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Magnetization Studies of Exchanged Coupled $CoFe_2/CoFe_2O_4$ Bilayers

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The focus of the paper is on an investigation of exchange coupled $CoFe_2/CoFe_2O_4$ bilayers. However, prior to this investigation we examined the growth conditions and related magnetic properties of epitaxial $CoFe_2O_4$ films. In general the results showed an out-of-plane easy direction of magnetization for $CoFe_2O_4$ films deposited in 30-mTorr oxygen pressure at 800 °C. However, for films deposited at 300 °C the easy direction depends on the film thickness. The temperature dependence of the magnetization and coercivity for both the $CoFe_2O_4$ films and the $CoFe_2/CoFe_2O_4$ bilayers was examined between 20 K and 300 K. The magnetization for both the $CoFe_2O_4$ films and bilayers shows a significant increase at low temperature and can be well fitted with a $T^{1.5}$ law. The results further show significant coupling for the $CoFe_2/CoFe_2O_4$, depending on the thickness of the $CoFe_2$ layer.

Key words: Magnetic properties, Exchange coupling, $CoFe_2$, $CoFe_2O_4$,

1- Introduction

Magnetic oxide films continue to be of considerable technological interest because of their potential applications in the microelectronics area. This is particularly true for ferrite films such as $CoFe_2O_4$. $CoFe_2O_4$ with its large magnetic anisotropy and reasonable magnetization, coupled with its excellent tribological characteristics, makes it an excellent replacement candidate for the current conventional metallic Co-based magnetic recording media. In addition to magnetic recording applications, the large magnetic anisotropy, coercivity [1], magnetostriction [2] and Faraday rotation [3-4] make $CoFe_2O_4$ particularly attractive as the material of choice for other applications such as high frequency microwave devices, magneto-optic wave guides and magnetostatic surface wave devices to name a few. Further, $CoFe_2O_4/CoFe_2/CoFe_2O_4$ are good candidates for a new class of materials, namely "exchange spring" materials. Exchange spring magnets consist of interspersed hard and soft magnetic phased materials exchanged coupled at the interface. In the past such interspersed bilayer materials were the basis for hard magnetic materials wherein a high magnetic anisotropy hard magnetic material, in our case $CoFe_2O_4$ and a high saturation magnetization soft magnetic material, $CoFe_2$, were interspersed to obtain a high (BH) energy product hard magnetic material.

With these and other applications in mind we initiated an investigation to examine the magnetic and structure related properties for a series of pulsed laser deposited epitaxial $CoFe_2O_4$ films, and $CoFe_2/CoFe_2O_4$ bilayers. Our study includes the temperature dependence of the magnetization of epitaxial $CoFe_2O_4$ films as well as $CoFe_2/CoFe_2O_4$ bilayers. Magnetic measurements have been performed with VSM and structural analyses have been carried out with x-ray diffraction and atomic force microscopy.

2- Experimental procedure

The $CoFe_2O_4$ films used in this investigation were prepared using pulsed laser deposition (PLD) technique. The soft magnetic layer, $CoFe_2$, used to form soft layer of the $CoFe_2/CoFe_2O_4$ bilayer was deposited by magnetron sputtering. Epitaxial $CoFe_2O_4$ films were achieved by growth on (100) MgO substrates. MgO has a good lattice match with Cobalt ferrite (0.48 % mismatch). The PLD system consists of vacuum chamber together with KrF eximer laser. Prior to each deposition the vacuum system was pumped down to base pressure (10^{-6} mbar). The eximer laser operates in the UV wavelength at 248 nm and delivers a beam, which is focused with a lens on a rotating $CoFe_2O_4$ target. Both the laser energy and the lens position were adjusted to obtain an energy density of 1.5 J/cm^2. During deposition the laser pulse frequency was fixed at 3 Hz and the oxygen pressure was maintained at 30 mTorr. Under these conditions stoichiometric films were obtained. Using these deposition conditions 170 nm to 350 nm thick $CoFe_2O_4$ films were deposited at various substrate temperature between 300 °C and 800 °C. The bilayer films ($CoFe_2/CoFe_2O_4$), on the other hand, were obtained by magnetron sputtering $CoFe_2$ on the $CoFe_2O_4$ films epitaxially grown on MgO. The sputtering conditions consist of 50 mTorr Ar pressure and 60 watts gun power. During the deposition of the $CoFe_2$ on $CoFe_2O_4$, the temperature of $CoFe_2O_4$ film was maintained at 300 °C (1) to avoid any change in the microstructure and magnetic properties of $CoFe_2O_4$ film, (2) to prevent interdiffusion at the interface between the soft and the hard layers, and (3) to achieve a full crystallization of the soft layer ($CoFe_2$). The thickness of $CoFe_2$ was varied between 9 and 40 nm by changing the sputtering time.

