



Exchange coupling driven omnidirectional rotatable anisotropy in ferrite doped CoFe thin film

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Isotropic magnetic materials with high resonant frequencies are useful for applications in microwave devices. Undoped CoFe thin films, as common soft magnetic materials with high saturation magnetization, show isotropic characteristics but no high frequency response. Here, we use ferrite doped CoFe thin film to realize a resonant frequency higher than 4.5 GHz at all orientations. The exchange coupling between ferrimagnet and ferromagnet is assumed to play a key role on the omnidirectional rotatable anisotropy.

Thin films of CoFe are widely used soft magnetic materials in static and low frequency applications because of its high saturation magnetization^{1,2}. For high frequency application, undoped CoFe single layer thin films have small in-plane anisotropic field and therefore no high frequency response can be found. With carefully chosen seed layers, the CoFe thin film can be fabricated with anisotropic field less than 40 Oe³⁻⁵. The anisotropic field of 40 Oe can only lead to a resonant frequency of less than 2 GHz which is still limited for microwave applications that require much higher frequencies⁴. Moreover, large eddy current loss caused by small resistivity also restricts its potential application in high frequency devices. Previous works show that the doping of non-magnetic dielectric can induce high resistivity and an in-plane uniaxial anisotropic field in such thin films^{6,7}. But, the doping of a nonmagnetic impurity decreases the saturated magnetisation and hence reduces the resonant frequency. In this report, we demonstrate that the CoFe films doped with NiZn ferrite could increase the resistivity by 7 times from 217 $\mu\Omega$ cm to 1480 $\mu\Omega$ cm while the saturated magnetization maintained at 9.8 kGs. The resonant frequency is above 4.5 GHz and is angular independent, which is valuable for applications. The static anisotropic field is 60 Oe, which is small compared with the dynamical anisotropic field of 292 Oe. Therefore, the high resonant frequency of the ferrite doped CoFe thin film is attributed to its dynamical anisotropic field. We propose a novel ferrimagnet and ferromagnet exchange coupling mechanism to explain the rise of dynamical anisotropic field.

In conventional exchange bias systems with antiferromagnet (AF)/ferromagnet (FM) multilayer structure, the unidirectional anisotropic (exchange bias field) could act as an internal magnetic field and push the resonant frequency to a higher level^{8,9}. Stiles and McMichael¹⁰ introduced a novel concept of rotatable anisotropic field to explain the enhancement of the coercivity and exchanged bias of the AF/FM exchanged biased system. The rotatable anisotropy can only be determined by a dynamic measurement method such as our measurement of permeability spectra¹¹ (see methods) and not by static methods such as vibrating sample magnetometer (VSM). According to Stiles and McMichael¹⁰, the AF grain in the exchange bias system can be classified into two types. The first type is frozen spin grains, with larger uniaxial anisotropic energy, K_{AF} , that will form a partial AF domain wall when FM moment rotates. These AF grains will spring and unwind back to their original direction when the FM moment reverses back to the positive saturation. These grains account for the exchange biased anisotropy observed in VSM measurements in the exchange biased system. The second type of the AF grain is rotatable spin grain, with weaker K_{AF} , which may not be able to form AF partial domain when FM moments rotate. The AF grains irreversibly flipped with their anisotropy direction following the FM moment direction.

The rotatable anisotropy can be determined experimentally by finding the difference between the dynamic anisotropy from a dynamic measurement and the static anisotropy obtained from a static measurement. Alternatively, the information on rotatable anisotropy can be extracted from magnetic field dependent permeability spectra measurement by applying small external magnetic field along various angular orientations. The rotatable anisotropy explains dynamics behaviours of exchange bias system well, including behaviours of FM and

