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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

NiZnCo ferrite films by spin spray technique: morphology and magnetic properties

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Abstract In the present study, highly crystallized spinel NiZnCo ferrite films were prepared by spin-spray ferrite plating, employing a reaction solution (containing Fe^{2+}, Ni^{2+}, Zn^{2+} and Co^{2+}) and an oxidizing solution (KNO_2 + CH_3COOK). The solutions were sprayed independently onto a glass substrate maintained at 90 °C. Series of films with various Zn and Co compositions were prepared and their structural and magnetic properties were studied. The films had a columnar structure perpendicular to the substrate surface as confirmed by scanning electron microscopy (SEM) studies and showed no preferential orientation confirmed by X-ray diffraction (XRD). The films had a saturization magnetization M_s of 325–520 emu/cc and H_c of 5–12 Oe. At the optimized compositions, we obtained an initial permeability of around 190 ($Ni_{0.18}Zn_{0.6}Co_{0.02}Fe_{2.2}O_{4-\delta}$) and resonance frequency f_r of 300 MHz ($Ni_{0.16}Zn_{0.2}Co_{0.02}Fe_{2.62}O_{4-\delta}$). Such films with high permeability can be employed as trimming layers of inductors to increase the inductance and films with high resonance frequency can be used as electromagnetic noise suppressors at high frequency.

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Introduction

Ferrites are known to have combination of properties that are unique to themselves, like high resistivity, chemical inertness, temperature-coefficient of permeability, magnetostriction and economy of materials and manufacturing [1, 2]. As an added advantage, the properties are easily tunable as required for a particular application. For most of the application, the main consideration is the permeability and resonance frequency [3]. Soft magnetic films with real permeability above several hundred megahertz can be used as trimming layers of planar inductors to increase their inductance [4]. Materials with high imaginary permeability in the gigahertz range can be used as conducted noise suppressors, which reduce the electromagnetic interference on printed circuit board [5]. Since high resistivity is required for these applications, ferrite films are one of the superior candidates.

Ferrite films are usually prepared by physical vapor deposition techniques such as, evaporation, sputtering, molecular beam epitaxy, pulsed laser deposition, etc [6–10], nevertheless these techniques are energy intensive and involves high temperature processing. On the other hand, wet chemical/soft solution processes attract a great interest because of its low process temperature, simplicity and economic considerations.

Spin-spray technique is a kind of soft solution process, an outstanding technique by which highly crystallized spinel ferrite films are obtained at low deposition temperature (<100 °C) without post annealing [11]. Spin-spray technique was previously employed for making various ferrite films ($M_xFe_{3-x}O_4$, where M = Mn, Zn, Co., etc.) [4, 12].

In this work, we prepared NiZnCo ferrite films with varying composition and the structure and morphology were analyzed. The dependence of magnetic properties like saturation magnetization (M_s), coercivity (H_c) and permeability on the composition of the films were studied. The purpose of this study, was to prepare ferrite films with a wide range of permeability and resonance frequency.

Experiments

Film preparation

The films were deposited by spraying a reaction solution of $FeCl_2 + NiCl_2 + ZnCl_2 + CoCl_2$ and an oxidizing solution of $KNO_2 + CH_3COOK$ independently onto a rotating disc mounted with glass substrates. The spin-spray apparatus and the experimental conditions are shown in Fig. 1. The temperature of the substrate surface was maintained constant at 90 °C by spraying distilled water before starting with the spraying of reaction and oxidizing solutions. Micro cover glass 30 × 40 mm were used after a preliminary plasma treatment for 2 min. The film composition was varied by changing the initial concentration of $ZnCl_2$ (0.2mM–0.8mM) and $CoCl_2$ (0.1 mM–0.6 mM) in the reaction solution. The concentration of $NiCl_2$ (5.2 mM) and $FeCl_2$ (16.6 mM) was kept constant in all the experiments. Spray duration was 30 min in all the experiments.

Characterization

X-Ray diffraction (XRD) studies were carried out to identify the crystal structure. Microstructure and film thickness were observed by cross-sectional scanning electron microscopy (SEM) images. The elemental composition was estimated by inductive coupled plasma spectroscopy (ICPS). The magnetic properties like saturation magnetization (M_s) and coercivity (H_c) were estimated with the hysteresis loops measured by a vibrating sample magnetometer (VSM). The complex permeability ($\mu' = \mu' - j\ \mu''$) of the films up to 3 GHz were measured by the Shielded loop coil permeance meter [13].

