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High-frequency magnetic properties of Zn ferrite films deposited by magnetron sputtering

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The effect of thermal annealing on structural and magnetic properties has been investigated for Zn ferrite films deposited on Si (111) substrates using radio frequency magnetron sputtering. The saturation magnetization at room temperature was enhanced upto 303 emu/cm^3 by annealing at relatively low temperature of 200 °C and decreased at higher temperatures. The complex permeability $\mu=\mu'-i\mu''$ values of the ferrite films as-deposited and annealed at 200 and 400 °C were measured at frequency upto 5 GHz. These films exhibited better high-frequency properties, especially, the film annealed at 200 °C had a large μ' of 19.5 and high resonance frequency f_r of 1.61 GHz. And the reason was investigated preliminarily based on the bianisotropy model.
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I. INTRODUCTION

Recently, there is considerable interest in thin films of nanometer-sized ferrite for their potential application in high-frequency devices and information storage devices.[1–8] As an important member of ferrite family, Zn ferrite ($ZnFe_2O_4$) film has attracted significant research interest based on its showing unusual magnetic properties compared to the bulk form.[9–14] Zn ferrite bulk has a normal spinel structure with antiferromagnetic properties below the Neel temperature of about 10 K and paramagnetism at room temperature since negative superexchange interaction occurs among Fe^{3+} cations on the octahedral sites.[15–18] However, large magnetization at room temperature has been observed for Zn ferrite films deposited by sputtering,[11,12,14] pulsed laser deposition,[10,13] and spray pyrolysis deposition.[8] The issue has been extensively researched and ascribed to a random distribution of Zn^{2+} and Fe^{3+} cations on the tetragonal (A) and octahedral (B) sites in the spinel structure.[10,12,13] The variation of cations distribution in the Zn ferrite films also could affect the high-frequency magnetic properties. Nevertheless, there has been little investigation in the recent reports.

In this paper, Zn ferrite films were prepared by radio frequency (rf) magnetron sputtering at room temperature. The structural and magnetic characteristics as well as the complex permeability of the films dependence on the annealed temperature (T_a) were investigated.

II. EXPERIMENTAL PROCEDURE

Zn ferrite films with thickness ~750 nm were deposited onto 10×10 mm^2 Si (111) substrates attached to a water-cooling system by rf magnetron sputtering at room temperature with a base pressure lower than 5×10^{-5} Pa. A $ZnFe_2O_4$ ferrite target with 76 mm in diameter and 3 mm in thickness was used. The rf power density was 4.4 W/cm^2 and a mixed gas of argon and oxygen was used during sputtering. The sputtering pressure was kept at 2.0 Pa, while the proportion of oxygen pressure to the total pressure was 20%. The as-deposited films were annealed at different temperatures of 200, 400, and 600 °C for 2 h in air atmosphere, respectively.

The compositions and thicknesses of the Zn ferrite films were measured by energy dispersive x-ray spectroscopy (EDS) and surface profiler meter (Vecco Dektak 8). The crystallographic and microstructure properties of the ferrite films were characterized by x-ray diffraction (XRD, X'Pert PRO PHILIPS with Cu K_α radiation) and field emission scanning electron microscope (SEM, Hitachi S-4800), respectively. The static magnetic measurements of the ferrite films were performed by using a vibrating sample magnetometer (VSM, Lakeshore 7304 model) and quantum design magnetic property measurement system magnetometer based on superconducting quantum interference device, and the applied field H was parallel to film plane. The complex permeability of the ferrite films were measured by a PNA E8363B vector network analyzer using shorted microstrip transmission-line perturbation method from 100 MHz to 5 GHz.[19] All the above observations and measurements of the Zn ferrite films were performed at room temperature.

III. RESULTS AND DISCUSSION

EDS analysis of the ferrite films quantifies the relative ferrite composition. The results show that the atom ratios of Zn and Fe in all the films are confirmed to be about 1:2. The thicknesses of Zn ferrite films at different annealed temperature are the same as that of as-deposited film with about 750 nm. Figure 1 shows XRD patterns of Zn ferrite films as-deposited and annealed at different temperature of 200, 400, and 600 °C, respectively. It is found that all the samples are well-crystallized and single-phase with a spinel crystal structure. The main peak is (311) peak and no preferential orien-

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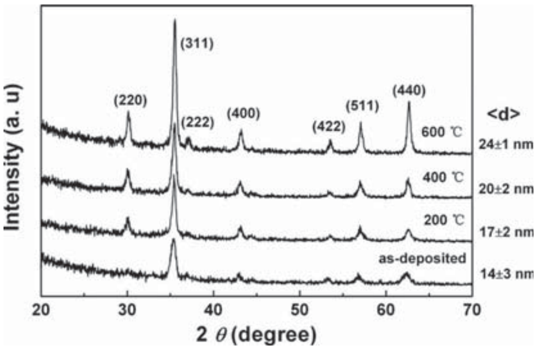

FIG. 1. XRD patterns of $ZnFe_2O_4$ films. The indices show those for spinel structure.

