ELECTROPLATING-BASED APPROACHES TO VOLUMETRIC NANOMANUFACTURING

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ABSTRACT

This paper focuses on electroplating-based volumetric nanomanufacturing to create highly-structured multilayer metallic materials, with precisely designed characteristic lengths in the hundreds of nanometers but volumes of manufactured material in the macro range. This electroplating-based approach also enables batch fabrication of nanostructures. The fabrication relies on automated and repeated multilayer electrodepositions of multiple metallic materials, followed by sacrificial etching of one metal. The remaining structure consists of individualized high-lateral-aspect-ratio sub-micron metallic films. As an example application, energy storage directly benefits from these approaches as nanostructuring improves specific energy storage performance and increasing volume improves the total amount of energy stored.

KEYWORDS: Electrodeposition, Nano-Laminations, Three-Dimensional

INTRODUCTION

Many nanomanufacturing approaches can be classified into two categories: precisely-controlled assembly approaches that rely on nano-scale manipulation techniques (e.g., AFM or e-beam lithography), and volumetric chemical syntheses (e.g., emulsion-based production of nanoparticles). The former approach has the advantage of exquisite control of the location and structure of the fabricated nanostructures, but is typically restricted to a surface patterned via serial processes. The latter approach allows larger volumes of nanostructures to be realized, at the expense of the exquisite control of the former.

The work presented in this paper describes efforts in electroplating-based volumetric nanomanufacturing to create highly-structured multilayer metallic materials, with precisely designed characteristic lengths in the hundreds of nanometers but volumes of manufactured material in the macro range. This electroplating-based approach also enables batch fabrication of nanostructures, combining the advantages of precisely-controlled assembly approaches and nano-scale manipulation techniques. Further, the fabrication process relies on established large area microfabrication techniques such as electroplating and chemical etching. As an example application, energy storage directly benefits from these approaches as nanostructuring improves specific energy storage performance and increasing volume improves the total amount of energy stored.

We previously demonstrated a variety of MEMS-based energy storage devices with micron-scale features fabricated using a similar conceptual approach; albeit some variations in the layer support techniques, plated materials, or aspect ratios. The electroplating-based technology was illustrated through three examples: laminated permalloy cores for reduced eddy current losses in high-frequency inductors [1]; high-surface-area MEMS-based electrolytic capacitors [2]; and high-current zinc-air micro-batteries [3], demonstrating compatibility with an extensive set of materials, including but not limited to copper, nickel, nickel-iron alloys, and zinc. The major limitations of the previously-published fabricated structures were caused by the plated material roughness and a limited layer count.

The major process improvements reported in this paper are the introduction of robotics into the electroplating system as well as low surface roughness of the electrodeposited materials, enabling automated and controlled nanostructuring of the materials during fabrication. The targeted application of the engineered materials is focused on magnetic materials for high-power high-frequency chip-scale inductors. Electroplating-based approaches enable the construction of nanolaminated materials that minimize core losses at high switching frequencies, while simultaneously maintaining not only the large overall core thicknesses required for large power handling. Furthermore, these approaches have the potential for scalable CMOS integration using existing back-end CMOS and packaging fabrication equipments.

CONCEPT

In order to create a multilayer structure with sub-micron characteristic lengths, alternating layers of two or more metals are sequentially electroplated through a standard photoresist mold defined using photolithography techniques. Figure 1 shows a conceptual rendering of the robotically-assiststed electroplating setup. By automatically alternating the plating materials and controlling the electrodeposition time and current density, it is possible to create a thick (several hundreds of microns) structure that consists of sub-micron-thick layers of metallic materials.

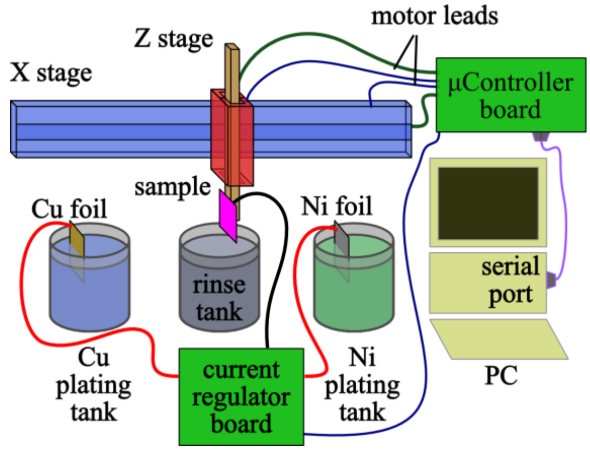


Figure 1: Conceptual rendering of the robotically-assisted sequential electroplating system

Figure 2 illustrates the fabricated multilayer structure after photoresist removal. Post-electrodeposition, one or more metals are selectively etched away as depicted in Figure 2(b) and Figure 2(c), creating a scaffold consisting of high-lateral-aspect-ratio metallic films. The metallic layers can be supported by metallic or polymer posts depending on the targeted application. For example, in highly-laminated magnetic cores, the layers must be electrically insulated from each other to efficiently reduce eddy current losses, preventing the use of metallic posts. Conceptually, this approach solely relies on established large area microfabrication techniques such as electroplating and chemical etching to develop a nanostructured material with improved performance.

