# **Development of Stable Baths for Electroplating**

# **CoFe and CoFeNi Soft Magnetic Thin Films**

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Conventional low pH (2.3-3.5) baths, for the electrodeposition of CoFe and CoFeNi thin films, suffer from stability problems. In addition, voids can form in the deposits due to the electroplating of hydrogen. New, more stable baths with relatively high pH levels have been developed by introducing a stabilizer. The effects of stabilizer dosage, bath Co/Fe concentration ratios and plating temperature on the deposition of CoFe and CoFeNi thin films have been investigated. CoFe and CoFeNi thin films with good magnetic properties have been plated out from the newly developed plating baths.

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#### Introduction

CoFe and CoFeNi alloys are the most studied soft magnetic materials because of their superior properties compared with FeNi alloys as write head core materials in hard disk-drives.<sup>1</sup> Electrodeposited Ni<sub>80</sub>Fe<sub>20</sub> was introduced as the core material of thin film inductive heads by IBM in 1979.<sup>2</sup> With increasing storage density, the need for recording heads to write on high-coercivity media has raised new requirements for the write-head material that cannot be met by Ni<sub>80</sub>Fe<sub>20</sub>.<sup>3</sup> Therefore, new soft magnetic materials, such as electroplated CoFe alloys<sup>4-7</sup>, CoFeNi alloys<sup>8-16</sup> and CoFeCu alloys<sup>3,17</sup>, sputtered FeN films<sup>18</sup> and other Fe-based alloys<sup>19, 20</sup>, have been developed.

Electroplating processes have major significance in the fabrication of thin-film recording heads, due to the advantages of simplicity, cost-effectiveness and controllable patterning. However, conventional CoFe and CoFeNi plating baths suffer from stability problems, i.e., precipitation occurs rapidly with time<sup>10</sup>, which is undesirable for commercialization. Precipitates can affect the film properties, uniformity and smoothness. Tabakovic and coworkers<sup>11</sup> equipped their plating cell with a filtered recirculation system to compensate for bath degeneration. Furthermore, the low pH employed in conventional baths leads to voids in deposited films, which degenerate film uniformity and magnetic properties, due to the electroplating of H<sub>2</sub>. Therefore, the development of a stable bath with a relatively high pH is important for commercial fabrication of CoFe and CoFeNi thin films with optimal soft magnetic properties.

New, stable baths with the addition of a stabilizer and relatively high pH levels have been developed for CoFe and CoFeNi alloy plating in this study. The effects of stabilizer dosage, Co/Fe concentration ratios and plating temperature on the deposition of CoFe and CoFeNi thin films have been studied. The magnetic properties of plated films have also been investigated.

#### **Experimental Methods**

Si wafers coated with Ti/Au blanket metallizations were used as cathodes. Platinum foil was used as the anode. All plating was done using pulsed current (PC) with a duty cycle of 10ms. Agitation was introduced at a speed of 600 rpm. For CoFe thin film deposition, the on-time was set at 6ms and off-time at 4ms, the current density (i) was 15mA/cm<sup>2</sup> (13.9 A/ft<sup>2</sup>) and the plating time was 25min. For CoFeNi plating, the on-time and off-time were set at 0.3ms and 9.7ms, respectively. The plating time was set by the product of plating time and current density at around 300 minutes\*mA/cm<sup>2</sup> (279 A/ft<sup>2</sup>), unless otherwise indicated. All plating experiments were conducted under ambient pressure. The pH levels of the newly developed CoFe and CoFeNi baths were natural without the addition of any acid or base. The compositions of baths for electroplating CoFe and CoFeNi alloys are listed in Tables 1 and 2, respectively, unless otherwise indicated.

Pourbaix diagrams were calculated with OLI Analyzer Version 1.3 Software. The compositions and microstructures of CoFe and CoFeNi deposits were characterized using a Hitachi S-2700 scanning electron microscope (SEM) equipped with an ultra thin window (UTW)

x-ray detector. A Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design) was applied to measure the magnetic properties of the CoFe and CoFeNi thin films.