3- Results and discussion

Structural analyses performed with XRD confirmed epitaxial growth for films all $CoFe_2O_4$ films. A good illustration of results obtained from the θ/2θ scan spectra is shown in Figure 1., which shows that all crystallographic orientations are parallel to the [100].

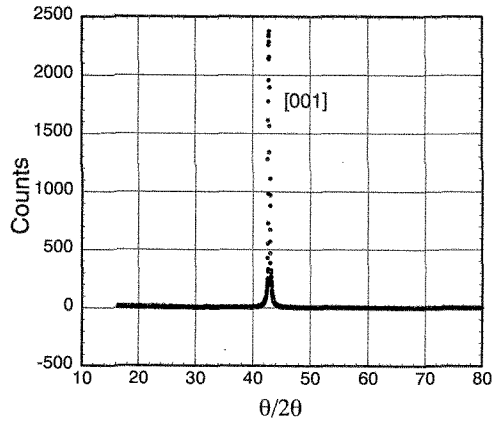

Figure 1. θ/2θ scan spectra (Figure 1.), which shows that all crystallographic orientations are parallel to the (100) texture.

The AFM and MFM analyses reveal a smooth film surface with cluster-like magnetic domains (Figures 2a and 2b). As we shall see below the magnetic properties are dominated by the growth conditions, particularly the substrate temperature and film thickness.

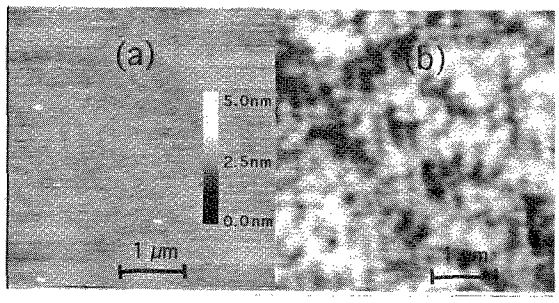

Figure 2. (a) AFM and (b) MFM of $CoFe_2O_4$ film deposited at 800 °C.

In general, it appears that stress is the dominant factor influencing the magnetic properties, particularly for films grown at low substrate temperatures despite the small mismatch between the lattices of $CoFe_2O_4$ and MgO [5]. This result can be well predicted from the large negative magnetostriction of Cobalt ferrite [6]. For example, films deposited at 300 °C with thicknesses between 170 nm and 300 nm show an in-plane or out of plane anisotropy depending on film thickness. At 170 nm an out-of-plane anisotropy is observed (Figure 3.); at 220 nm a spin reorientation appears to be occurring (Figure 4.); and at 300 nm the easy direction of magnetization is in-plane (Figure 5.). Because of its thickness and proximity to the MgO surface the 170 nm film is probably most sensitive to lattice mismatch and strain effects related to the substrate surface. The effects of these strains coupled with the negative magnetostriction of $CoFe_2O_4$ results in an out-of-plane anisotropy for the 170 nm film. However, at 300 nm these effect are somewhat relieved and the film assumes an in-plane easy direction. The 300 nm results are consistent with the results of Dorsey et al, [1].

