-shell nanowires with no stray field distribution

The hysteresis loops of individual nanowires with the magnetic field applied along the nanowires symmetry axis are presented in Fig. 5.4. The magnetic field has been varied from $+2\, \text{T}$ to $-2\, \text{T}$ with a step adjusted to each field interval. The corresponding magnetic textures are shown in Fig. 5.5, in which the cross-section of the core-shell nanowire along its symmetry axis indicates the inner configuration of the magnetic moments for the selected fields. The white arrows represent the initial magnetization direction, $m_z = +1$, while black arrows represent the remagnetized state, $m_z = -1$. The direction of the magnetic moments is represented by colored arrows according to the color code diagram on the right of each magnetic texture.

Initially the core diameter was increased, while the shell thickness and separation between the shell and core was fixed at 10 nm each. The length of the nanowire was fixed at 100 nm.

The core-shell nanowires obtained by electrochemistry usually have polycrystalline structure [241, 300], for which the constituent crystallites may be oriented randomly in space, resulting in an overall isotropic magnetocrystalline behavior of the samples. Hence, the magnetocrystalline anisotropy averages out, while each single crystallite itself exhibit a magnetocrystalline anisotropy [307–310]. The remagnetization of such core-shell nanowires is determined essentially by the shape anisotropy. This is ascribed not only to the polycrystallinity of the nanowires, but to their high length-to-diameter aspect ratio as well [300]. The micromagnetic simulation of individual core-shell nanorods, whose magnetic behavior is determined by shape anisotropy are presented. The hysteresis loops are characterized by two steps in the magnetization reversal Fig. 5.4, typical for systems composed of two magnetic phases (cf. chap. 4.3).

The shape of the hysteresis loop changes with increasing core diameter from a two-step hysteresis loop to a hysteresis loop for nanowires with a vortex-mediated remagnetization (Fig. 5.4 red and green lines). As shown in the corresponding magnetic texture (Fig. 5.5), the first step on the hysteresis loop is attributed to the remagnetization of the magnetically softer Fe$_3$O$_4$ external shell, which together with the external magnetic field contributes to the magnetization reversal of the magnetically harder Co core at a higher field, independent of the core diameter, for the whole simulated diameter diapason. This is in agreement with the experimental results obtained for core-shell microwires (cf. chap. 4.3). Nevertheless, for each core diameter, the remagnetization mechanism shows its peculiarities and reversal modes. The magnetization reversal of the simulated nanowires starts at their ends.
Fig. 5.4: Hysteresis loops simulated for individual Co-Fe₃O₄ core-shell nanowires with several core diameters and a 100 nm length: $d_{\text{core}} = 10$ nm (black line), $d_{\text{core}} = 30$ nm (red line) and $d_{\text{core}} = 50$ nm (green line).

This is related to the fact that the demagnetizing field has here its strongest value since it is practically parallel to the external field. For more details see chap. 5.1.

For core-shell nanowires with a small core diameter, in this case, 10 nm (Fig. 5.5 upper panel), the magnetization reversal of the Fe₃O₄ shell occurs at $B = -270$ mT in a single switching event between two stable remanent states (a large Barkhausen jump) via the depinning of a domain wall from the closure domain at one end, and its subsequent propagation along the whole microwire. This behavior is reflected in the first step of the hysteresis loop (Fig. 5.4, black line). The magnetization reversal of the Co core takes place at a higher magnetic field value, at $B = -756$ mT, in a single switching event between two well-defined magnetization states, a 180° magnetic moment flip along the nanorod axis, which is reflected in the hysteresis loop in the second step.

In the case of a 30 nm core diameter, the magnetization reversal starts by the rotation of the magnetic moments at the shell tube ends (Fig. 5.5, middle panel) at $B = +70$ mT with the subsequent domain wall propagation at $B = -53$ mT leading to a full shell magnetization reversal. This behavior is reflected in the corresponding hysteresis loop (Fig. 5.4 red line) with a smooth slight decrease in the magnetization before the magnetization jump occurs.

With the further increase of the magnetic field, at $B = -323$ mT, the remagnetization nucleation stage of the Co core starts at the nanowires ends as well. The magnetic moments coherently rotate on the nanowires ends (often referred as "curling" [50]), having an opposite rotation direction at the top and bottom ends. With increasing magnetic field more and more magnetic moments join the coherent rotation of the end domains inside the nanowire volume with a subsequent domain
wall propagation at $B = -361 \text{ mT}$. The initial point of the coherent rotation of the magnetic moment is seen in the hysteresis loop (Fig. 5.4 red line) as a small additional kink, followed by a short range with a smooth slope typical for an area with reversible coherent rotation of the magnetic moments. Until at $B = -362 \text{ mT}$ the hysteresis loop shows an irreversible jump of the magnetization.

I want to note, that for this core thickness a very peculiar behavior is observed: the remanent magnetization of the core-shell nanowire is zero at near-zero magnetic fields, precisely between $B = -53 \text{ mT}$ and $B = -32 \text{ mT}$. The core-shell nanowire shows an anti-parallel alignment of the magnetization along its axis over this field diapason, i.e., the shell is already reversed with $m_z = -1$, while the core is still in the initial state with $m_z = +1$. The core-shell nanowire is in a state, in which the stray field from the core and the shell compensate each other, thereby getting a zero magnetization at near-zero magnetic field. During the subsequent fabrication process, these specific material parameters and geometry will be used (cf. chap. 6).
At the core diameter of 50 nm the nanowire can no longer be approximated to a one-dimensional structure, and has to be treated as a three-dimensional structure [251], which leads to a change of the magnetization reversal mode.

For the 50 nm core diameter (Fig. 5.5, bottom panel): The reversal of the magnetization starts once again at the external shell. With the increase of the field, the magnetic moments at the shell ends start tilting at \( B = +200 \text{ mT} \) and continue until \( B = +85 \text{ mT} \). This behavior favors the nucleation of a vortex in the core. In the hysteresis loop (Fig. 5.4 green line) this is reflected as a smooth reduction of the magnetization value and a kink ascribed to the vortex nucleation in the core, right before the reversal of the shell magnetization occurs at \( B = +84 \text{ mT} \). This vortex is nucleated at each end of the core at \( B = 101 \text{ mT} \) with the same rotation direction in order to minimize the magnetostatic energy. The vortex axis is parallel to the nanowire axis. With a further increase of the magnetic field value, the magnetic moments adjacent to the vortex become part of it, expanding the vortices into the nanowire volume, until at \( B = -129 \text{ mT} \) it fills the whole nanowire. The domain structure of the Co core in this field interval has a combined structure: the central part of the wire along its axis consists of a large domain pointing in the initial magnetization direction, opposite to the magnetic field, covered by a large circular domain girdling the core domain. At \( B = -130 \text{ mT} \) the core remagnetizes in a single switching event. Nevertheless, the vortex is still visible at the nanowire ends until at \( B = -168 \text{ mT} \), when the nanowire is completely remagnetized.

On the hysteresis loop, such vortex-driven remagnetization of the core is reflected by an area with a gradual magnetization decrease over a field interval from \( B = 84 \text{ mT} \) to \( B = -129 \text{ mT} \), creating a concave down positive slope. This area is followed by an irreversible jump of the magnetization at \( B = -130 \text{ mT} \) to a state close to total remagnetization, after which the magnetic moments slowly align with the field direction to the fully reversed state, \( m_z = -1 \), at \( B = -168 \text{ mT} \). I want to note, that the switching field of the external shell decreases with the increasing of the core diameter, as a consequence of the magnetostatic coupling between the core and the shell: the stray field from the core acts with the magnetic field, contributing to the shell remagnetization.

### 5.3.3 Formation of 360° domain walls in magnetic coaxial nanorods

In this chapter the influence of the nanowire length is investigated for several nanowire lengths up to 800 nm, keeping the rest of the simulation parameters unaltered. For core diameters below 50 nm the influence of the length is neglectable, the remagnetization mechanism does not undergo major changes, remaining the
same as described in chap. 5.3.2 for all the studied lengths. For core diameters above 50 nm, the magnetization reversal mechanism changes drastically: for a 160 nm length and a 50 nm core diameter see Fig. 5.6 (the hysteresis loop, red line) and Fig. 5.7 (the magnetic textures in the bottom panel). For easier comparison the simulation results for core-shell nanowires with a 50 nm core diameter and a 100 nm length are presented as well in Fig. 5.6 (green line) and in Fig. 5.7 (upper panel). The details of the magnetization reversal mechanism for 100 nm long nanowires has been described in chap. 5.3.2.

![Fig. 5.6](image)

**Fig. 5.6:** Hysteresis loops simulated for individual Co-Fe$_3$O$_4$ core-shell nanowires with a $d_{\text{core}} = 50$ nm and a 100 nm length (green line) and 160 nm length (red line).

The magnetization reversal process of the core-shell nanowire starts, as in the previous cases at the shell and core ends, where the demagnetizing field has its strongest value. A simultaneous nucleation of a vortex at each of the core ends at $B = +85 \text{ mT}$, this time with opposite rotation directions, is found. The vortex axis is parallel to the nanowire axis. The minimization of the magnetostatic energy of the system leads to the formation of a $360^\circ$ domain wall in the shell, which remains stable (pinned) over a field region between $B = +35 \text{ mT}$ and $B = -63 \text{ mT}$, separating two regions with the same magnetization direction, collinear to the magnetic field direction, i.e., most of the shell has been remagnetized. When the $360^\circ$ domain wall is nucleated on the shell, the vortex at the core tips become less pronounced, the stray field from the shell tries to preserve the initial magnetization state of the core, protecting it from the external magnetic field influence. With the further increase of the field, the vortices expand into the core volume, until at $B = -64 \text{ mT}$ their stray field becomes strong enough to completely remagnetize the external shell in the opposite direction acting together with the external field.
With the further increase of the field, more and more magnetic moments join the vortices inside the nanowire volume, becoming part of them. At $B = -460 \text{ mT}$ the two vortices with different rotation directions meet at the nanowire center. The domain structure of the Co core at this point is complex: the central part of the wire along its axis consists of a very small single domain pointing in the initial magnetization direction, opposite to the magnetic field, covered by two circular domain structures girdling the core domain in opposite directions, divided by a domain in the horizontal plane at the nanowire center with the initial magnetization direction. For such a state the only energetically favorable solution is the core remagnetization through a single switching event at $B = -480 \text{ mT}$.

