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Microwave magnetic properties of spinel ferrite films deposited by one-step electrochemical method

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ABSTRACT

Spinel ferrites have been widely used in microwave devices due to their excellent electromagnetic properties. In this study, two kinds of spinel ferrite films, Fe_3O_4 and $Co_xFe_{3-x}O_4$, were grown on Pt(111)/Ti/SiO_2/Si substrates by one-step electrochemical deposition method. The XRD and SEM characterizations demonstrated that the orientation of the ferrite films changed from (111) to (100) with the increase of depositing time. The cobalt content within $Co_xFe_{3-x}O_4$ films was studied in detail by EDS analysis. The ferromagnetic resonance (FMR) responses of the ferrite films were measured by the flip-chip method using a vector network analyzer (VNA). It showed that the FMR frequency of Fe_3O_4 films reached to 10.5 GHz under an out-plane magnetic field of 5 kOe, while it reached to 27 GHz under an in-plane magnetic field of 5 kOe for $Co_xFe_{3-x}O_4$ films. Meanwhile, whether the magnetic field was applied parallelly or perpendicularly, the resonant peaks were increased linearly with increasing the magnetic field, indicating that the films are promising candidates for applications in tunable wave-absorbing materials or other tunable frequency devices.

1. Introduction

Microwave ferrite materials are ubiquitous from UHF (ultra-high frequency) to optical frequency during the transmit, acceptance and manipulation of electromagnetic signal within the microwave integration systems [1]. Ideal microwave magnetic materials are required to have high magnetization, high permeability, high dielectric properties, high resistance and low magnetic losses [2]. Fortunately, ferrite materials seem to meet the requirements above, which makes them particularly suitable for non-reciprocal passive microwave devices. To achieve the next generation of flat magnetic microwave devices, miniaturization, integration and multifunction should not lose out to what the current best technology can achieve. Thus, microwave ferrite materials, especially ferrite films, has attracted much attention during past several decades. There are many strategies to prepare ferrite films, of which PVD, CVD, electrochemical deposition, and spin coating inevitably require a heating process during the deposition or heat annealing at elevated temperature after the deposition, thus the substrates must withstand high temperature [3–6]. In comparison, one-step electrochemical deposition is of significant advantage to obtain thin films without any heating process involved. Thus, this approach is highly beneficial to design thin films upon organic substrates or alternative substrates for special applications in flexible materials, copper clad circuit board and semiconductor devices. In addition, it is rather difficult to obtain Ba or rare earth element in hexagonal ferrite films by electrodeposition in aqueous media. Compared with other materials like garnet and magnetoplumbite type ferrites, spinel ferrite films exhibit simple microstructures; and among common spinel ferrites, Fe_3O_4 possesses the simplest crystal structure, while $CoFe_2O_4$ has the highest magnetic anisotropy, making them suitable to be prepared through electrochemically depositing process [7]. Recently, some investigations have been reported upon such ferrite films by electrochemical deposition [8,9]. However, they were almost done on metals, and microwave responses were not given yet.

This work is mainly aimed at realizing Fe_3O_4 and $Co_xFe_{3-x}O_4$ films on Pt(111)/Ti/SiO_2/Si substrates by one-step electrochemical method and studying their magnetic properties as well. Meanwhile, the effects of deposition condition on the crystal structure, microstructure, orientation, and microwave response were investigated systematically. Both the oriented Fe_3O_4 and $Co_xFe_{3-x}O_4$ films can be directly applied in actual electromagnetic signal shielding

Abbreviations: CVD, chemical vapor deposition; EDS, energy disperse spectroscopy; SEM, emission scanning electron microscope; FMR, ferromagnetic resonance; NIST, National Institute of Standards and Technology; PVD, physical vapor deposition; TEA, triethanolamine; UHF, ultra high frequency; VNA, vector network analyzer; XRD, X-ray diffraction; XPS, X-ray Photoelectron Spectrometer.

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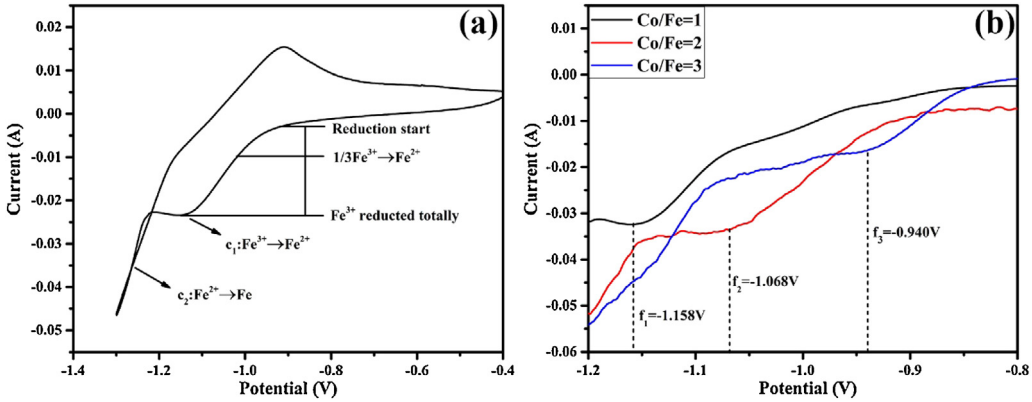

Fig. 1. Cyclic voltammetry curve of the deposition solution without Co precursor (a) and with Co precursor (b).

devices, such as isolators. In addition, the variations of orientation and surface microstructures during the deposition process were also discussed.

