Electroless Ni-Fe-B Alloy Plating Solution Using DMAB as a Reducing Agent

By D. Kim, H. Matsuda, K. Aoki and O. Takano

This paper describes the development of an electroless nickel iron boron plating solution using dimethylamine borane (DMAB) as a reducing agent. Two complexing agents, namely sodium citrate and sodium tartrate, are used. Satisfactory stability of the solution and relatively high deposition rate are achieved with this solution. Soft magnetic films having a coercive force of 20 A/m (0.25 Oe) are deposited from the solution.

Electroless nickel-iron alloy films are of interest as promising materials for computer storage[1-3] and undercoating of recording media.[4-6] In the nickel-iron solutions, deposition generally proceeds only in the alkaline region, because the driving force of the reducing agent is not sufficient in the acid region. This may produce a problem; that is, metallic ions naturally form hydroxide precipitates in alkaline solutions. In order to prevent precipitation, several organic chemicals have been used as complexing agents. Various nickel-iron solutions have been developed to obtain soft magnetic films. Most of them are Ni-Fe-P films deposited from solutions containing hypophosphite as reducing agent.[7] Electroless nickel-iron-boron films, however, have received less attention. We have already reported that the addition of ammonium sulfate is effective for improvement of stability in electroless Ni-Fe-P solutions.[7] This effect, therefore, may be expected in electroless Ni-Fe-B solutions.

In this study, an electroless cobalt-iron-boron solution was developed, using DMAB as a reducing agent. The relationship between the preparation conditions and deposition behavior is discussed.

Experimental Procedure

The selection and combination of complexing agents were crucial in ultimately determining the characteristics of the electroless plating solutions. From the result of preliminary investigations, we determined three basic solutions containing sodium citrate and/or sodium tartrate as the complexing agents. The composition of the solutions without the complexing agents was fixed at 0.10 mol/L metallic salt (nickel sulfate + ferrous sulfate), 0.03 mol/L dimethylamine borane (DMAB) and 0.50 mol/L ammonium sulfate. The pH of the solutions was adjusted with sodium hydroxide. The operating temperature was controlled at 90 °C, using a water bath. Copper sheet (0.3 mm thick) was used as substrate material.

The composition of deposited films was determined by an inductively coupled plasma (ICP) spectrometry system. The magnetic properties were measured using a Helmholtz coil-type magnetometer. The applied external field was 4 kA/m.

Results and Discussion

Basic Conditions

In electroless plating, the choice of complexing agents defines the basic plating conditions and limits the concentration regions of the components. To obtain the characteristics of each basic solution, a limited investigation was made into comparison of the stability and plating behavior of the basic solutions. The results are summarized in Table 1. In the case of the solution using citrate as its complexing agent (cit. solution), no spontaneous decomposition of the solution occurred and no precipitation of hydroxide. The plating rate of 4.7 µm/hr is not sufficient, however, for practical application. Conversely, for a solution containing sodium tartrate, a high deposition rate (11 µm/hr) was obtained; however, decomposition and precipitation were observed in the high pH region (pH 9). It was found that such disadvantageous effects are minimized by fixing the basic solution, using sodium citrate and sodium tartrate as the complexing agents. Further investigations were carried out using this solution.

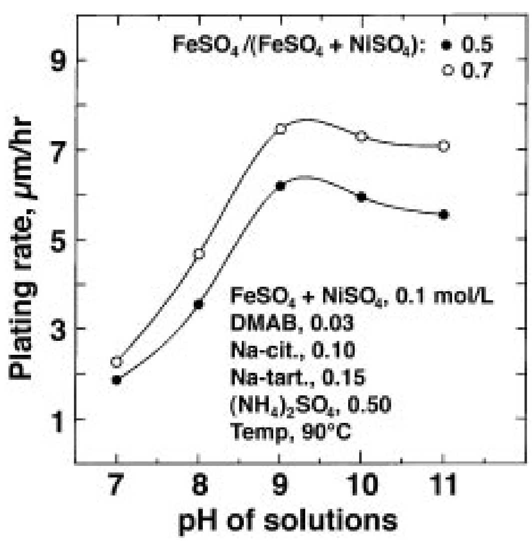

Fig. 1—Effect of solution pH on deposition rate.

