Structural and magnetic properties of co-sputtered Fe$_{0.8}$C$_{0.2}$ thin films

Prabhat Kumar, V. R. Reddy, V. Ganesan, and Mukul Gupta*
UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452 001, India
I. Sergueev, O. Leupold and H.-C. Wille
Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, D-22607 Hamburg, Germany

(Dated: July 12, 2019)

We studied the structural and magnetic properties of Fe$_{0.8}$C$_{0.2}$ thin films deposited by co-sputtering of Fe and C targets in a direct current magnetron sputtering (dcMS) process at a substrate temperature ($T_s$) of 300, 523 and 773 K. The structure and morphology was measured using x-ray diffraction (XRD), x-ray absorption near edge spectroscopy (XANES) at Fe L and K edges and atomic/magnetic force microscopy (AFM, MFM), respectively. An ultrathin (3 nm) $^{57}$Fe$_{0.8}$C$_{0.2}$ layer, placed between relatively thick Fe$_{0.8}$C$_{0.2}$ layers was used to estimate Fe self-diffusion taking place during growth at different $T_s$ using depth profiling measurements. Such $^{57}$Fe$_{0.8}$C$_{0.2}$ layer was also used for $^{57}$Fe conversion electron Mössbauer spectroscopy (CEMS) and nuclear resonance scattering (NRS) measurements, yielding the magnetic structure of this ultrathin layer. We found from XRD measurements that the structure formed at low $T_s$ (300 K) is analogous to Fe-based amorphous alloy and at high $T_s$ (773 K), pre-dominantly a Fe$_3$C phase has been formed. Interestingly, at an intermediate $T_s$ (523 K), a clear presence of Fe$_4$C (along with Fe$_3$C and Fe) can be seen from the NRS spectra. The microstructure obtained from AFM images was found to be in agreement with XRD results. MFM images also agree well with NRS results as the presence of multi-magnetic components can be clearly seen in the sample grown at $T_s = 523$ K. The information about the hybridization between Fe and C, obtained from Fe L and C K edges XANES also supports the results obtained from other measurements. In essence, from this work, experimental realization of Fe$_4$C has been demonstrated. It can be anticipated that by further fine-tuning the deposition conditions, even single phase Fe$_4$C phase can be realized which hitherto remains an experimental challenge.

I. INTRODUCTION

Tetra iron compounds (Fe$_4$X) are an interesting class of compounds known to exhibit higher (than Fe) magnetic moment ($M$), [1–4] and spin-polarization ratio (SPR) [5, 6]. In addition, metallic resistivity and corrosion resistance of Fe$_4$X make them attractive for applications. The structure of Fe$_4$X compounds have been classified as anti-perovskite [P43m (215)] and metalloid element such as X = B, C, N occupy the body center position within the face center cubic (fcc) lattice of host Fe. Theoretically predicted values of $M$ for Fe$_4$B, Fe$_4$C and Fe$_4$N are 2.57, 2.42 and 2.62 $\mu_B$ [1–4, 6], respectively. Such an enhancement in $M$ occurs due to volume expansion of Fe lattice. An expansion in volume produces higher density of states near the fermi level due to contraction of d-band (relative to Fe) and therefore results in higher $M$. The increase in $M$ due to volume expansion is known as magneto-volume effect [7]. Experimentally, $M$ of Fe$_4$N has been achieved close to its theoretical values ($\approx 2.4 \mu_B$) in several works [8–11]. Such enhancement in $M$ with respect to pure Fe ($M$ of Fe = 2.2 $\mu_B$) make them very useful in various applications e.g. spintronics, magnetic data storage devices [12], permanent magnets, spin-injection electrodes [5], etc. In addition, recent density functional theory calculation suggests that the SPR for Fe$_4$X (X = B, C, N) comes out to be 84, 88 and 61%, respectively [6].

Furthermore, Fe$_4$C is thermally more stable than others (e.g. Fe$_4$N or Fe$_4$B) due to smaller Fe–C bond distance [4, 6, 13–15]. Theoretical calculation suggests that Fe–C bond length at 1.8739 Å is smaller as compared to Fe–B (1.9027 Å) or Fe–N (1.8899 Å) [6]. Likewise, other transition metal carbides also show higher thermal stability than nitrides of similar composition. Their thermal stability can also be expressed in terms of Debye-temperature ($\theta_B$), which is a classical limit of quantum model of Einstein-Debye specific heat for solids. Guillermit et al. [16, 17] calculated $\theta_B$ for some transition metal carbides and nitrides and found that in general, $\theta_B$ of carbides are higher than that of nitrides.

