Growth and Magnetic Properties of RF Sputtered Fe-Ga Thin Films

Lalitha Raveendran Nivedita^a, Valiveti Venkata Siva Kumar^b, Kandasami Asokan^b,

Ramasamy Thangavelu Rajendrakumar^{a,c,*}

^aAdvanced Materials and Devices Laboratory, Department of Physics, Bharathiar University,
Coimbatore, India Pin - 641046

^bMaterials Science Division, Inter University Accelerator Centre, New Delhi, India Pin -110 067

^cDepartment of Nanoscience and Technology, Bharathiar University, Coimbatore, India Pin – 641046

Received: November 11, 2014; Revised: February 7, 2015

We report the growth and characterization of Fe-Ga thin films. These films were RF sputtered onto Si, MgO and quartz substrates by controlling the parameters such as the deposition time, power and substrate temperature. The deposited films were characterized using X-Ray Diffraction, Atomic Force Microscopy and Vibration Sample Magnetometry measurements. The effect of substrates on the structure and magnetic properties were studied. XRD pattern of the deposited films showed the formation of DO₃ phase with L1₂ ordered structure at higher sputtering power. The room temperature deposited films demonstrated higher magnetization (0.08 emu/g) as compared to higher substrate temperature (300 °C) deposited films. The M_T/M_s ratio was found to be 0.037 for films deposited at room temperature and 0.009 for the substrate temperature 300 °C. L1₂ order was observed in films deposited on MgO and Quartz substrates. Magnetization was also found to be high (M_s out of plane = 518 emu/cm³, M_s in plane = 707 emu/cm³) for films deposited on MgO substrate.

Keywords: Fe-Ga thin films, RF sputtering, annealing, in plane magnetization, out plane magnetization, lattice rearrangement

1. Introduction

Magnetostrictive thin films with lower saturation field and coercivity; and higher magnetostriction coefficient have applications in magnetic micromechanical systems¹. Since its inception into the world of advanced functional material research, FeGa alloys have gained much popularity and piqued the interest amongst the scientific community owing to their superior mechanical and magnetostrictive properties on comparison with its already in market counterparts like Terfenol-D and shape memory alloys. There are five phases that can co-exist in the FeGa alloys and thin films, namely, a disordered bcc α – Fe phase (A2), an ordered bcc superlattice phase (DO₃), an ordered fcc phase (L1₂), an ordered hexagonal close packed phase (DO₁₉) and an ordered bcc phase (B2) as per the currently available literature. The presence of DO₃ structure is said to be detrimental for obtaining high magnetostrictive property of FeGa alloys or films^{2,3}. It is proposed that one could extract maximum magnetostriction from these materials when it has A2 phase⁴. For magnetostrictive devices, magnetoelastic material in the form of thin films with high magnetostriction constant and low saturation field are desired. There are many results on single crystalline and polycrystalline bulk Galfenol with varying compositions. Gaudet et. al.³, have prepared Fe_{100-x}Ga_x alloys by mechanical milling and reports low degree of Ga clustering in as milled powders which is indicative to the

commencement of short range DO₃ ordering and shows the formation of DO₃ and L1₂ order in annealed samples. Basumatary et. al.⁵ have also reported the presence of all the three phases (A2, DO₃, L1₂) in FeGa alloy. Zhang et. al.⁶, found the DO₃ structure and Ga-rich cluster formation in melt spun ribbons which enhanced their giant magnetostriction. Limited literature is available on RF sputtered galfenol thin films¹. Morley et. al.⁷, prepared FeGa thin films of varying compositions using a customised deposition procedure using both co-sputtering and evaporation process. This was done to facilitate flexibility in the film composition by varying the evaporation rate and sputtering power of the target. Javed et. al.⁸, successfully deposited single phase b.c.c. FeGa thin films which had weak uniaxial anisotropy at lower Ar pressure and exhibited isotropic nature on increased Ar pressure. However, there was no change in magnetostriction constant with respect to varying pressure. Butera et. al.^{9,10}, have successfully grown FeGa films with cubic magnetic symmetry on MgO substrates. Basantkumar et. al.¹, fabricated FeGa films on thin glass cover slides using RF sputtering and studied how the forward power affects its composition and magnetic properties. These groups also succeeded in integrating these films with MEMS cantilevers for magnetic actuation. Present study attempts to fabricate Galfenol thin films by RF sputtering on different substrates varying the deposition parameters and understanding their structural and magnetic properties.

