CHIN. PHYS. LETT. Vol. 33, No. 11 (2016) 117304

Remanence Enhancement Effect in $Ni_{0.7}Zn_{0.3}Fe_2O_4/Co_{0.8}Fe_{2.2}O_4$ Ferrite Multilayer Film *

Cheng-Hua Fan(范程华)[1,2], Qun-Jing Wang(王群京)[1], Zhen-Fa Zi(訾振发)[2]**

[1]*School of Electrical Engineering and Automation, Anhui University, Hefei 230601*

[2]*School of Electrical and Information Engineering, Hefei Normal University, Hefei 230601*

(Received 24 May 2016)

$Ni_{0.7}Zn_{0.3}Fe_2O_4/Co_{0.8}Fe_{2.2}O_4$ (NZFO/CFO) multilayer films are fabricated on Si(100) substrates by the chemical solution deposition method. The microstructure and magnetic properties are systematically investigated. The results of field-emission scanning electronic microscopy show that the grain size of the NZFO/CFO multilayer film is quite uniform and the thickness is about 300 nm. The remanence enhancement effect of the NZFO/CFO multilayer film can be mainly attributed to the exchange coupling interaction between NZFO and CFO ferrite films, which is in favor of the design and fabrication of modern electronic devices.

PACS: 73.61.−r, 73.90.+f DOI: 10.1088/0256-307X/33/11/117304

In recent years, $Nd_2Fe_{14}B$-based nanocomposite magnets have been proposed to have a huge energy product far beyond theoretically that of traditional $Nd_2Fe_{14}B$ magnets.[1−5] Nanocomposite magnets combine the effect of two suitably dispersed and mutually exchange-coupled phases. The first of these phases is a magnetically hard material, with large anisotropy constant providing high coercivity. The second one is magnetically soft, with a higher magnetic ordering temperature together with higher saturation magnetization (M_s), thus providing enhancement of the remanence magnetization (M_r). An important characteristic of these nanocomposite hard magnets is the exchange coupling between magnetically hard and soft phases, thus the magnetization and anisotropy of the composite represent some average of the respective values for the constituent phases, and M_r is enhanced above $M_s/2$. Nanocomposite magnets combining the best properties of the soft and hard magnetic materials via exchange coupling on a nanometric-sized scale still need experimental efforts.[6−10] To date, the remanence enhancement effects have been observed in some nanostructured Ferich rare earth magnets, such as $SmCo_5/\alpha Fe$, $Nd_2Fe_{14}B/\alpha Fe$, and $Sm_2Fe_{17}C/\alpha Fe$.[11−14] However, there are very few reports on multilayer oxide thin films.

Some attempts have been made to deposit multilayer films by a variety of techniques including melt-spinning,[15,16] rapid-quenching process,[17] mechanical milling,[18] and sputtering.[19] However, most of them cannot be economically applied on a large scale because they require a high vacuum system, complicated experimental steps, and high reaction temperatures.

In this Letter, chemical solution deposition (CSD) is introduced to synthesize multilayer ferrite films on Si (100) substrates. The advantage of this chemical route is not only the low annealing temperature in favor of the crystallization process, but also forming more easily the small homogeneous grain size. $Ni_{0.7}Zn_{0.3}Fe_2O_4$ (NZFO) was selected as the soft magnetic phase because it has the highest M_s in the $Ni_xZn_{1-x}Fe_2O_4$ ($0 \leq x \leq 1$) system in previous reports.[20,21] Based on the previous studies, the magnetic properties (M_r and H_c) of $Co_{0.8}Fe_{2.2}O_4$ (CFO) are superior to those of other Co/Fe stoichiometric proportion[22,23] as the hard magnetic phase. We present and discuss the synthesis, microstructure, and magnetic properties of hard magnetic nanocomposites based on cubic spinel/hexaferrite phases. As a result, the remanence enhancement effect is observed in the NZFO/CFO multilayer film, which not only provides insight into the magnetism of nano-sized magnetic composites but also is a potential application for modern electronic devices.