On the hysteresis loop (Fig. 5.6, red line) the initial point, in which the vortices are nucleated on the core ends is reflected in the form of a small kink at $B = +85 \text{ mT}$, followed by a concave up positive slope, which corresponds to the deviation of the magnetic moments in the shell ends from the wire symmetry axis, with an irreversible jump of the shell magnetization at $B = -64 \text{ mT}$. Between $B = -64 \text{ mT}$ and $B = -480 \text{ mT}$ the vortex-driven magnetization reversal of the core takes place, reflected in the hysteresis loop by a concave down positive slope.
A more detailed representation of the magnetic texture of the $360^\circ$ domain wall, nucleated by the core, is shown in Fig. 5.8. On the left side of Fig. 5.8, a cross-section of the core-shell nanowire with the corresponding top and bottom views are presented. On the right side of Fig. 5.8, the 3D view of the magnetic texture, showing the $360^\circ$ domain wall girdling the shell, is depicted with the correspondent magnification of the magnetic moments forming the $360^\circ$ domain wall along the nanowires axis.

Fig. 5.8: Simulated magnetic texture of the $360^\circ$ domain wall nucleated in the nanowire shell from micromagnetic simulations. Left side- the cross-section of the core-shell nanowire with the corresponding top and bottom views; right side- the 3D view of the $360^\circ$ domain wall magnetic texture with a magnification of the magnetic moments forming the $360^\circ$ domain wall along the nanowire axis.

In order to understand, whether the $360^\circ$ domain wall is nucleated in the shell by the vortices arising at the core ends, independent simulations of the core, a Co nanowire with $d = 50$ nm and 160 nm length, and of the shell, an Fe$_3$O$_4$ nanotube with a tube diameter, $d_{NT} = 60$ nm, a wall thickness, $t_s = 10$ nm thickness, and a 160 nm length have been carried out.
Fig. 5.9: Hysteresis loops simulated for the core and the shell of the Co-Fe$_3$O$_4$ core-shell nanowire individually: a Co nanowire with $d = 50$ nm and 160 nm length (left side) and a Fe$_3$O$_4$ nanotube with a tube diameter, $d_{NT} = 60$ nm, a wall thickness, $t_s = 10$ nm thickness, and a 160 nm length (right side).

In Fig. 5.10 (bottom panel) the magnetization reversal of a Co nanowire with the correspondent hysteresis loop in Fig. 5.9 (left side) are presented. The Co nanowire is initially uniformly magnetized. When the external magnetic field is gradually changed from $+2$ T to $-2$ T the nanowire experience a vortex driven magnetization reversal. When $B = -115$ mT, a vortex is nucleated at each end of the nanowire with the same rotation direction, to minimize the magnetostatic energy which its the strongest at the nanowires ends. The vortex axis is parallel to the nanowire axis. In the hysteresis loop (Fig. 5.9, left side) this is reflected with a small kink at this value of the magnetic field, which typically reflects the vortex nucleation. With a further increase of the magnetic field value the adjacent to the vortex magnetic moments become part of it, expanding the vortices into the nanowire volume until at $B = -182$ mT it fills the whole nanowire volume. Like in the case of the core for a 100 nm long core-shell nanowire with a 50 nm core diameter, the domain structure of the Co core in this field interval have a combined structure: the central part of the wire along its axis consists of a large single domain pointing in the initial magnetization direction (opposite to the magnetic field), covered a large circular domain surrounding the core domain.

The vortex-driven magnetization reversal is reflected in the hysteresis loop by an area with a gradual magnetization decrease, creating a concave down positive slope, typical for reversible rotation of the magnetic moments. The irreversible magnetization jump occurs at $B = -184$ mT, fully remagnetizing the nanowire in the opposite direction, $m_z = +1$. I want to note, that the vortices have the same rotation direction, even though the length is 160 nm and not 100 nm. This is ascribed to the absence of the surrounding ferromagnetic nanotube, which incites as well the nucleation of the vortices with different rotation directions.

In Fig. 5.10 (upper panel) the magnetization reversal process of only the external
shell is presented. The Fe$_3$O$_4$ nanotube is initially uniformly magnetized, $m_z = +1$, in its saturation state. When the external field is reversed from $+2$ T to $-2$ T, the shell switches between two well defined magnetization states, $m_z = +1$, and $m_z = -1$, through a single switching event, a $180^\circ$ magnetic moment flip along the nanorod axis, precisely at $B = -103$ mT which results in a hysteresis loop of rectangular shape (Fig. 5.9, right side). The Fe$_3$O$_4$ shell can be regarded as magnetically bistable (cf. chap. 4.1). I want to note, that the observed magnetization reversal of the nanotube does not occur through a $360^\circ$ domain wall nucleation, like it has been described in the case of a core-shell nanowire with the same Fe$_3$O$_4$ tube as an external shell. Therefore, it is possible to conclude, that the $360^\circ$ domain wall is nucleated in the external nanotube by the vortices of opposite direction arising in the endsides of the core, as an attempt to minimize the magnetostatic energy of the core-shell system.

In this work a way of self-nucleation of a $360^\circ$ domain wall in the external shell of a core-shell nanowire by its core has been introduced. The natural creation of
such a domain wall in nanostructures has been a challenge so far, theoretically as the result of micromagnetic simulations, as well as experimentally (cf. chap. 6). Moreover, it has been shown as well, that the nucleated $360^\circ$ domain wall dwell in a metastable state, protected by the magnetostatic coupling between the core and the shell, i.e., it remains stable and unaffected by the external field over a significant field diapason (between $B = +35$ mT and $B = -63$ mT).

The formation of $360^\circ$ domain wall is restricted by the morphology, geometrical parameters, and materials selected for the nanostructure. For coaxial nanowires with a Co core and an Fe$_3$O$_4$ external shell, separated by a non-ferromagnetic material, a $360^\circ$ domain wall is nucleated only above a critical length and a critical core diameter, $l = 160$ nm and $d = 50$ nm in this case, respectively. Such a self-stabilizing, self- nucleated $360^\circ$ domain wall is very perspective for the use in technological applications, such as magnetic data storage and processing, especially in race-track memory, since it provides a solution to the instability problem of magnetic domain walls against stray fields.
5.4 Conclusions

Micromagnetic simulations have been used to identify material parameters of coaxial nanowire to obtain zero-remanence states at near-zero magnetic field. According to the simulation results, a 100 nm coaxial nanowire with a 30 nm diameter Co core and an 10 nm Fe$_3$O$_4$ shell, separated by a non-magnetic 10 nm insulating layer has to be fabricated.

The reversal mechanism is a typical two steps behavior: the first step occurs at low magnetic field, in the magnetically softer Fe$_3$O$_4$ shell, the second step occurs at higher fields in the magnetically harder Co core. The influence of the core diameter and the core-shell nanowire length on the magnetic properties and the magnetization reversal mode of the core-shell nanowire has been investigated.

The following reversal modes have been observed:

1. single switching event between two stable remanent states, $m_z = +1$ and $m_z = -1$, for $l < 160$ nm and $d_{\text{core}} < 30$ nm;
2. coherent rotation nucleated at the ends of the core for $l < 160$ nm and $30$ nm $\leq d_{\text{core}} < 50$ nm;
3. propagation of vortex domain walls nucleated at the ends of the core for $l < 160$ nm and $d_{\text{core}} \geq 50$ nm;
4. propagation of a 360° DW nucleated in the shell by the vortexes at the end of the core for $l \geq 160$ nm and $d_{\text{core}} \geq 50$ nm).

The influence of the length on the magnetization reversal mechanism of the core-shell nanowire:

- for core diameters below 50 nm is neglectable;

- for core diameters above 50 nm the magnetization reversal mechanism changes drastically, a 360° domain wall is nucleated in the shell to minimize the magneto-static energy by the vortices of opposite direction arising at the endsides of the core. The 360° domain wall remains stable and unaffected by the external field over a significant field region (between $B = +35$ mT and $B = -63$ mT), i.e., it is in a metastable state, stabilized by the magnetostatic coupling between the core and the shell.

For coaxial nanowires with a Co core and an Fe$_3$O$_4$ external shell, separated by a non-ferromagnetic material, a 360° domain wall is nucleated only above a critical length and a critical core diameter, $l = 160$ nm and $d = 50$ nm in this case, respectively.

The results of the present investigation has resulted in a US patent "Tubular nanosized magnetic wires with a 360° magnetic domain walls", released on April 7, 2020 [240].
A novel approach for the fabrication of Co-Fe$_3$O$_4$ core-shell nanowires: synthesis and characterization

"It is during our darkest moments that we must focus to see the light.

— Aristotle

This chapter starts with an introduction to core-shell nanowires and the different approaches existing for their fabrication in chap. 6.1. In chap. 6.2, a multi-step approach is introduced, which has been used to fabricate core-shell nanowires. A detailed description of each of the fabrication steps is provided, specifically:

(i) the description of polycarbonate (PC) membranes in chap. 6.2.1;
(ii) the deposition of a gold film on the PC membrane surface in chap. 6.2.2;
(iii) the subsequent controlled electrodeposition of Co nanowires in chap. 6.2.3;
(iv) the removal of the gold film from the PC membrane surface in chap. 6.2.4;
(v) the etching of the PC matrix by oxygen plasma and subsequent hydrogen plasma reduction of the oxidized nanowires in chap. 6.2.5;
(vi) the air oxidation of metals in chap. 6.2.6;
(vii) molecular beam epitaxy is used for the deposition of an external shell in chap. 6.2.7,
(viii) the core-shell nanowires redispersion in chap. 6.2.8.

Chap. 6.3 is dedicated to the compositional characterization and stray field visualization of single core-shell nanowires by means of scanning transmission electron microscopy (STEM) combined with energy-dispersive X-ray spectroscopy (EDX), i.e., STEM/EDX elemental mapping (chap. 6.3.1), and electron energy loss spectroscopy (EELS) (chap. 6.3.2) for the determination of the oxide types. In chap. 6.3.3 the results of electron holography, performed on single core-shell nanowires are presented and described.

Chap. 6.4 summarizes the findings of this chapter.
6.1 Introduction

The proposed particle morphology, as well as the obtained optimal material and geometrical parameters, leading to a zero magnetic stray field at remanence in a zero or near-zero external magnetic field, are shown in Fig. 6.1.

![Diagram of a core-shell nanowire with labels for core diameter, intermediate shell thickness, external shell thickness, and core-shell length.]

**Fig. 6.1:** Schematics of the core-shell nanowire with the respective material and geometrical parameters, obtained from micromagnetic simulations, which will be used for the fabrication. Here $d_{\text{core}}$ is the core diameter, $t_{sp}$ intermediate shell thickness, $t_{\text{shell}}$ external shell thickness, and $l_{\text{core}}$ core-shell length.