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Chemical	Concentration	Chemical	Concentration
$CoSO_4$	0.120 M	$H_3BO_3$	0.4 M
FeSO <sub>4</sub>	0.048 M	Sodium lauryl sulfate	0.01 g/L
Bath pH	= 4.4 (natural)	Bath stabilizer	5 g/L

 Table 1. Composition of newly developed bath for electroplating CoFe thin films

Table 2. Com	e 2. Composition of newly developed bath for electroplating CoFeNi thin films		
Chemical	Concentration	Chemical	Concentration
$CoSO_4$	0.08 M	$H_3BO_3$	0.4 M
FeSO <sub>4</sub>	0.015 M	Sodium lauryl sulfate	0.01 g/L
NiSO <sub>4</sub>	0.3 M	Bath stabilizer	50 g/L
	Bat	h pH = $5.3$ (natural)	

**Results and Discussion** 

The main differences in the newly developed baths for CoFe and CoFeNi alloy plating, relative to the conventional baths employed by other researchers, are the introduction of a stabilizer to improve bath stability and the relatively high pH levels for the new baths.

# Bath stability

Calculated Pourbaix diagrams for the Fe and CoFeNi systems are illustrated in Figures 1a and 1b, respectively. Thermodynamically, Fe(OH)<sub>3</sub> precipitates out at a pH  $\geq$ 3.1 for the Fe bath open to air. For the CoFeNi ternary plating bath without stabilizer, the bath stability is also dominated by the precipitation of Fe(OH)<sub>3</sub> at a pH  $\geq$ 3.1. Therefore, it is understandable that the bath pH was set in the range of 2.3 to 3.5 for the CoFe and CoFeNi plating systems by previous researchers.<sup>7-10</sup> Actually, in these cases, acids were employed as bath stabilizers.





Figure 1 Calculated Pourbaix diagrams for Fe and CoFeNi baths. The dashed lines a and b refer to the equilibrium lines for  $H^+/H_2$  and  $(O_2 + H_2O)/OH$ , respectively.

Bath composition	pН	Stability
0.120M CoSO <sub>4</sub> 0.050M FeSO <sub>4</sub> 0.4M H <sub>3</sub> BO <sub>3</sub> 0.01g/L sodium lauryl sulfate 5 g/L bath stabilizer	Around 4.4 (natural)	Plating bath was transparent after more than 2 weeks. Plating results were repeatable after 2 days.
0.048M CoSO <sub>4</sub> 0.050M FeSO <sub>4</sub> 0.4M H <sub>3</sub> BO <sub>3</sub> 0.01g/L sodium lauryl sulfate 0.28M NH <sub>4</sub> Cl 0 g/L bath stabilizer	2.4 (pH adjusted with dilute H <sub>2</sub> SO <sub>4</sub> )	Precipitate appeared in plated bath after less than 24 hours.

Table 3. Stability tests for CoFe plating baths with and without the addition of a stabilizer

#### Table 4. Stability tests for CoFeNi plating baths with and without the addition of a stabilizer

Bath composition	рН	Stability
0.08M CoSO <sub>4</sub> 0.015M FeSO <sub>4</sub> 0.3M NiSO <sub>4</sub> 0.4M H <sub>3</sub> BO <sub>3</sub> 0.01g/L sodium lauryl sulfate 50 g/L bath stabilizer	5.3 (natural)	Plating bath was transparent after more than one month. Plating results were repeatable after 6 days.
$\begin{array}{c} 0.08M \operatorname{CoSO}_4\\ 0.015M \operatorname{FeSO}_4\\ 0.3M \operatorname{NiSO}_4\\ 0.4M \operatorname{H}_3\mathrm{BO}_3\\ 0.01g/\mathrm{L} \text{ sodium lauryl sulfate}\\ 0.28M \operatorname{NH}_4\mathrm{Cl}\\ 0 \ g/\mathrm{L} \text{ bath stabilizer} \end{array}$	5.3 (natural)	Precipitate appeared in bath within 2 hours during plating.
0.08M CoSO <sub>4</sub> 0.015 M FeSO <sub>4</sub> 0.3M NiSO <sub>4</sub> , 0.4M H <sub>3</sub> BO <sub>3</sub> 0.01g/L sodium lauryl sulfate 0.28M NH <sub>4</sub> Cl 0 g/L bath stabilizer	2.7 (pH adjusted with dilute H <sub>2</sub> SO <sub>4</sub> )	Precipitate appeared in plating bath after less than 48 hours.

Bath stability tests on plating baths, with and without the addition of a stabilizer, have been conducted. The results are summarized in Tables 3 and 4, which demonstrate that the stabilizer can significantly improve the stabilities of CoFe and CoFeNi alloy plating baths. For stabilizer-free CoFeNi plating baths, the bath with lower pH is more stable, i.e., a lower pH bath is more resistant to the formation of metal hydroxide precipitates.