The NZFO/CFO ferrite film was fabricated by the CSD method. The starting materials were high-purity nickel nitrate hexahydrate $Ni(NO_3)_2{\cdot}6H_2O$, zinc nitrate hexahydrate $Zn(NO_3)_2{\cdot}6H_2O$, cobalt acetate $[Co(CH_3COO)_2{\cdot}4H_2O]$ and ferric citrate ($FeC_6H_5O_7{\cdot}5H_2O$). First, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and $FeC_6H_5O_7{\cdot}5H_2O$ were dissolved in 2-methoxyethanol at 70°C and stirred at this temperature for 20 min. The transparent solution with brown color was stirred at room temperature for 20 h to obtain well-mixed NZFO solution and its total concentration of the metal ions was 0.2 M. Secondly, CFO solution can be obtained in the same way. The films were synthesized by spin-coating on Si (100)

*Supported by the National Natural Science Foundation of China under Grant Nos 11274314, 11374304, 51102072, 21201052 and U1632161, the Natural Science Major Foundation of Anhui Provincial Higher Education Institutions under Grant No KJ2012ZD14, the Natural Science Foundation of Anhui Province under Grant No 1508085MA18, the Postdoctoral Science Foundation of China under Grant No 2013M541848, and the Foundation for University Key Teachers from Hefei Normal University under Grant No 2014136JKC08.

**Corresponding author. Email: zfzi@issp.ac.cn

© 2016 Chinese Physical Society and IOP Publishing Ltd

substrates by using rotation speed of 4000 rpm and time of 50 s, and then were dried at 300℃ for 30 min to expel out the organics. The spin-coating and dry procedures were repeated six times to obtain NZFO and CFO films with desired thickness. The $(Ni_{0.7}Zn_{0.3}Fe_2O_4/Co_{0.8}Fe_{2.2}O_4)_3$ multilayer film, denoted by NZFO/CFO, was spin-coated alternately. Finally, three dried films were annealed at 800℃ under air atmosphere for 20 min to obtain crystallized films.

The crystal structure was examined by a Philips X'pert PRO x-ray diffractometer (XRD) with Cu K_α radiation at room temperature. Field emission scanning electronic microscopy (FE-SEM, FEI designed Sirion 200 type) was carried out to check the morphology and thickness, and the compositions were examined by the energy dispersive spectroscopy (EDS) in FE-SEM. The thickness was checked by the cross section of the FE-SEM. Surface rms roughness was estimated by an atomic force microscope (AFM Park Scientific Instruments designed, Autoprobe CP type). Magnetic measurements were conducted with a SQUID magnetometer (MPMS, Quantum design).

The room-temperature XRD patterns of NZFO, CFO, and NZFO/CFO multilayer films are shown in Fig. 1. The peaks can be indexed to the pure-phase spinel structure with the space group $Fd3m$–O_h^7 apart from that of the Si substrate, and no additional and intermediate phase is observed within the sensitivity of experimental measurements. Based on the peak central positions obtained from the (311) peaks, the estimated NZFO, CFO, and NZFO/CFO ferrite lattice parameters were 0.8363±0.0002, 0.8391±0.0002 and 0.8376±0.0002 nm.

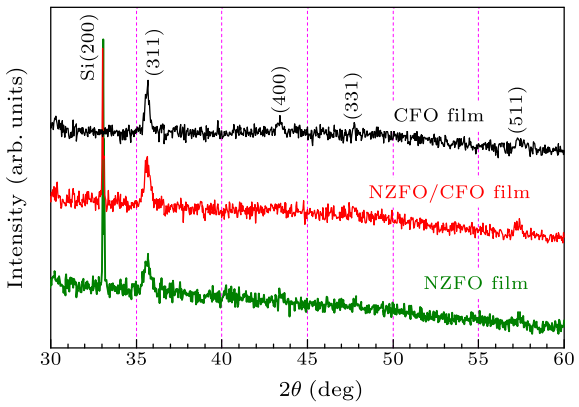

Fig. 1. XRD results of NZFO, NZFO/CFO, and CFO ferrite films on Si (100) substrates annealed at 800℃.

Surface morphology of the ferrite films was observed by FE-SEM images. FE-SEM micrographs of NZFO, CFO, and NZFO/CFO ferrite films annealed under air atmosphere at 800℃ are shown in Fig. 2. It is clearly seen that most of the grains are of homogenous grain sizes of 20–40 nm. The grains of the NZFO/CFO multilayer film are slightly larger than those of the NZFO and CFO ferrite films. The film thickness checked by the cross-sectional SEM micrograph is about 300 nm, as shown in Fig. 2(D).