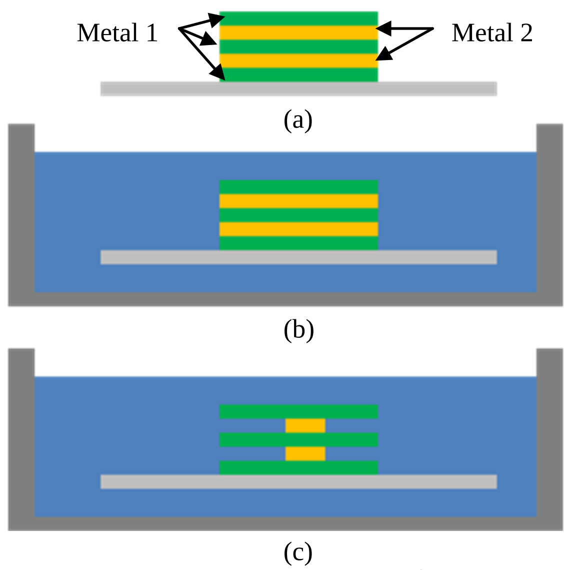


Figure 2: Electrodeposition-based approach to volumetric nanomanufacturing: (a) multilayer electrodeposition after photoresist mold removal, (b) sacrificial metal etching in chemical solution, (c) partially-released laminated structure

EXPERIMENTAL

The fabrication process starts with the deposition of a metal seed layer (Titanium/Copper/Titanium) onto a rigid substrate. After photoresist mold fabrication and pre-electrodeposition sample preparation (i.e., titanium etching and copper de-oxidation), alternating layers of ferromagnetic permalloy ($Ni_{80}Fe_{20}$) and copper are electroplated using the robotic multilayer electrodeposition system shown in Figure 3. The robotic plating system is a computer-controlled robotic arm that transfers the wafer from one bath to another. After electrodeposition of a single metallic layer, the wafer is rinsed into two DI water baths to avoid any cross-contamination between plating solutions. It is particularly critical to prevent the copper plating solution from being transferred to the permalloy plating bath because copper electrodeposits at a lower potential than permalloy. After rinsing, the wafer is transferred to the second plating solution for electroplating. This process is repeated as many times as desired and parameters such as plating current density, plating time, and bath temperature can also be adjusted.

The plating baths are continuously filtered and purged with nitrogen during electroplating. The filtering and purging also provide a slight fluid agitation to avoid diffusion-limited electrodeposition.

The selected sacrificial material must exhibit low resistance, low surface roughness, high adhesion to the magnetic material, and must be able to be selectively etched away without degrading or etching the magnetic material. Copper is a good material in this application. After a partial etch of the sacrificial metal, polymer posts are lithographically defined to support the metallic layers. Etching is carried on until the sacrificial metal is fully etched away.

