www.amlett.com, www.amlett.org, DOI: <u>10.5185/amlett.2012.ib.101</u> "Nanostructuring by electrons, photons and ions" Special Issue Published online by the VBRI press in 2013

Stabilization of FeCo alloy phase in FeCo-SiO₂ nanocomposites

Hardeep Kumar^{1,2}, S. Ghosh^{1*}, P. Srivastava¹, D. Kabiraj³, D. K. Avasthi³, L. Olivi⁴, G. Aquilanti⁴

¹Nanostech Laboratory, Department of Physics, Indian Institute of Technology, Delhi, New Delhi 110016, India

²Institute of Physics, University of São Paulo, São Paulo 05508-090, Brazil

³ Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi 110067, India

⁴Sincrotrone Trieste S.C.p.A. di interesse nazionale, Trieste, Italy

*Corresponding author. E-mail: ghoshsantanu1@yahoo.co.in

Received: 16 March 2012, Revised: 22 July 2012 and Accepted: 26 July 2012

ABSTRACT

A series of FeCo-SiO₂ granular films of different FeCo atomic concentration (33-54%) have been prepared by fast atom beam sputtering technique and post-annealed in inert (Ar) and reducing (H₂) gas environments. Fe and Co K-edge XANES analysis of as-deposited films indicate that both Fe and Co are present mainly in their elemental (Fe⁰, Co⁰) state. A partial oxidation of Fe and Co is observed, as the FeCo alloy content decreases (54 to 33%) due to reduced particle size. XANES/XAFS analysis shows the formation of FeCo alloy with bcc Fe structure in H₂ environment annealed films. The XRD and Raman analysis of Ar environment annealed films suggest the formation of Co₃O₄ and CoFe₂O₄ phases. The Ar environment is found not to be effective reducing medium to stabilize the FeCo alloy phase, while H₂ environment annealing (450-700 °C) leads to formation of bcc FeCo alloy. Copyright © 2013 VBRI press.

Keywords: Nanocomposite; fast atom beam sputtering technique; XANES analysis; XRD and Raman analysis.



Hardeep Kumar did Ph.D in Physics from Indian Institute of Technology Delhi in 2011. Currently, he is working as FAPESP postdoctoral fellow at DFMT-Institute of Physics, University of São Paulo, Brazil. His areas of interest are studies of magnetic nanocomposite and magnetic alloy thin films from fundamental and technological prospective.

Introduction

Magnetic granular films consisting of nanoparticles of magnetic transition metals (Fe, Co, Ni) or of their alloys (FeCo, FeNi etc.) embedded in an insulating matrix (SiO₂, Al₂O₃ etc.) have been extensively studied in past few years due to their peculiar magnetic and magnetotransport properties like enhance coercivity [1], superparamagnetism anomalous effect [2], Hall [3-5], tunneling magnetoresistance [6-10], high saturation magnetization with high permeability and low coercivity [11-15]. The aforesaid properties make magnetic granular films a good candidate for future technological applications like magnetic recording media, Hall sensors, read heads and magnetoresistive random access memory (MRAM), micro transducers and high frequency devices.

Among various transition metals and their alloys, FeCo alloy based granular films are the most promising candidates for technological applications as they show highest tunneling magnetoresistance (TMR) due to highest spin polarization, and better high frequency response due to large permeability and high saturation magnetization (M_s) of FeCo among all magnetic metals and alloys. In the last few years, several groups have studied the magnetotransport and high frequency response of FeCo alloy based granular films with different insulator matrices [8-13]. X- ray diffraction (XRD) is usually employed for the identification/formation of a phase based on its long range order. However, it is reported in recent past that XRD cannot prove the formation/stabilization of FeCo alloy in sol-gel prepared amorphous/nanocrystalline FeCo-SiO₂ granular solids (both in bulk and film form) due to the lack of long range order and very similar lattice parameters of α -Fe and FeCo.