In spite of very interesting magnetic properties, higher SPR and thermal stability, experimental reports on Fe$_4$C are almost non-existent and single phase Fe$_4$C has not yet been synthesized. Recently, interatomic potential for Fe-C systems were calculated using modified embedded atom method (MEAM) and it was predicted that the presence of C lowers the body center cubic (bcc) to face center cubic (fcc) transformation barrier [18, 19]. Also the activation energy for C diffusion in Fe was calculated and found to be very small at about 0.8 eV [20]. Both, the reduction in barrier for bcc to fcc and low activation energy point towards favorable conditions for Fe$_4$C phase formation. However, the enthalpy of formation energy ($\Delta H_f^\circ$) for Fe$_4$C is positive (about 0.1 eV [6, 21]). It may be noted that $\Delta H_f^\circ$ for early transition metal nitrides and
carbides is quite less e.g. \( \Delta H_f^\circ = -1.9 \text{ eV} \) for TiC and 
\(-3.5 \text{ eV} \) for TiN [16]. Therefore, synthesis of these compounds 
take place straight away using standard methods. Even with a slight negative \( \Delta H_f^\circ = -0.15 \text{ eV} \) [4, 6], single phase Fe3N has been reported in several works [2]. But 
for Fe2C, a positive value of \( \Delta H_f^\circ \) leads to a thermodynamically unfavorable condition that can not be achieved utilizing equilbrium processes e.g. Fischer-Tropsch synthesis (FTS). Recently, FTS was used to synthesize iron carbide (Fe-C) compounds and resulting phases were identified as \( \theta\)-Fe2C and \( \chi\)-Fe3C2 from x-ray diffraction and Mössbauer spectroscopy measurements [21].

However, using non-equilibrium processes that are typically found in physical vapor deposition (PVD) methods, formation of Fe4C may be feasible. It may be noted that \( \Delta H_f^\circ \) of Fe16N2 is also positive at about 0.88 eV/atom [22]. Using various thin film deposition techniques like e-beam evaporation, molecular beam epitaxy and sputtering, (partial) formation of Fe16N2 has been reported [23, 24]. Therefore, formation of Fe2C may also take place using such non-equilibrium processes.

Among PVD methods, co-sputtering is most convenient and effective to synthesize Fe-C compounds as: (i) the control of composition can be made precisely by varying the power of each sputter source (ii) in a confocal geometry, sputtered species from each source mix before depositing on to a substrate (iii) ad-atom energies in sputtering are much higher (typically 10 eV) than that of thermal evaporation (0.1-0.2 eV) [25]. Thus, non-equilibrium nature and higher energetics of the depositing species in sputtering have risen a possibility to prepare Fe3C.

Some attempts have been made to synthesize Fe-C thin films by sputtering of a compound [Fe+C] target [26–31], or sputtering of Fe using a mixture of Ar+CH4 [32] or Ar+C2H4 [33]. Utilization of compound target may not be useful to control the composition of Fe-C films and using gases like CH4 and C2H4 may also result in formation of undesired C-H bonds. On the other hand, co-sputtering of Fe and C from two different sources is a clean method providing a wide range of option to control the composition by changing the flux of each sources as demonstrated recently by Furlan et al. [34]. A survey of available literature suggests that most of the Fe-C thin films reported hitherto are either amorphous or nanocrystalline. For example, Jouanny et al. [32] prepared Fe3C thin films by sputtering of Fe target in Ar/CH4 gas environment at \( T_s = 373 \text{ K} \) and identified phases were Fe2C at lower CH4 gas flow and amorphous at higher CH4 gas flow. Tajima et al. deposited Fe-C thin films at 623 K by rf magnetron sputtering of a compound target [26] and phases identified were \( \alpha\)-Fe, Fe3C Fe2C2.

Weck et al. [30] deposited Fe-C thin films by ac magnetron sputtering and reactive cathodic arc evaporation of a compound target (12 and 16 at.% C). Resulting films were found to be nano-crystalline bcc-Fe. Subsequently, Babonneau et al. [28] deposited Fe1-xC x (0.26 \( \leq \) x \( \leq \) 0.74) thin films at various substrate temperatures but resulting films were found to be amorphous. Similarly, Mi et al. [29] deposited Fe-C thin films by sputtering of a compound target (at room temperature) and also found amorphous Fe-C phases. More recently, Furlan et al. [34] deposited Fe-C thin films by co-sputtering of Fe and C from two separate targets (at 300K) and varied C concentration from 20.8 to 71.8 at.%. It was observed that resulting Fe-C films were amorphous, irrespective of the amount of C in Fe.

In this work, we synthesized Fe-C thin films by co-sputtering of Fe and C at different substrate temperature (\( T_s \)) with a nominal composition of Fe0.8C0.2 so as to attempt the first ever experimental realization of Fe3C. Samples were characterized using x-ray diffraction (XRD) for their structure and the surface and magnetic morphology has been obtained from atomic and magnetic force microscopy (AFM, MFM) measurements, respectively. The information about the nature of bonding has been obtained from XANES measurements at C K and Fe L-edges. The magnetization of samples were studied using conversion electron Mössbauer spectroscopy (CEMS) and synchrotron based nuclear resonant scattering (NRS). In addition, from secondary ion mass spectroscopy (SIMS) depth-profiles measurements, Fe self-diffusion was estimated and compared with a pure Fe sample prepared under similar conditions. We found that at low \( T_s \) the addition of C suppresses Diffusion but at high \( T_s \) it augments. From above mentioned measurements, we found that the room temperature grown Fe0.8C0.2 film was amorphous but at high \( T_s \) phases formed are crystalline. At the highest \( T_s \) (773 K), predominantly a Fe3C phase has been formed but at an intermediate \( T_s \) of 523 K, a clear presence of Fe4C (along with Fe3C and Fe) can be seen. Observed results demonstrate the possibilities for formation of crystalline Fe-C phases by co-sputtering. The structural and magnetic properties of thus formed Fe-C phases are presented and discussed in this work.