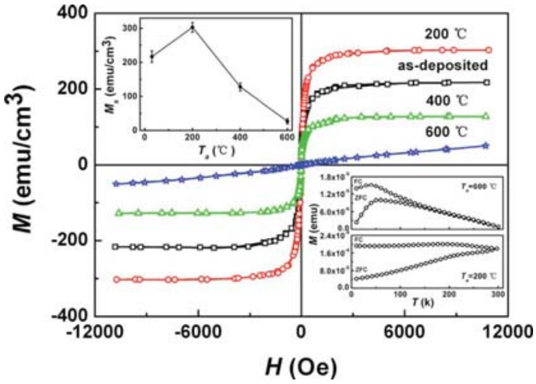

FIG. 3. (Color online) *M*-*H* loops of $ZnFe_2O_4$ films. The top left inset is M_s of the films as function of T_a and the bottom right is ZFC and FC curves of the films annealed at 200 and 600 °C.

tation appears in all the films, which is in agreement with other reports.[9,11–13] It can be seen that the peaks become narrow with the increasing of T_a, which indicates an increase in the average grain sizes $\langle d \rangle$ of the films. The values of $\langle d \rangle$ obtained from the Scherrer equation applied to the XRD patterns are shown in Fig. 1, which are in range of 14–24 nm. Figure 2 shows SEM images of the Zn ferrite films as-deposited and annealed at different temperature. As seen from Fig. 2, all the films are consisted of nanocrystalline particles in nature and the sizes increase as T_a increases, which are consistent with the results from XRD. It is noted that the compactability of the Zn ferrite films is pretty nearly with T_a increasing upto 400 °C. However, it becomes poor and there is much gap among the nanocrystalline particles as $T_a=600$ °C.

The *M*-*H* loops for Zn ferrite films were taken at room temperature using the VSM. The substrate contribution to the *M*-*H* loop was subtracted after obtaining the loops and the modified loops were shown in Fig. 3. The saturation magnetization (M_s) was evaluated from the loops of the ferrite films and shown in the top left inset. With the increase in T_a, M_s of the films first increases and then decreases. At $T_a=200$ °C, M_s of the film shows a maximum value of 303 emu/cm^3, which is much higher than the value of the Zn ferrite films reported recently.[9,11,13]

It is noted that the Zn ferrite films were deposited onto the substrates attached to a water-cooling system. Therefore, the film growth basically is a rapid cooling process from vapor phases to solid-state phases, which could lead to a random distribution of Zn^{2+} and Fe^{3+} ions on the A and B sites in the spinel structure.[18,20] The large magnetization in the Zn ferrite films at room temperature most likely results from occupation of the A sites by some Fe^{3+} ions. The initial increase of M_s might be due to the increase in the grain sizes and decrease in the superparamagnetic effect in the Zn ferrite films. However, as T_a increases further, M_s of the films decreases, which may arise from the Fe^{3+} ions tending to occupy the B sites more at high temperature.[12,21] Therefore, the static magnetic property of the Zn ferrite film at $T_a=600$ °C shows much as that of bulk which is paramagnetic at room temperature.

In order to verify above speculation, the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves in the temperature range of 2–300 K at a dc field of 50 Oe for the Zn ferrite films at $T_a=200$ and 600 °C are shown in the bottom right inset of Fig. 3. For the $ZnFe_2O_4$ film at $T_a=200$ °C, FC magnetization curve shows no obvious variety and ZFC magnetization curve monotonically increases with increasing temperature, which indicates that there is no blocking temperature appeared in this temperature range and Curie temperature of this sample is above 300 K.[22,23] However, for the film at $T_a=600$ °C, FC and ZFC magnetization curves first increase and then decrease, which show a maximum at about 50 K corresponding to blocking temperature. The variety of FC and ZFC for the film is similar to that observed for normal spinel $ZnFe_2O_4$.[15,24] In addition, the values of FC and ZFC magnetization curves of the film are quite small at 300 K, which is corresponding to the magnetic behavior at room temperature from *M*-*H* loop.

