

Microstructure and magnetic properties of NiZn ferrite thin films prepared by sol-gel method

NIE Xiao-liang(聂小亮), LAN Zhong-wen(兰中文), YU Zhong(余忠),
SUN Ke(孙科), LI Le-zhong(李乐中)

State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China

Received 15 July 2007; accepted 10 September 2007

Abstract: Ti⁴⁺ substitution for Fe³⁺ in Ni_{0.5}Zn_{0.5}Fe₂O₄ (NZF) ferrite thin films were realized by sol-gel method and annealing at 600 °C for 30 min in the air. Crystal structure and lattice constant determination was performed by X-ray diffractometer (XRD). Surface microstructure was observed by scanning electron microscope (SEM) and atomic force microscope (AFM), and the magnetic properties were measured by vibrating sample magnetometer (VSM). XRD analyses of the samples show that Ni_{0.5+x}Zn_{0.5}Ti_xFe_{2-2x}O₄ (NZTF) films with x varying from 0 to 0.15 in steps of 0.05 are composed of single phase with spinel structure. And the lattice parameter, particle size and the diffraction intensity of the films increase with substitution of Ti as the result of the larger radius ions entering the lattice. SEM and AFM show homogeneous grain size of each sample, but there is a few differences in grain size with different Ti-substitution contents. As the nonmagnetic Ti⁴⁺ substitutes Fe³⁺, both the saturation magnetization and coercivity decrease.

Key words: Ti-substitution; NiZn ferrite thin films; sol-gel method; microstructure; magnetic properties

1 Introduction

NiZn ferrite with spinel structure has a promising potential as high performance microwave devices owing to its high resistivity, mechanical hardness, high Curie temperature, chemical stability, and soft magnetic properties at high frequency. Presently, bulk NiZn ferrite components employed in discrete devices at microwave frequencies are not compatible with the rapid development of electronic applications towards miniaturization, high density, integration and multifunction. Thus, the ferrite thin films that are incorporated into magnetic integrated circuits (MAGIC) are expected to replace the currently used surface mounting modules in near future [1].

Besides basic formula and preparation process, dopant is also one of the most important factors which have great impact on the microstructure and magnetic properties of the thin films. Commonly used substituents in ferrite are Ca, Si, V, Bi, Ti, Sn, Ni, Co [2], etc. The function of Ti⁴⁺ added in certain ferrite films like Ti_xCo_{1+x}Fe_{2-2x}O₄ [3-4], BaFe_{12-2x}Co_xTi_xO₁₉ [5-6] and

NiMn_{0.05}Ti_xMg_xFe_{1.95-2x}O₄ thin films[7-8] was reported, while there are few reports about the influence of Ti substitution on the properties of NiZn ferrite thin films. In this study, phase characterization, microstructure and magnetic properties of Ti substituted Ni_{0.5+x}Zn_{0.5}Ti_xFe_{2-2x}O₄ ($x=0, 0.05, 0.10, 0.15$) (NZTF) ferrite thin films prepared by sol-gel method.

2 Experimental

2.1 Sample preparation

The samples of the Ni_{0.5+x}Zn_{0.5}Ti_xFe_{2-2x}O₄ ($x=0, 0.05, 0.10, 0.15$) ferrite thin films were prepared by sol-gel method. Zn(CH₃COO)₂·2H₂O (AR), Ni(CH₃COO)₂·4H₂O (AR), Fe(NO₃)₃·9H₂O (AR) and Ti(C₄H₉O)₄ (AR) were firstly dissolved in 2-methoxyethanol to form a mixed solution. After stirring the solution for 1 h, acetic acid was added to adjust the concentration of the solution to 0.2 mol/L. Meanwhile polyethylene glycol was added as a kind of surfactant, which can keep the colloidal particles of chelate from combining with each other. The prepared solution was then continuously stirred for 2 h and placed

for 36 h at room temperature to form the stable sol-gel precursor used for following process. Then wet films were deposited by a spin coating method on Si (100) layers. The speed and time of spin were controlled to get a uniform thin film. The obtained films were dried at 120 °C for 10 min to remove the mixed solvents, and then heated at 400 °C for 30 min to pyrolyze and exclude the organic substances. The operation of spin coating, drying and heating were repeated to get the required thickness of the films. Finally, the as-deposited films were annealed at 600 °C for 30 min in the air and cooled slowly in the furnace. And the thickness of the films was about 140 nm.

