

Study on different template-based production processes for magnetic nanowires

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Abstract. Nickel-iron (NiFe) nanowires with a high content of nickel and large aspect-ratio show promising characteristics for applications in modern micro-systems. In this study, nanowires with well-controlled diameter, height and composition are fabricated using nanoporous poly-carbonate (PC) and anodized aluminum-oxide (AAO) membranes. Differences between potentiostatic and pulsed deposition methods were studied with regard to their flexibility and a recommendation for the best use of the individual types is given. With the application of the presented processes, future technologies as magnetic energy-harvesting or nano-fluxgate sensors can be improved.

Keywords

magnetic nanowires, MEMS, template-based, electroplating

1. Introduction

Originally, magnetic sensors were developed and used almost exclusively for navigation and tracking purposes. However, in the last couple of years, expanding markets like consumer electronics with applications in smartphones, tablets and wearables have emerged for magnetic sensors. This development was enabled by advances in MEMS technology. Furthermore, due to these advances it is possible to realize energy self-sufficient circuits with micro energy-harvesters based on magnetic nanowires [1]. One possible implementation of a magnetic micro energy-harvester is presented in figure 1. An external magnetic field from a permanent magnet that magnetizes a series of wires during motion, inducing a voltage in a coil.

Understanding the concept of energy-harvesting with magnetic nanowires, various magnetic processes have to be taken into account. The amount of energy which can be harvested depends mainly on the magnetic properties of the used materials, described by its permeability μ . According to equation (1), the permeability is defined as the product

of the material dependent relative permeability μ_r and the vacuum permeability μ_0 :

$$\mu = \mu_0 \cdot \mu_r. \quad (1)$$

The impact of an external magnetic field H on a material with a permeability μ is the so called magnetic flux density B , which is described in equation (2). It is a vector pointing in the direction of the field lines and proportional to the magnetic field strength H :

$$\vec{B} = \mu \cdot \vec{H}. \quad (2)$$

Knowing the magnetic flux density, the magnetic flux ϕ can be calculated. By definition, it is the integral over the vectorial quantities B and area A which the magnetic flux passes [2]:

$$\phi = \int \vec{B} \cdot d\vec{A} = \int B \cdot dA \cdot \cos \theta \quad (3)$$

Thus, to maximize the magnetic flux it is important that the field passes through the material in an angle (θ) of 90° . If nanowires are affected by an external field, their magnetic flux can be changed. This effect will induce a voltage in a read out coil, as depicted in figure 1. The dependence of the induced voltage on the magnetic flux is described by Faraday's law [2]:

$$U_{\text{ind}} = -n \cdot \frac{\partial \phi}{\partial t}, \quad (4)$$

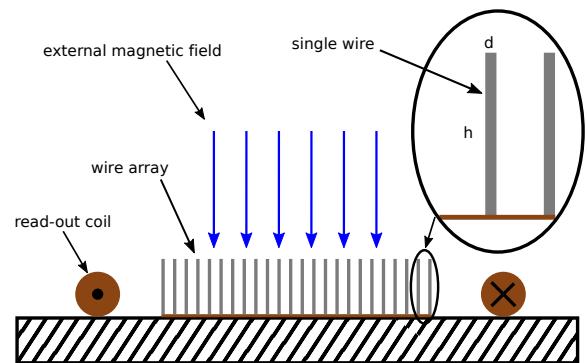


Fig. 1: Schematic of a magnetic micro energy-harvester.

with n being the number of windings of the coil.

Since the output power of an magnetic energy-harvester mainly depends on the used material, permeability must be as high as possible in order to achieve a high magnetic flux density. This allows the voltage yield to be maximized (see equation (4)).

Nickel-iron in the ratio 80% nickel and 20% iron, also called permalloy, is a very interesting material due to its high relative permeability of about 100,000 [2]. Together with a negligible magnetostriction it shows unique magnetic properties which make it favorable for application in magnetic energy-harvesting.