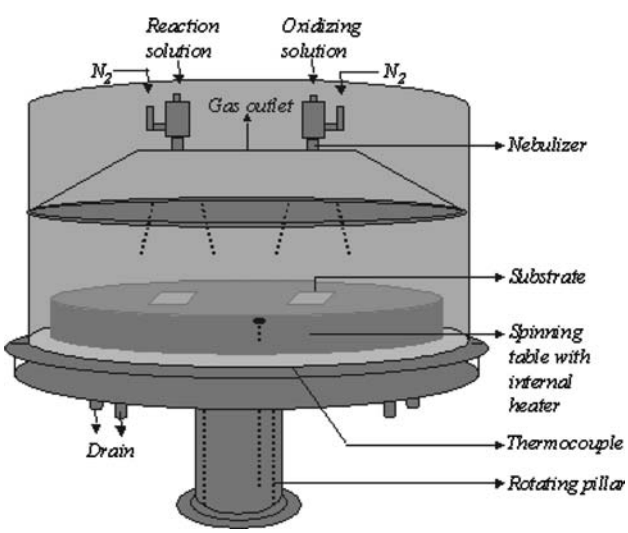

Fig. 1 Schematic illustration of ferrite plating apparatus

Results and discussion

Principle of ferrite plating

A schematic illustration of the mechanism involved in the ferrite plating is given in Fig. 2. The principle involves the adsorption of Fe^{2+} onto a substrate mediated by OH^- groups and further oxidation of Fe^{2+} to Fe^{3+}, when mixed with an oxidizing solution maintained at a suitable pH using a buffer. Fresh Fe^{2+} ions are again adsorbed on the pre-adsorbed layer of Fe^{2+} and Fe^{3+} forming a ferrite layer. Since the ferrite layer thus formed has OH^- group on the surface, the process is repeated and the film increases in thickness. The metal ions (Fe^{2+}, Fe^{3+}) are chemically bonded onto the substrate by coordination bonds intermediated by hydroxyl groups. Hence, the ferrite plated films have strong adhesion to the substrate, though prepared at low temperature. The main process parameters were concentration of metal chloride solution, oxidizing agents, pH of the oxidizing solution, etc.

Structure and morphology

By varying the concentration of $ZnCl_2$ and $CoCl_2$ in the reaction solution from 0.2 mM to 0.8 mM and 0.1 mM to 0.6 mM respectively their concentration in the film varied from 0.2 to 0.8 (C_{Zn}) and 0.01 to 0.06 (C_{Co}). The Ni content of the film was almost constant (0.17–0.2). The XRD results confirmed that the films had highly crystalline spinel structure without any preferential orientation. Figure 3a shows the XRD patterns of the prepared films with C_{Zn} = 0–0.6. A peak shift towards lower angles can be noticed in accordance with the lattice expansion with Zn concentration. Figure 3b shows the calculated lattice