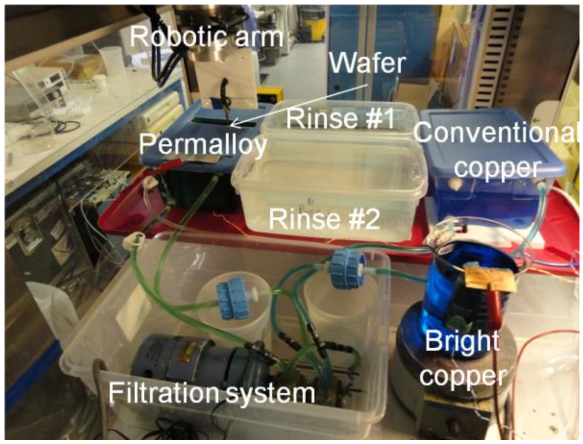


Figure 3: Photograph of multilayer robotic plating setup

RESULTS AND DISCUSSION

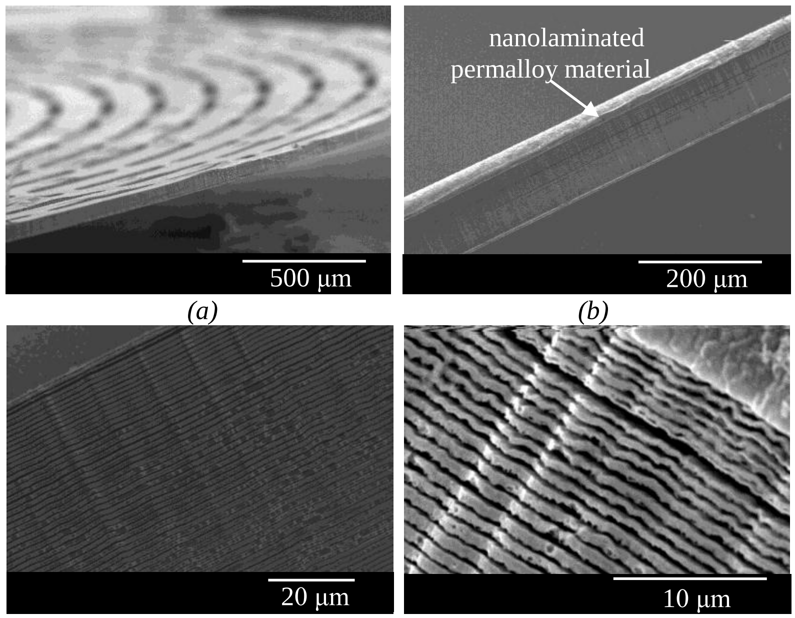
Figures 4 shows a photograph of a 100-layer permalloy structure with layer thicknesses and interlayer gaps measuring less than 500 nm. Layer thickness measurements were performed via scanning electron microscopy (SEM) metrology. The total device thickness is on the order of 100 μm, which consists of 50 μm of nano-laminated layers of permalloy, demonstrating volumetric nanomanufacturing. Figure 5 depicts a series of SEM micrographs focusing on the nano-structured material after sacrificial layer etching. Figure 5(a) shows a tilted view of the multilayer magnetic material, where designed hole patterns can be seen (also visible in Figure 4). The purpose of these holes is twofold. First, some of the features are utilized to efficiently etch the sacrificial metal layers by allowing the etchant to penetrate easily throughout the multilayer structure and reduce the lateral length to be effectively etched away. Second, the other patterns are filled with an epoxy to act as layer supports and material packaging.

Figure 4: 100-layer magnetic permalloy core electroplated using robotically-assisted multilayer electroplating setup and controlled-roughness electrodeposition. The total device thickness is on the order of 100 microns

As shown in Figure 5, the layers of magnetic material exhibit a high level of planarity. Controlled surface roughness was critical in achieving these nano-scale layers, and in overcoming technological limitations. Atomic force microscopy measurements on previously-plated and newly-plated copper films demonstrated surface roughness on the order of 300 nm and 30 nm, respectively. The low-roughness films were electroplated from a solution with leveler and brightener additives (*Grobet, Clean Earth Cu-mirror solution*). It should also be noted that the wavy patterns observable in Figure 5(c) and Figure 5(d) are attributed to the photoresist mold, and not to any layer degradation induced via multilayer plating or sacrificial etching.

Further, the low-roughness 100-layer structures demonstrated a 10x reduction in magnetic coercivity compared to previously-plated multilayer structures, resulting in measured coercivities below 5 Oe. It has been hypothesized that roughness and grain structure directly affect magnetic properties, as indicated in [4]. Moreover, the coercivity and magnetic saturation of this engineered material were comparable to the magnetic properties measured from a single electroplated film of permalloy ($Ni_{80}Fe_{20}$).

Although not imaged, we recently fabricated magnetic cores composed of 200 permalloy/copper layers with nominal film thicknesses of approximately 150 nm, demonstrating that the fabrication approach can still be scaled down.



(a) *(b)* *(c)* *(d)*

Figure 5: SEM micrographs of the multilayer magnetic core. The layers and interlayer gaps were measured at approximately 500nm or below. Increased magnification from (a) to (d) focusing on the multilayer construction

CONCLUSION

We demonstrated a CMOS-compatible nanomanufacturing technology to engineer highly-structured multilayer metallic materials that exhibit designed features in the hundreds of nanometers but total volumes of manufactured material in the µm-to-mm-scale range. Structures created via these electroplating-based approaches can consist of nano-laminated materials as demonstrated in this paper, or high-surface-area metallic scaffolds that can be further processed to create microfabricated batteries or capacitors. In such applications, large surface-area-to-footprint ratios are critical to enhance device performance.

Further, these high-lateral-aspect-ratio nano-scale features are defined by electrodeposition time, plating current density, and sacrificial etching time using existing back-end CMOS and packaging fabrication equipments, a major advantage towards large-scale nanomanufacturing development.

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