INCREASING THE THICKNESS AND DEPOSITION RATE OF HIGH-PERFORMANCE ELECTROPLATED CoPt PERMANENT MAGNETS

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ABSTRACT

This paper reports the fabrication and magnetic characterization of very thick (50+ μm) and high-performing (coercivity up to 850 kA/m; energy products up to 75 kJ/m³) electroplated permanent magnets microfabricated on silicon substrates. Intended for MEMS applications, an enhanced fabrication process yields higher areal magnetic energy density (5.6 J/m²) and faster plating rates (42 $\mu\text{m/hr}$) compared to previously published work. The magnetic CoPt alloy is co-plated in single electroplating bath and subsequently annealed at 675°C for 30 min to induce a phase transformation to the high-coercivity L1₀ CoPt phase. Four main accomplishments are reported: (1) optimization of the underlying seed layer metallurgy to improve film adhesion and prohibit silicon diffusion; (2) development of a warm-bath (50°C), high-current-density (300-2000 mA/cm²) electroplating process that dramatically increases plating rate while maintaining good magnetic properties; (3) demonstration of a mechanical planarization process yielding smooth surface with no delamination; (4) preliminary study of bath longevity.

INTRODUCTION

There are increasing technological needs for thick, process-integrable micrometer-scale permanent magnets that can provide high magnetic moment and/or large stray magnetic fields for various MEMS and microsystems. Examples include magnetic microactuators, magnetic field sensors, microfluidic devices, wireless power devices, and more (e.g. [1 - 4]).

Larger, thicker magnets are motivated by simple physics. First, the total magnetic moment of a magnet is proportional to its volume. Second, the “reach” of the stray magnetic fields produced by a magnet are also related to its size. At a given distance from the magnet surface, a larger magnet produces a larger magnetic field compared to a smaller magnet. To generate relatively strong fields at distances of tens of micrometers away from the magnet surface, micromagnets are needed with thicknesses of at least tens of micrometers.

Thick film rare-earth sputtered magnets (e.g. Nd-Fe-B, Sm-Co) have been studied for their high remanent magnetization and maximum energy density [5-6]. However, these sputtered magnets are difficult to be patterned into well-controlled shapes and are prone to oxidation, which limits their application in end devices. Alternatively, to provide large and stable bias fields, the L1₀ CoPt alloy offers desirable characteristics including strong magnetic properties, good thermal/chemical stability, and capability of fabricating thick films via aqueous electroplating processes (the rare-earth magnets cannot be electroplated from aqueous baths). For deposition, compared to physical or chemical vapor deposition methods, electroplating is more practical to realize multi-micron-thick films and easily scales to large substrates. Our group has previously reported electroplated CoPt magnets (250 $\mu\text{m} \times 2 \text{ mm}$ stripe shapes) with thicknesses of 15 μm electroplated at room temperature and current densities below 200 mA/cm², yielding excellent magnetic properties including intrinsic coercivity $H_{ci} \approx 800 \text{ kA/m}$, squareness > 0.8 , and energy product of $> 150 \text{ kJ/m}^3$ [7]. In this paper, efforts are focused on achieving larger (2 mm diameter round pattern) and thicker (50+ μm) magnet structures with equivalent or better magnetic properties by elevating the bath

temperature and also increasing the plating current-density and plating time. Ultimately, dense, thick-film magnets are achieved with 2.5X higher areal magnetic energy density (5.6 J/m²) and 3X increase in plating rate (42 $\mu\text{m/h}$) compared to the best previously published work [8-12].

EXPERIMENTAL METHODS

The overall fabrication process of electroplated CoPt thick film magnets includes three main steps. First, multiple thin-film underlayer (seed layers) and a masking layer are deposited on a silicon wafer. Second, 2 mm diameter CoPt films are electroplated using DC currents and an optimized electroplating bath. Third, the deposited CoPt films are annealed to induce strong magnetic properties. Scanning electron microscope (SEM) / energy-dispersive X-ray spectroscopy (EDS) (FEI NOVA 430, column voltage: 18 kV) and vibrating sample magnetometer (VSM) (ADE technologies) characterizations are performed to determine the surface/cross-section morphology, atomic composition and magnetic properties of plated films, respectively.

Underlayers and Masking Layer

N-type silicon wafer with $\langle 100 \rangle$ orientation is used as substrate and cleaned by buffered oxide etch (BOE) to remove the native oxide prior to deposition. The optimized seed-layer stack comprises (Fig. 1): 25 nm Cr adhesion, 50 nm titanium nitride (TiN) diffusion barrier, 25 nm Cr adhesion, 500 nm Cu conductive seed, and 500 nm photographically patterned Al₂O₃ (alumina) electroplating mask. All the layers except alumina are deposited by regular sputtering technique (KJL CMS-18 multi-source). The alumina layer is reactive sputtered by introducing oxygen during sputtering with an Al target. The TiN layer is used for preventing silicon atoms from diffusing into CoPt film and forming metal silicides [13]. Considering the high DC current that flows through the cross-section of conductive layer, Cu seed with thickness of 500 nm is chosen. Although photoresist electroplating molds are more commonly used for improved sidewall definition, the polymer-based photoresist suffers from deterioration and delamination in the heated baths. Consequently, a thin patterned alumina layer is used for its good adhesion and thermal stability. The alumina shows no sign of delamination in heated bath (up to 70°C) under high current density (up to 2000 mA/cm²) for at least 5 h.