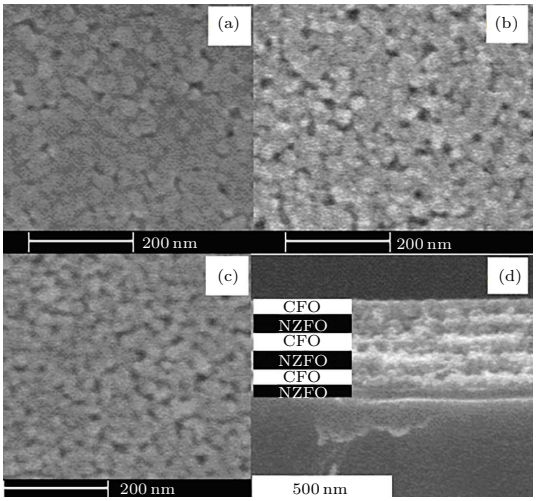

Fig. 2. FE-SEM micrographs of different ferrite films annealed at 800℃: (a) NZFO, (b) NZFO/CFO, (c) CFO, and (d) the cross-sectional SEM micrographs of the NZFO/CFO film.

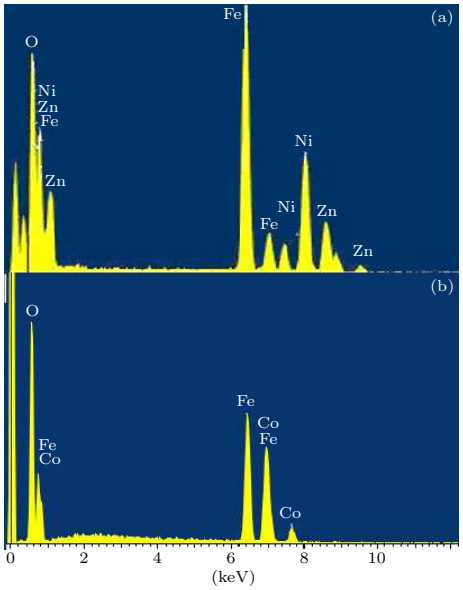

Fig. 3. EDS images of neighboring layer in NZFO/CFO ferrite films on Si (100) substrates.

Table 1. The values of Ni/Zn/Fe ratios in NZFO ferrite and Co/Fe ratios in CFO ferrite.

Sample	$Ni_{0.7}Zn_{0.3}Fe_2O_4$ (NZFO) Ratio of Ni/Zn/Fe	$Co_{0.8}Fe_{2.2}O_4$ (CFO) Ratio of Co/Fe
1	0.72/0.28/2.01	0.76/2.22
2	0.69/0.32/1.98	0.82/2.21
3	0.71/0.31/1.97	0.79/2.18

To rule out the possibility of the interdiffusion between NZFO and CFO interfaces, a quantitative energy dispersive x-ray spectroscopy (EDS) analysis is used to determine the composition of neighbouring NZFO and CFO layers. EDS was also conducted for three different areas of our sample. The results in Fig. 3 show that the molar ratios of NZFO and CFO

are consistent approximately with their nominal compositions. The molar ratios in detail from the EDS spectra NZFO and CFO ferrite are listed in Table 1, which indicates that there is no inter-diffusion between NZFO and CFO interfaces.

The surface morphologies of the films have been characterized by AFM. The typical images are shown in Fig. 4 for different samples annealed at 800℃, which indicates that all of our samples have smooth surfaces. For NZFO, CFO, and NZFO/CFO ferrite films, the surface roughnesses in the rms roughness are 2.5 nm, 3.4 nm, and 4.8 nm, respectively. The surface roughness is slightly dependent on the mean grain size of the sample. That is, the larger grains can enhance the surface roughness.

