



# Effect of Al doping on phase formation and thermal stability of iron nitride thin films



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## ABSTRACT

In the present work, we systematically studied the effect of Al doping on the phase formation of iron nitride (Fe–N) thin films. Fe–N thin films with different concentration of Al (Al = 0, 2, 3, 6, and 12 at.%) were deposited using dc magnetron sputtering by varying the nitrogen partial pressure between 0 and 100%. The structural and magnetic properties of the films were studied using x-ray diffraction and polarized neutron reflectivity. It was observed that at the lowest doping level (2 at.% of Al), nitrogen rich non-magnetic Fe–N phase gets formed at a lower nitrogen partial pressure as compared to the un-doped sample. Interestingly, we observed that as Al doping is increased beyond 3 at.%, nitrogen rich non-magnetic Fe–N phase appears at higher nitrogen partial pressure as compared to un-doped sample. The thermal stability of films were also investigated. Un-doped Fe–N films deposited at 10% nitrogen partial pressure possess poor thermal stability. Doping of Al at 2 at.% improves it marginally, whereas, for 3, 6 and 12 at.% Al doping, it shows significant improvement. The obtained results have been explained in terms of thermodynamics of Fe–N and Al–N.

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## 1. Introduction

Iron nitride compounds are known to exist in varieties of phases having distinct crystal structure and magnetic properties [1–13]. Different Fe–N phases can be formed just by increasing the nitrogen concentration in Fe. With the increasing nitrogen concentration, Fe–N phases that get formed are: nanocrystalline/amorphous  $\alpha$ -Fe–N (Nat.% = 0–11),  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> (Nat.% = 11.4),  $\gamma'$ -Fe<sub>4</sub>N (Nat.% ~ 20),  $\epsilon$ -Fe<sub>3–2</sub>N (0 ≤ z ≤ 1, Nat.% = 25–33),  $\zeta$ -Fe<sub>2</sub>N (Nat.% ~ 33),  $\gamma'''$ -FeN (Nat.% ~ 50). This essentially covers the whole phase diagram of Fe–N system [14]. These compounds have various applications such as in tribological coatings, magnetic read-write heads, memory devices etc. [5,7,15] However, thermal stability of Fe–N compounds is poor due to weak Fe–N bonding and since the heat of formation ( $\Delta H_f^\circ$ ) for Fe–N is high (compared to other transition metal nitrides e.g. Al–N, Ti–N etc.), Fe–N compounds are invariably less stable [16–22]. To improve the thermal stability of Fe–N

system, it was proposed that if a few atomic percentage of a third element X (X = Al, Ti, Zr, Ta etc.), which has low  $\Delta H_f^\circ$  for its nitrides and high affinity nitrogen, is added in the Fe–N system, then it can thermally stabilize the iron nitride compounds [20,23–28,3,29–33]. Very recent study elucidates that enhancement of thermal stability actually results from the suppression of Fe self-diffusion [34,35]. In addition, it was observed that Al doping is most efficient (compared to other dopants e.g. Zr, Ti) for the enhancement of thermal stability [34,35]. However, there were no reports mentioning the optimum amount of Al that would be required for the enhancement of the thermal stability. Moreover, as all the proposed dopants are non-magnetic the amount of dopants is very crucial, since it may alter the ingenious magnetic properties of Fe–N thin films. Therefore, it is required that an optimum doping level must be known so that it would not affect the desired properties of Fe–N thin films.

In the present work, we have addressed these issues by systematically studying the formation of different iron nitride phases by varying the doping level of Al. Structural properties of the films were investigated using X-ray diffraction (XRD). Polarized neutron

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reflectivity (PNR) was used to measure the magnetic properties of the deposited samples. We observed that at low doping of Al (2 at.%), nitrogen incorporation in the Fe–N system gets enhanced as compared to un-doped sample. Interestingly, we observed that with increasing the doping level of Al from 3 to 12 at.%, nitrogen incorporation in iron nitride system gets retarded. As expected, the thermal stability of un-doped samples is poor. With 2 at.% of Al, it only improves marginally. Whereas, Al doping at 3, 6 and 12 at.% shows significant enhancement in the thermal stability. The obtained results explained on the basis of interaction of Al with N.

