Electroplating of Nanocrystalline CoFeNi Soft Magnetic Thin Films from a Stable Citrate-Based Bath

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CoFeNi alloys are some of the most studied soft magnetic materials because of their superior properties over FeNi alloys as write head core materials in hard-disk-drives. Electroplating processes have major significance in the fabrication of thin-film recording heads due to their advantages of simplicity, cost-effectiveness, and controllable patterning. Conventional low pH (2.5−3.0) baths suffer from problems such as poor stability, low current density efficiency, and voids in deposited films due to the electroplating of hydrogen. A new, stable citrate-based bath has been developed in this study. Citrate can effectively improve the stability of CoFeNi plating baths, and denser CoFeNi films can be plated out because of the higher bath pH (>5). The effects of bath composition and plating conditions on the electroplating of CoFeNi thin films have been studied. CoFeNi thin films with preferred composition, mixed fcc-bcc phases, and 10−20 nm grain sizes have been plated out from the new citrate-based bath.

Introduction

CoFeNi alloys are some of the most studied soft magnetic materials in recent decades because of their superior properties over FeNi alloys as write head core materials in hard-disk-drives.[1] Electrodeposited permalloy ($Ni_{80}Fe_{20}$) was introduced as the core material of thin film inductive heads by IBM in 1979.[2] With increasing storage density, the need for recording heads to write on high-coercivity media at high frequencies has raised new requirements for the write-head material that cannot be met by $Ni_{80}Fe_{20}$.[3] New soft magnetic materials with higher saturation flux density B_s such as electroplated CoFe alloys,[4−6] CoFeNi alloys,[7−34] CoFeCu alloys,[3,35−37] other CoFe-based alloys,[38−40] sputtered FeN films,[41,42] and other Fe-based alloys[43−45] have been developed.

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Table 1. Composition of Bath for Electroplating CoFeNi Alloys

chemical	concentration	chemical	concentration
$CoSO_4$	0.03−0.0875 M	H_3BO_3	0.4 M
$FeSO_4$	0.005−0.045 M	sodium laury sulfate	0.01 g/L
$NiSO_4$	0.2 M	NH_4Cl	0.28 M
		bath pH = 2.5−3.0	

Table 2. Composition of Citrate-Based Bath for Electroplating CoFeNi Thin Films

chemical	concentration	chemical	concentration
$CoSO_4$	0.08 M	H_3BO_3	0.4 M
$FeSO_4$	0.015 M	sodium lauryl sulfate	0.01 g/L
$NiSO_4$	0.3 M	ammonium citrate	0.206 M
		bath pH = 5.3 (natural)	

Electroplating processes have major significance in the fabrication of thin-film recording heads with the advantages of simplicity, high cost-effectiveness, and controllable patterning. Andricacos and Robertson summarized the major properties of common plated soft magnetic materials for fabricating recording heads.[3] Among them, CoFeNi and CoFeCu alloys have the highest possible saturation magnetization. Therefore these two materials, especially CoFeNi alloys, have attracted the most attention of investigators. CoFeNi alloys can be readily plated from solutions whose compositions differ from that of a NiFe plating bath only by adding a Co^{2+} salt, usually a sulfate or chloride. Table 1 lists the composition of a sulfate bath for plating CoFeNi alloys,[7] which has a pH as low as 2.5 to 3.0 with the addition of acid.

However, conventional CoFeNi plating baths suffer from stability problems, that is, precipitation occurs rapidly with time,[9] which is undesirable for commercialization. Tabakovic and co-workers equipped the plating cell with a filtered recirculation system to compensate for bath degeneration.[10] Precipitates can affect the film properties of uniformity and smoothness. Furthermore, the low pH employed in conventional baths leads to voids in deposited films, which degenerate film uniformity and magnetic properties, and low current density efficiency due to the electroplating of H_2. Therefore, the development of a stable bath with a relatively high pH is important for commercial fabrication of CoFeNi thin films with optimal soft magnetic properties.

