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

Akhil Tayal\textsuperscript{a}, Mukul Gupta\textsuperscript{a}\textsuperscript{*} and Nidhi Pandey\textsuperscript{a}, Ajay Gupta\textsuperscript{b}, M. Horisberger\textsuperscript{c}, J. Stahn\textsuperscript{d}
\textsuperscript{a}UGC-DAE Consortium for Scientific Research, University Campus, Khaduwala Road, Indore 452 001, India
\textsuperscript{b}Amity Center for Spintronic Materials, Amity University, Sector 125, Noida-201 303
\textsuperscript{c}Laboratory for Developments and Methods, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland and
\textsuperscript{d}Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

(Dated: May 21, 2015)

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 to 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 3at.\%, 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 2at.\% improves it marginally, whereas, for 3, 6 and 12at.\% Al doping, it shows significant improvement. The obtained results have been explained in terms of thermodynamics of Fe-N and Al-N.

I. INTRODUCTION

Iron nitride compounds are known to exist in varieties of phases having distinct crystal structure and magnetic properties\textsuperscript{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$_{16}$N$_2$(Nat.\%=11.4), $\gamma'$-Fe$_3$N (Nat.\%=20), $\varepsilon$-Fe$_{3-z}$N(0$\leq$z$\leq$1, Nat.\%=25-33), $\zeta$-Fe$_2$N (Nat.\%=33), $\gamma'''$-FeN (Nat.\%=50). This essentially covers the whole phase diagram of Fe-N system\textsuperscript{14}. These compounds have various applications such as in tribological coatings, magnetic read-write heads, memory devices etc.\textsuperscript{5,7,15} However, thermal stability of Fe-N compounds is poor due to weak Fe-N bonding and since the heat of formation ($\Delta H_f^\parallel$) 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\textsuperscript{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 $\Delta H_f^\parallel$ for its nitrides and high affinity nitrogen, is added in the Fe-N system, then it can thermally stabilize the iron nitride compounds\textsuperscript{3,20,23–33}. Very recent study elucidates that enhancement of thermal stability actually results from the suppression of Fe self-diffusion\textsuperscript{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\textsuperscript{34,35}. However, there were no reports mentioning the optimum amount of Al that would be require 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 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 2at.\% of Al, it only improves marginally. Whereas, Al doping at 3, 6 and 12at.\% shows significant enhancement in the thermal stability. The obtained results explained on the basis of interaction of Al with N.

II. 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$_2$ 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$_2$ gas flow) between 0 to 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 to 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 ±0.5. All the samples at one particular concentration of Al were prepared simultaneously. The structural characterization of the samples was performed using a standard XRD system (Bruker D8-Advance) equipped with Cu-Kα x-ray source and a one dimensional position sensitive detector based on silicon strip technology (Bruker LynxEye) in θ–2θ 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.

III. RESULTS

A. Phase evolution in Fe-Al-N thin films

As such formation of different Fe-N phases with increasing RN₂ has been well-studied. Here to make an unambiguous comparison of phase formation for various Al doping, un-doped samples were also prepared under identical deposition conditions. Figure 1 shows XRD patterns of un-doped Fe-N thin films prepared for different RN₂. The observed Fe-N phases with increasing RN₂ and respective crystallite size are tabulated in the table I. Crystallite size in the samples was calculated using Scherrer formula. From the XRD pattern, it can be seen that up to RN₂ = 20% nanocrystalline/amorphous α-Fe(N) phase with bcc structure can be seen. For RN₂ between 30 and 70%, ε-Fe₃₋₂N(0 ≤ z ≤ 1) phase was observed. The ε phase exist in a wide range of nitrogen composition varying from 0 ≤ z ≤ 1. When 0 ≤ z ≤ 0.6 the phase is ferromagnetic at room temperature, whereas above this it becomes paramagnetic at room temperature. For RN₂ = 80 and 90%, ζ – Fe₂N phase having orthorhombic structure was observed while for RN₂ = 100%, γ′′′-FeN phase can be seen. These results are consistence with previous reports.