### II. EXPERIMENTAL DETAILS

Fe and C targets were co-sputtered to prepare iron-carbon (Fe-C) thin films. They were deposited at substrate temperature (\( T_s \)) = 300, 523 and 773 K with nominal stoichiometric composition for Fe3C or Fe0.8C0.2. Their layer structure was: C(5 nm)[natFe-C(70 nm)][natFe-C(3 nm)][natFe-
C(100 nm)]C(10 nm) sub.(Si/Quartz). The C concentration was evaluated using: (i) number of monolayer (n) per unit area per unit mole: \( n = \text{mass-number/mass-density} \) (ii) thicknesses of Fe and C equivalent to stoichiometric Fe0.8C0.2 is \( n_F = 0.8 \) and \( n_C = 0.2 \) (iii) deposition rates for Fe and C has been optimized to achieve thicknesses obtained for Fe0.8C0.2 composition.

The chamber was evacuated down to a base pressure of \( 2 \times 10^{-7} \text{ hPa} \). Sputtering was carried out using pure Ar (purity 99.9995%) gas at a working pressure of \( 3 \times 10^{-3} \text{ hPa} \) due to gas flow of 20 sccm. In this layer
structure, the natural Fe-C (hereafter Fe-C) was prepared by co-sputtering of a 0.8 inch Fe (purity 99.95%) and 0.3 inch C (purity 99.99%) target at the sputtering power of 100 and 156 W, respectively. On the other hand, for the 57Fe-C, the same C target and a 0.1 inch 57Fe (enrichment 95.0%, purity 99.95%) target was used and their sputtering powers were kept at 70 and 11 W, respectively. To prevent Si diffusion from the substrate and surface contamination of samples, a buffer and capping layer of C was always deposited at room temperature prior to or after the deposition of Fe(70 nm) and, (ii) pure Fe thin film with a 3 inch Fe (purity 99.95%) and 3 inch C (purity 99.999%) target at the sputtering power 70 and 11 W, respectively for the (110) plane becomes prominent. Generally, such variations in preferred orientations are not unexpected and have been observed in several cases like TiN [37–39], AlN [40] etc. and have been explained considering alterations in the adatom mobility, stress/strain, and surface energy due to enhanced $T_s$ [39, 40]. As shown later in this work (section III D), the Fe self-diffusion does not increase appreciably on increasing the $T_s$ (in fact it decreases slightly at 523 K), therefore arguments related to adatom mobility may not be valid for the change observed in the preferred orientation of Fe films. In a recent work, Schönecker et al. calculated the thermal surface free energy and stress of iron at different temperatures and found that surface stress for the (001) surface was much smaller than that of (110) surface at low temperature but at high temperatures they become similar [41]. The changes observed in the preferred orientation in our Fe films can be understood from this argument. On the other hand, the width of XRD peaks become narrow as $T_s$ increases. The crystallite size ($t$) has been calculated using Debye Scherrer formula, $t = 0.96 \lambda / \beta \cos \theta$, where $\lambda$ is wavelength of the x-rays, $\beta$ is angular full width half maxima of the Bragg reflection centered at $2\theta$. By increasing the $T_s$ from 300 to 523 and 773 K, $t$ increases from 18±0.5 to 28±0.5 and 46±2.0 nm, respectively.

The XRD pattern (fig. 1b) of the Fe$_{0.8}$C$_{0.2}$ thin film deposited at $T_s = 300$ K shows a broad reflection centered around $2\theta = (44.58±0.1)^\circ$ signifying that it has attained an amorphous structure. In an amorphous system, the average nearest neighbor distance ($d$) can be calculated using: $d = 1.23 \lambda / 2 \sin \theta$, where $\theta$ is the center of the broad reflection and 1.23 is a geometric factor which rationalizes the nearest neighbor distance with the spacing between, “pseudo-close packed planes” [42]. From here, we get $d = 2.5$ Å, a value typically found in iron-based amorphous alloys. [43]. On the other hand, samples deposited at higher $T_s$ show a number of peaks. Observed peak positions for the sample deposited at $T_s = 523$ and 773 K are similar and their intensity is increasing with $T_s$. These peak positions match well with that of $\theta$-Fe$_3$C (PDF#89-2867) and $\alpha$-Fe (PDF#870721) phases. A general observation shows that by increasing $T_s$, peak broadening decreases indicating increase in crystallite size. The crystallite size of the evolved phases in the sample deposited at $T_s = 523$ K comes out to be $17±1$ nm of $\theta$-Fe$_3$C phase corresponding to (210) reflection centered at $(43.74±0.01)^\circ$ and $26±1$ nm for $\alpha$-Fe phase corresponding to (110) reflection centered at $(44.75±0.01)^\circ$. Similarly, crystallite size is $42±2$ and $28±2$ nm for $\theta$-Fe$_3$C and $\alpha$-Fe phases, respectively for the sample deposited at $T_s = 773$ K.

The solubility of C in bcc Fe under ambient condition is very small ($\approx 0.2$ at%) [44]. Beyond this limit, the presence of C produces a disordered crystal structure due to immiscibility of C with Fe. This results in formation of an amorphous phase in our sample and show agreement with previous reports [34]. Increasing substrate temperature pushes C at interstitial position of the orthorhom-
The bicrystal lattice of Fe, this results in growth of $\theta$-Fe$_3$C phase. However, peaks corresponding to un-reacted $\alpha$-Fe are also visible.