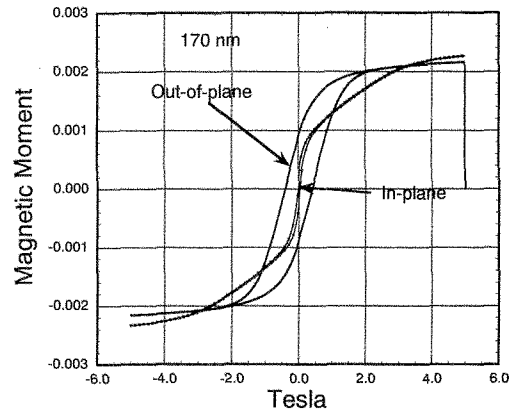

Figure 3. Out-of-plane easy axis for the 170 nm $CoFe_2O_4$ film epitaxially grown on [100] MgO at 300 °C.

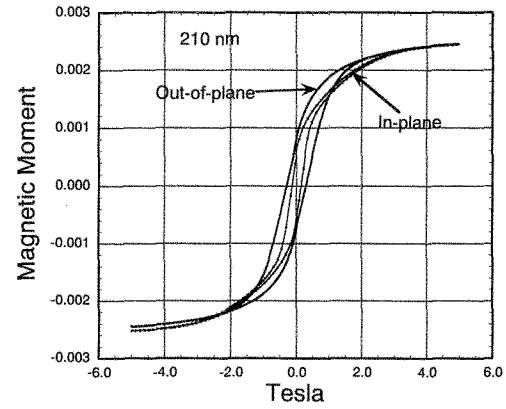

Figure 4. Out-of-plane easy axis for the 210 nm $CoFe_2O_4$ film epitaxially grown on [100] MgO at 300 °C that is near the spin reorientation threshold.

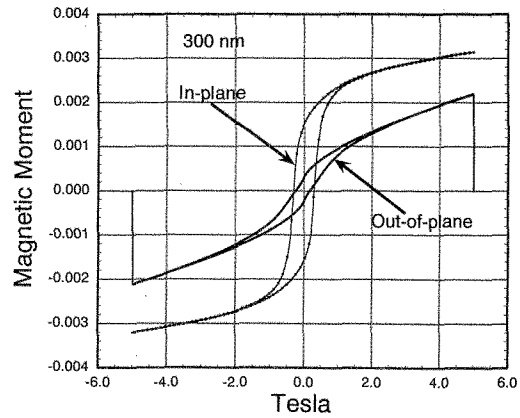

Figure 5. In-plane easy axis for the 300 nm $CoFe_2O_4$ film epitaxially grown on [100] MgO at 300 °C after stress relaxation.

However at 800 °C magnetocrystalline anisotropy is the unique prevailing form of anisotropy. At such growth temperatures any defects within the film that contribute to the internal stress are completely eliminated. Any remaining stress must be due to the differential thermal expansion between the film and the MgO substrate. In-plane and out of plane torque measurements reveal that both types of magnetocrystalline anisotropy (cubic and uniaxial) coexist in our films [5]. Typical magnetic loops of films deposited at 800 °C are shown in Fig. 6.

Despite the shearing induced by the demagnetizing field, the perpendicular loop exhibits a large hysteresis with coercivity $H_{c\perp}$ close to 4 kOe and a remanence of 0.5. However the in-plane loop is quasi linear and exhibits a vertical jump at low fields. The anisotropy field H_k is estimated to be larger than 15 kOe.

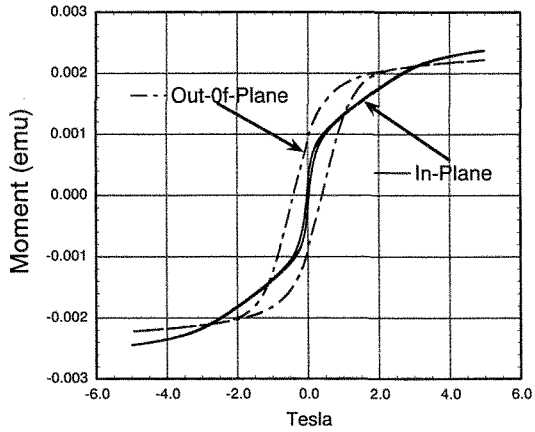

Figure 6. Typical in-plane and out-of-plane loops for epitaxial $CoFe_2O_4$ film deposited on [100] MgO.