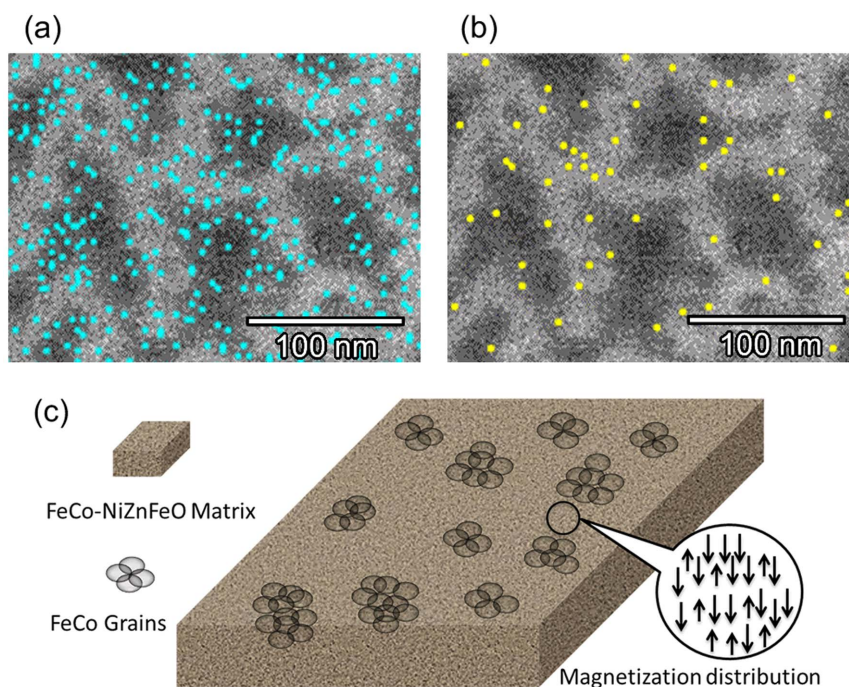


Figure 1 | (a) Co and (b) Ni mapping results of NiZn ferrite doped CoFe thin films. Blue and yellow dots show the distribution of Co and Ni element, respectively. The backgrounds are the corresponding SEM picture. (c) Microstructure sketch map of ferrite doped CoFe thin films to explain the “exchanged” interaction between the CoFe-NiZnFeO matrix and CoFe grains. The insert is a sketch map of magnetization distribution of the CoFe-NiZnFeO matrix.

AF thickness dependence of the coercivity and temperature dependent behaviour. It is also used in the report to explain our observation of the novel dynamic behaviour observed in the ferrite doped CoFe thin film.

A Ni-Zn ferrite is an insulator and ferrimagnet. A ferrimagnet has antiparallel spins similar to AF but with different magnitudes. Once it doped in the CoFe thin film, it will increase the resistivity of the film and do not dilute extensively the concentration of Fe magnetic component in the film. Furthermore, the interface of ferrimagnet and ferromagnet will support some form of exchange coupling to enhance anisotropic field contributing to the increase of the resonant frequency. The nature of the ferrimagnet-ferromagnet exchange coupling will be demonstrated and discussed in this report.

Results

Structure of NiZn ferrite doped CoFe thin films. The thickness of all the samples are fixed at about 110 nm by keeping the deposition time and rate constant and verified by scanning electron microscope (SEM) cross section measurements. From the XRD results of the undoped and ferrite doped CoFe thin films as shown in supplementary information, only a prominent peak at around 45 degree is observed which is ascribed to FeCo (110) bcc. There is no peak corresponding to ferrite phase detected in XRD scans. From this observation, we may suggest that our ferrite doped CoFe films are basically a granular thin film consists of CoFe nanocrystalline and amorphous phase. This argument is seemingly supported by the presence of the granular structure of the ferrite doped CoFe thin films as in the SEM picture with Energy Dispersive Spectrometry (EDS) mapping shown in Fig. 1 (a) and Fig. 1(b) with the mapping of Co and Ni in doped thin film, respectively. The blue dots in Fig. 1 (a) show the distribution of Co elements, and the yellow dots in Fig. 1 (b) represent the distribution of Ni elements. Here, we only give the mapping results of Co and Ni because of the distribution of Fe and Zn are similar with Co and Ni, respectively. With the mapping results, the blue dots are distributed throughout all fields of vision while the

yellow dots are all local at dark areas, which means the doping elements, Zn and Ni are scattered around the dark areas. This observation seems to suggest that the dark areas are those of CoFe alloy cluster, the bright area are those of CoFe-NiZnFeO matrix. The grain structure of the doped thin film can be schematically presented in Fig. 1 (c). The doping elements are embedded in CoFe-NiZnFeO amorphous matrix surrounding the CoFe grain.

