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Stress in electrodeposited CoFe alloy films

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CoFe alloys with 50–70% Fe have the highest magnetic moment of 2.4 T. There have been numerous research and development studies dedicated to achieving 2.4 T soft magnetic films by electrodepositing CoFe and CoFeNi alloys. The high tensile stress of the electrodeposited high moment films is one of the key causes slowing down the implementation of CoFe alloys. There have been few reported studies on the structure and stress evolution during the deposition of CoFe film either by vacuum processes or solution processes. This work reports on the preliminary finding related to the tensile stress in electrodeposited CoFe films as a function of grain size, alloy composition, and other deposition parameters. The residual tensile stress was found to increase with decreasing grain size in the film, which was accompanied by the increase of iron content in the films. Pulse plating study demonstrated to have little effect on film stress. Solution temperature was found to be highly effective in reducing tensile stress in the film, which is speculated to be attributed to the increased grain size from elevated deposition temperatures.

1. Introduction

CoFe alloys with 50–70% Fe are among the highest moment (2.4 T) soft magnetic materials [1]. Bulk CoFe alloys are used in aircraft turbo engines, due to its high magnetic moment, and high curie temperature of 1000 °C [2,3]. Electrodeposition of thin films has been widely used in microelectronics, hard disk drives, MEMS (microelectromechanical system), and also protective coatings. The unique capability of low cost, high throughput, and the versatility in creating various structures by electrodeposition has propelled breakthroughs and advancements in various applications over the years. Electrodeposited soft magnetic films have been widely used in hard disk applications. In particular, significant progress has been made during the past decades in the use of electrodeposited alloys with high magnetic moment for hard disk write heads [4,5]. The pole tip material in hard disk writing heads has evolved from permalloy (Ni79Fe19) of 1.0 T used in early generations of hard disk heads, to CoFe and CoFeNi alloys with 2.4 T magnetic moment [4,5].

There have been numerous research and development studies dedicated to electrodepositing 2.4 T CoFe and CoFeNi magnetic films [5–7]. The difficulty in making crack-free films in thickness over 2–4 μm has been one of the key challenges for the implementation [5–12]. The other challenge was their poor corrosion resistance. There have been very few reported studies on the stress of the deposited CoFe film either by vacuum processes or solution processes. This study reports on the preliminary findings related to the tensile stress in electrodeposited films as a function of grain size, alloy composition, and deposition parameters. The residual tensile stress was found to increase with the decreasing of the grain size of the films, which is closely related to the composition of the alloy. Pulse plating demonstrated to have little effect on film stress. Solution temperature was found to be highly effective in reducing tensile stress in the film, which is generally believed to be attributed to increased grain size at elevated deposition temperatures.

2. Electrodeposition of high moment soft magnetic materials

The instability of Fe^{2+} in aqueous solution is well known. In air ambient at room temperature, solvated ferrous (Fe^{2+}) ions are easily oxidized by O_2 to form ferric (Fe^{3+}) ions as follows:

$$4Fe^{2+}+O_2+2H_2O=4Fe^{3+}+4OH^- \qquad (1)$$

According to the hydrolysis study by Baes and Mesmer [13], the solubility of ferric hydroxides decrease rapidly with increasing pH, being approximately 100 times larger at pH 3 than at pH 4. Ferric hydroxide easily precipitates due to its low solubility in solution. The precipitation of hydroxides in a plating solution during electrodeposition leads to hydroxide incorporation in the

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deposited films. The hydroxide incorporation is known to embrittle the films, and at the same time it degrades the magnetic moment of the deposited film. It is crucial to control hydroxide incorporation to make high quality Fe films and Fe-containing alloys. The high moment CoFe alloys with 50–70% Fe are usually deposited from a solution containing significantly high Fe^{2+} concentrations. It is critical to stabilize Fe^{2+} ions in the plating bath and hence to minimize hydroxide inclusion in the film. Many methods have been reported to improve the film quality in depositing high magnetic moment CoFe and CoFeNi alloys. Below is a summary of methods reported in the literature:

- Keep the solution in inert atmosphere such as N_2. This is implemented in most laboratory experiments and in commercial production environments.
- Filtration of solution through iron powder due to the reaction is as follows [7]:

