

High Rate (>100 nm/min) Deposition of Ferrite Films from an Aqueous Solution

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By spin spray ferrite plating invented by the authors[1], we can fabricate ferrite films of a spinel structure from an aqueous solution at low temperature (>90°C). Because no heat treatment is required, we can use substrates of such no-heat-resistant materials as plastics. In our previous spin spray ferrite plating, a reaction solution of $\text{FeCl}_2 + \text{MCl}_2$ ($\text{M} = \text{Co}, \text{Ni}, \text{Mn}, \text{Zn}$ etc.) and an oxidizing solution of $\text{NaNO}_2 + (\text{NH}_4)\text{OCOCH}_3$ (a pH buffer) were simultaneously sprayed on to the rotating substrates[2]. The oxidizing agent, NaNO_2 , oxidizes Fe^{2+} to Fe^{3+} , which facilitates spinel formation. The pH buffer keeps the pH of aqueous solution to a desired value. Although the deposition rate of 20 nm/min was the same as or higher than that attained for ferrite films by sputtering and pulsed-laser deposition, further high deposition rate is preferable for industrial application. The deposition rate was increased up to 67 nm/min by adding NH_4OH in oxidizing solution[3]. However, the film surface was roughened as the amount of NH_4OH increased because of an unstable pH condition during film formation.

We focused attention on the work of pH buffers and seek the best pH buffer. In previous study, we found that a pH buffer having carboxylic group also works as a kind of a chelating agent to prevent the formation of hydroxide precipitation, and to promote ferrite film formation. In this study, we chose three types of pH buffers having a different number of carboxylic groups, i.e. potassium acetate, tri-sodium citrate, and di-sodium malate instead of ammonium acetate. In case of using tri-sodium citrate and di-sodium malate, they chelated Fe^{2+} so strong that we could not synthesize ferrite films. We could deposit ferrite films by using potassium acetate at the deposition rate of 60 nm/min, far higher than ammonium acetate. It is because potassium acetate keeps an aqueous solution at a higher pH, and Fe^{2+} combine with ferrite molecule more easily than ammonium acetate. That is why we decided to use potassium acetate as a chelating agent for ferrite plating.

As a result, we successfully increased the deposition rate exceeding 100 nm/min without deteriorating the quality of the films by optimizing the concentration of Fe^{2+} ions in reaction solution and potassium acetate in oxidizing solution. The film had very smooth surface and it was composed of fine grains grown perpendicular to a substrate plane as shown in Fig.2.

References

- [1] M. Abe, Y. Tamaura, "Ferrite Plating in Aqueous Solution for Preparing Magnetic Thin Film": *Advances in Ceramics*, 15, pp. 639-645 (1985).
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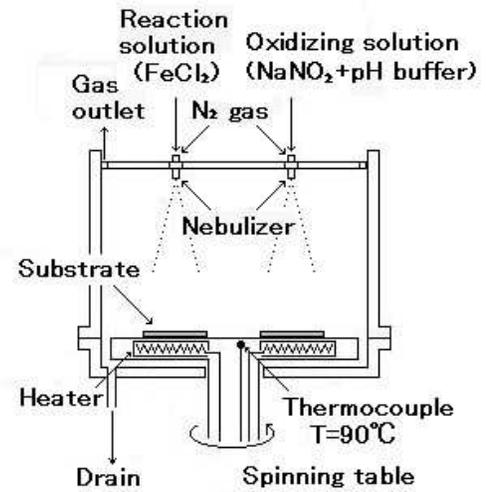


Fig.1 Spin-spray ferrite plating.

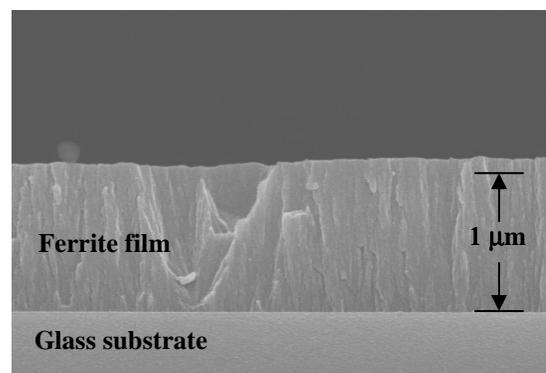


Fig.2 Cross-sectional SEM image of a ferrite film deposited for 10 minutes.