Resistivity ρ and saturation magnetization $4\pi M_s$. The resistivity of the ferrite doped CoFe thin films are increased with the doped ferrite concentration being increased from 0 to 11 at % as shown in figure 2. This behavior can be interpreted in terms of the percolation theory¹² where conducting paths are interrupted. The doping host

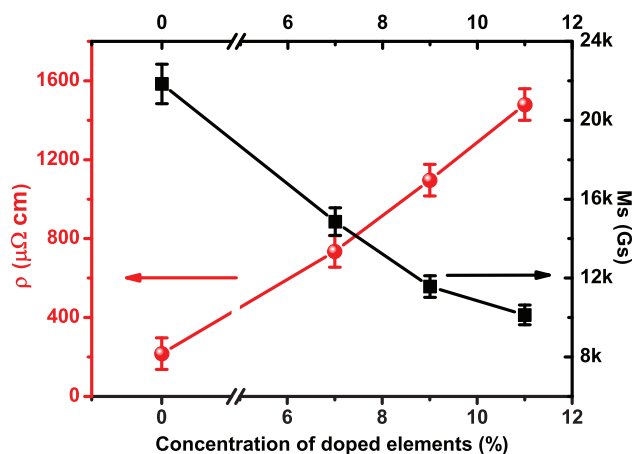


Figure 2 | Resistivity ρ and saturation magnetization $4\pi M_s$ behave as a function of the concentration of doped elements. The error bar comes from the contact resistance during measurement and the thickness measurement of the thin films.