$$Fe+2Fe^{3+}=3Fe^{2+} \tag{2}$$

- Add reducing agents, such as ascorbic acid [8].
- Separate anode and cathode chambers to prevent oxidized species on the anode from reaching cathode deposition surface [6].
- Use of $Fe(NH_4)_2(SO_4)_2$ salt instead of $FeSO_4$ in plating bath was found to be more stable in solution. However, these baths resulted in incorporation of N-containing impurities in the films and lead to lower magnetic moment of the deposited films [14]. Our study found $Co_{35}Fe_{65}$ films deposited from $Fe(NH_4)_2(SO_4)_2$ based solution only had a saturation magnetic moment of 2.2 T instead of the expected 2.4 T for the corresponding pure alloy.
- Use acetic acid as a more effective pH buffer than boric acid as reported by Cooper et al.[5].
- Myung and Nobe [15] used $CaCl_2$ based bath at very low solution $pH=0.3-0.4$. Usually at such low pH solutions, current efficiency is very low. But the $CaCl_2$ system as reported has achieved current efficiency comparable to most conventional baths operating at pH 2–4.
- Add vanadium salts ($VOSO_4$) to improve the maximum platable CoFe thickness without film cracking [8].
- Use new additive sodium benzenesulfinate as disclosed in US patent 6,855,240B2 and discussed by Cooper et al. to achieve 2.4 T CoFe alloys with thickness over 2 μm [5,16].

This preliminary study will report on stress in the electrodeposited CoFe alloys using the bath reported by Cooper et al. and disclosed in US patent 6,855,240B2 [5,16].

3. Tensile stress in electrodeposited CoFe alloys

3.1. Experimental

Electrodeposition was carried out using a three electrode IBM paddle cell setup [17], with one counter electrode made of cobalt sheet, one working electrode made of $4\times4\,cm^2$ square glass substrates seeded with 10 nm Ta/50 nm Rh, and a thief electrode made of stainless steel surrounding the working electrode with independent current control. The main purpose of the thief electrode is to ensure a uniform current density distribution over the working electrode surface. The current ratio of the working electrode versus the thief electrode was optimized to achieve the best thickness uniformity across the working electrode and was kept constant for the paddle cell. The solution temperature was kept at 25 °C if not noted otherwise. The paddle frequency was 1 Hz, and a permanent magnetic field of 700 Gauss was applied parallel to one direction along the substrate plane during electrodeposition, which became the easy axis direction. The saturation magnetic moment was measured by a vibrating sampling magnetometry (VSM).

The CoFe electrodeposition bath was composed of x g/l $FeSO_4\cdot7H_2O$+18.23 g/l $CoSO_4\cdot7H_2O$+5.75 ml/l acetic acid+0.2 g/l sodium benzenesulfinate (SBS). The cobalt salt concentration was varied to obtain different alloy compositions. The pH was adjusted to be 3.0. The current density was kept at $10\,mA\,cm^{-2}$ on the working electrode if not specified otherwise. During pulse plating experiments, the pulsing of working electrode was synchronized with the thief electrode by using a common function generator.

The bowing of the glass substrates was measured before and after deposition using a profilometry scan along the two diagonals of the substrates on the backside of the glass. The thickness of the deposit was measured using an average of step heights measured by a profilometer after etching off a narrow stripe along the diagonal using aqua regia (3:1 volume ratio of $HCl:HNO_3$ solutions). Stress was calculated using the Stoney's equation [18]

$$\sigma=\frac{4ET^2Z}{3L^2t(1-\nu)} \tag{3}$$

σ is the stress, E is the young's module of the glass substrates (70 GPa), T is the thickness of the glass substrates (0.4 mm), Z is the change of camber of the bowing measured from profilometry, L is the profilometry scan length, t is the deposited CoFe film thickness was 2 μm for this study, ν is the poisson's ratio of the substrate (0.22).

The composition of the deposited films was measured with X-ray fluorescence (XRF) using wavelength dispersive spectroscopy. The grain sizes of samples were estimated from TEM images.

3.2. Stress vs. grain size and composition

High tensile stress has been a major issue for electrodepositing CoFe alloys with iron composition above 65%. Tensile stress up to 700–850 MPa has been reported by Cooper et al.[5]. The high tensile stress can lead to film cracking. Fig. 1 shows a picture of a cracked and delaminated film on glass substrate upon standing in ambient for a few months. The sample was deposited from the SBS-containing CoFe bath with a composition of $Co_{35}Fe_{65}$ and a thickness of 4 μm.

As reported by Cooper et al., the deposition stress of CoFe films increases with the increase of iron composition in the alloy. This is accompanied by decrease in grain size, as shown in Fig 9(b) and 9(e) in Ref. [5]. The paper showed that the higher the iron content, the smaller the grain size. The Fe incorporation seems result in refining grains during deposition. By plotting the stress as a function of the reverse of grain size as in Fig. 2, it can be seen that a very good linear fit to the data is obtained. Grain boundary coalescence is a well-recognized phenomenon responsible for generating tensile stress during film growth. The finer the grains, the higher the tensile stress in a film[19–22]. This qualitatively explains the stress increase in CoFe alloys accompanied by decreasing grain size when iron content increases.

Atomic force microscopy (AFM) images of three CoFe samples with different iron content are shown in Fig. 3. It showed that the surface morphology changed with the film composition. The higher content of Fe, the smaller the surface features. At the same time, the surface roughness also decreases with increasing iron content in the film.