Electrodeposition of low-stress high magnetic moment Fe-rich FeCoNi thin films

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Abstract

Low-stress high magnetic moment Fe-rich FeCoNi thin films were electrodeposited from acidic chloride baths to investigate the effects of the deposition temperature, solution pH and L-ascorbic acid on film morphology, crystal structure, magnetic properties and film stress. As the deposition temperatures were increased from 23 to 70 °C, the film stress in the FeCoNi films decreased from 260 to 28 MPa at pH 1.5 in the absence of L-ascorbic acid. The film stresses further decreased to approximately 0 MPa when solution pH was increased to 2.15. However, the plating baths became unstable at pH higher than 2.15 because of precipitate formation. On increasing the deposition temperature, the deposit Fe content in the FeCoNi thin films decreased from 83 to 72 atomic percent (at.%) and the Co content increased from 17 to 27 at.%.

In the case of the deposit Ni content, it slightly increased with increasing deposition temperature. From the XRD analysis, the change of the preferred planes from the bcc (1 1 0) to bcc (2 0 0) with increasing deposition temperatures was observed. It is believed that the changes in the grain size and the incorporation of impurities during electrodeposition influenced the stress of the FeCoNi films. The presence of L-ascorbic acid enhanced the stability of the baths at high pH meanwhile reducing current efficiencies. With increasing deposit Ni content, magnetic saturation (B_s) and parallel squareness slightly decreased and increased, respectively.

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1. Introduction

Recently, electrochemical processes (electrodeposition and electroless deposition) have been widely used in electronic industries [1–8] including; computer read/write heads [2,3], microelectromechanical systems (MEMS) [4–6], ultra-large-scale integration (ULSI) devices [7,8], and electronic circuit packaging [9]. The electrochemical processes have many advantages over vacuum processes because of near room temperature operation, easy scale-up and maintenance, low-cost, relatively rapid deposition rate, the capability of handling complex geometries, and the ability to “tailor” deposit structure and properties [10]. Magnetic materials have recently been incorporated into MEMS devices such as sensors, microactuators, micromotors, and frictionless microgears because magnetically actuated MEMS are more durable for force applications and in severe environments compared to electrostatic-actuated MEMS [11,12]. In general, electroless deposits are less porous, more uniform and more corrosion resistant than electrodeposits [10]. However, they are more expensive and less stable, and have slower deposition rates than that of the electrodeposition process [13]. Therefore, electrodeposition process may be more suitable for integration of magnetic materials into computer read/write heads and MEMS devices.

In order to incorporate magnetic materials using electrodeposition process into devices, magnetic materials must have good adhesion, low-stress, high corrosion resistance and be thermally stable with excellent magnetic properties. In addi-
tion, film stress plays an important role in the incorporation of magnetic materials into MEMS devices. High stress in magnetic thin films may result in deformation or malfunction of MEMS devices because of detachment of thin films from the substrate (e.g., silicon (Si) substrate).