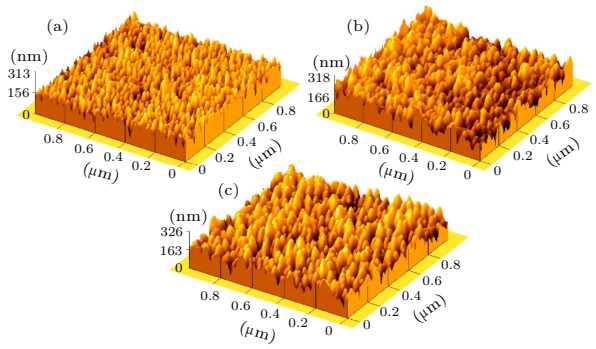

Fig. 4. AFM images of different film surfaces: (a) NZFO, (b) NZFO/CFO, and (c) CFO.

The $M(H)$ loops at 300 K under external fields of −20–20 kOe parallel to the film plane are shown in Fig. 5. It is seen that all ferrite films exhibit hysteresis behavior in the $M(H)$ curves, which indicates the characteristic of ferrimagnetism for our NZFO, NZFO/CFO, and CFO ferrite films. The saturation magnetizations M_s were approximated from the magnetization curves measured under 20 kOe in the parallel direction to the film plane, and M_s of NZFO, NZFO/CFO, and CFO ferrite films are 1410.45 emu/cm^3, 608.91 emu/cm^3, and 400.21 emu/cm^3, respectively. The remanent magnetization M_r can be extracted from the hysteresis loop at the intersections of the loop with the vertical magnetization axis. From Fig. 5 it can be seen that the loop of the NZFO/CFO multilayer film has a high remanent magnetization M_r (312.02 emu/cm^3) compared with that of the single-phase CFO film (207.94 emu/cm^3). Such an enhancement in magnetization can be attributed to the exchange coupling interaction between the soft magnetic NZFO and the hard magnetic CFO ferrite films, and this exchange coupling interaction can truly achieve enhanced magnetization. Furthermore, the hysteresis loop of the NZFO/CFO multilayer film shows a single-phase behavior without any observable kinks. The remanence ratio ($\frac{M_r}{M_s} = 0.513$) of the hysteresis loop is larger than the value of 0.5 predicted for randomly oriented, non-interacting Stoner–Wohlfarth particles,[24] which is the appropriated value for coherent magnetization rotation to occur in single-domain nanoparticles.[25,26] This further indicates the strong inter-grain exchange coupling in the NZFO/CFO multilayer film, with regard to the less saturated magnetization of the NZFO/CFO film than the average magnetization of CFO and ZNFO, which would be attributed to the magnetic moment angle at the interfaces between NZFO and CFO layers. Exchange coupling through multilayer interface can be used to drastically modify the magnetic properties of nanocomposite combining the high magnetization of a soft-magnetic phase NZFO ferrite film with the high anisotropy of a hard CFO ferrite film. Basically, the magnetic fields required to perform a reversible rotation of the magnetic moments in the NZFO soft magnetic phase film are defined by the anisotropy field of the CFO hard magnetic phase film, due to the adjacent magnetic moment angle resulting in the decreased saturated magnetization of the NZFO/CFO film.

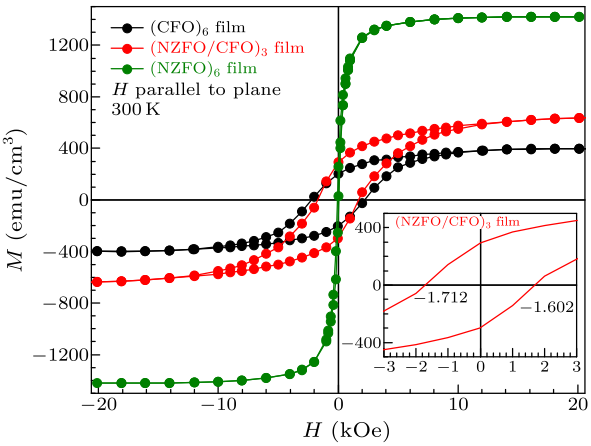

Fig. 5. Room-temperature $M(H)$ hysteresis loops of NZFO, NZFO/CFO, and CFO ferrite films on Si (100) substrates.