For the fabrication of ferromagnetic core-shell nanowires, two main routes are known and widely used [14, 246]: (i) deposition of the core-shell structure directly inside of a porous template by combining different fabrication methods and (ii) the coating of, grown on a substrate or in a solution.

The second approach allows the deposition of coaxial nanostructures, e.g., by depositing an external shell around free-standing chemical vapor deposited nanowires using sputter deposition [311], by focused electron beam-induced deposition [312], or atomic layer deposition [313, 314].

The template-based fabrication of core-shell nanowires is the most widely used and requires only one chemical method (e.g., electrodeposition, atomic layer deposition (ALD), or coxial lithography), as well as combining different methods (e.g., atomic layer deposition and electrodeposition, electrodeposition and sol-gel, electrodeposition and colloidal chemistry).

Template-assisted fabrication of core-shell nanowires provides a number of advantages, such as the control over the shape and dimensions of the nanowire by the proper selection of the template pore diameter and membrane thickness, high den-
sity of the fabricated nanowires (compared to coated free-standing nanowires), the parallel arrangement of the nanowires inside the templates, and the absence of unwanted interaction between the wires during fabrication. On the other hand, the fabrication of nanowires with diameters below 100 nm is challenging because of the high aspect ratio, which induces diffusion limitations [246]. Among the most known methods are:

A fully electrochemical deposition approach [315–317], in which the shell is initially electrodeposited within the template pores, followed by the electrodeposition of the core. Even though it is possible to get core-shell nanowires by this method, the control over the shell thickness, its homogeneous deposition, nanowire total length and the amount of shells remains an issue.

A combination of electrochemical and atomic layer deposition (ALD) [13], according to which the external shell(s) are deposited using ALD with high precision inside of the template pores in the form of concentric tubes, after which the core is electrodeposited inside the tubes. This method is known for providing high precision, homogeneity, and selection of materials for the core and shells.

A combination of electrochemical deposition and sol-gel [318–320], according to which nanotube/s are grown inside the template pores by sol-gel, after which the core is electrodeposited.

A coaxial lithography approach [321], which allows the deposition of coaxial nanowires by templated electrochemical deposition and subsequent selective wet-chemical etching processes. The approach provides precise control over material composition and geometry of the deposited coaxial nanostructures with sub-nanometer precision.

An electrochemical co-deposition approach with phase separation [322–324], in which the atoms of the desired materials for the core and shell are co-deposited into the template pores, and subsequent selective etching of one material, forming the shell. Additionally, there is a variety of combinations, leading to the fabrication of core-shell nanowires, which will not be explicitly described here. Details can be found elsewhere [14].

Since the desired dimensions of the core-shell nanowires, which I aim to fabricate are rather small with respect to those reported in the literature, and the presence of two shells is mandatory, the described methods are not suitable. Consequently, a novel approach for the fabrication of short coaxial nanowires (core-shell nanorods) has been developed, and subsequently successfully implemented. The approach provides the possibility of selecting the core diameter, length and shell thicknesses with high precision, as well as a wide selection of materials for the core and the shell, and the possibility of depositing several shells.
6.2 Sample preparation

Here, I introduce the 8-step approach for the fabrication of core-shell nanowires, combining a variety of techniques.

![Diagram of the 8-step approach](image)

**Fig. 6.2:** Schematic representation of the 8-step approach for the fabrication of core-shell nanowires, combining a variety of techniques, for more details see text.

A schematic representation of the steps to follow is presented in **Fig. 6.2**. Starting with a polycarbonate (PC) membrane with the desired pore diameter (1), on which a gold (Au) film is deposited (2), acting as the working electrode for the subsequent electrodeposition of short nanowires (500 nm to 1 µm). After the nanowires are electrodeposited (3), the gold film is removed from the polycarbonate membrane surface by sonofragmentation (4), before the subsequent controlled oxygen plasma etching of the membrane is performed to obtain free-standing nanowires with a desired "length" (5). Since the lower half of the nanowires are left inside of the membrane, the nanowires are free-standing from the membrane surface. As a side effect of the oxygen plasma etching, the nanowires are thoroughly oxidized (6); therefore, hydrogen reduction of the metal is performed (6). When the nanowires are brought in contact with air, a natural paramagnetic Co oxide shell is formed on the nanowire, serving as the non-ferromagnetic intermediate shell. Finally, a ferromagnetic shell is deposited around the nanowires using molecular beam epitaxy. Subsequently, the core-shell nanowires are redispersed in a solution, using a combination of wet chemical etching of polycarbonate, sonofragmentation, and
separation of core-shell nanoparticles by differential centrifugation. Each of these steps is described in more details below.

6.2.1 Polycarbonate membranes for template-assisted nanowire growth and their dissolution

Polycarbonate (PC) membranes or track-etched membranes are commonly used as templates for the fabrication of nanowires. They were first introduced by Penner [325] and Martin [326]. For the fabrication of polycarbonate membranes, polycarbonate foils are irradiated with heavy ions with kinetic energies of approximately $10 \text{ MeV/u}$ [67], generating ion “tracks” inside of the polycarbonate, which can be further widened by chemical track etching [327–330]. After this the foils are cut in the desired shape and size, according to the application. The most common shape is a disk related to the application of polycarbonate membranes as filters for general and high-purity filtration [331, 332].

PC membranes can be either prepared in a home laboratory, enabling the design of the membrane parameters according to the requirements of the experiment [67], or purchased from a distributor. The PC membranes, used in this work have been acquired from Whatman Nuclepore [333], which provides a wide variety of membrane shapes, diameters, thicknesses and coatings of PC membranes, as well as variety of pore diameters, ranging from 50 µm to 0.015 µm.

The Nucleopore PC membrane has two sides with different chemical activity, a hydrophobic and a hydrophilic side (see Fig. 6.3). Even though the membranes are initially designed to be hydrophobic, for many of their applications (e.g., filters [331]), one of the sides is functionalized with Polyvinylpyrrolidone (PVP) layer, a hydrophilic surfactant. It is possible to notice by eye that the membrane sides are
different: the hydrophobic side is opaque, while the hydrophilic PVP coated side is shiny. The PVP-coating is easily removable when needed, by boiling the membrane in deionized ultra-pure water for at least 1 h with subsequent air drying [334].

PC membranes provide some advantages, compared to alumina oxide membranes (AAO), for example. Their pores are randomly distributed over the surface, with an adjustable pore density, covering a wide range from 1 to $10^{10}$ pores/cm$^2$, enabling a nanowire deposition without interaction between the neighboring nanowires. Besides, PC is chemically inert to most electrolytes in a wide range of pH, from strongly acidic to alkaline solutions [332]. Moreover, the PC membranes can be easily handled due to their flexibility, and importantly, the PC membrane is easily dissolved in dichloromethane, chloroform, and a variety of other solvents or their combinations (see below), providing a fast, easy and clean way for the dispersion of the deposited nanowires in a solution, minimizing nanowire loss due to washing or etching.

For the fabrication of the core-shell nanowires, designed in the previous chapter, I selected PC membranes with an average pore diameter of 30 nm, pore density of $6 \cdot 10^8$ cm$^{-2}$ [78] and a nominal thickness of 6 µm (Tab. 6.1).

<table>
<thead>
<tr>
<th>Parameters of the used PC membranes</th>
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<tbody>
<tr>
<td>Rated pore size [µm]</td>
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<td>0.03</td>
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**Polycarbonate membranes dissolution**

To image and characterize the fabricated nanowires, the PC membrane has to be dissolved. Regarding the dissolution of the PC itself, the information about the chemical compatibility of PC membranes is presented on Sigma-Aldrich, Sterlich, and Merck webpages [334–337], for example. PC membrane can be dissolved with dipolar aprotic solvents (e.g., dimethyl sulfoxide, dimethylformamide, n-methyl-2-pyrrolidone), with organic chlorinated solvents (e.g., dichloromethane, chloroform), and with aromatic hydrocarbon solvents (e.g., toluene).

Nevertheless, the indicated solvents do not fully dissolve the PC. In this work, two alternative methods for the dissolution of PC membranes have been introduced and modified. For SEM imaging, the PC membrane is dissolved using a method, adapted from [68]. The membrane with the nanowires is submerged for 5 s in dichloromethane ($\text{Cl}_2\text{CH}_2$) heated up to 40°C (boiling point 39.6°C), fresh dichloromethane, chloroform ($\text{CHCl}_3$) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) sequentially. This procedure is repeated three times.
This dissolution protocol is sufficient for SEM imaging, even though the high-resolution images are still affected by the charging effects induced by the electron beam due to the residual organic layer on the surface of the nanowires. To get rid of this undesirable effect, the residual organic layer has to be removed. This is especially important for TEM investigations. For this reason, the nanowires are left additionally in a mixture of chloroform and dichloromethane (1:1) for 30 min, after which they are rinsed with absolute ethanol. All the used solvents have been purchased from Sigma-Aldrich.

### 6.2.2 Fabrication of the working electrode: gold film deposition

To get a reduction of ions from an electrolyte into the template pores, it is necessary to first get a working electrode on one of the surfaces of the PC membrane. Gold is often used in electrochemistry as a material for the working electrode due to its high electrical conductivity, low reactivity, and chemical resistance [14, 113]. In terms of electrical conductivity non-oxidized Ag has the highest value, but it tends to quickly oxidize in contact with air [338].

When depositing gold on PC, the correct side of the membrane has to be used. Even though for most PC membrane applications, the membrane "sidedness" does not play a role, it plays a crucial role in the electrodeposition of nanowires. The gold layer is deposited on the opaque hydrophobic side, ensuring that the hydrophilic side faces the electrolyte, favoring its penetration into the pores. Moreover, electrodeposition experiments have been performed using the shiny hydrophilic side as the working electrode side, and the hydrophobic side facing the electrolyte. In this case, no deposition of nanowires is observed.