In such epitaxial structure where the uniaxial anisotropy is highly oriented perpendicular to the film plane the unique way to interpret this vertical jump is to consider the cubic component of magnetocrystalline anisotropy as revealed by torque analyses. Low temperature measurements of magnetic hysteresis loops have been performed in both directions (field applied parallel and perpendicular to the film plane). Fig. 7 summarizes the results of such study and shows the dependence on temperature of the magnetization M_s and both coercivities (in-plane $H_{c//}$ and perpendicular $H_{c\perp}$). M_s shows a significant increase at low temperature and can be well fitted with a $T^{1.5}$ law. However both coercivities $H_{c//}$ and $H_{c\perp}$ show a considerable increase upon reducing the temperature. At 20 K $H_{c\perp}$ becomes larger than 10 kOe. This huge change in hysteresis and coercivity is certainly related to the strong dependence of magnetocrystalline anisotropy on temperature. It is important to point out that both components of anisotropy (cubic and uniaxial) contribute to $H_{c\perp}$ whereas the origin of $H_{c//}$ is purely cubic.

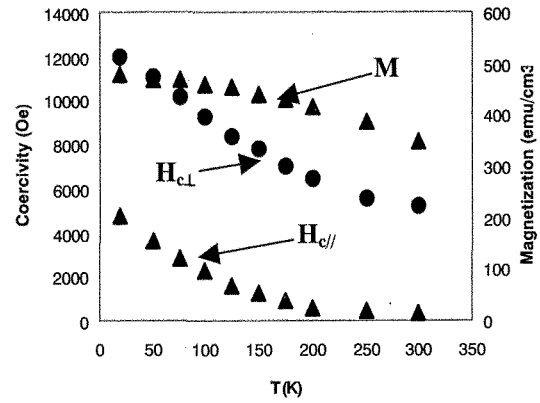

Figure 7. Temperature dependence of magnetization M_s and both coercivities ($H_{c//}$ and $H_{c\perp}$) of $CoFe_2O_4$ film deposited at 800 °C.

The bilayer system was formed by sputtering the $CoFe_2$ soft layer on $CoFe_2O_4$ films epitaxially grown on MgO at 800 °C. For the bilayer system the preference of sputtering rather than PLD to deposit the soft layer was motivated for several reasons. (1) The energy density required to ablate metals by PLD is relatively high and can exceed more than 3 J/cm^2 corresponding to about 300 ev; at these energies metals have a tendency to form "wet spots." (2) The energy of sputtering atoms is relatively low (3 eV) in comparison to that of PLD and allows the preparation of bilayer with a sharp interface. Fig. 8 shows both microstructure and magnetic domains of $CoFe_2$(9 nm)/$CoFe_2O_4$(300 nm), which have been imaged with MFM using tapping-lift mode.

In contrast to flat and continuous structure of epitaxially grown $CoFe_2O_4$ film, the topography of bilayer consists of a granular structure with small circular grains (40 nm) shown in Figure 8a. On the other hand, magnetic domains in the bilayer consist of a cluster-like structure (Figure 8b) and resemble those observed in $CoFe_2O_4$ (Figure 2b).

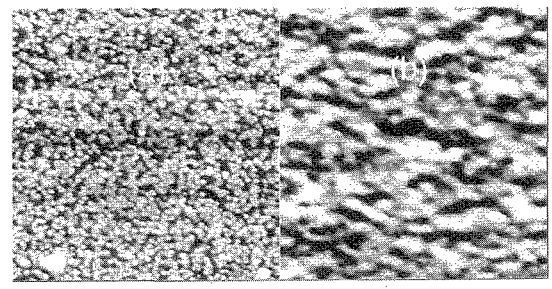

Figure 8. (a) – AFM topography of the $CoFe_2$ surface after deposition on the epitaxially grown $CoFe_2O_4$ film; (b) – MFM domain structure.

