Template electrodeposition of magnetic nanowire arrays

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Abstract

The controlled production of magnetic nanowire arrays with outstanding characteristics is attracting much interest recently owing to their applications in emerging technologies related with magnetic information storage. Template electrodeposition is an efficient approaching method to fabricate these magnetic nanowires. In this paper, progresses and developments on the electrodeposition of magnetic nanowire arrays using nanoporous templates and their properties are reviewed. First, most common nanoporous templates including track-etched polymers and anodic aluminium oxide membranes and their
preparation methods are outlined. Next; magnetic nanowires of 3d-ferromagnetic metals; Co, Ni and Fe, including elemental metal and amorphous nanowires, electrodeposited in different templates are described. Finally, deposition methods and magnetic and magnetotransport characteristics of the most interesting type of magnetic nanowires, superlattice or multilayered, are explained.

1. Introduction

Demands on micro- or nano-order science and technology have grown rapidly in recent years and electrochemistry, describing all processes of ions and molecules at charged interfaces, has played significant roles in the field of micro- and nano-fabrication [1,2]. Electrochemical fabrication techniques offer some unique advantages over competing technologies such as vapor phase methods and therefore find increasing applications in the electronics, magnetoelectronics, magnetic recording and microsystems industries [3,4].

One of the electrochemical fabrication methods is electrochemical deposition or electrodeposition which is well known as an inexpensive and simple process for the fabrication of metallic materials [5,6]. Although it is generally considered that electrodeposition can produce relatively thick metallic layers, recent developments have demonstrated that electrodeposition is able to make very thin metallic films and a wide range of nanostructured materials [7,8].

In some respects, the achievements demonstrate that electrodeposition is capable of depositing materials in extremely confined and ordered spaces which exist in nanoporous media called template. So far G.E. Possin [9] reported the fabrication of wires as small as 400 Å in diameter with a method involving electroplating into etched particle tracks in mica. Consequently, W. D. Williams and N. Giordano refined this technique and used it to routinely produce wires as small as 80 Å [10]. Most recent emerged researches on the method were pioneered by C. R. Martin, introduced template synthesis for fabrication of one dimensional nanostructures, i.e. nanowires. This method entails using the nanoscopic pores in a host membrane as templates to prepare monodisperse nanoscopic ultra-fine structures of a desired material [11-15]. In the past few years template electrodeposition, the subject of this review has been extensively used as a major and successful method to grow nanowires of various materials.

In this review, I aim to provide an overview on template electrodeposition of magnetic nanowire arrays and describe deposition parameters and properties of different classes of magnetic nanowires, including: ferromagnetic (Fe, Ni, Co and alloys) and superlattice nanowires. This review is divided into several sections. We first explain the fabrication of frequently used templates, track-etched polymeric membranes and anodic aluminium oxide films, and their properties. Next; I give a brief description on the design and methods of electrodeposition of magnetic nanowires into templates. The rest of the review
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will discuss ferromagnetic and magnetic superlattice nanowires electrodeposited in both types of the templates. Magnetic, magnetoresistance properties and substructures of electrodeposited nanowires will be compared with each other.

2. Template electrodeposition

Typically, template is known as an insulating host material which encompasses cylindrical pores with diameters in nanometer range [16, 17]. Template fabrication methods use prefabricated cylindrical nanopores in a solid material as templates. By filling the desirable materials into the nanopores, respected nanowires with a diameter predetermined by the diameter of the nanopores are fabricated [18]. There are several ways to fill the nanopores with metals or other materials to form nanowires, but the electrochemical deposition method [19-21] is a general and versatile method which has been successfully used for creating nanowires of magnetic [22], semiconductor [23,24], and superconductor [25-27] materials. If one dissolves away the host solid material, free-standing nanowires are obtained. This method may be regarded as a “brute-force” method because the diameter of the nanowires is determined by the geometrical constraint of the pores rather than by elegant chemical principles [18].

2.1. Nanoporous templates

Fabrication of suitable templates is clearly a critical step in template electrodeposition. Here, we describe fabrication method and characteristics of more conventional types of nanoporous templates and how electrodeposition can make metals as nanowires into the nanopores.

2.1.1. Track-etched membranes

All early works on templates electrodeposition of nanowires have been carried out using nuclear track filters (NTF) or so-called track-etched (TE) membranes [28]. When a heavy-charged particle such as Ar$^{+9}$ accelerated to 5.5 MeV/amu [29] from a nuclear radiation resource passes through certain materials such as mica or polymers in foil or film shape, it leaves a track of radiation damage in the film via a so-called Coulomb explosion phenomenon (Fig. 1a and 1b). The track can be selectively etched in a suitable reagent, such as hydrofluoric acid or NaOH, a technique that was originally introduced for the detection of charged radiation particles. The reagent “develops” and “fixes” the tracks, which results in fine cylindrical pores in the membrane along the tracks, while leaving the rest of the material essentially unchanged (Fig 1c). The pores are randomly distributed in the film but with a rather uniform diameter along their entire length.
Figure 1. A sketch represented for the steps of fabrication process of track-etched membranes (a) heavy-ion bombardments on surface (b) remained tracks after bombardments and (c) Etching the tracks to form cylindrical pores in membrane and (d) SEM image taken from top surface of a commercially available (Osmonics) PETE with pores of 100 nm nominal diameter. From reference [32].
Most of the works were designed to first provide the finest and critical
details of the geometry and dimensions of microstructural constituent elements -
the information which is most sought after, and the second, as a by-product, it
enables to study the various aspects of interaction of a nuclear particle with
given material leading to formation of tracks in NTF. It is well known that
parameters which control the shapes of tracks in NTF include the nature of the
material, the ion beam and energy deposition rate (dE/dx), pre- and post-
irradiation storage and environment, and the etching conditions [29-31].

Natural mica sheets, organic foils and polymers such as polycarbonate
(PCTE) and polyester (PETE) have been used to fabricate track-etched
templates among which PCTE is the most popular type. Nominal pore sizes
down to 10 nm in diameter have been reported in PCTE [30]. Furthermore,
pore density per area is in a range of 10^7-10^9/cm^2. Figures 1d illustrates a
scanning electron micrograph of a commercially available PETE membrane
from the top surface [32].

2.1.2. Anodic aluminium oxide (AAO)
Anodic aluminium oxide (AAO) or anodic oxide membrane (AAM) has
attracted much more interests recently due to its self-organizing hexagonally
arranged nanoporous structure, introduced by Masuda et al [33]. This kind of
self-organization of nanoporous anodic aluminum oxide is based on naturally
occurring long-range ordering, in which a highly regular polycrystalline pore
structures occurs only for a quite small processing window, whereas an
amorphous pore structure can be obtained for a very wide range of parameters
without substantial change in morphology [34-40]. Over the last decade, these
highly ordered nanoporous films have been used as templates for
electrodepositing metal and semiconductor nanostructures for various
applications such as magnetics and optoelectronics [41-47]. Fabrication
method of AAO templates, two step anodic oxidation or anodization, is very
flexible which makes it possible to provide pores with diameters less than 10
nm up to 200 nm and 10^9-10^11/cm^2 pore density. Moreover, thickness of
template, determining lengths of nanowires, only depends upon oxidation time
and leads to formation of 1-50 μm thick oxide layers.

In the anodization process, an electrical circuit is established between a
cathode and a film of aluminum which serves as the anode. Then, anodic oxidation
or anodization of the film occurs in accordance to the following reaction [45]:

\[ 2\text{Al} + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2, \Delta G^\circ = -864.6 \text{ kJ} \] (1)

where $\Delta G^\circ$ is the standard Gibbs free energy change. During the anodization,
initially a planar barrier film forms followed by pore development leading to
the formation of the relatively regular porous anodic film, which thickens in
time [45], shown schematically in Fig. 2. On the mechanism of self-ordering nature of AAO nanoporous materials, so far O’Sullivan and Wood presented a model which was based on an electric field distribution at the pore tip. This model is able to give microscopic explanations for the dependence of, e.g., pore diameters and pore distances on applied voltage or electrolyte composition, but cannot easily explain the self-ordering behavior. The self-organized arrangement of neighboring pores in hexagonal arrays can be explained by any repulsive interaction between the pores [46]. A possible origin of these forces between neighboring pores is the mechanical stress, which is associated with the expansion during oxide formation interface and leads to form curved shape metal/oxide interface. It is claimed that the pores are formed during electropolishing and/or anodizing on the aluminium surface and can become hexagonally ordered at certain voltages and times of the initial electropolishing [46] or by long-term anodization and reanodization [33] or also by a dynamic process depending on the mobility of ions within the barrier oxide and of Al atoms within the metal [47].