X-ray absorption spectroscopy, an elemental specific technique has been used by Corrias et al [16, 18] to study the structural evolution of FeCo-SiO₂ granular solids and the formation of intermediate products like metallic oxides and cobalt ferrites depending upon processing conditions and initial precursors used in the sol-gel technique [16]. Granular films may be prepared by a variety of methods like Sol-gel, ion-implantation, sputtering, thermal evaporation and pulsed laser deposition [17]. Out of these, sputtering is used on industrial scale due to uniform film thickness and large area deposition. Recently, atom beam source based sputtering method, called fast atom beam (FAB) sputtering has been employed by our group to synthesize FeCo-SiO₂ granular films under ambient conditions and its structural, electrical, magnetic and temperature dependent TMR properties were studied [10]. The structural characterization of the as-deposited FeCo-SiO₂ granular films was carried out using XRD and selected area electron diffraction, cannot prove the formation of FeCo alloy due to amorphous nature of the films. As stated earlier, X-ray absorption spectroscopy has been employed to study sol-gel prepared FeCo-SiO₂ granular solids [16, 18]. It has been observed in sol-gel prepared FeCo-SiO₂ granular solids that annealing in air at 350°C leads to the formation of Co₃O₄/CoFe₂O₄ phase depending upon the starting precursors used, while annealing in reducing atmosphere (H₂) at 800° C leads to the formation of FeCo alloy nanoparticles [16, 18]. Importance of H₂ atmosphere in avoiding the oxidation of FeCo nanoparticles is also indicated by Chaubey et al [19]. However, the effect of different annealing environments in FeCo-SiO₂ films prepared by sputtering and its study by X-ray absorption spectroscopy is not reported in the literature. In the present work, we have carried out X-ray absorption measurements to study in particular the FeCo phase formation in the silica matrix in as-deposited and annealed (in H₂ and Ar environment) FeCo-SiO₂ granular films.

Experimental

FeCo-SiO₂ granular films were prepared by FAB sputtering technique using 1.5 KeV energy neutral Ar atoms, as described elsewhere [10]. An Ar atom source was mounted at 45° facing towards a 3 in. diameter SiO₂ target partially covered with 5 mm × 5 mm Fe and Co foil pieces (purity >99.9%, Sigma-Aldrich). In this technique, energetic Ar atoms co-sputter SiO₂, Fe and Co together to form granular film structure. Relative area of Fe+Co to SiO₂ target and their sputtering yield decides the FeCo atomic concentration in the granular film. In the present study, the relative area covered by Fe+Co foil pieces on SiO₂ was maintained at 30, 35, 40 and 50% by varying the number of Fe and Co foil pieces on SiO₂ target and the Fe:Co area ratio was kept fixed to 1. The as-deposited granular films

are named as S1, S2, S3 and S4, respectively. The asdeposited films were annealed at 450-700°C in either Ar or H₂ environment in a tubular furnace. Film thickness and quantification of FeCo fraction was performed by analysis of Rutherford Backscattering spectrometry (RBS) plots using RUMP simulation code. It is not possible to distinguish Fe and Co profiles because of the similar masses of Fe and Co atoms, therefore energy dispersive xray spectroscopy (EDAX) is used to know the Fe:Co atomic ratio. Glancing angle x-ray diffraction (GAXRD) measurements were carried out using Cu-k_α radiation (λ =1.5406 Å) at grazing incidence of 1° at a scan rate of 0.03 deg/sec.

The X-ray absorption fine structure (XAFS) experiments were carried out at the XAFS beamline of ELETTRA Synchrotron Light Laboratory (Trieste, Italy) [20]. Data were collected at both Fe and Co K-edges using a Si(111) monochromator on as-deposited and H₂ annealed FeCo-SiO₂ granular films. Data were also collected on some reference compounds: commercial Fe₂O₃ (99.99%), Co_3O_4 (99.9 %), and bcc Fe and fcc Co foils. The energy was calibrated using a Fe foil placed between the I₁ and I₂ ionization chambers. The measurements have been performed in fluorescence mode using a large area Silicon drift detector. The sample was placed at 45° with respect to x-ray beams and to the detector in order to minimize the elastic peak. For FeCo-SiO₂ samples, an Al film was placed between the sample and the detector to absorb the fluorescence peak coming from silicon present in the fused silica substrate. The XANES K-edge spectra have been analyzed using the "fingerprint" method by comparing spectra from samples with those from reference compounds.



Fig. 1. GAXRD pattern of S1, S2, S3 and S4 sample having different FeCo atomic concentartion.

Results and discussion

As-deposited films

Rutherford backscattering spectrometry (RBS) studies show that FeCo atomic concentrations in S1, S2, S3 and S4 samples is 33, 39, 43 and 54% and The Fe:Co atomic ratio is 45:55 (± 2) as determined by EDAX analysis [10]. The

XRD pattern of S1, S2, S3 and S4 samples is shown in Fig. 1. It is clear from Fig. 1 that there are no diffraction peaks corresponding to either crystalline FeCo or silica. This indicates that FeCo particles are in amorphous phase or cluster. Electron diffraction (associated with TEM) analysis also showed that all as-deposited S1-S4 samples are amorphous in nature. Fig. 2(a) and 2(b) show the typical Co 2p and Fe 2p core-level XPS spectrum of S3 film recorded for different sputtering time: 0, 5, 15, 25, 40, 55 and 70 min and designated as A, B, C, D, E, F and G, respectively. In Fig. 2(a) the XPS spectrum of Co foil is also shown for comparison. It is found from XPS analysis that Co is present mainly in metallic (Co^0) state with Co^{2+} as minor phase; on the other hand Fe is present in partially oxidized state in the film as discussed elsewhere [10], due to larger resistance for oxidation of Co than Fe, in accordance with earlier observation [21].



