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Tuning transport and magnetic properties of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ thin films by Co content

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ABSTRACT

We systematically investigated the influence of the Co content on the magnetic and transport properties of spinel $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ($0 \leq x \leq 1$) thin films on MgO (001) substrates prepared by molecular beam epitaxy. Our films exhibited the spinel structure as expected. The Verwey transition was clearly observed in Fe_3O_4 and $\text{Co}_{0.6}\text{Fe}_2\text{O}_4$, while it disappeared with higher Co contents. Electrical resistivity increased with the Co content from $0.003 \text{ } \Omega\text{-cm}$ for $x = 0$ to $1.5 \text{ } \Omega\text{-cm}$ for $x = 1$ at 300 K. As expected, magnetization curves show an increase of the coercive fields of the samples with the Co content. In addition, the samples reveal complex magnetic properties that are explained by a reorientation of the anisotropy easy axis from the crystal (111) directions to the (100) directions with the Co content.

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Highlights:

1. We have successfully grown the epitaxial spinel $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ($0 \leq x \leq 1$) thin films on MgO (001).
2. We observed the tunable transport and magnetic properties by controlling the Co content.
3. Verwey transition temperature was shifted from 105 K in Fe_3O_4 to 115 K in $\text{Co}_{0.6}\text{Fe}_2\text{O}_4$, while it disappeared with higher Co content. The electrical resistivity increased with Co content.
4. We observed a shoulder in M-H curves in the samples $x = 0.6$ and 0.8 .

Keywords: Magnetic, Fe_3O_4 , CoFe_2O_4 , MBE, Spinel

PACS: 75.30.Cr, 75.30.Gw, 75.47.Lx, 75.50.Gg

I. INTRODUCTION

The first magnetic material, magnetite Fe_3O_4 , discovered and used during Ancient Greece, still attracts attentions because of its puzzling properties. It is a ferrimagnet with an inverse spinel structure (lattice constant, $a = 8.397 \text{ \AA}$), showing half-metallic nature and high Curie temperature (T_C) up to 850 K. This material has a first order metal-insulator transition at 120 K, called Verwey transition. The inverse spinel crystal structure of Fe_3O_4 can be expressed as $[\text{Fe}^{3+}]_A[\text{Fe}^{2+}\text{Fe}^{3+}]_B\text{O}_4$, where A denoted the tetrahedrally coordinated Fe^{3+} (A-site) and B denoted the octahedral sites (B-site) [1]. The ferrimagnetism in Fe_3O_4 is due to the antiparallel alignment of the magnetic moments between the two B cations and the single A cation. The electrical conduction in ferrite originates from the superposition of two transport mechanisms, small-polaron (sp) band and sp hopping conduction [2]. Recently, researchers have focused on mixed ferrite, especially with 3d transition metal such as Co, Mn, Zn, Ni, Cu and Cr. It has been reported that the di-valances like Cr^{2+} and Mn^{2+} tend to occupy the A sites, while ions Mg^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} tend to occupy the B sites in the inverse spinel structure [3, 4]. Among them, Co has very large magneto-crystalline anisotropy, which is expected to be of interest because the replacement of Fe ions by Co ions will not only affect the transport properties but also the magnetic properties of ferrite. The fraction of divalent cations that reside on the octahedral site was defined as inverse parameter, λ , where $\lambda = 0$ for normal spinel and 1 for inverse spinel; for example, in CoFe_2O_4 , λ ranges from 0.76 to 0.98 [5]; for random distribution between two kinds of site, $\lambda = 0.67$ [4]. Mössbauer spectra of CoFe_2O_4 supported $\lambda = 0.67$ [6] and Rahman *et al.* estimated $\lambda = 0.54$ [7]. This inverse parameter has a strong effect on the electrical and magnetic properties of bulk ferrite [8]. CoFe_2O_4 has been widely used in applications such as magnetic recording, magnetic stress sensors, spin filtering, millimeter-wave filters, telecommunication equipment, and bio-molecular drug delivery [8-11], etc. There were several reports on the influence of Co concentration to the

physical properties of ferrite. However, to the best of our knowledge, the systematic study of the effects of large Co content on the transport and magnetic properties in epitaxial ferrite thin films has not been reported.

