Swift heavy ions for controlled modification of soft magnetic properties of $Fe_{0.85}N_{0.15}$ thin film

2010 J. Phys.: Condens. Matter 22 226001

(http://iopscience.iop.org/0953-8984/22/22/226001)

J. Phys.: Condens. Matter **22** (2010) 226001 (7pp) doi:10.1088/0953-8984/22/22/226001

Swift heavy ions for controlled modification of soft magnetic properties of $Fe_{0.85}N_{0.15}$ thin film

Ranjeeta Gupta[1], Ajay Gupta[1], Ranu Bhatt[2], R Rüffer[3] and D K Avasthi[4]

[1] UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452 017, India
[2] Max-Planck-Institut für Metallforschung, Heisenbergstraße 3, 70569 Stuttgart, Germany
[3] European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France
[4] Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi 110 067, India

E-mail: agupta@csr.ernet.in

Received 1 February 2010, in final form 11 March 2010
Published 12 May 2010
Online at stacks.iop.org/JPhysCM/22/226001

Abstract

It is shown that the soft magnetic properties of amorphous $Fe_{0.85}N_{0.15}$ film can be modified in a controlled manner by irradiation with 120 MeV Ag ions. Irradiation causes relaxation of short range as well as long range stresses, resulting in an improvement in the soft magnetic properties. Nuclear resonance reflectivity has been used to measure the diffusion length of Fe atoms as a function of irradiation fluence. It is found that the atomic motion associated with irradiation is not expected to modify significantly the interfaces with substrate or other layers.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Soft magnetic films are important for several applications including tunnel magnetoresistance (TMR) devices, exchange spring magnets, soft magnetic cores in high frequency passive elements etc. As-deposited films in general contain a high density of structural defects and quenched-in stresses. These structural imperfections may result in severe deterioration of soft magnetic properties. Therefore, quite often post-deposition thermal annealing is required in order to relieve the stresses and structural defects so as to achieve the optimal magnetic properties. For example, in TMR multilayers, thermal annealing around 375 °C results in an increase in TMR from a few per cent to about 235% [1]. This enormous increase in magnetoresistance can partly be attributed to the improvement in the soft magnetic layer. However, with thermal annealing interdiffusion between different layers can also take place which is not desirable [2]. Therefore, alternative ways of relieving the structural imperfections in thin films in order to improve their soft magnetic properties without significant interdiffusion, are highly desirable.

High-energy heavy-ion beams have been well established as a powerful tool for modifying material properties of thin films. Low-energy ion beams (having energies of the order of keV/nucleon) have been in use for several decades for material modifications via ion implantation or ion beam mixing. More recently, material modifications produced by swift heavy ions (having energies of the order of MeV/nucleon), have been a subject of great interest. Swift heavy ions differ from the low-energy ions in their interaction with the atoms of the target: at low energies the interaction with the target atoms is via elastic collisions in which energy is directly transferred from the bombarding ions to the motion of the target atoms (termed as nuclear energy loss). On the other hand, at higher energies the inelastic collisions involving excitation and ionization of the target atoms become dominant [3, 4] and thus energy is transferred mainly to the electrons in the target (termed as electronic energy loss). A part of this energy subsequently gets transferred to the atomic motions, and may create substantial modifications in the target material. Swift heavy-ion irradiation of soft magnetic films can be an effective technique to improve the soft magnetic properties of thin films via stress relaxation. In general, metallic systems are known to be relatively insensitive to swift heavy-ion irradiation, and intermixing at the interfaces in multilayers is known to occur only above a threshold value

of electronic energy loss in the material [5]. Therefore, by appropriately choosing the energy and the species of the bombarding ions, it may be possible to improve soft magnetic properties of the films without significant interdiffusion at the interfaces. In the present work, it has been demonstrated that swift heavy ions can be used for tailoring the soft magnetic properties of thin films.

2. Experimental details

Iron nitride thin films of composition $Fe_{0.85}N_{0.15}$ were deposited on a float glass substrate using reactive ion beam sputtering of an iron target of purity 99.99% with a beam consisting of a mixture of Ar and N ions using a 3 cm broad beam Kaufman-type hot cathode ion gun. In order to facilitate Mössbauer measurements the Fe target was enriched in ^{57}Fe to about 50%. Two mass flow controllers were used in parallel in order to control the flow of Ar and N_2 gases into the ion source at 4 sccm Ar + 1 sccm N_2. The base vacuum in the chamber was of the order of 10^{-7} mbar. The purity of both Ar and N_2 gases was 99.995%. The accelerating voltage used in the ion source was 1000 V and a beam current of 25 mA was used. The deposition was carried out at room temperature. The target was kept at an angle of 45° with respect to the beam direction. The substrate was kept parallel to the target at a distance of about 15 cm. The thickness of the deposited $Fe_{0.85}N_{0.15}$ film as obtained from x-ray reflectivity measurement was 120 nm.