Figure 2 shows surface and magnetic morphology of the Fe$_{0.8}$C$_{0.2}$ thin films deposited at various $T_s$. Images were processed using WSxM software package [45]. For better understanding of grain and domain growth, we have plotted height and frequency distribution profile of the AFM (fig. 3(a)) and MFM (fig. 3(b)) images, respectively. In the AFM image of the sample deposited at $T_s = 300$ K (fig. 2(a)), the grains are very small. It is also clear from the height distribution ($H_d$) profile (fig. 3(a)). On the other hand, the AFM image of the sample deposited at $T_s = 523$ K shows enhancement in the grains (fig. 2(b)) and their $H_d$ profile shows that they are nearly equal in size. The sample deposited at $T_s = 773$ K have much larger grains compared to other two samples (fig. 2(c)). The $H_d$ profile of the AFM image shows uniform growth of larger grain along with smaller grains. This shows that increase in $T_s$ results in formation of larger grains. This is in agreement with the XRD results as the grains of $\theta$-Fe$_3$C become larger with increase in $T_s$.

The MFM images and their frequency distribution profile ($F_d$) show that the sample deposited at $T_s = 300$ K may have very small magnetic domains (fig. 2(b) and 3(b)) and they are not clearly visible. The sample deposited at $T_s = 523$ K have large magnetic domains (fig. 2(d)) with a systematic change in the cantilever frequency (fig. 3(b)). On the other hand, even larger magnetic domains can be seen in the MFM image (fig. 2(e)) of the sample deposited at $T_s = 773$ K. However, the magnetic domains in MFM image is following the pattern similar to topographic changes observed in the AFM (fig. 2(e)). In addition, the frequency distribution profile (fig. 3(b)) shows a change in the frequency similar to change in $H_d$ profile (fig. 3(a)). This is an indication of presence of two kinds of magnetic domain, one with larger and another with smaller size. The MFM image of the sample deposited at $T_s = 523$ K shows that the structural and magnetic morphologies are different. The $F_d$ profile shows various frequency maxima with different magnitude (fig. 3(b)). This change in the magnetic field of the sample deposited at $T_s = 523$ K may arise if several magnetic phases are present together. The presence of such magnetic phases can be investigated using a local magnetic probe e.g. Mössbauer spectroscopy based techniques like CEMS and NFS. Results of CEMS and NFS are presented in section III C.

B. Electronic structure

Local electronic structure was probed using synchrotron based XANES measurements at Fe $L_{3,2}$ and C K absorption edges. Fig. 4 shows Fe $L_{3,2}$-edge XANES spectra of the Fe$_{0.8}$C$_{0.2}$ thin film deposited at various $T_s$, following $2p \rightarrow 3d$ dipole transition. As indicated, the spectra consist of two prominent transitions occurring due to spin-orbit splitting of $2p$ orbital in $L_3$ (I) and $L_2$ (II) core-shell separated in energy by about 13 eV, which is a typical value for Fe. Each sub-spectrum further split in double sub-peak due to ligand field splitting marked as II and IV in fig. 4. Such splitting has been observed in several transition metal-carbides [34, 46–48]. The spectra show two characteristic change with $T_s$ (i) peak become narrow, and (ii) total integrated intensity of the feature is decreasing as shown in the inset of the fig.4.

Generally, a narrow Fe $L_{3,2}$ absorption lines for pure Fe are observed [34]. But, addition of smaller atom e.g. C, N, O produces splitting due to crystal field and results in broadening of the resonance lines [34]. Their intensity is proportional to the unoccupied Fe 3d states. Decreasing intensity indicates decrease in charge transfer with increasing $T_s$, this results in reduced unoccupied Fe 3d state at higher $T_s$. Earlier reports on Fe and Cr $2p$ XANES spectra of amorphous system have shown that, the peak intensity increases with increase in C concentration [34, 48]. Decrease in the unoccupied state show reduced carbide contribution at higher $T_s$. These variation of the spectra show, there can be a possibility of presence of C in un-hybridized states at higher $T_s$. Further
insight about the hybridization have been obtained from C K-edge XANES measurements.

Figure 5 shows C K-edge XANES spectra of the Fe-C thin film deposited at various \( T_s \). The prominent features are marked as a, b, c and d, and shoulders of a and c as \( a' \) and \( c' \), respectively. The feature a is related with empty \( \pi^* \) states, it is a combination of (i) \( sp^2 \) and \( sp^3 \) hybridized C states, and (ii) Fe 3d-C 2p hybridized states. In addition, the feature \( c' \) is also a combination of (i) Fe 3d-C 2p hybridized states, and (ii) C-O bonding states. These two features show opposite trend with \( T_s \), with increase in \( T_s \) the intensity of the feature a increases while the intensity of the feature c decreases. A comparison of the C K-edge spectra of the Fe\(_{0.8}\)C\(_{0.2}\) thin film with a-C thin film deposited at \( T_s = 300, 523 \) and 773 K shows that, the feature c is shifted by 0.4 eV at lower energy side for a-C thin films. This shows in case of Fe\(_{0.8}\)C\(_{0.2}\), the feature c is strongly related with Fe 3d-C 2p hybridized states. But decrease in the intensity of this feature shows reduction in carbide contribution as observed in the Fe \( L_3,2 \)-edge spectra. Consequently, increase in the intensity of the feature a signifies presence of higher fraction of \( sp^2 \) hybridized C states at higher \( T_s \). A shift in the feature a can be observed at higher energy side by 0.3 eV for the sample deposited at \( T_s = 523 \) K. This shows that, in addition with reduced carbide contribution at higher \( T_s \), the sample deposited at \( T_s = 523 \) K have different local structure compared to samples deposited at \( T_s = 300 \) and 773 K. In addition, a faint feature b is observed at 286.4 eV, although origin of this feature is yet not clear [49].

