Low Dimensional Materials and Catalysts

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TEM investigation of FeGa alloy nanowires electrochemically deposited within nanoporous templates

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Fe_{100-x} Ga_x (x = 20±5 at %), a low cost non rare-earth alloy with large magnetostriction ($_{max}$ = 400 ppm) and high mechanical strength is a promising material for miniaturized sensor and actuator applications. An economically priced method to produce low dimensional structures such as nanowires is the electrochemical deposition within nanoporous templates. The electrochemical co-deposition of Fe and Ga, however, is particularly challenging due to the low standard potentials of the involved metals and gallium's high tendency to hydrolyze and form insoluble oxidic species. Recently, enormous progress has been made in understanding the alloy deposition mechanism [1] and minimizing the oxygen content in Fe-Ga films by applying an alternating potential mode [2]. Moreover, the fabrication of Fe-Ga nanowires from a modified electrolyte was successfully demonstrated [3]. The objective of the present study is to investigate the local structure of the Fe-Ga nanowires in detail. The influence of the deposition technique on composition distribution, structure and microstructure is examined.

For preparation of nanowires a highly ordered hexagonally arranged nanopore array as the Anodized Aluminium Oxide (AAO) template for the following deposition process is generated. The freestanding membranes, an Au layer of 30nm thickness as the first electrical contact and a further Cu layer for mechanical stability of the template represent the working electrode [4]. Electrodeposition is performed in a three electrode arrangement and controlled by a HEKA PG 310 potentiostat/ galvanostat. A Pt foil is used as the counter electrode and a Saturated Calomel Electrode (SCE, E = 241 mV) as the reference electrode. The electrolyte contains 0.03 M $FeSO_4 \cdot 7H_2O$, 0.06 M $Ga_2(SO_4)_3 \cdot 18H_2O$, 0.5 M boric acid, 0.04 M ascorbic acid and 0.15 M sodium citrate as the complexing agent [3]. The pH value of the electrolyte is adjusted to 3 using sodium hydroxide.

Nanowires were electrodeposited by two different techniques, the potential pulse technique (A) [3] and the more simple, less time consuming potentiostatic mode (B). In mode (A) a deposition potential E_1 = -1.5 V_{SCE} is applied for t_1 = 10 s followed by a relaxation step E_2 = -0.9 V_{SCE} for t_2 = 10 s. These two steps are repeated 500 times, ending up with a total deposition time of 5000 s and a total process time of 10000 s. The length of the wires is 6.3± 0,2 µm. This approach is expected to create more homogeneous deposits through compensation of concentration gradients, interruption of hydrogen evolution and, therefore, easier escape of the smaller gas bubbles from the narrow nanopores.

Mode B is rarely used for alloy nanowire deposition due to numerous disadvantages:. Slow mass transport along the narrow nanopores can result in a significant composition gradient along the nanowire. The required low deposition potential leads to undesired bubble formation due to strong hydrogen evolution. Continued growth of these gas bubbles can block the pores and partially or even fully interrupt further nanowire growth. Simultaneous pH increase may cause the formation and incorporation of undesired hydroxides. However, complexing the metal ions with citrate is expected to significantly reduce the hydroxide formation and also seems to improve nanowire growth. Here, a constant potential of E = -1.48 V_{SCE} is applied for the overall deposition time of t = 5000 s. The length of the wires is measured to 6.1± 0,3 µm.

In order to investigate structure and microstructure transmission electron microscopy (TEM/ TECNAI T20, 200kV, LaB_6 filament) was performed. TEM samples of the FeGa nanowires embedded in aluminum oxide membrane were prepared to transparency by focused ion beam technique (FIB/ Helios Nano Lab 600 i). The sample was cut from the substrate side with an energy of 30kV to the beginning and 2kV during the finishing.

Figure 17 compares the cross sections of a) pulsed and b) non-pulsed nanowires. In both samples the nanowires appear continuous and smooth. Only few small defects are observed along the nanowire length following the surface morphology of the inner pore walls (marked with arrows in Figure 1b). The microstructure seems nanocrystalline. In some of the crystals the angle between lattice planes and the direction of the incident beam comply the Bragg`s condition exactly. In the imaging this crystals appear darker in contrast. In crystals with another incident beam conditions the contrast of the crystals come out brighter. The same effect can occur within a single stressed grain. Consequently different contrast can be

observed inside this grain. That is given in the pulsed or non- pulsed wires which exhibit strong stress. An accurate determination of the crystal size is not possible. The nanowires fabricated by pulsed deposition show a uniform stress pattern (marked with arrows in Figure 1a). These features might be attributed to the pulsed method as they are not at all observed for the potentiostatically deposited nanowires.