# Uniformity of deposited films



a. No stabilizer; pH=2.7; bath in Table 2b b. 0.206M stabilizer; pH=5.3; bath in Table 2b

Figure 2 SEM secondary electron (SE) images of CoFeNi films plated from a low pH bath (a) and the newly developed bath (b) at a current density of  $6mA/cm^2$  (5.57  $A/ft^2$ ).

Table 5. Equilibrium potentials of s	otentials of selected electrochemical electrodes <sup>3</sup>	
Electrochemical electrode	Equilibrium potential (V)	
$\mathrm{H}^{+}/\mathrm{H}_{2}$	0	
Ni <sup>2+</sup> /Ni	-0.23	
Co <sup>2+</sup> /Co	-0.28	
Fe <sup>2+</sup> /Fe	-0.44	

In addition to the stability problem, traditional low pH baths suffer from voids in deposited films, which will degenerate the magnetic properties and uniformity of the films, due to the electroplating of H<sub>2</sub> (Figure 2a). As shown in Table 5,  $H^+/H_2$  has a more positive equilibrium potential than the metal electrodes, which means hydrogen is more easily plated out than the metals. The H<sup>+</sup> concentrations in the newly developed baths are much lower than those in the conventional baths (pH = 2.3-3.5).<sup>7-10</sup> Therefore, more uniform and more dense films can be plated out (Figure 2b).

# Electroplating of CoFe alloys

The electrodeposition of CoFe thin films from stabilized baths (see Table 1) as a function of stabilizer dosage, Co/Fe concentration ratio and plating temperature has been studied.

# Effect of bath stabilizer

The effect of stabilizer dosage on the composition of CoFe deposits is shown in Figure 3. There is a linear relationship between deposit composition (in at%) and bath stabilizer dosage. The

Fe percentage in the deposit increases, while the Co percentage decreases, with increasing stabilizer dosage. Therefore, the stabilizer affects the plating activity of both the iron and cobalt ion species.



Figure 3 Effect of bath stabilizer dosage on deposit composition.

#### Effect of Co/Fe concentration ratio

Figure 4 illustrates the effect of Co/Fe concentration ratio in the plating bath on deposited CoFe film composition. The cobalt content in the deposit increases as the Co/Fe concentration ratio increases. Iron content in the deposit decreases as the bath Co/Fe ratio increases. This corresponds to the expected kinetics for electrodeposition, i.e., a higher metal ion concentration is beneficial for deposition of that metal. At a Co/Fe bath concentration ratio of 2.5, the deposited film has a composition corresponding to  $Co_{65}Fe_{35}$ .

For films plated from baths with the same Co/Fe concentration ratio but with different metal concentrations (Table 6), the compositions are very similar.



Figure 4 Effect of bath Co/Fe concentration ratio on deposit composition. The Fe concentration is fixed at 0.048M.

	concentrati	ons	
Co/Fe conc. ratio	Fe conc. (M)	Co (at%)	Fe (at%)
1	0.12	49.0	51.0
1	0.048	49.6	50.4
4	0.048	70.5	29.5
4	0.03	72.4	27.6

Table 6. CoFe films deposited from baths with the same Co/Fe concentration ratio but different metal

# Effect of plating temperature

The effect of plating temperature is illustrated in Figure 5. Generally, the cobalt content in the deposited film increases as plating temperature increases. For iron content in the plated film, the situation is reversed. Therefore, higher temperatures are more beneficial for cobalt deposition in contrast to iron. Increased plating temperature should accelerate the diffusion of metal ions to the cathode and help overcome the energy barrier for metal deposition; however the effect is more pronounced for cobalt.



Figure 5 Effect of plating temperature on deposit composiiton.

#### Electroplating of CoFeNi alloys

CoFeNi films with a composition of  $Co_{65}Fe_{23}Ni_{12}$  have been reported as having ideal soft magnetic properties.<sup>8,9</sup> The  $Co_{65}Fe_{35}$  alloy has a very high saturation magnetization,<sup>6</sup> so that the effect appears to be related to partial substitution of iron with nickel. The deposition of CoFeNi thin films from the newly developed bath (see Table 2), as a function of stabilizer dosage, bath Co/Fe concentration ratio and plating temperature, has been investigated.

