

Preparation of magnetite thin film using one-liquid ultrasonic spray plating

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Magnetite (Fe₃O₄) thin film was prepared by one-liquid ultrasonic spray plating using an aqueous solution containing FeCl₂, NaNO₂ and dextran. The starting solution was atomized into mist using an ultrasonic nebulizer and the mist was carried on to a substrate. Using this method, Fe₃O₄ film was deposited at 90°C; however, NaCl was coexisted with the film and the crystallinity and magnetic property of the film was low. After post deposition annealing at 850°C in N₂, NaCl was evaporated, and crystallinity and magnetic property of the film was improved. The mechanism and property of the film was compared with spin spray plating method invented by Abe et al.

Key words: magnetite, film, low temperature deposition, ultrasonic spray plating

1. INTRODUCTION

Ferrite films are promising for suppressing electromagnetic noises in GHz range. Ferrite films also have a potential to use novel memory devices [1]. Ferrite thin films have been deposited by several methods such as chemical vapor deposition (CVD) [2], sputtering [3], pulsed laser deposition (PLD) [4], chemical solution deposition (CSD) [5]. In addition to these methods, Abe and Tamaura invented "ferrite plating method" in 1983 with aqueous solution at 60-100°C [6]. Using this method, several spinel ferrite films with general formula; (Fe, M)₃O₄ where M=Fe, Co, Ni, Zn, Al, Cr, Ti etc. have been prepared so far. The process of ferrite plating in case of magnetite is in the following [7];

(1) Initial stage of the surface of the substrate is covered with OH⁻ by controlling pH.

(2) Aqueous solution of FeCl₂ is supplied on the surface of substrate. Then H⁺ is replaced by Fe²⁺, and the surface of the substrate is covered with Fe²⁺ ions.

(3) Aqueous solution of NaNO₂ is supplied on the surface of substrate as an oxidizing reagent. As the result, Fe²⁺ ions are partially oxidized into Fe³⁺ and the surface of the film is covered with O²⁻ ions. This means the Fe₃O₄ is formed as a result of electroless (electrochemical) plating.

(4) Aqueous solution of FeCl₂ is supplied on the surface again. Then Fe²⁺ ions are adsorbed on the surface of the film.

(5) The process of (3) and (4) is repeated until desired

thickness of Fe₃O₄ thin film.

For this process, Abe et al. invented a "spin-spray ferrite plating" apparatus shown in Fig. 1. The apparatus is composed of two nozzles; one nozzle is used for the supply of reaction solution (FeCl₂) and another is used for the supply of oxidizing solution (NaNO₂). The substrate is placed on the spinning table. In the oxidizing solution, CH₃COONH₄ (or CH₃COOK) is also added as a pH buffer. Therefore, this method requires two liquids for ferrite plating. Recently, Abe et al. developed "one-liquid" spin spray ferrite plating method [8]. In the "one-liquid" method, aqueous solution of FeCl₂ is mixed with NaNO₂+CH₃COOK solutions are mixed together with addition of dextran [(C₆H₁₂O₆)_n, n=1100-1700] as a complexing agent. By using this method, they succeeded to prepare Fe₃O₄ thin film at 90°C. This method is excellent because preparation of ferrite thin films can be carried out at low temperature below 100°C. Therefore, this method seems to be in harmony with the environment.

However, the spin spray ferrite plating method contains a fatal problem that a lot of amount of solution should be supplied to prepare the ferrite thin film. In other words, the yield to prepare the ferrite thin film is very low.

We think that another method should be proposed to increase the yield. Therefore, we tried to prepare Fe₃O₄ thin film by "ultrasonic spray plating method". The purpose of this work is to examine the possibility of ferrite plating by ultrasonic spray plating.

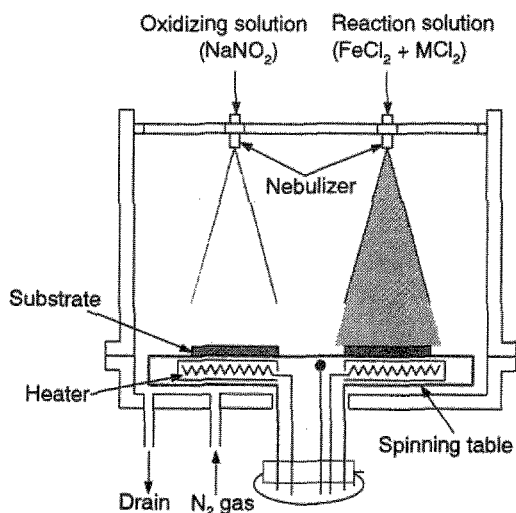


Fig. 1. Schematic drawing of spin spray ferrite plating apparatus invented by Abe et al.[7].