Few studies [14–18] have been carried out to investigate the stress of the electrodeposited CoNiFe thin films. Most of the works were focused on Co-rich alloys (Co contents >50 at.%), which have high magnetic saturation (\(B_S\) of 1.9–2.1 T) and low coercivity. Not only has little attention been given to the stress of the electrodeposited magnetic CoNiFe thin films, but also, only few studies were carried out to reveal the exact mechanisms leading to the origin of the film stress. Saito et al. [14] examined the temperature dependence on the internal stress in Co-rich alloys (with 60–70 at.% Co, 8–15 at.% Ni and 15–27 at.% Fe) electrodeposited at 5 and 15 mA/cm². They observed high stress CoNiFe thin films from saccharin-free baths. The stresses of the CoNiFe films electrodeposited at 5 and 15 mA/cm² in saccharin-free baths decreased from ~800 to ~500 MPa with increasing anodizing temperatures up to 250 °C. They observed a bending point in the stress curves of the CoNiFe films and attributed the bending point to the recrystallization process of the films. Rasmussen et al. [15] measured the stresses of the pulse-reverse electrodeposited Co-rich alloys (with ~53 at.% Co, 36–24 at.% Ni, 10–20 at.% Fe) with deposition temperature of 40 °C and solution pH varying from 3.9 to 4.2. The CoNiFe films exhibited the stress ranges of 69–101 MPa and the film stresses increased with increasing current density of (is it or/off) the deposit Fe contents in the plating baths. Tavakovic et al. [16] investigated the stress changes in Co-rich alloys (with 62–67 at.% Co, 13–16 at.% Ni, 18–22 at.% Fe) electrodeposited on two different substrates (Pd_{50}Ni_{50} and Ni_{60}Fe_{40}) in mild-acidic chloride baths, with additives. The stresses of the CoNiFe films electrodeposited on Pd_{50}Ni_{50} substrates decreased with increasing thickness of the CoNiFe films. On the other hand, the stresses of the CoNiFe films electrodeposited on Ni_{60}Fe_{40} substrates showed a transition from compressive to tensile stress with increasing thickness of the CoNiFe films. It was also observed that the stresses of the CoNiFe films electrodeposited on Ni_{60}Fe_{40} substrates decreased with increasing saccharin concentration in plating baths. They suggested that lattice mismatch between the electrodeposited CoNiFe alloys and the sputtered Pd_{50}Ni_{50} or Ni_{60}Fe_{40} seed layers may result in the stress changes of the films, in the presence of additives. Liu et al. [17] reported that current density strongly affected the deposit contents of the CoNiFe films electrodeposited from sulfate baths. As the current density increased from 5 to 50 mA/cm², the deposited Fe, Co and Ni contents changed from 41 to 9, 49 to 30, and 10 to 61 at.% respectively. The CoNiFe films exhibited tensile stresses and decreased from 800 to 190 MPa with increasing current density from 5 to 20 mA/cm². The stresses increased up to 300 MPa at above 25 mA/cm² and then leveled off at above 35 mA/cm².

Although numerous studies had been carried out to investigate the ternary CoNiFe thin films [18–21], there are a few studies exploring the Fe-rich ternary alloys. Osuka [22] and Osuka et al. [23] suggested a Co-rich ternary alloy \([\text{Co}_{65}\text{Ni}_{12}\text{Fe}_{23} \text{(at.%)}}]\) electrodeposited from mild acidic sulfamate baths as a possible candidate for merged-GMR head with high-density magnetic recording. It was pointed out that the saturation of the write head core and the thermal relaxation of recording medium might become serious problems in ultra-high density recording for the future. They observed that the Co$_{65}$Ni$_{12}$Fe$_{23}$ films exhibited high magnetic saturation \((B_S \sim 2.1 \text{T})\), low coercivity \((H_C \sim 1.2 \text{Oe})\), low magnetorestriction \((\lambda_A \sim 1.8 \times 10^{-5})\) and low electrical resistivity \((23 \mu\Omega \cdot \text{cm})\). They suggested that the high \(B_S\) and low \(H_C\) in the Co$_{65}$Ni$_{12}$Fe$_{23}$ film might be attributed to the very fine grain sizes (10–15 nm) because of the mixed phases of the bcc and fcc microstructures, and inclusion of small amount of sulfur. In a consequent study, Ohashi et al. [24] suggested that Co$_{65}$Ni$_{12}$Fe$_{23}$ films with mixed body-centered cubic (bcc) and face-centered cubic (fcc) phases exhibit higher magnetic saturation \((B_S \sim 2.0–2.1 \text{T})\), improved corrosion resistance and good thermal stability compared to the other Co$_{60}$Ni$_{33}$Fe$_{7}$ films with bcc phases. Zhuang and Podlaha [25–27] carried out an experimental kinetic study on the influence of electrolyte concentration at steady state, and suggested a mathematical model to describe CoNiFe ternary alloy deposition. The Ni deposition in the ternary system appeared to be inhibited and the Fe deposition was enhanced; both catalytic and inhibiting effects were observed in Co deposition. Liu et al. [28] reported that the Co$_{65}$Fe$_{25}$Ni$_{20}$ alloy films electrodeposited from sulfate baths without additives have a saturation magnetization \((M_S \sim 2 \text{T})\), coercivity \((H_C \sim 1 \text{Oe})\), resistivity \((\rho \sim 22 \mu\Omega \cdot \text{cm})\) and saturation magnetization \((\lambda_A \sim 10^{-5})\). They reported that the Co$_{65}$Fe$_{25}$Ni$_{20}$ alloy films with the best soft magnetic properties consisted of the mixed phases with the bcc and fcc microstructures. Tavakovic et al. [29] thoroughly examined the effects of organic additives such as thiourea, sodium lauryl sulfate, DPS and saccharin on current efficiencies, alloy compositions, magnetic properties, and stresses in the Co-rich CoNiFe films. A strong influence of different additives in plating baths on the above properties was observed. They obtained the highest values of \(B_S \sim 1.2 \text{T}\) in the baths with DPS, \(B_S \sim 1.7 \text{T}\) in the baths with TEAOTAc and saccharin, \(M_S \sim 1.75 \text{T}\) in the baths with TEATPS and saccharin, \(B_S \sim 1.8 \text{T}\) in the baths with sodium lauryl sulfate, and \(M_S \sim 1.86 \text{T}\) in the baths with sodium lauryl sulfate and saccharin. The Fe-rich FeCo alloys (i.e., Fe content of 50–70%) possess the highest known room-temperature magnetic saturation \((B_S \sim 2.4–2.45 \text{T})\). Therefore, electrodeposition of high quality FeCo thin films are considered to be the ultimate objective for making new high magnetic moment soft magnetic thin films for data storage industry [30]. Compared to NiFe alloys and Co-rich CoNiFe alloys, limited works have been reported because of the difficulty in electrodepositing films with good properties [30]. Previously, we
demonstrated electrodeposition of high magnetic moment low-stress FeCo thin films ($B_S$ of 2.3 T) from acidic chloride baths [31]. Fe-rich FeCoNi thin films with small addition of Ni are important because it may enhance the corrosion resistance of the film without sacrificing magnetic saturation. In this study, we systematically investigated changes in the film stress, microstructure, and magnetic properties of the Fe-rich FeCoNi thin films as a function of deposition temperature, solution pH, and l-ascorbic acid concentration in the plating baths.

