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Microstructure and thickness dependent magnetic properties of nanogranular Co–Zn–O thin films for microwave applications

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ABSTRACT

Co-based granular thin films with in-plane anisotropy were deposited on Si substrate by magnetron sputtering. The films have a phase structure of Co nanocrystallites and amorphous Zn–O inter-granular phases. The Co nanograins with uniform size of 8–10 nm are evenly distributed in the amorphous matrix. This structure gives the films relatively high resistivities. The as-deposited films with thickness larger than 100 nm have low coercivity (<10 Oe) along both easy and hard directions. The dynamic properties in the frequency range up 5 GHz for the films with various thicknesses have been investigated. High values of permeability (μ' up to 560 and μ'' up to 1000) and ferromagnetic resonance frequency (FMR) up to 4.1 GHz have been obtained in these films. The FMR frequency decreases with increasing thickness, because of the increases in real and imaginary permeabilities. The high frequency characteristics have complicated dependences on the resistivity, anisotropy field, and magnetization. The microwave properties of Co–Zn–O films can be adjusted in a relatively wide range by changing film thickness, which makes these films promising for absorber applications.

1. Introduction

Nanogranular systems, i.e. composites comprising of nano-sized metallic grains embedded in an insulating host matrix, exhibit special optical, electrical and magnetic properties [1]. Magnetic nanogranular films have been actively studied due to their potential applications as the materials with giant magnetoresistance [2], hard magnetic properties [3] and high resistivity soft magnetic properties [4]. In particular, granular films such as CoAlO, FeSiO and FeCoZrO have been extensively studied [5–8]. These films have relatively high electrical resistivity (ρ), large saturation magnetization (M_s), large anisotropy field (H_k) and low coercivity (H_c), therefore they have excellent $\mu - f$ response and are excellent candidates for Gigahertz applications. Most previous investigations on Co based nanogranular films were focused on Al–O or Si–O matrix; Co–Zn–O system has received relatively little attention. Actually, Co doped ZnO with low Co concentration has been extensively studied as a diluted magnetic semiconductor (DMS). Recently, Song et al. [9] studied the Co–Zn–O thin films with various oxygen contents and found that with decreasing oxygen concentration, the behavior of as-deposited film transferred from DMS to nanogranular soft magnets. As a good insulation material with high resistivity, ZnO can be used as the matrix for magnetic nanogranular films. Increase of Co concentration in Co:ZnO system will also lead to soft magnetic film. Following our previous work on the continuous FeTaN [10], FeZrN [11] films and granular CoAlO [12], CoFeSiN [13] films, here we report the structure and high frequency behavior of the CoZnO thin films with various thicknesses.

2. Experiment

Co-based granular thin films were fabricated on the Si substrates with size of 5 mm × 10 mm at room temperature using rf magnetron sputtering. A 2 in. Co disc with five ZnO chips was employed as the target. The ZnO chips are of circular shape with a diameter of 8 mm and are fabricated by sintering ZnO powders at 1200 °C. An alignment magnetic field of ∼120 Oe was applied parallel to the substrate surface to induce an in-plane magnetic anisotropy during deposition. The target-substrate distance was fixed as 80 mm. The base pressure was 3×10^{-7} Torr. The ambient Ar-gas pressure was 3.0 m Torr and the rf power was 75 W for sputtering. The as-deposited films were subjected to examination and measurement without post annealing. The film phase structure and grain size were investigated by small angle X-ray diffraction (XRD, Philips 1710, 40 kV/40 mA) with Cu-Kα radiation using thin film attachment. The thickness of the film was measured in SEM. The microstructure was characterized by high resolution transmission electron microscopy (HRTEM) using a JEOL JEM 3010 equipped with an energy dispersive X-ray spectrometer (EDXS). Ion milling was used to prepare TEM samples for plane-view. X-ray absorption fine structure spectroscopy (EXAFS) and X-ray-absorption near-edge structure (XANES) at the Co K-edge has been performed on selected sample at the Singapore Synchrotron Radiation Center. The electrical resistivity at room temperature was determined by a conventional four-probe method. The static magnetic properties were measured

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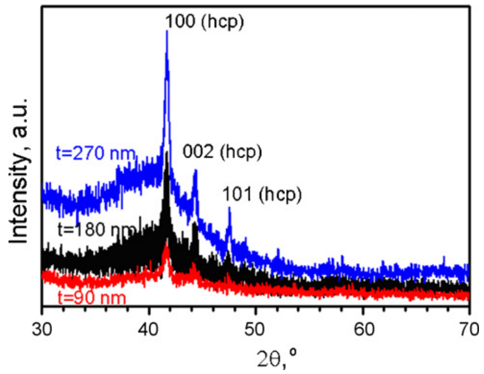

Fig. 1. XRD patterns for the films with various thicknesses.

using an M–H loop tracer and a vibrating sample magnetometer (VSM). The permeability spectrum over the frequency range of 0.1–5.0 GHz was characterized by shorted microstrip transmission-line perturbation method using a fixture developed in National University of Singapore (NUS) and the measurement error for this method has been found less than 10% [14].