Different pieces of the film were irradiated with 120 MeV Ag ions at room temperature for different fluences using the 15UD pelletron at Inter University Accelerator Centre, New Delhi. The ion beam was allowed to fall at normal incidence and was scanned to cover an area of 1 cm × 1 cm. The structural characterization was carried out with x-ray diffraction (XRD) at grazing incidence and x-ray reflectivity (XRR) using a Bruker D8 x-ray diffractometer with Cu Kα radiation, while magnetic properties were measured using conversion electron Mössbauer spectroscopy (CEMS) and magneto-optic Kerr effect (MOKE). The CEMS measurements were carried out using a ^{57}Co-radioactive source in a Rh matrix and a gas flow proportional counter (He + 4%CH_4) for detection of conversion electrons.

For measuring the self-diffusion of Fe using nuclear resonance reflectivity (NRR) [8], another set of samples was prepared in the form of isotopic multilayers with structure: [$^{nat}Fe_{0.85}N_{0.15}$ (3.6 nm)/$^{57}Fe_{0.85}N_{0.15}$ (2.6 nm)] × 30, by using two different targets, one with natural Fe and the other one enriched in ^{57}Fe (enrichment ∼95%). NRR has been done at the beamline ID18 of the European Synchrotron Radiation facility, Grenoble [6]. The storage ring operated in 16 bunch mode, providing short pulses of x-rays every 176 ns. The radiation from the undulator source optimized for 14.4 keV transition in iron, was filtered by double Si(111) reflection followed by a high resolution monochromator. The detector used in the experiment was an avalanche photodiode which has a time resolution of 1 ns. While the prompt events (0–5 ns) gave the usual electronic reflectivity, the delayed events (10–160 ns) were used to obtain the NRR.

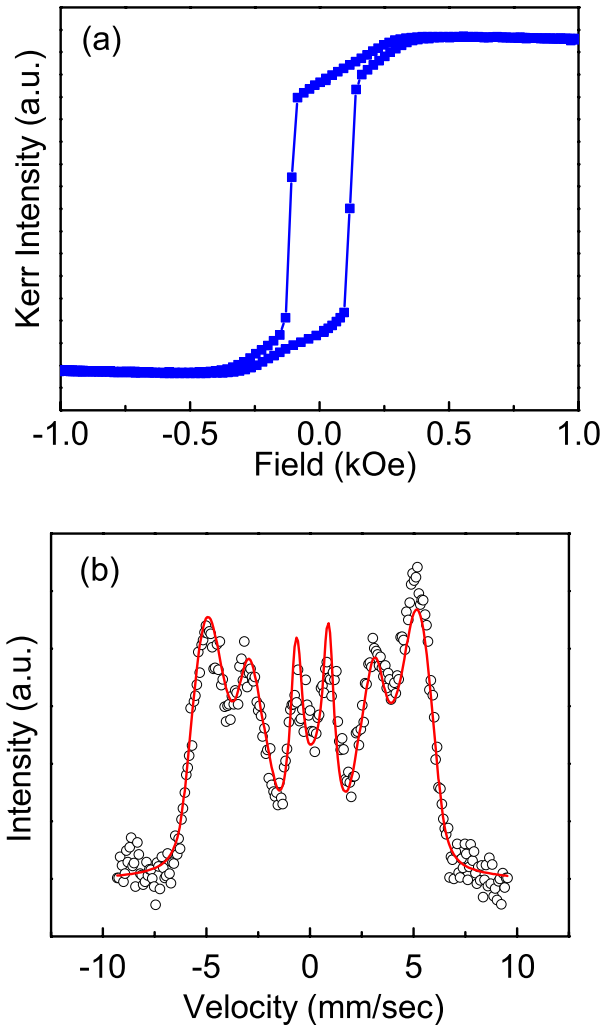

Figure 1. (a) MOKE hysteresis loop and (b) Mössbauer spectrum of as-deposited $Fe_{0.85}N_{0.15}$ film.