Fig. 2. X-ray photoelectron spectroscopy spectrum for Co 2p core-level (a) and Fe 2p core-level (b) of S3 sample recorded after different sputtering times: 0, 5, 15, 25, 40, 55 and 70 min. Vertical line indicate the binding energy position of different components. In Fig. 2(a) Spectrum of Co foil is shown for comparison.

Fig. 3(a) and **3(b)** shows the normalized XANES spectra of S1-S4 samples (as-deposited FeCo-SiO₂ films) at Fe and Co K-edges, respectively. The K-edge spectra of Fe foil, Fe₂O₃, Co foil and Co₃O₄ are also provided as reference. In Fe and Co K-edge of S1-S4 samples (see **Fig. 3**), two main features are identified: the pre-edge/shoulder (A) and the broad main peak (B). The interpretation of

XANES K-edge spectra for 3d transition metals and metal oxides is well established **[22-24]**. XANES K-edge spectra of 3d transition metals (say Fe and Co) is associated with the transition of 1s electron to empty 4p states. Generally, the absorption edge of transition metal oxides shifts to higher energy with respect to corresponding 3d transition metal. In addition, the XANES spectra of metal-oxides consist of pre-edge peak (s) due to 1s to 3d transitions with 3d-4p mixing.



Fig. 3. Typical XANES spectra for as-deposited S1, S2, S3, S4 samples, reference bcc Fe, fcc Co and reference oxides at (a) Fe K edge, and (b) Co K edge.

On comparing the XANES spectra of S1-S4 samples with reference samples (bcc Fe and fcc Co foils, Fe₂O₃ and Co₃O₄) in Fig. 3 and also with other reference compounds (Fe₃O₄, FeO, CoO and Co₂O₃) from literature **[25]**, it is found that Fe and Co K-edge of S1-S4 are very close to that of their respective metal foils but lower in energy with respect to the reference metal oxides, Fe₂O₃ and Co₃O₄ (see **Table 1**). In Fe K-edge spectra of S1, a pre-edge peak (A) similar to the one observed in the iron oxides is present suggesting the presence of some iron oxide content. The pre-edge peak (A) progressively becomes more broad similar to the one observed in bcc Fe foil as the FeCo concentration increases (S1 to S4), suggesting that the contribution of iron oxide content decreases as the FeCo alloy content increases from S1 to S4. In Co K-edge spectra of S1, a broad feature (A) is observed which is more similar to the shoulder observed in fcc Co foil than the pre-edge of Cobalt oxides suggesting the negligible content of cobalt oxide in S1. The shoulder (A) progressively becomes more similar to the broad one observed in fcc Co foil as the FeCo concentration increases (S2, S3 and S4), suggesting that the contribution of cobalt oxide content (if any) decreases as the FeCo alloy content increases. This is similar to the observations of Carta et al [26].

Table 1. XANES Fe and Co K-edge energy position for S1-S4 samples, Fe and Co foils, Fe_2O_3 and Co_3O_4 oxides.

Come also	Energy (eV)			
Sample	Fe K-edge	Co K-edge		
Fe foil	7120.2			
Fe ₂ O ₃	7125.8			
Co foil		7718.3		
Co_3O_4		7722.0		
S 1	7120	7718.3		
S2	7120.2	7717.9		
S3	7120.3	7718.2		
S4	7120.6	7718.2		

In order to confirm our XANES findings, relatively far edge features (~ 200 eV from the edge) at Fe and Co Kedges of same samples are also compared to that of Fe and Co metal foils. It should be mentioned here that data has not been accumulated in the full energy window available for proper EXAFS (Extended X-ray fine structure) analysis. Therefore, a complete quantitative EXAFS analysis is not attempted with the present data. Fig. 4(a) and (b) shows the XAFS spectra at Fe and Co edge, respectively. The Fe and Co edge energy is rescaled wrt. 7112 and 7009 eV (the first inflection point of bcc Fe and fcc Co foil), respectively. Spectra of S1-S4 samples at Fe K-edge (see Fig. 4(a)) show a significant difference with respect to that of bcc Fe foil, this is expected due to involvement of Fe atoms in a phase other than bcc Fe metal, such as iron oxide. On the other hand, the XAFS Co K-edge spectra of S1-S4 samples (see Fig. 4(b)) show similar far edge oscillations to that of fcc Co foil, but significantly different than that of bcc Fe foil. This indicates that Co is in Co⁰ state and also there is no formation of bcc FeCo alloy in all as-deposited samples. The XANES spectra of nanocrystalline samples are known to be influenced also by size and morphology of particles [27]. It is found from TEM analysis that these samples contain nanometer size particles and particle size increases with FeCo content i.e. from S1 to S4 [10]. It is clear from above analysis that the oxide contribution becomes more important with decrease in FeCo content (from S4 to S1), which is expected due to the variation in particle size with FeCo content. Also, the amplitude of Co far edge oscillations of all samples is lower than that of fcc Co foil and it increases progressively with increase in FeCo content (S1 to S4). The XAFS results are further supported by XPS analysis (see **Fig. 2**) that Fe and Co are present in their metallic state (Fe⁰, Co⁰) as main phase with their corresponding oxides as minor phases. Further Fe is more oxidized than Co, which leads to reduce the amplitude of post-edge oscillations in Fe than Co much sharply.



