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Characterization of FePt film electrodeposited with a ferric electrolyte

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Abstract−The electrodeposition of FePt alloy film in a novel ferric electrolyte that could be an alternative electrolyte to the usual non-stable baths was investigated. The influence of the applied current density and electrolyte temperature on the composition of the alloy was studied. It was found that co-deposition of oxygen can be reduced by deposition at higher temperature of 65 °C than room temperature. The as-deposited film had a face-centered cubic (γ-Fe,Pt) structure, and after an additional annealing process, the structure was changed to a face-centered tetragonal structure. The as-deposited FePt film also shows good resistance to corrosion and its coercivity was about 0.1 T, which makes it suitable for use in applications compatible with silicon technology.

Key words: Alloys, Electromechanical Techniques, Magnetic Structures

INTRODUCTION

Recently, the electrodeposition of FePt and CoPt binary alloys has been extensively studied, due to their superior magnetic properties due to the high magnetocrystalline anisotropy of the face centered tetragonal (fct) $L1_0$ phase [1-5]. So far, all the electrolytes used in practical electrodeposition processes are acidic solutions of ferrous iron (II) salts. Thus, iron-platinum electrolytes can be broadly divided into those based on chloride [6,7] and those based on sulfate [1-5,8-11]. In these electrolytes, the presence of ferric iron (III) ions is undesirable, because it lowers the cathode efficiency and causes the deposited film to be brittle, stressed, and pitted [12]. Moreover, controlling the stability of these electrolytes in the presence of ferric ions is very difficult. It is known that Fe^{2+} ions are easily oxidized to Fe^{3+} ions at the anode during electroplating or by oxygen in air [13], which results in an increase in the quantity of ferric ions in the electrolyte. These Fe^{3+} ions are not stable and are inclined to be hydrolyzed, which leads to the precipitation of $Fe(OH)_3$. Therefore, it is necessary to avoid or minimize the production of Fe^{3+} in the electrolyte [14].

More recently, however, Barbosa et al. [15] showed the possibility of the deposition of Fe-Zn alloy from a ferric bath. In their electrolyte, ferric ions are complexed by sorbitol and can be reduced to metallic iron. In the electrodeposition of Fe-W alloy by Zakharov et al. [16], the reduction of metal ions occurs most likely from ferric ions, rather than from ferrous ions. This indicates that the FePt bath based on a ferric salt can be an alternative electrolyte to chloride or sulfate baths.

In this work, we report a study on fabrication and characterization of FePt films on a Cu plate by direct current electrodeposition with a novel stable ferric bath.

EXPERIMENTAL

FePt films were deposited on a polycrystalline Cu substrate from an amino-citrate-based aqueous bath containing 0.05 M of $FeC_6H_5O_7$ (unless otherwise mentioned), 10 mM Pt P-salt $[Pt(NO_2)_2(NH_3)_2]$, 0.1 M of ammonium citrate, and 0.1 M of glycine. The pH value of the electrolyte was adjusted to 2.5 by adding a small amount of CH_3COOH. Cyclic voltammetry (CV) was carried out on a platinum electrode to investigate the electrodeposition process. Before the investigation, the platinum plate (working electrode) was cleaned by cycling the potential between 0.2 V and 1.5 V for 10 minutes with a scanning rate of 20 mV/s in a solution of 0.1 M $HClO_4$. All of the CV curves were taken with a scan rate of 10 mV/s. To determine the influence of the bath temperature on the film properties, the deposition was carried out at room temperature and at 65 °C. For the deposition of the FePt films, a platinum plate with a size of 1 cm×5 cm was used as the counter electrode and an Ag/AgCl electrode filled with 1 M KCl served as the reference electrode. To prepare the working electrodes, 0.5 mm thick Cu foil was cut into 5 mm ×10 mm pieces. A Cu wire was soldered to the back side of the working electrode to insure the electrical contact, and the back side of the Cu plate and the wire was covered with varnish. Just before the electrodeposition, the working electrode was rinsed in 10 vol% H_2SO_4 solution in water to remove the oxide layer and then cleaned with de-ionized (DI) water. The annealing was performed in a mixture of 1.5% hydrogen in argon at a temperature of 700 °C for 30 min.