Now the effect of Al doping on the phase formation can be compared. Figure 2 shows XRD patterns of samples prepared with different amount of Al doping at 2%(a), 3%(b), 6%(c), and 12%(d). It can be seen that as compared to the un-doped samples, the doping of Al has altered the order of phase formation while the phases that occur are similar to the un-doped case. The observed Fe-N phases and their crystallite size are given in the table I. With 2at.% Al doping (figure 2(a)), up to RN₂ = 20% the phases formed are similar to those in the un-doped sample. However, the ε phase can only be seen between RN₂ = 30, 40 and 50%. Above this value of RN₂, γ′′′ phase gets formed. No signature of ζ – Fe₂N phase can be seen for samples prepared with Al doping.

We find that as the Al doping levels are increased, the value of RN₂ at which the ε phase starts shifts to a higher value. For 3at.% it is 40%, for 6at.% it is 50% and for 12at.% it is 60%. This also suggests that value of RN₂ for which nanocrystalline/amorphous α-Fe(N) phase is seen gets extended with an increase in Al doping. Other variations remain almost similar as shown in figure 2(a), (b) and (c) for samples prepared with Al doping of 3, 6 and 12at%, respectively. A general trend that emerges out is that with successively increasing Al doping, formation of nitrogen rich phases occurs at higher RN₂.

B. Study of magnetic properties using polarized neutron reflectivity

To investigate the implication of doping concentration on the magnetic properties of deposited samples, we have performed PNR measurements on all set of samples. PNR is a well known technique for the measurement of magnetic moment in thin films. Magnetic moment obtained from this technique as compared to conventional magnetization technique has an unique advantage, that it is free from errors that are generally occurred in measuring sample mass. PNR measurements on all sets of samples were carried out up to the value of RN₂, where spin-up (R⁺) and spin-down (R⁻) reflectivities equals. When R⁺ = R⁻, it suggests that the sample has become non ferromagnetic at the measured temperature. Figure 3 shows PNR patterns of samples deposited at varying RN₂ for Al=0at.%(a), 2at.%(b), 3at.%(c), 6at.%(d), and 12at.%(e).

Raw PNR data even without fitting can be used to get vital information about the magnetic structure of the samples. Spin asymmetry (SA= (R⁺ – R⁻)/(R⁺ + R⁻))
can be used to observe variation in its intensity which is proportional to magnetic moment of the sample. Figure 4 show a plot of SA for samples deposited at varying $R_{N_2}$. If the relative intensity at around $q_{1}^\gamma$ is monitored, it gives qualitative information regarding the variation in magnetic moment with increasing $R_{N_2}$. In the un-doped sample, SA intensity at $q_{1}^\gamma$ falls to zero for sample deposited at $R_{N_2}=40\%$. For 2at.% Al, SA intensity is zero for $R_{N_2}=40\%$ sample, however, for 30% sample, SA intensity at $q_{1}^\gamma$ is slightly reduced compared to un-doped sample deposited at same $R_{N_2}$. This indicates that at 2at.% Al doping, nitrogen rich non-ferromagnetic Fe-N phase gets formed at relatively less $R_{N_2}$. On contrary, at 3at.% Al doping, SA intensity is zero for sample deposited at $R_{N_2}=50\%$. With further increasing Al concentration to 6 and 12 at.%, SA intensity is zero for 60% samples. However, on comparing these two set of samples SA intensity falls more rapidly for 6at.% Al doping as compared to 12at.% Al doping. To get quantitative information about the variation of magnetic moment in the samples, PNR data was fitted using a computer program. Obtained values of the av-
occurs at relatively lower $R_{N_2}$ formation of nitrogen rich Fe-N phases to a higher $R_{N_2}$ fall in the value of magnetic moment continuously shifts magnetic moment get altered. For low doping (2at.%) to zero in all samples. However, with doping the fall in samples. On contrary to this, as doping concentration be seen that with increasing $R_{N_2}$ average magnetic moment are plotted in figure 3(f). It can be seen that with increasing $R_{N_2}$ magnetic moment falls to zero in all samples. However, with doping the fall in magnetic moment get altered. For low doping (2at.%) moment fall more rapidly as compared to un-doped samples. Whereas, with increasing Al doping beyond 3at.% fall in the value of magnetic moment continuously shifts to a higher $R_{N_2}$. These results indicate that at low Al doping (2at.%) formation of nitrogen rich Fe-N phases occurs at relatively lower $R_{N_2}$ as compared to un-doped samples. On contrary to this, as doping concentration of Al increases, nitrogen rich Fe-N phase get formed at relatively higher $R_{N_2}$ as compared to successive lower Al doping. These results are consistence with the XRD measurements discussed in section III A.