Fig. 4. Typical XAFS spectra at (a) Fe K-edge, and (b) Co K-edge for asdeposited S1, S2, S3, S4 samples and reference metal foil. In 4(b) Fe Kedge spectra of bcc Fe foil is also included to compare far edge oscillations (C,D, E) of S1-S4 samples with both bcc Fe and fcc Co foils. The energy scale of Fe and Co K-edge is rescaled to zero wrt. 7112 and 7709 eV, respectively

Effect of annealing

FeCo-SiO₂ granular films of different compositions (S1, S2, S3 and S4) have been annealed in H_2 or Ar atmosphere at 450-700°C temperature. The annealed samples are

designated as SX_T_{ann}_Y. Where SX stands for S1, S2, S3 and S4, T_{ann} stands for annealing temperature (in $^{\circ}$ C) and 'Y' stands for annealing environment (either H₂ or Ar). XRD measurements of all samples were carried out to examine variation in structure and phases as a function of annealing environment and annealing temperature. XANES/XAFS and Raman spectroscopy measurements have been carried wherever required.



Fig. 5. XRD pattern of H₂ environment annealed S2_450_H₂, S2_600_H₂ and S2_700_H₂ samples having 39 at% FeCo. Inset Fig. shows the XRD pattern of H₂ environment annealed S1_700_H₂, S2_700_H₂, S3_700_H₂ and S4_700_H₂ samples at 700°C having 33, 39, 43 and 54 at% FeCo, respectively. XRD pattern of Fe foil is also shown in the Fig. and its inset to distinguish α -Fe and α -FeCo phases.

Annealing in H₂ environment

Fig. 5 shows the XRD pattern of $S2_450_H_2$, $S2_600_H_2$ and S2_700_H₂ samples (in 2θ - θ mode) along with XRD pattern of reference Fe foil (θ - θ mode) to distinguish α -Fe and a-FeCo phase. The XRD pattern of Fe foil contains crystalline peak around $2\theta=44.7^{\circ}$ (marked by "+") and has been indexed to (110) plane of α -Fe using standard XRD data (JCPDF file 06-0696). The XRD pattern of all annealed films contains a single peak around 44.9° (marked by "*"), whose intensity increases and FWHM (full width at half maxima) decreases with increase in annealing temperature from 450 to 700°C i.e. from S2_450_H₂ to S2_700_H₂. The other peaks are barely detectable; therefore XRD data is not shown for higher 20 range. Inset of Fig. 5 shows the XRD pattern of samples annealed at 700°C having different FeCo atomic concentration (from 33% to 54%) i.e. S1_700_H₂, S2_700_H₂, S3_700_H₂ and S4_700_H₂. These films contain a single peak around 44.9° (marked by "*"), its intensity increases and FWHM decreases with increase in FeCo concentration. On comparing the XRD pattern of annealed films with that of Fe foil, standard XRD data of Fe (JCPDF file 06-0696, 03-1050 and 01-1267) and FeCo (JCPDF file 49-1568, 44-1433), it is concluded that crystalline peak around 44.9° (marked by "*") could be assigned to (110) plane of either bcc α -Fe or α -FeCo for annealed films. Since the lattice parameter of bcc α -Fe and α -FeCo are very similar. No additional phase is detected. Therefore, it is evident that due to very similar lattice parameters of bcc α -Fe and α - FeCo phase, XRD cannot give conclusive information on the formation of FeCo alloy in H_2 annealed films.



Fig. 6. Typical XANES spectra at (a) Fe K edge, (b) Co K edge and (c) XAFS spectra at both Fe and Co-K edge for H_2 environment annealed $S1_700_H_2$, $S2_700_H_2$ and reference samples.