This result suggests that even with the $CoFe_2$ soft layer the stray field of the hard layer ($CoFe_2O_4$) is still strong and dominates the magnetic image of bilayer. In such structure most of domains are elongated and the correlation length where the local magnetization is supposed to be uniform can exceed 1 μm. This result also suggest strong coupling between the soft and hard magnetic materials.

In order to illustrate the evidence of magnetic coupling between the soft and hard layers, we examined the hysteresis loops for the bilayer. In the case of a weak interaction a two phase system develops and the resulting loop will be a linear superposition of the soft and hard loops.

An interesting method to probe the coupling in such systems is to examine difference between the hysteresis loop of the hard layer ($CoFe_2O_4$) and the bilayer ($CoFe_2/CoFe_2O_4$). The difference between the loops should reflect the coupling of the soft $CoFe_2$ layer.

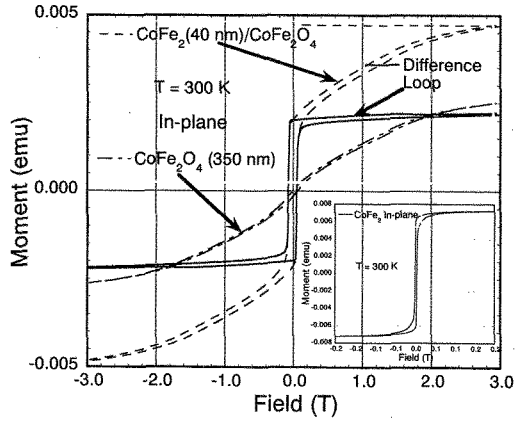

Figure 9. In-plane hysteresis loops measured at 300 K for $CoFe_2O_4$, $CoFe_2$(40 nm)/ $CoFe_2O_4$ bilayer and the difference between $CoFe_2O_4$ and the bilayer.

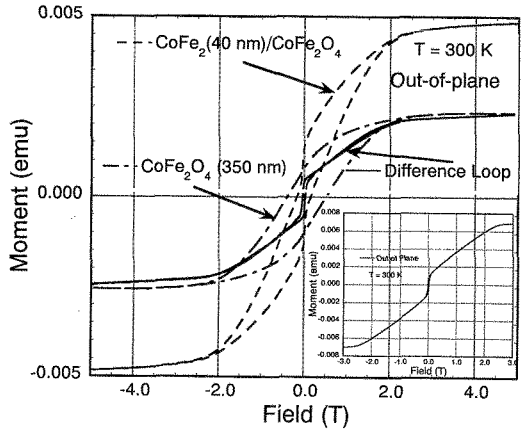

Figure 10. Out-of-plane hysteresis loops measured at 300 K for $CoFe_2O_4$, $CoFe_2$(40 nm)/ $CoFe_2O_4$ bilayer and the difference between $CoFe_2O_4$ and the bilayer.

Examples are shown in Figures 9 and 10 which show the in-plane and out-of-plane loops, respectively for a 350 nm hard $CoFe_2O_4$ film; the same film with a 40 nm layer of $CoFe_2$ deposited ($CoFe_2/CoFe_2O_4$); and the difference between the loops (or "difference loop"), obtained by subtracting the $CoFe_2O_4$ loop from the $CoFe_2/CoFe_2O_4$ bilayer. If there is weak or no coupling the "difference loops" should be similar to the in-plane and out-of-plane hysteresis loops for $CoFe_2$, shown in the inserts in Figures 9 and 10. However, if there is coupling then it should be reflected in the "difference loops."

A comparison of the in-plane and out–of-plane "difference loops" for the 40 nm $CoFe_2$ bilayer with the $CoFe_2$ loops in the inserts shows there is very little difference between the loops. Thus we concluded the $CoFe_2$(40 nm)/$CoFe_2O_4$ bilayer is a two phase system dominated by the in-plane anisotropy of the 40 nm $CoFe_2$ layer. However, when the we examined a 9 nm $CoFe_2$ bilayer significant coupling is observed, (Figures 11 and 12), indicated by the changes in-plane and out-of plane "difference loops."