In addition, the shoulder \( a' \) can be solely due to formation of metal carbide [34, 46–48]. The intensity of this shoulder is faint and does not show any significant change. On the other hand, the intensity of the shoulder \( c' \) is decreasing with increase in \( T_s \). Another report on nano-crystalline TiC/a-C, shows that the intensity of these features increases with increasing grain sizes as the carbide contribution increases. Unlike TiC/a-C, decrease in the intensity shows decrease in carbide contribution with increasing \( T_s \). This shows presence of a-C in unhybridized state at higher \( T_s \).

C. Magnetic structure

Magnetic structure of sandwiched 3 nm \(^{57}\)Fe-C layer was probed using CEMS and NRS measurements. Fig. 6 shows experimental CEMS spectra of samples deposited at various \( T_s \) along with fitted data. The CEMS spectrum of the sample deposited at 300 K shows broad resonance lines. The broadening of the resonance lines can be related to lack of long-range ordering arisen due to im-
miscibility of C [50–52]. This spectrum was fitted using one sextet with hyperfine field (B$_{hf}$) of 25.65±0.34 T. A B$_{hf}$ = 26-30 T depending on C content can be observed in amorphous Fe-C alloys [53, 54]. This also in a way confirms the amorphous nature of the sample deposited at $T_s = 300$ K. In comparison to this, the spectrum of the sample deposited at $T_s = 523$ K shows narrow resonance lines. It was fitted assuming two sextets S1 and S2 with their B$_{hf}$ = 33.20±0.08 and 20.51±0.13 T, respectively. Where, S1 and S2 can be assigned to $\alpha$-Fe (57%) and $\theta$-Fe$_2$C (43%) phases, respectively [21].

On the other hand, the CEMS spectrum of the sample deposited at $T_s = 773$ K does not show any prominent resonance even after long counting time (one week). The active % of Mössbauer signal was already low at about 0.5% due to ultrathin $^{57}$Fe-C layer (3 nm) but at higher $T_s$ (773 K) the $^{57}$Fe-C layer gets diffused across the entire depth of sample (shown later from SIMS depth profiles), active % of Mössbauer signal will reduce further. It may be noted that the escape depth of electrons in CEMS is (≈80 nm) which is shorter than the total thickness of sample. The large spread of $^{57}$Fe with $T_s$ reduces the effective number of resonating nuclei leading to poor statistics. Therefore, ensuing magnetic phases that can be observed in MFM measurements, could not be resolved from CEMS measurement. Such experimental limitation can be overcome by doing synchrotron radiation based NRS measurements.

NRS is a fourier transform of Mössbauer spectroscopy. This technique is very sensitive to spatial phase factors due to coherent scattering of radiation with matter. It gives a possibility to correlate internal fields with the spatial arrangement of the atoms [56]. Now a days, the availability of enormous brilliance of the synchrotron radiation sources have made it possible to perform such kind of measurements. This technique is frequently used to investigate magnetic properties and phase transitions under high pressure/temperature of nano-structure, ultrathin films, clusters [36] and diffusion in the layered systems [57].

NRS spectra of of the Fe$_{0.8}$C$_{0.2}$ samples deposited at various $T_s$ are shown in the fig.7. The spectrum of the
Figure 7. (Color online) Nuclear resonant scattering spectra of the Fe$_{0.8}$C$_{0.2}$ samples deposited 300, 523 and 773 K measured at grazing incidence of 0.21° at P01 PETRA III, Germany.

D. Depth profiling and Fe self-diffusion measurements

Fig. 8(a) and (b) shows SIMS depth-profiles of Fe$_{0.8}$C$_{0.2}$ and pure Fe samples deposited at different $T_s$. The sandwiched $^{57}$Fe layer in both sets of sample results in a peak and it becomes broadened with increase in $T_s$. In Fe$_{0.8}$C$_{0.2}$ samples $^{57}$Fe peak width ($\Delta_{Fe}$) is about 4 and 8 nm at $T_s = 300$ and 523 K, respectively and at $T_s = 773$ K it has completely diffused throughout the film. On the other hand, $^{57}$Fe profile in pure Fe is significantly broader already at 300 K but the broadening does not increase as much as in Fe-C at higher $T_s$. In addition, C concentration has also been estimated from SIMS depth profiles (not shown) and it comes out to be 20, 17 and 13 at. % in samples deposited at $T_s = 300$, 523 and 773 K, respectively. This shows, C content decreases significantly for the sample deposited at $T_s = 773$ K. In accordance with XANES spectra, decrease in C content with $T_s$ shows that C is moving out from the bulk of the sample.

As can be seen in Fig. 8(a), the trailing side of SIMS profiles are broader than the rising side. Such broadening is observed due to involvement of sputtering and small intermixing produced by 3 keV O$^+$ ions. Such profiles can be corrected using following equation [59–61]:

$$c_c(x + h) = c_c(x) + h \frac{dc_c(x)}{dx}$$

(1)

where, $c_c$ is corrected and $c_c$ is experimentally measured concentration profiles and $h$ is a parameter representing the strength of intermixing. The value of $h$ was kept constant for a series of samples.