2.2 Properties measurement

Crystal structure of the films was investigated with Philips X'Pert PRO X-ray diffractometer (XRD), with Cu K_α radiation (used $\bar{\omega}/(2\theta)$ mode, $\omega=1.0$, step angle was 0.01, dwelling time was 0.3 s) and JEOL JSM-6490LV scanning electron microscope (SEM) was used to estimate the thickness of the films. The surface morphology and grain size were studied by atomic force microscope (AFM). The magnetic properties were measured by using the Model BHV-525 vibrating sample magnetometer (VSM) at room temperature.

3 Results and discussion

3.1 Phase characterization

The XRD patterns of NZTF ferrite thin films with various contents of Ti substitutions are shown in Fig.1. It can be seen from Fig.1 that films for substitution contents $x \leq 0.15$ are composed of single phase with the spinel structure. And the main peak (311) of NZTF ferrite thin films is in agreement with that in Ref.[9]. An increase in the concentration of Ti⁴⁺ yields an increasing intensity of the major peak. Table 1 shows the influence of Ti substitution on the structural parameters of NZTF ferrite thin films. The lattice parameter of NZTF ferrite thin films is obtained with the help of the Nelson-Riley function[4, 10]. And the particle size is determined from the diffraction peak broadening with the use of the Scherrer equation [10]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where λ is wavelength of the target Cu K_α, 0.154 05 nm; β is full width at half maximum of diffracted (3 1 1) peak. The result shows that along with the increase of Ni²⁺ and Ti⁴⁺ contents, lattice parameter and particle size increase slightly. The reason that lattice parameter increases is that the ion radius of Ti⁴⁺ ($r=0.069$ nm) and Ni²⁺ ($r=0.078$ nm) is very near that of Fe³⁺ ($r=0.067$ nm) [11], which indicates that the dopant Ti⁴⁺ and Ni²⁺ can easily diffuse into the lattice to substitute Fe³⁺ at the octahedral site

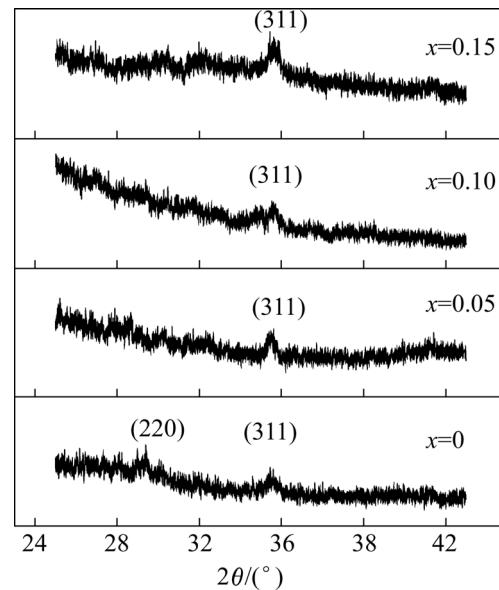


Fig.1 X-ray diffraction patterns of $\text{Ni}_{0.5+x}\text{Zn}_{0.5}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ ferrite thin films

Table 1 Structural parameters of $\text{Ni}_{0.5+x}\text{Zn}_{0.5}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ ferrite thin films

Sample	a/nm	D/nm
$x=0$	0.838 1	24.4
$x=0.05$	0.838 4	27.1
$x=0.10$	0.838 6	29.6
$x=0.15$	0.839 0	30.9

a Lattice parameter; *D* Grain size

(B site). However, their radius is bigger than that of Fe³⁺, so Ti⁴⁺ and Ni²⁺ enter into the lattice, and swell the lattice, then enlarge the lattice parameter, which results in lattice aberrance. So, the higher activity of particles can be obtained. That is to say, under the same annealing conditions, grain growth is more easily. Eventually, the more the Ti substitution in the ferrite thin films is, the larger the lattice parameter and grain size are.