Nanowires, which are manufactured in such a way that all their magnetic moments point in the same direction, could allow so-called large Barkhausen jumps [3]. In general, Barkhausen jumps occur in any kind of ferromagnetic material (see figure 2). However, large Barkhausen jumps only occur if a large number of magnetic moments point in the same direction. Such an alignment of the magnetic moments is called single domain behavior. If an external magnetic field magnetizes the nanowires, the magnetic moments suddenly switch over as soon as a certain field strength is reached [3]. Since, according to equation (4), the induced voltage is proportional to the time derivative of the magnetic flux, short switching times allow for larger induced voltages, which increases the output power of the harvester.

The dependency of stray field interaction within a nanowire array was investigated by Nielsch et al. in 2001 [4]. He found that the critical diameter below which they are theoretically single-domained is described by

$$D_{crit} = 3.68 \sqrt{\frac{A}{\pi M_s^2}}, \quad (5)$$

where A represents the exchange stiffness constant and M_s represents the saturation magnetization. The exchange

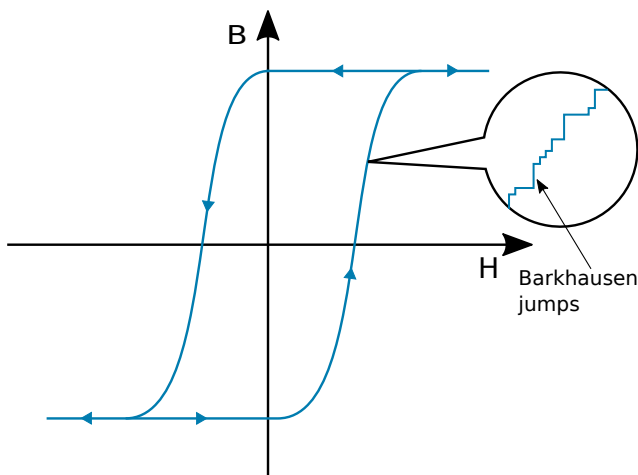


Fig. 2: Magnetic hysteresis loop with barkhausen jumps.

stiffness constant for $\text{Ni}_{80}\text{Fe}_{20}$ is 10^{-6} erg/cm [5] and the saturation magnetization is according to Dragos et al. [5] 800 emu/cm^3 . Applying these values for $\text{Ni}_{80}\text{Fe}_{20}$ a critical diameter for one nanowire D_{crit} of about 30 nm is obtained.

In this work, we systematically investigate the galvanic deposition process of permalloy in terms of template material, electrolyte and voltage with respect to achieve single domain nanowires.

2. Methods and Materials

Characterization methods

The morphology and size of nanowires were characterized by scanning electron microscopy (SEM) (Phenom ProX) and the composition of the formed wires was characterized by energy dispersive X-ray spectroscopy (EDX) attached to the SEM. In addition, the topography of the AAO and PC membranes was characterized by atomic force microscopy (AFM) (Asylum Research MFP-3D) using intermittent contact mode.

Membranes and deposition material

For all galvanic growth processes two types of membranes were used: track etched poly-carbonate (PC) (Merck KGaA, Darmstadt, Germany) and anodized aluminum-oxide membranes (AAO) (SmartMembranes GmbH, Halle a. d. Saale, Germany).

Atomic-force-microscope measurements of the topology of the used membranes are shown in figure 3. While the AAO templates show very regular inter-pore-pitch, the PC membranes do not have a defined structure. The pore density as well as the interpore distance varies strongly across the whole membrane. This can be explained by their different production processes, with the PC membranes being produced by ion beaming and the AAO membranes are produced in an anodizing process. However, the regular AAO membranes are very brittle, which complicates the handling of the membranes. PC membranes are flexible, easy to

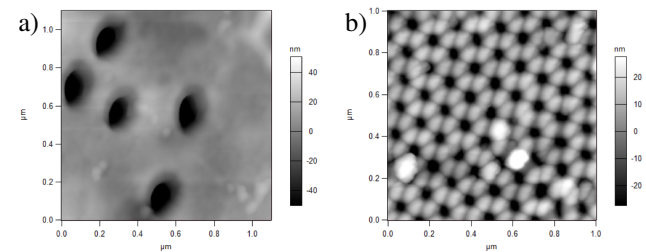


Fig. 3: AFM measurements of a) PC template with pore diameter of approx. 200 nm and b) AAO templates with pore with diameter of approx. 35 nm.

handle and can easily be dissolved in acetone, to remove the template after production. As AAO and PC are non-magnetic materials, it is generally not necessary to remove the template [6].