On the contrary, XANES analysis at the Fe K-edge and Co K-edge can provide very detailed information. In particular, the definitive evidence of the formation of the bcc FeCo alloy can be obtained by comparing the XANES spectra of the annealed films at the Fe K-edge and Co Kedge with the XANES spectra of bcc Fe and fcc Co foils. Fig. 6(a) and 6(b) show the typical normalized XANES spectra of S1_700_H2 and S2_700_H2 along with bcc Fe foil, fcc Co foil, F₂O₃ and Co₃O₄ reference samples at Fe and Co K-edge, respectively. It may be noted from Fig. **6(a)** that the spectrum of S1 700 H_2 and S2 700 H_2 at Fe K-edge present the same oscillations as that of bcc Fe foil. However, the Co K-edge spectrum of S1_700_H₂ and S2_700_H₂ do not matches with fcc Co foil spectra nor with that of Co_3O_4 (see Fig. 6(b)), but appear similar to bcc Fe foil spectra. This indicates the formation of bcc FeCo alloy in H₂ environment annealed (S1_700_H₂ and $S2_700_H_{2}$ samples. In order to clearly show the formation of bcc FeCo alloy, both the Fe and Co K-edge spectra of annealed samples S1_700_H2, S2_700_H2, bcc Fe and fcc Co foil are shown in extended energy range together in Fig. 6(c). In Fig. 6(c), a striking similarity in post edge oscillations can be seen for the spectra recorded at Fe and Co-K edges of S1_700_H₂ and S2_700_H₂ and bcc Fe foil. The Fe spectra of annealed samples present the same oscillations as that of bcc Fe foil. This furthers strengths our conclusion that annealing in H₂ environment results in bcc FeCo alloy formation. Similar result was observed for sol-gel prepared FeCo-SiO₂ granular films by Casula et al [18].

Annealing in Ar environment

Fig. 7 shows the typical XRD pattern of S1_600_Ar, S2_600_Ar and S4_600_Ar samples. The XRD pattern contains many crystalline peaks but none corresponds to (110) and (200) plane of α -Fe and α -FeCo in the scanned 20 range. The crystalline peaks in Fig. 7 have been indexed as (311), (222), (400), (511), (400) planes of Co₃O₄ (marked by '•`) and (220), (311), (400), (422), (511), (411) planes of Fe₃O₄/γ-Fe₂O₃/CoFe₂O₄ (marked by "o"). The same phases are observed for samples annealed at 450 and 700 °C in Ar environment (Figs. not shown). Bulk Fe₃O₄ (T>T_v, where T_v is Verwey transition), γ -Fe₂O₃ and CoFe₂O₄ are reported having similar inverse-spinal structure with O_h^{\prime} (Fd3m) space group. Due to similar structure and lattice parameter of Fe_3O_4 (T>T_v), γ -Fe₂O₃ and CoFe₂O₄, XRD analysis cannot conclude the actual phase (s) present in S1_600_Ar, S2_600_Ar and S4_600_Ar samples.



Fig. 7. XRD pattern of Ar environment annealed S1_600_Ar, S2_600_Ar and S3_600_Ar samples.

Therefore, Raman spectroscopy was further used to investigate the S1 600 Ar, S2 600 Ar and S4 600 Ar samples. For the cubic symmetry, one expects five Raman active $(A_{1g}, E_g \text{ and } 3T_{2g})$ modes according to group theory. At room temperature $(T>T_v)$, Fe₃O₄ exhibit five Raman active modes around 670 cm⁻¹ (A_{1g}), 410 cm⁻¹ (E_g), 190 cm⁻¹ 1 [T_{2g}(1)], 540 cm⁻¹ [T_{2g}(2)] and 300 cm⁻¹ [T_{2g}(3)] according to group theory. But generally only three modes around 308, 540 and 670 cm⁻¹ are reported experimentally [28-31]. In γ -Fe₂O₃, three Raman modes around 350 (T_{2g}), 500 (E_g) and 700 cm⁻¹ (A_g) are generally observed [29, 31, 32], while remaining two modes around 1370 and 1580 cm⁻¹ (T_{2g}) are observed rarely in some studies [28, 33, 34]. For CoFe₂O₄ five Raman modes are observed around 195, 300, 470, 620 and 690 cm⁻¹ [35-38]. Co₃O₄ crystallizes in the normal spinal structure with O_{h}^{\prime} space group and exhibit five Raman active modes (A_{1g} , E_g and $3F_g$) around 194 $[F_{1g}(1)]$, 482 (E_g), 521 $[F_{1g}(2)]$, 618 $[F_{1g}(3)]$, and 690 (A_{1g}) cm⁻¹ [39, 40]. Raman spectra of S1_600_Ar, S2_600_Ar

and S4_600_Ar consist of six Raman peaks around 190-193, 303-305, 472-475, 514-515, 610-613, 671-683 cm⁻¹ (see **Fig. 8**).



Fig. 8. Raman spectra of Ar environment annealed S1_600_Ar, S2_600_Ar and S3_600_Ar samples.