2. Experimental

The FeCoNi thin film alloys were electrodeposited from acidic chloride baths. The solution compositions for chloride baths are listed in Table 1. CaCl$_2$ was added to enhance the current efficiency and l-ascorbic acid to minimize precipitate formation. Solutions were exposed to air and the solution pH was adjusted with KOH or HCl. Electrodeposition of the films was conducted galvanostatically at 5 mA/cm$^2$, pH 0.34–5.5, total charge of 300 C (on deposit area of 7.74 cm$^2$) and from room temperature to $\sim$90$^\circ$C without stirring the solution. The cathode current efficiency was calculated from differential mass measurements (Mettler Toledo XS105 with resolution of 10$^{-9}$g). The effects of the deposition temperature on the stress, the film composition, the current efficiency, the surface morphology, and the microstructure of the Fe-rich FeCoNi films were examined by varying deposition temperatures from 23 to 90$^\circ$C. The effects of solution pH were also studied by varying solution pH from 0.3 to 2.15 in the absence of l-ascorbic acid. In the presence of l-ascorbic acid, solution pH was varied from 0.3 to 5.0. The FeCoNi films were electrodeposited on Cu substrates (PN 1194, Specialty Testing & Development Co.) to measure film stresses; iron sheets were used as soluble anodes. The deposited stress of FeCoNi thin films was measured with a deposit stress analyzer (Model 683, Specialty Testing & Development Co.). The surface morphology and the deposited Fe, Co and Ni contents were examined using SEM (Model JSM-6300, JEOL Ltd.) and EDS (Model ISIS, Oxford Instruments), respectively. An X-ray diffractometer (XRD) (Model D/MAX 2500H, RIKAKU) with Cu K$_\alpha$ radiation was used for the identification of the phases and for the measurement of grain size in the electrodeposits. The conditions of the XRD were a scanning range (20–100$^\circ$) with 0.03$^\circ$ increments and a 1-s dwell time.