3. Results and discussion

Figures 1(a) and (b) give a MOKE hysteresis pattern and the Mössbauer spectrum, respectively, of the as-deposited specimen. The coercivity of the film is 130 Oe which is quite high for soft magnetic applications. Further, the shape of the loop is typical for films with perpendicular magnetic anisotropy (PMA). Existence of PMA is also evidenced from the Mössbauer spectrum in which the intensity of the second and fifth lines relative to the inner ones is only 1.21. The angle between the average spin direction and the film normal, β, as obtained from Mössbauer spectroscopy comes out to be 43°. Earlier studies have shown that this magnetic anisotropy in iron nitride thin films is due to the presence of compressive stresses [7].

Swift heavy-ion irradiation is known to induce substantial atomic motion in the target. This may relieve the internal stresses, resulting in a possible improvement in the magnetic properties. Figure 2 gives the relevant part of the XRD pattern as a function of fluence, Φ, of 120 MeV Ag ions. The as-deposited film exhibits a broad hump at $2\theta = 43.4°$, suggesting that the film is x-ray amorphous. As a result of irradiation, a

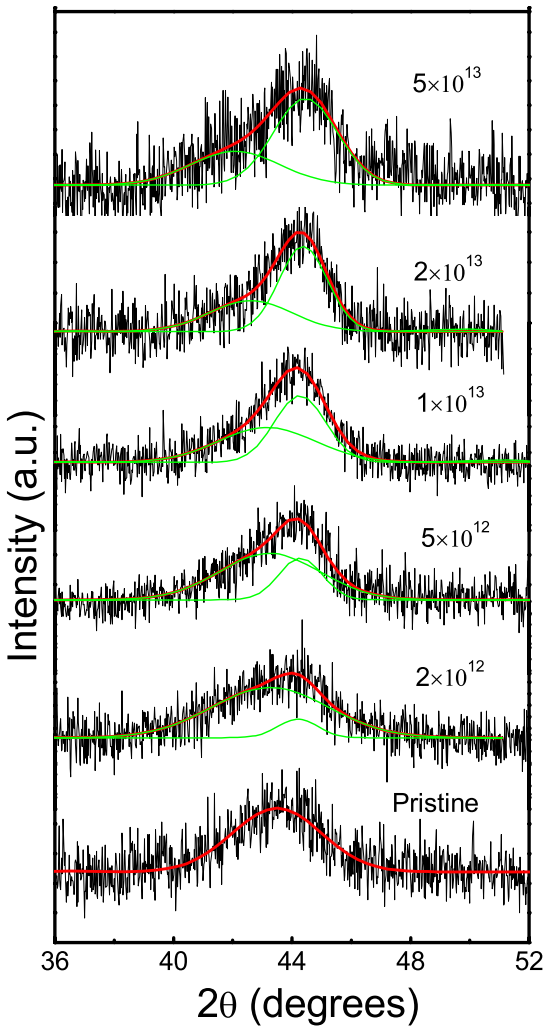

Figure 2. XRD pattern of as-deposited as well as irradiated films. The continuous curve represents a fit to the data with two Gaussian peaks, as described in the text.

second broad peak starts appearing which is shifted to a higher angle with respect to the first one. Accordingly, XRD patterns of irradiated samples have been fitted with two overlapping broad peaks. The second peak is shifted by 1.0° with respect to the original peak. This shift is of the same order as that observed in some amorphous alloys due to structural relaxation with thermal annealing [8]. Therefore, the appearance of the second peak in the irradiated samples can be understood if one conjectures that the region of the film that is influenced by the irradiation gets structurally relaxed; the irradiated samples thus consist of two regions namely the unrelaxed amorphous region and the relaxed amorphous region, the second peak in the XRD pattern corresponds to the relaxed amorphous region. In amorphous alloys the average first-near-neighbor distance can be obtained from the position of the broad hump using the relation $d = 1.23\lambda/2\sin\theta$ [9]. The value of average near neighbor distance corresponding to the two peaks come out to be 0.26 nm and 0.25 nm respectively. A lower average near-neighbor distance in the irradiated region may be attributed to partial annihilation of excess free volume. As discussed in section 1, if the electronic energy loss S_e