C. Investigation of thermal stability

To investigate the effect of Al concentration on the thermal stability of Fe-N thin films, we studied Al doped and un-doped samples after annealing them at different temperatures. We selected five samples deposited at $R_{N_2}$=10% for various Al doping. At this value of $R_{N_2}$ the structure of all samples is similar (nanocrystalline $\alpha$-Fe-N phases) and samples are expected to show soft magnetic properties. When N atoms are incorporated in $\alpha$-Fe, they occupy interstitial sites within the Fe lattice. Since the radius of the interstitial site is almost half of a N atom, N incorporation give rise to lattice strain. In this process strain energy dominates over grain boundary energy that leads to reduction in grain size. If the grain size in the films reduces below ferromagnetic exchange length, in such condition, films displays excellent soft magnetic properties as explained by the random anisotropy model. Therefore, such kind of films are important for device application and hence their thermal stability is necessary to investigate.

To study the effect of Al doping on the thermal stability all sample prepared at $R_{N_2}$=10% were annealed in a vacuum furnace for 2 hours. To reduce any thermal gradient, all samples were annealed together. After an annealing at a temperature, XRD measurements were performed. Figure 5 shows XRD patterns of annealed samples at various temperatures. It can be seen in
properties on similar samples were done in earlier studies. The measurement of magnetic properties deteriorate as the grain size increase. The grain size obtained from XRD data for annealed samples are shown in figure 5(f). As expected in the un-doped sample, improvements as no additional peaks corresponding to any other Fe-N phase can be detected even after annealing at 673 K.

Although thermal stability improves significantly when Al doping in Fe-N system exceeds 3at.%, it is immensely important that the grain growth should be avoided as annealing temperature increases. For grain sizes below the ferromagnetic exchange length, soft magnetic properties deteriorate as the grain size increase. The grain sizes obtained from XRD data for annealed samples are shown in figure 5(f). As expected in the un-doped sample, sudden grain growth was observed above 573 K. Whereas with Al doping grain size remains stable throughout the annealing temperatures. The measurement of magnetic properties on similar samples were done in earlier studies. It was found that with doping soft magnetic properties of films shows significant improvement.

IV. DISCUSSION

The obtained results can be understood from the interaction of N atoms with Fe and Al. It is know that the $\Delta H_f^\circ$ for aluminum nitrides is significantly smaller than that of iron nitrides ($\Delta H_f^\circ$ for Al-N is typically -321 kJmol$^{-1}$; for Fe-N it is about -10 kJmol$^{-1}$) and Al has far more affinity for N as compared to Fe$^{34}$. As N is added in Fe, the magnetic moment falls due the formation of non-magnetic covalent bonds between Fe and N. However, as concentration of Al doping increases, the formation of non-magnetic iron nitride shows a non-monotonic behavior with $R_{N_2}$ as compared to un-doped samples. This can be understood from the thermodynamics of Al-N. When Al is doped in Fe, it may either get dissolved substitutionally or may get incorporated in the grain boundary region. Al atoms present within the Fe lattice enhance the N incorporation since $\Delta H_f^\circ$ is small and high affinity for N. Enhanced N content increases the interaction of Fe with N that results in the formation of non-magnetic Fe-N phase at relatively smaller $R_{N_2}$ as compared to un-doped sample. This phenomenon was indeed observed with 2at.% Al doping in the present study as well as in previous reports$^{33,36}$. However with increasing Al concentration beyond 3at.% a reverse effect can be observed. Higher doping level enhance the probability for Al atoms to be present in the grain boundary region. During the deposition, N atoms interact with these Al atoms to form Al-N. This behavior shields a direct interaction between Fe and N atoms. Due to reduced interaction between Fe and N formation of non-magnetic Fe-N phases shifts to higher $R_{N_2}$ with increasing doping concentration. The grain boundary precipitate layer in the form of Al-N also act as a diffusion barrier layer that suppress Fe self-diffusion which results in the observed enhancement in the thermal stability of Fe-N films at 3, 6 and 12at.% of Al. Moreover no grain growth is observed at these doping level attributed to suppression in
atomic diffusion. From the obtained results, it can be concluded that to get good soft magnetic properties and remarkable thermal stability, optimum doping level of Al in the Fe-N thin films must be about 3at.%.