3. Results and discussion

Using optimized magnetron sputtering process, CoZnO thin films with thicknesses from 25 nm to 400 nm were fabricated on the Si substrates by adjusting the time of deposition. A shiny and smooth surface was observed for all films. Fig. 1 shows the XRD patterns for the films with thicknesses of 90, 180 and 270 nm, indicating a nanocrystalline structure. The three strong peaks in XRD patterns are corresponding to (1 1 0), (1 0 1) and (0 0 2) crystal planes of hcp structured Co phase. No ZnO or cobalt oxide diffraction peaks were detected in the films. With increase of thickness, the diffraction peaks become narrower and stronger, indicating an approach to high crystallinity, possibly because of the increase of substrate temperature due to extended sputter time. The grain sizes of Co particles in the as deposited films were estimated from Scherrer equation to be roughly 8–12 nm.

The granular structure of the film was confirmed by TEM investigations. As shown in Fig. 2(a) for a film with thickness (t) of 405 nm, nanogranular structure consisting of Co nanocrystallites and amorphous phase has been observed. The nanograins have spherical shape and a very uniform size of ~10 nm, which is in good agreement with above calculation results from XRD patterns. The nanograins are evenly distributed in the amorphous matrix. To verify amorphous structure, we have also examined the film with thickness of 90 nm by HRTEM and the image is showed as Fig. 2(b). An average Co particle size of 8 nm was demonstrated. The EDS analysis (not shown here) also confirmed that Zn and O atoms existed in the film, indicating the proposed structure. Together with the conclusions based on similar alloy system, such as CoAlO films [6], we conclude that the matrix is amorphous. This nano-granular structure is believed to be responsible for the excellent high frequency properties of the films, as discussed later.

To investigate the local structure of the Co dopant in ZnO lattice, we performed X-ray absorption fine structure spectroscopy (EXAFS) and X-ray-absorption near-edge structure (XANES) measurements at Co K-edge. Fig. 3 is the Fourier Transform (FT) of the EXAFS spectrum for a 270-nm-thick Co–Zn–O film. To obtain the FT, the raw absorption spectra were background subtracted. The first peak around $R = 2$ Å is the contribution to the EXAFS signal of the first NN shell, which can be fitted in a single scattering approximation for the quantitative determination of the interatomic distances [15]. The other peaks ($R > 2.6$ Å) reflect the contribution of the more distant neighbors where multiple scattering events become important. The pattern is very similar to the pure cobalt particles or films [16]. Co^0 was detected in the films and No Co–O or Co–Zn bond was detected. The results confirmed that Co exists in the films in the form of Co particles and the oxygen atoms combine with zinc atoms.

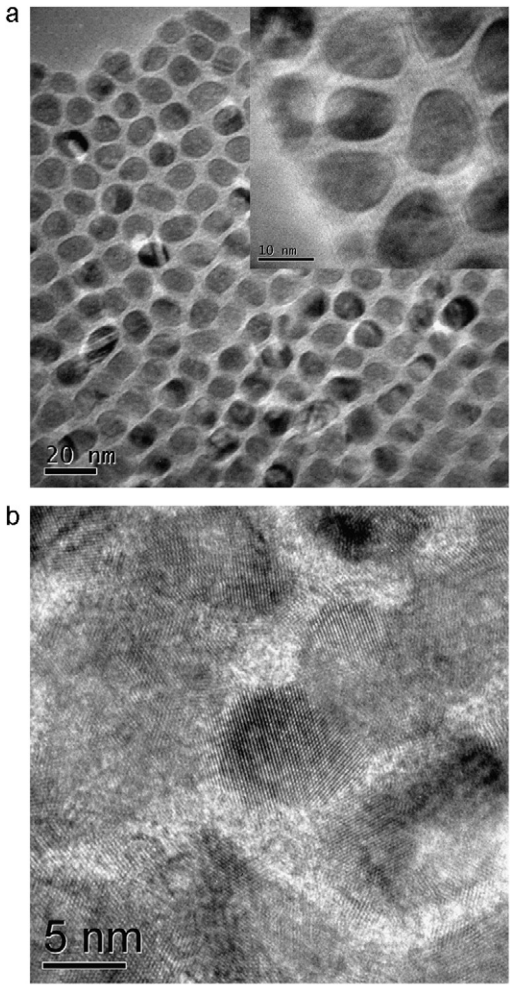

Fig. 2. Microstructure of CoZnO film showing nanogranular structure ((a). TEM for 405 nm thick film; (b). HRTEM for 90 nm thick film).