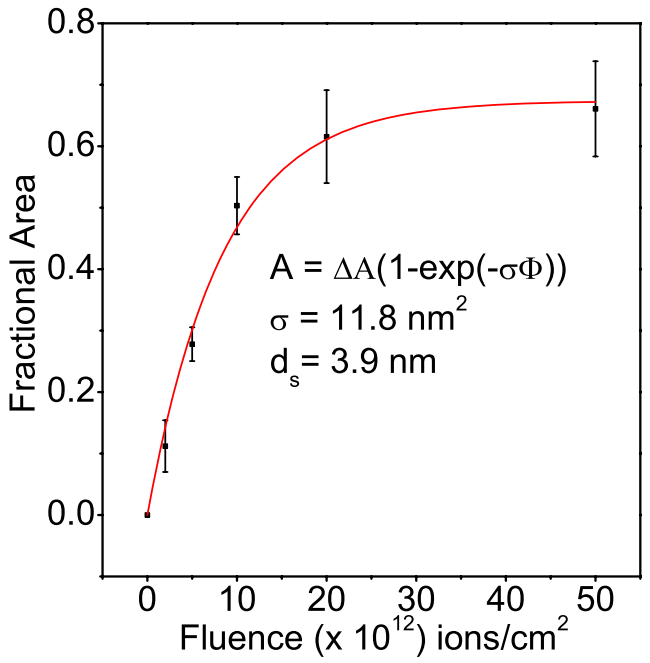

Figure 3. Fluence dependence of fractional area A under the second peak in the XRD pattern. The continuous curve represents a theoretical fit to the data.

associated with irradiating ions is below a threshold value then defect annihilation may take place. In the present case S_e comes out to be 26 keV nm^{-1}. The fact that the irradiation results in an annihilation of free volume, which is equivalent to defect annihilation in crystalline systems, suggests that this S_e value is below the threshold for defect generation in $Fe_{0.85}N_{0.15}$.

With irradiation fluence the area under the second peak grows continuously at the expense of the first one. The area under the second peak gives the fraction of the film which is structurally relaxed as a result of irradiation. Figure 3 gives the variation of the fractional area A under the second peak as a function of fluences. The fluence dependence of A can be fitted with the relation [10]:

$$A = \Delta A(1 - \exp(-\sigma\Phi)), \quad (1)$$

where σ is the average area of the film over which structural relaxation occurs on the passage of a single ion. The fit of the data shown by the continuous curve gives the value of $\sigma = 11.8 \pm 0.04$ nm^2, giving an effective track diameter $d_s = 3.9$ nm, where d_s is the average diameter of the area over which structural relaxation occurs due to a single ion.

Figure 4 gives the Mössbauer spectra of the film as a function of ion fluence. A broad Mössbauer spectrum is again typical of amorphous or highly disordered phase. The spectrum has been fitted with a distribution of hyperfine fields. The average hyperfine field as well as the width of hyperfine field distribution does not change much, suggesting that there is no significant change in the nitrogen content of the film with irradiation fluence. However, the intensity of the second and fifth lines relative to the inner ones exhibits a systematic increase with irradiation fluence, suggesting that the

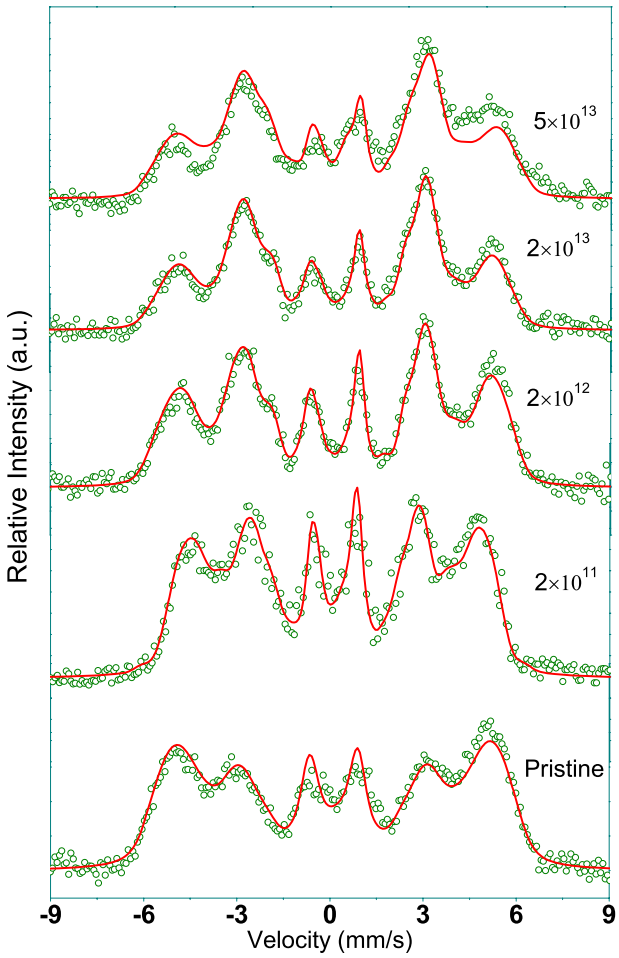

Figure 4. Mössbauer spectrum of as-deposited as well as irradiated films.