Figure 1: Substrate seed layers with lithographically patterned alumina electroplating mask.

CoPt Electroplating Process

The seed layer/masking layers are processed on 100 mm wafers, and the wafer is then singulated for electroplating one magnetic structure at a time using 100 mL of bath. The electroplating bath chemistry is critical to the entire CoPt magnet fabrication process. The electroplating bath contains three

components: dinitrodiamine-platinum solution (Sigma Aldrich), cobalt sulfamate salt (Alfa Aesar) and ammonium citrate salt (Sigma Aldrich), which serve as platinum source, cobalt source, and pH buffer, respectively [7]. Since the cobalt sulfamate salt has unknown number of intramolecular combined water (depends on humidity and storage conditions), inductively coupled plasma mass spectrometry (ICP-MS) (Perkin-Elmer Corp.) is used to accurately determine the molecular weight of the cobalt sulfamate hydrate as well as the concentration of the platinum content of the commercial dinitro-diamine platinum solution. The pH of the bath is adjusted to 7 by adding diluted sodium hydroxide (NaOH) into mixed solution. Platinum foil and silicon wafer (with seed layers) are used as anode and cathode, respectively, with anode-to-cathode gap of 2.5 cm and no stirring. Bath temperatures of 50°C and 70°C are explored, as are DC current densities from 300 – 2000 mA/cm².

To achieve desired L1₀ CoPt crystal phase, an equiatomic CoPt alloy is desired. The film alloy ratio (measured via energy dispersive x-ray spectroscopy, EDS) is controllable by adjusting the concentration of Pt and Co ions in the electroplating bath (measured by ICP-MS) as shown in Fig. 2, and the optimized bath recipe (yielding near equiatomic films) is shown in Table 1.

Figure 2: Pt/Co atomic ratio in plated film vs. Pt/Co ion ratio in electroplating bath.

Table 1: Optimized bath composition.

Chemicals	Concentration [M]
Dinitrodiamine-platinum [Pt(NH ₃) ₂ (NO ₂) ₂]	0.05
Cobalt sulfamate [Co(SO ₃ NH ₂) ₂ •xH ₂ O]	0.0515
Ammonium citrate [C ₆ H ₁₇ N ₃ O ₇]	0.1

According to the Arrhenius law, the reduction rate of metal ions increases exponentially with temperature. So, elevated bath temperature from room temperature to 70°C is investigated to increase deposition rate [14].

Figure 3: Comparison of film quality between samples plated at 50 °C (left) and 70 °C (right), 1000 mA/cm² for 1 h.

High temperatures of 70°C allow layers of ~30 μm to be deposited in only 20 min, and if the time is extended over 45 min, films of 60–80 μm can be obtained. SEM analysis, however, shows that the quality (e.g. coercivity <100 kA/m) and density of the films is compromised at such rapid plating rates. In contrast, a plating bath temperature of 50°C yields much denser films (Fig. 3).

Film Annealing

After film deposition, an annealing step is used to induce a phase transformation of the CoPt alloy from the disordered, low-coercivity A1 phase to the ordered, high coercivity L1₀ phase (Fig. 4) [15]. All the plated films are annealed using a tube furnace (Lindberg Blue) with forming gas (96% N₂ + 4% H₂) ambient at 675°C for 30 min with the ramping up rate of 28°C/min.

Figure 4: Schematic diagram of CoPt phase transformation from disordered A1 phase (fcc) to the ordered L1₀ phase (fct).

EXPERIMENTAL RESULTS

Magnetic Properties vs. Plating Conditions

Using 50°C bath temp., current densities from 300 to 2000 mA/cm² are applied for 1 h. Fig. 5 and Fig. 6 shows the plating rate as a function of current density, and the resulting magnetic properties (post annealing). The plating rate increases monotonically with current density ranging from 0.29 μm/min up to 0.71 μm/min, which is important for reaching desired thickness in a reasonable amount of time. The magnetic properties are relatively consistent: coercivity up to 844 kA/m and maximum energy density up to 57 kJ/m³.

While the highest current densities yielded the fastest plating rate, to maintain such high current density for full-wafer plating with much larger plating area would require a very high-current power supply and may lead to the potential issue of uneven distribution of electric current across the wafer.

Figure 5: Plating rate and coercivity of electroplated CoPt magnets at various current densities. All the films are plated at 50 °C for 1 h.

Figure 6: Full hysteresis loops of electroplated CoPt magnets at various current densities. All the films are plated at 50 °C for 1 h.

Consequently, current densities of 400-600 mA/cm² and temperature of 50°C have proven to be the optimized electroplating conditions. At these conditions, extending the plating time to 5 h allows layer with thickness ranging from 46 to 98 μm to be successfully plated (Fig. 7).

