Template synthesis of different metal nanowires with applying of magnetic field

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Abstract. This paper presents an investigation of electrodeposition of metal in pores of track etched membranes in presence of magnetic field. Where were obtained as homogeneous and heterogeneous nanowires. There is shown that magnetic field affects both on deposition process and on structure of metal nanowires. Particularly, samples obtained were investigated with help of methods of scanning electron microscopy, X-ray analysis and magnetometry.

1. Introduction
It is known that track membranes can be used both for filtration and matrix synthesis [1,2]. Matrix synthesis method, using track membranes, allows to obtain arrays of thin rods – nanowires (NWs) [3]. The use of matrix synthesis allows to adjust many parameters of both the matrix and the process – and choose the optimal modes for obtaining NWs with the desired properties. One of the factors affecting the electrodeposition of NWs may be an external magnetic field (MF). There are a few paper devoted to this method, but results seem to be contradictory. For example, in [4, 5] the magnetic field increases the deposition current, whereas in [6] on the contrary – reduces. Some features of magnetohydrodynamics (MHD) are given in the review article [7]. According to published data there are three main effects of the magnetic field on the deposition process: 1) the Lorentz Force (in the case \( \vec{B} \perp \vec{E} \) ) 2) the paramagnetic force, and 3) the ponderomotive force. But the question of how the field affects the growth of magnetic metal in nanoscale pores has not been studied carefully yet. In this work we made an attempt to investigate effect of external magnetic field to the process of NWs electrodeposition and to the properties of obtained samples.

2. Experiment
Track etched membranes with a pore diameter of 100 nm (JINR, Dubna) were used (figure 1). Electrolytes of the following composition were used: for the deposition of homogeneous Ni-Fe NWs: \( \text{H}_3\text{BO}_3 - 15 \text{ g/l; NiCl}_6\text{H}_2\text{O} - 40 \text{ g/l; NiSO}_4\cdot7\text{H}_2\text{O} - 16 \text{ g/l; FeSO}_4\cdot7\text{H}_2\text{O} - 16 \text{ g/l, stabilizing additives.} \)
For the deposition of cobalt NWs: \( \text{CoSO}_4\cdot7\text{H}_2\text{O} 320 \text{ g/l H}_3\text{BO}_3 - 40 \text{ g/l.} \)
For the deposition of layered NWs Cu/Ni: \( \text{NiSO}_4\cdot7\text{H}_2\text{O} - 196.7 \text{ g/l; CuSO}_4\cdot5\text{H}_2\text{O} - 6.25 \text{ g/l; H}_3\text{BO}_3 - 31.6 \text{ g/l. Conductive layer of copper was deposited on one side of the matrix for electrical conductivity. Elin P-2X potentiostat was used.} \)
used as a source. For synthesis of Fe-Ni NWs, a voltage of 1.5 V was applied (in [8] it was shown that such a voltage makes it possible to obtain an alloy with a ratio of 1:1). For Co NWs voltage was equal to 0.8 V. For the synthesis of heterogeneous NWs the voltage of 0.8 V was used for deposition of Cu layers, and for Ni layers it was 1.8 V. The deposition was carried out in a specially designed galvanic bath (figure 1), the design of which allowed to apply permanent magnets (neodymium, with an induction of ≈ 0.15; 0.2 and 0.3 T) just close to the growing sample.

Thus, the magnetic field was collinear to the growing wires and its intensity in the growth zone was maximal and. The magnet was applied by the "North" and "South" poles. Current vs time dependencies were recorded during the growth.

3. Results
3.1. Electrodeposition
It is shown that the growth time both of homogeneous and heterogeneous NWs (Ni-Fe, Co and Cu/Ni) depends on the presence of the magnetic field. (The time of full filling of pores was estimated based on a sharp increase in the current). In particular, in the experiment the growth time of homogeneous nanoparticles (Fe-Ni) without a magnetic field was about 480 seconds, whereas in the case of a magnet ≈ 420 seconds (figure 2).

The effect of magnetic field on deposition of layers NWs is shown in figure 3.

Figure 1. Schematic representation of the electrolytic cell: 1) Track etched membrane 2) working electrode (cathode) 3) anode 4) magnet.

Figure 2. Current vs time dependences of alloyed FeNi NWs grown in "south", "north" and without MF. (Arrows indicate the time when pores were filled by metal).
So, it can be concluded that magnetic field accelerate the electrodeposition process. Generally, the effect is the same for both cases- for alloyed NWs and for the layered NWs

3.2. Structure investigation

X-ray data were obtained for all samples (Diffractometer RIGAKU, Cu-anode). As an example the spectra for Co NWs obtained with different magnetic field are given in figure 4.

Figure 3. Current vs time dependences of layered Ni/Cu NWs grown in “south”, “north” and without MF.

Figure 4. X-ray analysis. Spectra of cobalt NWs grown in different field (0.15, 0.1, 0.06, 0.04, 0 T and without field – from top to bottom respectively).
It could be concluded that external field leads to appearance of texture. It is interesting that the effect doesn’t depend on field intensity.

3.3. Microscopy
SEM showed that the magnetic field doesn’t affect the topography of homogeneous nanowires (Ni-Fe and Co). On the other hand, for layer NWs the result was different- the SEM image presented in figure 5.

![Figure 5](image)

**Figure 5.** SEM of layered Ni/Cu nanowires grown without MF (a), in the "South" (b) and "North" (c) pole.

It is easy to see that in heterogeneous Ni/Cu NWs the applying of the magnetic field leads to formation of cavities in Ni layers (figure 6, b).

3.4. Magnetometry
Hysteresis loops were obtained for samples of alloyed Fe_{0.2}Ni_{0.8} NWs and Co NWs. It was carried out for two orientations – “out of plane” and “in plane”. The study showed that the magnetic properties of cobalt NWs do not depend on the presence of a magnetic field during deposition.

On the contrary, magnetic field affects the growth of alloy NWs. The data obtained for Fe_{0.2}Ni_{0.8} NWs presented in figure 6.

![Figure 6](image)

**Figure 6.** H-B loops for alloyed Fe_{0.2}Ni_{0.8} NWs.
From these magnetic hysteresis curves, it could be supposed that Fe-Ni NWs consists of two phases: Ni and Fe-Ni. This is confirmed by a residual magnetization hysteresis (figure 7).

![Figure 7. Residual magnetization hysteresis of Fe$_{0.2}$Ni$_{0.8}$ NWs.](image)

Another interesting fact was the influence of MF homogeneity on magnetic properties in plane. In particular, the residual magnetization and coercive force are reduced by 2-3 times in cases when the magnet is at a certain distance from the growth zone. This effect has not yet been explained and is subject for further studies.

4. Conclusions

Thus, it is shown that the applying of the magnetic field leads to an increase in the growth rate of both homogeneous (Co and Ni-Fe) and heterostructural (Ni/Cu) NWs. We can assume that it occurs due to ponderomotive force. X-ray analysis showed that magnetic field leads to the appearance of texture. Microscopy showed in the case of layered NWs, to cavities in nickel layers (Ni/Cu NWs). The applying of a magnetic field parallel to the NWs axis during growth has no effect on the magnetic properties of Co NWs, but it has been noticed that the inhomogeneous MF affects the magnetic properties of alloyed Ni-Fe NWs. In particular, the coercive force and residual magnetization of NWs grown in inhomogeneous MF is 2-3 times less than NWs grown in homogeneous and without MF.

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