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Integrated CoPtP Permanent Magnets for MEMS Electromagnetic Energy Harvesting Applications

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Abstract. This work reports the development of integrated Co rich CoPtP hard magnetic material for MEMS applications such as Electromagnetic Vibration Energy Harvesting. We report a new method of electrodeposition compared to the conventional DC plating, involving a combination of forward and reverse pulses for optimized deposition of Co rich CoPtP hard magnetic material. This results in significant improvements in the microstructure of the developed films as the pulse reverse plated films are smooth, stress free and uniform. Such improvements in the structural properties are reflected in the hard magnetic properties of the material as well. The intrinsic coercivities of the pulse reverse deposited film are more than 6 times higher for both in-plane and out-of-plane measurement directions and the squareness of the hysteresis loops also improve due to the similar reasons.

1. Introduction

Microfabricated permanent magnets with thickness of the order of microns to hundreds of microns are the key building blocks for a number of magnetic MEMS (Micro-Electro-Mechanical Systems) applications. Development in this particular field is necessary for complete integration of electromagnetic transducers [1-3] in CMOS compatible processes for scavenging electrical energy from mechanical vibrations. Therefore, a number of fabrication techniques including powder-based fabrication methods [4, 5] (such as dry-packing, screen printing etc.) and conventional thin film deposition techniques [6, 7] (sputtering, electrochemical deposition etc.) have emerged over the years depending on the application requirements. Electrochemical deposition is an attractive choice among them due to its low cost and relatively high deposition rate at CMOS compatible temperature. Growth of transition metal alloys Co/Fe-Pt with equi-atomic ratios has received extensive attention [8] due to the high magneto-crystalline anisotropy which require high temperature, post-deposition annealing. On the other hand, Co rich Co₈₀Pt₂₀P alloy exhibit a relatively high coercivity, squareness and remanent magnetization in its as deposited state making it a suitable choice for different Magnetic MEMS applications [7, 9].

In this work, we have reported the deposition, structural and magnetic characterization of Co rich CoPtP magnetic material for magnetic MEMS applications.

2. Magnetic Material Deposition

Co-rich CoPtP films are electrochemically deposited using a bath consisting of 0.1M Cobalt Sulfamate, 0.01M Diammine-Dinitro-Platinum, 0.1M Sodium Hypophosphite, 0.1M Dibasic Ammonium Citrate, 0.1M Glycine and 0.25M Saccharin. Among the used chemicals in the bath,



Cobalt Sulfamate, Diammine-Dinitro-Platinum and Sodium Hypophosphite act as the source of cobalt, platinum and phosphorous impurity ions. Dibasic Ammonium Citrate acts as the complexing agent to bring the reduction potentials of cobalt and platinum close together. Glycine reduces the surface tension between the electrolyte and the working electrode whereas saccharin is added in the electrochemical bath as stress-relieving additive. The pH of the solution was adjusted to 8. Cobalt pieces were used as anode and silicon pieces (1 cm² area) with sputtered (200/20 nm) Cu/Ti seed layer were used as cathode and deposition is carried at room temperature. First film is deposited using DC plating technique at a current density of 20 mA/cm² whereas a second film is electroplated using Pulse Reverse Plating (PRP) technique using a current waveform as shown in Fig. 1. This consists of forward and reverse current densities 20 mA/cm² (20 ms) and 10 mA/cm² (0.5 ms) respectively with intermediate off times of 0.5 ms. The cycle is repeated for the entire deposition duration. The magnetic measurements of the deposited films are carried out in Quantum Design SQUID magnetometer (MPMS-XL5) for applied field up to 5 Tesla.

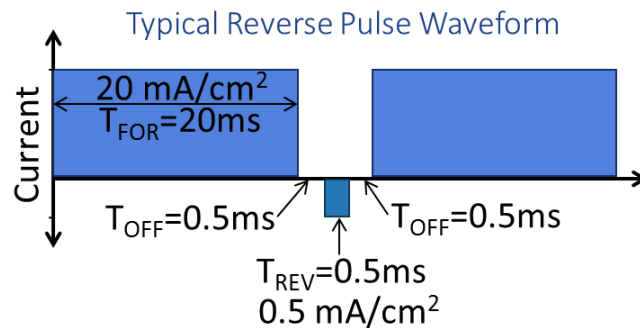


Figure 1. Current waveform for Pulse Reverse Plating (PRP) deposition of CoPtP.