perpendicular magnetic anisotropy is relieved gradually. The variation of β with irradiation fluence is shown in figure 5. Fluence dependence of β is very similar to that of A. The passage of each bombarding ion will influence certain areas in its wake, in which the stresses will be relieved, resulting in a decrease in the perpendicular magnetic anisotropy in that region. If d_β is the diameter of this effective area and $\Delta\beta$ is the change in the anisotropy in this affected zone due to the passage of an ion, an argument similar to that used in deriving equation (1) [10] will lead to a fluence dependence of β, as

$$\beta = \beta_0 + \Delta\beta(1 - \exp(-\sigma\Phi)). \qquad (2)$$

Fitting of the fluence dependence of β with equation (2) gives an effective track diameter $d_\beta = 5.6$ nm, where d_β is the average diameter over which magnetic anisotropy is influenced by a single ion. One can see that the effective area over which magnetic anisotropy is influenced by a single bombarding ion is comparable to that over which structural relaxation occurs. The perpendicular magnetic anisotropy in the present system originates because of long range compressive stresses in the film [7]. Thus, the present result suggests that relaxation of long range stresses is associated with structural relaxation of the amorphous phase.

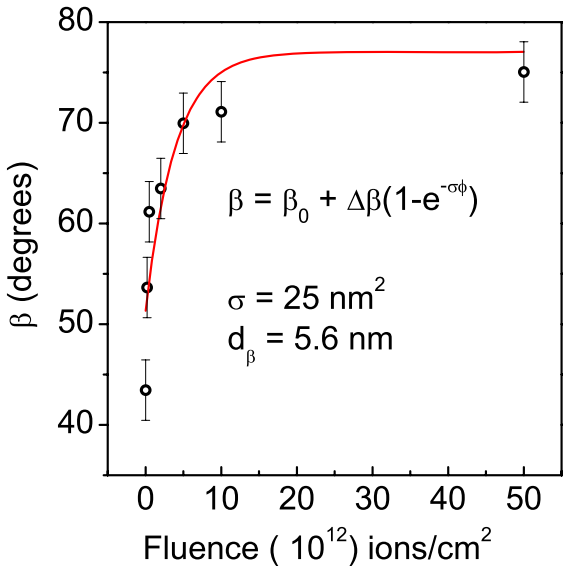

Figure 5. Fluence dependence of angle β as obtained from Mössbauer spectra. The continuous curve represents the theoretical fit to the data.

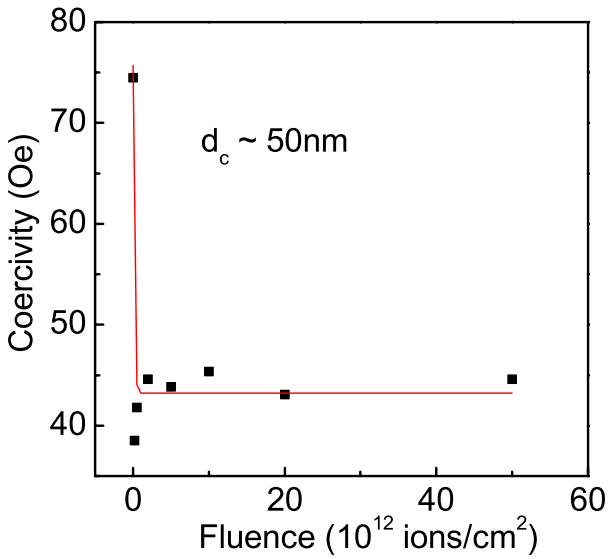

Figure 6. Fluence dependence of coercivity in $Fe_{0.85}N_{0.15}$ film. The continuous curve is a guide to the eye.

The fluence dependence of the coercivity of the film as obtained from MOKE measurements is shown in figure 6. One may note that even at the lowest fluence of 2×10^{11} ions cm^{-2} the coercivity exhibits a sudden decrease to 38 Oe. For higher fluences coercivity remains almost constant. This suggests that even at the lowest fluence chosen in the present experiment the coercivity has already reached its saturation value. Measurements at still lower fluences would have shown a gradual decrease of coercivity with fluence. Therefore, the data in figure 6 cannot be fitted in order to yield the effective diameter d_c over which coercivity gets influenced. However, a lower bound to d_c can be obtained using the following argument. One can see that the coercivity reaches its saturation value at a fluence below 2×10^{11} ions cm^{-2} which is about two

orders of magnitude less than that needed for saturating A or β. Thus the effective diameter d_c over which the coercivity gets affected by a single ion should be an order of magnitude larger than d_s and d_β. This gives $d_c \sim 50$ nm.