In Table 2, the observed Raman peak positions for S1_600_Ar, S2_600_Ar and S4_600_Ar is compared to Raman spectra of Fe₃O₄, γ -Fe₂O₃, CoFe₂O₄ and Co₃O₄ from literature. It is clear from Table 2 that position of some of Raman peaks of CoFe₂O₄, Co₃O₄ and Fe₃O₄ are very near and therefore it is hard to identify a single phase. However, it is known that Raman spectra of γ -Fe₂O₃ contain much stronger Raman peaks at 1378 and 1576 cm⁻¹ than those of $CoFe_2O_4$ [41, 42]. Only weak and broad Raman peaks are observed above 800 cm⁻¹, which indicates the absence of γ - Fe_2O_3 phase. As mentioned earlier for Fe_3O_4 that only three Raman modes A_{1g} (strongest, 670 cm⁻¹), T_{2g} (2) (medium, 540 cm⁻¹) and E_g (weak and broad, 308 cm⁻¹) are generally observed together. In contrast, in our case no Raman peak is observed around 540 cm⁻¹, which indicates the absence of Fe₃O₄ phase in S1_600_Ar, S2_600_Ar and S4_600_Ar samples. It can be concluded from Fig. 8 and Table 2 that S1_600_Ar, S2_600_Ar and S4_600_Ar samples contain Co₃O₄ and CoFe₂O₄ phases. In conclusion, XRD and Raman analysis (see Figs. 7 and 8) indicate that there is no formation of FeCo alloys in Ar environment annealing, but there exist Co_3O4 and $CoFe_2O_4$ phases in these samples.

Table 2. Raman peak positions for $S1_{Ar_600}$, $S2_{Ar_600}$, $S3_{Ar_600}$ and Co_3O_4 , $CoFe_2O_4$, Fe_3O_4 and Fe_2O_3 from literature.

S1_Ar_600	S2_Ar_600	S4_Ar_600	Co ₃ O ₄ 38	CoFe ₂ O ₄ ³⁶	Fe ₃ O ₄ ²⁸	γ-Fe ₂ O ₃ ²⁸
193	193	190	194.4	193	193	
305	303	303		301	308	350
475	472	472	482.4	470		500
515	514	514	521.6		540	
613	612	610	618.4	618		
683	679	671		686	670	700

Conclusion

In the present work we have prepared the FeCo-SiO₂ granular films of different FeCo atomic concentration, x = 33-54% (S1-S4) by atom beam sputtering technique. Fe and Co K-edge XANES analysis indicate that in the asdeposited samples both Fe and Co are present mainly in their elemental state (Fe⁰, Co⁰). However a partial oxidation of Fe and Co is observed, which increases as the FeCo alloy content decreases. By comparing the far edge oscillations at Fe and Co K-edge in XAFS spectra of asdeposited samples with bcc Fe and fcc Co metal foils, it is concluded that in as-deposited samples there is no formation of bcc FeCo alloy. The XRD and XANES/XAFS analyses of H_2 environment annealed samples (SX_T_{ann}_H₂) suggest the formation of FeCo alloy particles with bcc Fe structure. Raman analysis of S1_600_Ar, S2_600_Ar and S4_600_Ar samples suggest the presence of Co₃O₄ and CoFe₂O₄ phases. Therefore H₂ environment annealing is found to effectively reduce the presence of oxides and leads to the stabilization of bcc FeCo alloy, which could not be achieved with annealing in Ar environment.

Acknowledgements

One of the authors (H.K.) acknowledges CSIR India for providing financial support as SRF during this study. The help of Dr. D. C. Agarwal (RA, IUAC Delhi) during sample preparation and Dr. A. Kanji Lal for providing Raman facility is acknowledged. The authors (S.G and P.S.) acknowledge ICTP (Trieste, Italy) for financial support and ELETTRA (Trieste, Italy) for XANES facility. The authors acknowledge the support of XPS facility at IIT Delhi.