In this paper, we report on the influence of Co content on the magnetic and transport properties of spinel $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ($0 \leq x \leq 1$) thin films. With the increase of Co content the Verwey metal-insulator transition of Fe_3O_4 was shifted to higher temperature and eventually disappeared with large Co content. With increasing Co concentration the electrical resistivity can be tuned over 3 orders of magnitude. Coercive field increased, while saturation magnetization decreased with Co content. More surprisingly a non-zero remanence is observed in the out of plane magnetization curves. This is attributed to an enhancement of the out of plane magnetic anisotropy due to the strains in the films.

II. EXPERIMENT

$\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.0, 0.6, 0.8$, and 1.0) thin films were epitaxially grown on MgO (001) substrates by MBE (VG Semicon, Inc.). The MgO substrate was initially cleaned with methanol before being loaded into the vacuum chamber. After pre-heating at $600\text{ }^\circ\text{C}$ for 30 minutes in ultra-high vacuum (UHV), the substrate was cooled down to $400\text{ }^\circ\text{C}$, and maintained at that temperature during the growth. The base pressure of the growth chamber was $\sim 10^{-9}$ Torr. Atomic oxygen gas was then applied using an oxygen cracking cell. The films were grown by the co-deposition of Co and Fe using effusion cells under an oxygen partial pressure of 10^{-6} Torr. The evaporation rates were determined using a quartz crystal thickness monitor. The expected film thickness was 200 nm. The quality of the films was monitored by *in-situ* reflection high energy electron diffraction (RHEED). The crystal structure of the samples was characterized by X-ray diffraction (XRD). The composition of films was determined after deposition by electron probe micro-analyzer (EPMA). A four-

probe Van der Pauw configuration was employed to measure electrical resistivity. The charge carrier type in the samples was deduced from the slope of ΔV vs ΔT curves using a differential method. The magnetic properties of the films have been examined in-plane and out-of-plane by an alternating gradient field magnetometer (AGFM) and a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, Inc.) with the applied magnetic field up to 25 and 75 kOe, respectively.

III. RESULT AND DISCUSSION

Figure 1 shows the RHEED patterns of the $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ films along the [100] azimuth taken after film growth. The cleaned MgO substrate showed a good RHEED pattern with Kikuchi lines, as shown in the inset of Fig. 1 (a). Streaky RHEED patterns were observed in all samples, indicating the epitaxial growth and smooth surface of the samples on MgO substrate. The pattern also indicated a surface reconstruction in our films. The relation between lattice constant of a crystal and its RHEED lines spacing is expressed as

$$a \sim \frac{1}{d} \quad (1)$$

where a is a -axis lattice constant of the crystal and d is the RHEED lines spacing. Based on the relation (1), we may estimate the lattice constant of the film with standard error of 0.1%. The lines spacing of MgO is two times larger than that of the films, indicating the double lattice constant of the films compared to that of the substrate in agreement with theoretical values.

The crystalline structures of the $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ films on MgO (001) substrate were examined by θ - 2θ scan XRD experiment, as illustrated in Fig. 2. All films exhibited a single phase with an excellent crystalline quality on MgO (001) substrate, which can be indexed in a spinel structure. With the presence of Co, there is a slight shift of (008) peaks toward to the

right. The lattices constants were calculated from (008) peaks; 8.365, 8.357, 8.360, and 8.360 Å for samples $x = 0.0, 0.6, 0.8,$ and 1.0 , respectively. These values indicated a decrease of lattice constants with the presence of Co. Compared to the bulk values of Fe_3O_4 (8.397 Å) and CoFe_2O_4 (8.388 Å), our films exhibited tensile strains; 0.38% and 0.36% for $x = 0.0$ and $x = 1.0$, respectively. These observations are consistent with the substitution of Co into Fe site because of the smaller atomic radius of Co (135 pm) compared to the one of Fe (140 pm) [12].