From the above results we see that relaxation of magnetic anisotropy is very well correlated with that of the structural relaxation, and d_s is comparable in magnitude to d_β. On the other hand, d_c is an order of magnitude larger than both d_s and d_β. Moreover, there are several studies in the literature on the visual tracks generated by swift heavy ions in various materials. These tracks which are amorphous regions formed along the trajectory of the bombarding ions, have typical diameters of a few nanometers in various materials [11]. These tracks are formed due to melting of a narrow region along the ion track and subsequent rapid solidification resulting in amorphization. Thus, depending upon the property being investigated (structural change, magnetic anisotropy or coercivity) the obtained effective diameter of the track varies. The effective track diameter here is defined as the diameter of the area over which that specific property is influenced by a bombarding particle. These results can be understood qualitatively in terms of the thermal spike model for swift heavy-ion-induced modifications in materials as follows. Swift heavy ions primarily deposit energy in the electronic system of the target material through excitation and ionizations of atoms. A part of this energy gets transferred to the lattice via electron–phonon coupling. The temperature of the electronic system as well as the lattice as a function of time t and distance r from the track can be calculated using coupled equations for energy flow [12].

$$C_e(T_e)\frac{\partial T_e}{\partial t} = \nabla(K_e(T_e)\nabla T_e) - g(T_e - T) + A(r,t), \quad (3)$$

$$C(T)\frac{\partial T}{\partial t} = \nabla(K(T)T) + g(T_e - T), \quad (4)$$

where various symbols have been defined in [12]. Equations (3) and (4) can be solved numerically to get the electronic and lattice temperatures at a distance r from the core as a function of time. The time dependence of the lattice temperature exhibits a peak. The larger the distance from the core of the ion track, the lower will be the value of the peak lattice temperature. Now, if T is the temperature needed to modify a given physical property (e.g. structural relaxation), the modification will take place in a cylindrical zone of radius r within which the peak temperature is greater than or equal to T. The lower the value of T the larger will be the radius of the cylindrical zone in which the corresponding property gets modified. It may be noted that the coercivity is related to some random stresses, which act as pinning centers for the domain walls, while magnetic anisotropy is related to long range stresses. Relaxation of random stresses would occur at a lower temperature as compared to that needed for relaxation of long range stresses. Therefore, random stresses and hence the coercivity will get affected over a larger radius as compare to the long range stresses, which are responsible for magnetic anisotropy. This can qualitatively explain different track diameters obtained for magnetic anisotropy and coercivity. Therefore, d_s and d_β are smaller than d_c.

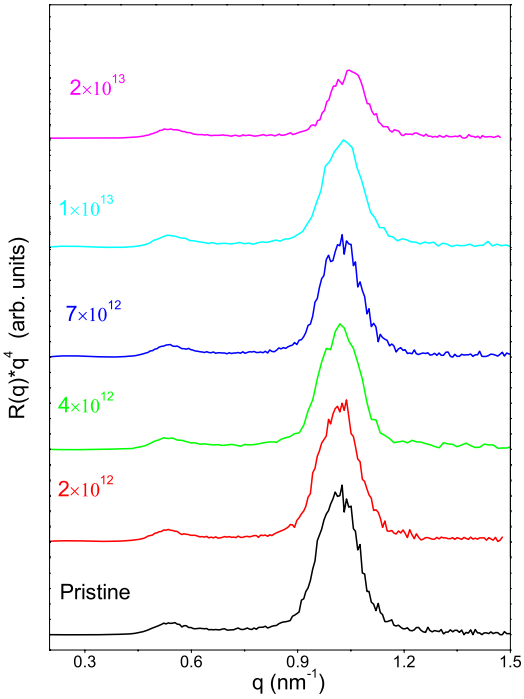

Figure 7. Nuclear resonance reflectivity of a $Fe_{0.85}N_{0.15}$ isotopic multilayer taken at the Mössbauer resonance energy of ^{57}Fe 14.413 keV, as a function of irradiation fluences. The Bragg peak around $q = 1.1$ nm^{-1} corresponds to the isotopic periodicity of the multilayer.