The first and second anodization steps could be conducted in the same condition and the oxide layer formed in the first step is removed by wet chemical dissolution in a mixture of suitable chemicals for an appropriate time, depending on the anodizing time. Based on the applied anodizing voltage and also the type of electrolyte, pores with diameters up to 200 nm are produced. A.P. Li et al demonstrated a formula between interpore distance (D) and anodizing voltage (V) [39]:

\[ D_{(nm)} = -1.7 + 2.81V_{(volts)} \]  

(2)

Figure 2. Schematic of AAO template containing barrier and porous layers on aluminium substrate. From reference [32]
We have used different processes (A, B and C) of anodic oxidation, summarized in Table 1, for fabrication of AAO with different pore sizes. Note that working temperature is kept constant in the mentioned study. The variation of working temperature may affect anodization and self-ordering processes. Details of the effects of temperature on the self-organization of nanopores are found in ref. [47]. The self-ordered anodic aluminium oxide (AAO) membranes have been generally characterized by removing the aluminum substrate and the structure has been observed from the bottom view of grown layer, in which the pore ordering can be achieved easily than the top surface of grown films which is more important in application. Recently, we have demonstrated the topographical properties of AAO films, which contribute into ordering the nanopore domains using atomic force microscopy (AFM) [48, 49].

In this respect, growth sequence of highly ordered AAO templates were investigated by contact-mode AFM including electropolishing, first-step anodizing, dissolution of first oxide layer and second step anodizing, shown in Figs. 3a-d, respectively. After electropolishing (Fig. 3a), aluminium has an almost flat surface, exhibiting small etch pits and bumps, which could be seeds for pore nucleation. Consequently, the electropolished aluminium was anodized for first time. It has been shown that the pits or pores nucleate on the natural barrier layer or in the bottom of porous layer during the initial stages of anodization. However, it is assumed that the pits formed in the electropolishing contributing in the nucleation of pores on the aluminium in the order of $10^{10}$-$10^{12}$.

Figure 3b shows the topography of aluminium anodized for 6 hr in 0.3M oxalic acid at 0°C, obtained in contact mode-AFM. As it can be seen, pores occur on the top surface randomly and have a broad size distribution. During the first step anodization process, the pores nucleate on the electropolished surface at almost random positions, i.e., lattice imperfections or pits formed by electropolishing. As the anodization time is increasing the pores merge and form the curved metal/oxide interface due to stress inducing by volume expansion. Because of the random nucleation positions of initial pores, the hexagonally ordering of pores is just achieved in the first stages of anodizing at the bottom of porous oxide layer and cannot grow up to the thick anodized layers.
Figure 3. Atomic force micrographs obtained after (a) electropolishing aluminium (99.999%) foil in 1 HClO₄/4 EtOH below 5°C for 10 min., (b) First step anodization of aluminium in 0.3M oxalic acid for 6 hr at 40 V, (c) Removing oxide layer, formed during first step anodization and (d) second step anodization at the same conditions as mentioned in the first step. Reprinted from reference [49]. Copy right (2007) with kind permission from Elsevier.

After removing the first anodized oxide layer, the curved shape interface remains on the aluminium substrate. This structure is shown in Figure 3c, which demonstrates the AFM image of aluminium surface after removing the oxide layer. The uniform hemispherical shape of barrier layer covers the substrate surface. Anodizing the sample for second time develops the pore growth exactly on the concave pattern created during the first step anodization, shown in Fig. 3d. As the first step anodizing time increases the hexagonally ordered pore areas, domains, in the bottom of porous oxide layer are formed over the larger surfaces. In fact, nanopores exactly grow upon the relevant hemispheres and form direct pillars, which can be detected on top surfaces of AAO films. Moreover, extension of first step anodizing time increases domain size in a particular regime [48,49].

Consequently, the effect of second step anodizing time has been investigated. In Figure 4, the fracture surfaces of highly ordered AAO films,
2.2. Electrodeposition into nanoporous template

2.2.1. Synthesis methods

Principle of electrodeposition is known for the years. Generally, a given metal is electrodeposited from a cell consisting two conductive electrodes, an electrolyte and a power supply for conducting an electrical current through the cell or applying an external electric field in the electrolyte. As the current flows into the cell, an oxidation reaction occurs on one electrode (called anode) by charging growth species (typically positively charged metal ions) into the electrolyte and consequently a reduction reaction takes place on the other electrode (called cathode), reducing the charged growth species at the growth or deposition surface as a metallic layer. Controlling the process can be carried out using potentiostatic or galvanostatic deposition, depending upon whether applied potential or current is adjusted precisely for the given material to be deposited.

A similar method has been frequently used for electrodeposition of metallic nanowires into nanoporous template, when it has been made electrically conductive. Furthermore, direct current (dc) power supply can easily apply desirable deposition potential or current through electrodeposition cell. For track-etched polymeric templates, there exists an advantage which is obtained in different reanodizing time, elucidate the same through pore arrangement. Thus, as the pore ordering takes place, increasing the second step anodizing time does not affect the achieved arrangement. The thicknesses of AAO films were measured approximately 1 and 6 \( \mu \text{m} \) after 45 min and 6 hr anodizing in second step, respectively [48,49].
the same pore openings on both sides of the template. In this case, the metallic thin layer such as Au or Cu is evaporated or sputtered to fill the pores from one side, forming a conductive layer, reserving the cathode in electrodeposition cell.

For AAO templates, developed barrier layer at pore bottoms during anodizing process only leaves pores open from one side. For such template, two approaches have been developed to make nanowire electrodeposition possible into nanopores. First method involves the procedure mentioned above for dc electrodeposition of nanowires in track-etched polymers before which porous aluminium oxide layer has to be removed from the substrate. Moreover, it is crucial to dissolve barrier layer from pore bottom to make pores open at both sides. The second method is developed based on using barrier layer as a rectifying source for an alternative current (ac) to supply electrons for reduction reaction at cathode (pore bottoms)/electrolyte interface. Alternating current is needed either because of the rectifying nature of the Al metal/oxide junction, or because of diffusion barriers with the deep nanopores [50].

Figure 5a illustrates the common set-up for the template-based growth of nanowires using electrochemical deposition. Template is attached onto the cathode, which is subsequently brought into contact with the deposition solution. The anode is placed in the deposition cell parallel to the cathode. When an electric field is applied, cations diffuse toward and reduce at the cathode, resulting in the growth of nanowires inside the pores of template [51, 52].

![Figure 5a](image_url)  
**Figure 5a.** Schematic illustration of the electrode arrangement for electrodeposition of Ni and Co nanowires, (b) growth stages during nanowire electrodeposition in template. Reprinted from reference [53], Copy right (2007) with kind permission from P.C. Searson and Science).
2.2.2. Growth mechanism

The film growth during a complete pore filling process into template nanopores has a well-defined sequence, described first time by Whitney et al [53]. Figure 5b schematically shows the related results of current density versus deposition time (current transient) when a constant electric field is applied. The curve depicts different stages that can be divided to four regions. A pre-growth stage occurs when a sudden drop of current takes place once the potential is applied through the cell during which nucleation starts at the pore bottoms. S. Valizadeh et al pointed out that this markedly reduction of current happens due to the mass transport limitation [54, 55]. Consequently, a slightly increased current is observed at which the metal is growing in the pores, stage (I). As pores are filled, current increases with a large gradient versus time, stage (II). At final step hemispherical caps, originating form each nanowires, form a coherent planar layer that expanded to cover the whole surface of the template, stage (III). Thus, the effective cathode area increases and a rapidly increasing deposition current can be observed.