In this study, a new, stable citrate-based bath with higher pH (>5) has been developed. Stability diagrams of CoFeNi plating baths with and without the addition of citrate have been calculated. The effects of bath composition and plating conditions on the electroplating of CoFeNi thin films have been investigated. Phase formation in films plated from the newly developed bath has been studied with thin film X-ray diffraction (XRD) and transmission electron microscopy (TEM). Grain sizes have been determined using TEM.

Experimental Methods

Si wafers coated with Ti/Au blanket metallizations were used as cathodes, with Au acting as a seed layer for plating. A deposition area of about 0.5 cm^2 was defined with lacquer. Platinum foil was used as the anode. Composition of the citrate-based plating bath is listed in Table 2, unless specified otherwise. The pH of the bath was natural without the addition of any acid or base. The volume of the electrolyte was 33 mL in every test. All plating, unless otherwise indicated, was done using pulsed current (PC) with a duty cycle of 10 ms − 0.3 ms of on-time (t_{on}) and 9.7 ms of off-time. Agitation was introduced by a mechanical stirrer at a speed of 600 rpm, unless specified otherwise. Plating time was set by the product of plating time and current density at around 300 min·mA/cm^2. Plating experiments were conducted under ambient temperature unless otherwise indicated.

Stability diagrams (Pourbaix diagrams) were calculated with OLI Analyzer Version 1.3 software purchased from OLI systems, Inc. The compositions and microstructures of CoFeNi deposits were characterized using a Hitachi S-2700 scanning electron microscope (SEM) equipped with an ultrathin window (UTW) X-ray detector. A Rigaku rotating anode XRD system, with a thin film camera attachment, was employed to identify specific CoFeNi phases. A Cu anode operating at 40 kV and 100 mA was used, with an incident angle of $2\theta = 2°$. A JEOL 2010 TEM, also equipped with a UTW X-ray detector, was used to observe the crystallization process and grain size, and to obtain diffraction patterns. A superconducting quantum interference device (SQUID) magnetometer (Quantum Design) was applied to measure the magnetic properties of CoFeNi thin films.

Results and Discussion

Stability of Plating Bath. The stability of the plating bath can be studied through stability diagrams. Unfortunately, no stability diagram calculations have been made in the reviewed references. Usually complexing agents are employed to stabilize a metal or alloy plating bath. The main differences in the newly developed bath (Table 2) relative to the conventional bath (Table 1) are the introduction of citrate as a complexing agent and a higher pH (>5).

Figure 1a, b, and c are the calculated Pourbaix diagrams for CoFeNi alloy plating baths with no citrate addition, addition of 0.206 M potassium citrate ($K_3(C_6H_5O_7)$), and addition of 0.395 M ammonium citrate ($(NH_4)_3(C_6H_5O_7)$), respectively. It can be seen that, thermodynamically, the stability of a CoFeNi alloy plating bath open to air is dominated by the precipitation of $Fe(OH)_3$ at pH ~3.1 (Figure 1a). Therefore, it is easy to understand the selection of bath pH in the range of 2.5 to 3.0 by previous researchers.[7−9] Actually, in their cases, acids are employed as the bath stabilizer. After the addition of 0.206 M potassium citrate, the CoFeNi alloy plating bath is thermodynamically stable until pH ~4.7 under the given concentrations of metal ions (Figure 1b). With the introduction of 0.395 M ammonium citrate, the CoFeNi alloy plating bath is thermodynamically stable until the precipitation of $Fe(OH)_3$ at pH = 5.8 (Figure 1c), due to the formation of stable complexing species, $FeC_6H_5O_7$, $Co[C_6H_5O_7]^-$, and $Ni[C_6H_5O_7]^-$. The adoption of ammonium citrate

