Iron/Nickel Nanowire growth in Anodic Aluminum Oxide Templates: Transfer of Length Scales and Periodicity

H D Yan¹,², P Lemmens¹,², H Dierke³, S C White¹, F Ludwig³ and M Schilling²,³

¹ Institut für Physik der Kondensierten Materie, 38106 Braunschweig, TU-Braunschweig, Germany
² International Graduate School of Metrology, 38106 Braunschweig, TU-Braunschweig, Germany
³ Institut für Elektrische Messtechnik und Grundlagen der Elektrotechnik, 38106 Braunschweig, TU-Braunschweig, Germany

E-mail: p.lemmens@tu-bs.de

Abstract. Anodic oxidation allows the preparation of aluminum oxide (AAO) templates with self-organized, ordered pores and diameters ranging from 10 nm to 200 nm. Electrochemical deposition of metals, semiconductors and oxides has been demonstrated. As a case study, we investigated the growth of Fe/Ni nanowires in the AAO templates. Transmission and scanning electron microscopy are used to optimize growth parameters and to demonstrate that length scales and periodicities of the templates can be transferred to the wire arrays. This paves the way for the preparation and investigation of tailored matter on nanoscales with emerging applications in photonics, sensorics and information technology.

1. Introduction
Nanomaterials are currently of great interest among researchers because of their promising applications in a large variety of fields. Well-established examples can be found in magnetic recording media, ferrofluids, catalysts, colour imaging and pigments in paints and ceramics[1,2]. Functionalization and self-organization also allows investigation of fundamental physical questions related to mesoscopic and microscopic properties of the nanostructures. Nanomagnetism serves as a fruitful example, as the properties of magnetic nanoparticles depend on size, shape, particle distribution, and arrangement, and can be easily investigated using both macroscopic and thermodynamic properties of the ensembles, as well as with respect to microscopic properties using local magnetic probes. Magnetic nanostructures have been prepared with electron beam lithography that realize artificial, frustrated materials with interesting properties from a fundamental point of view[3]. Another example is given in the field of nanophotonics, where enhanced light-matter interaction in nanostructured metallic or molecular systems is established in the electromagnetic fields of photonic crystal-like, periodic environments. For all examples the precise control of length scales and function is critical.

Anodic aluminium oxide (AAO) can be prepared as a transparent template with uniform and periodic nano-pores, whose diameters are controllable between 10 nm and 200 nm. Within this kind of template, the preparation of tubal or wire-like materials with sizes controlled by the pores has been demonstrated[4–10]. In our work, an electrochemical method is explored to grow Fe/Ni nanowires...
directly in the AAO templates. Nanostructures with fixed diameter and well-controlled height and periodicity are obtained.

2. Experimental
Alumina foil was polished in perchloric acid, the electrochemical anode oxidation action occurred in oxalic acid with a voltage of 50 V for 4 h. After that, the oxide layer was removed in a mixed solution of phosphoric acid and H₂CrO₄ at 60°C for 4 h. A second oxidation step under the same conditions as the first anodizing step was started. This oxidation process is finished after 15 h. With a fixed 10% H₂SO₄ aqueous solution, nanochannels with small pore diameters can be obtained by applying a 20 V anodizing potential.

In the following, the AAO template was placed in a solution of 120 g/l NiSO₄·6H₂O, 80 g/l FeSO₄·7H₂O and 30 g/l H₃BO₄. Titanium was used as an anode with a voltage of 1.8 V for deposition of nanowires. The electrodeposition is carried out at room temperature and a pH value of 3.5 – 4.0. After the nanotube array was formed, the template was etched in a 2 M NaOH solution to allow an investigation of the individual wires. The resulting precipitate was dispersed in ethanol and investigated with transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

3. Results and Discussion
Fig. 1(a) shows an SEM image taken from the AAO template prepared by oxalic acid. It is observed that a triangular array of nanopores is formed, with a pore-diameter of around 80 nm. The pore diameter depends on the electrolyte, voltage, etc. Some defects are visible related to the collapse of a pore to a very small diameter of approximately 5 nm.

Fig. 1 (b) shows the template prepared in sulphuric acid resulting in a pore diameter of approximately 30 nm. A comparison with Fig. 1 (a) shows that the pores formed in sulphuric acid are smaller and the template is thinner. During pore formation an insulating barrier layer remains on the bottom of the pores. We removed the barrier from the bottom side with phosphoric acid to achieve continuous pores all the way through the template. For the further preparation steps, we evaporated a 500 nm Ag film on one side of the template as an electrode.

Fig. 1(c) represents the characterization of the templates with the SEM from the side view. Pores are identified as straight columns. The respective walls and diameters depend on the parameters oxidation time, voltage (current density), pH value, temperature, etc. Usually, the dimension of these pores is...
less than 100 nm. The smaller the pore diameter is, the thicker the walls of a hole will be. The depth of these holes depends on the oxidation time. There are no intercrossing phenomena observed among these holes, which demonstrates a controlled pore formation beneficial for the preparation of nanowires.

In order to investigate individual wires with electron microscopy, the templates are dissolved in NaOH solution. Fig. 2(a) and (b) show the respective TEM images. There are wire-like Fe/Ni nanostructures, which are of consistent size and have a very sharp distribution of diameters. The diameter is essentially controlled by the pore size. Fig.2 (a) shows a diameter of approx. 90 nm, which is similar to the pore size in Fig. 1(a). The length of the wires is approximately 150 µm, leading to an aspect ratio of 1600. Fig. 2(b) presents nanowires synthesized in small pore templates using sulfuric acid as the electrolyte. Their diameter is around 35 nm, and the aspect ratio is reduced to 300. Experiments show that the diameter of the nanowires is larger than the pore diameter, because the depositing acid solution etches the walls of the pores to enlarge their size. The length of the nanowires depends linearly on deposition time. In the present experiment, the growth speed is 0.3 µm/min.

![Figure 2(a). TEM image of Fe/Ni nanowires grown in larger-pore templates with diameters of about 90 nm. In the background, remains from the NaOH solution are observed, which was used to remove the template.](image)

![Figure 2(b). TEM image of Fe/Ni nanowires grown in small-pore template. The diameter is around 35 nm and the wire length is approximately 10 µm.](image)

During the deposition process, the metal ions obtain an electron and finally discharge at the end of their pathway. However, the metal ions are not immobilized and diffuse irregularly before they arrive at a point with lowest potential energy. Usually, such a point is the pore bottom, so that metal ions gather in the nanopores and the nanowires grow from the metallized back of the template through the pores\[11\]. Effects that point to an interplay of confinement effects versus the influence of the pore-wall have recently also been demonstrated using the growth of liquid crystalline nanowires in similar porous alumina\[12\].

The empty template is highly insulating and weakly diamagnetic. Magnetization hysteresis loops were measured using SQUID magnetometry and the susceptibility is $10^8$ emu/Oe at room temperature. There are strong dipolar interactions between the nanowires grown in template due to their high-density \[13\]. Significant changes of the hysteresis loops are observed as function of the geometric properties of the wire arrays.
4. Conclusion
AAO is a good template material in the sense that length scales and periodicities established in the self-organized growth process of the template can be transferred to an array of nanowires. The width of the ordered pores is controllable between 10 nm to 200 nm. A method for Fe/Ni nanowire preparation is introduced. The size of nanowires strongly depends on the diameter of the pores and deposition conditions. Most of the properties of this process depend in a linear way on growth parameters and can therefore be tuned to achieve the desired nanostructures. We managed to remove the AAO template with NaOH solution. It is remarkable how well the critical dimensions of the nanowires match to those of the templates.

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