2.3. Magnetic nanowires

In this section, ferromagnetic materials including Co, Ni, Fe and their alloys will be discussed in the form of nanowires. Fundamental interest in ferromagnetic nanowire arrays lies in the emergence of novel magnetic and transport properties as the dimension approaches the length scale of a few nanometers to a few tens of nanometers. Current interest in research on ferromagnetic nanowires is stimulated by the potential application to future ultra-high-density magnetic recording media [56]. Electrodeposited nanowires are as well as stimulating great interest because they provide a relatively simple and inexpensive way to study the magnetic properties of nano-scale objects. Due to the shape anisotropy, those elements are predominantly magnetized along their length. However, there are still open questions about the mechanisms responsible for the magnetization reversal [57].

The ultimate density of magnetic storage media depends on the minimum spacing between magnetic domains, their quality and the interaction between adjacent magnets. Miniaturization of the magnets can now be explored through the use of electrodeposited nanowires, whose typical dimensions may vary routinely from 500 down to 30 nm or even smaller. Magnetic order and reversal processes which have been extensively studied since the last century are consequently being re-examined for nanostructured magnets.

This group of nanowires can be easily electrodeposited into the templates using dc or ac currents from salt-based solutions such as CoSO₄, FeSO₄ and NiSO₄ by the method mentioned previously. For example, Co nanowires is either deposited under -0.75~0.95 V (in respect to Ag/AgCl reference electrode) from a typical aqueous electrolyte containing cobalt sulphate salt.
(40 g/l CoSO$_4$.7H$_2$O) in a boric acid solution (40 g/l H$_3$BO$_3$) [58] or using a sulfate electrolyte (CoSO$_4$ /H$_3$BO$_4$) under 20 V$_{\text{rms}}$ at 200 Hz at 25 °C [50]. For alloying, the relevant salt of appropriate concentration must be added to the composition of electrolyte.

This section is divided into two types of magnetic nanowires including elemental nanowires and amorphous nanowires of which most recent achievements on their magnetic properties will be reviewed. Generally, the factors determining the final magnetic response of nanowire arrays are, (i) the magnetic nature of individual nanowires, preferably having strong longitudinal magnetic anisotropy for data storage purposes, and (ii) the characteristics of the geometrical arrangement of the nanopore/nanowire array, which determines the strength of the magnetostatic interaction among neighboring nanowires [59]. Thus, the template used to electrodeposit magnetic nanowires is extremely effective on magnetic properties of nanowire arrays.

2.3.1. Cobalt, nickel and iron nanowires

The magnetic properties of arrays of elemental and alloyed ferromagnetic nanowires electrodeposited inside the void spaces of anodic aluminium oxide (AAO) and of polymer membranes have been extensively investigated. Because of different pore arrangements of each template, the consequent magnetic properties of nanowires are considerably influenced which are described.

2.3.1.1. Electrodeposited nanowires in AAO templates

Porous anodic aluminium oxide (AAO) is considered as particularly attractive template materials for fabricating nanowires, because the pore density is high, the pore distribution is uniform and the diameter of the pores is small [59,60]. However, due to very high surface pore density (typically $10^{-8}$-$10^{-12}$/cm$^2$) of AAO templates, a considerable dipolar interaction occurs between nanowires that affects magnetic properties of the filled templates [22,61]. The ideal result which is looked for, from the magnetic point of view, is the fabrication of controlled long range ordered arrays of nanowires with packing density as high as possible where individual nanowires should ideally keep its own magnetic state and consequently give rise to individualized response under the action of external magnetic field. Figure 6 shows a comparison between two hysteresis loops of Ni nanowire arrays, electrodeposited in AAO templates with different hexagonal order degree defined by the first anodization time [48, 49]. Clearly, the array with only 3 hr of first anodization (lower order degree) presents an effective axial anisotropy less defined than that of the array that underwent 24 hr of first anodization [59, 62].
Figure 6. Hysteresis loops of Ni nanowire arrays grown within nanoporous alumina film previously synthesized in oxalic acid solution (pore diameter=35 nm and spacing=105 nm). —: 24 h and □: 3 h of first anodization times. Reprinted from reference [59], Copyright (2007) with kind permission from M. Hernandez-Velez and Elsevier.

Another advantage of AAO template for magnetic studies is capability of producing wires with diameters comparable to the important length scale for such a magnetic system which is the thickness of a domain wall ($\lambda_w$). For Fe, Ni, and Co, $\lambda_w$ is of the order of 10-50 nm which is obtainable in nanowires by electrodeposition in AAO templates [63].

Details of magnetic properties of nanowires with diameters less than domain wall have been explained by Kroll et al [64]. The magnetisation curves for Ni and Fe nanowires within AAO membranes with an average pore diameter of 12 nm are presented in Fig. 7a. This figured behavior clearly indicates two stable orientations of the magnetic moments, namely pointing parallel and antiparallel to the long axis of the wire. These two orientations are separated by an energy barrier. The slight hysteresis that can be seen for the perpendicular measurement is probably due to a slight misalignment of the wires and due to the influence of the rather weak magnetocrystalline anisotropy. Furthermore, it is obvious that the hysteresis loops for the parallel measurement are slightly sheared. This can be attributed to dipolar interactions between the wires due to very high pore density of the template. Thus, it is concluded for Fe and Ni the easy direction for the magnetization lies preferentially parallel to the long axes of the wires.

The modes of magnetization reversal in such arrays of Fe [65-67] and Ni [68-70] nanowires were tentatively extracted from the dependence of the coercive field on diameter. For Fe nanowires, most of the results suggest that coercivity increases as the diameter of nanowires deceases in a range of 7-160
Figure 7. (a) Hysteresis loops for 12 nm Fe and Ni nanowires measured at 4.2K and (b) Magnetisation curves for Co nanowires at 314 and 5K. *Reprinted from reference [64], Copyright (2007) with kind permission from Elsevier.*

Figure 8. Dependence of the coercivity vs the pore-widening time, i.e., nanowire diameter. The corresponding hysteresis loops for Ni nanowires with diameter of 8, 18, and 21 nm are shown as inset. *Reprinted from reference [72], Copyright (2007) with kind permission from D.J. Sellmyer and American Physical Society (APS).*
nm [71]. Most of studies on Ni nanowires have demonstrated the same variation of coercivity with pore diameter. However, more recently Zheng et al [72] investigated the magnetic properties of Ni nanowires electrodeposited into self-assembled porous alumina arrays. By anodizing aluminum in sulfuric acid and immersing the as-anodized template into phosphoric acid, called pore-widening process, for different lengths of time, a wide variety of pore diameters between 8 and 25 nm was obtained. Figure 8 illustrates that the coercivity measured along wire axis first increases with the wire diameter, reaches a maximum of 950 Oe near a diameter of 18 nm, and then decreases with further increase of wire diameter. Some tentative explanations for this behavior can be found in ref. [72].

Cobalt nanowires not only show the strong shape anisotropy that can be observed for Fe and Ni wires, but also a temperature- and size dependent magnetocrystalline anisotropy along the hexagonal c-axis of HCP-Co. This c-axis is known to be perpendicular to the long axis of the wire. It is well known that the HCP structure favors an easy magnetization axes perpendicular to the wire length, while in the FCC phase the easy magnetization axis lies mainly parallel to the wire axis [63, 64, 73-77].

Measurements on crystalline structure of Co nanowires in some respects show the existence of two Co phases including hexagonal cobalt phase (HCP) and cubic cobalt phase (FCC). Paulus et al [63] pointed out that the amount of FCC phase probably increases if the wire diameter is decreased and the shape anisotropy becomes predominant in small Co wires even at low temperatures. On the other hand, other studies exhibit a relationship which does exist between structure of Co nanowires and pH [59, 78]. Li et al showed that Co nanowires electrodeposited in AAO with diameter size of 15-70 nm, are FCC structure at pH = 2.7, a mixture of structures of FCC and HCP at pH = 3.5, and HCP structure at pH = 5.0. The effective anisotropy along the nanowire axis of the FCC Co nanowire array is obviously stronger than that of the HCP Co nanowire array, and the coercivity of the FCC structure is also larger than that of the HCP structure when they are the same diameter [78].