3. Results & Discussions

The samples are electroplated for one hour each. The deposition rate for DC plated film is 1.7 μm/hr whereas that for the PR plated film is 2.9 μm/hr. The deposition current density is varied for both the electrodeposition techniques in order to observe the consequences on the developed films. In case of PRP technique, the reverse current density is always maintained to half of the forward current values with the previously mentioned durations. The variation of the plating rates with current density is shown in the Fig. 2.

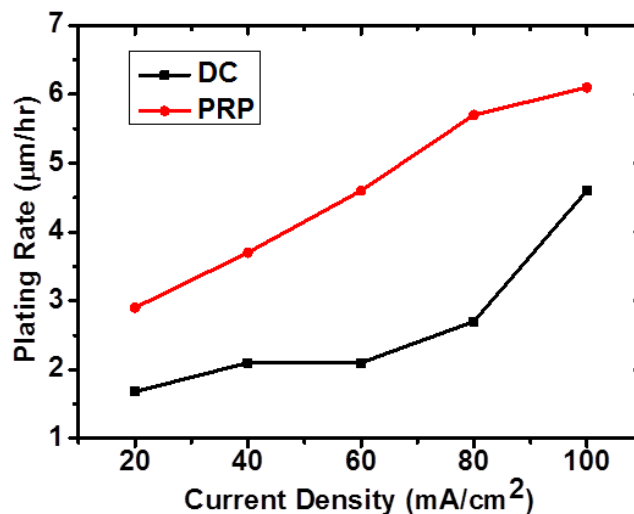


Figure 2. Variation of plating rate with the current density for DC and PRP plating.

The surface morphology of the deposited films is characterized using Scanning Electron Microscopy (SEM) and shown in Fig. 3. The DC plated film is full of micro-cracks [Fig 3(a)] even without using the stress relieving agent. To overcome this and in order to develop smooth and stress free films of CoPtP, we adapted the PRP technique with the above mentioned parameters. The nano-scale roughness from the surface of the deposited film is etched away in each cycle due to the reverse current of the PRP process which results in smooth film with uniform composition [Fig 3(b)]. The cross-section images of the electrodeposited films are shown in Fig. 3 (c) and (d). The uniform columnar growth of the film in case of PRP technique can be easily observed even at a high current density whereas the DC plated film become more and more non-uniform and the grain size increases significantly with the deposition current.