## 2. Experimental

Iron nitride films were deposited using a dc magnetron sputtering (dcMS) technique. Pure Fe and [Fe + Al] composite targets were sputtered using a mixture of Ar and N<sub>2</sub> gases. Nitrogen concentration in the films was varied by varying the nitrogen partial pressure defined as:  $R_{N_2} = P_{N_2} / (P_{Ar} + P_{N_2})$ , (where  $P_{Ar}$  is Ar gas flow and  $P_{N_2}$  is N<sub>2</sub> gas flow) between 0 and 100%. Total gas flow was kept constant at 10 sccm. Before deposition a base pressure of  $1 \times 10^{-5}$  Pa was achieved, during the deposition chamber pressure was maintained at 0.4 Pa. Total five sets of samples were prepared by varying the  $R_{N_2}$  between 0 and 100% at Al doping of 0, 2, 3, 6, and 12 at.%. Concentration of Al in the samples was measured using energy dispersive X-ray analysis, typical error bars in the measurement are of the order of  $\pm 0.5$ . All the samples at one particular concentration of Al were prepared without venting the vacuum chamber to atmosphere. The structural characterization of the samples was performed using a standard XRD system (Bruker D8-Advance) equipped with Cu-K $\alpha$  x-ray source and a one dimensional position sensitive detector based on silicon strip technology (Bruker LynxEye) in  $\theta$ – $2\theta$  geometry. PNR measurements were carried out at AMOR reflectometer at SINQ-PSI Switzerland. To saturate the sample magnetically a magnetic field of 0.5 T was applied during the PNR measurements.

## 3. Results

### 3.1. Effect of Al doping in Fe

We will first compare the effect of Al doping on sample prepared using argon gas only ( $R_{N_2}=0\%$ , no nitrogen). For pure Fe sample (110) reflection corresponding to  $\alpha$ -Fe phase can be seen in the XRD pattern as shown in Fig. 1 (a). With Al doping this peak shifts

**Table 1**

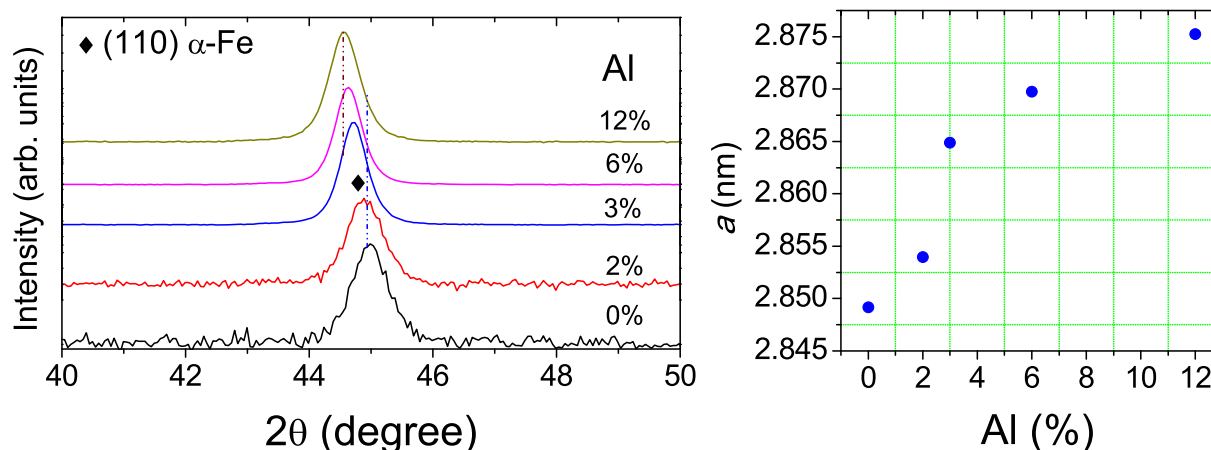
Crystallite size (CS in nm) and phases formed in Fe–Al–N thin films samples with Al doping of 0, 2, 3, 6 and 12 at.% deposited by varying the nitrogen partial pressures between  $R_{N_2} = 0 - 100\%$ . Here *am* denotes amorphous phase. The error bar in measurement of crystallite size is about  $\pm 0.5$  nm. Indexation of various Fe–N phases was done following the JCPDS database and XRD data reported in the literature, for  $\alpha$ -Fe–N (JCPDS No. 85-1410),  $\gamma$ -Fe<sub>4</sub>N (JCPDS No. 86-0231),  $\epsilon$ -Fe<sub>3-2</sub>N (JCPDS No. 03-0925 and Ref. [46]),  $\zeta$ -Fe<sub>2</sub>N (JCPDS No. 86-1025 and Refs. [47,48]) and  $\gamma$ -FeN (JCPDS No. 88-2153 and Ref. [49]).