Therefore, ferromagnetic FCC modification does not influence the magnetic anisotropy of Co nanowires and only for HCP-dominant structured cobalt nanowires at low temperatures a competition between shape anisotropy and magnetocrystalline anisotropy can be observed (Fig. 7b). At room temperature, however, the magnetic properties are predominated by the shape anisotropy. This can be explained by the strong temperature dependence of the magnetocrystalline anisotropy constant. The competition between the two kinds of anisotropies is also controlled by the diameter of the wires. The smaller the pore diameter the less important the magnetocrystalline anisotropy becomes even at low temperatures [64].
2.3.1.2. Electrodeposited nanowires in track-etched polymers

Nanoporous polycarbonate (PCTE) membranes extensively used to electrodeposit magnetic nanowires can present a low pore density and offer the possibility of investigating the magnetic properties of almost magnetically isolated magnetic nanowires. Co [79-86], Ni [87,88] and Fe [89] nanowires successfully electrodeposited in PCTE exhibit an almost similar behavior to that were demonstrated earlier for the nanowires electrodeposited in AAO. Moreover, some particular studies have shown the dependency of structural and magnetic properties of nanowires on the synthesis parameters. Most investigations have been focused on the properties of Co nanowires because of its complex behavior and particular emphasis has been given to the competing shape and crystal magnetic anisotropies that exist in the Co nanowire system.

V. Scarani et al. [81] showed that the microstructure of Co nanowires can be varied by changing the composition of the electrolyte and they produced nanowires in which Co was dominated by the HCP or the FCC phase. As a rule of thumb, low deposition rates were shown to be necessary to grow an HCP phase. This could be obtained by decreasing the ions concentration and diminishing the deposition voltage (or current). The other extreme is the deposition of Co at high rate with the presence of Cu impurities which incorporate into the structure of deposit in a form of CoCu alloy. In such a case, the FCC phase was shown to be dominant. Another investigation by Kazadi et al [83] on the effect of addition of citrate to simple acidic electrolyte demonstrated a decrease in the crystalline grain size and the maximum magnetic moment and it was ascribed, from the electrochemical point of view, to a reduction of current density as the concentration of citrate ion is increased in the bath at the same deposition potential. Overall, citrate generates two effects: slowing down the synthesis rate and diminishing the size of crystalline domains.

The effects of the electrolytic bath acidity, or pH, on the magnetic properties in arrays of electrodeposited Co nanowires and their correlation with the crystalline properties have been also studied [90, 91]. The results showed that, depending on the value of the pH of the electrolyte, appreciable changes in the effective anisotropy can be induced. These changes are attributed to modifications in the microstructure of the Co nanowires. In particular, quantification of the effective anisotropy field implied that the microstructure of the deposited Co wires can be set to contain a dominant fraction of the Co-HCP phase with the c-axis oriented perpendicular to the wires for pH values of 3.8–4.0, and parallel to the wires for pH values ~6.0. This could result in a competitive or additive magnetocrystalline contribution to the total anisotropy field. Furthermore, at a pH value of 2.0, no contribution from the magnetocrystalline anisotropy is present, indicating a lack of texture in the Co microstructure.
In addition, in the range of the synthesis conditions presented by Kazadi et al [82], the magnetic behavior of nanowires electrodeposited from a simple salt bath depends neither on the synthesis reduction potential nor on the electrolyte concentration. It was shown that in a range of diameters (100–200–400 nm) the shortest wires have an easy axis of magnetization parallel to the axes of the wires, and the longest wires present a crossover towards perpendicular directions. This has been explained by a simple magnetostatic model, which corresponds to competition between the dipolar interactions, demagnetizing field, and the Co magnetocrystalline anisotropy [85]. It is worth noting that if dipolar coupling acts as an additional magnetic anisotropy favoring an easy axis of magnetization perpendicular to the wires, then the effective anisotropy field of the wires will decrease as they are brought closer together [92].

2.3.2. Amorphous magnetic nanowires

In the previous section, it was pointed out that in nanowires the magnetic behavior is governed both by shape and magnetocrystalline anisotropies. However, the magnetocrystalline anisotropy of structures made from amorphous magnetic materials is absent, and the magnetic behavior is primarily determined by shape. Electrodeposition has been widely used for the synthesis of amorphous alloys including binary transition-metal–metalloid glasses such as Ni-P, Co-P, and Fe-P. The microstructure and magnetic properties of the materials depend on the composition, and can be controlled by varying the electrodeposition conditions such as the electrolyte and the current density [93].

Ge et al [94] demonstrated that amorphous and crystalline Co nanowires can be electrodeposited into polycarbonate membranes by varying deposition potential. As the deposited cobalt nanowires at −1.2 V (in respect to Ag/AgCl), 250 mA/cm² shows perpendicular anisotropy, but the deposited at −1.0 V (in respect to Ag/AgCl), 125 mA/cm² has no perpendicular anisotropy any more. This different magnetic behavior was explained from their different microstructures the former sample is amorphous, and the latter is polycrystalline. Consequently, easy axis of magnetization lies along wires in the former sample due to only shape anisotropy.

To the author's knowledge, the idea of studying electrodeposited amorphous metal-non metal alloy magnetic nanostructures has been developed since the work of Ross et al [95]. Arrays of low-aspect-ratio cylindrical amorphous CoP nanomagnets with diameters near 100 nm have been fabricated using electrodeposition into a lithographically patterned template. The remanence of individual particles and the easy axis direction are consistent with the predictions of a micromagnetic model by considering zero magnetocrystalline anisotropy, but the behavior of the arrays is dominated by magnetostatic interactions, because the switching fields of the particles are low...
compared to the magnitude of the nearest-neighbor interactions. After this principle study, some other groups have investigated properties of this category of amorphous nanowires in track-etched and AAO templates [96-99]. Arrays of amorphous NiP and CoP nanowires with diameters near 200 nm have been dc electrodeposited into PCTE and AAO. The microstructure and magnetic properties of the nanowire arrays were demonstrated to strongly depend upon the composition, i.e. content of phosphorous (%P) and could be controlled by varying the composition, pH and the temperature of the electrodeposition bath. It was implied that the replacement of Ni with Co results in both the decrease of the coercive field and the increase of the Curie temperature [96]. More recently, CoP nanowires were synthesized in AAO by ac electrodeposition [97] that showed the existence of a relationship between bath composition, i.e. sodium hypophosphite concentration on the P content of nanowires.

Amorphous FeCoP ternary alloy nanowire arrays with diameters of about 40 nm were fabricated in AAO templates by ac electrodeposition method, indicating that the nanowires are amorphous in structure. The magnetic hysteresis loops (when magnetic field is applied parallel to wire axis) showed that $H_c$ and squareness ($M_r/M_s$) increase with increasing Co content. Other results demonstrated that magnetic moments of the Fe atoms are almost parallel to the wire axis, and the easy magnetizing axis is parallel to the nanowires, which indicates that the nanowire arrays have obvious shape anisotropy. With increasing Co content the saturation magnetization of Fe atoms decreases which is in consistent with the decrease of saturation magnetization of nanowires [98].