2. EXPERIMENTAL

One aqueous solution containing dextran (0.8 g/l), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (160 mM), CH_3COOK (60 mM) and NaNO_2 (5 mM) were prepared. The one-liquid solution was poured into the conical flask. The solution in the conical flask was atomized by ultrasonic nebulizer and the mist was carried to the surface of Vycor glass substrate by N_2 carrier gas. The substrate was heated to 90°C by hotplate. Schematic drawing of the apparatus used in this work was shown in Fig. 2.

The film was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and vibration sample magnetometer (VSM).

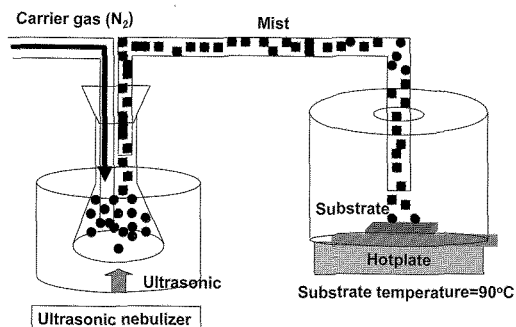


Fig. 2. Schematic drawing of ultrasonic spray plating apparatus.

3. RESULTS AND DISCUSSION

Figure 3(a) shows XRD pattern of as-deposited thin film. This figure indicates that Fe_3O_4 is formed; however, the intensity of diffraction peak was very weak and broad. This suggests that the Fe_3O_4 is amorphous-like or nano-crystalline. Figure 4(a) shows SEM photograph of the as-deposited film. This figure suggests that the surface of the film is rough and deposition of fine particles having less than $1\ \mu\text{m}$ in diameter are dispersed. In this figure, deposition of string-like objects shown in bright color due to charging up is also observed. This stringlike objects seems to be dextran. Figure 5(a) shows

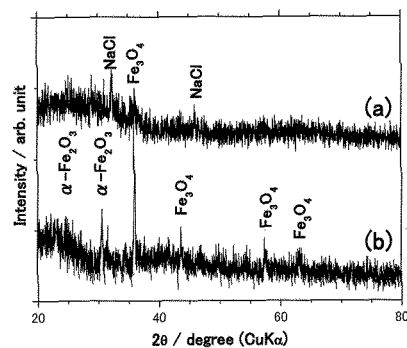


Fig. 3. XRD pattern of (a) as-deposited thin film deposited at 90°C and (b) after post deposition annealing in N_2 at 850°C .

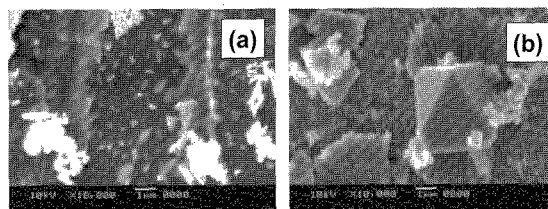


Fig.4. SEM photograph of (a) as-deposited thin film deposited at 90°C and (b) after post deposition annealing in N_2 at 850°C .

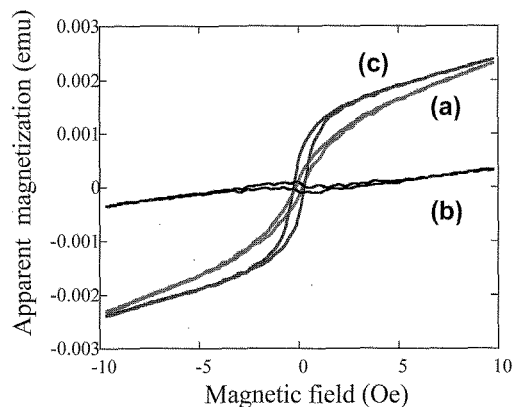
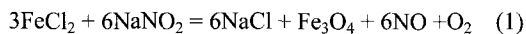


Fig. 5. M-H curves of (a) as-deposited thin film deposited at 90°C , after post deposition annealing at 850°C in (b) air and (c) N_2 , respectively.

an M-H curve for the as-deposited film. In this work, it was difficult to determine the volume of the film; therefore, the vertical axis in Fig. 5 is not magnetization. However, the area of the sample is same and the films were deposited by the identical deposition procedure, it is possible to compare the shape of the M-H curves. Figure 5(a) indicates that the as-deposited film shows slight hysteresis, suggesting ferrimagnetic property. By comparing Fig. 3(a) and Fig. 5(a), it can be considered that as-deposited film is composed of the aggregating fine Fe_3O_4 particles. This means that preparation of

Fe₃O₄ thin film by one-liquid ultrasonic spray plating is possible.