Figure 3(a) shows the effects of Co doping content on the electrical resistivity of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ in the temperature range from 410 K down to 85 K, which is below the Verwey transition temperature of Fe_3O_4 . For all samples the electrical resistivity decreased with increasing temperature. The introduction of Co atoms into ferrite shows an increasing electrical resistivity over three orders of magnitude from $0.003 \text{ } \Omega\cdot\text{cm}$ for $x = 0.0$ to $1.5 \text{ } \Omega\cdot\text{cm}$ for $x = 1.0$ at 300 K. A Verwey transition was clearly observed in the Fe_3O_4 at around 105 K in agreement with previous report [13, 14]. The observation of a Verwey transition also confirmed the high quality of our un-doped film. With the introduction of small Co content, the Verwey transition temperature increases up to 115 K in the $\text{Co}_{0.6}\text{Fe}_3\text{O}_4$ film. On the other hand, the Verwey transition was not observed for higher Co contents. The conduction in ferrites can be explained by hopping models, where the electrical conduction of ferrite is dominated by electron hopping between Fe^{2+} and Fe^{3+} cations present at octahedral B sites. Hopping rate increases with temperature due to the increase in thermal energy compared to the hopping barrier height [15]. In contrast, in CoFe_2O_4 electron hopping is not possible anymore and electron conduction can only occur by thermal activation of electrons from the valance band to the conduction band. Therefore, the resistivity mainly depends on the size of band gap. J. A. Moyer *et al.* [5] reported that when doping CoFe_2O_4 with Fe the introduction of Fe^{2+} ions produces an increase of the density of states at the fermi level resulting in a shift of the Fermi level with respect to the top of the valance band. In summary the resistivity

measurements show that the replacement of Fe ions by Co ions results in an increase in electrical resistivity originating from the gradual suppression of the electron hopping mechanism, and in a shift and eventually the disappearance of Verwey transition. Interestingly, a transition in the temperature dependent resistivity was observed at 365 K in CoFe_2O_4 as shown in Fig. 3 (a). Note that in bulk form, CoFe_2O_4 exhibited no transition above room temperature [16]. However, a similar transition has been reported in the CoFe_2O_4 nanostructures around 330 K [7] and 370 K [17] assigned to a semiconductor to metallic transition. These authors interpreted this transition by the coexistence of cation-anion-cation (c-a-c) and cation-cation (c-c) interaction in rock-salt-structures.

Figure 3(b) shows the temperature dependent Seebeck coefficient. The sign of the Seebeck coefficient was negative, indicating dominant n-type conduction. The Seebeck coefficient increase with the increase in Co concentration is consistent with the trend in electrical resistivity; from $-63 \mu\text{V/K}$ for $x = 0.0$ to $-215 \mu\text{V/K}$ for $x = 1.0$ at 300 K. A peak at 350 K was also observed in sample CoFe_2O_4 that is consistent with the transition already mentioned in the electrical resistivity.

In order to investigate the influence of the Co content on the magnetic properties of the ferrites we have measured the magnetization as a function of magnetic field using an AGFM set up. Figure 4 shows room temperature in-plane and out-of-plane M-H curves of our films. However, the AGFM maximum magnetic field is 25 kOe and even if this field was large enough to reach the reversible part of the magnetization processes, it was not possible to fully saturate the magnetization of the samples. Therefore, the AGFM measurements were complemented by SQUID measurements in order to properly evaluate saturation magnetizations. The evolution of saturation magnetization versus Co content is shown in Fig. 4(c). Saturation magnetization is decreasing, with the Co content. The decrease of saturation magnetization with the Co content can be interpreted as following. The net

magnetization of spinel ferrite can be given by $M = \sum M_{B\text{-sites}} - \sum M_{A\text{-sites}}$, where $\sum M_{A\text{-sites}}$ and $\sum M_{B\text{-sites}}$ are the contributions to the net magnetization by the cations on the tetrahedral A and octahedral B-sites, respectively [16]. The Co^{2+} ions (magnetic moment $3\mu_B$) in the Co-ferrite system tend to replace Fe ions (magnetic moment $4.9 \sim 6.7 \mu_B$) in either the tetrahedral A-sites or octahedral B-sites, resulting in an overall decrease in the total magnetic moment. The Fig. 4 (c) and (d) also show the evolution of the remnant magnetizations (M_r/M_s) and of the coercive fields as a function of the Co content. It is surprising that the out of plane remnant magnetizations and coercive fields are increasing with the Co content and eventually decrease again when $x=1$. In plane coercive fields only increase with the Co content. An increase of the coercive fields is expected with the introduction of Co because Co ions provide a strong contribution to the magneto crystalline anisotropy. The most likely explanation of the evolution of the out of plane remnant magnetizations and coercive fields is that a reorientation of the magneto crystalline anisotropy takes place with the Co content. Indeed, in bulk Fe_3O_4 the magnetic anisotropy easy axes are along the (111) directions while in bulk CoFe_2O_4 the magnetic anisotropy easy axes are along the (100) directions. When a small content of Co is introduced, the anisotropy is enlarged but the Fe_3O_4 magnetic anisotropy directions are not modified. Since the growth direction of the samples is (100), increasing the anisotropy along the (111) direction will result in an out of plane contribution of the magnetic anisotropy that overcomes (at least partly) the demagnetizing energy. This explains the increase of the out of plane remnant magnetizations and coercive fields until the Co content becomes large enough to allow a reorientation of the magnetic easy axes along the (100) directions. (100) directions are situated as well out of the film plane as in the film plane, therefore no out of plane contribution should be found and in such case out of plane remnant magnetizations and coercive fields should be negligible. Our experimental results show that in agreement with this description the remnant magnetization and out of plane coercive field