The variations of coercivities with the film thickness are shown in Fig. 4(a), where H_{ce} is the coercivity along easy direction and H_{ch} the hard direction. Compared to the Co film without (Zn,O) addition, whose coercivity is around 50 Oe [4], the granular films have lower coercivities ($H_{ce} = 5$–28 Oe, $H_{ch} = 3$–13 Oe). The reason is that the Co particles with such a small size in the films are approaching the superparamagnetic limit. The general tendency for the

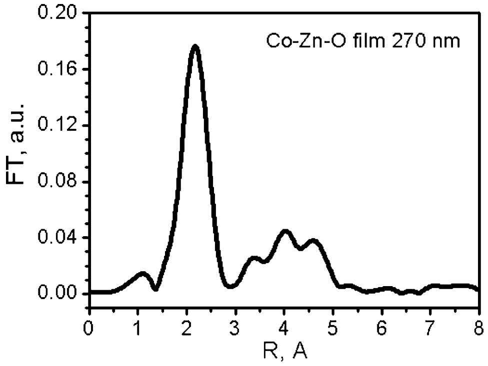

Fig. 3. Experimental EXAFS spectrum for the 270-nm-thick Co–Zn–O film.

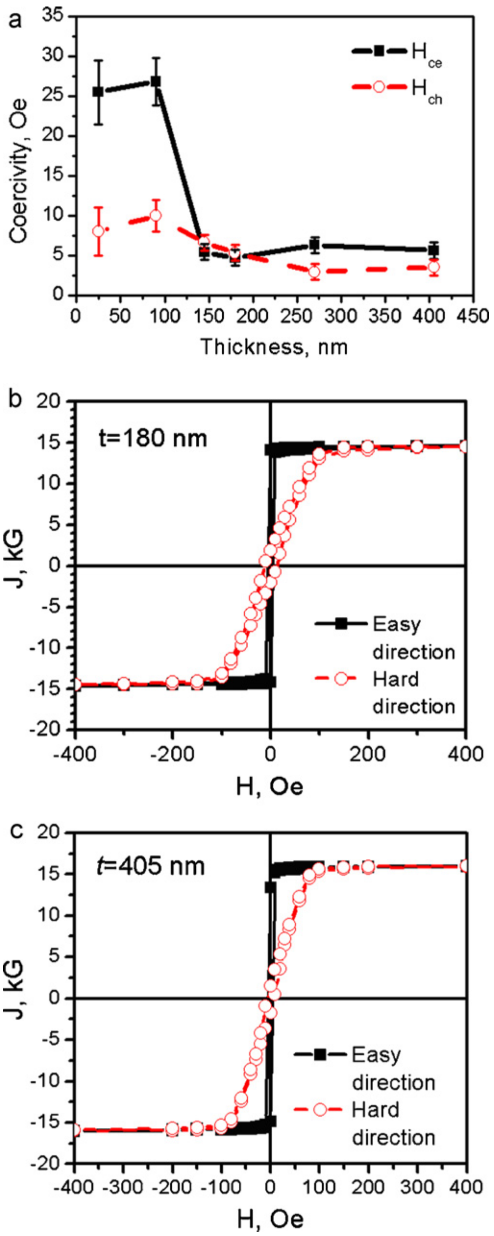

Fig. 4. Thickness dependent coercivities (a) and typical hysteresis loops for CoZnO thin films with thicknesses of 180 nm (b) and 405 nm (c).

thickness dependent coercivity is that the coercivity decreases with increasing thickness. An exemption only occurs in the very thin films with thickness of 25 nm, possibly due to the effect of film-substrate interaction. This is different from our previous finding in Co–Al–O films, where the coercivity increased with thickness due to the perpendicular anisotropy for thicker films [12]. Fig. 4(b) and (c) are the typical M–H loops parallel and perpendicular to the aligning field in the film plane for the films with $t = 180$, and 405 nm, respectively. The results indicate that in-plane anisotropy has been induced by the applied field. This is different from Fe–Al–O granular thin films where field-induced anisotropy is hard to obtain [17]. High anisotropy and the dependence of the coercivity on the thickness in present films indicate that it is also easier to obtain in-plane anisotropy in Co–Zn–O film than that in Co–Al–O film and Fe–Al–O films. The coercivity of the Co–Zn–O film is believed to be dependent on both thickness and grain structure.