A comprehensive study has been carried out on another ternary alloy nanowire arrays (CoFeB) by a pulse electrodeposition (PED) method into AAO [99]. It was found that the density of nanowires in the array can be modified by changing the ratio $t_{on}/t_{off}$ for PED, as the lower the duty cycles, the higher the packing density of wires were obtained. This affects the magnetic behavior of arrays by magnetostatic interactions. It may be observed that as $t_{on}/t_{off}$ increases, there is an increase of out-of-plane coercivity and squareness ($M_r/M_s$). A further observation on the effect of the peak current density ($i_p$) showed that, at constant value of $t_{on}/t_{off}$ ratio, a decrease in $i_p$ tends to produce an increase in the out-of-plane $H_c$ and squareness, and an inverse change for the in-plane $H_c$ and squareness. The main magnetization characteristics of the arrays – high field of saturation and low remanence – were determined by the superposition of effects due to the shape anisotropy of the individual nanowires and the inter-wire magnetostatic interactions. The easy axis of magnetization of the alloy arrays can be perpendicular or parallel to the wire, depending on the wire diameter and length. This behavior was explained in terms of the geometry-dependent magnetostatic interactions [99].
Cobalt-platinum alloy nanowires may be classified as another category of electrodeposited magnetic nanowires exhibiting amorphous structure, although some investigations reported crystalline microstructure in these alloy nanowires. Li et al. reported the formation of amorphous as-deposited Co$_{0.71}$Pt$_{0.29}$ nanowires by dc electrodeposition into AAO with 50 nm pore diameter. However, an argon atmosphere annealing of the nanowires at 700 °C leads to development of FCC phase in the structure [100]. Another report by Chen et al. showed that Co$_x$Pt$_{1-x}$ ($x>0.5$) as-deposited and annealed nanowires consist of FCC phase. The as-deposited nanowires with Pt content of about 50 atomic % consist of a single ferromagnetic phase; FCC CoPt. When the Pt content of the nanowires varies from about 55 to about 75 at.%, the nanowires comprise a soft phase of FCC CoPt$_3$ and a relatively hard phase of FCC CoPt, where two phases are separate as seen from the hysteresis loops. After annealing at 600 °C, two phases coupled completely and the coupled phase has the same coercivity equal to the original hard one [101].

Mallet et al. [102] demonstrated the formation of a disordered single phase FCC structure in as-deposited Co$_{0.65}$Pt$_{0.35}$ nanowires with a range of diameters (48, 74, 240, and 470 nm). Their nanowires exhibited both shape and magnetocrystalline anisotropy leading to large coercivity and high remanence along the wire axis. More recent investigations by T.H. Shen group on the structure and magnetic properties of 14 nm diameter cobalt platinum (Co$_x$Pt$_{1-x}$, 0.09 ≤ x ≤ 0.86) nanowires obtained by ac electrodeposition into AAO [103], indicated that the crystal structure of the as-deposited nanowire arrays changes progressively from HCP to a mixture of HCP and FCC phases and finally to pure FCC with increasing Pt content. An earlier work of this group explained the effect of annealing on the structure of cobalt-rich Co$_{0.96}$Pt$_{0.04}$ nanowires, fabricated by a similar procedure. Crystalline structure after annealing was shown to be predominately HCP with a preferred texture along long axis of nanowires and the optimum properties required for a recording medium e.g., coercivity and squareness are attained at an annealing temperature of 600 °C [104, 105].

2.4. Multilayered or superlattice nanowires

Since the discovery of giant magnetoresistance by Baibich et al. [106] in magnetic multilayers, a great deal of attention has been devoted to the magnetic and magnetotransport properties in multilayered structures for possible potential in high density magnetic storage applications, i.e. spin valves. First works were usually carried out by vacuum deposition systems like sputtering or molecular beam epitaxy. Consequently, the electrodeposition method, cheaper and simpler to implement, has been successfully used to fabricate
multilayers exhibiting GMR by Schwarzacher group at Bristol [107]. All the earlier studies were based on resistivity measurements with the current in-plane (CIP) geometry. However, it was shown theoretically how it would be possible to detect the contributions of the interfaces and of the bulk properties and the influence of the spin diffusion length (SDL) on spin-polarized electron transport in current perpendicular to plane (CPP) geometry, proposed by Valet and Fert [108]. In practice, the extremely low resistance perpendicular to the plane of thin film samples renders such experiments extremely complicated and a few groups were able to measure it by using superconducting connections at limited low temperatures and lithography techniques with pillar structures [109,110]. In the CIP geometry, the anti-ferromagnetic coupling is crucial and an optimum bi-layer width of about electron mean free path (MFP) [111] is necessary to maximize the effect. In the CPP geometry, the interface resistance and the ferromagnetic bulk resistance both contribute to the magnetoresistance and the optimum scale is affected by spin- or spin-flip diffusion length which is an order greater than MFP [112-115].

One of the most exciting achievements in the recent development of electrodeposition is fabrication of multilayered or superlattice nanowires into template, demonstrated by two groups almost at a same time, Piraux et al. [116] and Blondel et al. [117]. These nanowires are of great importance because of their very small cross sections which can be easily obtained by electrodeposition. It facilitates magnetoresistance measurements along wire axis. In addition, such a system is able to conduct electrons almost perpendicular to the interfaces of layers and thus CPP geometry is formed. Rather than mentioned achievements by electrodeposited nanowires, there are some more advantages such as easy production of very large number of bilayers along wires, the possibility of controlling the interface or electrochemistry, the possibility of controlling the coercive field either by varying the thickness or by changing the pore diameter and so on which are described later [117]. More details of GMR in the electrodeposited films were presented in a review paper by Schwarzacher and Lashmore [118].

2.4.1. Deposition methods of superlattice nanowires

Most of the investigations on the electrodeposition of magnetic multilayered nanowires have been performed by, so called, single bath method. In this method, ions of all the metals to be deposited are contained in a single electrolyte and the composition of the film is modulated by dc potentiostatic or galvanostatic deposition [118]. The groups demonstrating primary results on CPP-GMR of Co/Cu [116,117] and NiFe/Cu [117], used single bath method to electrodeposit the nanowires into PCTE membranes. For example, consider electrodeposition of Co/Cu nanowires in which an electrolyte containing ions of two metals Co and Cu, with Cu is nobler than
Template electrodeposition of magnetic nanowire arrays

Co, is used. At some potential which is sufficiently negative to reduce Cu, but not to reduce Co, pure Cu will be deposited as wire into the template. When the potential is changed to a value sufficiently negative to reduce Co, both metals will be deposited, but if the concentration of Cu is sufficiently kept low, because of its diffusion-controlled deposition [116], the resulting alloy will be predominantly Co. Researchers have reported the composition of multilayered nanowires with (i.e., Co-Cu/Cu) and without (i.e., Co/Cu) considering the codeposition occurred as mentioned above. In this review, the composition of nanowires are shown as same as what exist in the literature. More details of single bath electrodeposition parameters will be given later in Co-Ni-Cu/Cu nanowires.

Although not too comprehensive, a preliminary result was presented by Blondel et al. [119], pointing out that another synthesis technique, called double bath electrodeposition, can be used to produce CPP-GMR in Co/Cu nanowires, where the Co and Cu baths are separated and the sample exchanged between the two baths. It was of interest since it could avoid the co-deposition of Cu in the Co layers. However, the observed CPP-MR ratios do not exceed 10%.

Figure 9 illustrates a comparison between samples made by the two techniques, with equal Co and Cu thickness [119]. In addition, the study of the

![Figure 9](image.jpg)

**Figure 9.** CPP-MR measured at 20 K for layered Co/Cu 80 nm wires into PCTE. *Solid line:* Sample (A), 8 nm of layers thickness, produced by a single bath technique. *Dotted line:* Sample (B), 10 nm of layer thickness, produced by the dual bath method. *Reprinted from reference [119], Copy right (2007) with kind permission from J. Ph. Ansermet and Elsevier.*
temperature variation of the resistivities revealed that the interface resistance severely decreases in the samples produced by the double bath technique compared to the single bath, limiting the magnetoresistance to 10%. The limited temperature variation of the Co wires produced by the dual bath electrodeposition technique indicated that the Cu impurities do not play the dominant role in the observed large resistivity of electrodeposited nanowires. To the author's knowledge, there is no other report describing the effect of dual bath electrodeposition on GMR of multilayered nanowires.

2.4.2. Cobalt/copper nanowires

Since the first reports of the attainment of CPP-GMR in superlattice nanowires [116,117], cobalt/copper structure has been brought under consideration to study by several groups. The investigations not only demonstrate exhibited CPP-GMR of Co/Cu nanowires electrodeposited in PCTE [119-126], but also higher values of GMR more recently achieved in electrodeposited nanowires into AAO [127,128]. Generally, cobalt/copper nanowires were deposited from single sulphate-based bath by modulating potential between ~1.0 VSCE for Co layers and ~0.2 to ~0.5 VSCE for Cu layers.