To determine diffusion that is taking place during the growth of our samples, the shape of the tracer profile can be represented as a function of depth ($x$) as:

$$c(x, t) = \frac{c}{2\sqrt{2Dt}} \exp[-(x^2/4Dt)]$$

(2)

where, $c$ is a constant, $t$ is annealing time and $D$ is diffusion coefficient. Therefore, profiles can be fitted using a Gaussian function and diffusion coefficient can be calculated using the following equation [60]:

$$D(t) = \frac{\sigma_t^2 - \sigma_0^2}{2t}$$

(3)

where, $D(t)$ is time average diffusion coefficient and $\sigma_t$ is standard deviation of the Gaussian depth profile over an annealing time of $t$ or when $t = 0$.

Obtained $\Delta_{Fe}$ in Fe$_{0.8}$C$_{0.2}$ and Fe samples are compared in fig. 8 (c). As can be seen that $\Delta_{Fe}$ is about 10 times smaller in Fe$_{0.8}$C$_{0.2}$ as compared to Fe sample deposited at $T_s = 300$ K. Such a large variation in $\Delta_{Fe}$ is somewhat puzzling and unexpected. It is known that fast grain boundary (gb) diffusion takes place in Fe due to defects or voids that are incorporated during the growth.

sample deposited at $T_s = 300$ K shows few quantum beats (QBs) with a period of about 15 ns confirming the magnetic nature of this sample in accordance with CEMS results [52]. But the NRS signal decays soon after 40 ns which can be understood due to disordered local structure present in the amorphous phase [52]. The NRS signal lasts much longer times (> 165 ns) in samples deposited at higher $T_s$. The QB period of 523 K sample varies from 5 to 15 ns. On the other hand, it varies from 10 to 15 ns for the sample deposited at 773 K. The smaller QB period reveals presence of a high magnetic moment phase at 523 K. To get more detail information, we fitted NRS spectra of samples deposited at high $T_s$ using REF-TIM software package [58]. The spectrum of the sample deposited at $T_s = 523$ K can be best fitted using combination of three hyperfine fields, $B_{hf} = 21, 33, 34.3$ T. As already discussed, $B_{hf} = 21$ and 33 T are respectively related to $\theta$-Fe$_3$C and $\alpha$-Fe, the additional component with larger $B_{hf} = 34.3$ T can be assigned to Fe$_4$C [21] phase only. Their relative volume fractions comes out to be 45% for $\theta$-Fe$_3$C, 35% for $\alpha$-Fe and 20% for Fe$_4$C. On the other hand, the spectrum of the sample deposited at $T_s = 773$ K can be best fitted assuming two components with $B_{hf} = 21$ and 33 T and their relative volume fractions are 70 and 30%, respectively. The absence of $B_{hf} = 34.5$ T shows that higher $T_s$ (773 K) is not favorable for the growth of Fe$_4$C phase.
Addition of C seems to suppress them significantly. Generally, it is anticipated that gb diffusion would take place at moderate temperatures. In our case, the information about Fe self-diffusion during growth is obtained, it is new and unique information and can be suitably used to understand the growth of Fe based thin films and also C can be used as an effective dopant to suppress Fe diffusion.

As we increase the $T_s$, $\Delta s$ increases albeit a small drop in pure Fe deposited at $T_s = 523$ K. Such a drop in $\Delta s$ can be due to an interface sharpening effect which happens due to release of defects and voids. Such interface sharpening was also evidenced recently in Fe thin films grown at 573 K [62] and also observed in earlier works [63–66]. At $T_s = 523$ K, $\Delta s$ in Fe$_{0.8}$C$_{0.2}$ sample is still significantly smaller as compared to Fe but when samples were grown at $T_s = 773$ K, a sudden rise in $\Delta s$ can be seen in Fe$_{0.8}$C$_{0.2}$ sample. It appears that at low $T_s$ the presence of C suppress Fe self-diffusion but when the $T_s$ increases beyond a particular value, Fe diffusion gets augmented. Such kinetics of Fe self-diffusion affects formation of Fe-C phases and will be discussed later. The schematic of diffusion process is shown schematically in fig. 9.

Using the values of $\Delta s$, Fe-C and Fe samples grown at $T_s = 773$ K, we estimated Fe self-diffusion and it comes out to be about an order of magnitude faster in Fe$_{0.8}$C$_{0.2}$ as compared to Fe ($6 \pm 1 \times 10^{-19}$ m$^2$/s in Fe-C and $7 \pm 3 \times 10^{-20}$ m$^2$/s in Fe). Fe self-diffusion coefficient obtained in our sample is close to the value found in earlier works [67–69].