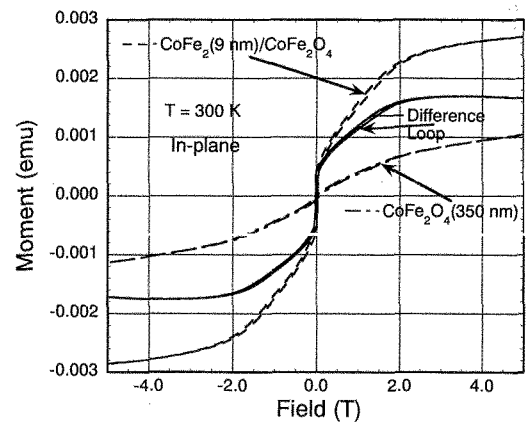

Figure 11. The in-plane magnetic hysteresis loops for $CoFe_2O_4$, $CoFe_2$/ $CoFe_2O_4$ bilayer, and "difference loop" at 300 K.

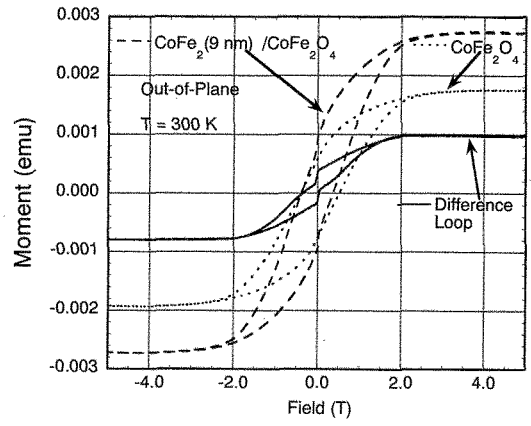

Figure 12. The out-of-plane magnetic hysteresis loops for $CoFe_2O_4$, $CoFe_2$/ $CoFe_2O_4$ bilayer, and "difference loop" at 300 K

The in-plane and out-of-plane "difference loops" no longer resemble $CoFe_2$ loops shown in the inserts, but more closely resemble the $CoFe_2O_4$ loops. In the 9 nm $CoFe_2$ bilayer the magnetic anisotropy of the $CoFe_2O_4$ film dominates the coupling. This result is consistent with the earlier MFM observations that showed very little difference between the magnetic stray field image of the bilayer (Figure 8b) and that of the hard layer ($CoFe_2O_4$, Figure 2b). The $CoFe_2O_4$ hard layer dominates the magnetic image of bilayer.

It is well known in other exchange coupled systems that the coupling is related to the magnetic anisotropy of the hard layer and this coupling increases with decreasing temperature. We found this to be true in our $CoFe_2$/ $CoFe_2O_4$ bilayer system as well. At 20 K and 150 K, both the "difference loop" and the bilayer hysteresis show a significant coupling. This is not only true for the 9 nm $CoFe_2$ layer (Figure 13), but also for the 40 nm $CoFe_2$ layer (Figure 14) where at 300 K appeared to be a two phase system.

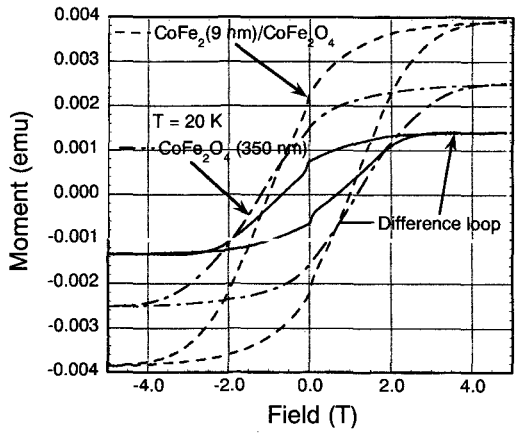

Figure 13. Out-of-plane hysteresis loops measured at 20 K for $CoFe_2O_4$, $CoFe_2$(9 nm)/ $CoFe_2O_4$ bilayer and the "difference loop."