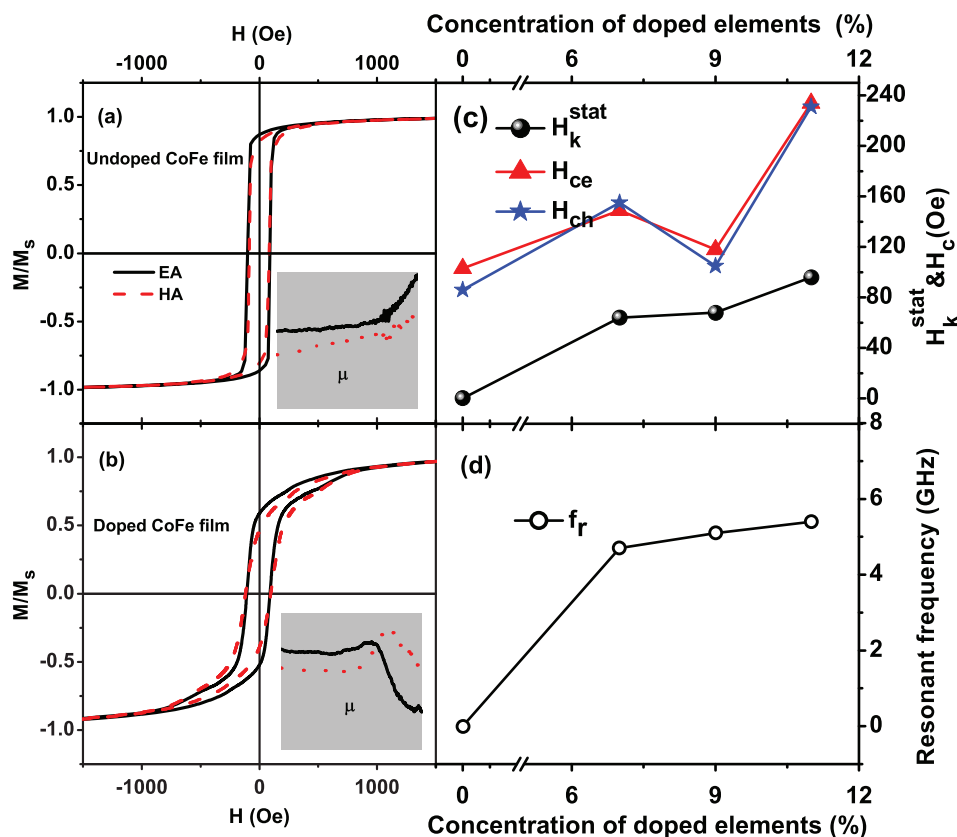


Figure 3 | (a), (b) M-H loops of undoped (a) and ferrite doped (b) CoFe thin films, black and red loops are picked from different direction with largest differences. Inserts are the magnetic permeability spectra of corresponding sample. (c) The changes of coercivities and in plane uniaxial anisotropic fields with the concentration of doped elements. (d) The changes of the resonant frequency of magnetic permeability spectra with the concentration of doped elements.

amorphous matrix increases the separation of CoFe grains and enhances the energy barrier between them. The increase of the resistivity of the granular MTF is due to the broken conducting paths of CoFe grains by insulating doping-host amorphous matrix. The more ferrite is doped, the larger resistivity is as the insulating doping-host amorphous component increases. Simultaneously, as the $4\pi M_s$ of NiZn ferrite is smaller than that of CoFe, the quantity $4\pi M_s$ of the whole films decrease linearly from about 22 kG to 10 kG with the doping composition increase as shown in figure 2.

Static magnetic anisotropic fields. In plane M-H loops of undoped and ferrite doped CoFe thin films are shown in Fig. 3(a) and (b). The undoped FeCo thin film shows magnetic isotropic behavior in the film plane, where the doped films reveal a small magnetic anisotropy with anisotropic field H_k^{stat} about 60 Oe (see Methods for the measurement). As doping elements concentration increase, the changes of coercivities and in plane magnetic anisotropic field with doping elements concentration are shown in Fig. 3 (c). The coercivities and anisotropic fields increase with increasing ferrite doped ratio. The magnitude of coercivity is proportional to the effective anisotropic field of the thin films. According to random anisotropy model^{13,14}, the effective anisotropic fields in magnetic thin film increase as the separation of the grains increases. Thus, the effective anisotropic fields and coercivity increase with the ferrite doped rate increases.

High frequency permeability spectra. The high frequency permeability spectra of undoped and ferrite doped CoFe thin films are shown in the insets of Fig. 3. The undoped thin films do not have visible resonant peak, however, the spectra of doped thin films have a clear resonance peak at about 4.5 GHz along easy axis. The

permeability spectra were fitted to the dynamic Landau-Lifshitz-Gilbert (LLG) theory¹⁵ to obtain dynamic magnetic properties. The fitting results of resonant frequency are shown in Fig. 3 (d). The resonance frequency increases while the doped ferrite increase from 7 at% to 11 at%. Further experiments as shown in Fig. 4 (a) is to study the angular dependence of the high frequency permeability spectra^{16,17}. The results shown in Fig. 4 (b) indicates that the high frequency response of these films are isotropic. The contribution from the uniaxial anisotropy to the total effective anisotropy is small in comparison with the dynamic anisotropy.

Dynamic magnetic anisotropic fields. The dynamic anisotropic field of the ferrite doped CoFe thin films is obtained from field dependence permeability spectra with applied external magnetic field at different directions. Fig. 4(c) presents the dependence of resonant frequency squared (f_r^2) as a function of applied magnetic field H_{app} for $\theta = 0, 40, 90$, where θ is the angle between applied field and easy axis of the thin film. The intercept of a linear regression of f_r^2 versus H_{app} on H_{app} axis is the in plane dynamic anisotropic field H_k^{dyn} . The angular dependence of the H_k^{dyn} is shown in Fig. 4(d) which can be fitted by the expression $H_k^{\text{dyn}} = H_k^{\text{rot}} + H_k^{\text{stat}} \cos 2\theta$. The first term is contributed from the AF rotatable grain as described earlier which is isotropic and only responds to dynamics measurements. The second term is contributed from the uniaxial anisotropy which responds to static magnetic field. We obtained the values of H_k^{rot} and H_k^{stat} as 292 Oe and 60 Oe respectively, the value of H_k^{stat} is consistent with the result obtained from static M-H loops. As the ratio of $H_k^{\text{rot}} / H_k^{\text{stat}}$ is around 5, we conclude that the doped ferrite grains scattering in the film provide pools of rotatable grain to enhance isotropic anisotropy and raise the resonant frequency.