For the production of the wires in an electroplating processes, the following chemicals were used: NiSO_4 and NiCl_2 as a source for nickel and FeSO_4 for iron respectively. H_3BO_3 was used for enhanced solubility and ion transport [7].

3. Technology

Process overview

The general process was the same for both types of membranes, schematically depicted in figure 4. In the beginning, a glass substrate is metallized with 200 nm of copper using a sputter process. After the metallization, a photo resist is spin coated and structured on the metallic layer to form a passivation layer which determines the nanowires growth area (Fig. 4a)). In the next step, the membrane is placed on the prepared substrate and gently pressed down using a sponge (Fig. 4b)). As the flexibility of the used PC membranes is very high, this is necessary to avoid any large gaps between the cavity and the membrane which would result in irregular deposition. It should be noted, that this is only necessary for the PC membranes, as the AAO membranes are not flexible. Figure 4c) shows the first part of the deposition process, which is the filling of the air-gap between substrate and membrane. After this step, the growth of the nanowires starts (Fig. 4d)). The length of the wires can be adjusted by controlling the deposition time, as the growth-height increases linear with time. Finally, as an optional step, the

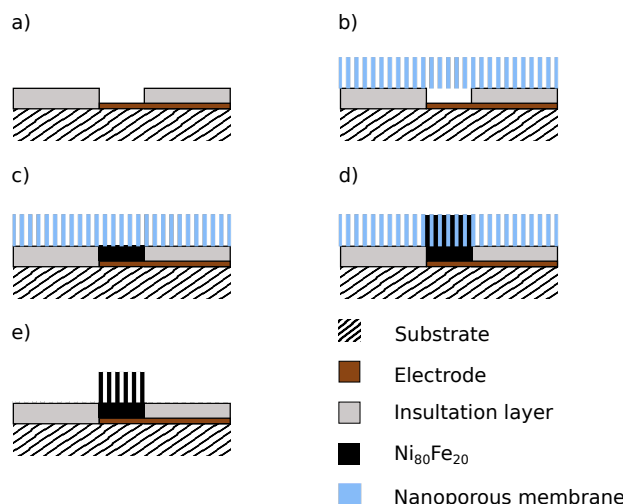


Fig. 4: Fabrication process of nickel-iron nanowires using nanoporous membranes.

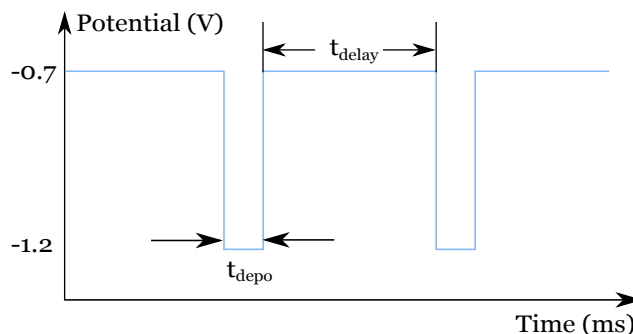


Fig. 5: Illustration of the electrochemical pulse employed for the deposition of NiFe nanowires.

membrane is dissolved with acetone releasing free standing nanowires (Fig. 4e)).

Deposition processes

The electrochemical deposition of permalloy was carried out at 35 °C. Two hours prior to and during deposition, the electrolyte was mixed with nitrogen, to avoid oxidation of iron ions. The deposition processes were carried out in a three electrode setup, whereas a platinum wire was used as counter electrode and Ag/AgCl acted as a reference electrode.

Deposition processes can be carried out using two different methods. Potentiostatic deposition is the simplest method for the growth of nanowires. A constant voltage is applied and the resulting current during deposition is measured. Based on the current trend, conclusions about the progress of the deposition can be drawn. The second method used for deposition is pulsed electrochemical deposition, with which the composition of the nanowires is controlled by different potential pulses (see Fig. 5). This technique has been described to achieve homogeneous growth of wires [8]. Delay time of the pulse ensures a constant material transport through the pores and helps to renew the concentration of the metal ions at the pore-electrolyte interface.