V. CONCLUSION

In conclusion, Fe-N films were deposited using dc-MS by varying the R$_{N}$. Phase formation in the Fe-N system was compared for different Al doping (2, 3, 6 and 12at.%). At low Al doping (2at.%) nitrogen rich Fe-N phases gets formed at lesser R$_{N}$, as compared to un-doped samples. On the contrary, successive increase in Al doping levels shift the formation of non-ferromagnetic Fe-N phase to higher R$_{N}$. Thermal stability of un-doped sample deposited at R$_{N}$=10% is found to be poor. With 2at.% thermal stability only improves marginally. Whereas, for 3, 6 and 12at.% thermal stability improves remarkably while the grain size remains almost constant. We find that when doped sufficiently, Al atoms are not only substitutionally dissolved but also present in the grain boundary region. Formation of a diffusion barrier layer in the grain boundary region prevents grain growth and leads to remarkable thermal stability.

ACKNOWLEDGMENTS

A part of this work was performed at AMOR, Swiss Spallation Neutron Source, Paul Scherrer Institute, Villigen, Switzerland. We acknowledge Department of Science and Technology, New Delhi for providing financial support to carry out PNR experiments. We would like to acknowledge Dr. A. K. Sinha and Dr. V. Ganesan for support and encouragement. One of the authors (AT) wants to acknowledge CSIR, New Delhi for the senior research fellowship.