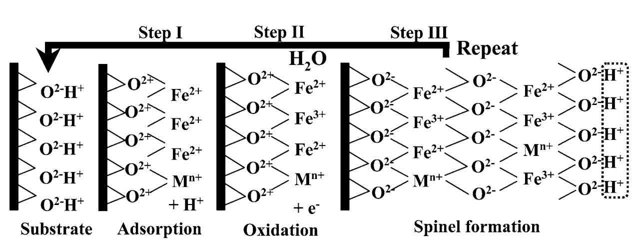

Fig. 2 Schematic illustration of the mechanism of ferrite plating

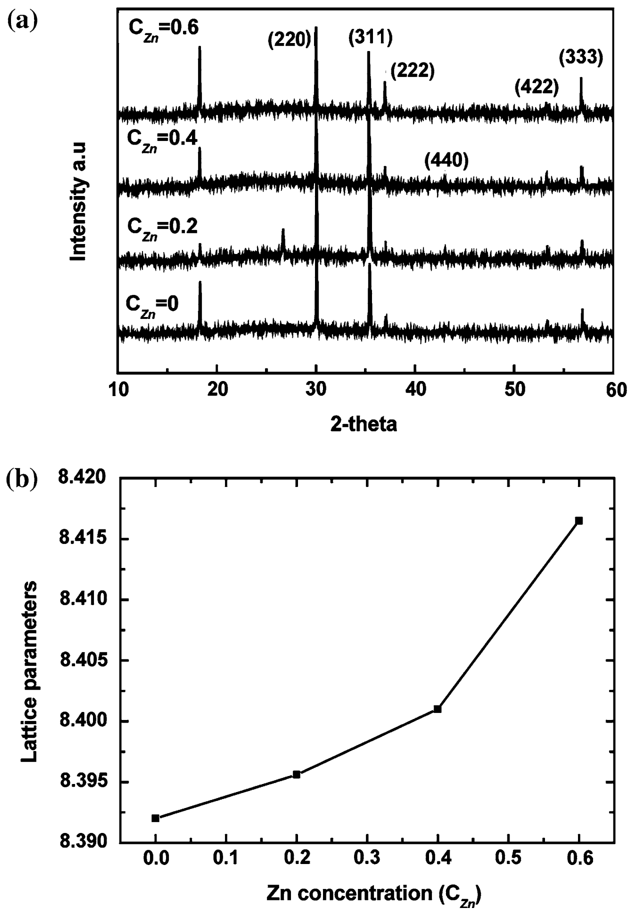

Fig. 3 (**a**) XRD spectra of NiZnCo ferrite; (**b**) lattice constant in MnZnCo Ferrite films plotted as a function of C_{Zn}

constants for Zn = 0–0.6. By replacing the Fe ions with Zn ions, the lattice constant increased because the ionic radius of Zn is larger than that of Fe [14].

Figure 4 shows the representative SEM image of the film. From the SEM image, it can be inferred that the film had a columnar structure grown perpendicular to the substrate surface. The deposition rate can be estimated to be 35.6 nm/min. The columnar diameter of the ferrite-plated films generally varies between few hundred nanometers. Smaller grains are formed at the initial stages of the growth that becomes distinct columns later. Recently, we succeeded in preparing fine-grained films with uniform columnar diameter throughout the length, which is an important factor in controlling the film resistance, results to be published.

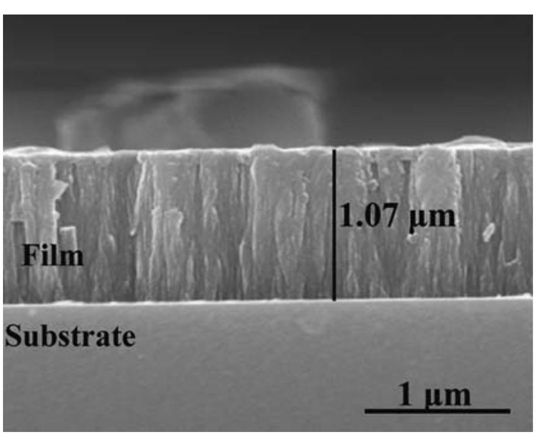

Fig. 4 Representative cross sectional SEM image of the as-prepared NiZnCo ferrite film

Magnetic properties

Figure 5 describes the dependence of M_s and H_c on the Zn and Co content (C_{Zn} and C_{Co}) of the film. With an increase in Zn, both M_s and H_c decreased. Although M_s and H_c remained constant with increase C_{Co} up to 0.03, it decreased on further increase of C_{Co}. The Fe content (C_{Fe}) in the film decreased from 2.5 to 2.2 with an increase of C_{Zn} (or C_{Co}) while the Ni (C_{Ni}) remained almost constant. Figure 6a and b shows the dependence of real permeability and resonance frequency on C_{Zn} of the film respectively. The real permeability μ' at lower frequency increased with Zn concentration, a maximum μ' of 189 was obtained with