4. Results and discussion

All deposition processes were carried out using a VersaStat4 (Princeton applied research, Oakridge, USA), since this instrument allows a very precise adjusting of the required parameters. For the pulsed deposition an electrolyte was developed which consists of the following components (I): $300 \text{ g L}^{-1} \text{ NiSO}_4 + 6 \text{ H}_2\text{O}$, $45 \text{ g L}^{-1} \text{ NiCl}_2 + 6 \text{ H}_2\text{O}$, $43.27 \text{ g L}^{-1} \text{ FeSO}_4 + 7 \text{ H}_2\text{O}$, $45 \text{ g L}^{-1} \text{ H}_3\text{BO}_3$ [7]. Nickel content was adjusted by nickel-containing chemicals. Used chemical based on iron provide sufficient iron even when varying pulses. Boric acid is used to enhance the ion trans-

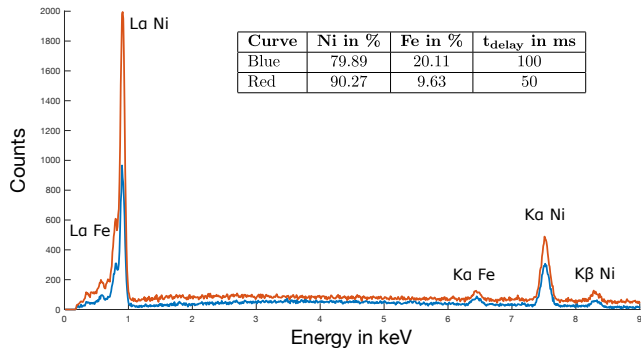


Fig. 6: EDX spectrum of $\text{Ni}_{80}\text{Fe}_{20}$ and $\text{Ni}_{90}\text{Fe}_{10}$ nanowire arrays fabricated using PC membrane. Differences in the composition were accomplished by using different delay times in the pulsed deposition process.

port and the solubility of the other components. During pulsed deposition, constant deposition pulse time (t_{depo}) of 10 ms and a delay time (t_{delay}) of 100 ms were applied, with -1.2 and -0.7 V respectively, which resulted in a uniform nanowire growth over the whole active area. A decrease in the iron content in nanowires can be achieved by decreasing the pulse delay time. Figure 6 shows an EDX spectrum for $\text{Ni}_{80}\text{Fe}_{20}$ nanowires grown in the PC template (see Fig. 8). Compared to nanowires grown at a delay time of ($t_{\text{delay}} = 50$ ms), the iron content was halved (see red spectrum). The area below the peaks is estimated to show the relative composition of the corresponding element. In both samples, no oxygen contamination was found as they were kept under a constant nitrogen atmosphere. Through this method a rapid prototyping of differently composed wires is achievable, since the composition of the nanowires can be controlled with the delay time.

If only a certain composition is required, the use of potentiostatic deposition is advisable. As the requirements on the voltage source are less demanding, but good results can nevertheless be achieved. Since a deposition with elec-

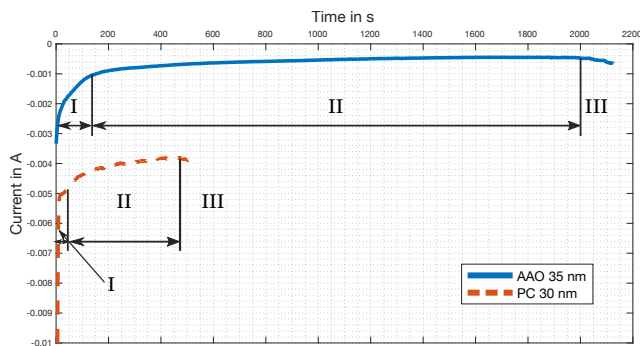


Fig. 7: Resulting current over time for a potentiostatic deposition through a PC membrane and a AAO membrane. Pore-diameters of 30 and 35 nm respectively.