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creates an additional stable region of $Co(NH_3)_6^{+3}$ from pH 6.6 to 10 because of the complexing effect of NH_3 on Co^{3+} ion. From Figure 1b and c, it is apparent that citrate has the strongest complexing power for Fe ions, followed by Ni^{2+} ion, and the weakest complexing effect for Co^{2+} ion. The main complexing reactions in the above CoFeNi alloy plating bath with the addition of 0.395 M ammonium citrate can be summarized as follows:

$$Fe^{+2} + [C_6H_5O_7]^{-3} = Fe[C_6H_5O_7]^{-}$$

$$4Fe[C_6H_5O_7]^{-} - 4e =$$
$$4Fe[C_6H_5O_7],\ O_2 + 2H_2O + 4e = 4OH^{-}$$

$$Co^{+2} + [C_6H_5O_7]^{-3} = Co[C_6H_5O_7]^{-}$$

$$Ni^{+2} + [C_6H_5O_7]^{-3} = Ni[C_6H_5O_7]^{-}$$

The calculated stability diagrams demonstrate that, thermodynamically, citrate can effectively stabilize the CoFeNi alloy plating baths, preventing the precipitation of metal hydroxides at higher pH.

Bath stability tests on baths with and without the addition of citrate have been conducted. Table 3 summarizes these results and demonstrates that citrate can significantly improve the stability of a CoFeNi alloy plating bath. For citrate-free baths, a low pH bath is more stable.

Effect of Ammonium Citrate. Besides the stability problem, traditional low pH baths suffer from low current density efficiency and voids in deposited CoFeNi films (which will degenerate the magnetic properties and uniformity of the films) due to the electroplating of H_2 (Figure 2a). As shown in Table 4, H^+/H_2 has a more positive equilibrium potential than the metal electrodes, which means hydrogen is more easily plated out than the metals. The H^+ concentration in the newly developed citrate-based bath (pH > 5) is hundreds of times lower than that in the conventional bath (pH = 2.5−3.0).[7−9] Therefore, more uniform and denser films have been plated out (Figure 2b).

The effect of ammonium citrate on the composition of CoFeNi deposits is shown in Figure 3a. Generally, ammonium citrate has the most prominent effect on Fe content, followed by Ni content, and only a minor effect on Co content. The results agree with the calculated stability diagrams (see Figure 1b and c), which demonstrate that citrate has the most powerful complexing effect on Fe ions, then Ni^{2+}, and finally Co^{2+}. At low citrate dosage, the Fe content in the deposited films is lowered, whereas as the citrate dosage is increased, the Fe content goes up. This is because at low citrate dosage only Fe ions are complexed; as citrate dosage increases, the Ni and Co ions will also be complexed. Metals are more difficult to plate out from the complexed metal ions due to higher activation energies and lower diffusivities to the cathode.

At an ammonium citrate dosage of 50 g/L (0.206 M), a film with a composition of $Co_{65}Fe_{24}Ni_{11}$ has been plated out. This film is very close in composition to the film with optimal soft magnetic properties, which has a composition of $Co_{65}Fe_{23}Ni_{12}$ with a high saturation flux density B_s of 2.1 T and low coercivity H_c of 1.20 Oe, claimed by Osaka and co-workers.[7, 8]