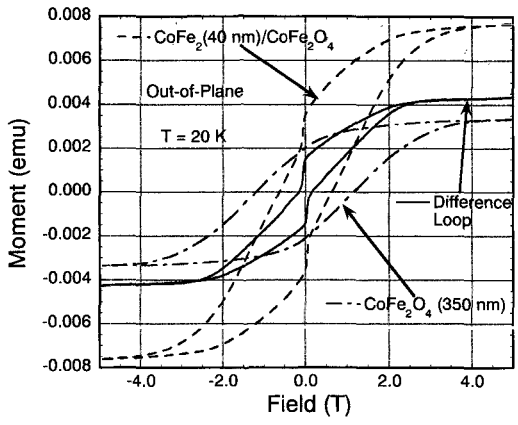

Figure 14. Out-of-plane hysteresis loops measured at 20 K for $CoFe_2O_4$, $CoFe_2$(40 nm)/ $CoFe_2O_4$ bilayer and the "difference loop."

In general ferri/ferromagnetic coupling is much weaker than ferro/antiferromagnetic coupling. In the latter one observes in many instances well-defined shifts in the hysteresis loops; however, in the case of ferrimagnetic/ferromagnetic coupling, a shift in the loop is generally not observed. However, Suzuki et al. [7] did observe a substantial in the hysteresis loop for ferrimagnetic/ferrimagnetic coupling in $CoFe_2O_4$/$(Mn,Zn)Fe_2O_4$ bilayers, where $CoFe_2O_4$ is the hard layer and $(Mn,Zn)Fe_2O_4$ is the soft layer. Ideally in a coupled ferrimagnetic/ferromagnetic system the coercive force of the bilayer should scale reasonably well with the coercive force of the hard ferrimagnetic material and the magnetization should scale with the soft layer, as with most interspersed hard magnetic material. The temperature dependence of the coercive forces for the 9 nm and 40 nm $CoFe_2$ bilayer and their respective $CoFe_2O_4$ films (i.e. the $CoFe_2O_4$ film on which the $CoFe_2$ layer was deposited) is shown in Figure 15. A comparison of the coercivities of the 9 nm and 40 nm $CoFe_2$ bilayer films with coercivities of the $CoFe_2O_4$ films on which they were deposited shows the coercivity of the 9 nm bilayer scales reasonably well with the coercivity of the $CoFe_2O_4$ film as would be expected based on our earlier discussions. On the other the 40 nm $CoFe_2$ bilayer is two phase and coercivity does not track well. The coercivity of the 9 nm $CoFe_2$ bilayer on average is about 0.25 Tesla greater than the coercivity of the 40 nm $CoFe_2$ bilayer over the temperature range between 20 K and 300 K. As expected, the "difference loops" reflect a similar behavior. If one compares the temperature dependence of the coercivities for these curves we see that the coercivity of the 9 nm bilayer increases at a much greater rate with decreasing temperature Figure 16.

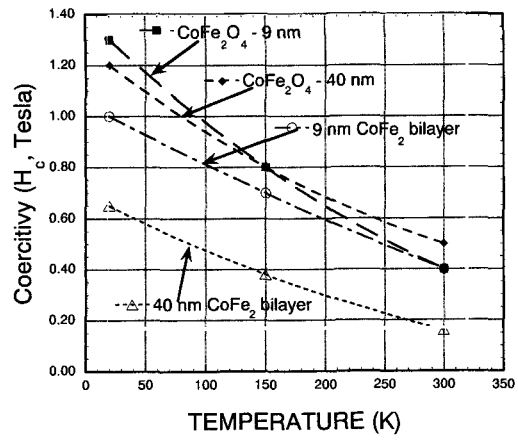

Figure 15. The temperature dependence of the coercivities of the $CoFe_2O_4$ films on which the 9 nm $CoFe_2$ film ($CoFe_2O_4$-9 nm) and 40 nm $CoFe_2$ film ($CoFe_2O_4$-40 nm) were deposited and coercivities of the 9 nm and 40 nm bilayer films.

