Ion-beam modifications in Fe-N thin films

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Thin films of transition metal nitrides are interesting systems due to their important properties such as high hardness and chemical inertness. An amorphous iron nitride thin film was deposited onto glass and silicon substrate using reactive ion-beam sputtering of iron in nitrogen atmosphere. The structural and magnetic properties of the film have been studied using grazing incidence x-ray diffraction, x-ray photoelectron spectroscopy, elastic recoil detection analysis, and magneto-optic Kerr-effect measurements. Ion-beam induced effects on thin films were observed using Au ions of 100 MeV energy at $1x10^{14}$ ions/cm^2 fluence. GIXRD of irradiated thin film samples shows a broad maximum around 2θ ≈ 43^0 showing no change in the nature of film. The film is found to transform into a mixture of ε- Fe_3N and α- Fe phases at 568 K. MOKE results show increase in coercivity after irradiation.

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1. Introduction

Iron nitride has been extensively investigated due to their excellent magnetic properties, which make them suitable for applications in high-density magnetic recording media. It plays an important role in the technical applications concerning the iron-based materials. It has a very complex phase diagram and can exist in many different phases such as α'' - $Fe_{16}N_2$, γ′ -Fe_4N, ε -Fe_3N, ζ - Fe_2N and FeN.

Irradiation of thin films with ion beams can improve the optical, chemical and electrical properties [1-2]. The ion beam technique, in various forms, has been applied to semiconductors, metals, ceramics, polymers and glasses in producing stable, metastable or even non-equilibrium phases [3-10]. A large number of studies on ion-beam induced effects in various bilayers [11-16] have been carried out. These investigations include (i) production of stable and metastable alloys (ii) improvements of the structural, optical and electrical properties.

In the present work, we have discussed irradiation effects on FeN/Glass system Phase formations in as deposited and irradiated samples have been studied using GIXRD. Nitrogen content in iron nitride thin film has been determined using X-ray photoelectron spectroscopy (XPS) and elastic recoil detection analysis (ERDA). Magnetic properties have been studied by magneto optic kerr effect (MOKE).

2. Experimental work

The experimental processes can be discussed in the following sections.

2.1 Deposition of thin films

The iron nitride thin film (80 nm) was deposited on silicon and glass substrate by reactive ion beam sputtering. Iron plates of purity 99.999% have been used as target. Nitrogen and argon gases were used in the ion gun for sputtering. The ion gun used was a broad beam Kaufman-type hot cathode gun (3 cm Commonwealth Scientific Corporation). The vacuum chamber was flushed with argon gas to remove contamination of other gases. Total gas flow rate was kept 3 sccm and the ratio of argon and nitrogen gas was kept 2.4:0.6. Ultimate vacuum of chamber was maintained at 2.2×10^{-7} torr. During the deposition overall pressure of argon and nitrogen was 1.2×10^{-4} torr. Sputtering was performed at room temperature with current 18 mA.

2.2 Irradiation

In order to see irradiation induced effects in near surface region, Fe-N thin film samples were irradiated by Au^{+8} at 1 pna (particle nanoampere) current with 100 MeV energy from the Pelletron accelerator of Inter University Accelerator Centre, New Delhi at 1×10^{14} ion/cm^2 fluence. The irradiation was carried out over an area of 1×1 cm^2 of samples. The irradiation induced compositional changes were monitored by GIXRD, XPS, ERDA and MOKE.

3. Results and discussion

3.1 Grazing incidence X-ray diffraction

The crystalline structure of as-deposited and irradiated Fe-N thin films deposited onto glass was confirmed by Grazing Incidence X-Ray Diffraction (GIXRD) using CuKα (λ = 1.5406Å) radiation at IUAC, New Delhi. These measurements were carried out in the 2θ range of 30^0 to 60^0. Fig. 1 shows the diffraction pattern of pristine Fe-N thin film sample indicating amorphous nature of iron nitride thin film. After the irradiation of this system at 1×10^{14} ions/cm^2 fluence a broad maximum is obtained around 2θ ≈ 43^0 showing no change in the nature of film (Fig. 2). It was difficult to determine the phase formation in iron nitride thin film by X-ray diffraction experiment, because the diffraction peak was very broad, Fe-N as-deposited sample was annealed in $1x10^{-6}$ torr vacuum for one hour at University of Rajasthan. It is observed that as-deposited system gets crystallized at 568 K into a mixture of α- Fe and stoichiometric ε- Fe_3N phases as shown in Fig. 3.