However, it should be noted that formation of NaCl is also detected as shown in Fig. 3(b). NaCl is formed as the byproduct of Fe₃O₄ according to the following reaction;



We compared our results (ultrasonic spray plating) with those reported by Abe et al. (spin spray plating). Coexistence of NaCl and dextran was not reported by spin spray plating, while the coexistence of these was apparent by ultrasonic spray plating. It should be noted that the amount of solution for the deposition of Fe₃O₄ thin film is absolutely different. By ultrasonic spray plating, the amount of solution needed to prepare the film is small (around 50 ml); on the other hand, by spin spray plating, the amount is so large (around several liters). Since the raw material of Fe₃O₄ is aqueous solutions of FeCl₂ and NaNO₂, it is reasonable to form NaCl as shown above. Therefore, we thought that the reason why the formation of NaCl is not detected by spin spray plating is following;

NaCl is actually formed by the spin spray plating; however, since the amount of supplied solutions is too many, the NaCl would be flushed and does not remain on the surface of the film. As well as NaCl, the dextran deposited on the surface of the film is also flushed by the supplied solutions. On the other hand, by ultrasonic spray plating, all amount of supplied solution remains on the surface of the film; therefore it is impossible to remove NaCl and dextran from the surface of the film. This consideration is also supported by the crystallinity of the Fe₃O₄ thin film. By spin spray plating, the crystallinity of the Fe₃O₄ is high; while that of Fe₃O₄ is very low by ultrasonic spray plating as shown in Fig. 3(a). It is speculated that the decrease of crystallinity is brought about by the coexistence of NaCl.

As mentioned above, it was impossible to prepare single phase Fe₃O₄ with high magnetization in the as-deposited form, post deposition annealing was carried out at 850°C in air and in N₂. The film after annealing in air was composed of single phase α-Fe₂O₃ (XRD patterns are not shown here) and M-H curve showed paramagnetic like property as shown in Fig. 5(b). On the other hand, the film after annealing in N₂, resultant phase is Fe₃O₄ with trace α-Fe₂O₃. SEM image of the film after annealing in N₂ is shown in Fig. 4(b). After annealing, stringlike objects were not observed and large grains with octahedral morphology were observed. The octahedron seems to be Fe₃O₄ after abnormal grain growth. Since Fe₃O₄ has cubic spinel structure (space group; Fd3m), automorphic form is octahedron. It was also found that NaCl was not detected after the post deposition annealing. This indicates that the NaCl was evaporated during annealing process. M-H curve after annealing in N₂ was shown in Fig. 5(c). This figure indicates that the ferrimagnetic property was improved by the annealing; however, the curve shows the magnetization is not saturated and the magnetization at 10 kOe is almost same with that of as-deposited film. This suggests that magnetization of as-deposited film is almost same with that of film after annealed in N₂.

4. CONCLUSIONS

We developed an ultrasonic spray plating method using one-liquid source and prepared Fe₃O₄ thin film on glass substrate at 90°C. Starting materials were same with those used in the spin spray plating method reported in the literature (aqueous solution of FeCl₂, NaNO₂ and dextran). It was found that considerable amount of NaCl and dextran are coexisted with Fe₃O₄ by the ultrasonic spray plating though the coexistence is not detected by the spin spray plating method. It was suggested that ultrasonic spray plating method has an advantage that the amount of solutions needed to prepare the film is much smaller than that in the spin spray plating. However, it is impossible to remove NaCl and dextran on the surface of the film by ultrasonic spray plating. Therefore, post deposition annealing in N₂ was used to remove the NaCl and dextran and to improve the crystallinity and magnetic property of the Fe₃O₄ film.

References

- [1] N. Wakiya, K. Shimizu, S. Mizukami, K. Shinozaki and N. Mizutani, *Appl. Phys. Lett.*, **85**, 3772-3774 (2004).
- [2] P. Gibart, M. Robbins and A. B. Kane, *J. Crystal Growth*, **24-25**, 166-171 (1974).
- [3] M. Naoe, Y. Hoshi and S. Yamanaka, *J. Crystal Growth*, **45**, 361-364 (1978).
- [4] N. Wakiya, K. Shinozaki and N. Mizutani, *Appl. Phys. Lett.*, **85**, 1199-1201 (2004).
- [5] Jae-Gwang Lee, Hi Min Lee, Chul Sung Kim and Oh Young-Jei, *J. Mag. Mag. Mater.*, **177-181**, 900-902, (1998).
- [6] M. Abe, Y. Tamaura, *Jpn. J. Appl. Phys.*, **22**, L511 (1983).
- [7] M. Abe, *Electrochim. Acta*, **45**, 3337-3343 (2000).
- [8] J. Miyasaka, M. Tada, M. Abe and N. Matsushita, *J. Appl. Phys.*, **99**, 08M916-1-3 (2006).

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