One of the main issues in the deposition of gold films is their weak adhesion, which becomes a problem in the case of gold deposition on PC. The homogeneous film growth, forming a continuous film over the PC membrane surface, is a required criterion as well. Therefore, the selection of a suitable gold deposition technique is crucial. The first attempts to achieve a homogeneous gold film deposition over the PC membrane surface have been made using a Q150R Rotary Pumped Coater [218, 339, 340], like in the case of glass-coated microwires (chap. 4.2). In Fig. 6.4 SEM images of the Au film deposited over the PC membrane surface are presented, showing a gold columnar growth, leading to the formation of gold nanopillars. It is visible that the gold adhesion to the PC surface is poor. As a result, the gold layer, consisting of nanopillars, detaches from the surface. Similar growth has been reported in [341] where the aim has been to obtain gold nanoparticles. As it has been shown, this method is not suitable for the deposition of homogeneous gold films, covering the membrane pores.
To solve the adhesion issue, adhesion promoting processes are usually used to improve the adhesion of gold, e.g., the use of a 2 nm to 5 nm thick intermediate oxidative metal, like chromium or platinum [342, 343]. However, these processes are not suitable for the current work, considering that the removal of the gold film must be performed during the next steps of the fabrication process, without inducing major damages to the PC surface or the deposited nanowires. To improve the adhesion of gold films, to tune their morphology, and to provide control over the film roughness, thermal evaporation has been used [343, 344].

Thermal evaporation is a physical vapor deposition process during which the metal is transformed into vapor using thermal energy for thin film deposition on a substrate [345]. Using higher deposition temperatures, improved gold adhesion to the PC surface and a different growth mechanism are expected, thereby achieving a homogeneous working electrode surface over the membrane and its pores. For
the deposition of gold films a conventional thermal evaporation chamber has been used (work group of A. Lorke, University Duisburg-Essen [346]) (Fig. 6.5). The gold pellets, purchased from Agosi [347], have been placed in one of the two available tungsten filament boats (source 1 and source 2 in Fig. 6.5), each of which provides a different gold deposition (see Fig. 6.7), i.e., oblique angle deposition and perpendicular deposition, respectively. The membranes are fixed on a sample holder with the hydrophobic surface facing the beam and mounted 20 cm above source 2 on a movable substrate table at the level of the quartz crystal microbalance thickness monitor. The thickness of the evaporated material is monitored by two quartz crystal microbalances. The gold is heated in the filament boat above 1673 K [348]. The evaporation has been conducted under high vacuum, at a base pressure of $10^{-6}$ mbar, and a deposition rate of $0.17 - 0.19$ nm/s.

![Fig. 6.6: Schematic representation of different growth models of initial metal film growth: (i) Frank-van der Merwe mode, i.e., layer by layer or epitaxial growth; (ii) Volmer-Weber mode, i.e., island growth; and (iii) Stranski-Krastanov mode, i.e., intermediate growth or Stranski-Krastanov mode. Adapted from [349].](image)

It is well known that the initial growth of metal films occurs in three main ways [349]: (i) layer by layer or epitaxial growth, known as the Frank-Van der Merwe mode, in which material growth is related to the crystallographic orientation of the substrate; (ii) island growth, known as the Volmer-Weber mode; (iii) intermediate growth, which combines the formation of a monolayer at the beginning followed by the nucleation and island growth on top of this monolayer, known as the Stranski-Krastanov mode.

In the case of PC, the defects on the membrane surface, thermal processing, and impurities may induce modifications on the gold film growth, making the gold-PC (metal-polymer) interface non-ideal [350]. Nevertheless, the evaporation of gold on PC is smooth and uniform [350], and according to literature gives rise to the formation of crystallites with pronounced $\langle 111 \rangle$ texture [350, 351]. The gold film growth on PC occurs following the intermediate growth model, starting by the formation of a monolayer, which is followed by nucleation on the monolayer surface and subsequent island growth [350].

During the thermal evaporation of gold a high number of clusters is formed, facilitating the immediate formation of a thin gold film [344]. Next to it, gold spitting has been observed for deposition rates over 0.2 nm/s, as a side effect during gold
evaporation due to the ejection of liquid droplets from the filament filled with molten gold simultaneously with the gold evaporation [345], forming solid particles on the membrane surface. For this reason, the deposition rate has to be kept at $0.17 - 0.19$ nm/s. A 500 nm gold layer is deposited for a PC membrane with 30 nm pore diameter. The membranes are removed after allowing the setup to cool down to room temperature.

![Oblique angle deposition](image1.png) ![Perpendicular deposition](image2.png)

**Fig. 6.7:** SEM image of the inner side of a 700 nm thick gold film deposited on the hydrophobic surface of a PC membrane with 30 nm pore diameter using oblique angle deposition (left side) and perpendicular deposition (right side). The white "dots" on the left image correspond to the Au deposited inside of the pores.

The adhesion of the gold films has been tested before electrodeposition manually, scratching its surface with tweezers and checking it afterward with an SEM. The morphology of the deposited gold films, their continuousness, and homogeneity have been characterized by SEM. The membranes are fixed using the gold side on a Si substrate, and the PC is completely dissolved, exposing the "inner" side of the gold film. In Fig. 6.7 the SEM images of the gold surface after PC removal are presented: on the left side the gold film deposited using source 1, i.e., *the oblique angle deposition* is imaged, while on the right side the gold film deposited using source 2, i.e., *the perpendicular deposition* is imaged. The qualitative analysis of the SEM images allows to image the morphology for the two types of deposition. During oblique angle deposition, the gold penetrates $100 - 200$ nm inside the pores, depositing on one side of the pore walls forming a semi-shell (Fig. 6.7, left side). On the other hand, during perpendicular deposition, the gold is deposited in the form of a continuous film (Fig. 6.7, right side) with small "islands," which penetrate the pores during the pore closure. The latter has been selected as a suitable working electrode for the subsequent electrodeposition of nanowires inside the PC membrane pores.
6.2.3 Controlled electrodeposition of cobalt nanowires: growth rate development

The electrodeposition of nanowires has been carried out in a home-built three-electrode electrodeposition setup. A saturated calomel electrode (SCE) is used as the reference electrode, a Pt net as the counter electrode, and a Au-sputtered PC membrane as the working electrode with a working area of 1 cm². To control the experiments a potentiostat Amel 2049 [114] has been used. All the potentials have been measured with respect to the SCE. For more details about the setup see chap. 3.1.4.

The electrodeposition of nanowires has been carried out, in contrast to the core-shell microwires (cf. chap. 4.2), potentiostatically, using a cobalt electrolyte, containing 0.36 M cobalt sulfate heptahydrate (CoSO₄·7H₂O) and 0.16 M boric acid (H₃BO₄) aqueous solutions (using milli-Q water) [111]. Boric acid has been used as the supporting electrolyte. The pH during electrodeposition has been kept constant, at a value of 3, and adjusted using 0.30 M sulfuric acid (H₂SO₄) aqueous solution to decrease the pH or 0.30 M sodium hydroxide (NaOH) aqueous solution to increase it. The deposition has been performed at room temperature. All the used reagents have been purchased from Sigma-Aldrich.

Before starting the electrodeposition, the PC membrane is soaked for 30 min in the cobalt electrolyte, allowing the Co²⁺ ions to penetrate inside the membrane pores. The electrolyte was purged with Argon thoroughly, providing vigorous stirring and replacing the oxygen in the solution, therefore avoiding the electrodeposition of Cobalt oxide in the selected potential range.

After the electrodeposition the membranes are rinsed with milli-Q water to remove the residual electrolyte and left to dry in air. To be able to image the nanowires during their growth the PC has been dissolved using the method described in chap. 6.2.1 at each growth stage, leaving free-standing nanowires on the Au film. For TEM characterization, the Au film is removed using sonofragmentation, after which the PC is dissolved (described in detail in chap. 6.2.8).

Cyclic voltammetry

Firstly electrochemical characterization of the system has been carried out in the Co aqueous electrolyte described above in order to elucidate important details of cobalt electrodeposition. The cyclovoltamogramm reveals the effect of the electrolyte and the deposition conditions.
In Fig. 6.8 three subsequent cycles of a cyclovoltammogram are presented. The potential has been scanned from $+1\, \text{V}$ to $-0.9\, \text{V}$ at a scan rate of $0.05\, \text{V/s}$, recording the so-called *cathodic curve*, during which the deposition of the material takes place, i.e., the *reduction*, and back to the initial value of the potential, from $-0.9\, \text{V}$ to $+1\, \text{V}$, recording the *anodic curve*, during which the dissolution of material occurs, i.e., the *oxidation*.

On the forward scan a near-zero current is observed until at $E = -0.28\, \text{V}$ the current, named *cathodic current*, starts slowly increasing, and at $E = -0.79\, \text{V}$ rapidly increases once the nucleation process is initiated until the potential reaches $-0.9\, \text{V}$. A further increase in the cathodic current can be ascribed to irreversible hydrogen generation due to the aqueous solvent decomposition \[116, 117, 352, 353\], which does not happen within the selected potential range. Once $-0.9\, \text{V}$ is reached the scanning direction is reversed. The current shows a high value until it reaches zero current at $E = -0.52\, \text{V}$, and with a further increase of the potential an oxidation peak is recorded in the vicinity of $E = -0.37\, \text{V}$ (a little shifted for each cycle). Here the dissolution of the material takes place. Even though, only one oxidation peak has been expected, a second peak is observed in the vicinity of $E = -0.30\, \text{V}$ (a small shift is observed for each cycle as well).

Two peaks during the dissolution of a single metal can be interpreted in different ways \[354\]: (i) the dissolution of an underpotential deposited phase \[355\], (ii) differences in the crystal lattice orientation \[356\], (iii) passivation due to oxide/hydroxide formation \[357, 358\], (iv) dissolution of a codeposited hydrogen-rich metallic phase preceding the dissolution of the bulk phase \[359\].
Since the electrodeposited cobalt resulted to be polycrystalline (see chap. 6.3), the most likely reason for having a second peak is the differences in the crystal lattice orientation. Nevertheless, an experimental confirmation is difficult. The reduction and oxidation peaks correspond solely to the electrodeposition of Co, which has been shown in [360], were cyclovoltammetric study has been performed to confirm this using the supporting electrolyte and the electrolyte with Co ions separately.

The Co electrolyte shows good stability upon repeated cycling, i.e., the 3 cycles of the cyclovoltammograms show the same notable features: a well defined oxidation peak in the vicinity of $E = -0.30\, V$ and a reduction starting at $E = -0.75\, V$ with its peak at the highest scanning potential, $E = -0.9\, V$. Details about the kinetics of the process can be found elsewhere [354].

**Potentiostatic deposition of Co nanowires**

In Fig. 6.9 SEM images of potentiostatically deposited nanowires at various applied potentials, $-0.8\, V$, $-0.9\, V$, and $-1.0\, V$, with a deposition time of 120 s are presented after the dissolution of PC.