3.2 Surface microstructure observation

Fig.2 shows the surface microstructure of the ferrite thin films with $x=0$ by SEM and AFM. This reveals that grains are very uniform and the average grain size is 40 nm. Other film samples also appear to consist of regular grains and with a narrow distribution of grain size. Moreover, the increasing trend is consistent with the results obtained from the particle sizes *D* calculated by Scherrer equation from XRD, although the grain size measured by AFM is larger than that of *D*.

3.3 Magnetic properties

Fig.3 shows the in-plane hysteresis curves of the NZTF ferrite thin films in the external maximum field of

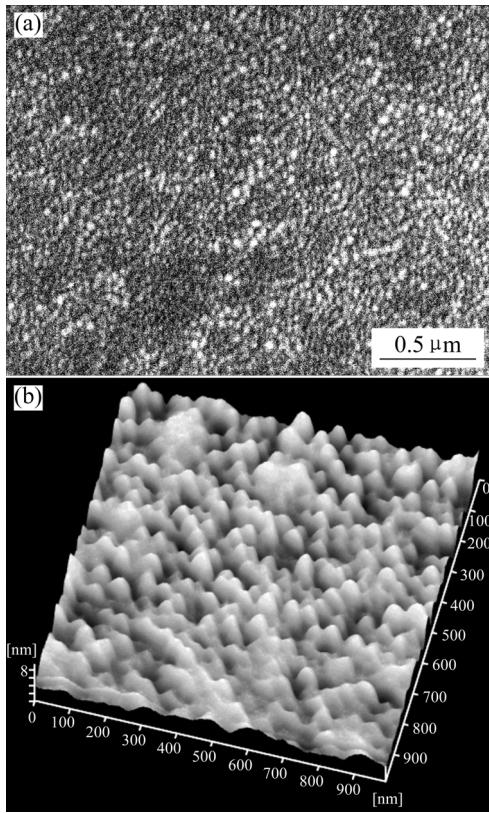


Fig.2 Surface microstructure of $\text{Ni}_{0.5+x}\text{Zn}_{0.5}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ thin films with $x=0$: (a) SEM image; (b) AFM image

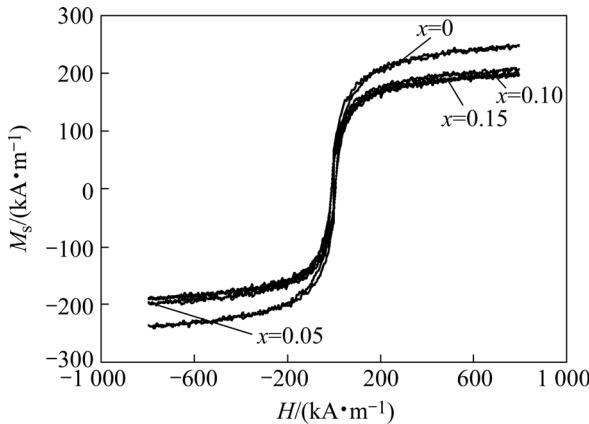


Fig.3 Relationship between M_s and H of $\text{Ni}_{0.5+x}\text{Zn}_{0.5}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ thin films