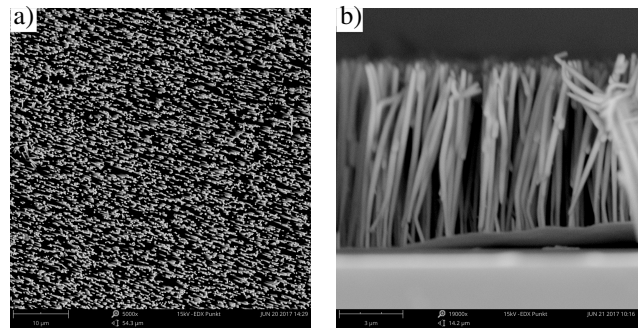


Fig. 8: SEM micrograph of 200 nm diameter NiFe wires, in a) top and b) side view.

trolyte (I), which was optimized for pulsed deposition, led to poor results concerning homogeneity and composition of the nanowires, a new electrolyte had to be developed. The new electrolyte (II) consisted out of the following components: $131.5 \text{ g L}^{-1} \text{ NiSO}_4 + 6 \text{ H}_2\text{O}$ and $36.61 \text{ g L}^{-1} \text{ FeSO}_4 + 7 \text{ H}_2\text{O}$. This composition showed at a constant voltage of -0.7 V good results for nanowires with a permalloy composition of 80 % nickel and 20 % iron. During the deposition process, the current flow was monitored for (Fig. 7) for PC membrane with pore-diameter of 30 nm and AAO membrane with 35 nm respectively. Looking at figure 7, the deposition process can be divided into three sections. For PC membranes, the first section lasts from 0 to 20 s (1). During this time the cavities below the template are filled. In the section between 20 and 500 s (2), the nanowire deposition process takes place, with wires now growing evenly in the nanopores of the membrane. This results in an almost constant current. Finally, the last range (3), which starts at approx. 500 s, indicates an overgrowth of the wires. As overgrowing occurs, the area of the working electrode increases, which explains higher current values. As the increase in amperage is a very good indicator for identifying overgrowth *in-situ*, it can be efficiently reduced to a minimum. Generally both membranes show similar characteristics, but the AAO membrane time spans are longer because it is more than twice as thick as the PC membrane. The small absolute current of the AAO membrane is due to the size of the membrane itself, which measures only 49 mm^2 , whereas the PC membrane has an area of 201 mm^2 .

Nanowires grown in PC had a constant length of $20 \mu\text{m}$, whereas nanowires grown in the AAO template had a length of about $55 \mu\text{m}$. Nanowire lengths were controlled by monitoring the resulting current and total charge during deposition. Figure 8 a) shows a SEM micrograph of the produced nanowires. It is clearly visible that the nanoporous PC membrane used allows for uniform wire growth. A high quality membrane is very important as it determines the density and geometry of the wires. Figure 8 b) shows a SEM measurement in the side view.

5. Summary and Outlook

In this work we showed the fabrication of $\text{Ni}_{80}\text{Fe}_{20}$ nanowire arrays with well-controlled diameter, height and compositions using nanoporous PC and AAO membranes as templates. Differences between potentiostatic and pulse guided electrochemical depositions were discussed. Emphasis was placed on the importance of a good electrolyte for successful deposition.

For rapid prototyping we recommend the pulsed deposition, as different compositions can be produced quickly by variation of the pulse delay time. If only a certain composition is required, we recommend the use of potentiostatic deposition, as the requirements for the voltage source are less demanding but still good results can be achieved.

In the near future, we are going to establish an alternative process that can be started by directly metallizing the membranes. This would allow faster fabrication times. Since the layer thickness of this method is considerably smaller than that of the used method, the handling of the nanowire array produced in this method is more difficult. The biggest advantage of the new method is its flexibility, as the nanowire arrays can be cut into any desired shape.

Moreover, first magnetic measurements of the fabricated nanowire arrays are planned. Considering the critical diameter of the wires of 30 nm, the 30 nm diameter PC membranes could possess a single domain structure, whereas the 400 nm pore diameter wires should have a multi domain structure.

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