An adequate selection of the deposition potential is crucial to ensure a homogeneous controllable growth of short nanowires. For low deposition potentials, e.g., $-0.7\, V$, the nanowires will grow very slowly and inhomogeneously inside the membrane pores, filling only a few of them. Such a case is imaged in Fig. 6.9, comparing the amount of nanowires deposited inside a PC membrane over an area of $7\, \mu m^2$ at $-0.7\, V$ (Fig. 6.9, left upper panel) and $-0.9\, V$ (Fig. 6.9, right upper panel). On the other hand, an extremely high deposition potential will lead to a sudden overgrowth of material in the form of dendritic superstructures, which is the case of $-1\, V$, showing an overgrowth of material over the PC membrane surface in the shape of nanoroses and nanoleaves after a deposition time of only 60 s (Fig. 6.9 lower panels).

The potential $-0.9\, V$ has been found to be the most suitable for the electrodeposition of Co nanowires, enabling the homogeneous growth of short nanowires inside the membrane pores and the possibility of controlling their length. In order to follow the deposition process and control the material growth, the current has been recorded as a function of the deposition time. The resulting curve is named current vs. time ($I$ vs. $t$) curve or chronoamperogramm.

In Fig. 6.10, the current vs. time curve recorded at $-0.9\, V$ is shown together with the nanowire growth rate corresponding to each part of the $I$ vs. $t$. Four different stages of Co growth can be distinguished (in agreement with the literature [67–69, 361]): (i) Co nucleation, charging of the electrical double layer and formation of the diffusion layer; (ii) Co growth inside the pores; (iii) hemispherical caps formation on the membrane surface; (iv) growth of the hemispherical caps into...
films on the membrane surface and the subsequent film growth. In Figure 6.11 the correspondent SEM images for each of the growth stages obtained during Co nanowires growth are presented.

Region (i) starts with a sharp increase of the current when the potential is applied, which is ascribed to the charging of the electrical double layer and formation of the diffusion layer. During this stage, the concentration of the electrolyte at the mouth of the pores and in the bulk electrolyte are the same (see Fig. 6.11, left upper panel). As a consequence of the linear diffusion front passing along the pores, Co ions are transported from the bulk electrolyte inside the pores, diffusing to their bottom to initiate the nanowire growth. Once the nanowires are nucleated and the growth starts, the electrolyte concentration changes within the pores. An abrupt decrease in the current-time plot is observed in this region, which indicates the diffusion layer formation [362].

In region (iii), the diffusion front reaches the pore mouth and propagates in three dimensions, forming a hemispherical front, creating an ion concentration gradient between the pore mouth and the bulk electrolyte. In region (ii) of the potentiostatic curve on Fig. 6.10 the current remains nearly constant until the nanowires reach the

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Fig. 6.9: SEM images of the deposited nanowires at $E = -0.7\, \text{V}$ and $E = -0.9\, \text{V}$ (upper panel left and right respectively), and dendritic cobalt superstructures deposited on a PC membrane at $E = -1\, \text{V}$ in the shape of nanoleaves (left bottom panel) and nanoroses (right bottom panel). The magnification of selected regions are indicated with white squares on the images.
Fig. 6.10: Electrochemical reduction current as a function of the deposition time for the potentiostatic electrodeposition of Co \(-0.9\) V in PC membrane pores with a 30 nm pore diameter. The schematics displays four different stages of the growth process: (i) nucleation of Co and initial growth, (ii) Co nanowires growth, (iii) hemispherical caps formation, (iv) Co film growth over the membrane surface. The lower panel shows the growth rate, measured for each of the deposition times.

membrane surface indicating constant growth rate, where the current increases at the end of the region, increasing the diffusion of ions towards the nanowire growth front (see Fig. 6.11, right upper panel).

In region (iii), the diffusion is linear inside the pore and in the bulk electrolyte. During this stage, the nanowires fill the pores completely, reach the mouth of the electrolyte, forming mushroom-like hemispherical caps on top of the nanowires. This is reflected on the I vs. t curve with an increase of the current, ascribed to the increased surface once the hemispherical caps start to grow. Linear diffusion at this stage provokes nanowire growth instability, which means that some nanowires will grow faster than the others, forming single early mushroom-like structures (see Fig. 6.11 middle panel) [363]. The mushroom-like hemispheres grow further, merging and forming a film on top of the membrane. In this region, the current saturates emphasizing the start of region (iv), the film growth, during which the current increases continuously and slowly (see Fig. 6.11, lower panel).

For the subsequent development of core-shell nanowires, I selected the 1 µm long nanowires, deposited at \(-0.9\) V and 30 s deposition time. The diameter of the nanowires, grown inside PC porous membranes, tend to slightly differ from the PC membrane pore size, showing a higher diameter. For the 30 nm pore diameter membrane nanowires with a 39 ± 2 nm diameter are obtained. There are two possible explanations for this effect [69, 352]: (i) the shape of the pore inside the
membrane is not fully cylindrical, but a conical taper shape; (ii) the flexibility of PC, which stretches, expands the pore in all directions when the metal is grown inside of them.

Fig. 6.11: SEM images of the Co nanostructures, formed in the membrane pores during each of the four different stages of the growth process, corresponding to the current-time plot (see Fig. 6.10). The magnification of selected regions are indicated with white squares on the images.
6.2.4 Working electrode removal by sonofragmentation

Before proceeding with the etching of the PC membrane to free the nanowire ends for the subsequent deposition of the shells, the gold layer must be removed. Although chemical wet etching methods are widely used to etch gold using potassium iodide ($\text{KI}$) solution, this method will be avoided, since it partially etches away the metal nanowires. The overall length of the nanowires inside of the membrane is 1 $\mu$m, thus they occupy only $1/6$ of the membrane, and the free PC surface is hydrophilic, the $\text{KI}$ infiltrates inside the membrane pores and fully etches away the nanowires.

![SEM images of the PC membrane surface (Au side): left side - 700 nm thick Au film on the PC membrane surface, right side - PC membrane surface after Au removal by sonofragmentation.](image)

Thus, the gold film deposited on the PC membrane surface is removed using sonofragmentation as a method for the film breakage. Sonofragmentation is described in detail in chap. 6.2.8. The membrane is suspended in Milli-Q water under constant stirring with the gold film facing down, providing better interaction with the cavitation bubbles, which leads to the breakage of the gold film into nano-sized fragments. An ultrasonic power of 140 W is applied, and the exposure to ultrasound has been limited to 1 min. This method has been found to be very efficient, but precise control of the sonication time is required to avoid possible damages of the nanowires inside of the membrane, even though they are not directly affected by the cavitation bubbles. When the ultrasound time is longer than required, the membrane curls, making the following preparation steps difficult. In Fig. 6.12 SEM images of the PC membrane surface with the gold layer (left side) and after gold removal (right side) are presented. It is possible to see the nanowire tips on the membrane surface, as well as part of the nanowires showing through the membrane. Additionally, it is possible to see as well that the nanowires did not
grow inside each of the pores, leaving some of them empty. The PC surface is free from gold and ready for the subsequent O₂ plasma etching.

6.2.5 **Oxygen plasma etching of polycarbonate and the subsequent hydrogen reduction of CoOₓ**

The methods for the controlled etching of surfaces, especially those with nanometer precision, are very limited. Regarding PC, there are few works reported on the controlled wet chemical etching of PC membranes with the aim of achieving partially liberated from PC free-standing nanowires [332, 364–367], which cannot be done with a high enough precision and satisfactory repeatability.

An alternative to wet chemical etching of a PC membrane is reactive plasma etching, specifically oxygen plasma etching, having the highest PC etch rate [368–371] and surface modification [369, 371–377]. And it has been found to be a good method to strip out nanowires from PC membranes. Even though some works have been dedicated to the etching of PC membranes using oxygen plasma with the aim of achieving partially liberated free-standing nanowires [364, 367, 378–381], no precise control over the etching has been achieved, i.e., no length estimation of the free-standing nanowires is performed. In the current work, the precision of the etching has a crucial role, since it will determine the length of the end-product core-shell nanowire. Thus, it is crucial to develop a protocol to etch away PC with nanometer precision.

Plasma etching of the PC membranes containing Co nanowires after removing the gold layer has been performed with the help of M. Stevens using a home-built ultra-high vacuum (UHV) chamber (assembled by U. Wiedwald) [382]. The operational parameters have been optimized experimentally: power of 100 W, rf-excitation at 13 MHz, and oxygen pressure of 1.2 mbar have been kept constant.

The thickness of etched PC, i.e., the length of the exposed nanowires, can be controlled by varying the etching time. The PC has been exposed to oxygen plasma for a duration of 5 – 40 min with a step of 5 min, in order to find the optimal etching time to achieve free-standing Co nanowires with 500 nm length. The resulting PC membrane surface has been imaged after each of the etching procedures by SEM, determining the free-standing nanowire length (for details see [382]). Fig. 6.13 shows representative images of the membrane surfaces following 5 min, 10 min, 15 min, 20 min, 30 min, and 40 min oxygen plasma exposure, showing the increasing length of the freed nanowires. The etching depth increases linearly with the etching time. Over a 5 – 40 min time range including the time zero for the untreated membranes, the etch rate was calculated to be 20 ± 5 nm/min, which is plotted in Fig. 6.14.
It is necessary to point out that the length estimation of the nanowires after oxygen plasma etching is a non-trivial task with several complications. The released nanowires tend to agglomerate in bunches, due to electrostatic interaction. Details about the length estimation can be found in [382]. Processing PC membranes with oxygen plasma results in changes to the membrane surface and pore structure, increasing the root-mean-square roughness [375, 383], very little at short etching times [384], and becoming more pronounced for exposure times over 30 min (see Fig. 6.13), developing a texture composed of raised nodules [385].

The etching of PC starts around the nanowires since thermal dissipation occurs not uniformly (unevenly) around the metal nanowires. As the etching time increases, some additional features arise. For instance, due to the plasma-induced heating of

Fig. 6.13: SEM images of the PC membrane surface with the free-standing nanowires after etching with oxygen plasma for 5 – 40 min.
the nanowires, the area near the nanowires gets etched away faster, widening the membrane pores (see Fig. 6.13). Regardless of this, the oxygen plasma etching is consistent across the PC surface, yielding to a generally flat morphology. Since the etching conditions are selected to have a mild action on the membrane, it does not undergo any shape transformation or deformation, like it has been reported in other works, e.g., shrinking and curling of the membrane [370].