*e-mail: rtrkumar@buc.edu.in

2. Experimental Methodology

Thin Films of FeGa were prepared by RF Magnetron sputtering under different deposition conditions. The RF sputtering unit was a custom made instrument in the Inter University Accelerator Centre (IUAC), New Delhi. The films were prepared at different conditions by varying sputtering parameters such as sputtering power and substrate temperature. FeGa alloy 2" diameter target was RF sputtered with power P_{sp} , which was varied as 80, 100, 120 and 140 W. The typical base chamber pressure was 6.5×10^{-5} torr and the argon working pressure was kept constant for all depositions at 6.5×10^{-2} torr. The films were deposited onto Si substrates at room temperature and at 300 °C by varying the time of deposition and substrate temperature along with sputter power. By varying the time of deposition as 45 min, 90 min and 180 min, we obtained films of thickness ~20nm, ~40nm, ~100nm. 20nm films were deposited at all the four P_{sp} at both room temperature and 300 °C, 40 nm films at P_{sp} of 100W at room and 300 °C substrate temperature and 100nm films at P_{sp} 80W and 140W at room and 300 °C substrate temperature. The structural analysis of the films was done by taking their 2 θ X-Ray scans using glancing incidence X-ray diffractometer (GIXRD), Bruker, D-8 model and Surface morphology analysis was done by Atomic Force Microscopy (AFM), Veeco Instruments Inc.. Magnetic properties of these films were measured by Vibration Sample Magnetometer (VSM), EV-9, Microsense.

3. Results and Discussion

The XRD pattern of the alloy target had two main peaks with (110) reflection at 43.6° and (200) reflection at 63.4° that corresponds to A2 structure. Though this is the most likely crystal structure, it could also be that of DO₃ (Fe₃Al type, α''), which have X-ray diffraction reflections at (220) for 43.6° peak and (400) for 63.4°^[2,11], since the alloy composition is in the range of 25 between 25 and 30%. The same peaks were expected in the sputtered films also. But the XRD showed a predominant peak at ~52° in all the films deposited at different sputtering powers. There were some other reflections present along with this predominant peak under selected sputtering conditions.

The XRD 2 θ scans of 20 nm, 40 nm and 100 nm thick films fabricated by varying P_{sp} were taken. For 20 nm and 40 nm thick films, two peaks were observed at ~52° and ~55° corresponding to the (311) and (222) reflections originating from DO₃ ordering. The high intensity reflection at ~52° clearly identifies the presence of DO₃ ordering^{2,6}. The (222) reflection is of much less intensity. From all the films deposited on Si at various P_{sp} 's, we have concentrated on 100 nm thick films under extreme P_{sp} conditions, namely, 80W and 140W. The films deposited at other conditions were not uniform. Figure 1 shows the XRD patterns of 100nm thick films fabricated at two P_{sp} , 80W and 140W. We observed the presence of DO₃ structure in all the films. Room temperature prepared films deposited at both the P_{sp} demonstrates the presence of the (311) reflection while (222) reflection is absent in higher P_{sp} deposited film. There is evolution of a peak at ~35° in these films, which corresponds to that of (110) reflection of L1₂. Sputtering at higher P_{sp} could have resulted in mixed phase

formation of FeGa, with both L1₂ and DO₃ structure presence in the film. The above mentioned room temperature deposited films were annealed in vacuum for three hours at 500 °C. The (110) reflection was found to completely vanish after annealing. This indicates the probable rearrangement of lattice system of FeGa where L1₂ phase gets rearranged to form DO₃. The crystallite size calculated using Debye-Scherrer formula was in the range of 75 – 90 nm for all the films. There was substantial increase in the crystallite size (~135 nm) after the films were annealed. We have optimised the ambient deposition condition for the films on Silicon to be 140W with 300 °C substrate temperature for a deposition time of 180 min, because it delivers uniform and homogenous films.

There are various reports of FeGa films deposited onto metallic underlayers^{9,12-14} and substrates other than Si and glass. After optimisation, a set of films were deposited on MgO and Quartz substrates along with Si, at P_{sp} 140W, 300 °C substrate temperature for 180 min to see how substrate affects the films. The films were approximately 100 nm thick. The as-prepared films were also annealed in vacuum at 500 °C for three hours. The XRD scans of the as-prepared and annealed films are given in Figure 2a and b.