The chemical composition of the deposited thin films was measured by energy dispersive X-ray spectroscopy (EDS) performed in a scanning electron microscope (JEOL JSM-7000F) system. Scanning electron microscopy (SEM) was used for the investigation of the morphology. The structural properties were examined by X-ray diffractometry (XRD) (Bruker AXS with Cu - Kα, 40 kV, 40 mA). X-ray photoelectron spectroscopy (XPS) was also carried out to examine the chemical state of the FePt alloys. The magnetic proper-

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ties were measured by vibrating sample magnetometry (VSM).

RESULTS AND DISCUSSION

To prepare the electrolyte, all of the chemicals except for the platinum salt were dissolved in DI water. The obtained brown turbid solution was then heated to 65 °C while adding the Pt P-salt till it became yellow-green and transparent. The prepared electrolyte retained its color and transparency for a long period of time (up to a few months) and was used for the deposition of FePt alloy. No Pt electroless deposition or Pt decomposition occurred on the Cu electrode. In addition, there were no visible colloids in the electrolyte either, which indicates the good stability of the electrolyte.

The FePt films deposited over a wide range of current densities (j=0.5-50 mA/cm^2) exhibited a typical metallic luster, which demonstrates the good leveling performance of the electrolyte. The deposition process with a low current density leads to the formation of deep dark films, and with increasing current density, the film color changes to a bright metallic one. We believe that this is related to the variation of the platinum content in the FePt alloys or to the change of the film morphology. Typically, the films deposited from the heated electrolyte with small currents were darker than the ones deposited at room temperature. The typical film thickness was in the range of a few hundred nanometers and we were able to deposit film with thickness up to a few micrometers by increasing the deposition time. It is worth mentioning that there was no evidence of film corrosion even after a few months. Such a film can be a good candidate for metal layers in various magnetic MEMS/NEMS applications.

Fig. 1(a) presents the typical CV curves for the Pt electrode in the presence of Fe (solid line) and Pt (dashed line) ions in the solution. The CV curves for the electrolyte containing both Fe and Pt ions are also shown in Fig. 1(b). The onset of Pt deposition starts below 0.0 V, whereas the onset of the reduction of Fe ions is observed at a more positive voltage of about 0.25 V. It is believed that this corresponds to the reduction of Fe^{3+} to Fe^{2+} ions, which is more negative than the equilibrium potential of the Fe^{3+}/Fe^{2+} couple. The following two waved diffusion limited peaks can be seen at more negative potentials of around −0.0 V and −0.44 V, which are assigned to the reduction of ferric ions to ferrous ions and the deposition of iron metal, respectively. In the solution containing both Fe and Pt ions, the onset of deposition appears at a more positive potential, as shown in Fig. 1(b). There is also no evidence of an Fe^{2+}/Fe^{3+} oxidation peak at 0.2 V, which indicates that the platinum ions stabilize the iron in the electrolyte. As mentioned above, the deposition of Fe appears at a more negative potential than that of Pt, which implies that a higher Pt content in the FePt films is obtained with smaller current densities. The EDS data, presented in Fig. 2(a), confirm this conjecture. At low current densities, the films are platinum rich and the Pt content decreases with increasing cathodic current. For the FePt films obtained at higher current densities than 20 mA/cm^2, the Pt/Fe ratio reaches about 0.3. It can also be seen that increasing the electrolyte temperature leads to an increase in the Pt content at relatively small and moderate current densities. This indicates that equiatomic FePt alloy is more easily deposited at higher temperatures.

