Preparation and Characterization of NiZn Ferrite Thin Films by a Spray Pyrolysis Deposition Method

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スプレー熱分解法による NiZn フェライト薄膜の作製とその特性

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Nickel-zinc (NiZn) ferrite thin films were successfully prepared from nickel, zinc, and iron nitrates aqueous solutions at a substrate temperature between 350 and 500°C in air by a spray pyrolysis deposition method (SPD), where the film thickness was held at about 1 μm and the deposition rate was varied between 100 and 200 nm/min depending on the substrate temperature. The crystallinity of as-prepared NiZn ferrite films became higher with increasing substrate temperature, but it could not reach a suitable value to produce magnetic properties suitable for practical applications. It was then necessary to anneal the films at higher temperatures above 600°C. Magnetic properties comparable with those of bulk NiZn ferrite and applicable to practical magnetic devices were obtained by annealing at 750°C. Furthermore, we attempted the preparation of well-crystallized NiZn ferrite thin films by adding hydrogen peroxide to the starting solutions.

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1. Introduction

High frequency electronic devices have been used for high performance signal transmission recently, in which electro-magnetic immunity (EMI) is required for noise reduction.¹⁾ The formation of magnetic thin films is essential for integrated and miniaturized EMI components and other magnetic devices. NiFe²⁾⁻⁴⁾ and CoZrNb⁵⁾ films were investigated for this purpose, but their eddy current losses due to their low resistivity caused low magnetic properties in high frequency range.

Bulk ferrites are good magnetic materials with high resistivity, which are widely used for EMI components and transformers. Then the preparation of ferrite thin films is essential for the downsizing of these components. Many kinds of techniques such as sputtering,^{6),7)} sol-gel,⁸⁾ CVD⁹⁾ and ferrite plating^{10),11)} have been attempted for ferrite film formation, but production cost, deposition speed and/or magnetic properties unsatisfied yet.

Of thin film formation methods, a spray pyrolysis deposition method (SPD)¹²⁾ is possibly carried out by using simple equipments without complicated vacuum system different from vapor deposition and sputtering. This method is a versatile technique for producing various materials in wide range of composition, size and morphology.¹³⁾⁻¹⁷⁾ The spray pyrolysis deposition of cobalt ferrite films from iron(III) chloride and cobalt sulfate solutions has been reported.¹⁸⁾ We have also reported that well-crystallized spinel zinc ferrite thin films could be prepared from mixed zinc and iron nitrates aqueous solution at a low temperature under 400°C by SPD.¹⁹⁾

In this paper, we have further studied the preparation of NiZn ferrite thin films probably applicable to practical integrated magnetic devices. The crystal structure, morphology and magnetic properties of these sprayed films have been related to the preparation conditions such as substrate temperature, annealing and hydrogen peroxide addition.

2. Experimental procedure

Reagent grade Ni(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were used as starting chemicals. These three metal nitrates of 0.0072 M Ni²⁺, 0.0128 M Zn²⁺ and 0.040 M Fe³⁺ were dissolved separately in deionized water, followed by mixing all of solutions in 1:1:1 volumetric proportion for a spray solution. NiZn ferrite thin films were deposited by spraying the above mixed solution onto glass substrates (Corning 1737) with 25 mm × 25 mm × 1 mm in size.

Detailed illustration of the setup of SPD used is shown in Fig. 1. A glass substrate was mounted on a holder, which was put on the surface of a hot plate. A temperature controller was used to keep the deposition temperature within ±5°C through a thermocouple connected to the glass substrate. A spray solution was atomized in air via a pneumatic spray system under an air pressure of 0.25 MPa. The atomized droplets were transferred onto the heated glass

Fig. 1. Experimental setup of SPD apparatus.

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Table 1. Experimental Parameters

Starting materials	Ni (NO ₃) ₂ 6H ₂ O Zn (NO ₃) ₂ 6H ₂ O Fe (NO ₃) ₃ 9H ₂ O
Solvent	Water
Concent. Ni / Zn / Fe	0.0072 / 0.0128 / 0.04 (M)
Ferrite composition	Ni _{0.36} Zn _{0.64} Fe ₂ O ₄
Film thickness	~1 μ m
Spray rate	0.3 ml/s
Duration of one spray	0.5 s
Number of times	30 ~ 60
Substrate temperature	350 ~ 500°C

substrate for 0.5 s intermittently. Because the substrate temperature was lowered under the effect of spraying, several seconds of intervals were required to recover the pre-set temperature after each spraying. Solution flow rate and nozzle-substrate distance were kept at 0.5 ml/s and 30 cm, respectively. Experimental parameters are summarized in Table 1.