The film deposited on Si substrate had (311) reflection of DO₃ which was the predominant peak. The other reflections at ~35° and ~62° with (110) and (211) orientations identify the presence of partial L1₂ ordering in the film. There is also the presence of a reflection at ~55° which could be either (222) orientation of DO₃^[2] or (210) orientation of L1₂ ordering². The films on Quartz substrate exhibits only (110) and (211) reflections of L1₂. The dominant reflection on MgO substrate is at ~43° which belongs to (111) reflection of L1₂. The only other peak corresponds to (211) orientation of L1₂.

The X-ray data of films on different substrates (Figure 2) confirms the partial long range ordering of DO₃ and L1₂ structures on different substrates. While Si is the only substrate that favours the development of DO₃ long range order (though with the presence of L1₂ order), MgO and Quartz substrate favours the film deposition in L1₂ ordered structure. The L1₂ (110) and (211) reflections in annealed film on Quartz substrate slightly improves in intensity with

Figure 1. X-Ray diffraction patterns of 100 nm thick FeGa thin films deposited at Room temperature and 300 °C substrate temperature.

Figure 2. X-Ray diffraction patterns of FeGa thin films on different substrates a) as-deposited b) annealed at 500 °C.

a shift of 0.2° to higher 2θ value while they show a shift of ~0.1° to the lower 2θ value in Si substrate with the complete disappearance of the previously dominant DO₃ reflection. The disappearance of DO₃ reflection can only mean that lattice rearrangement occurred. But this is at total contradiction with the result from what we observed in the room temperature deposited films. There, the lattice rearrangements lead to complete formation of DO₃ whereas, here the inverse effect is observed. The shift in the peak 2θ value can also be attributed to the lattice rearrangements. The L1₂ reflections of FeGa on MgO increases in intensity on annealing which manifests betterment of crystallinity of the film.

The calculation of microstrain on films (Table 1) due to the substrate was carried out and it was found that the films on MgO substrates indicated low strain thus manifesting the fact that it may be a better suited substrate for the nucleation and growth of thin films. The microstrain on quartz and Silicon substrates were 3 times greater when compared with MgO. The microstrain was calculated for the dominant peak present in the films in each substrate. The earlier reports mentioning that the lattice mismatch is minimal for FeGa/MgO is affirmed by the minimal strain in thin films.

The surface morphology of the deposited thin films was observed using Atomic Force Microscopy. Figure 3 shows the AFM images of the as-deposited and annealed 100 nm thick FeGa thin films. The films deposited were uniform and the line scans across the AFM images gave the average grain diameter to be in the range of 75-120 nm in as deposited films while it was 45-55 nm in annealed thin films.

It was seen from XRD that the grain size increased on annealing the as deposited film. But this was contrary to what we observed in AFM data. The grain size here reduced drastically from ~110 to ~55nm. It can be inferred that there is columnar grain growth during annealing. The variation in grain size could be due to the presence of inhomogeneous strains in the film⁸. The RMS values of the surface roughness of the films were below 2 nm.

The M-H hysteresis loops for the 100nm thick films (140W) fabricated on Si substrates are shown in Figure 4.

Table 1. The microstrain values calculated from Fe-Ga thin films on different substrates.

Substrate	Microstrain (x10 ⁻³)		
	As prepared	Annealed	As prepared / annealed
MgO	2.7248	1.7278	1.5770
Silicon	8.3445	2.0556	4.0594
Quartz	8.01	4.2496	1.8849

Both room temperature and 300 °C substrate temperature deposited films demonstrate soft magnetic property.

The room temperature deposited films showed higher saturation magnetisation (0.08 emu/g) than the higher substrate temperature deposited films (0.06 emu/g). The coercivity of films deposited at room temperature is 87.697 G with M_r/M_s ratio of 0.03724 while for higher substrate temperature deposited film, coercivity is 12.809 G and the M_r/M_s ratio is 0.00918.

The hysteresis loops for the films deposited on different substrates are plotted in Figure 5. The effect of substrate on M of the films manifests in as deposited films. The magnetization is highest for films on MgO with M_{s//}=512 emu/cm³ and M_{s⊥}= 699 emu/cm³ (Refer Table 2). Magnetization of films deposited on Si and Quartz substrates are in the similar range. On annealing, the overall magnetization reduces with its value being comparable in all substrates, though a slight higher M_{s⊥} value is observed for quartz. The M_{s⊥} / M_{s//} ratio was found to be more or less the same for MgO and Si substrate whereas this is much higher for quartz.