800 kA/m measured by VSM. The relationships between the saturation magnetization M_s , coercivity H_c and contents of Ni^{2+} and Ti^{4+} can be seen more obviously in Fig.4. It can be seen that the saturation magnetization and the coercivity decrease from 242, 8.36 kA/m to 193 and 7.48 kA/m, respectively, with the increase of Ni^{2+} and Ti^{4+} substitution. Magnetic properties would be variable with the shape of the samples, thickness, particle size, internal strain and cation distribution[2]. In this work, the decrease of saturation magnetization is due to a combination of more lattice defects and weaker magnetic

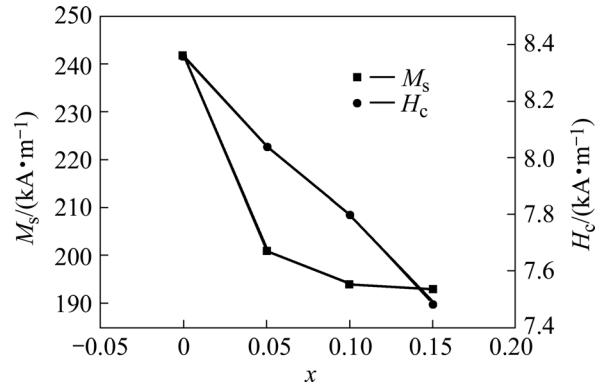


Fig.4 Relationship among M_s , H_c and x of $\text{Ni}_{0.5+x}\text{Zn}_{0.5}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ thin films

superexchange interactions between the tetrahedral (A) sites and octahedral (B) sites. In detail, for cubic structure ferrite thin film, there is

$$M_s = \frac{8M}{a^3} \quad (2)$$

where M is the net overall magnetic moment; a is the lattice parameter. The cation distribution of the NZTF ferrite thin films is $(\text{Zn}_{0.5}\text{Fe}_{0.5})[\text{Ni}_{0.5+x}\text{Ti}_x\text{Fe}_{1.5-2x}]\text{O}_4$. Due to antiferromagnetic coupling, the net overall magnetic moment is equal to the result of magnetic moment from B sites minus magnetic moment from A sites, $M=M_B-M_A$. Ti^{4+} is nonmagnetic and the molecule magnetic moment of Ni^{2+} and Fe^{3+} is $2\mu_B$ and $5\mu_B$, respectively. While Ti^{4+} and Ni^{2+} substitute Fe^{3+} , the magnetic moment on B sublattice reduces, resulting in decrease of the net overall magnetic moment. However, the lattice parameter increases with the increase of the substitution of Ti^{4+} , as listed in Table 1. Therefore, saturation magnetization decreases. In addition, the nonmagnetic Ti^{4+} that enters into B sites will also decrease the A—O—B superexchange interaction, which also makes the saturation magnetization decrease more quickly. The reason that the coercivity decreases is as follows. The addition of nonmagnetic Ti^{4+} weakens the magnetocrystalline anisotropy (K_1), and coercivity is proportional to magnetocrystalline anisotropy ($H_c \propto K_1$), therefore, the coercivity decreases with the increase of the concentration of Ti^{4+} . Furthermore, with the increase of substitution content, particle size increases (see Table 1); consequently, coercivity decreases [9]. It also can be found that the saturation magnetization of ferrite thin films is somewhat lower than that of the bulk with the same basic formula. The reasons are: 1) incomplete saturation; 2) films having smaller density than that of bulk NZF; 3) 20% uncertainty in determining the values of thickness [12].

4 Conclusions

1) Single phase with spinel structure are confirmed by analyzing XRD of the Ti-substituted NZF thin films. And the lattice parameter, grain sizes and the diffraction intensity of the films increase with the increase of the substitution of Ti.

2) AFM observation shows regular grains and the trend that grain size increases slightly with the Ti substitution, which is consistent with the results obtained from the grain sizes D calculated by Scherrer equation.

3) Both saturation magnetization and coercivity decrease with the Ti substitution. And the saturation magnetization is lower than that of the bulk with the same basic formula.

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(Edited by CHEN Can-hua)