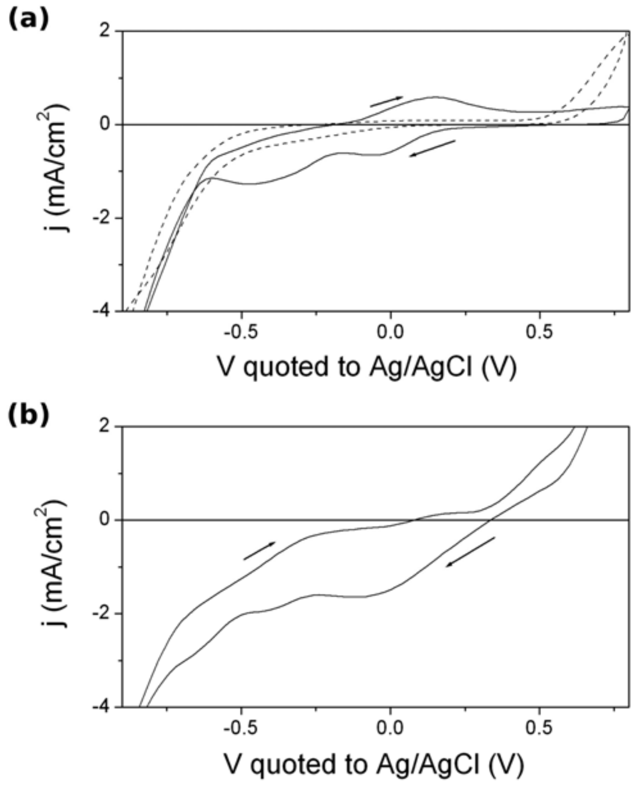

Fig. 1. Current-voltage curves for platinum electrode in the electrolytes consisting of (a) Fe salt (solid line) and Pt salt (dashed line) and (b) a mixture of Fe and Pt salts.

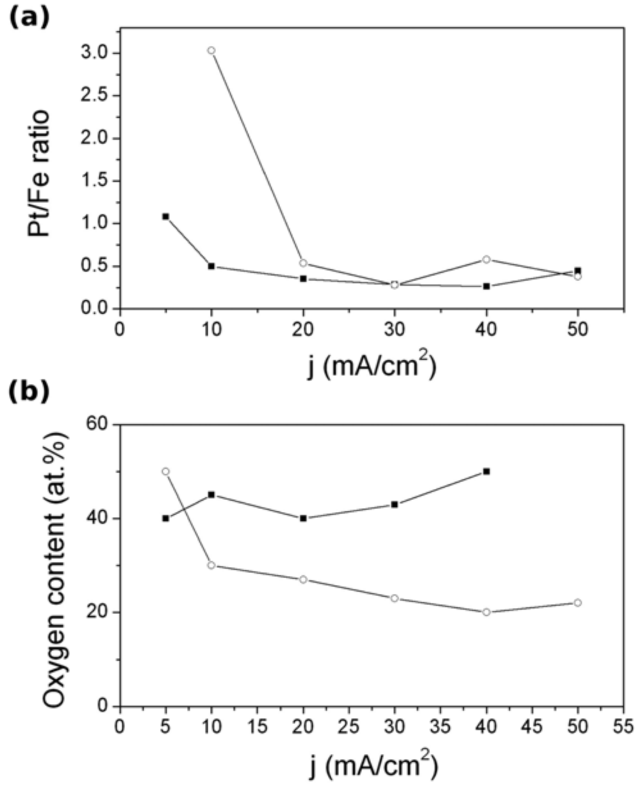

Fig. 2. Effect of current density on (a) Pt/Fe ratio and (b) oxygen content in FePt alloy films deposited at 65 °C (open circles) and room temperature (solid squares).

It has been reported that oxygen is usually incorporated during the electrodeposition of iron or iron alloys, which is undesirable [17]. It is believed that the mechanism of such pollution is as follows. The co-deposition of hydrogen, which accompanies the deposition of the main elements, leads to the change of the local pH value near the cathode electrode and leads to the formation of Fe-O-H species [17]. Assuming that $Fe(OH)_3$ compound is formed, each iron atom in the obtained film could be accompanied by three atoms of oxygen. In this case, the maximum amount of oxygen should be three times larger than that of iron [18]. Fig. 2(b) presents the oxygen content in the FePt film. Only in the case of current density j= 5 mA/cm^2 was the amount of oxygen in the film deposited at 65 °C larger than that in the film deposited at the room temperature. In the range of current densities of 10-50 mA/cm^2, it can be seen that the electrodeposition at room temperature results in a larger amount of oxygen. At 65 °C, moreover, the oxygen incorporation in the films reduces with increasing current density. A comparison of the oxygen content with that of Fe in the film reveals that the oxygen content is smaller than its maximum value, which indicates that a part of the iron ions were deposited in the metallic state. Indeed, the amount of oxygen in the FePt film obtained from deposition at 65 °C is similar to the literature data for the usual sulfate electrolyte [17].

