Coupled, Simultaneous Displacement and Dealloying Reactions into Fe-Ni-Co Nanowires for Thinning Nanowire Segments

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Introduction

The use of nanowires in microfluidic devices and sensors require the tip size of the nanowire to be of the order of molecules, *e.g.* ~2 nm for nucleotides, to be detected, while integrating them into micro and macro-scale connectors. Template-assisted electrodeposition of metals and alloys is an efficient nanowire fabrication method, popularly used with polymeric, or aluminum oxide membranes.[1-2] The availability of commercial templates with pore size ranging from 10 nm to 2000 nm has enabled the field to rapidly expand, but templates with pore size < 10 nm are limited, making it difficult to create nanowires with diameters below 10 nm. Ultra-thin metallic nanowires can be fabricated electrochemically, either by resorting to high-end instrumentation to create ultra-small, nanopatterned templates, such as by using electron beam lithography[3] or EUV (extreme ultraviolet) lithography[4], or by generating in-house, porous alumina substrates with careful control of the anodization step. Ultra-thin metallic nanowires can also be generated without a hard template, such as gold[5] and PtFe[6] with an oleylamine reducing agent and stabilizer, producing a dispersion of sub 10 nm wires with finely controlled diameter dimensions.

The work presented here describes creation of multiscale wires through a coupled dealloying and galvanic displacement reaction and a subsequent etching procedure. Nanosized, rod-like structures were generated from electrodeposited Fe-Ni-Co nanowires, followed by displacement of a part of the Fe-Ni-Co by Cu. A second Fe-Ni-Co layer was then deposited onto the Cu layer. Once the wires are released from the template, a part of the Cu was selectively etched to achieve a thinning effect for the Cu displacement region. Experiments with varying $[H^+]$ and [Cu(II)] concentrations were implemented to investigate their influence on the penetration rate of copper ions into Fe-Ni-Co nanowires

Experimental

Fe-Ni-Co nanowires were fabricated with a pulsed current electrodeposition method, 2 s on (-50 mA/cm^2)/2 s off (0 mA/cm^2),[7,8] in a polycarbonate membrane having pores of ~100 nm, from a boric acid-sulfate-sulfamate electrolyte. A displacement reaction of Cu(II) on iron and nickel was carried out in a copper citrate solution and the etching step for thinning the copper displacement region was completed in a citrate-boric acid electrolyte (Figure 1). The resulting structure was characterized with Field Emission Scanning Electron Microscope (FESEM) and High-resolution transmission electron microscopy (HRTEM).

Results and Discussion

FESEM and TEM results indicate that rod-like regions occurred between two supporting Fe-Ni-Co regions in the nanowires (Figure 2), with the diameter of the rods on the order of 10 nm. Inner rods were formed at low pH = 0 (Figure 2a), and pH = 1 (Figure 2b)) however gaps were generated at a relatively high pH (pH=4). SEM-EDS analysis show that there is indeed Fe and Ni remaining in the rod-like region. Varying the $[H^+]$/[Cu(II)] concentration ratio indicated that either insufficient $[H^+]$ or insufficient [Cu(II)] will produce a slow penetration rate for Cu(II) going into Fe-Ni-Co nanowires in the axial direction. Thus, it is determined that a balance exists between the amount of proton and copper species required for the Cu(II) propagation phenomenon to occur. A model was created to capture this effect, assuming a first order

reaction occurs for the displacement and the proton corrosion reactions to give a comprehensive understanding for the Cu(II) penetration process.

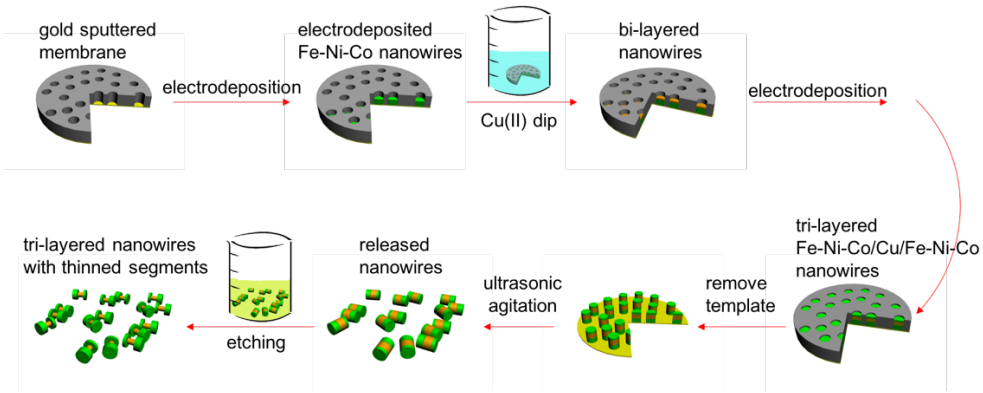

Figure 1. Procedure: electrodeposition Fe-Ni-Co into a gold sputtered membrane, exposure of the membrane containing the deposit structure into an acid copper solution resulting in a bi-layer structure, removal of the template, and release of the nanowires facilitated by ultrasonic agitation, followed by a selective copper etch resulting in a multi-scale diameter wire.

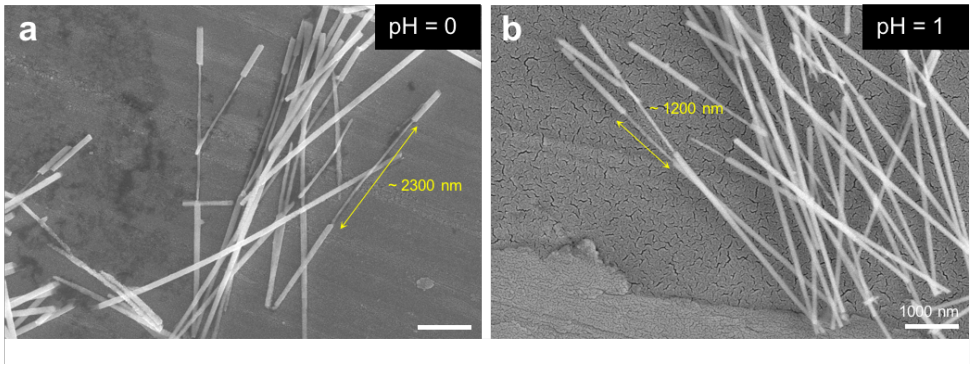

Figure 2. SEM image of tri-layered Fe-Ni-Co/Cu-Fe-Ni-Co/Fe-Ni-Co nanowires after exposure to the copper-citrate electrolyte at pH 0(a), and 1(b) for 2 min.

Conclusion

A novel method was developed to create nanowires with smaller, inner rod regions via electrodeposition, displacement/dealloying and a subsequent etching step. The proton and copper concentration ratio, $[H^+]/[Cu(II)]$, and total moles of reactants during the dipping step, are determined to be key to drive the displacement reaction of iron by copper ion reduction into the iron-rich nanowire axially for creating a copper-rich region to be selectively etched forming thinner segments.

Acknowledgement

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