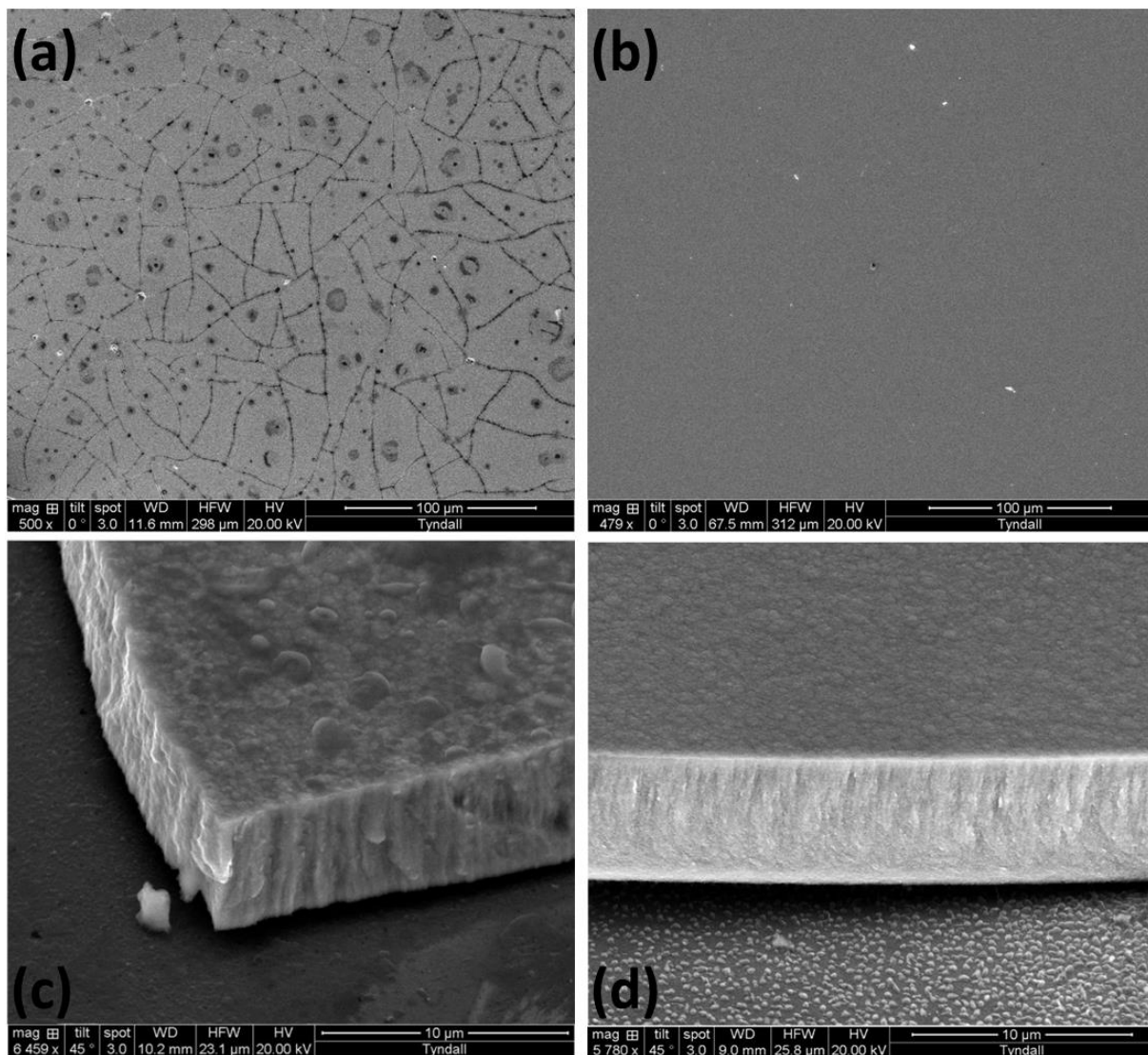


Figure 3. Surface morphology of the films deposited at 20 mA/cm² density (a) DC (b) PRP. The cross-section image of the films deposited at 100 mA/cm² density (c) DC (d) PRP.

As shown in Fig. 4, the Co percentage increases significantly (over 90%) along with further increase of current in both the deposition processes. As Co is soft magnetic in nature, the consequently developed films also lose their hard magnetic nature. Therefore, the above mentioned parameters are identified as the optimized deposition conditions.