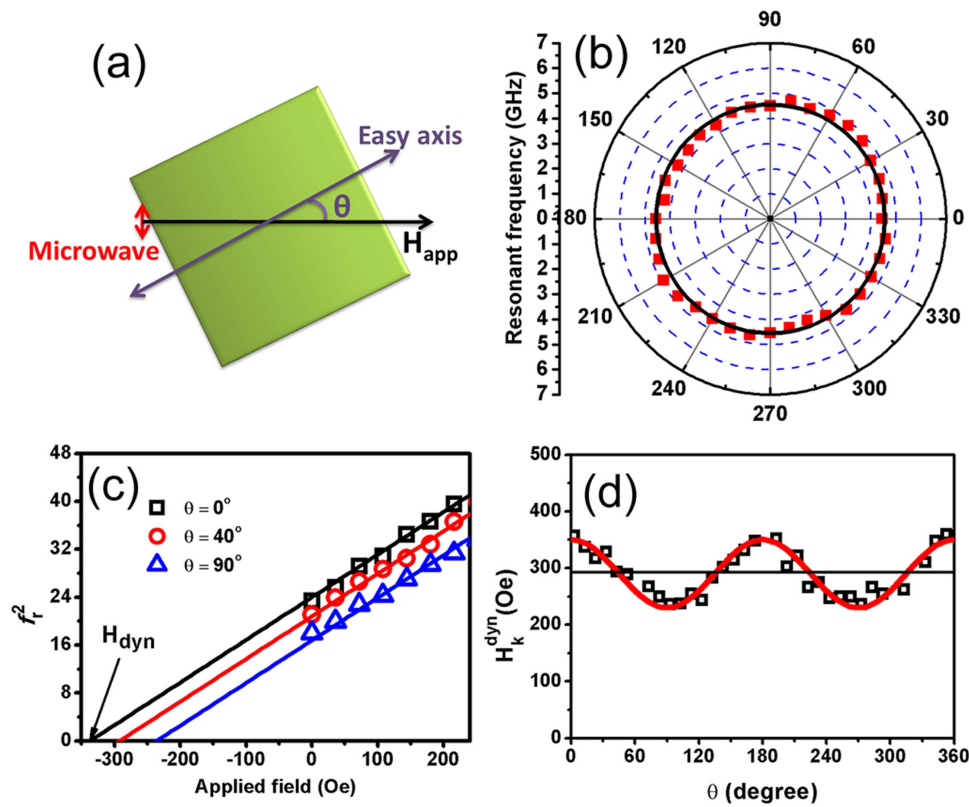


Figure 4 | The high frequency properties of ferrite doped CoFe thin films. (a) The geometry of the measurement, θ is the angle of the magnetic easy axis to the applied magnetic field. (b) The angular dependence of the resonant frequency for ferrite doped CoFe thin film without additional magnetic fields, the dark circle correspond to $f_r = 4.55$ GHz. (c) The dependence of resonant frequency squared (f_r^2) as a function of additional magnetic field H_{app} are shown for $\theta = 0^\circ, 40^\circ, 90^\circ$. (d) The dependence of H_k^{dyn} on θ for ferrite doped CoFe thin films. The line are the fitted curves to the equation $H_k^{dyn} = H_k \cos 2\theta + H_k^{rot}$. The horizontal line is $H_k^{rot} = H_k^{dyn} - H_k^{stat} = 292$ Oe.