Swift heavy-ion irradiation may also result in substantial atomic motion which is undesirable as it would result in blurring of the interfaces in a multilayer structure [2]. Therefore, it is meaningful to estimate the range of atomic motions associated with various irradiation fluences needed for improving the soft magnetic property. In order to determine the diffusion length of Fe atoms associated with various irradiation fluences, NRR of x-rays in isotropic multilayers has been used. When the energy of the incident x-ray beam is tuned to the 14.4 keV Mössbauer transition of ^{57}Fe, a strong scattering contrast develops between $^{nat}Fe_{0.85}N_{0.15}$ and $^{57}Fe_{0.85}N_{0.15}$ layers resulting in a Bragg peak in the NRR of the multilayer [13]. Figure 7 gives the NRR of the isotopic multilayer irradiated to different fluences of 120 MeV Ag ions. The intensity scale is multiplied by q^4, in order to remove the background due to Fresnel reflectivity [14, 17]. In addition to the peak at critical angle for total reflection ($q = 0.56$ nm^{-1}), the first Bragg peak due to isotopic periodicity is clearly visible. This is due to a strong scattering contrast between ^{57}Fe and ^{nat}Fe layers at the nuclear resonance energy corresponding to the first excited state of a ^{57}Fe nucleus (Mössbauer transition) [13, 15, 16].

As the Fe atoms diffuse the boundary between $^{nat}Fe_{0.85}N_{0.15}$ and $^{57}Fe_{0.85}N_{0.15}$ layers becomes blurred and the height of the Bragg peak comes down. The average diffusion length L_d for self-diffusion of Fe can be obtained using the relation [8, 17]

$$\ln\left(\frac{I(\Phi)}{I(0)}\right) = -\frac{4\pi^2 n^2 L_d^2}{\lambda^2}, \quad (5)$$

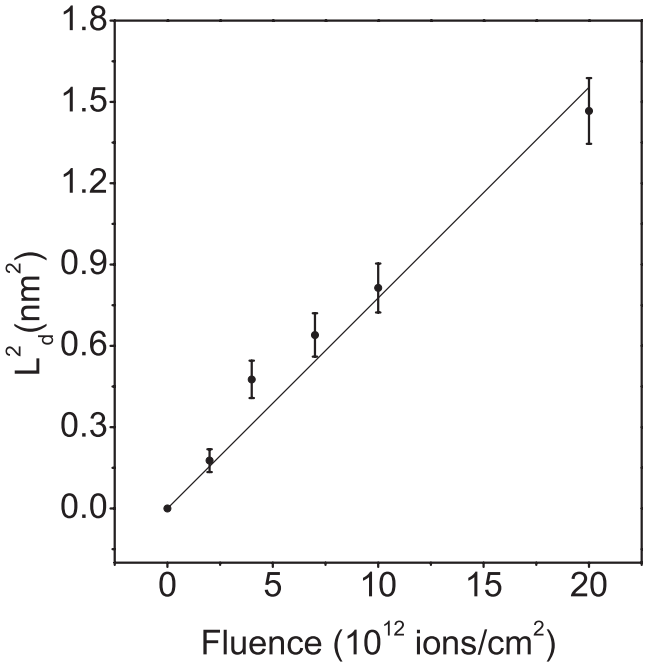

Figure 8. Square of the diffusion length L_d^2 of Fe as a function of the fluence, as determined from NRR.

where $I(0)$ is the intensity of the nth order Bragg peak at zero fluence, $I(\Phi)$ is the intensity of the nth order Bragg peak after a fluence Φ, L_d is the average diffusion length and λ is the periodicity of the multilayer. Typical accuracy with which the diffusion length can be measured in this technique is of the order of 0.1 nm [13].

The fluence dependence of L_d^2 is given in figure 8. One finds that L_d^2 varies linearly with irradiation fluence. A linear dependence of L_d^2 with fluence is similar to that observed in thermal diffusion and can be understood in terms of the thermal spike model discussed above. If T is the temperature in the thermal spike region and t is its lifetime, the diffusion length corresponding to a single bombarding ion can be written as: $L_d^2 = 2D(T)t$, where $D(T)$ is the diffusivity at temperature T. Similar behavior has been observed in swift heavy-ion-induced intermixing experiments [4, 18–21], where the interface broadening is found to vary linearly with fluence:

$$\Delta s^2 = k\phi. \tag{6}$$

However, as discussed in the literature [4], it is often difficult to estimate the diffusion time t, and therefore it is not possible to extract the effective diffusion coefficient D. In some studies on the interface mixing the fluence dependence of Δs^2 is found to have a quadratic term in ϕ [22, 23]

$$\Delta s^2 = k\phi + m\phi^2. \tag{7}$$

The quadratic term has been attributed to a solid state reaction occurring under ion bombardment. However, in the present case, the multilayer structure is chemically homogeneous and the contrast is only isotopic. Therefore, there is no chemical driving force for the movement of atoms and therefore a ϕ^2 dependence of L_d^2 is not expected to be observed.