Fig. 3 shows the plane-view scanning electron microscopy images of the films deposited at current densities of 10 mA/cm^2 (a and c) and 40 mA/cm^2 (b and d) at room temperature (a and b) and at T= 65 °C (c and d). The deposition time varies 12 min (b and d) and 48 min (a and c) to obtain the same charge amount of 28.8 °C/cm^2 during the electrodeposition. By analyzing the cross-sectional view, it was found that the thicknesses of the films shown in Fig. 3(a)-(d) are about 0.3 μm, 1 μm, 2 μm, and 1 μm, respectively. With increasing electrolyte temperature, the deposition rate increases in the case of a low current density. On the other hand, at a high current density, the deposition temperature does not have much influence on the deposition rate. The films deposited at room temperature are smoother and consist of smaller grains. Electrodeposition with a low current density results in a less brittle, but not uniform film. With increasing cathodic current, the film deposition becomes more uniform, but the film obtained is more brittle. When electrodeposition was carried out at 65 °C, a spongy and powdery structure was obtained at small current densities which changes to a smoother and more uniform morphology at moderate and higher currents. The powdery structure obtained at a low current density of 10 mA/cm^2 at 65 °C has a dark color, which is possibly due to the large amount of co-deposited carbon and oxygen. Thus, the variation of both temperature and current density results in changes in the film morphology and the deposition rate. Comparing Fig. 3(b) and 3(d) reveals that the film obtained at 40 mA/cm^2 and 65 °C shows relatively better morphology in terms of absence of cracks. As mentioned above, the film obtained at this condition contains less amount of oxygen in the film.

It is known that the hard magnetic properties of FePt alloy are associated with the presence of the (fct) structure. To examine the formation of such a phase, an XRD study was performed for the as-deposited and annealed samples. Fig. 4 shows the XRD patterns of the $Fe_{35}Pt_{65}$ and $Fe_{63}Pt_{37}$ films obtained by electrodeposition at 65 °C and a current density of 40 mA/cm^2, when the concentrations of Fe ions were 0.05 M and 0.1 M, respectively. The as-deposited films can be indexed as a (γ-Fe,Pt) (fcc) structure, due to the presence of the (fcc)(111) peak in the XRD pattern. The disappearance of the (fcc)(111) peak and appearance of the (fct)(111) and (fct)(200) peaks indicate that the (fcc) phase was transformed into the (fct) phase after annealing. It should be noted that the positions of these peaks are slightly shifted to higher diffraction angles, which may be related to the effect of the Cu substrate during annealing.

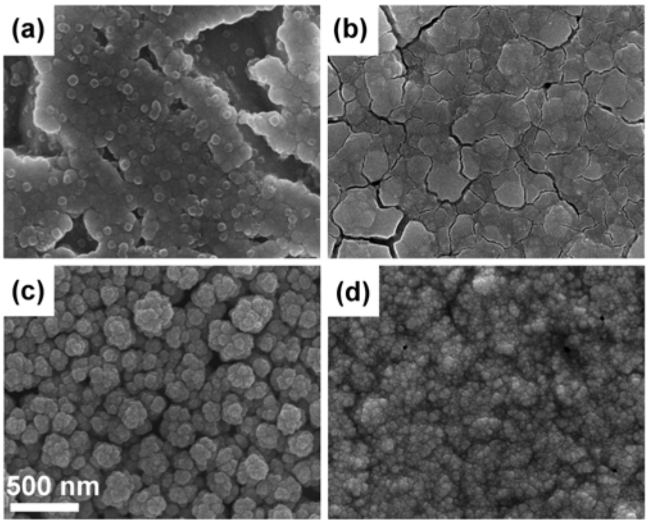

Fig. 3. FE-SEM images of surface morphologies of FePt films deposited with the conditions of (a) 10 mA/cm^2 at room temperature, (b) 40 mA/cm^2 at room temperature, (c) 10 mA/cm^2 at 65 °C, and (d) 40 mA/cm^2 at 65 °C.