**E. Phase transformation mechanism**

From the results obtained in this work, a phase transformation mechanism can be drawn to understand the formation of Fe-C phases during the co-sputtering process. In co-sputtering process two or more targets are sputtered simultaneously (here $\alpha$-Fe (bcc) and graphite C targets). The mixing of sputtered Fe and C adatoms takes place when they are still in the vapor phase. In the sputtering process typically the adatom energy is about 10 eV and as adatom condense on a substrate they lose this energy in picosecond time yielding quenching rates of the order of $10^{16}$ K/s [70]. These rates are about 10 orders of magnitude higher as compared to melt roller quenching [70]. Generally, with such a high quenching rates, the resulting phase should become amorphous but this is certainly not the case as metallic samples produced by sputtering do possess a long range ordering. This can be amply seen from the XRD patterns of pure Fe films shown in fig. 1. Films grown at 300 K are poly crystalline with an average grain size of $18 \pm 0.5$ nm and with an increase in $T_s$, the grain size increases to $28 \pm 0.5$ nm at 523 K, $45 \pm 1.5$ nm at 648 K and $46 \pm 2$ nm at 773 K. This clearly indicates that after condensation on a substrate, the adatom mobility driven diffusion process results in formation of long range ordering and with an increase in $T_s$, it increases. As such this is trivial information which is well-known for growth of thin films with sputtering [71, 72]. However, this will be useful to understand the role of C in affecting phase formation in Fe-C thin films.

Aforementioned, we placed a 3 nm $^{57}$Fe marker layer
between natural Fe layers, and through this we could measure Fe self-diffusion that is taking place during the growth of film. We found that already at 300 K, the broadening in $^{57}$Fe profile, $\Delta_{Fe}$ is quite large at about 40 nm which is more than ten times of the thickness of marker layer. However, with an increase in $T_s$, $\Delta_{Fe}$ does not increase as much. Therefore, it appears that Fe self-diffusion takes place rapidly during the initial stages of growth and thereafter it reduces significantly. Fu et al. [73] did multi-scale modelling of defect kinetics in iron and found that the activation energy (E) for interstitial migration can be as low as 0.3 eV in $\alpha$-Fe. In an experimental study on Fe self-diffusion in Fe/$^{57}$Fe multilayers, it was also found E was small ($E<1$ eV) and has been explained in terms of structural defects in Fe that lead to fast Fe diffusion during initial stages which subsequently becomes smaller when defects relaxation process gets completed [74]. In a recent study also, fast Fe diffusion has been observed and explains in terms of triple junctions leading to short-circuit diffusion [62]. In a way, the fast Fe diffusion during initial stages can be understood as grain boundary (gb) diffusion. When the gb diffusion gets over, annihilation of defect causes Fe atoms to diffuse through a classical volume type diffusion via thermal vacancies with very high E $= 3$ eV.

The addition of C in Fe affects the gb diffusion process, so much that $\Delta_{Fe} \rightarrow 0$. Instead of 40 nm for Fe, the $\Delta_{Fe}$ in Fe-C was about 4 nm, close to its nominal thickness of 3 nm. And within experimental accuracy it can be inferred that $\Delta_{Fe} \approx 0$ in Fe-C as compared to pure Fe. In this scenario, C atoms restrict the path of Fe atoms thereby leading to formation of an amorphous structure as observed in our Fe-C samples and also in previous studies [28, 29, 34]. However, when $T_s$ increases to 773 K even more rapid Fe diffusion takes place, compared to the case when C was not added as shown in fig. 8 (c). Such an enhancement clearly indicates that in presence of C, the concentration of defects may become even higher leading to faster Fe diffusion through gb. But at an intermediate temperature of 523 K, we found that Fe diffusion was still low and crystalline Fe-C phases like Fe$_3$C and Fe$_4$C start to nucleate. And at this temperature regime, it seems that kinetics of Fe-C phase formation is driven by C diffusion. Recently, it has been revealed in a computational ReaxFF study (based on bond order concept [75]) that C diffuses through gb [20] and E for C diffusion is typically about 0.8 eV. Also, as suggested by theoretical calculations, the energy barrier for $\alpha$ (bcc) $\rightarrow \gamma$ (fcc) phase transformation of Fe is about 0.137 eV/atom but it gets reduced to 0.127 eV/atom in presence of C [18, 19]. On the other hand, for the reverse case i.e. $\gamma \rightarrow \alpha$ phase it is much smaller at about 0.025 eV/atom for Fe but it increases marginally to 0.047 eV/atom for Fe-C. The presence of C in Fe lattice produces local stress field, resulting enhancement in the energy barrier for $\gamma \rightarrow \alpha$ [18, 19]. Therefore, the presence of C prevents $\gamma \rightarrow \alpha$ and favors the $\alpha \rightarrow \gamma$ phase transformation. These conditions are suitably met at the intermediate temperature of 523 K and by further fine tuning the amount of C and $T_s$ around 523 K, it may be possible increase the fraction of Fe$_2$C phase or even a single phase Fe$_3$C phase can be obtained.

### IV. CONCLUSION

In conclusion, in the present work we systematically studied the role of substrate temperature and phase formation in Fe-C thin films around Fe$_{0.8}$C$_{0.2}$ composition. A comparison of Fe$_{0.8}$C$_{0.2}$ films together with pure Fe films grown under similar conditions exhibited the effect of C inclusion of on the long range crystalline ordering. In addition, the comparison of Fe$_{0.8}$C$_{0.2}$ films with C thin films yielded vital information about the hybridization between Fe and C. By inserting a thin $^{57}$Fe or $^{57}$Fe$_{0.8}$C$_{0.2}$ marker layer in between thick Fe or Fe$_{0.8}$C$_{0.2}$ layers, Fe self-diffusion that is taking place during the growth itself was measured. We found the Fe self-diffusion was appreciably large even at 300 K, but the addition of C in Fe inhibits Fe self-diffusion remarkably. At the high $T_s$ of 773 K, C addition leads to very rapid Fe self-diffusion. However, at an intermediate temperature of $T_s$ of 523 K, Fe self-diffusion is still slow and controllable so that formation of Fe$_3$C phase could be realized. It can be anticipated that by further fine tuning of $T_s$ and C composition, the fraction of Fe$_3$C can be further enhanced. The information about such Fe diffusion process in Fe-C system is new and can be suitably used to synthesize challenging Fe-C phases.