The coercivity (H_c) value refers to the intensity of the magnetic field required to reduce the magnetization of the magnetic sample to zero after the magnetization has reached saturation. The value of H_c (1.657 kOe) of the NZFO/CFO multilayer film decreases slightly compared with that of the CFO film (2.102 kOe), and this phenomenon has been found in the $SmCo_5/Fe_x$ nanocomposites.[27,28]

To further make the magnetism clear, the $M(H)$ loop of the NZFO/CFO multilayer film is shown in the inset of Fig. 5 on an enlarged scale. It is evident that the loop of the NZFO/CFO multilayer film is shifted towards negative fields. This exchange bias effect can be attributed to the magnetic moment angle between NZFO and CFO interfaces, since single-phase NZFO and CFO films do not exhibit any loop displacement. Hence the exchange-bias phenomenon of the NZFO/CFO multilayer film provides indirect evidence for the existence of the magnetic moment angle between NZFO and CFO interfaces.

In conclusion, the CSD method has been used to

prepare NZFO/CFO multilayer films. The FESEM results show that the NZFO/CFO multilayer film grains are uniform and the thicknesses of films are about 300 nm. The excellent magnetic properties including room-temperature M_r, M_s, H_c are explained by the interlayer exchange-coupling, which might make it a potential candidate for modern electronic devices in magnetic recording media and permanent magnet field.

References

[1] Cui W B, Takahashi Y K and Hono K 2012 *Adv. Mater.* **24** 6530
[2] Hou F C, Cheng Y, Lou L et al 2013 *Mater. Lett.* **108** 186
[3] Zhang Y M, Li W, Li H L et al 2014 *J. Phys.* D **47** 015002
[4] Sepehri-Amin H, Liu J, Ohkubo T et al 2013 *Scr. Mater.* **69** 647
[5] Liu Z W, Qian D Y, Zhao L Z et al 2014 *J. Alloys Compd.* **606** 44
[6] Ma Y L, Shen Q, Liu X B et al 2014 *J. Appl. Phys.* **115** 17A704
[7] Kneller E F and Hawig R1991 *IEEE Trans. Magn.* **27** 3588
[8] Skomski R and Coey J M D1993 *Phys. Rev.* B **48** 15812
[9] Zhang J, Takahashi Y K, Gopalan R et al 2005 *Appl. Phys. Lett.* **86** 122509
[10] Fullerton E E, Jiang J S, Grimsditch M et al 1998 *Phys. Rev.* B **58** 12193
[11] Horikawa R, Fukunaga H, Nakano M et al 2014 *J. Appl. Phys.* **115** 17A707
[12] Pop V, Gutoiu S, Dorolti E et al 2013 *J. Alloys Compd.* **581** 821
[13] Gong W and Hadjipanayis G C 1994 *J. Appl. Phys.* **75** 6649
[14] Cheng Z H, Zhang J X, Guo H Q et al 1998 *Appl. Phys. Lett.* **72** 1110
[15] Withwanawasam L, Murphy A S, Hadjipanayis G C et al 1994 *J. Appl. Phys.* **76** 7065
[16] Kobayashi T, Yamasaki M and Hamano M 2000 *J. Appl. Phys.* **87** 6579
[17] Hirosawa S, Kanekiyo H and Uehara M 1993 *J. Appl. Phys.* **73** 6488
[18] Zhang J, Zhang S Y, Zhang H W et al 2001 *J. Appl. Phys.* **89** 2857
[19] Liu J P, Liu Y, Skomski R et al 1999 *J. Appl. Phys.* **85** 4812
[20] Zhang H E, Zhang B F, Wang G F et al 2007 *J. Magn. Magn. Mater.* **312** 126
[21] Zi Z F, Lei H C, Zhu X D et al 2010 *Mater. Sci. Eng.* B **167** 70
[22] Júnior A F, Zapf V and Egan P 2007 *J. Appl. Phys.* **101** 09M506
[23] Zi Z F, Zhang S B, Wang B et al 2010 *J. Magn. Magn. Mater.* **322** 148
[24] Stancu A and Ppusoi C1994 *IEEE Trans. Magn.* **30** 4308
[25] Betancourt I, Barrera V and Elizalde-Galindo J T 2016 *J. Supercond. Novel Magn.* **29** 2407
[26] Soares J M, Cabral F A O, Araújo J H de et al 2011 *Appl. Phys. Lett.* **98** 072502
[27] Hou Y L, Sun S H, Rong C B et al 2007 *Appl. Phys. Lett.* **91** 153117
[28] Choi Y, Jiang J S, Pearson J E et al 2007 *Appl. Phys. Lett.* **91** 022502