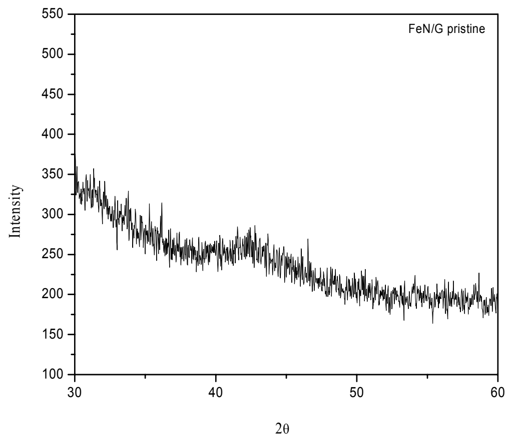

Fig. 1. GIXRD of as-deposited Fe-N thin film.

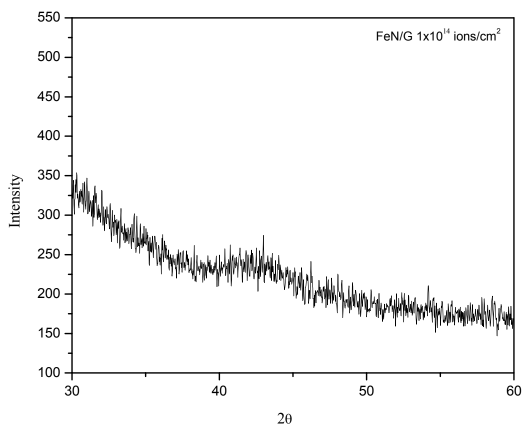

Fig. 2. GIXRD of irradiated Fe-N thin film at 1×10^{14} ion/cm^2 fluence.

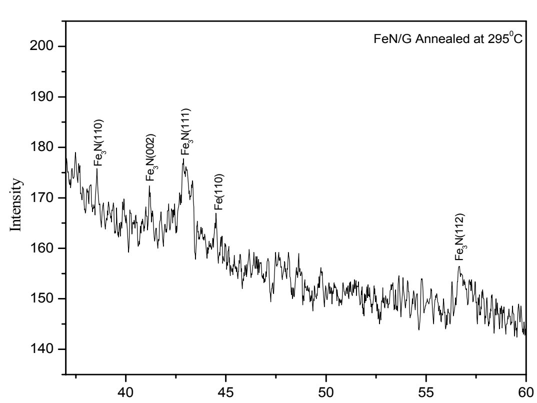

Fig. 3. GIXRD of annealed Fe-N thin film.

3.2 X-ray photoelectron spectroscopy

XPS measurements of iron nitride thin film onto glass substrate were used to determine the film composition and to analyze chemical shift. The AlKα (λ = 1486.6Å) line was used as the X-ray source to investigate chemical composition of as-deposited and irradiated samples. $Fe2p_{3/2}$ and N-1s levels of pristine FeN thin film are shown in Figs. 4 & 5. After normalizing the areas under the peaks corresponding to iron and nitrogen by their cross sections, the stochiometric ratio of iron and nitrogen was found to be 1 : 0.243, i.e. at. % of nitrogen is approximately 19.54 %.

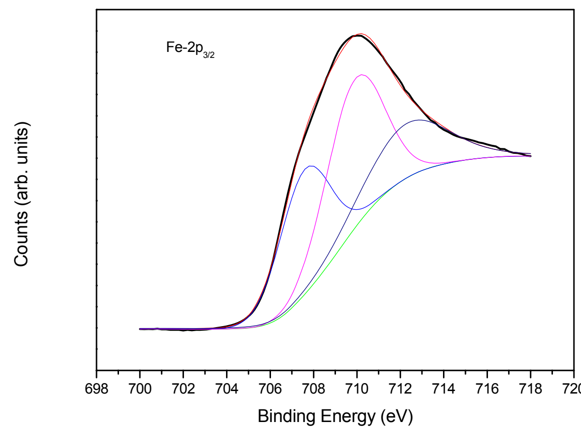

Fig. 4. Fe 2p3/2 core level spectrum of pristine Fe-N surface.

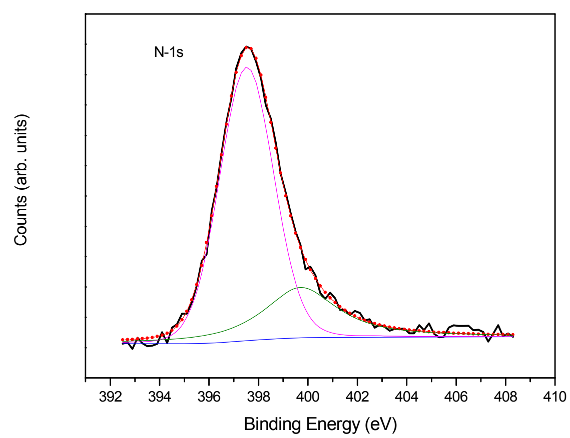

Fig. 5. N-1s core level spectrum of pristine Fe-N surface.