$R_{N_2}$ (%)	0 at% Al		2 at% Al		3 at% Al		6 at% Al		12 at% Al	
	Phase	CS	Phase	CS	Phase	CS	Phase	CS	Phase	CS
0	$\alpha$	15	$\alpha$	14.9	$\alpha$	23.3	$\alpha$	24.1	$\alpha$	19.6
10	$\alpha$	4.6	$\alpha$	7.7	$\alpha$	12.9	$\alpha$	14.7	$\alpha$	15.9
20	$\alpha$	<i>am</i>	$\alpha$	<i>am</i>	$\alpha$	7.4	$\alpha$	9.6	$\alpha$	11.0
30	$\epsilon$	10.6	$\epsilon$	13.9	$\alpha$	3	$\alpha$	<i>am</i>	$\alpha$	<i>am</i>
40	$\epsilon$	14.9	$\epsilon$	20.7	$\epsilon$	15.8	$\alpha$	<i>am</i>	$\alpha$	<i>am</i>
50	$\epsilon$	21.2	$\epsilon$	29.5	$\epsilon$	24.8	$\epsilon$	14.9	$\alpha$	<i>am</i>
60	$\epsilon$	17.5	$\gamma$ <sup>'''</sup>	10.2	$\epsilon$	24.8	$\epsilon$	15.4	$\epsilon$	4.0
70	$\epsilon$	14.7	$\gamma$ <sup>'''</sup>	6.0	$\epsilon$	19	$\epsilon$	14.4	$\epsilon$	4.0
80	$\zeta$	19.7	$\gamma$ <sup>'''</sup>	3.3	$\gamma$ <sup>'''</sup>	7.4 ( $\epsilon+\gamma$ <sup>'''</sup> )	10.5	$\epsilon$ <sup>'''</sup>	<i>am</i>	
90	$\zeta$ <sup>'''</sup>	7.6	$\gamma$ <sup>'''</sup>	3.0	$\gamma$ <sup>'''</sup>	5.4	$\gamma$ <sup>'''</sup>	4.4	$\gamma$ <sup>'''</sup>	2.5
100	$\gamma$ <sup>'''</sup>	5.0	$\gamma$ <sup>'''</sup>	3.2	$\gamma$ <sup>'''</sup>	3.8	$\gamma$ <sup>'''</sup>	3.4	$\gamma$ <sup>'''</sup>	2.4

towards lower angles, indicating an expansion of the lattice. Obtained variation in the lattice constant is shown in Fig. 1(b). We find that as Al doping level is increased from 2 to 3%, there is a sudden jump in the lattice constant. For higher doping levels, the variation in the lattice constant is linear with Al concentration, as expected from Vegard's law [37]. As shown later, the behavior of 2% doped sample is different than samples doped with higher amount of Al, while in 2% doped sample, the Fe–N nitridation process is somewhat accelerated (compared to undoped case) while at the higher doping levels it is retarded. This suggests that with 2 at.% doping, Al is predominantly substituting a Fe atom within the bcc unit cell. At higher doping levels, Al gets incorporated in the grain boundary region and micro strain produced by such doping results in expansion of lattice constant. It interesting to note that the grain size increases somewhat for doping beyond 3 at% of Al (see Table 1). Such enhancement in grain size with a dopant is due to an increase in the grain nucleation rate in agreement with previous reports [23,36].

### 3.2. Phase evolution in Fe–Al–N thin films

As such formation of different Fe–N phases with increasing  $R_{N_2}$  has been well-studied [33,36]. Here to make an unambiguous



**Fig. 1.** XRD pattern of Fe–Al samples for different Al doping (a) and relation between lattice constant and Al doping (b). Typical error in estimation of lattice constant are the size of scatters.

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