Mitigation of interfacial silicide reactions for electroplated CoPt films on Si substrates

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Abstract. We report in this paper the influence of film thickness on the material and magnetic properties of electroplated CoPt permanent magnets. Layers of CoPt magnets with film thicknesses ranging from 0.5 \( \mu \text{m} \) to 5 \( \mu \text{m} \) are deposited into photoresist molds (3.5 mm x 3.5 mm square and 5 \( \mu \text{m} \times 50 \mu \text{m} \) arrays) on a (100)Si substrate coated with 10 nm/100 nm Ti/Cu adhesion/seed layer. Results show an unexpected reduction in magnetic properties for films below 2 \( \mu \text{m} \) thick. This effect is determined to be a consequence of metal-silicide reactions at the substrate interface during annealing leading to the formation of a non-magnetic layer at the interface. Subsequently, a TiN diffusion-barrier layer is added to inhibit the silicide reaction and thereby maintain strong magnetic properties (\( H_{ci} \sim 800 \text{ kA/m} \), \( M_r/M_s = 0.8 \)) in micron-thick electroplated CoPt layers.

1. Introduction

Equiatomic CoPt in the ordered \( L_1_0 \)-phase is known to exhibit strong magnetic properties (\( K_u = 4.9 \text{ MJ/m}^3 \), \( \mu_0 H_{ci} \geq 1 \text{ T} \), and \( M_s = 1 \text{ T} \)) and excellent corrosion resistance [1]–[3], making it a magnetic material of considerable interest to the PowerMEMS community. In the as-deposited state, CoPt films possess a disordered A1 crystallographic phase, with relatively soft magnetic properties (\( \mu_0 H_{ci} < 0.0125 \text{ T} \), \( M_r/M_s < 0.05 \)). The films typically require a thermal anneal (usually > 500°C) to induce a crystallographic ordering from the disordered A1 phase with a face-centered cubic structure to an ordered \( L_1_0 \) equilibrium phase having a face-centered tetragonal structure. The tetragonal crystal lattice yields high magnetocrystalline anisotropy and plays a key role in yielding the hard magnetic properties.

Because of the advantages offered by electroplating (such as cost efficiency, ease of fabrication and scalability, shape controllability, and general integrability within MEMS processes), the electrodeposition of CoPt permanent magnets has been widely studied as an attractive and practical fabrication technique for various MEMS applications [4]–[12]. However, like many fabrication methods, electroplating is a variation-prone process, in that factors such as plating conditions (pH, current characteristics, temperature, agitation, deposition time), electrolyte composition, and substrate (or seed layer) impact the morphology and overall properties of the plated layer. For example, our group has previously reported the deposition of 3 – 20 \( \mu \text{m} \)-thick CoPt magnets and investigated the influence of current density, seed layer, anneal temperature/time on the crystallographic structure and magnetic properties of the plated CoPt magnets [4]–[12]. While most of the above studies have focused on multi-micron thick films, film thicknesses of hundreds of nanometers to a few microns...
may be desired for certain microsystem device applications. In this work, we study the effects of film thickness variation on the magnetic properties of electroplated CoPt magnets and investigate an unexpected reduction in magnetic properties observed in films with thickness below 2 µm. The deterioration in magnetic properties is identified to be the result of metal-silicide reactions between the metal layers and silicon substrate, which occurs during the post-deposition annealing step. The use of a TiN diffusion barrier is shown to eliminate the silicide reaction and thereby improve the magnetic properties of thinner layers.

2. Experimental Procedure

2.1. Fabrication process

The CoPt magnetic layers are electroplated into photoresist molds, 3.5 mm x 3.5 mm and 5 µm x 50 µm array, on a (100)Si substrate using one of two types of seed layers. Type A samples use a 10 nm Ti adhesion layer and a 100 nm Cu conductive layer. Type B samples use a 25 nm TiN diffusion barrier, followed by 10 nm Ti and 100 nm Cu. The Ti and Cu are DC sputtered, and the TiN is achieved by reactive sputtering of Ti in nitrogen. The electroplating bath consists of 0.1 M of cobalt sulfamate, 0.025 M of diamine dinitrito platinum (II), and 0.1 M of ammonium citrate salts in a 100 mL solution. Films are plated at room temperature, at a pH of 7 using 100 mA/cm² currents and subsequently annealed in a forming gas ambient (4% H₂ + 96% N₂) at 700°C with a ramp rate of 20°C/min for 40 min [11]. Figure 1 shows example optical images of CoPt magnets deposited into photo-defined molds. Film thicknesses between ~0.5 µm and ~5 µm are obtained by varying the time of deposition. Table 1 presents the deposition time and corresponding film thickness.