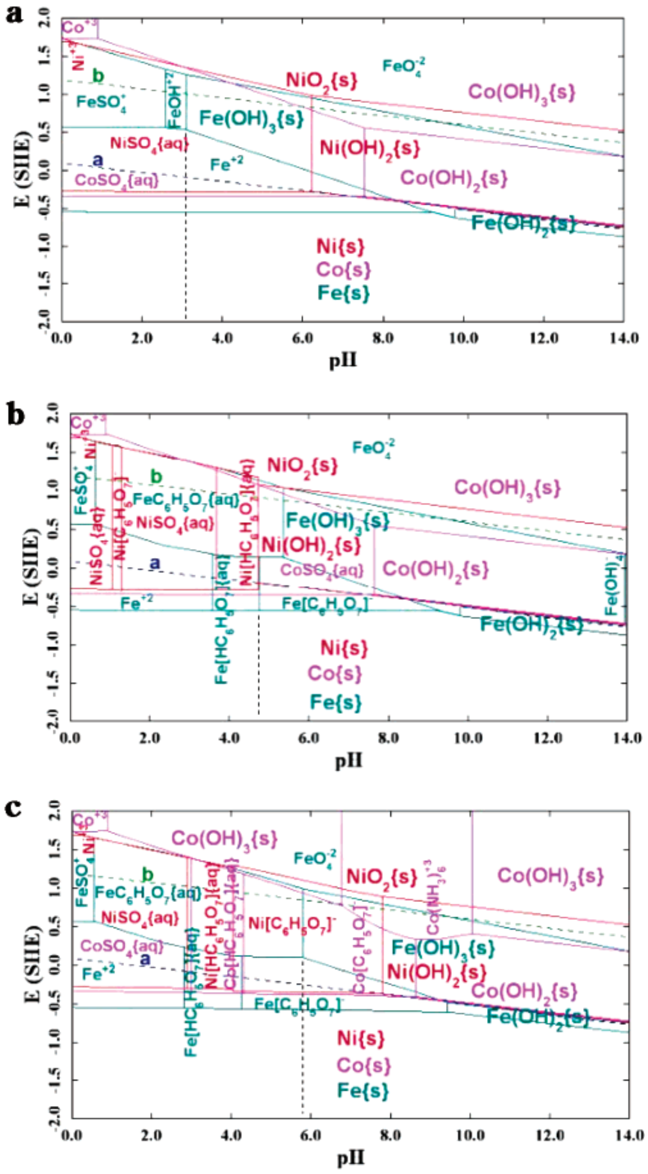

Figure 1. Pourbaix diagrams for CoFeNi alloy plating baths with and without the addition of citrate: (a) 0.015 M $FeSO_4$, 0.08 M $CoSO_4$, and 0.3 M $NiSO_4$ bath; (b) 0.08 M $CoSO_4$, 0.015 M $FeSO_4$, 0.3 M $NiSO_4$, and 0.206 M $K_3(C_6H_5O_7)$ bath; and (c) 0.08 M $CoSO_4$, 0.015 M $FeSO_4$, 0.3 M $NiSO_4$, and 0.395 $(NH_4)_3(C_6H_5O_7)$ bath. The dashed lines a and b refer to the equilibrium lines for H^+/H_2 and $(O_2 + H_2O)/OH^-$, respectively. The predominant areas of Co species, Fe species, and Ni species are defined by purple, green, and red lines, respectively.

The effect of ammonium citrate dosage on plating rate is shown in Figure 3b. The ammonium citrate dosage has a minor effect on plating rate up to a concentration of 50 g/L, but the plating rate drops rapidly at high ammonium citrate dosages.

Effect of Cobalt Concentration. The effect of cobalt concentration in the plating bath on deposit composition is illustrated in Figure 4. Co content in the deposit increases rapidly, while Fe and Ni contents decrease, as the cobalt concentration increases. This corresponds to the kinetics of the plating process.

Effect of Iron Concentration. Iron concentration tests (Figure 5) demonstrate that deposit iron content increases, and cobalt content decreases, with increasing iron concentration in the plating bath. It is interesting

Table 3. Bath Stability Tests on Baths With and Without the Addition of Citrate

bath composition	pH	stability
0.08 M $CoSO_4$ 0.015 M $FeSO_4$ 0.3 M $NiSO_4$ 0.4 M H_3BO_3 0.01 g/L sodium lauryl sulfate 0.206 M $(NH_4)_3(C_6H_5O_7)$	5.3 (natural)	plated bath was transparent after more than one month; plating results were repeatable after 6 days
0.08 M $CoSO_4$ 0.015 M $FeSO_4$ 0.3 M $NiSO_4$ 0.4 M H_3BO_3 0.01 g/L sodium lauryl sulfate 0.28 M NH_4Cl	5.3 (natural)	precipitate appeared in bath within 2 h during plating
0.08 M $CoSO_4$ 0.015 M $FeSO_4$ 0.3 M $NiSO_4$, 0.4 M H_3BO_3 0.01 g/L sodium lauryl sulfate 0.28 M NH_4Cl	2.7 (pH adjusted with dilute H_2SO_4)	precipitate appeared in plated bath after less than 2 days