3.3 Elastic recoil detection analysis

The areal concentration of nitrogen has been confirmed for iron nitride thin film sample deposited on silicon substrate using elastic recoil detection analysis. In the ERD analysis, 100 MeV Au^{+8} ions were delivered by 15UD Pelletron accelerator at Inter University Accelerator Centre, New Delhi, India. On-line ERDA technique with a large area ΔE-E detector telescope was employed to monitor the change of nitrogen content of the films. Total accumulated fluence of projectile ions for FeN/Si system was of the order of 1×10^{13} ions/cm^2. After the irradiation beam spot area was manually measured to 3.8 mm^2. Ions recoiling from the sample during ERD analysis were detected using large area ΔE-E detector telescope with a detection solid angle ΔΩ = 5.5 msr, where the detector was fixed to a 45^0 port of a high vacuum chamber. Isobutane gas was passed through the detector at a pressure 26 mbar. Figs. 6 & 7 show areal concentration of iron and nitrogen respectively.

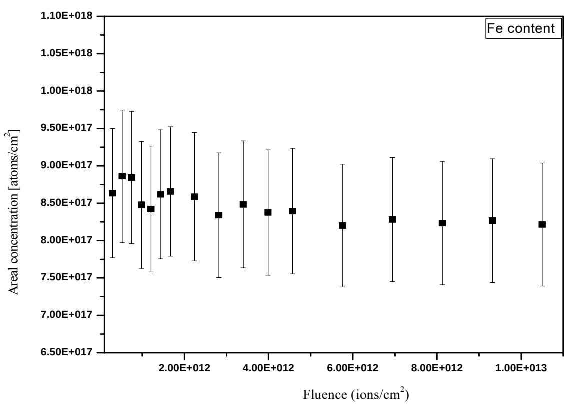

Fig. 6. Iron content versus fluence of Au ions.

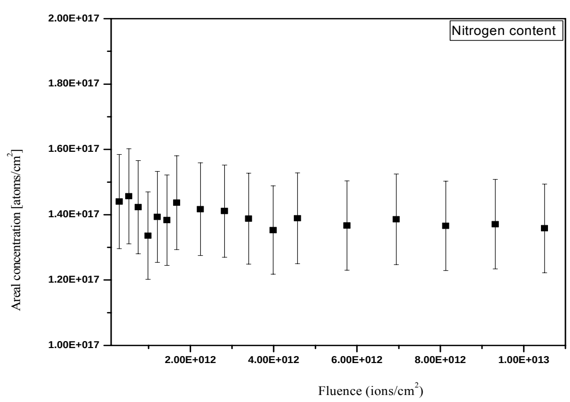

Fig. 7. Nitrogen content versus fluence of Au ions.

The concentration of sample atoms N_r (in atoms/cm^2) is determined by the following relation:

$$N_r = Y \sin\alpha / N_p \Omega d\sigma/d\Omega \qquad (1)$$

Where Y is the number of recoils detected in the detector subtending a solid angle of Ω, N_p is the number of incident ions, α is the sample tilt angle and dσ/d Ω is the Rutherford recoil cross section. For iron and nitrogen atom Rutherford recoil cross section is 126 barn and 101 barn respectively. From above equation we found the ratio of N/Fe equal to 0.208, i.e. atm% of nitrogen is approximately 17.2 %.

3.4 MOKE measurements

The magnetic properties of the samples were characterized by MOKE at room temperature. Measurements in the longitudinal geometry were performed with the magnetic field applied in the sample plane in the plane of incidence (parallel magnetization). Fig. 8 shows the magnetization measurements carried out using MOKE technique for as-deposited Fe-N thin film. The coercivity of as-deposited sample is found to be 14.28 Oe. After irradiation coercivity of Fe-N thin film sample is obtained 22.32 Oe as shown in Fig. 9. Hysteresis loop, measurements have been characterized by the coercivity H_c which can be defined as the displacement and the half-width of the loop. From recorded hysteresis loops, it has been observed clearly that all the samples show well-saturated magnetization with applied magnetic field.

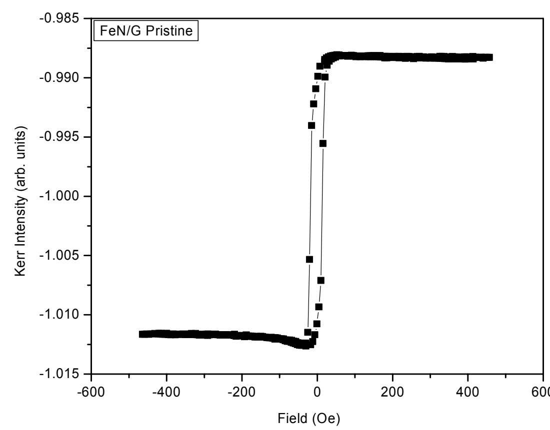

Fig. 8. Longitudinal Kerr signal versus applied magnetic field of Fe-N pristine system.