* ngupta@csr.res.in/dr.mukul.gupta@gmail.com

1. M. Gupta, A. Gupta, P. Bhattacharya, P. Misra, and L. Kukreja, J. Alloys and Compounds 326, 265 (2001).
2. R. Gupta and M. Gupta, Phys. Rev. B 72, 024202 (2005).
3. Y.-K. Liu, M. H. Kryder, D. H. Ryan, and Z. Altounian, J. Appl. Phys. 93, 6471 (2003).
4. L. Rissanan, M. Neubauer, K. P. Lieb, and P. Schaaf, J. Alloys and Compds. 274, 74 (1998).
5. P. Schaaf, Prog. Mater. Sci. 47, 1 (2002).
6. E. Y. Jiang, D. C. Sun, H. Liu, H. L. Bai, and X. X. Zhang.
7. R. Dubey, A. Gupta, and J. C. Pivin, Phys. Rev. B 74, 214110 (2006).
8. D.-L. Peng, K. Sumiyama, and K. Suzuki, J. Alloys and Compounds 355, 50 (1997).
9. E. B. Easton, T. Buhrmester, and J. Dahn, Thin Solid Films 493, 60 (2005).
10. D. Moszyński, I. Moszyńska, and W. Arabczyk, Materials Letters 78, 32 (2012).
11. W. Li Li, X. Hiang Zheng, and W. dong Fei, Vacuum 83, 949 (2009).
12. T. Hinomura and S. Nasu, Physica B: Condensed Matter 237-238, 557 (1997).
13. X. Wang, W. Zheng, H. Tian, S. Yu, W. Xu, S. Meng, X. He, J. Han, C. Sun, and B. Tay, Appl. Sur. Sci. 220, 30 (2003).
14. N. Kardonina, A. Yurovskikh, and A. Kolpakov, Metal Science and Heat Treatment 52, 457 (2011).
15. C. Navio, J. Alvarez, M. J. Capitan, F. Yndurain, and R. Miranda, Phys. Rev. B 78, 155417 (2008).
16. M. Gupta, A. Gupta, S. Rajagopalan, and A. K. Tyagi, Phys. Rev. B 65, 214204 (2002).
17. S. Chakravarty, M. Gupta, A. Gupta, S. Rajagopalan, A. Balamurugan, A. Tyagi, U. Deshpande, M. Horisberger, and T. Gutterlet, Acta Materialia 57, 1263 (2009).
18. Y. Ding and C. A. Jr., IEEE Trans. Mag. 42, 5 (2006).
19. M. Gupta, A. Tayal, A. Gupta, R. Gupta, J. Stahn, M. Horisberger, and A. Wildes, J. Appl. Phys. 110, 123518 (2011).
20. N. G. Chechenin, A. van Veen, H. Schut, A. R. Chezan, D. O. Boerma, T. Vystavel, and J. T. M. D. Hosson, J. Phys. Cond. Mat. 15, 7663 (2003).
21. F. Tessier, A. Navrotsky, R. Niewa, A. Leineweber, H. Jacobs, S. Kikkawa, M. Takahashi, F. Kanamaru, and F. J. DiSalvo, Solid State Sciences 2, 457 (2000).
22. M. Kopciewicz, J. Jagielski, G. Gawlik, and A. Grabias, J. Appl. Phys. 78, 1312 (1995).
23. B. Viala, M. K. Minor, and J. A. Barnard, J. Appl. Phys. 80, 3941 (1996).
24. H. Y. Wang, E. Y. Jiang, H. L. Bai, P. Wu, Y. Wang, and F. F. Gong, J. Physics: Condensed Matter 9, 8443 (1997).
25. L. Varga, H. Jiang, T. J. Klemmer, W. D. Doyle, and E. A. Payzant, J. Appl. Phys. 83, 5955 (1998).
26. Y.-K. Liu and M. H. Kryder, Appl. Phys. Lett. 77, 426 (2000).
27. A. Chezan, C. Craus, N. Chechenin, L. Niesen, and D. Boerma, physica status solidi (a) 189, 833 (2002).
28. J. Rantscher, Y. Ding, S.-C. Byeon, and C. Alexander, J. Appl. Phys. 93, 6671 (2003).
29. A. Kamzin, F. Wei, Z. Yang, and S. Kamzin, Tech. Phys. Lett. 31, 461 (2005), 10.1134/1.1969763.
30. J. Das, S. S. Kalarickal, K.-S. Kim, and C. E. Patton, Phys. Rev. B 75, 094435 (2007).
31. S. S. Kalarickal, P. Krivosik, J. Das, K. S. Kim, and C. E. Patton, Phys. Rev. B 77, 054427 (2008).
32. F. Xu, S. Li, and C. K. Ong, J. Appl. Phys. 109, 07D322 (2011).
33. R. Gupta, A. Tayal, S. M. Amir, M. Gupta, A. Gupta, M. Horisberger, and J. Stahn, J. Appl. Phys. 111, 103520 (2012).
34. A. Tayal, M. Gupta, N. P. Lalla, A. Gupta, M. Horisberger, J. Stahn, K. Schlage, and H. C. Wille, Phys. Rev. B 90, 144412 (2014).
35. A. Tayal, M. Gupta, D. Kumar, V. R. Reddy, A. Gupta, S. M. Amir, P. Korelis, and J. Stahn, Journal of Applied Physics 116, 222206 (2014).
36. A. Tayal, M. Gupta, A. Gupta, M. Horisberger, and J. Stahn, Thin Solid Films 536, 39 (2013).
37 P. Scherrer, news from the Society of Sciences in Göttingen, Mathematics and Physical Class 1918, 98 (1918).
38 B. D. Cullity, Elements of X-ray Diffraction (Addison-Wesley, MA, 1978).
39 G. Chen, N. Jaggi, J. Butt, E. Yeh, and L. Schwartz, Journal of physical chemistry 87, 5326 (1983).
40 P. Schaaf, C. Ilgner, M. Niederdrenk, and K. P. Lieb, Hyp. Int. 95, 199 (1995).
41 Y. Cai, A. Li, J. Cao, X. Ni, G. Zhang, G. Yu, and W. Xu, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 168, 422 (2000).
42 D. Rechenbach and H. Jacobs, J. Alloys and Compounds 235, 15 (1996).
43 I. Jouanny, P. Weisbecker, V. Demange, M. Grafouté, O. Peña, and E. Bauer-Grosse, Thin Solid Films 518, 1883 (2010).
44 S. J. Blundell and J. A. C. Bland, Phys. Rev. B 46, 3391 (1992).
45 F. Ott, SIMULREFLEC (V1.7 2011).
46 A. Tayal, M. Gupta, A. Gupta, V. Ganesan, L. Behera, S. Singh, and S. Basu, Surface and Coatings Technology , (2015).
47 G. Herzer, I.E.E.E. Trans. Mag. 25, 3327 (1989).
48 J. F. Loffler, J. P. Meier, B. Doudin, J.-P. Ansermet, and W. Wagner, Phys. Rev. B 57, 2915 (1998).