3. Results and discussion

The dependence of film compositions on the deposition temperature in the FeCoNi thin film alloys is shown in Fig. 1. With increasing the deposition temperature in plating baths from 23 to 70$^\circ$C, the deposit Fe contents decreased from 83 to 73 at.%; the deposit Co contents and the deposit Ni contents increased from 17 to 27 and 0.1 to 0.8 at.%, respectively. Current efficiencies slightly increased with increasing deposition temperature as shown in Fig. 2. Tabakovic et al. [29] reported that the current efficiencies of the CoNiFe films electrodeposited from mild-acidic sulfate baths containing thiourea increased from $\sim$45 to $\sim$90% with increasing FeSO$_4$ concentration in plating baths up to 0.06 M. Current efficiency decreased from $\sim$80 to $\sim$50% with increasing current density from 5 to 30 mA/cm$^2$. They suggested that the decrease of current efficiency at higher current densities is attributed to the partial current density for hydrogen evolution, which becomes more important at higher current densities. In their system, current efficiencies become higher at higher Fe concentration in the plating baths and low current densities (<10 mA/cm$^2$). In this study, the high current efficiencies (>80%) observed at high Fe concentration and low current density (5 mA/cm$^2$) observed in the absence of other additives (e.g. l-ascorbic acid) are in agreement with Tabakovic et al.’s results. Myung and Nobe [32] also observed a high current efficiency ($\sim$82%) in the CoFe alloys electrodeposited from mixed chloride and sulfate baths (Watts (Model DMAX 2500H, RIKAKU) with Cu K$_\alpha$ radiation was used for the identification of the phases and for the measurement of grain size in the electrodeposits. The conditions of the XRD were a scanning range (20–100$^\circ$) with 0.03$^\circ$ increments and a 1-s dwell time.)
They reported that the current efficiency was independent of Fe\textsuperscript{2+} concentrations in the plating baths. Because the Ni contents in the FeCoNi thin film alloys in this study are relatively small (<1 at.%) compared to the Fe and Co contents, it is reasonable that the current efficiencies of the FeCoNi thin film alloys should be high like the CoFe alloys.

As deposit temperature increases from 23 to 30 °C, the surface morphology of FeCoNi electrodeposits changed from an acicular to polyhedral crystallites. The increases of the sizes of polyhedral crystallites were observed with increasing deposit temperature further, up to 70 °C. These observations are similar to binary FeCo films [31].

Fig. 4 shows the dependence of the stresses in the FeCoNi films. The stresses decreased from 260 to 28 MPa, on increasing the deposition temperatures from 23 to 70 °C. The FeCoNi thin films electrodeposited at 23 °C consisted of bcc structures [the (1 1 0) and (2 1 1) planes] with the pre-

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Fig. 3. The effects of deposit temperatures on the surface morphology of the ternary FeCoNi films (a) 23 °C, (b) 30 °C, (c) 45 °C, and (d) 70 °C (CD = 5 mA/cm\(^2\), pH 0.3).
ferred (1 1 0) planes as shown in Fig. 5. Myung and Nobe [32] have observed that the microstructures in the binary CoFe alloys electrodeposited from mixed sulfate and chloride baths (Watts type) changed from fcc (at the Fe contents <16 wt.%) to bcc (at the Fe contents >16 wt.%), on increasing the deposit Fe contents. Because the chemical composition of the FeCoNi thin film alloys in this study were measured to be 72–84 at.% Fe, 18–27 at.% Co and 0.1–1 at.% Ni, the bcc microstructures at the high Fe contents in this study appear to be in good agreement with the above reported observation [32]. According to Osaka’s results [22], in the electrodeposited CoNiFe alloys, the bcc microstructures are obtained as the deposit Fe contents were increased.

As the deposition temperatures increased up to 45 °C, the intensity of the preferred (1 1 0) planes increased as well; the bcc (2 1 1) planes always existed and were independent of the deposition temperatures. However, the FeCoNi films electrodeposited at 45, 55 and 70 °C showed the changes of the preferred planes from the bcc (1 1 0) to bcc (2 0 0).

The dependence of average grain sizes on the deposition temperatures are shown in Fig. 6. The average grain sizes were calculated from the broadening of each peak in the X-ray diffraction patterns using the Scherrer formula from the bcc (1 1 0), (2 0 0) and (2 1 1) planes. The average grain sizes in the FeCoNi films increased from 48 to 64 nm, on increasing the deposit temperatures from 45 to 70 °C. The inset shows the dependence of stresses on the average grain sizes of the FeCoNi films. As the average grain sizes increased, the deposit stresses decreased. Therefore it is believed that the stress changes in the FeCoNi films on varying the deposition temperatures may mainly attribute from the changes of the average grain sizes. The detailed mechanisms of stress changes by varying the deposit temperature have not been revealed yet.