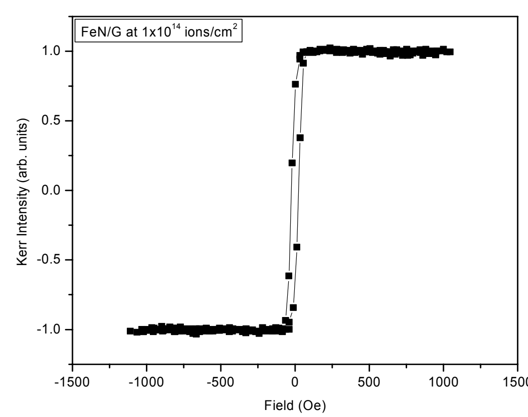

Fig. 9. Longitudinal Kerr signal versus applied magnetic field of Fe-N irradiated system.

Increase in coercivity after irradiation shows the formation of nanocrystalline grains [17- 19]. However, the type of the formed iron nitride phase is not clear due to amorphous nature. Phase diagram [20] of iron nitride describes that α- Fe and stochiometric ε- Fe_3N phases should co-exist in given conditions.

4. Conclusion

We have investigated the structural, magnetic and optical properties of iron nitride film containing both amorphous and nanocrystalline grains. It has been observed that diffraction pattern of pristine and irradiated Fe-N thin film samples indicates amorphous nature of iron nitride thin film and after annealing, as-deposited system gets crystallized into a mixture of α- Fe and stochiometric ε- Fe_3N phases. X-ray photoelectron spectroscopy and elastic recoil detection analysis gives nitrogen concentration in iron nitride thin films for glass and silicon substrate respectively. It has been concluded that substrate affects the concentration of nitrogen. For glass substrate the concentration of nitrogen is found to be higher than silicon substrate. Increase in coercivity in irradiated samples is upon nanocrystallization.

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References

[1] A. Polman, J. Appl. Phys. **82** 1, (1997).
[2] C. A. Straede, Nucl. Instrum. Methods. B **113**, 161 (1996).
[3] W. Bolse, Mater. Sci. Eng. R **12**, 53 (1994).
[4] J. Desimoni, A. Traverse, Phys. Rev. B **48**, 13266 (1993).
[5] S. Dhar, Y. N. Mohapatra, V. N. Kulkarni, Phys. Rev. B **54**, 5769 (1996).
[6] Nastasi, J. W. Mayer, Mater. Sci. Eng. R **12**, 1 (1994).
[7] Y. T. Cheng, Mater. Sci. Rep. **5**, 45 (1990).
[8] P. Sigmund, A. Gras-Marti, Nucl. Instrum. Methods B **182-183**, 25 (1981).
[9] G. S. Was, Prog. Surf. Sci. **32**, 211 (1990).
[10] B. X. Liu, Phys. Status Solidi A **94**, 11 (1986).
[11] S. Kumar, R. S Chauhan, S. A. Khan, W. Bolse, D. K. Avasthi, Nucl. Instrum. Methods. B **244**, 194 (2006).
[12] S. Dhar, L. Rissanen, K. Engel, M. Wenderoth, K. P. Lieb, Nucl. Instrum. Methods. B **178**, 297 (2001).
[13] S. Kumar, R. S. Chauhan, D. C. Agarwal, M. Kumar, A. Tripathi, W. Bolse, D. K. Avasthi, Nucl. Instrum. Methods. B **266**, 1759 (2008).
[14] R. E. Joohnson, B. U. R. Sundqvist, Phys. Today March 305 (1992).
[15] S. Ghosh, A. Tripathi, T. Som, S. K. Srivastava, V. Ganesan, A. Gupta, D. K. Avasthi, Radiat. Eff. Defects Solids **154**, 151 (2001).
[16] M. Toulemonde, J. M. Costantini, C. Dufour, A. Meftah, E. Paumier, F. Strder, Nucl. Instr. and Meth. B **116**, 37 (1996).
[17] C. Lal, R. Dhunna, I. P. Jain, Materials Science in Semiconductor Processing **11**, 1 (2008).
[18] R. Dubey, A. Gupta, Journal of Applied physics **98**, 083903 (2005).
[19] H. Naganuma, R. Nakatani, Y. Endo, Y. Kawamura, M. Yamamoto, Science & Tech. of Adv. Materials **5**, 101 (2004).
[20] E. H. Du, Marchie Van Voorthuysen, N. C. Chechenin, D. O. Boerma, Metallurgical and Materials Transactions A, **33A**, 2593 (2002).

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