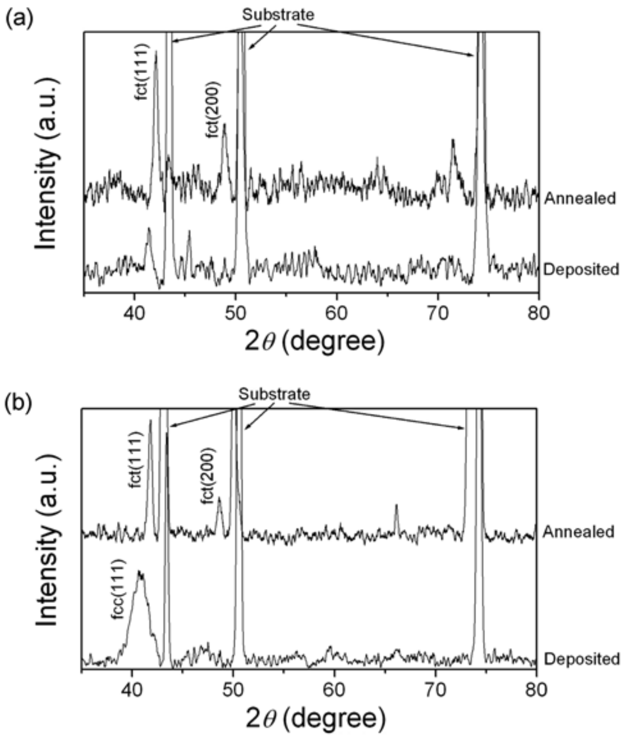

Fig. 4. X-ray diffraction patterns of (a) $Fe_{35}Pt_{65}$ and (b) $Fe_{63}Pt_{37}$ films deposited at 40 mA/cm^2 and 65 °C with concentrations of Fe salt of 0.05 M and 0.1 M, respectively.

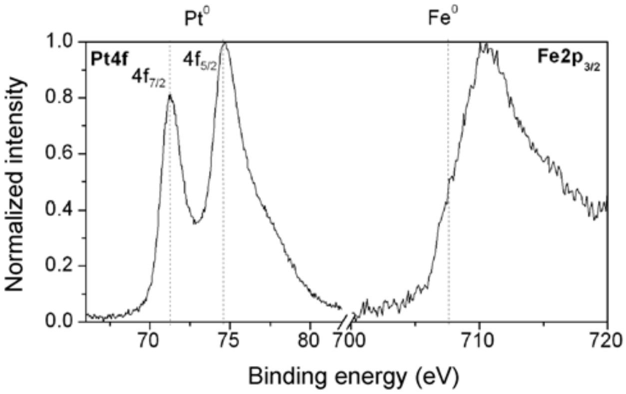

Fig. 5. XPS spectrum of the FePt alloy deposited at 40 mA/cm^2 and 65 °C.

To examine the chemical state of the FePt film, X-ray photoelectron spectroscopy was also carried out. The XPS spectra of the FePt film deposited at 65 °C and 40 mA/cm^2 in the range of Fe 2p and Pt 4f are shown in Fig. 5. The XPS peaks of Pt show the presence of only metallic platinum in the film, while the superposition of the signals from the analyzed film and the copper substrate results in a relatively high intensity of Pt $4f_{5/2}$. On the other hand, the iron is mostly present in the iron oxide and iron hydroxides states. The amount of metallic iron is relatively small.

The magnetic measurements showed that the as-deposited Fe rich films exhibit a coercivity of up to 0.1 T in the direction parallel to the plane and up to 0.07 T in a perpendicular field. However, the films with a high Pt content do not show reasonable magnetic properties. As mentioned above, the near equiatomic FePt films had to be annealed to form ordered (fct) phase and possess hard magnetic properties. Hence, the magnetic properties of the samples after annealing were not changed, which indicates the absence of magnetically hard phases.

CONCLUSION

FePt alloy was electrodeposited with a novel stable amino-citrate-based aqueous bath. The composition of the films was adjusted by controlling the current density. The amount of co-deposited oxygen was analyzed. It was found that the oxygen content in the electrodeposited films is similar to that in the films obtained from the known sulfate electrolytes. The co-deposition of oxygen could be reduced by conducting the electrodeposition at higher temperatures. The crystallographic structure of the as-deposited films consisted of a face-centered cubic (γ-Fe,Pt) phase that changed to face-centered tetragonal after annealing. The EDS results showed that a small amount of oxygen was incorporated into the film obtained by electrodeposition at high temperature, and the XPS analysis indicated that iron was present mostly in the form of oxides or hydroxides. Since even the un-annealed films showed moderate coercivity values, this FePt film can be a good candidate for magnetic applications compatible with silicon technology where annealing is unacceptable.

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