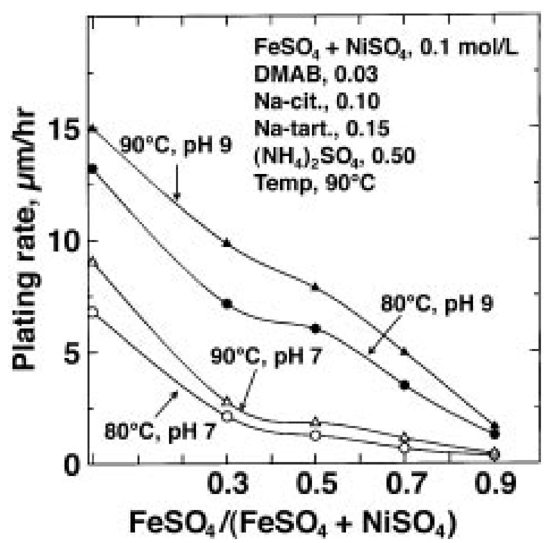

Fig. 2—Effect of metallic salt ratio $FeSO_4/(FeSO_4 + NiSO_4)$ on deposition rate.

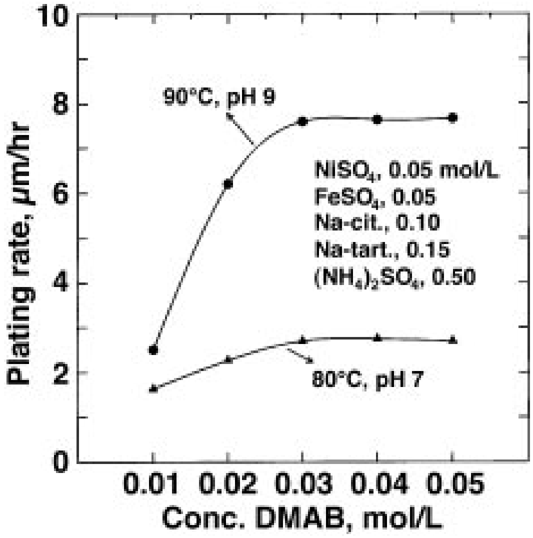

Fig. 3—Effect of DMAB concentration on deposition rate.

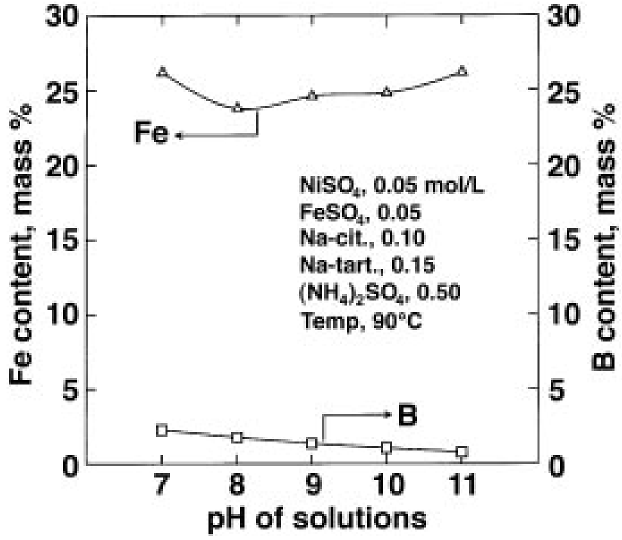

Fig. 4—Effect of solution pH on film compositions.