The hysteresis loops for films deposited on different substrates for both as deposited and annealed conditions were plotted as in Figure 6. It is observed that the magnetisation value is higher for as-deposited film on MgO. On annealing, the magnetization of film decreases in both in plane and out of plane directions. The magnetization values improve after annealing for films on Quartz and Silicon. For fcc L1₂ order, the easy axis of magnetization is (111) which is present in the films deposited on MgO substrate. The higher value

Figure 3. a) AFM images of FeGa thin films deposited at 140W at a) Room temperature b) 300 °C substrate temperature c) 140W Annealed @ 500 °C for three hours d) 80W deposited at Room temperature e) 300 °C substrate temperature f) 80W Annealed @ 500 °C for three hours.

Figure 4. Magnetic field dependence of Magnetisation of as-deposited (140W) FeGa thin films on Si substrate. In the inset, we have the zoomed in view.

Figure 5. Magnetic field dependence of Magnetisation of as-deposited (140 W, 300 °C substrate temp.) FeGa thin films measured a) parallel to the film b) perpendicular to the film c) annealed (500 °C) FeGa thin films measured parallel to the film d) perpendicular to the film.

Table 2. The saturation magnetisation values of 140W, 300 °C substrate temp. deposited thin films as obtained from the VSM measurement.

Substrate	Measurement parameters	As prepared	Annealed
MgO	$M_{s//}$ (emu/cm ³)	518	139
	$M_{s\perp}$ (emu/cm ³)	707	182
	$M_{s\perp}/M_{s//}$	1.365	1.309
Quartz	$M_{s//}$ (emu/cm ³)	79.56	117
	$M_{s\perp}$ (emu/cm ³)	204	229
	$M_{s\perp}/M_{s//}$	2.55	1.957
Si	$M_{s//}$ (emu/cm ³)	64.96	107
	$M_{s\perp}$ (emu/cm ³)	86	119
	$M_{s\perp}/M_{s//}$	1.323	1.112

of magnetization for as deposited films on MgO may be attributed to the presence of (111) plane which favours easy axis of magnetization. The DO_3 has (311) plane present which corresponds to the hard axis of magnetization for a bcc crystal as can be seen from the hysteresis loop. The miller planes in as prepared film on MgO exhibited increase in intensity on annealing, with both (111) and (211) planes equally increasing in intensity. The decrease in magnetization after annealing, in MgO substrate, could be due to the miller planes

being present in opposite direction which may annihilate the magnetization achieved by both miller planes. Quasilinear loops are obtained when magnetization was measured parallel and perpendicular to the deposited film. There is enhanced magnetisation and retention of $L1_2$ order in the film which could be attributed as an influence of MgO on the film. The microstrain calculation also indicated the favourability of MgO as a suitable substrate for Fe-Ga film growth. It has been mentioned elsewhere¹⁰ that relative

Figure 6. In plane and Out-of-plane M-H curves of as-deposited and annealed Fe-Ga thin films on different substrates a) MgO b) Quartz c) Silicon.

small lattice mismatch between MgO and FeGa (cubic with $\sim 0.7\%$ lattice mismatch) favours good nucleation and growth of thin films.

4. Conclusions

The structure and magnetic properties of FeGa thin films grown by RF magnetron sputtering technique have been investigated. It was found that long-range ordered DO_3 structure was formed in all sputter conditions, but for high sputter power of 140W in 100 nm thick films, coexistence of L1_2 and DO_3 phases were observed. On annealing this film, lattice rearrangement occurred leading to the disappearance of L1_2 phase, leaving only DO_3 in the film. The effect of substrates on the structure and magnetic properties were

also studied and it was observed that the MgO substrate favoured higher magnetization when compared to Si and Quartz substrates. An anomalous behaviour was observed when 100 nm thick 300 °C deposited film on Si substrate was annealed. The films on MgO and Quartz retained L1_2 order and there was enhanced magnetization for films on MgO substrate.

Acknowledgements

The authors RTR and NLR would like to thank University Grants Commission - Inter University Accelerator Centre, New Delhi for the financial support provided through the UGC – IUAC project (IUAC/XIII.7/UFR-51311/2677).