The crystal structure of deposited films was determined by X-ray diffraction (XRD), and film morphology was observed by a scanning electron microscopy (SEM). Film thickness was estimated from a fundamental parameter method²⁰⁾ using an X-ray fluorescence analysis (XFA), and magnetization measurement was carried out using a vibrating sample magnetometer (VSM) under an applied magnetic field of 800 kA/m at room temperature.

3. Results and discussion

3.1 Crystalline state and morphology of film

In the X-ray diffraction pattern of the film deposited at a temperature of 350°C, the (311) plane of spinel ferrite was clearly shown together with the slight profiles of the (400) and (440) planes (Fig. 2). It was noteworthy that NiZn ferrite film was possibly prepared from metal nitrates solution at this low-temperature by SPD and composed of spinel structure without another phase. This fact means that the pyrolysis of all metal nitrates occurred and the chemical reaction among resulting metal oxides was completed throughout the process. It is also shown that the crystallization of spinel ferrite increased with an increase in substrate temperature. The well-defined X-ray patterns corresponding to spinel ferrite were all observed for the films prepared here at temperatures higher than 350°C, in the same way as Zn ferrite films prepared by SPD.¹⁹⁾

Figure 3 shows the SEM images of the surface and cross section of NiZn ferrite thin films prepared at temperatures from 350 to 500°C. The surface of the thin film prepared at temperatures below 400°C was flat and dense. The thin film thickness was held at about 1 μ m in this study, as shown in Table 1, where required 30 times of intermittent spraying with each interval of 10 s at the substrate temperature of 400°C. The deposition rate at a temperature of 400°C was about 200 nm/min, and was several times higher than that in the ferrite plating method.²¹⁾ The unevenness and porous structure was observed in the film deposited at temperatures above 450°C. The film formation processes via SPD have been divided into four steps according to the substrate temperature, as shown in Fig. 4.^{22),23)}

It has been assumed that droplets of sprayed solution reach heated glass substrate as a liquid phase, although the size of droplet becomes small accompanied by slow evaporation of solvent below 400°C, corresponding to A process in

Fig. 2. XRD profiles of NiZn ferrite films prepared at substrate temperatures between 350 and 500°C.

Fig. 3. SEM images of surface and cross section of NiZn ferrite thin films prepared at substrate temperatures from 350 to 500°C.

Fig. 4. Subsequently, the metal nitrates are pyrolyzed and the resulting metal oxides react mutually after the completion of the evaporation of solvent. At a high temperature of 450°C, the rapid evaporation of solvent, the pyrolysis and reaction of starting materials and then the precipitation of the final product occur intensively before the drops reach the substrate (B process). As a result, uneven and powdery film was formed as a temperature increased above 450°C, corresponding to C and/or D process in Fig. 4.

3.2 Magnetic properties

Figure 5 shows the saturation magnetic flux densities, B_s , of the NiZn ferrite thin films as a function of the substrate temperature. The dense but poor crystallized thin film prepared at 350°C as described above, showed low saturation magnetic flux density of 0.06 T, however, the saturation

Fig. 4. Schematic representation of a spray pyrolysis deposition process according to the substrate temperature based on Viguie's model.²²⁾

Fig. 5. Saturation magnetic flux densities (B_s) of ferrite thin films prepared at substrate temperatures from 350 to 500°C.

magnetic flux density of the dense and well-crystallized film prepared at 400°C had the highest value of 0.21 T. Furthermore, the films prepared at a temperature higher than 450°C show a low saturation magnetic flux density of 0.12 T, because these films were good crystalline but porous. Here, the saturation magnetic flux density of 0.21 T corresponds to about 60% of that of the bulk ferrite with the same composition,²⁴⁾ and then it is suggested that the film consists of super-paramagnetic phase with size-effect and/or non-magnetic phases such as amorphous state in addition to predominant magnetic phase.