Deposition Rate

Under the above basic conditions, the individual effects of the components, namely, solution pH, metallic salt ratio ($FeSO_4$/[$FeSO_4$ + $NiSO_4$]) and a concentration of DMAB, on the deposition rate were investigated. First, the effect of solution pH is illustrated in Fig. 1. Here, the metallic ratio and DMAB concentration were fixed at 0.5 or 0.7, and 0.03 mol/L, respectively. Figure 1 shows that deposition proceeds within the pH range 7.0 to 11.0. Below pH 7.0, deposition is scarcely initiated. The solutions become unstable at higher pH, especially above pH 11. Precipitation of metallic hydroxide occurs during heating to the operating temperature. Both curves are found to have a peak deposition rate around pH 9.0. The decrease in deposition rate below the peak probably originates from the decrease in driving force of the reducing agent. It is inferred that the decrease of the deposition rate in the higher pH region results from the decrease of net metallic ions because of precipitation of the hydroxide.

Second, the effect of the metallic salt ratio on the deposition rate was investigated. The result is shown in Fig. 2. In this case, the solution temperature and pH were varied as indicated by the parameters. As shown in the figure, under every condition, deposition rate is reduced monotonically as the metallic salt ratio rises. At the ratio of 1.0, no deposition is observed. This may result from relatively low catalytic activity of iron in this process.

Figure 3 shows the influence of DMAB concentration on the deposition rate, as well as the operating conditions without the DMAB concentration. As shown, in both curves, the deposition rate is found to saturate at a DMAB concentration near 0.03 mol/L. It is considered that for DMAB concentration less than 0.03 mol/L, the concentration is the rate determining factor and that above 0.03 mol/L, the rate determining factor may be the supply of metallic ions. The deposition rate, therefore, remains constant as the reducing agent increases.

Film Composition

The relation between the pH of the solutions and the composition of the deposited films is illustrated in Fig. 4. The operating conditions without pH are shown in the figure. The iron content is almost independent (equal to 24 to 26 mass percent) of the change of pH. The boron content decreases slightly as the pH rises, and is reduced to as little as 0.8 mass percent at pH 11.0.

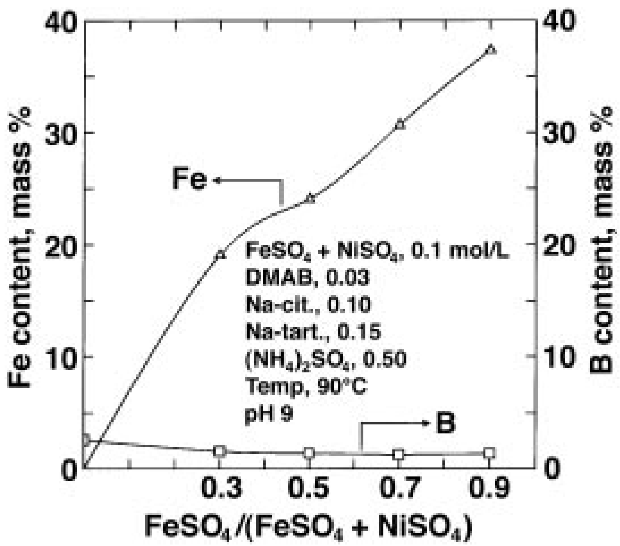

Fig. 5—Effect of metallic salt ratio $FeSO_4$/($FeSO_4$ + $NiSO_4$) on film composition.

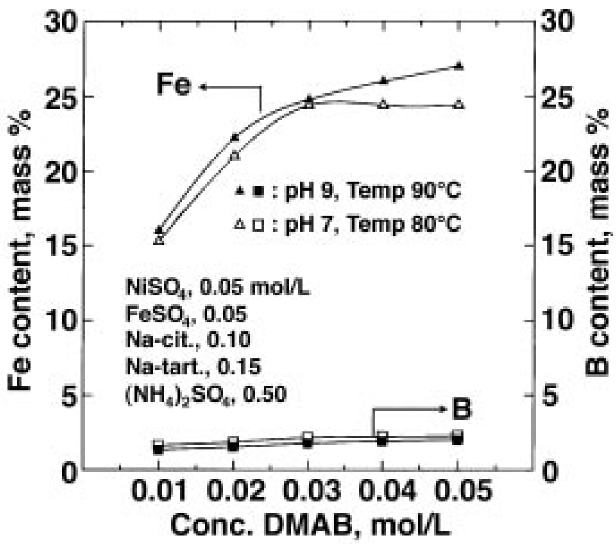

Fig. 6—Effect of DMAB concentration on film composition.