Figures 4(a) and 4(b) show the frequency dependence of the complex permeability spectra for the $ZnFe_2O_4$ films as-deposited and at $T_a=200$ and 400 °C in the range of 100 MHz–5 GHz. With the increasing of T_a, the real part of permeability μ' and the resonance frequency f_r, around which the imaginary part of permeability μ'' reaches a maximum value, first increase and then decrease, which reach a maximum value of about 19.5 and 1.61 GHz as the film was annealed at 200 °C. It is very well evident that the film with $\mu'=19.5$ and $\mu''=0$ upto 500 MHz might be applied to film

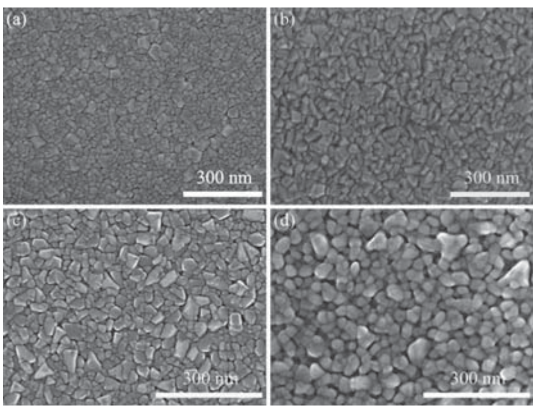

FIG. 2. SEM images of $ZnFe_2O_4$ films (a) as-deposited and annealed at (b) 200, (c) 400, and (d) 600 °C.

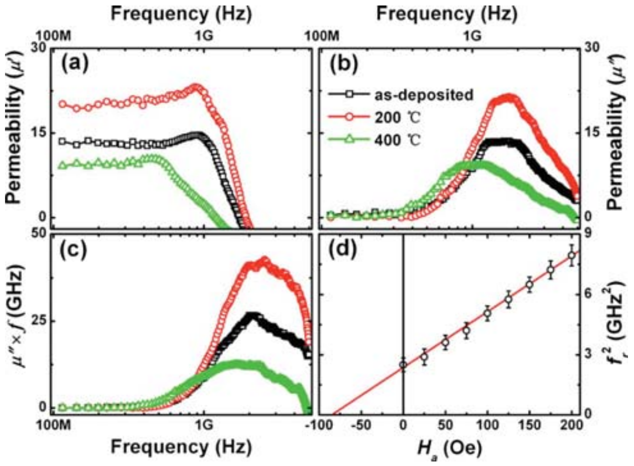

FIG. 4. (Color online) (a) Real and (b) imaginary parts of the complex permeability spectrums of $ZnFe_2O_4$ films. (c) Frequency spectrums of $\mu'' \times f$ for the ferrite films. (d) Square of resonance frequency of f_r as a function of in-plane applied magnetic field H_a. The symbols are experimental results for the $ZnFe_2O_4$ film annealed at 200 °C and the solid line is the fitting curve.

inductors operated hundred MHz range. The $\mu'' \times f$ spectra, which can be accounted as similar to the noise suppression property of the film,[25] are shown in Fig. 4(c). It is seen that all the films have better noise suppression property in the gigahertz region. Especially the film at $T_a=200$ °C has a large value in GHz region, which is equal to the commercial composite sheet noise suppressors.[25,26]

In order to investigate the high-frequency resonance mechanism of the Zn ferrite films, the resonance frequency f_r as a function of in-plane applied magnetic field H_a was measured. According to the results of uniform precession of magnetization, viz., ferromagnetic resonance, when the H_a applied in-plane, a linear relationship between f_r^2 and H_a can be witnessed.[27,28] Therefore, in Fig. 4(d), the data of f_r^2 (symbols) for the film at $T_a=200$ °C are plotted as a function of H_a, which follows linear fit by solid line. The good agreement between the fitting line and the experimental data proves that the resonance model of Zn ferrite films is the uniform precession model.

The reason why the Zn ferrite films have high f_r in the gigahertz region could be explained by using the bianisotropy model presented Xue *et al.*,[29] which is similar to the Ni–Zn ferrite films expatiated in Ref. 4. Taking the model into account, it is considered that spontaneous magnetization M of the crystallites in the Zn ferrite films is exchange coupled to each other and yields a macroscopic magnetization M_s, which is almost restricted in the films plane. And due to the demagnetizing effect of the film, the Zn ferrite films are divided into magnetic domains.[30] Certainly, the further investigation on high-frequency of the Zn ferrite films has been working on and will be presented in a forthcoming paper.

IV. CONCLUSION

In summary, Zn ferrite films were successfully prepared by rf magnetron sputtering at room temperature and thermal annealing effect on their structural and magnetic properties has been investigated. All the films are well-crystallized and single-phase with a spinel crystal structure. The films as-deposited and annealed at 200 and 400 °C show strongly ferromagnetic properties at room temperature, especially the film at $T_a=200$ °C has a large M_s of 303 emu/cm^3. At $T_a=600$ °C, the film shows paramagnetic properties which is due to cation distribution going back to that of a normal spinel.

Zn ferrite films as-deposited and annealed at 200 and 400 °C have exhibited better high-frequency properties, in particular, the film at $T_a=200$ °C has not only a large μ' of 19.5 and high f_r of 1.61 GHz but also better noise suppression property in the gigahertz region. Based on the bianisotropy model, the reason was investigated preliminarily.

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