The etching of material occurs as the result of a chemical reaction between the reactive gas and the material, here, PC, which depends on the energy transfer from the plasma to the material surface [386]. The etching of PC during exposure to oxygen plasma is attributed to the reaction of PC with atomic oxygen (influenced by ions impinging on the surface [387]) and photochemical degradation of the ester group [388], forming volatile products, H₂, H₂O, CO₂ and CO [383, 385, 388, 389], which are pumped away. The formation of H₂ can be initiated as a result of UV radiation and ion bombardment [388], while CO₂ and CO are formed as a result of photochemical degradation of ester groups (carboxyl and carbonyl radicals are formed, which leads to the formation of CO₂ and CO), and, mostly, by oxygen addition [390]. Finally, I selected a 30 min exposure to oxygen plasma, which leads to 500 nm etching of PC, stripping out 500 nm long nanowires. These were used for the subsequent fabrication of core-shell nanowires.

**Hydrogen plasma reduction of metals**

Since oxygen plasma is well-known for its oxidizing properties, and it is used as a method to prepare metal oxides, e.g., copper and zinc oxides [391–393], nickel oxide [394]), YBaCuO films [395], an undesirable side effect of the oxygen
plasma etching of PC is the oxidation of the free-standing part of the Co nanowires. Consequently, an important step is the hydrogen reduction of the outstanding nanowires, after which CoO$_x$ is reduced back to metallic Co [396]. The membrane with the freed nanowires is exposed to hydrogen plasma directly after oxygen plasma etching at a power of 100 W, and a pressure of 1.5 mbar for a duration of 40 min. Hydrogen plasma is less reactive than oxygen plasma, and has no visible effect on the PC etching. But it reduces CoO$_x$ created during oxygen plasma etching.

### 6.2.6 Intermediate shell formation: air oxidation of Co.

After the reduction from CoO$_x$ back to Co using hydrogen plasma, the membrane with the nanowires is taken out of the chamber, and kept under atmospheric conditions. The interaction of Co with oxygen [397–400] or air [399–402] at normal atmospheric conditions and room temperature leads to the formation of a few monolayers of cobalt hydroxide [400] or hydroxylated oxide [399, 401] within seconds [402, 403].

In [402] has been shown that exposure to air for one day at room temperature, leads to 8 – 10 Å of oxidized Co.

In [396], it has been shown that spherical Co nanoparticles form a CoO$_x$ shell with a 2 – 2.5 nm thickness when brought in contact with air, which does not change significantly over two weeks.

**Fig. 6.15:** STEM images of a Co nanorod showing the formed oxide shell thickness on its surface after 24 h exposure to air at different magnifications. The dotted line on the right side image roughly denotes the border between the Co core and the CoO$_x$ shell.

I used the effect of the natural oxidation around the nanowire surface for the creation of a non-ferromagnetic intermediate layer. In **Fig. 6.15** STEM images with different magnifications are depicted, showing the thickness of the CoO$_x$, which has
been formed after the exposure of the nanowires to air before the external Fe shell is deposited. The CoO$_x$ shell passivates the inner metallic Co. Regarding the type of oxide, it is known from literature [402] that a thin film of Co(OH)$_2$ is formed at low temperatures and Co$_3$O$_4$ at high temperatures [404], while at room temperature CoO is formed in most cases. CoO is a p-type semiconductor [405, 406], which is paramagnetic above 292 K [407–409].

To determine the Co oxide type of the electrodeposited nanowires, EELS has been performed on the redispersed nanowires right after hydrogen plasma reduction (see chap. 6.3.2).

### 6.2.7 External shell deposition by molecular beam epitaxy

Homogeneous growth of an external Fe shell on the nanowire has been successfully achieved using molecular beam epitaxy (MBE). Molecular beam epitaxy (MBE) is an ultra-high vacuum (UHV) deposition technique for high quality and high purity layer by layer thin film growth as a result of the reaction of a well-defined thermal beam of atoms or molecules at the surface, towards which it is directed [410]. This growth can be epitaxial in the case of a single crystal substrates [411, 412], however, for polycrystalline Co nanowires, it will not be the case. MBE provides such advantages as a clean ultra-high vacuum environment for material deposition, a precise control of the deposited material thickness (with angstrom precision), and a homogeneous layer by layer growth on the surfaces, including those with curvatures, which is perfect for the deposition of an external shell on free-standing nanowires, still being able to control its thickness precisely.

The deposition of the Fe external shell has been performed by MBE using a home-built MBE setup from the group of H. Wende [413] with the help of N. Rothenbach. In Fig. 6.16, a schematic representation (left side) and a picture (right side) of the MBE-chamber are presented. The membrane with the free-standing nanowires is placed and fixed on a sample stage, which can be used to heat the sample before, as well as during the deposition depending on the required growth conditions. In the case of PC membranes, heating to elevated temperatures is not possible due to the low melting temperature of PC [78]. The Fe source material is inside a Knudsen effusion cell (an Al$_2$O$_3$ crucible) and heated by a Wolfram coil above its sublimation temperature, 1523 K [414], creating a well-defined thermal beam of Fe atoms directed towards the membrane, which can be obstructed to cease material deposition by the shutter, when the desired material thickness is reached. The used MBE-chamber additionally allows the co-evaporation of different materials onto the
substrate, as well as their subsequent evaporation using different Knudsen effusion cell.

Fe has been grown at a sample temperature of 300 K, and a base pressure of \(2 \times 10^{-9}\) mbar during deposition with a growth rate of \(0.05\) Å/s. The evaporation rate is monitored during growth using a calibrated quartz-crystal microbalance.

Three thicknesses of the external Fe shell have been deposited, specifically 5 nm, 10 nm and 20 nm, which are listed in Tab. 6.2. Furthermore, the small deposition rate should lead to a homogeneous Fe coating of the free-standing nanowires. However, the influence of the wire orientation, as well as the absence of rotation of the sample during deposition leads to a gradient of the Fe shell thickness, i.e., the shell is thicker on the side of the nanowire facing the beam. The thickness of the deposited external shell has been checked directly after deposition by SEM. The thickness estimation using SEM has been performed making images of the membrane with the sticking out nanowires prior and posterior to Fe deposition, which is a rough but fast estimation of the deposited Fe shell (see Fig. 6.17).

The PC plays a crucial role in the defined homogeneous growth of an external shell around the nanowire surface. An experiment using a gold film, instead of PC, with free-standing nanowires on its surface has been performed (Fig. 6.18, right side), in which the Fe grows over the whole surface forming a film, "gluing" the nanowires to
**Fig. 6.17:** SEM images of the free-standing nanowires after the Fe external shell deposition.

**Tab. 6.2:** List of all fabricated core-shell nanowires with the respective geometrical parameters of its constituents. For the Fe external shell the nominal thickness is presented due to asymmetrical deposition (see text).

<table>
<thead>
<tr>
<th>Core-shell nanowires</th>
<th>Material</th>
<th>Core</th>
<th>Internal shell</th>
<th>External shell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>CoO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>Fe</td>
<td></td>
</tr>
<tr>
<td>Thickness [nm]</td>
<td>39 ± 2 nm</td>
<td>4 ± 1 nm</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>39 ± 2 nm</td>
<td>4 ± 1 nm</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>39 ± 2 nm</td>
<td>4 ± 1 nm</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

the surface. On the other hand, in the case of PC, the Fe external shell is deposited differently, leaving the free-standing nanowires well-defined and standing, growing around the nanowire surface, and in a different manner over the PC (Fig. 6.18, left side).

To determine the type of Fe oxide of the external shell, EELS investigation has been performed (cf. chap. 6.3.2).
6.2.8 Core-shell nanowires redispersion

To extract the nanowires from the PC membrane the following steps are conducted: (i) dissolution of the PC membrane, (ii) sonofragmentation of the Fe film, and (iii) separation of core-shell nanoparticles by differential centrifugation.

(i) Dissolution of the polycarbonate membrane

As it has been described in chap. 6.2.1, the PC membrane dissolution is performed by following a modified multi-step dissolution protocol (see chap. 6.2.1).

The membrane with the nanowires is subsequently submerged in dichlormethane (Cl₂CH₂) heated up to 40°C (boiling point 39.6°C), fresh dichlormethane, chloroform (CHCl₃) and ethanol (C₂H₅OH), each for 5 s. This procedure is repeated three times.
To avoid charging effects induced by the electron-beam due to the presence of a residual organic layer on the nanowires surface, the nanowires are left additionally in a mixture of chloroform and dichloromethane (1:1) for 30 min, after which they are rinsed with absolute ethanol.

In Fig. 6.19, the resulting nanowires embedded in a Fe layer are imaged by SEM. It is possible to see the core-shell nanowires rising over the Fe film and the single Co nanowires below it.

(ii) Sonofragmentation of the Fe film
To perform the breakage of the Fe layer, which fixes the nanowires, and break the nanowires at the core-shell nanowire/Co nanowire interface, sonofragmentation was used.

To break the Fe layer, binding the nanowires, sonofragmentation of the nanowires embedded in the Fe film is performed in milli-Q using an ultrasonic power of 140 W, with a frequency of 35 kHz during 10 s with a repetition of five times.

(iii) Separation of core-shell nanoparticles by differential centrifugation
After sonofragmentation a mixture of core-shell nanowires and unwanted side-products, like Fe particles generated due to Fe film breakage and Co nanowires (mostly also broken in smaller pieces), suspended in the solvent is obtained. To separate the core-shell nanowires from the rest of the particles, differential centrifugation is used. Differential centrifugation is one of the forms of particle separation by centrifugation, according to which particles with different sizes or densities in a suspension will sediment at different rates [415]. The particles with higher mass sediment faster. Therefore, core-shell nanowires will sediment faster, than the unwanted side-products.

![Fig. 6.20: TEM images: left side - Supernatant 1 containing Fe particles and film fragments (Fe film visible in the image), center - Supernatant 2 containing Co nanowires, right side - core-shell nanowires. For details see text.](image)
The initial step of size separation involves the removal of Fe particles. The suspension containing the mixture of core-shell nanowires, Co nanowires, and Fe particles and film fragments is centrifuged at 2000 RPM for 40 min. The resulting supernatant, named Supernatant 1, containing the smallest particles, i.e., Fe particles and free Fe film flakes, is removed and investigated by TEM (see Fig. 6.20, left side). The remaining part of the particles is subsequently redispersed in ethanol and subjected to ultrasound for a duration of 5 s five times consecutively to achieve re-suspension of the wires. The suspension is then re-centrifuged at 2000 RPM for 20 min. The nanowires with lower aspect ratios will remain in the Supernatant 2 (see Fig. 6.20, center), i.e., the Co nanowires, while the core-shell nanowires will sediment [415] the supernatant is once again removed, and the sediment redispersed in ethanol, obtaining the core-shell nanowires dispersed in ethanol (see Fig. 6.20, right side). The obtained suspension is used for the subsequent elemental and structural characterization and electron holography.
6.3 Element specific characterization and stray field visualization

To reveal the morphology and elemental composition of the core-shell nanowires they are investigated by means of scanning transmission electron microscopy (STEM) combined with energy-dispersive X-ray spectroscopy (EDX), i.e., STEM/EDX elemental mapping (chap. 6.3.1). Quantitative information on the oxidation state of the core, intermediate, and external shells is obtained using electron energy loss spectroscopy (EELS) (chap. 6.3.2). The STEM/EDX and STEM/EELS investigations have been conducted with the help of Dr. M. Heidelmann using the ICAN facility [134].