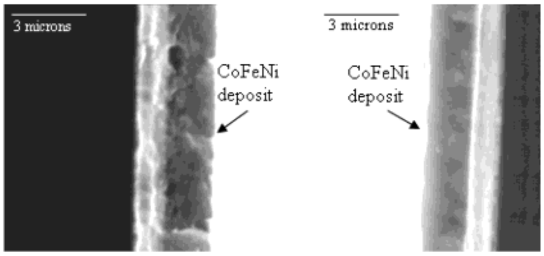

Figure 2. CoFeNi films plated from a low pH bath and the newly developed bath at a current density $i = 6$ mA/cm^2: (a) no citrate, pH 2.7 bath in Table 3, and (b) 0.206 M citrate, pH 5.3 bath in Table 3.

Table 4. Equilibrium Potentials of Selected Electrochemical Electrodes (ref 3)

electrochemical electrode	equilibrium potential (V)
H^+/H_2	0
Ni^{2+}/Ni	−0.23
Co^{2+}/Co	−0.28
Fe^{2+}/Fe	−0.44

that Ni content is almost constant as the iron concentration is varied, which may be due to the much lower solution concentration of iron relative to that of nickel.

Effect of Nickel Concentration. The effect of nickel concentration on CoFeNi alloy deposition is shown in Figure 6. The deposit Ni content increases, while Co and Fe contents oscillate, as nickel concentration in the bath goes up. From the plating bath composition (Table 2), it is clear that the metal contents in the deposits are not proportional to the metal concentrations in the plating bath. By referring to Figures 4−6, Ni is the most difficult metal to be plated out. However, from Table 4, Ni^{2+}/Ni has the most positive potential among the three metal electrodes, so it should be the metal plated out first. This anomalous phenomenon for Ni plating has been reported previously by several researchers.[14,46,47]

Effect of Current Density. Tests on the effect of current density (Figure 7) demonstrate that, at low current densities, the composition of deposited CoFeNi films varies as the current density increases. At current densities higher than 6 mA/cm^2 the deposited metal contents are almost constant.

Effect of Agitation. The introduction of agitation changes the composition of plated CoFeNi films (Figure 8). This is because agitation accelerates the diffusion of metal ions to the cathode and affects the metal ion ratio near the cathode surface. The Fe and Ni compositions are more affected, with little change in Co.

Effect of On-Time (t_{on}). To obtain uniform composition in deposited film along thickness (i.e., to avoid metal content gradients) pulsed current plating is usually employed for maintaining initial metal ion concentrations around the cathode.[25] Figure 9 shows the effect of on-time, t_{on}, of the duty cycle on the plating of CoFeNi alloys. The metal contents in deposits have very little fluctuation with t_{on} variation. The films have a composition around $Co_{67}Fe_{22}Ni_{11}$.

Generally, the effects of plating conditions on CoFeNi film composition are not as pronounced as that of bath composition.

Phase Formation and Grain Size in Deposited Films. Phase formation control in plated CoFeNi films is necessary for obtaining optimal soft magnetic properties. Ideal properties are obtained when both bcc and fcc phases coexist. Osaka et al.[7] found that CoFeNi films have close to zero saturation magnetostriction ($\lambda s = 0$) around the fcc−bcc phase transformation boundary. Saito and co-workers[11] reported that magnetic properties, such as saturation magnetic flux density B_s, coercivity H_c, and saturation magnetostriction λ_s, are affected by the ratio of bcc to fcc phase content. When the ratio of bcc to fcc phase content was low and the grain size was small, the coercivities of plated films were lower than 2 Oe. The λ_s and B_s values increased with an increasing bcc to fcc phase ratio in the film.