2. Material and methods

2.1. Electrochemical deposition of spinel films

The spinel ferrite films were deposited on platinum-plated silicon substrates of Pt(111)/Ti/SiO_2/Si by one-step electrochemical deposition, as described in literatures [8,9]. A mixed solution of $FeSO_4$, $CoSO_4$ and triethanolamine (TEA) were used as the raw materials. To better study the influences of the solution composition on the crystal structures, orientations, and microwave properties of the as-prepared films, four kinds of solutions with different Co/Fe ratio (0, 1, 2, 3) were designed. Different deposition potentials were selected in a range of $-0.95 \sim -1.05\,V_{Ag/AgCl}$ for Fe_3O_4 films and $-0.90 \sim -1.025\,V_{Ag/AgCl}$ for Co $_xFe_{3-x}O_4$ films, respectively. During the depositing process, the solution temperature was fixed at 65 °C, and the solutions were stirred continuously. The cyclic voltammograms of solutions were measured before depositing, as shown in Fig. 1. For this deposition process, the possible electrochemical reactions on the eletrodes can be described as follow:

$$Fe(TEA)^{3+} + e^- \rightarrow Fe^{2+} + TEA \quad (1)$$

$$Fe^{2+} + 2Fe(TEA)^{3+} + 8OH^- \rightarrow Fe_3O_4 + 2TEA + 4H_2O \quad (2)$$

$$Co^{2+} + 2Fe(TEA)^{3+} + 8OH^- \rightarrow CoFe_2O_4 + 2TEA + 4H_2O \quad (3)$$

With respect to the valence change of iron element in the reaction equations above, it is necessary to discuss the deposition of pure Fe_3O_4 first. Fig. 1 shows the cyclic voltammograms of the deposition solutions with and without Co precursor. In deposition solution without Co precursor, the cyclic voltammogram (shown in Fig. 1a) displays two cathodic peaks, c_1 and c_2, implying that two-step reduction of iron takes place with the decreasing potential, in which c_2 corresponds to the transformation from Fe^{2+} to Fe, and c_1 is associated with the reduction of Fe^{3+} to Fe^{2+}. The platform of curve before the appearance of c_1 suggests that all Fe^{3+} ions contacting with the cathode electrode have been reduced to Fe^{2+} while further reduction would not happen. This observation indicates that the reaction rate of Eq. (1) depends on the reducing potential when the it is lower than 1.16 V. However, such reaction rate will depend on the diffusion of Fe^{3+} when the reducing potential is higher than 1.16 V. From Eq. (2), with one-third of Fe^{3+} ions are reduced, pure Fe_3O_4 would be processed theoretically. Both upper and lower fluctuation in the degree of the reduction of iron element would result in the variations of the compositions in final materials, which would directly affect their magnetic performances. In a proper depositing potential range, if the cobalt precursor is added into the deposition solution, the chemical composition of as-prepared films would be changed from Fe_3O_4 to Co $_xFe_{3-x}O_4$. With the increase of Co content, the first cathodic peak of Fe^{3+} enlarges as the shift of f_1, f_2 and f_3 shown in Fig. 1b. The introduced Co promotes the reduction of Fe^{3+}, because Fe^{3+} could be immobilized near the cathode easily. Eq. (2) and Eq. (3) are competitive during the depositing process, so it pretty difficult to form pure $CoFe_2O_4$ and the x is definitely smaller than one. By means of monitoring the productivity of Fe^{2+} influenced by depositing potential, the composition of the ferrite films can be adjusted accordingly.

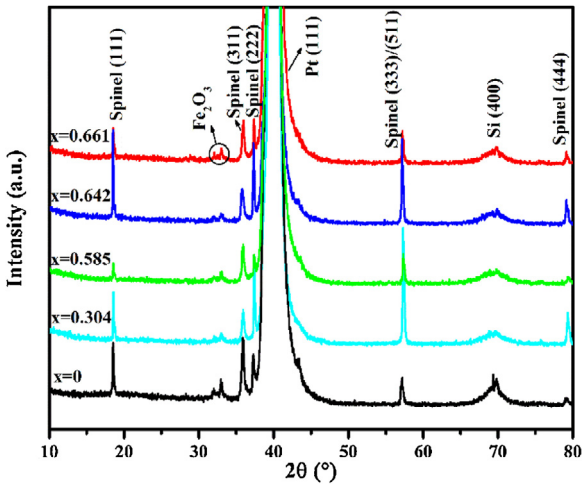

Fig. 2. XRD patterns of Fe_3O_4 and Co $_xFe_{3-x}O_4$ with different x.

2.2. Structure, composition and properties measurement

The crystal structure and orientation behavior of as-deposited ferrite films were characterized by using an X-Ray Diffractometer (D8 Advance A25, Bruker, Germany) through θ-2θ scanning and pole figure measurement. The micro-morphology was observed with a field emission scanning electron microscope (SEM, JSM-7001, JEOL, Japan). The elementary composition of the films was analyzed with an energy disperse spectroscopy (EDS) system while observing the films by SEM. The ratios of Fe^{3+} to Fe^{2+} were measured by an X-ray photoelectron spectrometer (XPS) microprobe (ESCALAB 250X, Thermo Scientific, America). The fundamental magnetic hysteresis loop was measured by a vibrating sample magnetometer (7307, LakeShore, China). To characterize