Blondel et al made their Co$_{5nm}$/Cu$_{5nm}$ nanowires in PCTE membranes having an average pore diameter of 80 nm and a length of 6 µm. The thickness of layers were estimated by calculations obtained from pore filling time and therefore the accuracy of the estimated thicknesses was probably reduced, however, by Co dissolution during deposition of Cu layers. They obtained a maximum percentage change in magnetoresistance (MR) (measured relative to the resistance in zero applied field) rather than the resistance at saturation field) of ~14% at room temperature and ~18% at 20K [117, 118].

Piraux et al obtained very similar results for their Co/Cu nanowires, electrodeposited in PCTE membranes comprising pores with 40 nm average diameters and 10 µm lengths. The applied potential and the duration of each potential square pulse were used as determination criteria for the thicknesses of the layers of both constituents. Clear evidence of CPP-GMR was shown for example 15% and 19% MR for Co$_{7nm}$/Cu$_{3nm}$ at room temperature and 4.2K, respectively. Moreover, larger coercivity was measured from magnetisation curve at lower temperature due to significant in-plane anisotropy. Co dissolution may be recognized from transmission electron micrograph illustrating relatively rough and irregular interfaces between layers [116].

A further study of electrodeposited Co/Cu nanowires in PCTE was carried out by Liu et al [125]. The electrodeposition process was almost similar to the previous groups, where the thicknesses of the layers were controlled by a coulometer, integrating the passed charge between substrate and counting
electrode. Current efficiencies of Co and Cu were individually measured so that hydrogen evolution during Co deposition taken into account to gain exact layer thickness. Another precaution taken was a few seconds open-circuit interruption during the transition between Co to Cu potentials to avoid severe cobalt dissolution during copper deposition cycle which could damage the interfaces and leave the Co thickness inaccurate [125].

For \( \text{Co}_{5\text{nm}}/\text{Cu}_{0.8\text{nm}} \) with a length of equal to 1000-bilayer thickness, CPP-MR was measured 11% and 22% at room temperature and 5K, respectively. One interesting point argumented by the calculation of bulk resistivities of Co and Cu in form of nanowire, was that the most contribution to resistivity of nanowires come from the effect of interfaces due to their CPP geometry. Further points of interest were the estimation of SDL for Co/Cu structure and observation of oscillatory GMR behavior in electrodeposited Co/Cu nanowires when copper layer thickness \((t_{\text{Cu}})\) is less than 10 nm. Figure 10 shows the variation of MR ratio of 400nm length \( \text{Co}_{5\text{nm}}/\text{Cu}_{t_{\text{Cu}}} \) versus \( t_{\text{Cu}} \) at two different temperatures. It was observed that the GMR decreases with increasing \( t_{\text{Cu}} \) and approaches zero when \( t_{\text{Cu}} \approx 21\text{nm} \) and remains constant so far larger \( t_{\text{Cu}} \). Liu et al considered this length as SDL because GMR diminished to zero at this Cu layer thickness [125]. Voegeli et al [121] and Piraux [124] have carried out comprehensive analyses of magnetotransport data for Co/Cu multilayered nanowires based on the Valet-Fert Model [108] and calculated SDL of Cu and Co for a series of samples.

Almost same results were obtained for Co/Cu superlattice nanowires electrodeposited in AAO. However, Ohgai et al [128] made a comparison between Co/Cu nanowires electrodeposited in PCTE and AAO with similar bi-layer thicknesses. They fabricated Co/Cu by dc electrodeposition into AAO nanopores after barrier layer removal by a direct chemical dissolution in phosphoric acid from the top surface of the membrane. The sample with a bi-layer thickness of 5 nm shows 5.0% MR ratio in AAO and \( \approx 3.1\% \) MR ratio in PCTE. For both these samples, saturation is not reached at 10 kOe. This is attributed to a non-ordered layer structure similar to an alloy deposit. By increasing the bi-layer thickness up to 10 nm, the GMR value is changed to 20% and 12% in AAO and PCTE, respectively. The saturation fields of these samples decreased to around 5 kOe, much lower than the value of the sample with a layer thickness of 5 nm. A further increase of the bi-layer thickness from 10 nm to 15 nm can reduce both the GMR and saturation fields. Therefore, the pore bottom treatment technique using phosphoric acid was successful in removing most or the entire barrier layer and in making a good metallic electrical contact between the aluminium substrate and the electrodeposited nanowires.
2.4.3. Cobalt-nickel-copper/copper nanowires

Another magnetic superlattice nanowire system which has been extensively studied is Co-Ni-Cu/Cu, as the addition of Ni appears to reduce problems experienced for the Co-Cu/Cu system which were associated with dissolution of the magnetic layer during deposition of the non-magnetic one. Following the discovery of GMR in Co-Ni-Cu/Cu multilayers by Bristol group, this system was chosen as another candidate to fabricate superlattice nanowires. Primary investigations were performed on the electrodeposition of Co-Ni-Cu/Cu nanowires into PCTE from a suphamate single bath under the same condition as used in the electrodeposition of multilayers [129].

The results indicated the successful formation of 80 nm wire shape Co-Ni-Cu/Cu in addition to the formed parallel and smooth interfaces between layers, exhibiting CPP-GMR values of 15-20%. Energy dispersive X-ray spectroscopy (EDX) measurements showed that the ratio of Co to Ni in the Co-Ni-Cu layers was ~7:3 which is consistent with the anomalous co-deposition, well known in the electrodeposition of Iron group alloys [130]. More recent study by Heydon et al [131] was carried out on identification of the composition of Co-Ni-Cu/Cu/Co-Ni-Cu multilayered nanowires and Co-Ni-Cu pulse-deposited nanowires. They showed that the multilayered nanowires with nominal layer thicknesses of 5 and 3.5 nm for the magnetic and non-magnetic layers respectively, have the Co:Ni ratio equal to 6:4 which could be explained by some re-dissolution of the less noble metal (in this instance Co) and H₂ gas.
evolution, occurring at the Co-Ni-Cu/Cu interface. For the pulse-deposited Co-Ni-Cu nanowires the Co: Ni ratio was 7:3, with an overall Cu concentration of 40%. The extended periodical Co-Ni-Cu pulse-deposited nanowire structures in this study were grown within the nanopores by alternating between the Co-Ni-Cu deposition potential and a potential which was controlled to keep the net current in the external circuit at zero, called ‘rest-state potential’. The latter short-period was held for 200 ms during which time Co (and possibly Ni) could dissolve and be replaced by Cu. This electrochemical process which does not require any current to flow in the external circuit was considered to be responsible for the 40% Cu in the pulse-deposited nanowire [131].

Most of the researches carried out on using polycarbonate track-etched (PCTE) [131,132] and anodic aluminium oxide (AAO) [133] templates and considerable values of giant magnetoresistance (GMR) and multilayered microstructures have been reported in both templates. Recently, we have shown that another type of track-etched polymeric templates, polyester track-etched (PETE), is appropriate for growing Co-Ni-Cu/Cu superlattice magnetic nanowires that exhibit current perpendicular to plane giant magnetoresistance (CPP-GMR) [134,135]. Although much less commonly used as a template for electrodeposition than PCTE, this membrane has the major advantage over PCTE of being naturally hydrophilic. There is therefore no need to add a surfactant as is done during the manufacture of PCTE membranes. Furthermore PETE is very resistant to chemical attack and is both durable and stable.