Reference

- Chien, C.L. J. Appl. Phys. 1991, 69, 5267. DOI:<u>10.1063/1.348946</u>
- Gittleman, J.I.; Abeles, B.; Bozowski, S. *Phys. Rev. B* 1974, *9*, 3891.
 DOI: <u>10.1103/PhysRevB.9.3891</u>
- Pakhomov, A.B.; Yan, X.; Zhao, B. Appl. Phys. Lett. 1995, 67, 3497. DOI: <u>10.1063/1.115259</u>
- Socolovsky, L.M.; Oliveira, C.L.P.; Denardin, J.C.; Knobel, M.; Torriani, I.L. J. Appl. Phys. 2006, 99, 08C511. DOI: 10.1063/1.2171013
- Kumar, H.; Ghosh, S.; Bürger, D.; Zhou, S.; Kabiraj, D.; Avasthi, D.K.; Grötzschel, R.; Schmidt, H. J. Appl. Phys. 2010, 107, 113913. DOI: <u>10.1063/1.3410986</u>
- Milner, A.; Gerber, A.; Groisman, B.; Karpovsky, M.; Gladkikh, A. *Phys. Rev. Lett.* **1996**, *76*, *475*.
 DOI: <u>10.1103/PhysRevLett.76.475</u>
- Mitani, S.; Takahashi, S.; Takanashi, K.; Yakushiji, K.; Maekawa, S.; Fujimori, H. *Phys. Rev. Lett.* **1998**, *81*, *2799*. DOI: 10.1103/PhysRevLett.81.2799
- Vovk, A.Y.; Wang, J.Q.; Zhou,W.; He, J.; Pogoriliy, A.M.; Shypil, O.V.; Kravets, A.F.; Khan, H.R. J. Appl. Phys. 2002, 91, 10017. DOI: <u>10.1063/1.1480113</u>
- Wang, C.; Xiao, X.; Rong, Y.; Hsu, T.Y. Mater. Sci. Eng. B 2007, 141, 126.
 DOI: 10.1016/j.mseb.2007.06.010
- Kumar, H.; Ghosh, S.; Bürger, D.; Li, L.; Zhou, S.; Kabiraj, D.; Avasthi, D.K.; Grötzschel, R.; Schmidt, H. J. Appl. Phys. 2011, 109, 073914.
 DOI: 10.1063/1.3561438
- Ohnuma, S.; Kobayashi, N.; Masumoto, T.; Mitani, S.; Fujimori, H. J. Appl. Phys. 1999, 85, 4574.
 DOI: <u>10.1063/1.370412</u>
- Ge, S.; Yao, D.; Yamaguchi, M.; Yang, X.; Zuo, H.; Ishii, T.; Zhou, D.; Li, F. J. Phys. D 2007, 40, 3660. DOI:10.1088/0022-3727/40/12/016
- Russek, S.E.; Kabos, P.; Silva, T.; Mancoff, F.B.; Wang, D.; Qian, Z.; Daughton, J.M. *IEEE Trans. Magn.* 2001, *37*, 2248. DOI: <u>10.1109/20.951138</u>