#### Effect of bath stabilizer

The effect of bath stabilizer on the composition of CoFeNi deposited films is shown in Figure 6. In general, the stabilizer has the most prominent effect on Fe content, followed by Ni content, and only a minor effect on Co content. At a stabilizer dosage of 50g/L, 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 Tesla and low coercivity  $H_c$  of 1.20 Oe.<sup>8,9</sup>

#### Effect of Co/Fe concentration ratio

Figure 7 illustrates the effect of Co/Fe concentration ratio in the plating bath on deposit composition. Cobalt content in the deposit increases rapidly, while iron and nickel content decrease, as the Co/Fe bath concentration ratio rises. This reflects the expected kinetics of the plating process.

For films deposited from baths with the same Co/Fe concentration ratio, but different metal concentrations (Table 7), the compositions are not similar. This is in contrast to the FeCo alloy plating system (Table 6).



Figure 6 Effect of bath stabilizer concentration on the electroplating of CoFeNi films. The plating current density is  $6mA/cm^2$  (5.57  $A/ft^2$ ).



Concentration ratio of Co/Fe in bath

Figure 7 Effect of bath Co/Fe concentration ratio on the composition of deposited CoFeNi films. The Fe concentration is fixed at 0.015M and the plating current density is  $6mA/cm^2$  (5.57 A/ft<sup>2</sup>).

Table 7. CoFeNi films deposited at same bath Co	<b>Co/Fe concentration ratio but different metal concentrations</b>
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Co/Fe conc. ratio	Fe conc. (M)	Co (at%)	Fe (at%)	Ni (at%)
4	0.015	64	21	15
4	0.020	61	29	10

#### Effect of plating temperature

The effect of plating temperature is shown in Figure 8. Similar to the CoFe alloy plating system, the cobalt content in deposited films increases, while the iron content decreases, as the plating temperature increases. Increasing the plating temperature also facilitates the deposition of nickel.



Plating temperature, degrees centigrade

Figure 8 Effect of plating temperature on the composition of deposited CoFeNi films. Plating current density is  $12mA/cm^2$  (11.15 A/ft<sup>2</sup>) and the plating time is 30min.

#### Magnetic properties of plated CoFe and CoFeNi thin films

The hysteresis loop of a CoFe film corresponding to a composition of  $Co_{66}Fe_{34}$ , deposited from the newly developed bath, is illustrated in Figure 9. The film has a coercivity of 9 Oe, and a saturation magnetization  $M_s$  of 1.93 Tesla, which are similar to the magnetic properties of  $Co_{90}Fe_{10}$ films plated by Liao.<sup>5</sup> The coercivity of the deposited  $Co_{66}Fe_{34}$  film is lower than the coercivity for  $Co_{35}Fe_{65}$  films plated by Osaka and coworkers,<sup>7</sup> but the saturation magnetization is also lower for the deposits in this work.



Magnetic field, Oe

Figure 9 Hysteresis loop for CoFe film deposited from stabilizer-added bath (film composition is  $Co_{66}Fe_{34}$ ).

	newly developed bath				
Plating bath	Film	Coercivity	Saturation flux		
	composition	Hc (Oe)	density $B_{\rm s}$ (Tesla)		
Low pH bath	$Co_{64}Fe_{24}Ni_{12}$	1.5	2.01		
(pH 2.7)	Co <sub>65</sub> Fe <sub>24</sub> Ni <sub>11</sub>	5.5	1.91		
	Co60Fe29Ni11	18	1.84		
Newly	Co <sub>61</sub> Fe <sub>29</sub> Ni <sub>10</sub>	11	1.98		
developed bath	CociFearNin	15	2 10		

Table 8. Magnetic properties of representative CoFeNi films plated from the traditional low pH bath and the

The magnetic properties for representative CoFeNi films plated from conventional low pH baths and the newly developed bath are listed in Table 8. CoFeNi films with ideal soft magnetic properties (high  $B_s$  and low  $H_c$ ) have been plated out from the conventional low pH bath. The results are close to those reported in the literature.<sup>8,9</sup> For films plated from the newly developed bath with the stabilizer, the saturation flux density  $B_s$  exceeds 2 Tesla, which is desired. However, the coercivities of the films are larger than those of the films plated from low pH bath. Compared with CoFe films deposited from the stabilizer-added bath, the CoFeNi films plated from the newly developed bath have higher saturation magnetizations and slightly higher coercivities. The coercivities are still lower, however, than those for CoFe films obtained with vacuum techniques for recording head fabrication, which are around 20 to 60 Oe.<sup>4, 6</sup>

In summary, optimal soft magnetic properties for CoFe and CoFeNi thin films can only be achieved by optimizing their chemical composition, phase formation, grain sizes and electroplating process.