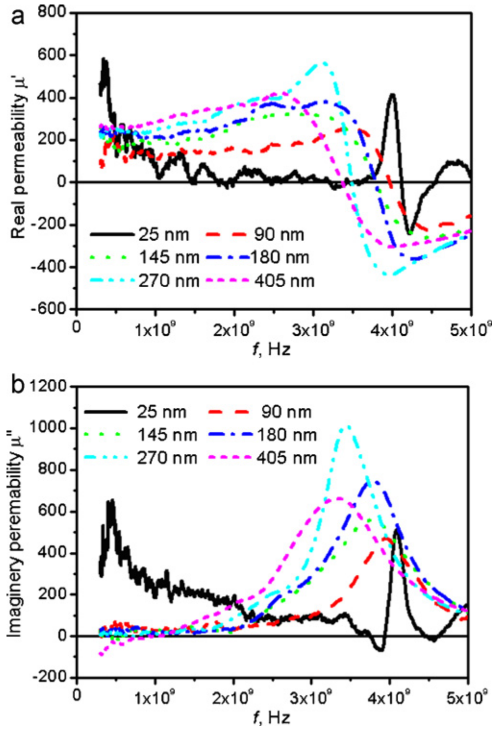

Fig. 5. Real permeability spectra (a) and imaginary permeability spectra (b) for the thin films with various thicknesses.

Fig. 5(a) and (b) shows the real permeability spectra and imaginary permeability spectra over the frequency range 0.3–5.0 GHz for the films with various thicknesses, respectively. The resistivity, static and dynamic magnetic properties of the Co–Zn–O films are shown in Table 1. Based on the common definition, the complex permeability μ is related with real permeability μ' and imaginary permeability μ'' by $\mu = \mu' + i\mu''$. The permeability μ' up to 560, μ'' up to 1000 and ferromagnetic resonance (FMR) frequency (f_r) up to 4.1 GHz have been obtained in these films. The results also show that the values of permeability and resonance frequency strongly depend on the film thickness. Increasing the film thickness generally leads to a shift of the main resonances towards the low frequencies and an increase in the level for both real permeability and imaginary permeability. From Table 1, the real permeability at low frequencies μ'_{low}, the peaks of real permeability $\mu'_{\max}$, the peak of imaginary permeability $\mu''_{\max}$ all increase with the increasing thickness from 90 to 270 nm. For the 270-nm-thick film, the values of μ' and μ'' are up to 564 and 1014, respectively. Figs. 4 and 5 show that the high frequency behavior of 25 nm thick film is quite different from other samples. This is corresponding to its relatively large coercivities (Fig. 3(a)). The reason for this abnormal behavior is not quite clear, but it may be attributed to both film-substrate interaction and structure difference. It is possible that a very thin layer with different structure modified the properties of the 25 nm films. The permeability decreases as the thickness increases from 270 nm to 405 nm possibly due to the appearance of eddy current loss. As we know, the film thickness is an important factor to control eddy current loss. If an ac field is applied to a conducting material, eddy currents are induced inside the material. These currents depend on the materials resistivity, permittivity, permeability, and the ac field frequency. Based on the equation for calculating skin depth $(\delta=(2\rho/(2\pi f\mu_r\mu_0))^{1/2}$, where μ_r is relative permeability, μ_0 is permeability in vacuum) and the values in Table 1. The estimated skin depths of the Co–Zn–O materials based on the following equation are in the range of 0.5–0.9 μm. For very thin films, the eddy current loss should not be responsible for the variation in perme-

Table 1
The resistivity ρ, saturation magnetization M_s, coercivity H_c, anisotropy field H_k, real permeability at low frequencies μ'_{low}, the peaks of real permeability μ'_{max}, the peak of imaginary permeability μ''_{max} and FMR f_r for the Co–Zn–O films with various thicknesses t.

t (nm)	ρ ($\mu\Omega$ cm)	M_s (kG)	H_{ce} (Oe)	H_{ch} (Oe)	H_k (Oe)	μ'_{low}	μ'_{max}	μ''_{max}	f_r (GHz)
25	220	14.2	25.5	8.0	68	20–230	409	512	4.10
90	201	14.5	26.8	10.0	60	130–160	255	468	3.96
145	185	15.0	5.4	6.6	78	180–215	325	563	3.79
180	190	14.7	4.7	5.3	100	215–250	382	745	3.78
270	176	15.0	6.3	2.9	110	235–280	564	1014	3.44
405	175	15.9	5.6	3.5	82	255–360	420	661	3.32

ability since the thickness is less than the skin depth. Only the film with large thickness may be subjected to eddy current loss. This explains the reduced permeability of 405 nm-thick film in our experiment.