To image the stray field distribution of single core-shell nanowires electron holography has been done by Dr. Zi-An Li in the Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons (Jülich Research Centre) [416] (chap. 6.3.3).

6.3.1 Element-specific characterization by STEM/EDX

In Fig. 6.21 the STEM images (left side) and the respective elemental mapping (right side) of core-shell nanowires with two different external Fe shell nominal thicknesses, $t_{Fe} = 10\, \text{nm}$ (upper panel) and $t_{Fe} = 20\, \text{nm}$ (bottom panel) are presented. In the STEM image, a core-shell structure is visible. The different constituents are represented by different colors, red for the Co core, blue for the oxidized layer, and green for the external Fe shell. The Co and Fe maps are fully consistent with the expected core-shell morphology, while the O signal appears over the whole external shell surface. It is not possible to visualize the intermediate CoO$_x$ shell in the elemental map. To obtain more details about the oxidation states, EELS was carried out (see chap. 6.3.2).

The obtained core-shell nanowires exhibit a length of $460 \pm 10\, \text{nm}$, a Co core diameter of $d_{Co} = 39 \pm 2\, \text{nm}$, an intermediate CoO$_x$ layer of $t_{CoOx} = 4 \pm 1\, \text{nm}$ (as concluded from chap. 6.2.6), and a well-defined external shell covering the whole nanowire surface. Nevertheless, the Fe external shell shows some peculiarities. In Fig. 6.21 it is visible that the growth of the external shell does not occur homogeneously around the nanowire surface, but exhibit a gradient-like thickness evolution, which is especially visible for higher thicknesses, i.e., nominal $t_{Fe} = 20\, \text{nm}$ (Fig. 6.21, lower panel). The influence of the wire orientation during the shell growth, as well as the absence of rotation of the sample holder during deposition (cf. chap. 6.2.7), lead to the formation of a gradient of the Fe shell thickness from front to the backside of the nanowire, e.g., the shell may be thicker on the side of the nanowire facing the beam.
Fig. 6.21: Left side: STEM images of Co-Fe core-shell nanowires with a 37 nm Co core diameter and a 10 nm Fe shell thickness (upper panel) and a 20 nm Fe shell thickness (lower panel). Right side: STEM/EDX elemental mapping of Co (red), Fe (green) and O (blue) for the respective core-shell nanowires.

Thus, for nominal $t_{Fe} = 10$ nm (Fig. 6.21, upper panel) the thickness is $10 \pm 1$ nm and $8 \pm 1$ nm, left, while for nominal $t_{Fe} = 20$ nm the shell is more pronounced on the right side $19 \pm 1$ nm with only $8 \pm 1$ nm on the left side (Fig. 6.21, lower panel).
6.3.2 Determination of the oxide type by EELS

The EELS measurements have been carried out on a Co-Fe core-shell nanowire, a 20 nm free Fe film (center), and a 37 nm Co nanowire. Fig. 6.22 depicts the STEM images of the respective areas from which the measurements have been performed.

![STEM images of core-shell nanowire, free Fe film, and Co nanowire](image)

**Fig. 6.22:** STEM images of the areas of the core-shell nanowire (left side), free Fe film (center), and Co nanowire (right side) from which the EELS measurements have been performed.

Fig. 6.23 shows an EELS spectrum of the Co-Fe core-shell-nanowire in the electron energy region of $510 - 810 \text{ eV}$, i.e., the O K-, Fe L$^{3,2}$-, and Co L$^{3,2}$ absorption edges. The EELS spectrum has been processed in the following way: after subtraction of the zero-loss peak and the subsequent subtractions of a linear background, which has been extracted from the respective pre-edge region, the part of the spectrum in the vicinity of the relevant absorption edges was normalized so that the post-edge region is equal to one.

![EELS spectra comparison](image)

**Fig. 6.24** (upper panel) shows the EELS spectra of the core-shell nanowire (black), with the spectrum of a free 20 nm thick Fe layer (red) extracted as a side-effect from the sonofragmentation process, and of the partially oxidized Co nanorod (green), representing the core with the intermediate shell (cf. chap. 6.2.6). **Fig. 6.24** (lower panel) shows literature spectra of the most common types of Fe and Co oxides from the EELSdb.eu database [417], which will be used in the following to attempt to qualitatively determine the oxide type of the constituents of the core-shell nanowire. I want to note, that the absolute electron energy axis of the measured spectra was unfortunately not calibrated, which will restrict the comparison solely on the spectral shape and relative energy shifts of the spectra. Furthermore, I note that only the reference spectra for Co$_3$O$_4$ from the database showed an offset of the electron energy, and was therefore subsequently corrected by $-5.6 \text{ eV}$ to the energetic position of the Co L$_3$ absorption edge.
Starting with the Fe constituent, the spectral shape of both measurements reflects a broad single-peak structure of the $L_3$-edge as well as of the $L_2$-edge. It is difficult to attribute the spectral shape unambiguously to either Fe, Fe$_3$O$_4$ or Fe$_2$O$_3$, due to the energy resolution and the signal-to-noise ratio. However, since the O K-edge shows a clear signal for both, the free Fe layer and the core-shell nanowire, some oxide contribution has to be present in the measured EELS spectra of the Fe constituent, i.e., Fe$_3$O$_4$, or Fe$_2$O$_3$. Nevertheless, within the limits of accuracy of the measurements, one might attempt to exclude contributions of Fe$_2$O$_3$, which exhibits a clear feature at the rising edge of the $L_3$-edge, but is not visible in the measurements. The broadened, nearly double-peak like structure at the $L_2$-edge of the oxide is hardly visible in the measurement due to the signal-to-noise ratio, and does not allow a clear distinction of the spectra. Furthermore, since the Fe reference spectrum of pure Fe exhibits a 2 eV relative energy shift to the spectra of the Fe-oxides, a mixed state of Fe and Fe-oxide might be excludable. Consequently, the EELS measurements show that the outer Fe shell of the Fe-Co core-shell nanowire presumably entirely consists of Fe$_3$O$_4$. However, I want to emphasize once more that an unambiguously clear attribution of the measured spectra to the reference spectra is with the accuracy of the measurements not possible, also making the other contributions from Fe, Fe$_3$O$_4$ or Fe$_2$O$_3$ possible.

Similarly, the spectral shape of the measurement of the Co nanorod shows a clear single-peak like structure within the energy resolution and the signal-to-noise ratio. I want to note that the Co spectrum of the core-shell nanowire shows an overall smaller intensity than the spectrum of the Co nanorod, which will not be relevant for
the qualitative attribution of the type of Co-oxide and can presumably be attributed to the background resulting from the surrounding Fe shell. I showed above (cf. Fig. 6.24), that a CoO$_x$ contribution is expected to be very small for the Co nanorod ($3 - 5$ nm). Furthermore, it was reported in the literature that Co$_3$O$_4$ is formed mostly at high temperatures [404], while at room temperature, the formation of CoO is favored. Therefore, the $3 - 5$ nm thick CoO$_x$ shell most likely presents CoO, not Co$_3$O$_4$. Consequently, the measured EELS spectra of the Co constituent almost certainly presents mainly pure Co, with a small CoO shell on its outside, even though the measured spectra of the nanorod can not resolve the feature-rich L$_3$-edge structure of CoO.

The spectral shape of the measured O K-edge spectra alone does not allow qualitative analysis of the type of oxide. That is why I restricted the discussion on the comparison of the transition metal absorption edges. Following the discussion above, the first, sharp peak in the measured O K-edge spectrum of the core-shell-nanowire might be a fingerprint of the Fe$_3$O$_4$ contribution, while the second broadened peak resembles a combination of Fe$_3$O$_4$ and CoO, even though the Fe oxide contribution dominates clearly.

Fig. 6.24: Upper panel: EELS spectra for the Co-Fe core-shell nanowire (black), the spectrum of a free Fe layer (red), and of the partially oxidized Co nanorod (green). Lower panel: References literature spectra of the most common types of Fe and Co oxides from the EELSdb.eu database [417].
6.3.3 Electron Holography

Fig. 6.25: Electron holography images of Co-Fe$_3$O$_4$ core-shell nanowires with a 37 nm Co core diameter, 3 – 5 nm CoO intermediate shell, and 10 nm Fe$_3$O$_4$ external shell. Electrostatic and magnetic phase images are shown in the left and right upper panel, respectively. The distribution of the magnetic flux lines, represented as $\cos(20 \cdot \phi_M)$, and the colored representation of phase contours of the magnetic phase image are depicted in the left and right lower panel, respectively. The inset represents the color scale of the magnetic induction orientation in arbitrary units.

To image the stray field distribution of one single coaxial nanowire off-axis electron holography [141] measurements have been conducted.

The obtained interference pattern contains the electron-optical phase shift, combining the electrostatic and magnetic phase shifts. For the analysis of magnetic samples, it is necessary to retrieve the electrostatic and the magnetic contributions to the total phase shift from the hologram [131, 142]. The approach used here is based on the in-situ magnetization of the sample.
Two magnetic states of the sample are defined. For the first state the sample is firstly vertically tilted and then magnetized by a magnetic field of \( B = 1.5 \, \text{T} \) generated by the objective lens. The second oppositely magnetized state of the sample is reached after subsequently changing the tilting angle to the opposite ones. The tilting angle was set to 70°. By adding state 1 and state 2 the electronic phase (\( \phi_E \)) (Fig. 6.25 left upper panel) is obtained, while the magnetic phase (\( \phi_M \)) (Fig. 6.25 right upper panel) is obtained by their subtraction.