From figure 8 one also finds that for a fluence of 2×10^{11} ions cm^{-2}, at which the coercivity reaches its minimum value, the diffusion length is only 0.1 nm, while after a fluence of 1×10^{13} ions cm^{-2} at which most of the PMA disappears, the diffusion length is about 0.9 nm. These diffusion lengths are of the order of the interface roughness in a typical multilayer structure and therefore a diffusion length of this order would not have a large effect on the quality of the interfaces. Thus, swift heavy-ion irradiation can be used to improve soft magnetic properties of thin films without having a large effect on the quality of multilayers.

4. Conclusion

In conclusion, it is shown that swift heavy ions can be used as an effective tool to tailor the soft magnetic properties of thin films. Irradiation of $Fe_{0.85}N_{0.15}$ thin film with 120 MeV Ag ions results in a decrease in its coercivity as well as magnetic anisotropy. The coercivity reaches its minimum value at a much lower fluence as compared to that needed for removal of PMA. For high frequency soft magnetic applications a certain amount of uniaxial anisotropy is needed in order to achieve a flat frequency response. Therefore by appropriately choosing the ion fluence, films with minimum coercivity and desired magnetic anisotropy can be achieved. Diffusion measurements done using NRR show that the Fe diffusion length, even after a fluence of 1×10^{13} ions cm^{-2}, is 0.9 nm which is comparable to the interface roughness in multilayers. Therefore irradiation is not expected to significantly modify the interface structure.

Acknowledgments

Thanks are due to Mr Satish Potdar for depositing Fe–N films. Partial support from the Indo-French Center for Promotion of Advanced Research, New Delhi and the Department of Science and Technology, New Delhi is also acknowledged.

References

[1] Scola J, Polovy H, Fermon C, Pannetier-Lecoeur M, Feng G, Fahy K and Coey J M D 2007 *Appl. Phys. Lett.* **90** 252501
[2] Wang Y, Zeng Z M, Han X F, Zhang X G, Sun X C and Zhang Z 2007 *Phys. Rev.* B **75** 214424
[3] Gupta A 2000 *Vacuum* **58** 16
[4] Bolse W 2002 *Surf. Coat. Technol.* **158** 1
[5] Dunlop A, Lesueur D, Legrand P, Dammak H and Dural J 1994 *Nucl. Instrum. Methods* B **90** 330
Lesueur D 1993 *Radiat. Eff. Defects Solids* **126** 123
[6] Rüffer R and Chumakov A I 1996 *Hyperfine Interact.* **97** 589
[7] Gupta A, Dubey R, Leitenberger W and Pietsch U 2008 *Appl. Phys. Lett.* **92** 052504
[8] Gupta A, Chakravarty S, Tayagi A K and Rüffer R 2008 *Phys. Rev.* B **78** 214207
[9] Guinier A 1994 *X-Ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies* (New York: Dover)
[10] Bauer Ph *et al* 1997 *J. Appl. Phys.* **81** 116

[11] Dunlop A, Dammak H and Lesueur D 1996 *Nucl. Instrum. Methods* B **112** 23
[12] Wang Z G *et al* 1994 *J. Phys.: Condens. Matter* **6** 6773
[13] Gupta A, Gupta M, Chakravarty S, Rüffer R, Wille H C and Leupold O 2005 *Phys. Rev.* B **72** 014207
[14] Parratt L G 1954 *Phys. Rev.* **95** 359
[15] Gupta A, Gupta M, Dasannacharya B A, Yoda Y, Kikuta S and Seto M 2004 *J. Phys. Soc. Japan* **73** 423
[16] Chumakov A I, Smirnov G V, Baron A Q R and Salashchenko N N 1993 *Phys. Rev. Lett.* **71** 2489
[17] Mizoguchi T, Tanabe S and Murata M 1993 *J. Magn. Magn. Mater.* **126** 96
Greer A L and Spaepen F 1985 *Synthetic Modulated Structures* ed L L Chang and B C Giessen (Orlando: Academic) p 419
[18] Nastasi M and Mayer J W 1994 *Mater. Sci. Eng.* R **12** 1
[19] Cheng Y T 1990 *Mater. Sci. Rep.* **5** 45
[20] Bolse W 1994 *Mater. Sci. Eng.* R **12** 53
[21] Bolse W 1998 *Mater. Sci. Eng.* A **253** 194
[22] Harbsmeier F 2000 *Doctoral Thesis* Göttingen
[23] Desimoni J and Traverse A 1995 *Phys. Rev.* B **48** 13266