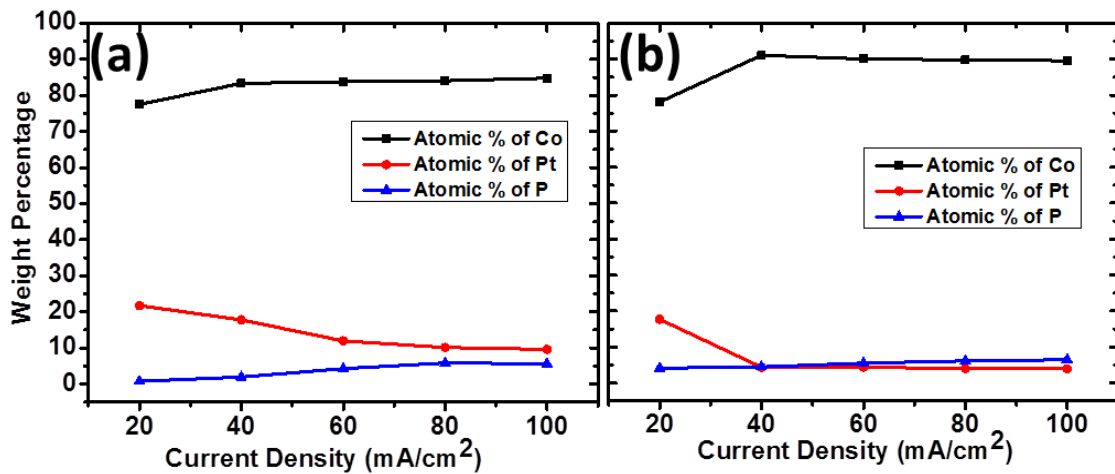


Figure 4. Effect of deposition current density on the alloy composition: (a) DC plated film (b) PRP plated film.

The PRP method improves the magnetic properties significantly too as compared in Fig 5. The perpendicular and parallel coercivities of the DC plated film are 515 Oe and 300 Oe respectively whereas the same values for the PRP deposited film are 3345 Oe and 1904 Oe. This huge improvement in the magnetic property can be attributed to the structural uniformity of the PRP deposited film. The squareness factor ($S=M_R/M_S$) of the PRP deposited film in perpendicular and parallel directions are 0.3 and 0.42 respectively. Corresponding values for the DC plated films are significantly low too. However, further improvements in the squareness and remanence properties of the developed films will be needed to increase the energy product which is essential for hard magnetic applications. Further study will also include development of thick films of CoPtP with preserved magnetic properties for MEMS electromagnetic energy harvesting applications.

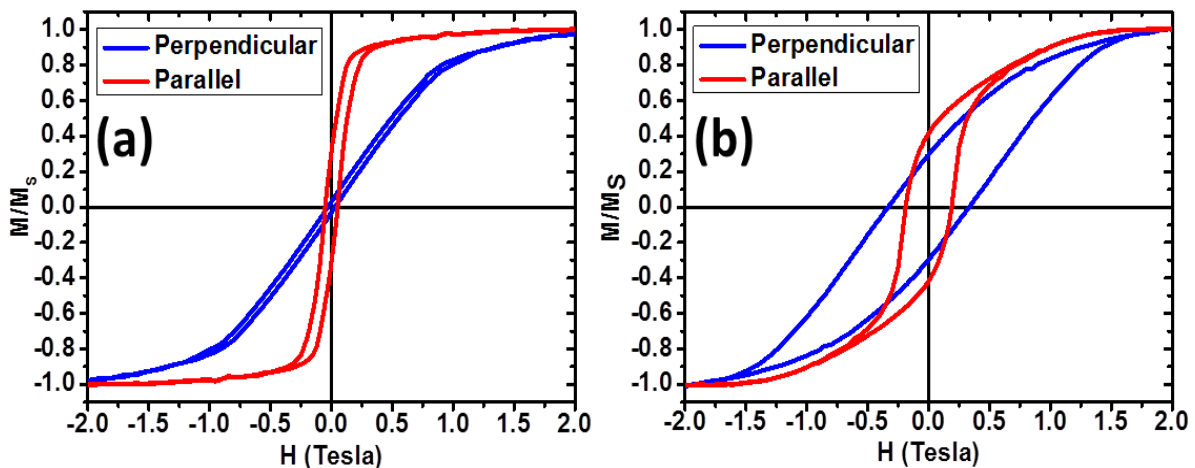


Figure 5. Magnetic hysteresis loop measurement of the deposited films at room temperature: (a) DC plated film (b) PRP plated film..

4. Conclusion

In this work, we report a new method of electrodeposition compared to the conventional DC plating, involving a combination of forward and reverse pulses for optimized deposition of Co rich CoPtP hard magnetic material. This results in significant improvements in the microstructure of the developed films as the PRP deposited films are smooth, stress free and uniform. Such improvements in the structural properties are reflected in the hard magnetic properties of the material as well. The intrinsic

coercivities of the PRP deposited film are more than 6 times higher for both in-plane and out-of-plane measurement directions and the squareness of the hysteresis loops also improve due to the similar reasons. Further optimized and thick films of the developed CoPtP material will be used for complete integration of MEMS electromagnetic energy harvesting devices.

Acknowledgements

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