The diffraction ring patterns presented in the insets in Figures 1a) and b) indicate a multitude of nano crystals that can be attributed to α-Fe_3Ga with a preferred {110} orientation. In case of the pulsed wires lots of strong discrete reflexes along the diffraction pattern rings were found. This hints for a larger crystal size in the pulsed wires compared to the non-pulsed wires. Both diffraction patterns give no indications for the presence of the undesired GaOOH phase. Fast Fourier transformation (FFT) filtered high resolution TEM images suggest isolated small regions consisting of GaOOH shown on a pulsed wire in Figure 18.

EDX measurements along both types of wires indicate no gradient in chemical composition. The average composition of the non-pulsed wires amounts 68±3 at % Fe and 32±3 at % Ga. The pulsed wires were measured to 78±3 at % Fe and 22±3 at % Ga. This correlates much better with the desired composition of $Fe_{80}Ga_{20}$.

In summary, our TEM investigations reveal only minor differences in structure and microstructure of differently prepared FeGa nanowires. The pulse deposited nanowires exhibit slightly larger crystals and more pronounced stress patterns. Unexpectedly, potentiostatic deposition yields similar nanowire quality.

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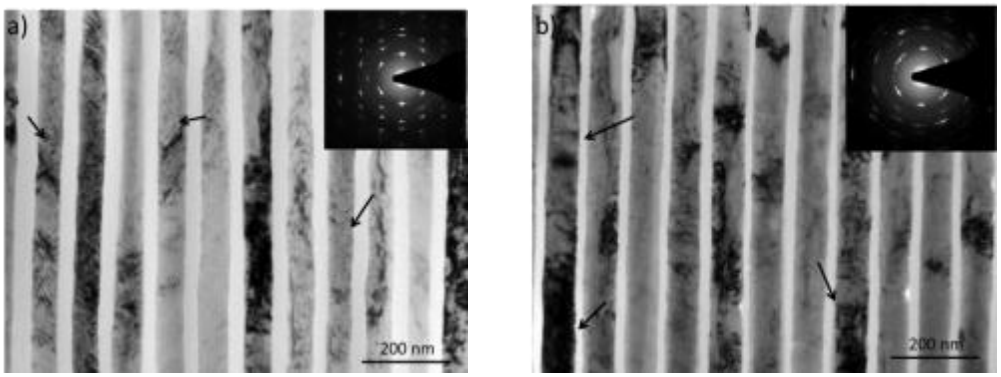

Figure 17. TEM bright field images and corresponding SAD of cross sections of a) pulsed wires (arrows point on the uniform stress pattern) and b) non- pulsed wires (arrows point on defects following the surface morphology of the inner pore walls).

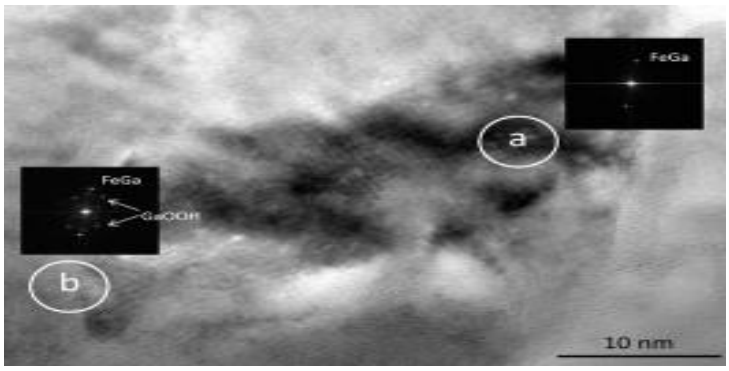

Figure 18. HRTEM image of the cross section of a pulsed wire and FFT: a) main reflexes FeGa and b) main reflexes FeGa and side reflexes GaOOH.