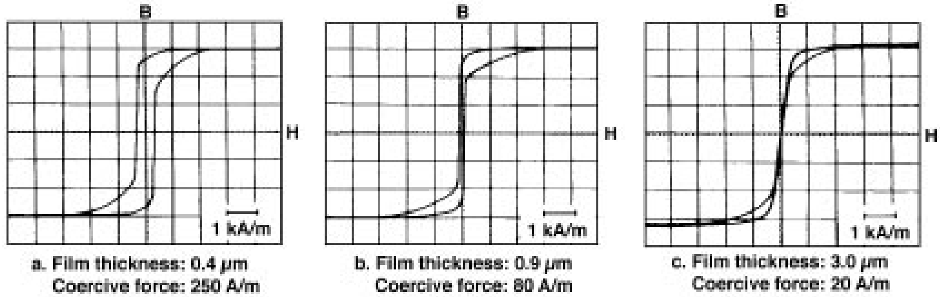

Fig. 7—Magnetic hysteresis loops of electroless Ni-Fe-P films.

Figure 5 shows the effect of the metallic salt ratio on the iron and boron content. The content of iron increases linearly and that of boron is reduced slightly as the ratio rises. It is notable that high-iron films with iron content of 38 mass percent can be produced in this solution. In Fig. 6, the relation between DMAB concentration and the alloy content is shown. Boron content is almost constant, while iron content rises with increasing DMAB concentration.

Optimum Conditions

From the above results, optimum operating conditions were determined after general consideration of the performance of solutions, namely, the stability of the solution, the deposition rate and film composition. The plating conditions are summarized in Table 2. Under these conditions, the films with optional iron content from 0 to 38 mass percent can be prepared by varying the metallic salt ratio from 0 to 0.9. In these solutions, soft magnetic films with extremely low coercive force can be obtained. Typical examples of magnetic hysteresis loops of the films are shown in Fig. 7. Here, the coercive forces are 240 A/m (3 Oe), 80 A/m (1.0 Oe) and 20 A/m (0.25 Oe) at thicknesses of 0.4, 0.91 and 3.0 µm, respectively.

Table 1
Comparison of Deposition Behavior With Various Complexing Agents

Complexing Agent mol/L	Stability of Solutions	Plating Rate µm/hr
Na-citrate 0.20	stable up to pH 10	4.7
Na-tartrate 0.25	unstable at pH 9	11.1
Na-cit 0.10 + Na-tart 0.15	stable up to pH 11	7.4

Metallic salt ratio $FeSO_4/(FeSO_4 + NiSO_4)$ and operating temperature were adjusted at 0.5 and 90 °C.

Table 2
Optimum Operating Conditions In an Electroless Ni-Fe-P Plating Solution

Component	Concentration mol/L
Nickel sulfate	0.05
Ferrous sulfate	0.05
Sodium citrate	0.10
Sodium tartrate	0.15
DMAB	0.03
Ammonium sulfate	0.50

Conditions: pH 9 (with NaOH); 90 °C

Summary

An electroless nickel iron boron plating solution using DMAB as reducing agent, and sodium citrate and sodium tartrate as complexing agents has been developed. The optimum conditions are shown in Table 2. Under these conditions, the films with optional iron content from 0 to 38 mass percent can be prepared by varying the metallic salt ratio of (ferrous sulfate/[ferrous sulfate + nickel sulfate]) from 0 to 0.9. This solution can be used to deposit soft magnetic films with coercive forces under 20 A/m (0.25 Oe).

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