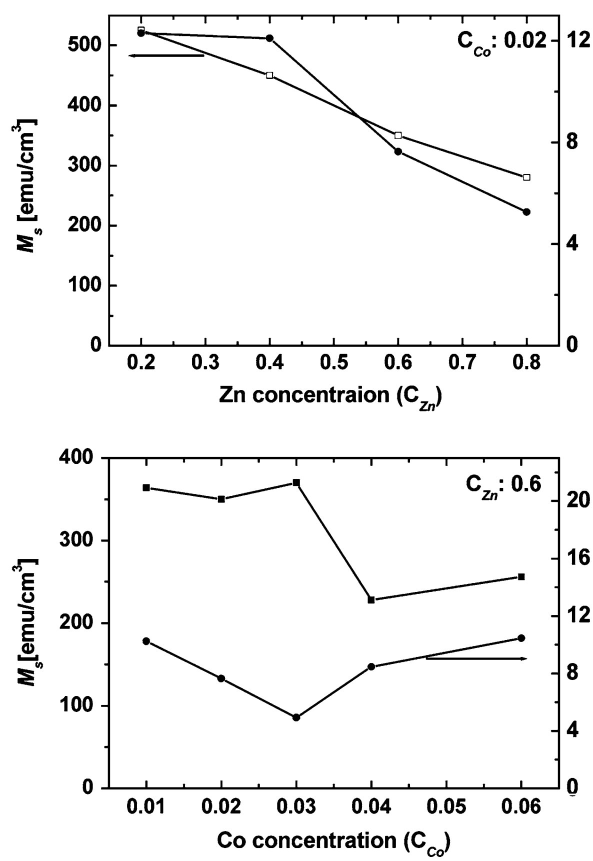

Fig. 5 M_s and H_c for different Zn and Co concentration (C_{Zn} and C_{Co}) of the films

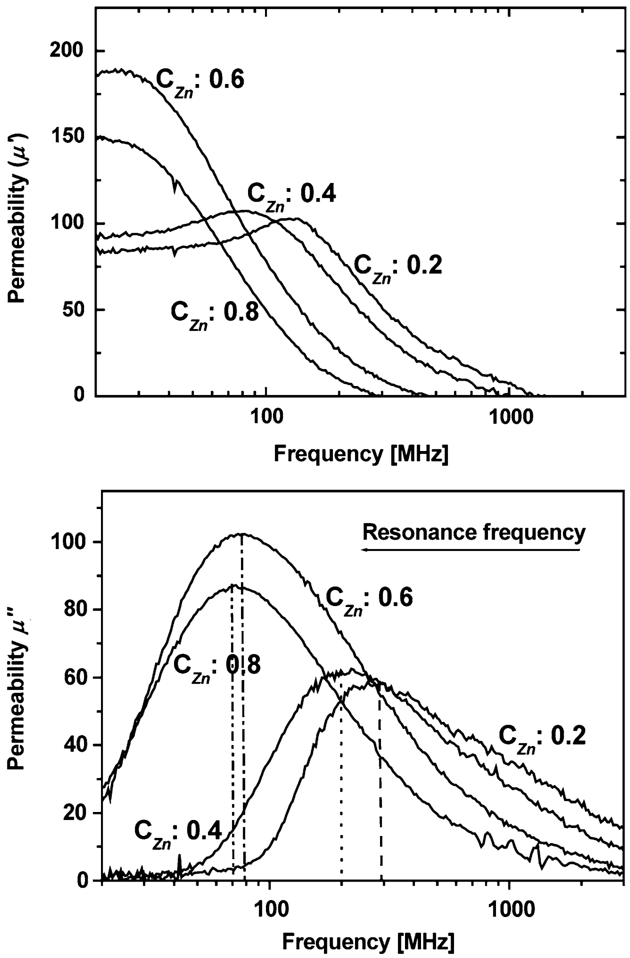

Fig. 6 Permeability and resonance frequency of NiZnCo ferrite films with C_{Zn} = 0.2–0.8 (Co concentration was maintained at C_{Co} = 0.02)