To visualize the stray field distribution, the magnetic phase is shown in terms of \( \cos(20 \cdot \phi_M) \), giving rise to a fringe pattern, corresponding to the distribution of the magnetic flux lines, produced by the nanowires (Fig. 6.25 left lower panel) [418]. Additionally, the phase contours are derived from the magnetic phase image to trace the projected magnetic induction flux lines inside and around the sample (Fig. 6.25 right lower panel). The contour spacing is inversely proportional to the in-plane magnetic induction of the nanowires, integrated in the incident electron beam direction. The colormap is generated from the magnetic phase images and superimposed onto it to represent the direction of the projected lateral magnetic induction field by the color, and the magnitude by the intensity.

In Fig. 6.25 two core-shell nanowires with a 30 nm Co core diameter and a nominal 10 nm Fe shell thickness are presented. One can notice that the upper nanowire broke into two halves right in the middle, creating a separated core-shell nanowire with a 250 nm length (mini core-shell nanowire). Additionally, on the upper side of the image, one can see a 10 nm Fe film flake, a side product from the nanowires redispersion.

First, the focus will be held upon the upper nanowire. Inside the upper half of the nanowire, the flux lines are aligned mostly along the nanowire axis (see Fig. 6.25 left and right lower panel). The more densely packed the contour lines, the highest is the magnetization. The lines are not entirely straight and parallel to the nanowire axis, they "oscillate" along it. This observation suggests that the longitudinal (axial) alignment of the magnetization varies along the nanowires. The alignment of the magnetization along the nanowire longest direction, i. e. along their symmetry axis, is the result of the shape anisotropy dominating over the magnetocrystalline anisotropy in cylindrical nanowires (cf. chap. 5.3.2). This favors the observed orientation of the magnetization in order to minimize the magnetostatic energy. Similar results have been reported in [56].

The vicinity of a second nanowire and the Fe film flake induces a more complex flux line configuration, where the stray field from the first nanowire penetrates the neighboring wire. The flux lines bend as they approach the lateral sides of the nanowires and their ends, forming a flux closure configuration of the stray field around the nanowires, and the Fe film flake (see Fig. 6.25 right and left lower
panels). To make further observations the resolution of the recorded electron holography images is not sufficient. Inside the lower mini core-shell nanowire, no flux lines are visible in the phase contour of the magnetic phase image (Fig. 6.25 right lower panel). The mini core-shell is not visible as well in the magnetic phase (see Fig. 6.25 right upper panel) and the magnetic flux lines distribution images (see Fig. 6.25 left lower panel). The absence of a magnetic induction geometry inside of the mini core-shell nanowire can correspond to a state with (i) compensated magnetic stray fields (which has been the desired outcome), or (ii) non-ferromagnetic constituents of the core-shell nanostructure. Since HRTEM investigation proved that CoOₓ forms a 3 – 5 nm shell around the Co core (chap. 6.3.1), and EELS measurements confirm, that the Co core is not thoroughly oxidized (chap. 6.3.2), the latter state (ii) can be excluded. Consequently, proving that the 250 nm long core-shell nanowire is in a state where the stray fields from the Co core and Fe₃O₄ shell compensate each other completely. Longer nanowire lengths lead to a state with uncompensated magnetic stray fields (see Fig. 6.25, right upper and left lower panels).
6.4 Conclusions

In this chapter, I introduced, developed, and successfully implemented a novel fabrication approach for the fabrication of core-shell and core-multishell coaxial nanowires. The approach provides the possibility of selecting the core diameter, length, and shells thicknesses with high precision, a wide selection of materials for the core and the shells, and depositing several shells.

The proposed particle morphology and the obtained optimal material and geometrical parameters, leading to a zero magnetic stray field at remanence in a zero or near-zero external magnetic field, have been obtained using micromagnetic simulations.

The approach is a multi-step process consisting of 8 steps, combining electrochemistry, plasma etching, and molecular beam epitaxy. Each of the fabrication steps has been in detail described, and the resulting sample is visualized using SEM at each of the steps.

As a result, Co-Fe$_3$O$_4$ core-shell nanowires with a 37 nm Co core diameter, 3 − 5 nm CoO intermediate shell, and several thicknesses of the Fe$_3$O$_4$ external shell, precisely 5 nm, 10 nm, and 20 nm, have been fabricated and subsequently characterized.

The morphology and elemental composition of the obtained core-shell nanowires have been investigated using a single nanowire using scanning transmission electron microscopy (STEM) combined with energy-dispersive X-ray spectroscopy (EDX). The oxidation state of the core-shell nanowire constituents have been quantitatively investigated using electron energy loss spectroscopy (EELS) measurements. The stray field distribution of single core-shell nanowires has been obtained using electron holography. The distribution of the magnetic flux lines evidences the presence of a state, in which the magnetic stray fields from the core and external shell compensate each other. However, this is observed for a 250 nm long core-shell nanowire. On the other hand, higher lengths lead to a state with uncompensated magnetic stray fields, which is the case of 500 nm long core-shell nanowires.
Conclusions and perspectives

This thesis was dedicated to the fabrication, and investigation of ferromagnetic core-shell cylindrical structures at the micro- and nanoscale, ultimately aiming to the development of nanoparticles consisting of two ferromagnetic phases separated by a non-ferromagnetic intermediate layer, which show no magnetic stray fields.

Fully and partially covered core-shell microwires

Core-shell microwires with amorphous FeSiB and crystalline CoSiB cores and Co, CoNi, and FeNi external shells separated by a Pyrex layer, were fabricated by the combined Ultitowski-Taylor, sputtering and electrodeposition technique. In particular, a partially covered core-shell microwire has been fabricated for the very first time. The external shell drastically modifies the magnetic behavior of the microwire, enabling the possibility to tune the overall magnetic properties via the magnetostatic and magnetoelastic coupling between the magnetic core and shell. All the fully covered core-shell microwires showed a two step behavior of the magnetization process, until a critical shell thickness $t_{crit}$ is reached, where the external shell dominates the remagnetization process. For both, magnetically soft (i.e., FeSiB) and magnetically hard cores (i.e., CoSiB), the strongest effect on the magnetic properties of the wire was found to be exerted by the soft FeNi shell. I demonstrated that the coercivity, $H_c$, increases/decreases (soft/hard core) with the shell thickness. It is determined by the combination of the core and shell coercivities. The saturation magnetization $M_s$ increases linearly with the shell thickness for both types of core. Partially covered core-shell microwires exhibit a clear two-step remagnetization behavior for all the investigated thickness up to 9.5 $\mu$m, with a significantly smaller magnetization than for fully covered microwires with the same external shell thicknesses. The magnetic bistability of the FeSiB core deteriorates with increasing the shell thickness, but is not fully destroyed in the studied thicknesses range (up to $t_{CoNi} = 9.5 \mu$m). Moreover, a near-zero remanence state at near-zero magnetic field is achievable for partially covered wires, which is, in contrast, not possible for the fully covered case, due to critical length effects.

Temperature changes lead to additional magnetic phase transitions and structural transformations of the core and the shell independently, hence affecting the overall magnetic response. In particular, the magnetic phase transitions from the ferromagnetic to paramagnetic phase, and structural transformations of the core are still distinguishable when a shell is deposited until its $t_{crit}$ is reached, after which the temperature dependence of the magnetic moment is determined by the shell.
High temperatures (up to $T = 1200 \text{K}$) induce irreversible changes in the magnetic properties of the core-shell microwires due to modification of the material microstructure.

The presented study, especially the very-first demonstration of a successful fabrication of partially covered microwires, has been proven to have promising technological application, particularly as magnetostrictive sensor devices and actuators. This investigation has served as a basis for a patent by M. Vazquez et al. [214].

**Micromagnetic simulations of a Co-Fe$_3$O$_4$ core-shell nanowire**

Micromagnetic simulations identified the optimal particle parameters for the miniaturization of the cylindrical core-shell structures to the nanoscale in order to obtain a zero-remanence state at near-zero magnetic field. According to the micromagnetic simulations, a 100 nm long coaxial nanowire with a Co core of 30 nm diameter, and a 10 nm thick Fe$_3$O$_4$ shell, separated by a non-magnetic 5 nm thick insulating layer has to be fabricated to fulfill the desired compensation of stray fields, i.e., the zero-remanence state.

Additionally, I reported on the influence of the core diameter and the nanowire length on the magnetic properties and the magnetization reversal mechanism of the whole core-shell system. The reversal mechanism of the simulated core-shell nanowire showed the typical two step behavior. The length has no effect for core diameters below 50 nm. The magnetization reversal mechanism changes drastically for core diameters above 50 nm, and eventually results in the propagation of a 360° domain wall for a nanowire length of 160 nm and above. The 360° domain wall was shown to be nucleated in the shell to minimize the magnetostatic energy by the vortices of opposite direction arising at the endsides of the core. The 360° domain wall remains stable and unaffected by external fields between $+35 \text{ mT}$ and $-63 \text{ mT}$.

The results of this part of the thesis have resulted in a US patent "Tubular nanosized magnetic wires with a 360° magnetic domain walls" [240].

**Fabrication of Co-Fe$_3$O$_4$ core-shell nanowires**

Finally, I introduced a novel multi-step approach, which consists of 8 individual steps, combining electrochemistry, plasma etching, and molecular beam epitaxy, for the fabrication of core-shell nanowires with several external shells. The approach provides the possibility of tailoring the geometrical parameters, i.e., the core diameter, nanowire length, and shell thicknesses, and allows a wide selection of materials for both the core and the shell materials. I fabricated Co-Fe$_3$O$_4$ core-shell
nanowires with a 37 nm Co core diameter, 3 – 5 nm CoO intermediate shell, and an Fe₃O₄ external shell, with thicknesses of 5 nm, 10 nm, and 20 nm, representing the very-first successful fabrication of short bi-shell core-shell nanowires. Additionally, to the structural analysis of each of the fabrication steps using scanning electron microscopy (SEM), I performed a compositional characterization of the single core-shell nanowires. I visualized the stray field distribution of single core-shell nanowires using electron holography, demonstrating that the magnetic stray fields from the core and external shell indeed are able to compensate each other, as predicted by the simulations. While this state was observed for a 250 nm long core-shell nanowire, higher lengths led to a state with uncompensated magnetic stray fields, e.g., for a 500 nm long core-shell nanowire.

In conclusion, the developed fabrication approach allows to tailor the parameters of the core-multi-shell nanowires according to the needs of specific future applications. In particular, the successful fabrication of short core-shell nanowires with compensated magnetic stray fields demonstrate and emphasize great perspectives for future biological applications, i.e., preventing unwanted agglomeration of the nanowires and still allowing the easy manipulation via external magnetic fields.
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