3.3 Effect of annealing

Oka et al. reported that the saturation magnetic flux den-

Fig. 6. B-H curves of NiZn ferrite films prepared. (a) as-deposited, annealed at (b) 600°C and (c) 750°C.

Fig. 7. XRD profiles of NiZn ferrite films as-deposited, and annealed at 600 and 750°C.

sity of MnZn ferrite thin films prepared by sputtering at room temperature was improved by annealing at 800°C in N_2 because of the increase in grain growth and crystallization.²⁵⁾ Then, NiZn ferrite thin films that were prepared at 400°C by SPD were further annealed for in air 2 h at 600 and 750°C for 2 h in air separately. As-deposited film showed a low saturation magnetic flux density of about 60% of the bulk ferrite (Fig. 5), however the saturation magnetic flux density of this film became higher with an increase in annealing temperature, as shown in Fig. 6. The saturation magnetic flux density of NiZn ferrite film by annealed at 750°C is 0.37 T, which is the same as that of bulk NiZn ferrite. This annealing effect is probably due to the transformation of super paramagnetic or non-magnetic amorphous phase to the ferromagnetic spinel phase and grain growth by the annealing. Matsushita et al. also reported that the saturation magnetic flux density of well-crystallized NiZn ferrite thin film prepared by a spin-spray-coating method was comparable with that of the bulk.²¹⁾ The XRD patterns of NiZn ferrite films annealed at 600°C and 750°C are shown in Fig. 7. It seems that poorly-crystallized spinel ferrite were formed in as-deposited film, but the crystallinity of the film became higher with an increase in annealing temperature. Figure 8 shows the SEM photographs of the cross section of

Fig. 8. Cross sectional views of NiZn ferrite films prepared. (a) as-deposited and (b) annealed at 750°C.

Fig. 9. XRD patterns of NiZn ferrite films prepared from starting spray solution added hydrogen peroxide of 0.01 to 0.1 M.

NiZn ferrite films. As-deposited film consisted of small particles of several nanometers that were grown up to the size of about 100 nm by annealing at 750°C.

3.4 Effect of hydrogen peroxide addition

Okuya et al. have successfully realized the enhanced deposition of SnO_2 films by adding hydrogen peroxide (H_2O_2) which is expected as pro-oxidant to the starting solutions.²⁶⁾ The addition of H_2O_2 of 0.01–0.1 M to starting solutions was tested for the low temperature formation of NiZn ferrite film. The XRD pattern of the spinel was seen slightly in the film prepared without H_2O_2 , as shown in Fig. 9. The crystallinity of the spinel was improved effectively with increasing H_2O_2 amount added until 0.04 M, but the crystallinity became poor at 0.1 M. The addition of the adequate amount of H_2O_2 to starting solution could promote the formation of the spinel ferrite by making oxygen-rich atmosphere. It is possibly that excess addition of H_2O_2 made more stable metal complex as precursors and then inhibited the formation of the spinel ferrite.

The saturation magnetic flux density of NiZn ferrite thin films prepared at 350°C with various amounts of H_2O_2 added are shown in Fig. 10. The saturation magnetic flux density

Fig. 10. Saturation magnetic flux densities (B_s) of ferrite thin films prepared from the starting spray solution added hydrogen peroxide of 0.01 to 0.1 M.

showed the similar tendency to the crystallinity shown in Fig. 9. The saturation magnetic flux density of the film prepared by the addition of hydrogen peroxide of 0.04 M is 0.27 T that is equivalent to that annealed at 600°C.

4. Conclusions

We have successfully prepared well-crystallized spinel $\text{Ni}_{0.36}\text{Zn}_{0.64}\text{Fe}_2\text{O}_4$ ferrite thin films from mixed metal nitrates aqueous solution at a substrate temperature from 350 to 500°C in air by SPD. The surface of the thin film deposited at a temperature below 400°C was flat and dense. The saturation magnetic flux density of the film deposited at a substrate temperature of 400°C was 0.21 T, which was about 60% of that of bulk NiZn ferrite with the same composition. Further annealing of as-prepared film above 600°C was needed to get enough magnetic properties. The same saturation magnetic flux density of 0.37 T as the bulk ferrite was, thus, obtained by annealing at 750°C. The deposition of NiZn ferrite film was also possible at a low substrate temperature of 350°C by adding H_2O_2 of 0.04 M to starting solution, but the saturation magnetic flux density was 0.27 T.

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