Coercivity, H_c, generally decreases as the grain size decreases. According to Herzer's model,[48] H_c is proportional to the sixth power of the average grain size (D^6). Therefore, only nanocystalline alloys can have low coercivities and achieve optimal soft magnetic properties. It is believed that the competitive nucleation and

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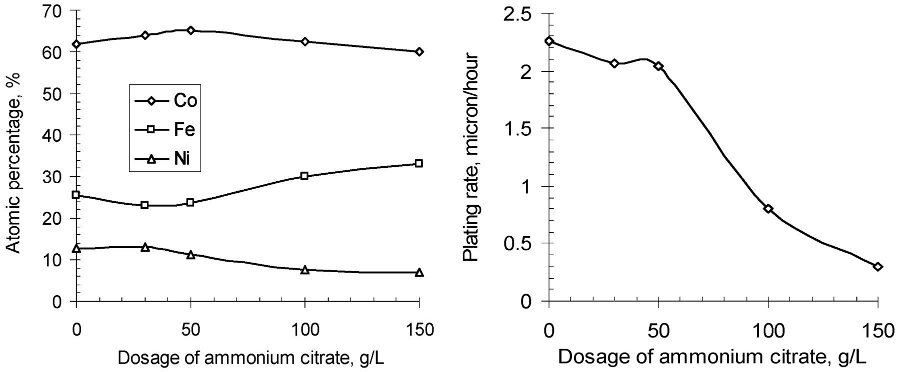

Figure 3. Effect of ammonium citrate on the electroplating of CoFeNi films: (a) effect on deposit composition, and (b) effect on plating rate. Plating current density $i = 6$ mA/cm^2.

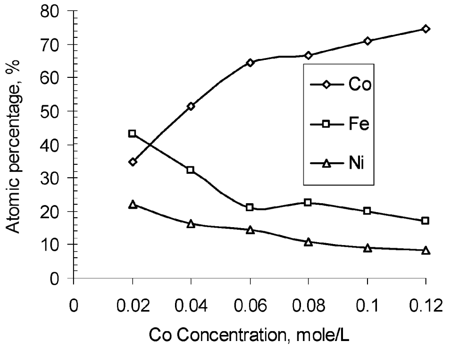

Figure 4. Effect of cobalt concentration on the composition of deposited CoFeNi films. Plating current density $i = 6$ mA/cm^2.

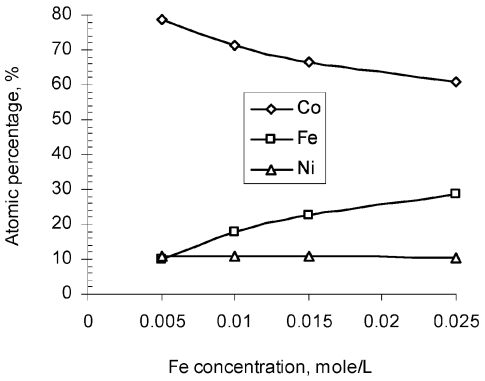

Figure 5. Effect of iron concentration on the composition of deposited CoFeNi films. Plating current density $i = 6$ mA/cm^2.

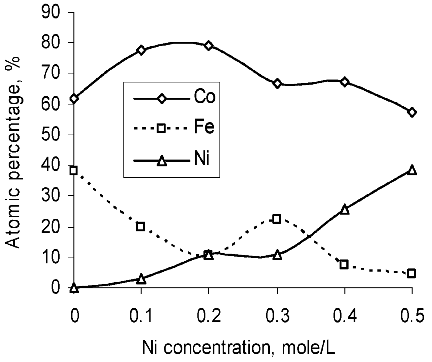

Figure 6. Effect of nickel concentration on the composition of deposited CoFeNi films. Plating current density $i = 6$ mA/cm^2.