decrease when $x=1$ but stay however significantly larger than zero. This might be due to an enhancement of the out of plane magnetic anisotropy due to the strains in the films that have been discussed in a previous paragraph. It can also be noticed that with the presence of Co, a shoulder is observed in sample $x = 0.6$ and more clearly in sample $x = 0.8$ but disappeared in sample $x = 1.0$. Similar shoulders are observed in $\text{CoFe}_2\text{O}_4/\text{Fe}_3\text{O}_4$ bi-layer systems or in any bi-layer systems which consist of one soft and one hard magnetic layers [18 - 21]. However, we do not think that the observation of a shoulder in the magnetization curves of samples $x = 0.6$ and 0.8 is due to the coexistence of soft and hard magnetic phases since this would require a non-homogeneous distribution of the Co ions into the samples. The observation of this shoulder is probably related to the complex magnetic anisotropy orientations discussed above that might lead to complex magnetization reversal processes in samples in which canted and/or perpendicular anisotropy directions compete with demagnetizing field.

IV. CONCLUSION

Through the Co content we have shown that it is possible to tune the magnetic and transport properties of epitaxial $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ($0 \leq x \leq 1$) thin films. The Verwey metal-insulator transition was clearly shown in the samples with $x = 0.0$ and 0.6 but disappeared in the samples with $x = 0.8$ and 1.0 . The electrical resistivity increased with the Co content and can be tailored over more than 3 orders of magnitude. A semiconductor to metallic transition was observed at 365 K in the CoFe_2O_4 film. The samples reveal complex magnetic properties that are explained by a reorientation of the anisotropy easy axis from the (111) directions to the (100) directions with the Co content. In summary the magnetic and transport properties of the films can be easily controlled by changing the Co concentration, indicating a possibility to incorporate $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ films as ferromagnetic electrodes in spintronic devices.

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Figure captions

FIG. 1 (Color online) RHEED patterns of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ thin films; (a) $x = 0.0$, (b) $x = 0.6$, (c) $x = 0.8$, and (d) $x = 1.0$. The inset in Fig. 1 (a) is that of MgO substrate.

FIG. 2 (Color online) XRD patterns of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ thin films on the MgO (001) substrate at various Co concentrations; $x = 0.0$, $x = 0.6$, $x = 0.8$, and $x = 1.0$. All films show spinel crystal structure.

FIG. 3 (Color online) Temperature dependence of (a) electrical resistivity and (b) Seebeck coefficient with different Co concentrations; $x = 0.0$, 0.6 , and 0.8 , and 1.0 . The inset of Fig. 1(a) is a magnification of temperature dependent resistivity of sample $x = 1.0$.

FIG. 4 (Color online) (color online) Room temperature magnetic field dependent magnetization by AGFM for (a) in-plane and (b) out of plane for samples; $x = 0.0$, 0.6 , 0.8 , and 1.0 . (c) saturation magnetization taken from in-plane SQUID measurements and squareness ratio M_r/M_s where M_r is taken from AGFM measurements as a function of Co content. (d) in and out-of-plane coercive fields taken from AGFM measurements as a function of Co content.

FIG. 1, Nguyen *et al.*

FIG. 2, Nguyen *et al.*

FIG. 3, Nguyen *et al.*

FIG. 4, Nguyen *et al.*