The dependence of film composition in the FeCoNi thin film alloys on solution pH is shown in Fig. 7. The deposit Fe, Co and Ni contents remained fairly constant and are independent of solution pH. Fig. 8 shows the dependence of the stresses on the solution pH in the FeCoNi films electrodeposited from chloride baths. The stresses were almost constant in the range from 37 MPa (pH 0.3) to 28 MPa (pH 1.5), and slightly decreased to 0 MPa at pH 2.15. Inset figure presents the relationship between stress and average grain size at different pH. In this case, lower stresses were achieved with smaller grain size, which is opposite to the results seen with stress–grain size relationship at different temperature. It strongly implies that there is another factor affecting the film stress. According to Weil [33], not only crystal defects like grain boundary, but incorporations of foreign materials can affect the stress. As increasing the pH, the possibility of incorporation of hydroxide or oxide is increased, which could compensate stress of FeCoNi thin films. The FeCoNi films electrodeposited at pH 0.3 showed the highly preferred
Fig. 8. Dependence of film stresses in the ternary FeCoNi films on solution pH in the absence of 0.05 M L-ascorbic acid (CD=5 mA/cm², temperature = 70 °C).

Fig. 9. XRD patterns of the ternary FeCoNi films as a function of solution pH (CD=5 mA/cm², temperature = 70 °C). S represents the X-ray diffraction peaks from Cu–Be substrate.

bcc (200) planes as shown in Fig. 9. As the solution pH was increased from 0.3 to 2.15, the dominant phases changed from the highly preferred bcc (200) planes to the bcc (110), (200) and (211) planes. The FeCoNi films with zero stress could be obtained at the deposition temperature 70 °C, pH 2.15 and 10 mA/cm².

Fig. 9 shows the dependence of surface morphology on solution pH of the electroplating baths. All the FeCoNi films electrodeposited from pH 0.3 to 2.15 showed the polyhedral crystallites. The sizes of the polyhedral crystallites (no grain sizes) were measured to be about 4.8 μm for solution pH 0.3–1.5, measured using a point counting method [32]. However, the FeCoNi thin films electrodeposited at pH 2.15 exhibited the finer crystallite sizes of about 1.8 μm.

Fig. 10 shows the dependence of magnetic saturation for Fe-rich FeCoNi films on deposited Ni content. Magnetic saturation decreased with increased deposited Ni content as expected from bulk alloys. However, when deposit Ni content is less than 2%, magnetic saturation was independent of deposit Ni content. Fig. 11b and c shows the parallel coercivity and parallel squareness as a function of deposit Ni content, respectively. Coercivity was ranged from 30 to 40 Oe (Fig. 11b) and squareness increased slightly with increased deposit Ni content (Fig. 11c).

Fig. 10. The effects of solution pH on surface morphology in the ternary FeCoNi films (a) pH 0.3, (b) pH 1.0, (c) pH 1.5, and (d) pH 2.15 (CD=5 mA/cm², temperature = 70 °C).
Fig. 11. Dependence of magnetic properties of FeCoNi electrodeposits on deposit Ni content (CD = 5 mA/cm², temperature = 70°C, pH 0.3).

Figs. 12 and 13, shows the dependence of the film stresses and the current efficiencies on solution pH with/without l-ascorbic acid in the plating baths. As the solution pH was increased up to 2.15 for baths without l-ascorbic acid and 5.0 for baths with l-ascorbic acid, the stresses of FeCoNi films with/without l-ascorbic acid decreased from ~40 to 0 MPa. In the presence of 0.05 M l-ascorbic acid, solution pH was able to adjust up to 5 without formation of precipitate. However, baths in the absence of 0.05 M l-ascorbic acid, solution pH was only raised up to 2.15 because of precipitate formation at higher pH. Low stresses (~0 MPa) of the FeCoNi films were obtained at solution pH 2.15 in l-ascorbic acid free baths and pH 5.0 in baths containing l-ascorbic acid. The plating baths without l-ascorbic acid were stable up to pH 2.15 and the operating pH range in the plating baths containing 0.05 M l-ascorbic acid was increased up to pH 5.5.

In the presence of 0.05 M l-ascorbic acid, the current efficiencies of the FeCoNi films electrodeposited is lesser than the current efficiencies of the FeCoNi films electrodeposited.
from the bath without L-ascorbic acid. This reduction of current efficiency is still unclear.

4. Conclusion

The low-stress high magnetic moments FeCoNi thin films were electrodeposited from acidic chloride baths. The stresses in the FeCoNi thin films decreased with increasing the electrodeposition temperature. From XRD analysis, it is suggested that the stress changes in the FeCoNi films may be a result of grain sizes. As the electrodeposition temperatures were increased, the grain sizes increased.

L-Ascorbic acid extended the life of solution baths and allows operation at higher pH range while maintaining low-stress film deposition to prevent precipitate formation.

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