References

1. Basantkumar RR, Stadler BJH, Robbins WP and Summers EM. Intergration of thin-film galphenol with MEMS cantilevers for magnetic actuation. *IEEE Transactions on Magnetics*. 2006; 42(10):3102-3104. <http://dx.doi.org/10.1109/TMAG.2006.879666>.
2. Lograsso TA, Ross AR, Schlager DL, Clark AE and Wun-Fogle M. Structural transformations in quenched Fe-Ga alloys. *Journal of Alloys and Compounds*. 2003; 350(1-2):95-101. [http://dx.doi.org/10.1016/S0925-8388\(02\)00933-7](http://dx.doi.org/10.1016/S0925-8388(02)00933-7).
3. Gaudet JM, Hatchard TD, Farrell SP and Dunlap RA. Properties of Fe-Ga based powders prepared by mechanical alloying. *Journal of Magnetism and Magnetic Materials*. 2008; 320(6):821-829. <http://dx.doi.org/10.1016/j.jmmm.2007.08.029>.
4. Javed A, Szumiata T, Morley NA and Gibbs MRJ. An investigation of the effect of structural order on magnetostriction and magnetic

- behaviour of Fe-Ga alloy thin films. *Acta Materialia*. 2010; 58(11):4003-4011. <http://dx.doi.org/10.1016/j.actamat.2010.03.023>.
5. Basumatary H, Palit M, Arout Chelvane J, Pandian S, Manivel Raja M and Chandrasekaran V. Structural ordering and magnetic properties of $\text{Fe}_{100-x}\text{Ga}_x$ alloys. *Scripta Materialia*. 2008; 59(8):878-881. <http://dx.doi.org/10.1016/j.scriptamat.2008.06.034>.
 6. Zhang MC, Gao XX, Jiang HL, Qiao Y and Zhou SZ. Effect of Ga content on the magnetostriction and microstructure of Fe-Ga ribbons'. *Journal of Alloys and Compounds*. 2007; 431(1-2):42-44. <http://dx.doi.org/10.1016/j.jallcom.2006.05.093>.
 7. Morley NA, Yeh SL, Rigby S, Javed A and Gibbs RJ. Development of a cosputter-evaporation chamber for Fe-Ga films. *Journal of Vacuum Science & Technology: A, Vacuum, Surfaces, and Films*. 2008; 26(4):581-586. <http://dx.doi.org/10.1116/1.2924416>.
 8. Javed A, Morley NA and Gibbs MRJ. Structure, magnetic and magnetostrictive properties of as-deposited Fe-Ga thin films. *Journal of Magnetism and Magnetic Materials*. 2009; 321(18):2877-2882. <http://dx.doi.org/10.1016/j.jmmm.2009.04.039>.
 9. Butera A, Gomez J, Barnard JA and Weston JL. 'Magnetic anisotropy in $\text{Fe}_{81}\text{Ga}_{19}/\text{MgO}$ (100) films sputtered at different powers. *Physica B, Condensed Matter*. 2006; 384(1-2):262-264. <http://dx.doi.org/10.1016/j.physb.2006.06.005>.
 10. Butera A, Gomez J, Weston JL and Barnard JA. Growth and magnetic characterization of epitaxial $\text{Fe}_{81}\text{Ga}_{19}/\text{MgO}$ (100) thin films. *Journal of Applied Physics*. 2005; 98(3):033901. <http://dx.doi.org/10.1063/1.1996829>.
 11. Kawamiya N, Adachi K and Nakamura Y. Magnetic properties and mossbauer investigations of Fe-Ga alloys. *Journal of the Physical Society of Japan*. 1972; 33(5):1318-1327. <http://dx.doi.org/10.1143/JPSJ.33.1318>.
 12. Adolphi B, McCord J, Bertram M, Oertel C-G, Merkel U, Marschner U, et al. Improvement of sputtered Galfenol thin films for sensor applications. *Smart Materials and Structures*. 2010; 19(5):055013. <http://dx.doi.org/10.1088/0964-1726/19/5/055013>.
 13. Butera A, Weston JL and Barnard JA. Ferromagnetic resonance of epitaxial $\text{Fe}_{81}\text{Ga}_{19}$ (110) thin films. *Journal of Magnetism and Magnetic Materials*. 2004; 284:17-25. <http://dx.doi.org/10.1016/j.jmmm.2004.06.015>.
 14. Weston JL, Butera A, Lograsso T, Shamsuzzoha M, Zana I, Zangari G, et al. Fabrication and characterization of $\text{Fe}_{81}\text{Ga}_{19}$ thin films. *IEEE Transactions on Magnetics*. 2002; 38(5):2832-2834. <http://dx.doi.org/10.1109/TMAG.2002.802468>.