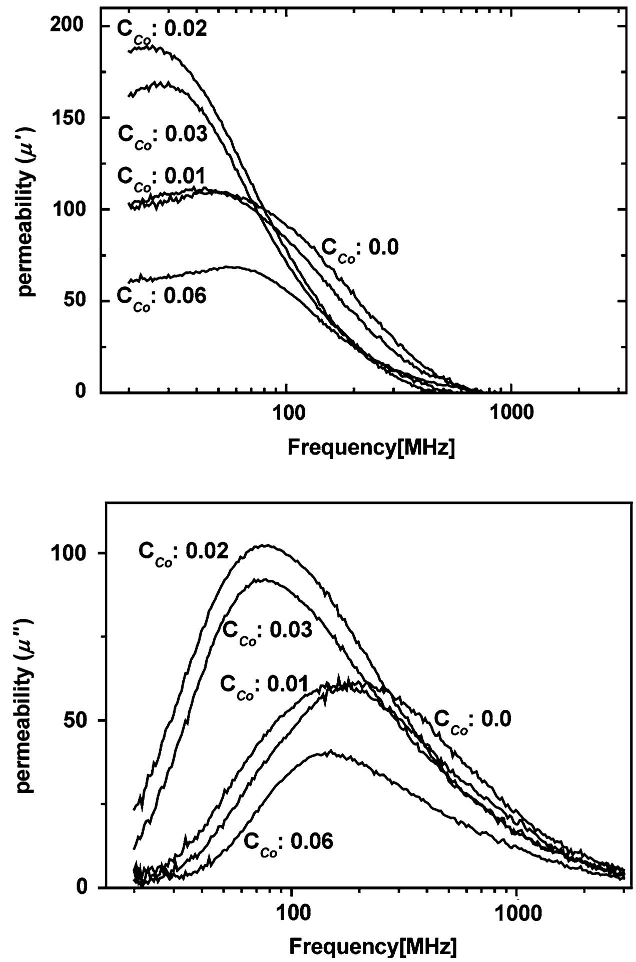

Fig. 7 Permeability and resonance frequency of NiZnCo ferrite films with C_{Co} = 0.0–0.06 (Zn concentration was maintained at C_{Zn} = 0.6)

C_{Zn} = 0.6. The films with permeability above 100 (C_{Zn} = 0.4–0.8) can be used as trimming layers for inductors. The resonance frequency f_r (where μ'' becomes maximum) decreased from around 300 MHz to less than 100 MHz with increase in C_{Zn}. Further maintaining C_{Zn} at 0.6, the content of Co was varied. When C_{Co} = 0.02, the highest real permeability of about 189 was recorded (Fig. 7). This indicates that a small amount of Co helped to increase the low frequency permeability. In accordance with the Snokes' limit, films with high initial permeability has to compromise for the resonance frequency [15]. A maximum resonance frequency was noticed when C_{Co} = 0. The decrease in the f_r can be ascribed to the local magnetocrystalline anisotropy field, which decreases with increasing the Zn/Co content in the film. The increased permeability of these films can be due to decrease in the H_k. When C_{Co} was further increased up to 0.2, the μ' decreased and f_r increased, and a very high resonance frequency of 3.3 GHz was attained for $Ni_{0.23}Zn_{0.34}Co_{0.23}Fe_{2.2}O_4$ [16], though with a low initial permeability.

Figure 8 is the plot of the product of imaginary permeability and frequency ($\mu'' x{\cdot}f$), which is proportional to the noise suppression effect of the film [10]. By varying the

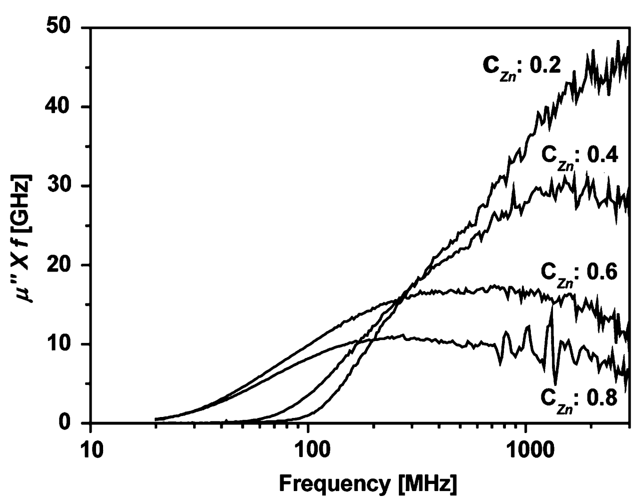

Fig. 8 Plot of $\mu'' \times f$ for NiZnCo ferrite films

Zn concentration (C_{Zn} = 0–0.8), the frequency from where the noise absorption starts can be tuned. When C_{Zn} = 0.2, the noise suppression effect was found to be relatively good, since it had an absorption of up to 48% at 3 GHz and almost zero at 100 MHz. These types of films can be used as low pass filters.

Conclusion

Ferrite films were prepared by spin-spray technique, a kind of soft solution process, at a very low temperature of 90 °C. The obtained films were highly crystallized and had columnar structures perpendicular to the substrate surface. Composition of the films was optimized in order to get high initial permeability or high resonance frequency. Permeability of around 190 was obtained for $Ni_{0.18}Zn_{0.6}Co_{0.02}Fe_{2.2}O_{4-\delta}$ film having a resonance frequency of 80 MHz. Film having high resonance frequency of 300 MHz had an initial permeability of 100 ($Ni_{0.16}Zn_{0.2}Co_{0.02}Fe_{2.62}O_{4-\delta}$). From the output of the study, it is clear that the ferrite films with a wide range of permeability and resonance frequency can be prepared by spin-spray technique depending on specific requirements.

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