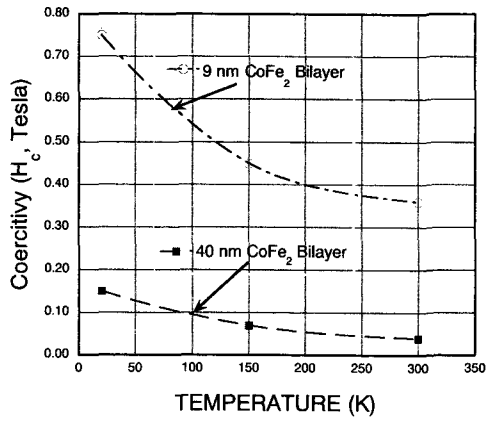

Figure 16. The temperature dependence of the coercivity of the difference curves for the 9 nm and 40 nm $CoFe_2$ bilayer films.

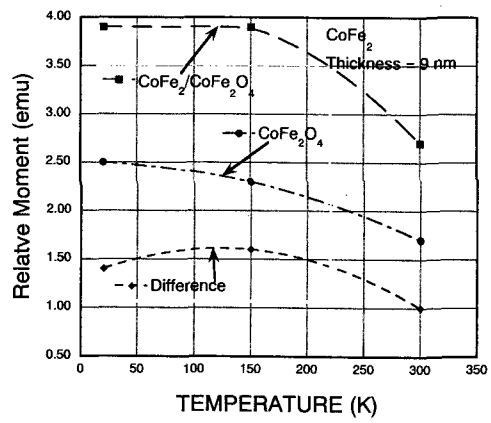

Figure 17. The temperature dependence of the relative magnetic moments for $CoFe_2O_4$, 9 nm $CoFe_2$ bilayer, and the difference

The temperature dependence for the relative magnetic moments for the magnetization of $CoFe_2O_4$, 9 nm $CoFe_2$ bilayer, and the difference between the moments (Figure 17) shows the bilayer magnetic moment increases almost a factor of 1.6 over the $CoFe_2O_4$ moment over the entire temperature range between 20 K and 300K

4-Summary

This investigation gives clear evidence that ferrimagnetic/ferromagnetic coupling exist in the $CoFe_2$/ $CoFe_2O_4$ bilayer system. Both magnetization and magnetic force microscopy support this result. The increase in magnetic moment with little compromise in the coercive force of the hard layer makes the materials potential candidates for a number of applications which include magnetic recording, exchange spring as well as microwave devices. Further we have shown that the spin direction in $CoFe_2O_4$, which is directly related to the anisotropy and intern the coercive force, depends on the deposition temperature and film thickness. At 300 K for thickness around 210 nm the onset of a spin reorientation from out-of-plane to in-plane was observed with increasing film thickness.

5-References

[1] P. C. Dorsey, P. Lubitz, D. B. Chrisey, and J. S. Horwitz, J. Appl. Phys. **79**, 6338 (1996)

[2] M. D. Sturge, E. M. Gyorgy, R. C. LeCraw, J. P. Remeika, Phys. Rev. **180**, 413 (1969)

[3] K. Suzuki, T. Namikawa, and T. Yamazaki, Jpn. J. Appl. Phys., Part 1 **27**, 361 (1988)

[4] L. Bouet, P. Thailhades, and A. Rousset, J. Mag. Mag. Mat. **153**, 389 (1996)

[5] A. Lisfi and C. M. Williams, accepted in J. Appl. Phys.

[6] Y. Suzuki, G. Hu, R. B. van Dover, R. J. Cava, J. Mag. Mag. Mat. **191**, 1 (1999)

[7] Yuri Suzuki, Annual Reviews of Materials **31**, 265-289 (2001).

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