(pH 5.3)

#### Conclusions

Conventional low pH CoFe and CoFeNi plating baths suffer from stability problems, as well as voids in deposited films due to the electroplating of hydrogen. Bath stability is important for commercial fabrication of CoFe and CoFeNi thin films with optimal magnetic properties. A bath stabilizer can effectively improve the stabilities of both CoFe and CoFeNi plating baths. Denser films can also be plated out from the newly developed baths because of their relatively high pH.

A linear relationship between deposit concentration and stabilizer dosage was found for CoFe plating. For CoFeNi deposition, the behavior was non-linear, with the stabilizer having the most prominent effect on Fe content, followed by Ni content, and only a minor effect on Co content.

Generally, Co content in deposited films increases, while Fe content decreases with an increasing Co/Fe concentration ratio in the plating bath. For CoFe plating, films deposited from baths with the same Co/Fe concentration ratio, but with different metal concentrations, had almost the same composition. For CoFeNi plating, a change in bath metal concentration while maintaining the same Co/Fe ratio resulted in different deposit composition.

The cobalt content in deposited films increases, while the iron content decreases, as plating temperature increases. For CoFeNi plating, higher plating temperatures facilitate nickel deposition.

Soft magnetic CoFe thin films with a coercivity of 9 Oe, and a saturation magnetization  $M_s$  of 1.93 Tesla, have been plated out from the new stabilizer-added bath. The saturation flux density  $B_s$  for CoFeNi films plated from the newly developed bath, exceeds 2 Tesla; however, the coercivities are slightly larger than the best values reported in the literature.

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### References

- 1. T. Osaka, *Electrochimica Acta*, **45**, 3311 (2000).
- A. Chiu, I. Croll, D. E. Heim R. E. Jr. Jones, P. Kasiraj, K. B. Klaassen, C. D. Mee & R. G. Simmons, *IBM J. Res. Develop.*, 40, 283 (1996).
- 3. P. C. Andricacos & N. Robertson, *IBM J. Res. Develop. (Electrochemical Microfabrication)*, **42**, 671 (1998).
- 4. S. H. Liao & C. H. Tolman, US Patent 4,756,816 (1988).
- 5. S. H. Liao, *IEEE Trans. Magn. Mag.*, 23, 2981 (1987).
- 6. W. Yu, J. A. Bain, Y. Peng & D. E. Laughlin, *IEEE Trans. Magn.*, **38**, 3030 (2002).
- 7. T. Osaka, T. Yokoshima, D. Shiga, K. Imai & K. Takashima, *Electrochemical and Solis-State Letters*, **6**, C53 (2003).
- T. Osaka, M. Takai, K. Hayashi, K. Ohashi, M. Saito & K. Yamada, *Nature*, **392**, 796 (1998).
- T. Osaka, M. Takai, K. Hayashi, Y. Sogawa, K. Ohashi & Y. Yasue, *IEEE Trans. Magn.*, 34, 1432 (1998).
- 10. X. Liu, G. Zangari & M. Shamsuzzoha, J. Electrochem. Soc., 150, C159 (2003).
- 11. I. Tabakovic, V. Inturi & S. Riemer, J. Electrochem. Soc., 149, C18 (2002).
- 12. M. Saito, N. Ishiwata & K. Ohashi, J. Electrochem. Soc., 149, C642 (2002).
- 13. X. Liu, P. Evans & G. Zangari, J. Magn. Magn. Mater., 226-230, 2073 (2001).
- 14. Y. Zhuang & E. J. Podlaha, J. Electrochem. Soc., 150, C219 (2003).
- 15. C. Chen, K. Lin & J. W. Chang, US Patent Application no. 20030044303 (2003).
- 16. T. Osaka, M. Takai, Y. Sogawa, T. Momma, K. Ohashi, M. Saito & K. Yamada, J. *Electrochem. Soc.*, **146**, 2092 (1999).
- 17. P. C. Andricacos, J. W. Chang, W. J. Horkans, J. D. Olsen, B. Petek & L. T. Romankiw, US Patent 5,582,927 (1996).
- 18. S. Wang & M. H. Kryder, J. Appl. Phys., 67, 5134 (1990).
- 19. Y. Yoshizawa, S. Oguma & K. Yamauchi, J. Appl. Phys., 64, 6044 (1988).
- 20. T. J. Klemmer, K. A. Ellis, L. H. Chen, B. Dover & S. Jin, J. Appl. Phys., 87, 830 (2000).