It is found in Table 1 that the resistivity slightly decreases with the increasing thickness. Relatively higher resistance for a thinner film demonstrates the effects of substrate-film interface. The values of the resistivity for the films are larger than $1.7 \times 10^{-4}\ \Omega$ cm, which is larger than the value ($\sim 0.8 \times 10^{-4}\ \Omega$ cm) for FeTaN films [18] and similar to that of Co–Al–O films [12]. The high resistivities result from the nanogranular film with both the amorphous + nanocrystalline structure and the insulation + conducting structure. The high resistivity is obviously an advantage for the application of the soft magnetic film since the eddy loss can be reduced by an increasing electrical resistance due to an increasing skin depth [19].

According to calculations based on the Laudau–Lifshitz equation, the frequency characteristics of the permeability in magnetic films is known to be improved by increase not only in resistivity but also in the magnitudes of saturation magnetization M_s and the film anisotropy field H_k [20]. The values of anisotropy field H_k for each film are also shown in Table 1. For the film thickness of 25–270 nm, the real part of permeability μ_i'' shows a low resonance peak at a high H_k, which well agrees with the theoretical calculation by Sohn et al. [21]. The magnitude of real permeability also roughly agrees with that expected from the Stoner and Wolfarth theory, which gives the permeability at a low frequency. $\mu' = 4\pi M_s/H_k$ [22]. Fig. 4 and Table 1 also show that the thinner films have larger value of resonance frequency f_r. As we know, the resonance frequency f_r for the film sample is related to the anisotropy field H_a and magnetization, i.e., $f_r = (\gamma/2\pi)\mu_0\sqrt{H_a M_S}$, where γ is the gyromagnetic ratio. However, if we consider H_a in above equation as H_k in Table 1, the experimental results do not agree with the theoretical values. The reason is not quite clear, but according to Spenato et al. [22], the anisotropy field should be the effective anisotropy field H_i not the conventional anisotropy field H_k due to so-called magnetization ripple in the films. “Magnetisation ripple” has been frequently used to explain the domain pattern and anisotropy of nanograin-matrix heterogeneous system such as CoFeHfO [23], FeCoAlO [24] films and multilayer systems such as FeCoSiN/Al_2O_3 [25] and NiFe/Co-oxides [26] films. Spenato et al. [22] found that, in thin amorphous ferromagnetic films with induced in-plane anisotropy, the magnetic ripples are strongly frequency dependent at the frequency higher than 280 MHz. As our films were excited by GHz frequency field, we can thus suggest that the magnetic ripples have an important effect on the high frequency microwave properties of the present Co–Zn–O films. The domain under hard-axis applied fields probably corresponds to formation of magnetic ripples caused by local variations in anisotropy.

Overall, the results in Table 1 also indicate that, for various applications, the permeability of the Co–Zn–O can be adjusted in a wide range and f_r can be adjusted in the frequency range of 3.3–4.1 GHz by changing the film thickness from 405 nm to 25 nm. High values of μ', μ'', and f_r can be obtained in the films with a range of thicknesses. The superior static and dynamic soft magnetic properties of the Co–Zn–O films with relatively high electric resistivity exhibit the potential applications in micromagnetic integrated devices such as inductors for high-frequency integrated dc-to-dc converters and transformers for power delivery and signal conditioning. They are also promising coatings for microwave absorbers at GHz frequency to be used as magnetoelectric wave shield in laboratory, home electric appliance or communication devices.

4. Conclusions

Anisotropic CoZnO nanogranular films have been fabricated on the Si substrates by rf magnetron sputtering. The films comprise of Co-based nano-crystallites and small amount of (Zn,O) inter-granular amorphous phase, which gives them high resisivities. The films with thickness larger than 100 nm have relatively better magnetic properties. The real permeability up to 560, imaginary permeability up to 1010 and FMR up to 4.1 GHz have been obtained in the films. By controlling the thickness of the granular thin films, the resonance frequencies and the values of the permeability are adjustable in the Gigahertz range. It is believed that the Co-based nano-granular films using Zn-O as matrix can find their wide applications in microwave devices at high frequencies for various purposes, such as applications as inductors in micromagnetic integrated devices and high frequency microwave absorbing coating.

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