![Image](image_url)

Figure 1: Example top-view optical images of CoPt magnets electroplated into photoresist molds.

| Sample | Layers       | Deposition Time (min) | Film Thickness (µm) |
|--------|--------------|-----------------------|---------------------|
| A1     | Si/Ti/Cu     | 5                     | 0.4                 |
| A2     | Si/Ti/Cu     | 15                    | 1.3                 |
| A3     | Si/Ti/Cu     | 30                    | 2.6                 |
| A4     | Si/Ti/Cu     | 45                    | 3.5                 |
| A5     | Si/Ti/Cu     | 60                    | 5.2                 |
| B1     | Si/TiN/Ti/Cu | 5                     | 0.4                 |
| B2     | Si/TiN/Ti/Cu | 15                    | 1.3                 |
| B3     | Si/TiN/Ti/Cu | 30                    | 2.6                 |

2.2. Characterization

Energy dispersive x-ray spectroscopy (EDS) was used to confirm the chemical composition (~50:50) of the CoPt films. A FEI Nova NanoSEM 430 scanning electron microscopy was used to image the films and to measure the film thickness. Crystallographic structure analysis was carried out using x-ray diffraction (XRD) patterns from a Panalytical X’Pert Powder diffractometer. In-plane and out-of-plane magnetic measurements were made with an ADE EV9 vibrating sample magnetometer (VSM).
3. Results and Discussion
This section presents experimental results of the material and magnetic characterizations of CoPt samples deposited on Si/Ti/Cu and Si/TiN/Ti/Cu.

3.1. SEM Imaging
Figure 2 shows cross-section SEM images of samples with different thicknesses after annealing. For samples without TiN layer (samples A1–A5), a rough, pulverized appearance of the metal-substrate interface is observed, particularly in the 0.4-μm-thick film. This damaged interface is a consequence of a reaction between the Si substrate and the metal layers at temperatures ≥ 200°C [13], [14] (later confirmed by XRD). It is noted that as the film thickness increases, the effects of the interface reactions become less noticeable and the microstructure of the CoPt film becomes clearly defined. The use of the 25-nm TiN layer (Type B samples) shows a dramatic improvement of the interface, although a new problem arises in the poorer adhesion of the electroplated layer to the TiN barrier layer on Si. The larger area 3.5 mm x 3.5 mm films delaminated from the substrate, but the smaller 5 μm x 50 μm patterned films did not.

![Figure 2: Cross section SEM images of annealed CoPt magnets of various film thicknesses (A1-A3) without TiN layer; and (B1-B3) with TiN diffusion barrier layer.](image)

3.2. Crystallography
Figure 3 shows XRD measurements for the CoPt samples with different film thicknesses. The diffraction patterns confirm the presence of Co- and Cu-silicides in the Type A samples, with strong peak intensities notable for the 0.4-μm-thick sample. The figure also confirms the elimination of the silicides in the Type B samples with the introduction of the TiN barrier layer. Figure 4 shows the L10 phase volume fraction [9] of samples A1 – A5 (without TiN) and B1 – B3 (with TiN). It is seen here that an increase in the L10 volume fraction is observed with increasing film thickness for both sets of samples. The low volume fraction obtained in the thinner films is attributed to the formation of metal silicides from the interface reactions inhibiting the progress of the transformation, for the case of the Type A samples.

3.3. Magnetic Properties
Figure 5 presents out-of-plane magnetization curves of the CoPt samples deposited with and without TiN. Very poor magnetic properties are exhibited by the 0.4-μm-thick sample without TiN layer,
owing to the large volume fraction of non-magnetic silicides. The magnetic properties improve with thickness suggesting the existence of a “good” magnetic layer on top of a “poor” layer, as illustrated in figure 6. Films at 3.5 μm and above show properties consistent with the previously reported 3 to 20-μm-thick layers [10], [11].

Figure 3: X-ray diffraction patterns of annealed CoPt magnets showing the presence of non-magnetic Cu-silicide and Co-silicide in the Type A samples, with subsequent mitigation of these silicides in the Type B samples.

Figure 4: $L_{10}$ phase volume fraction of CoPt magnets without (A1 – A5) and with TiN (B1 – B3) for various film thicknesses.

Figure 5: Out-of-plane magnetic hysteresis curves for CoPt samples with various thicknesses (A1-A5) without TiN layer and (B1-B3) with TiN diffusion barrier layer.

Substantial improvements in magnetic properties are observed for samples on TiN layer with film thickness of 1.3 μm and above, although the 0.4 μm-thick film still exhibit relatively poor magnetic
properties. Lastly, Figure 7 shows a strong correlation between the $L_{10}$ volume fraction and the coercivity of the CoPt magnets, the highest volume fraction of 0.83 yielding a high coercivity of close to 900 kA/m.

4. Conclusion
The mitigation of metal-silicide reactions at the substrate interface of an electroplated CoPt magnetic layer is reported in this paper. More than 4X reduction in coercivity is observed for films with thicknesses less than 2 µm as a result of the silicide reaction. By using a TiN barrier layer, the metal-substrate interface is improved, the silicide reaction is prevented and a coercivity of ~800 kA/m is maintained for micron-thick films.

5. References
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