Discussion

As the NiZn ferrite is a ferrimagnet, the coupling between doping-host amorphous matrix and the FeCo grain would form an exchange coupling to enhance exchange anisotropy similar to those in ferromagnet/antiferromagnet (FM/AF) exchange biased system and hard/soft magnet coupling in exchange spring magnet^{18,19}. In FM/AF system, the spins in AF are classified into two categories, namely, frozen spins and rotatable spins^{5,6}. The frozen spins are responsible for unidirectional anisotropy and the rotatable spins are responsible for rotational anisotropy. However, exchange bias has not been found in our ferrimagnet/ferromagnet in VSM measurements as most of the spins follow the FM moment when it rotates. We assume the ferrite matrix system play the role of AF in FM/AF system with very thin AF thickness smaller than a critical thickness for the onset of exchange bias¹⁰. In such a system, only rotatable AF spins are presence accounting for the emergence of rotational anisotropy since the AF domain wall is not fully formed. The existence of the rotational anisotropy explains why the magnetization curves obtained from VSM measurement shows quasi-isotropic characteristics while a large magnetic anisotropy is still present in the dynamic permeability spectra through the emerge of resonance frequency peaks. It also accounts for the angular behavior of H_k^{dyn} as in Fig. 4 (d) where rotational anisotropy is present in any measured direction while the measured direction is the same as the FM magnetization.

In summary, we demonstrate that CoFe thin films with small in plane static magnetic uniaxial anisotropic field and thus poor high frequency property can be doped with NiZn ferrite to achieve a large isotropic resonant frequency. This suggests a new route to tailor high frequency magnetic thin film. The mechanisms were explained with a high omnidirectional rotatable anisotropic field with a model similar to exchange bias systems.

Methods

Samples preparation. The NiZn ferrite doped CoFe thin films were deposited in a radio frequency (RF) magnetron sputtering chamber. The 3-inch $\text{Co}_{50}\text{Fe}_{50}$ target with varying numbers of equal dimension of the $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite chips on top of the target. The compositions of the thin films were controlled by changing the number of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite chips. The substrates of the thin films were those of $5\text{ mm} \times 10\text{ mm} \times 0.10\text{ mm}$ MylarTM flexible substrates. The substrates were attached to a water-cooling system at the room temperature with background pressure lower than 5×10^{-7} Torr. During sputtering, an Ar flow rate of 16 SCCM (SCCM denotes cubic centimeter per minute at STP) was needed to maintain an Ar pressure of 2×10^{-3} Torr, and the RF power density was 2.7 W/cm^2 .

Measurement. The compositions of the films and target were measured by energy dispersive X-ray spectroscopy (EDS on Hitachi S4800 SEM). The surface images were taken by field emission scanning electron microscope (SEM, Hitachi S4800). The crystalline structure was characterized by grazing incidence X-ray diffraction (GIXRD, Panalytical Empyrean with Cu K α radiation). The hysteresis loops of the samples at room temperature were taken by a vibrating sample magnetometer (VSM). The resistivities were taken by Keithley 6430 Sub-FA Remote Source Meter. The permeability spectra over the frequency range from 0.5 GHz to 10 GHz were obtained by a shorted micro-strip transmission-line perturbation method¹¹ using a fixture developed in our laboratory, applied fields up to 250 Oe were applied with Helmholtz coils to study the field dependence of the high frequency complex magnetic permeability spectra. The vector network analyzer that was used in the present study is Agilent N5230A.

The static magnetic anisotropic fields were taken by calculating the measured easy axis and hard axis loops of the reduced magnetization²⁰. In this method, the anisotropic energy between easy and hard axis can be calculated by

$$H_k = 2 \int_0^{H_{up}} [m_{ea}(H) - m_{ha}(H)] dH$$

where, m_{ea} and m_{ha} means the reduced magnetization ($m = M / M_s$) taken from the measured easy axis and hard axis loops. The upper integration boundary H_{up} was chosen higher than the saturation field. This method is an effective



method to determine H_k^{stat} for samples which do not have typical easy and hard loops.

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Author contributions

C. K. O. initiated the research project. G. C. did the experiment, measurement and analysis of the results. All the authors discussed the results and put forward the model. G. C. and C. K. O. wrote the manuscript. All the authors proof read the full paper.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

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