### ACKNOWLEDGMENTS

Authors would like to acknowledge Layanta Behera for technical help, Anil Gome for CEMS, Mohan Gangade for AFM and MFM, Rakesh Sah for XANES and Nidhi Pandey for NRS measurements. We are thankful to A.K. Sinha for support and encouragements and Seema for fruitful discussions. Portions of this research were carried out at the light source PETRA III of DESY, a member of the Helmholtz Association (HGF). Financial support by the Department of Science & Technology (Government of India) provided with in the framework of the India@DESY collaboration is gratefully acknowledge.

### REFERENCES
[48] M. Magnuson, M. Andersson, J. Lu, L. Hultman, and U. Jansson, Journal of Physics: Condensed Matter 24, 225004 (2012).
[49] P. Kumar, M. Gupta, U. Deshpande, D. Phase, V. Ganeshan, and J. Stahn, Diamond and Related Materials 84, 71 (2018).
[50] M. Miglierini and J.-M. Greneche, Journal of Physics: Condensed Matter 9, 2303 (1997).
[51] T. Glaser, Angewandte Chemie International Edition 50, 10019, https://onlinelibrary.wiley.com/doi/pdf/10.1002/anie.201104962.
[52] M. Miglierini and P. Mat, Pure and Applied Chemistry 89, 405 (2017).
[53] F. Miani, P. Matteazzi, and D. Basset, Journal of Alloys and Compounds 204, 151 (1994).
[54] S. Amagasa, N. Nishida, Y. Kobayashi, and Y. Yamada, Hyperfine Interactions 237, 110 (2016).
[55] F. Moutinho, C. Rojas, and L. D’Onofrio, in LACAME 2008, edited by J. Desimoni, C. Ramos, B. Arcondo, F. D. Saccone, and R. Mercader (Springer Berlin Heidelberg, Berlin, Heidelberg, 2009) pp. 141–147.
[56] R. Röhlberger, Nuclear Condensed Matter Physics with Synchrotron Radiation (Springer Berlin Heidelberg, 2005).
[57] A. Gupta, M. Gupta, S. Chakravarty, R. Rüffer, H.-C. Wille, and O. Leupold, Phys. Rev. B 72, 014207 (2005).
[58] M. A. Andreeva, Hyperfine Interactions 185, 17 (2008).
[59] G. Brebec, R. Seguin, C. Sella, J. Bevenot, and J. Martin, Acta Metallurgica et Materialia 38, 283 (1990).
[60] Y. Loirat, J. Bocquet, and Y. Limoge, Journal of Non-Crystalline Solids 265, 252 (2000).
[61] M. Gupta, A. Gupta, S. Rajagopalan, and A. K. Tyagi, Phys. Rev. B 65, 214204 (2002).
[62] A. Tiwari, M. K. Tiwari, M. Gupta, H.-C. Wille, and A. Gupta, Phys. Rev. B 99, 205413 (2019).
[63] H. L. Bai, E. Y. Jiang, C. D. Wang, and R. Y. Tian, Journal of Physics: Condensed Matter 8, 8763 (1996).
[64] J. B. Kortright, S. Joksch, and E. Ziegler, Journal of Applied Physics 69, 168 (1991).
[65] M. Ishino, M. Koike, M. Kanehira, F. Satou, M. Terauchi, and K. Sano, Journal of Applied Physics 102, 023513 (2007), https://doi.org/10.1063/1.2756741.
[66] S. Amir, M. Gupta, and A. Gupta, Journal of Alloys and Compounds 522, 9 (2012).
[67] M. Lbbhusen and H. Mehrer, Acta Metallurgica et Materialia 38, 283 (1990).
[68] Y. Iijima, Journal of Phase Equilibria and Diffusion 26, 466 (2005).
[69] S. Chakravarty, N. Shukla, A. Devishvili, A. Vorobiev, and G. Amarendra, Materials Research Express 3, 085001 (2016).
[70] K. Wasa, in Handbook of Sputtering Technology (Second Edition), edited by K. Wasa, I. Kanno, and H. Kotera (William Andrew Publishing, Oxford, 2012) second edition ed., pp. xi – xii.
[71] V. Bhavanasi, C. B. Singh, D. Datta, V. Singh, K. Shahi, and S. Kumar, Optical Materials 35, 1352 (2013).
[72] X.-Y. Li, H.-J. Li, Z.-J. Wang, H. Xia, Z.-Y. Xiong, J.-X. Wang, and B.-C. Yang, Optics Communications 282, 247 (2009).
[73] C.-C. Fu, J. D. Torre, F. Willaime, J.-L. Bocquet, and A. Barbu, Nature Materials 4, 68 (2005).
[74] S. Chakravarty, H. Schmidt, U. Tietze, D. Lott, N. P. Lalla, and A. Gupta, Phys. Rev. B 80, 014111 (2009).
[75] A. C. T. van Duin, S. Dasgupta, F. Lorant, and W. A. Goddard, The Journal of Physical Chemistry A 105, 9396 (2001), https://doi.org/10.1021/jp004368u.