Pulse Electrodeposition of Multi-segmented Super Invar/Au Nanowires

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Introduction

One dimensional metal nanowires, nanotubes, and multi-segmented nanowires are of interest due to their use as a sensor in the fabrication of micro- and nano-devices. Electrodeposition is a preferred technique because of the low cost, precise control over segment dimensions, and offers a wide range of metals and alloys that can be deposited depending on the material's functionality.[1] In particular, the multi-segmented nanowires with magnetic and nonmagnetic segments are attractive for biosensor applications. The magnetic part of the nanowire is to be used to align them in a microfluidic channel and the nonmagnetic region is to provide the freedom to functionalize its end.

In this work, the multi-segmented Super Invar/Au nanowires have been fabricated by using galvanostatic pulsing for the Super Invar layers (64 wt % Fe, 31 wt % Ni, and 5 wt % Co) and dc deposition for the Au layers. The robustness of the nanowires are investigated, with particular emphasis on the integrity of the Super Invar and Au interface.

Experimental

The Super Invar/Au segmented nanowires were fabricated by sequential electrodeposition within nanoporous membranes, such as alumina oxide (AAO) and polycarbonate (PC). The nanoporous membranes with a sputtered Au layer on one side, served as the working electrode. A platinum mesh was employed as a counter electrode. For deposition of Super Invar alloys, a rotating cylinder Hull cell was used to survey conditions use for the recess deposition.[2] The Super Invar alloy was deposited from an electrolyte containing: 0.72 M nickel sulfamate, 0.155 M ferrous sulfate, 0.005 M cobalt sulfate, 0.5 M boric acid, 0.001 M sodium lauryl sulfate, 0.011 M ascorbic acid, at a pH of 2 and temperature of 40 ^{0}C. Au segments were fabricated at a current density of -1 mA/cm^2 by using cyanide free gold solution (TG-25E RTU) at a temperature of 60 ^{0}C. The membrane was dissolved in dichloromethane and then washed with ethanol three times.

A substrate for magnetic alignment was prepared by electrodepositing a thin film of cobalt onto a copper substrate. The Co electrolyte composition was 0.25 M cobalt sulfate and 0.5 M boric acid. The film was cut in cross-section, embedded in an epoxy resin, polished and cleaned. A drop of released nanowires in ethanol was added onto this surface and then examined by FE-SEM.

Results and Discussion

Super Invar nanowires were electrodeposited into AAO membranes (200 nm) with and without 2-butyne-1,4-diol (BD). A long "off" time was used 27 s relative to the deposition time of 2 s in order to facilitate diffusion of ions during the "off" relaxation time. Without BD significant layering of corrosion products resulted, however these were largely eliminated with the addition of BD to the electrolyte.

Segment nanowires of Super Invar with Au were deposited into PC membranes and the "off" time for the Super Invar deposition was reduced to 2 s in order to circumvent corrosion during the "off" time but still allowing for some relaxation to minimize local pH changes within the nanopore. Figure 1 shows FE-SEM images of Super Invar/Au/Super Invar tri-layered nanowires without (a) and with (b) a sulfuric acid treatment. A dilute sulfuric acid treatment (5 vol %) was critical between the deposition of the Au layer and the Super Invar layer. Figure 1 (a) shows that without the sulfuric acid treatment only two segments of Super Invar/Au nanowires were observed intact, suggesting that the Super Invar layer deposited onto the Au layer can easily break apart. As evident in Figure 1 (b) when the sulfuric acid pre-treatment was added prior to the Super Invar layer deposition all three layers were observed.

On the microscale, Figure 2, clumps of Super Invar/Au nanowires were attracted to the only magnetic Co edge, of a thin film, but not to the non-magnetic edge, Cu. Continued work to align the nanowires will be presented.

Conclusions

Super Invar nanowires were fabricated by pulsed galvanic electrodeposition for the purpose of avoiding local pH changes in the recessed membrane, but introduced corrosion during the relaxation time that can be circumvented with the use of BD and also decreasing the "off" time. The Super Invar nanowires were used as a magnetic cap onto Au nanowires to direct them onto a magnetic surface.

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References

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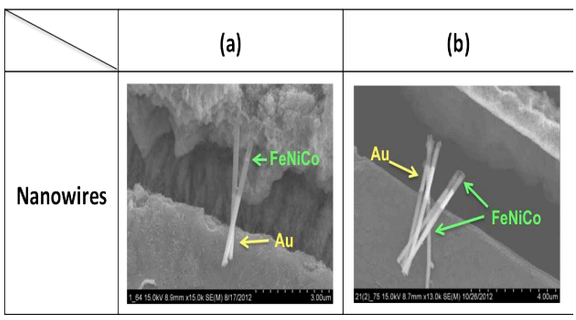

Figure 1: Multi-segmented Super Invar/Au/Super Invar nanowires: (a) without and (b) with dilute sulfuric acid treatments between Au and FeNiCo deposition

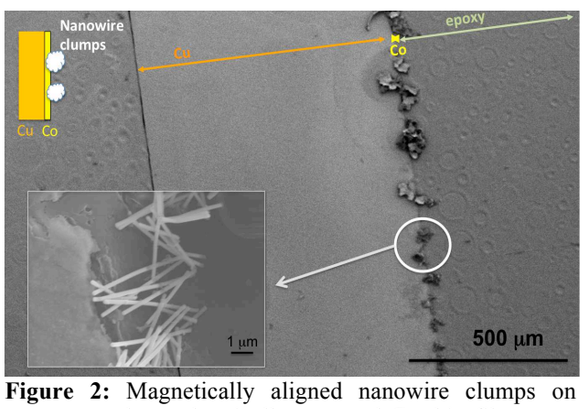

Figure 2: Magnetically aligned nanowire clumps on electrochemically prepared Co thin films onto the Cu substrate