In each case an Au film was evaporated onto one face of the membrane to act as a contact. The multilayered nanowires were electrodeposited from an electrolyte containing 2.3 mole/L H₂O Ni sulphamate, 0.4 mol/L H₂O Co sulphate, 0.05 mol/L H₂O Cu sulphate and 30 g/L boric acid in a standard 3-electrode cell and the deposition potentials used were –0.15 to -0.3V for Cu and -1.6 to –1.8V for Co-Ni-Cu alloy relative to a saturated calomel reference electrode. Deposition was carried out under computer control, and the current during deposition was recorded. Figure 11 illustrates part of a typical current transient associated with the applied switching potentials for deposition of Co-Ni-Cu/Cu nanowires in PETE. The high negative currents correspond to deposition at -1.8 V_{SCE} for Co-Ni-Cu layers, while the low negative currents correspond to deposition of Cu layers at -0.2 V_{SCE}. Note that when the deposition potential is switched from -1.8 V to -0.2 V, the current is initially positive or anodic. Although it is not completely clear, this current may be attributed to the dissolution of the less noble metal or double layer discharge [136].

A comparison between growth mechanism of superlattice nanowires in PCTE and PETE is shown in Figure 12 showing the Co-Ni-Cu current as a function of time during deposition of (a) Co-Ni-Cu (6 nm) / Cu (6 nm)
superlattice nanowires in polycarbonate membranes and (b) Co-Ni-Cu (3.3 nm) / Cu (3.3 nm) superlattice nanowires in polyester membranes. The Co-Ni-Cu current was recorded at the end of the deposition of each Co-Ni-Cu layer, just before switching to the potential for Cu deposition. As usual for nanowire electrodeposition, the current transients show four distinct growth stages [53].

These are (1): initial nucleation and growth of the nanowires at the ends of the pores, (2): growth of wires within the pores, (3) pore filling and (4) overgrowth. Stage (2) may be subdivided into a time during which the current increases (2-1) and a time during which the current changes much more slowly (2-2). A probable explanation of the increasing current during stage (2-1) is that poor wetting leads to a delay in nucleation in some pores, so that the number of pores in which growth takes place and therefore also the current rise gradually [53]. The increase in current during stage (2-1) and its duration are significantly greater for the polycarbonate membranes than for the polyester ones, consistent with poorer wetting in the former case. According to Fokkink et al. [137], poor pore-wetting also leads to a smearing out of the transition to bulk growth and it is noticeable that stage (3) is much longer for the polycarbonate than for the polyester membranes.

On the magnetotransport properties of Co-Ni-Cu/Cu nanowires, there exist several studies on the variation of MR percentage with copper spacing layer thickness, mostly done by Schwarzacher's group at Bristol and the largest CPP-GMR in electrodeposited nanowires (Co-Ni-Cu/Cu) was reported in AAO membranes; 55% and 115% at room temperature and 77K, respectively.
Figure 12. Co-Ni-Cu current as a function of time during deposition of (a) Co-Ni-Cu (6 nm) / Cu (6 nm) superlattice nanowires in polycarbonate and (b) Co-Ni-Cu (3.3 nm) / Cu (3.3 nm) superlattice nanowires in polyester membranes. Reprinted from reference [134], Copy right (2007), with kind permission from Elsevier.

For Co-Ni-Cu/Cu superlattice nanowires electrodeposited in PCTE (80 nm pore diameter) the variation of GMR as a function of the Cu layer thickness $t_{Cu}$ was reported for a series of superlattice nanowire with a fixed nominal Co-Ni-Cu layer thickness of 5 nm. Measurements were made at room temperature with the applied field parallel to the membrane surface, i.e. in the plane of the magnetic layers. As Fig. 13a shows, the GMR first increases (up to ~22% at $t_{Cu} \approx 3.5$nm), and then decreases with increasing $t_{Cu}$. The decrease in the GMR for large $t_{Cu}$ is expected from theory [108], while the decrease for very small $t_{Cu}$ suggests that for the thinnest Cu layers the GMR is destroyed by ferromagnetic coupling arising from defects. There is additional indirect evidence for ferromagnetic coupling at small $t_{Cu}$ because the easy direction of magnetization changes from in the plane of the layers to along the wire axes for these films. The (111) growth direction observed for many of the Co-Ni-Cu/Cu superlattice nanowires could favour defects causing ferromagnetic coupling [132].

AAO membranes were used very successfully to grow Co-Ni-Cu/Cu nanowires, presented by Evans et al [133]. As pointed out, AAO has two significant advantages over the polycarbonate; (1) possibility of preparing samples with much higher CPP-GMR: 55% at room temperature (even on cycling the applied field), compared to 22% for the same system electrodeposited in PCTE and (2) stable at higher temperature opening up the possibility of studying the effect of annealing treatment on the CPP-GMR of multilayered nanowires. The reason for a greater GMR obtained in AAO than PCTE was not explained clearly, though more easily diffusion of reactive species of electrolyte along the pores in the aluminum oxide membranes may have been an effective factor, both because of their greater diameter over most
of their length, and because of hydrophobic nature of PCTE, only treated with a wetting agent by the manufacturer. It is also exciting that at 77 K, the CPP-GMR of the nanowires electrodeposited in porous oxide membranes was recorded 115% before the application of a magnetic field and slightly less ~112% on cycling the applied field [133]. Figure 13b illustrates CPP-GMR data for at room temperature for a series of Co–Ni– Cu/Cu nanowires, electrodeposited in AAO with 300 nm actual diameter having fixed nominal magnetic layer thickness $t_{\text{Co-Ni-Cu}}$ 55.4 nm and varying Cu layer thickness.

Experimental data were adopted with the corresponding parameters presented by the CPP-GMR theory of Valet-Fert as equation (3):

$$\left( \frac{R_{(AP)} - R_{(P)}}{R_{(P)}} \right)^{1/2} = \frac{\rho^{*}_{\text{CoNiCu}} t_{\text{CoNiCu}} + 2\gamma^{*}_{b}}{\beta \rho_{\text{CoNiCu}} t_{\text{CoNiCu}} + 2\gamma^{*}_{b}} + \frac{\rho^{*}_{\text{Cu}} t_{\text{Cu}}}{\beta \rho_{\text{Cu}} t_{\text{Cu}} + 2\gamma^{*}_{b}}$$

\[ (3) \]

Figure 13. (a) Maximum change in resistance (GMR) as a function of Cu layer thickness for a series of Co-Ni-Cu/Cu superlattice nanowires with a fixed nominal Co-Ni-Cu layer thickness of 5 nm, electrodeposited in PCTE with 80 nm actual nanometer. The change in resistance is expressed as a percentage of the resistance in the maximum applied field (8 kOe). Measurements were made at room temperature with the applied field parallel to the membrane surface. The solid line is a guide to the eye. Reprinted from reference [132], Copyright (2007) with kind permission from W. Schwarzacher and Elsevier. (b) CPP-GMR data for a series of Co-Ni-Cu/Cu nanowires electrodeposited in AAO with 300 nm actual diameter with fixed nominal Co-Ni-Cu layer thickness 55.4 Å and varying nominal Cu layer thickness. $R_{\text{max}}$ and $R_{\text{min}}$ are the maximum and minimum CPP resistances measured when cycling the applied field between 0 and 8 kOe. The solid squares represent data for the as-grown nanowires, whereas the crosses represent data for the same nanowires after vacuum anneals of 30 min at 200, 300, 400, and 500 °C, successively. Reprinted from reference [133], Copyright (2007) with kind permission from W. Schwarzacher and American Institute of Physics (AIP).
Here, $\rho_{Cu}^{*}$ is the resistivity of the nonmagnetic metal, $\rho_{CoNiCu}^{*}$ is a resistivity characteristic of the ferromagnetic metal, $\beta$ and $\gamma$ are the bulk and interfacial spin asymmetry coefficients, and $r_{b}^{*}$ is a resistance per unit area characteristic of a single interface [108, 133]. $R_{AP}$ and $R_{P}$ were approximated by the maximum and minimum CPP resistances $R_{\text{max}}$ and $R_{\text{min}}$, measured for one or more multilayered nanowires in parallel when cycling the applied field. It was shown clearly that the obtained data can be fitted by a straight line, as predicted by Eq. (1). It was also demonstrated that except for the smallest and largest $t_{Cu}$, the CPP-GMR for the annealed nanowires exhibited the linear dependence predicted by the Valet–Fert model [133].