- Yamaguchi, M.; Suezawa, K.; Arai, K.I.; Takahashi, Y.; Kikuchi, S.; Shimada, Y.; Li, W.D.; Tanabe, S.; Ito, K. J. Appl. Phys. 1999, 85, 7919.
 DOI: 10.1063/1.370608
- 15. Liu, Y.; Tan, C.Y.; Liu, Z.W.; Ong, C.K. J. Appl. Phys. 2007, 101, 023912.
- DOI: <u>10.1063/1.2427099</u>
 16. Corrias, A.; Casula, M.F.; Ennas, G.; Marras, S.; Navarra, G.; Mountjoy, G. J. Phys. Chem. B 2003, 107, 3030.
 DOI: <u>10.1021/jp027078h</u>
- Cody, G.D.; Geballe, T.H.; Sheng, P. In *Physical Phenomena in Granular Materials*, Mater. Res. Soc. Symp. Proc.; MRS: USA, 1990, Vol. 195,
 DOI: <u>10.1080/10426919408934910</u>
- Casula, M.F.; Corrias, A.; Falqui, A.; Serin, V.; Gatteschi, D.; Sangregorio, C.; Fernandez, C.de Julin; Battaglin, G. *Chem. Mater.* 2003, 15, 2201.
 DOI: <u>10.1021/cm0217755</u>
- Chaubey, G.S.; Barcena, C.; Poudyal, N.; Rong, C.; Gao, J.; Sun, S.; Liu, J.P. J. Am. Chem. Soc. 2007, 129, 7214. DOI: 10.1021/ja0708969
- Cicco, A.D.; Aquilanti, G.; Minicucci, M.; Principi, E.; Novello, N.; Cognigni, A.; Olivi, L. J. Phys. :Conf. Ser. 2009, 190, 012043.
 DOI: 10.1088/1742-6596/190/1/012043
- Dong, X.L.; Zhang, Z.D.; Zhao, X.G.; Chuang, Y.C.; Jin, S.R.; Sun, W.M. J. Mater. Res. 1998, 14, 398.
- DOI: 10.1557/JMR.1999.0058
 22. Grunes, L.A. Phys. Rev. B 1983, 27, 2111.
 DOI: 10.1103/PhysRevB.27.2111
- Garcia, M.F.; Arias, A.M.; Hanson, J.C.; Rodriguez, J.A. Chem. Rev. 2004, 104, 4063.
 DOI: <u>10.1021/cr030032f</u>
- 24. Groot, F.D. Chem. Rev. 2001, 101, 1779. DOI: 10.1021/cr9900681
- Ko, Y.D.; Kang, J.G.; Choi, K.J.; Park, J.G.; Ahn, J.P.; Chung, K.Y.; Nam, K.W.; Yoon, W.S; Kim, D.W. J. Mater. Chem. 2009, 19, 1829. DOI: 10.1039/B817120C
- Carta, D.; Mountjoy, G.; Gass, M.; Navarra, G.; Casula, M.F.; Corrias, A. J. Chem. Phys. 2007, 127, 204705.
 DOI: 10.1063/1.2799995
- Bazin, D.; Rehr, J.J. J. Phys. Chem. B 2003, 107, 12398. DOI: <u>10.1021/jp0223051</u>
- 28. de Faria, D.L.A.; Silva, S.V.; de Oliveira, M.T. J. Raman Spectrosc. 1997, 28, 873.
 DOI: 10.1002/(SICI)1097-4555(199711)28:11<873::AID-
- JRS177>3.0.CO;2-B
 29. Chamritski, I.; Burns, G. J. Phys. Chem. B 2005, 109, 4965.
 DOI: 10.1021/jp048748h
- Phase, D.M.; Tiwari, S.; Prakash, R.; Dubey, A.; Sathe, V.G.; Choudhary, R.J. J. Appl. Phys. 2006, 100, 123703. DOI: <u>10.1063/1.2403849</u>
- Gasparov, L.V.; Tanner, D.B.; Romero, D.B.; Berger, H.; Margaritondo, G.; Forro, L. *Phys. Rev. B* 2000, 62, 7939. DOI: <u>10.1103/PhysRevB.62.7939</u>
- 32. Jubb, A.M.; Allen, H.C. ACS Applied materials and interfaces 2010, 2, 2804.
 DOI: 10.1021/am1004943
- 33. Sousa, M.H.; Rubim, J.C.; Sobrinho, P.G.; Tourinho, F.A. J. Magn. Magn. Mater. 2001, 225, 67.
 DOI: 10.1016/S0304-8853(00)01229-4
- Bersani, D.; Lottici, P.P.; Montenero, A. J. Raman Spectrosc. 1999, 30, 355.
 DOI: 10.1002/(SICI)1097-4555(199905)30:5<355::AID-
- JRS398>3.0.CO;2-C 35. Yu, T.; Shen, Z.X.; Shi, Y.; Ding, J. J. Phys. :Conds. Mat. 2002, 14, L613.
- **DOI:** <u>10.1088/0953-8984/14/37/101</u> 36. Wang, W.H.; Ren, X. J. Crys. Growth **2006**, 289, 605.
- **DOI:** <u>10.1016/j.jcrysgro.2005.11.115</u> 37. Liu, Y.; Zhang, Y.; Feng, J.D.; Li, C.F.; Shi, J.; Xiong, R. J. Exp.
- S7. Liu, Y.; Zhang, Y.; Feng, J.D.; Li, C.F.; Sni, J.; Xiong, R. J. Exp. Nanosci.2009, 4, 159.
 DOI: 10.1080/17458080902929895
- Nakagomi, F.; da Silva, S.W.; Garg, V.K.; Oliveira, A.C.; Morais, P.C.; Júnior, A.F.; Lima, E.C.D. J. Appl. Phys. 2007, 101, 09M514. DOI: 10.1063/1.2712821
- Hadjiev, V.G.; Iliev, M.N.; Vergilov, I.V. J. Phys. C :Solid State Phys. 1988, 21, L199.

DOI: <u>10.1088/0022-3719/21/7/007</u>

- Wang, G.; Shen, X.; Horvat, J.; Wang, B.; Liu, H.; Wexler, D.; Yao, J. J. Phys. Chem. C 2009, 113, 4357.
 DOI: 10.1021/jp8106149
- 41. Tang, D.; Yuan, R.; Chai, Y.; An, H. *Adv. Funct. Mater.* **2000**, 17, 976.
- DOI: 10.1002/adfm.200600462
 42. Sousa, M. H.; Tourinho, F. A.; and Rubim, J. C. J. Raman Spectrosc. 2000, 31, 185.
 DOI: 10.1002/(SICI)1097-4555(200003)31:3<185::AID-JRS511>3.0.CO;2-B

Advanced Materials Letters

Publish your article in this journal

ADVANCED MATERIALS Letters is an international journal published quarterly. The journal is intended to provide top-quality peer-reviewed research papers in the fascinating field of materials science particularly in the area of structure, synthesis and processing, characterization, advanced-state properties, and applications of materials. All articles are indexed on various databases including DOAJ and are available for download for free. The manuscript management system is completely electronic and has fast and fair peer-review process. The journal includes review articles, research articles, notes, letter to editor and short communications.