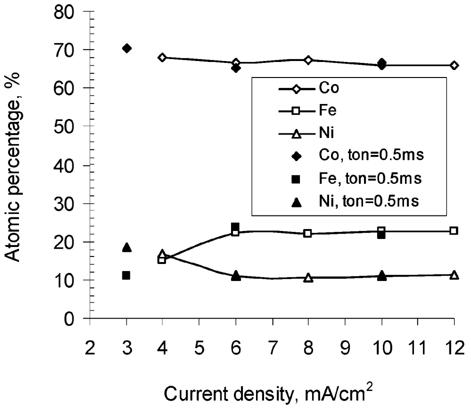

Figure 7. Effect of current density on the composition of CoFeNi films.

growth of the two phases could lead to a smaller average grain size.[12,13] Osaka et al. attributed the high B_s values, as well as the soft magnetic properties, of plated CoFeNi films to small grain sizes in the range of 10−20 nm.[8]

Thin film XRD and TEM methods were employed to analyze the phase formation and grain size in deposited CoFeNi films. The major XRD peaks for fcc and bcc phases are (111) for fcc at $2\theta \approx 44.1°$ and (110) for bcc at $2\theta \approx 45.2°$, respectively.[9,10] As shown in Figure 10, both fcc and bcc phases can be co-deposited from the newly developed bath.

Electron diffraction (Figure 11c) further verifies the coexistence of fcc and bcc phases in films plated from the citrate-based bath. TEM bright field and dark field images (Figure 11a and b) show that the grains in CoFeNi deposits are 10−20 nm in diameter, which is similar to the grain sizes in CoFeNi films with the best soft magnetic properties obtained by Osaka et al.[7,8] The dark field image was formed from part of the fcc (111) and bcc (110) diffraction rings (Figure 11c).

Magnetic Properties of Plated CoFeNi Thin Films. The magnetic properties of representative CoFeNi films plated from conventional low pH baths and the newly developed citrate-based bath are listed in Table 5. CoFeNi films with optimal soft magnetic properties (high B_s and low H_c) have been plated out from the low pH bath. The results are close to those reported in the literature.[7,8] For the films plated from the citrate-based bath, the saturation flux density B_s exceeds 2 T, which is desired. However, the coercivities of the films are larger than those of the films plated from the low pH bath. The coercivities of CoFeNi films plated from the newly developed bath are lower than those for CoFe films obtained with vacuum techniques for recording

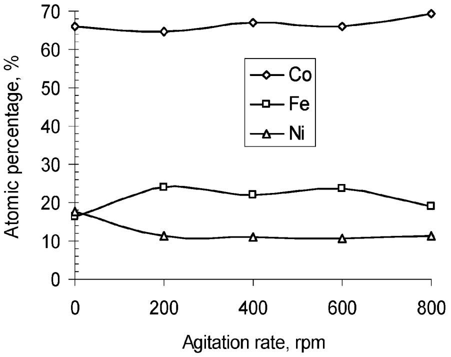

Figure 8. Effect of agitation on the composition of CoFeNi films. Plating current density $i = 6$ mA/cm^2.

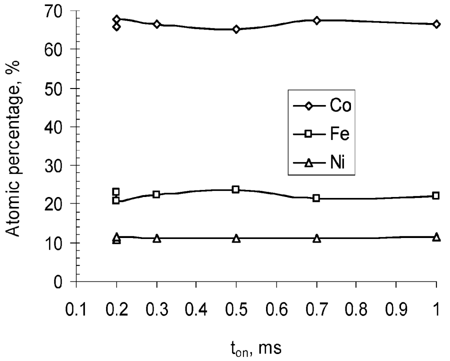

Figure 9. Effect of t_{on} on the composition of CoFeNi films. Plating current density $i = 6$ mA/cm^2.