The experimental results show that the magnetic properties are affected by the applied current density to some extent, but not as much as the plating temperature. Best results are obtained at 400 mA/cm², yielding a thickness of ~60 μm, coercivity of 820-850 kA/m, a remanence of 0.62 T, saturation magnetization of 0.73 T, squareness of 0.85, and (BH)_{max} of 65-75 kJ/m³.

Figure 7: SEM pictures a 2 mm diameter round manually polished CoPt sample (left) and cross-section view of a 58 μm thick unpolished CoPt sample (right) plated at 400 mA/cm², 50 °C for 3 h. Delamination due to manual cleaving for cross-section view.

Mechanical Polishing

Due to the uneven distribution of current density at the edge of plating area, a super thick “ring” (up to 200 μm) appears around the edge of the sample (Fig. 8). More uniform, cylindrical magnets with smooth surface are typically desired.

Figure 8: Optical image and profilometer measurement of a 2 mm diameter sample with thick “ring” prior to polishing.

A flatter and smoother surface can be easily achieved by polishing the CoPt magnet on a rotation polishing machine with 0.3 μm alumina polishing pad for only 20 s. No sign of delamination is observed after the polishing step.

Longitudinal Study of Bath Chemistry

Most of the aforementioned results were obtained using relatively “fresh” electroplating baths. However, we have observed deterioration of the magnetic properties after continued use of a given bath. To study this effect more systematically, we initiated a longitudinal study of CoPt bath chemistry. Starting with a freshly mixed 100 mL bath, a series of 13 samples are plated without any bath refreshment, each at 50°C and current density of 400 mA/cm² for 3 hr. This process typical yields ~20 μm/h plating rates, equivalently ~60 μm thick samples.

Fig. 9 shows the trends in magnetic properties. All samples show relatively consistent coercivity. However, there is more variation in remanence (and saturation). The initial seven samples show relatively high remanence and saturation magnetization. The highest value appears at the 7th sample. After ten samples are plated from the same bath, significant decrease of remanence and saturation magnetization. This change in magnetic properties coincided with the bath color changing from purple to wine red. [Several data points from this set of experiments are missing due to samples that were lost during testing due to machine failure.]

Figure 9: (top) Coercivity, remanence and (bottom) in-plane hysteresis loop comparison of CoPt samples (after annealing) plated from a single bath. All of samples are plated at 400 mA/cm², 50 °C for 3 h.

The metal ion consumption in the electroplating bath can be roughly calculated. Using the optimized bath recipe (Table 1), 100 mL bath contains 975 mg of Pt and 304 mg of Co. The average mass of single 60 μm thick, 2 mm diameter round equiatomic CoPt magnet is assumed to be 2.86 mg (2.02 mg Pt, 0.84 mg Co) by

averaging the density of Pt and Co. According to this calculation, thirteen 60- μm -thick samples would only correspond to 26 mg of Pt (a reduction of only 2.6%) and 11 mg of Co (a reduction of only 3.6%). Hence, a depletion of metal ions in the bath due is unlikely to be the reason that leads to the decrease of magnetic properties. Further investigation and confirmation by more systematic chemical analysis of the CoPt electroplating bath is still needed.

CONCLUSIONS

A complete fabrication process is demonstrated for yielding high-performance CoPt thick film micro-magnets on Si substrates. Multiple functional layers including Cr adhesion, TiN diffusion barrier, Cu seed and alumina mask layer with optimized thickness are deposited through sputtering and patterned by HF on silicon wafer. Warm electroplating baths and relatively high current densities are shown to increase the plating rate, yielding very thick films while retaining strong magnetic performance. Specifically, CoPt magnets with thicknesses over 50 μm are obtained using optimized electroplating conditions: current densities 400-600 mA/cm^2 , bath temperature of 50°C, and plating times of 3-5 h. After post-annealing at 675°C for 30 min, the magnets consistently exhibit coercivities up to 850 kA/m, remanence of 0.62 T, saturation magnetization of 0.73 T, squareness of 0.85 and maximum energy density up to 75 kJ/m^3 . Li et al. suggested areal magnetic energy density $t_{\text{film}} \times (\text{BH})_{\text{max}}$ as a good figure of merit for magnetic films for MEMS [8]. Herein, we demonstrate magnets with more than 2.5X improvement in areal magnetic energy density compared other reported electroplated films on Si substrates (Fig. 10) [7-13].

Longitudinal study of bath chemistry is also conducted, which shows the changing trends of magnetic properties of CoPt samples plated continuously from single electroplating bath. Theoretical calculation indicates that the degraded magnetic performance is not attributed to simple metal ion consumption during electroplating.

Figure 10: Maximum areal magnetic energy density (figure of merit) vs. film thickness for our results vs. previous work.

ACKNOWLEDGEMENT

This work is sponsored in part by DARPA MTO and the Army Research Office (Grant Number W911NF-17-1-0050). The authors thank the staff of the UF Research Service Centers for their assistance in the microfabrication and material characterization.

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