In very recently studied Co-Ni-Cu/Cu nanowires, we have shown that track-etched polyester membranes (PETE) are an appropriate template for growing superlattice nanowires that exhibit CPP-GMR. Figure 14 shows a TEM image of such nanowires as a clear evidence of a well-developed layered structure. Figure 15a shows the measured MR percentage (% MR) for a series of Co-Ni-Cu / Cu superlattice nanowires with fixed nominal Co-Ni-Cu layer thickness $t_{Co-Ni-Cu}$ and varying Cu layer thickness $t_{Cu}$. The %MR in this investigation was defined as equation (4):

$$\%\text{MR} = \frac{R(H) - R(H_{\text{max}})}{R(H_{\text{max}})} \times 100$$

where $R$ is the resistance, $H$ is the applied field and $H_{\text{max}}$ the maximum applied field that could be applied in our MR apparatus (~3 kOe). In each case, the %MR

Figure 14. Low magnification (a) and high magnification (b) TEM images of Co-Ni-Cu (3.3 nm) / Cu (3.3 nm) superlattice nanowires electrodeposited in a polyester membrane. From reference [135].
curve is broad, with changes in the MR continuing to be recorded even for $H > 2$ kOe. There is also hysteresis (as well as some drift) in the MR data. For comparison, Figure 15 (b) shows the magnetization curve measured at 300K with the applied field in the plane of the membranes, as for the MR measurements, for the Co-Ni-Cu (3.3 nm) / Cu (2nm) sample. Comparison of Figures 15a and 15b show that the maximum % MR occurs close to $H = H_c$ (the coercive field) [134,135].

It is worth noting that from Figure 15 (a) the maximum measured % MR increases with decreasing $t_{Cu}$ as is expected according to the Valet-Fert (VF) model for CPP-GMR. Because decreasing $t_{Cu}$ decreases the component of the resistance that is independent of magnetization [108, 135]. This simple model will only apply, however, if decreasing $t_{Cu}$ does not influence e.g. the effective $t_{Co-Ni-Cu}$. For example, if interlayer roughness or pinholes lead to strong ferromagnetic coupling between the Co-Ni-Cu layers when $t_{Cu}$ is reduced, the VF model will break down. Hence the observation of increasing %MR with decreasing $t_{Cu}$ is an important criterion by which the structural quality of superlattice nanowires may be judged.

![Graph](a)

**Figure 15.** (a) Measured percentage magnetoresistance (% MR) for series of Co-Ni-Cu / Cu superlattice nanowires with fixed nominal Co-Ni-Cu layer thickness and varying Cu layer thickness electrodeposited in PETE; (b) Magnetization curve measured at 300 K with the applied field in the plane of the membrane for the Co-Ni-Cu (3.3 nm) / Cu (2 nm) sample. Reprinted from reference [134], Copy right (2007) with kind permission from Elsevier.

### 2.4.4. Nickel-iron/copper and nickel/copper multilayered nanowires

There are some investigations on the electrodeposition of other superlattice nanowires including Ni-Fe/Cu [117,138-142] and Ni/Cu [143-148]. Permalloy/copper (Ni$_{80}$Fe$_{20}$/Cu) nanowire arrays were firstly electrodeposited from a sulphate bath showing a succession of formed Ni-Fe and Cu layers. Wires containing layers of 5–10 nm in thickness exhibited a CPP-MR of 10% for Ni-Fe/Cu at ambient temperature [117]. Then, Dubois *et al* [138] reported
successful achievement to the electrodeposited Ni-Fe/Cu nanowires. Consequently, the magnetotransport and microstructures of this nanowire system were studies for those which were electrodeposited into both PCTE and lithographically patterned templates [139-142]. As indicated, precisely layered structure of Ni-Fe/Cu nanowires could be seen from transmission electron micrographs (TEM) and CPP-MR ratios as high as 80% obtained at 4.2K. Two types of structures have been studied: conventional Ni$_{80}$Fe$_{20}$/Cu multilayers and multilayers composed of Ni$_{80}$Fe$_{20}$/Cu/Ni$_{80}$Fe$_{20}$ trilayers magnetically isolated by long Cu rods. It was explained that for Ni-Fe/Cu, the magnetic arrangement of successive layers is more difficult to control and made it not possible to determine the SDL from data of the first series. A second series of samples was made with Ni-Fe/Cu/Ni-Fe trilayers having $t_{Cu} = 10$ nm, 7 nm$< t_{NiFe} < 30$ nm, separated from each other by Cu layers of 100 nm. As shown, the magnetization of the two NiFe layers, for layers thinner than about 90 nm, in a trilayer is approximately antiparallel at zero field. Using the Valet-Fert model, they analyzed the GMR data, estimating that the spin diffusion length in Ni$_{80}$Fe$_{20}$ is between 3.3 and 5.3 nm.

Nickel/copper multilayered nanowires have been also electrodeposited in both PCTE and AAO membranes. Wang et al presented microstructural properties of Ni/Cu nanowires which were electrodeposited from single sulphate bath into PCTE of 80 nm in pore diameter. It was noticed that the thickness of the bilayers is not constant along the whole wire, whereas the nickel layer thickness enlarges more quickly than that of copper layer. They mentioned also that Ni and Cu layers grow epitaxially and the multilayers have a preferred growth direction parallel to wire axis [143].

Afterthought, John-Hopkins group reported [144,145] on the fabrication of disc-shape segments (particles) in Ni/Cu nanowire arrays, electrodeposited in PCTE in a range of 30-130 nm in diameter. The segments were magnetically single domain in the size regime and exhibited large coercivity and remanence due to the inherent shape anisotropy and reduced dimensions. In contrast, the axis perpendicular to the nanowire axis is the magnetic hard axis with small coercivity and remanence. It was appeared that the coercivity and remanence along the easy axis are dependent on the nanowire diameter and hence could be tuned by the selection of the appropriate nanowire dimensions. Moreover, according to the M–H curves the magnetic response of Ni/Cu was classified in terms of three micromagnetic states (rod-shape, disc-shape and an intermediate state) depending on the diameter and aspect ratio of the nickel segments. Their magnetic behavior, however, was explored a dependent property on the thickness of the nonmagnetic layer due to the dipolar interactions between the ferromagnetic segments [145].
Bristol group have recently studied the magnetic behavior of Ni/Cu nanowires, electrodeposited in PCTE [146,147] using remanence and relaxation measurements. Robinson et al found that demagnetizing interactions take place between the ferromagnetic layers of Ni–Cu/Cu superlattice nanowires, the strength of which decrease with increasing layer separation, giving rise to flux closure configurations between layers like antiferromagnetic coupling. However, the weakly interacting component, decreased with decreasing $t_{\text{Cu}}$, was believed to be caused by large individual nickel islands (corresponding to inter-layer interactions), while the strongly-interacting component was believed to be due to fragmented nickel islands (corresponding to intra-layer interactions).

Guo et al mentioned that by using an AAO template, a highly ordered composite Ni/Cu nanowire array was prepared by pulsed electrodeposition. The Ni segments alternated with nonmagnetic Cu layers showed single crystal microstructure with a preferred (111) orientation. By MFM observation, it was revealed that all the Ni segments are single magnetic domain and aligned to the same direction after magnetizing under an external field (perpendicular or parallel to the axes of the nanowires). Magnetization measurement on the array of ordered Ni-Cu nanowires demonstrated a remarkably enhanced coercivity and a similar high saturation magnetization compared to that of bulk nickel [148].

3. Summary and concluding remarks

Progresses on the template electrodeposition of magnetic nanowires were reviewed. It was noticed that type of template, rather than its physical properties like pore diameter and density, causes explicit effects on the magnetic and structures of the nanowires. Magnetic nanowires was divided to two major groups, elemental or alloy nanowires and superlattice nanowires. In the former group, 3d-ferromagnetic metal nanowires, of which there exists a firm historical knowledge of electrodeposition, explore potential applications in the data storage industry. As well as, amorphous magnetic nanowires may be under consideration for more structural and magnetic studies. In the later, superlattice nanowires, in addition to be useful in the GMR reading heads, show the existence of stack of fine magnetic particles which might be another potential candidate for various applications.

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5. References