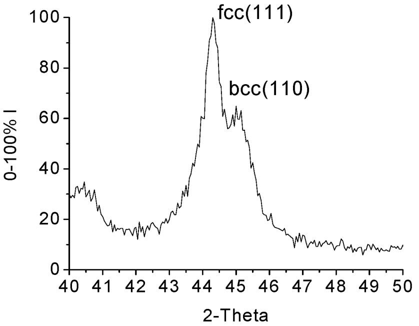

Figure 10. Thin-film XRD spectrum of CoFeNi film plated at an ammonium citrate dosage of 50 g/L and $i = 8$ mA/cm^2. The film composition is $Co_{65}Fe_{24}Ni_{11}$.

head fabrication, which are around 20 to 60 Oe.[4,6] The optimal soft magnetic properties of CoFeNi thin films can be achieved only by optimizing their chemical composition, phase formation, grain sizes, and electroplating process.

Conclusions

Conventional low pH electroplating baths suffer from stability problems, as well as low current density efficiency and voids in deposited films due to the electroplating of hydrogen. Bath stability is important for commercial fabrication of CoFeNi thin films with ideal properties. Citrate can effectively improve the stability of CoFeNi plating baths. Denser CoFeNi deposits can be plated out from the new citrate-based bath because of higher bath pH. The calculated Pourbaix diagrams demonstrate that citrate has the strongest complexing effect on Fe ions, then on Ni^{2+} ion, and the weakest complexing effect on Co^{2+} ion.

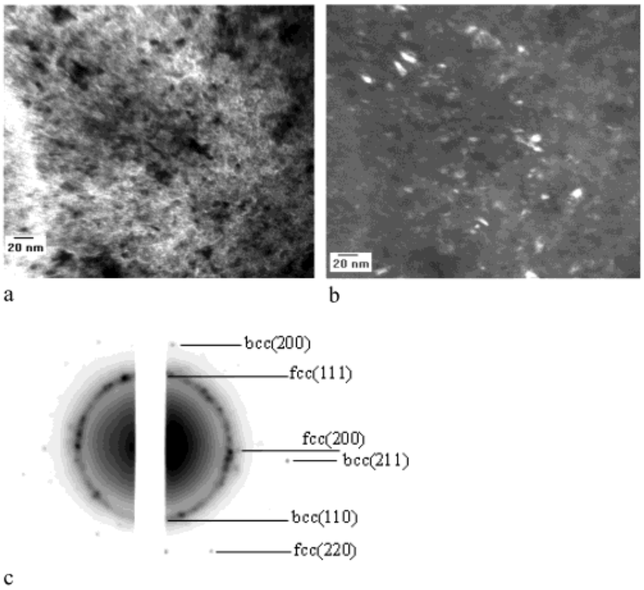

Figure 11. TEM (a) bright field and (b) dark field images, and c) electron diffraction pattern of a CoFeNi film plated at ammonium citrate dosage of 100 g/L and $i = 10$ mA/cm^2. The film composition is $Co_{72}Fe_{21}Ni_7$.

Table 5. Magnetic Properties of Representative CoFeNi Films Plated from a Low pH Bath and the Newly Developed Bath

plating bath	film composition	coercivity H_c (Oe)	saturation flux density B_s (T)
low pH bath (pH 2.7)	$Co_{64}Fe_{24}Ni_{12}$	1.5	2.01
	$Co_{65}Fe_{24}Ni_{11}$	5.5	1.91
	$Co_{60}Fe_{29}Ni_{11}$	18	1.84
newly developed bath (pH 5.3)	$Co_{68}Fe_{22}Ni_{10}$	11	2.03
	$Co_{64}Fe_{26}Ni_{10}$	15	2.10

Generally, metal content in deposited films increases with the metal concentration in the plating bath. The anomalous behavior of Ni plating was also observed during the plating with citrate-based bath. The effects of plating conditions on deposited CoFeNi film composition are not as prominent as that of bath composition.

CoFeNi thin films with preferred composition, mixed fcc–bcc phases, and 10–20 nm grain sizes, which are necessary for achieving ideal soft magnetic properties, can be plated out from the new citrate-based bath.

The saturation flux density, B_s, of films plated from the citrate-based bath exceeds 2 T; however, the coercivities are relatively large, but better than those of CoFe films obtained with vacuum techniques for recording head fabrication.

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