# Mössbauer study on the magnetic state of iron particles in Fe–N and Fe–Zr–N soft magnetic thin films

T. KOMATSU, K. SHIMAGAMI, K. MATUSITA
*Department of Chemistry, Nagaoka University of Technology, Nagaoka 940-21, Japan*

K. TERUNUMA
*R and D Laboratory, Data Storage Components Group, TDK Co., Higashi-Ohwada, Ichikawa 272, Japan*

M. MIYAZAKI
*R and D Laboratory, Data Storage Components Group, TDK Co., Kousai-cho, Nakakumagun, Yamanashi 400-04, Japan*

The magnetic state of $\alpha$-Fe particles and the behaviour of nitrogen and zirconium during annealing in $Fe_{96}N_4$ and $Fe_{85.6}Zr_{7.6}N_{6.8}$ magnetic thin films have been studied by conversion electron Mössbauer spectroscopy for $^{57}Fe$. The crystalline phases present in the Fe–N annealed films were $\alpha$-Fe and $\gamma'$-$Fe_4N$, and those in the Fe–Zr–N annealed films were $\alpha$-Fe and ZrN. In the Fe–N films annealed below 300 °C, about 60% nitrogen is incorporated interstitially into $\alpha$-Fe and the rest is used for the formation of $\gamma'$-$Fe_4N$. In the Fe–N film annealed at 500 °C, almost all nitrogen participates in the formation of $\gamma$-$Fe_4N$, leading to the grain growth of $\alpha$-Fe particles and an increase in coercive force. The values (291–325 kOe) of internal magnetic field of iron sites in $\alpha$-Fe in the Fe–Zr–N films are much smaller than that (333 kOe) of the iron site in pure $\alpha$-Fe. Even if the Fe–Zr–N films were annealed at 500–700 °C, some zirconium and nitrogen is still incorporated substitutionally and interstitially into $\alpha$-Fe, respectively. In particular, the substitutional zirconium depresses the grain growth of $\alpha$-Fe particles, perhaps due to a chemical interaction between zirconium and iron.

## 1. Introduction

Recent magnetic recording-head materials require both high-saturation magnetic-flux densities and excellent soft magnetic properties at high frequencies, as well as satisfactory thermal stability and corrosion resistance. Fe–N films have attracted much attention because the addition of a small amount of nitrogen to pure iron does not significantly reduce its saturation magnetization but can provide a lower coercivity [1, 2]. Fe–N films, however, have not been used practically for new recording-head materials because of their poor thermal stability [3]. It is known that the coercivity increases dramatically on annealing at temperatures above 350 °C [2]. Any thermal degradation of magnetic properties with annealing is undesirable, because films are usually subjected to high-temperature (around 500 °C) annealing conditions in head fabrication. The addition of a small amount of aluminium, silicon, tantallum, zirconium or other elements to Fe–N has been proposed as a method to improve its thermal stability [3–5].

It is well recognized theoretically and experimentally that the magnetic anisotropy constant in ferromagnetic particles decreases rapidly with de-

creasing particle size [3–7]. Alben *et al.* [6] and Herzer [7] have proposed that the coercivity steeply increases following a $D^6$ power law with increasing grain size, $D$. In order to retain the soft magnetic properties of iron-based films, therefore, the grain growth of iron particles during annealing has to be depressed. For example, Terunuma *et al.* [3] found that the addition of zirconium or titanium was highly effective in improving the thermal stability of Fe–N films because it prevented the grain growth of $\alpha$-Fe particles. So far, many authors have studied the structure and magnetic properties of Fe–N based thin films. To our knowledge, however, detailed information on the magnetic and electronic state of $\alpha$-Fe particles themselves, and on the role of nitrogen or other elements on the grain growth of $\alpha$-Fe particles is still insufficient. For example, it is unclear what amount of nitrogen is incorporated into $\alpha$-Fe particles in the annealed films.

In this work, we prepared Fe–N and Fe–Zr–N films by using an r.f. sputtering method and examined the magnetic and electronic state of $\alpha$-Fe particles and the behaviour of nitrogen or zirconium during annealing with a conversion electron Mössbauer (CEM) spectroscopy for $^{57}Fe$. Mössbauer studies of Fe–N based

films are few so far [8–10], although CEM spectroscopy is very powerful for the study of microscopic state of iron or iron compounds in thin films.

## 2. Experimental procedure

Fe–N and Fe–Zr–N films were deposited on crystallized glass substrate (F, Corning Co.) in a nitrogen atmosphere by using an r.f. planar magnetron sputtering method. In order to avoid oxidation of films during annealing, silicon dioxide ($SiO_2$) films were coated with a thickness of about 0.05 μm. As-sputtered films were annealed at 200–700 °C for 1 h in a nitrogen atmosphere. The coercive force, $H_c$, was measured with an inductive B–H loop tracer at an applied field of 10 Oe. The crystalline phase and grain size of crystals present in the films were analysed by X-ray diffraction (XRD) using $FeK_\alpha$ radiation. The conversion electron Mössbauer (CEM) spectroscopy for $^{57}Fe$ for as-sputtered and annealed films were carried out using an electron detector of gas(He 90%–$CH_4$ 10%) flow type at room temperature. For the γ-rays, 20 mCi $^{57}Co$ in metallic Rh was used. The incident γ-rays were perpendicular to the films. The velocity calibration was obtained from the spectrum of iron thin films with a thickness of 1 μm, which was deposited on a crystallized glass substrate by r.f. planar magnetron sputtering.

## 3. Results and discussion
### 3.1. Fe₉₆N₄ film

The composition of r.f. sputtered Fe–N films, which was determined by using electron probe microanalysis (EPMA), was $Fe_{96}N_4$ (in atomic per cent). Prior to analysing the Mössbauer spectra, it is worth examining magnetic properties, crystalline phases and grain sizes of α-Fe particles for the annealed films. The values of $H_c$ for as-sputtered and annealed (200–500 °C) films are shown in Fig. 1. The values for as-sputtered and annealed (200 and 300 °C) films are very small, around 0.3–0.4 Oe. On increasing the annealing temperature from 400–500 °C, the value of $H_c$ increases rapidly, indicating that the annealing at temperatures higher than 400 °C deteriorates greatly the soft magnetic properties. These results are very consistent with those reported by Wang and Kryder [2] and Terunuma et al. [3] for Fe–N films.

The XRD patterns at room temperature for as-sputtered and annealed films are shown in Fig. 2. The patterns indicate that the as-sputtered and annealed (200 °C) films consist of α-Fe but two kinds of crystalline phase, α-Fe and γ'-$Fe_4N$, are present in the films annealed at 300 and 500 °C. From the full-width at half-maximum of the (1 1 0) peak, the grain size of α-Fe was estimated. It was found that the grain sizes in the as-sputtered and annealed (200 and 300 °C) films are almost the same, i.e. the mean diameter is around 15 nm. On the other hand, the grain size in the film annealed at 500 °C is about 50 nm and is much larger than those (15 nm) in other films annealed below 300 °C. These results on the formation of α-Fe and
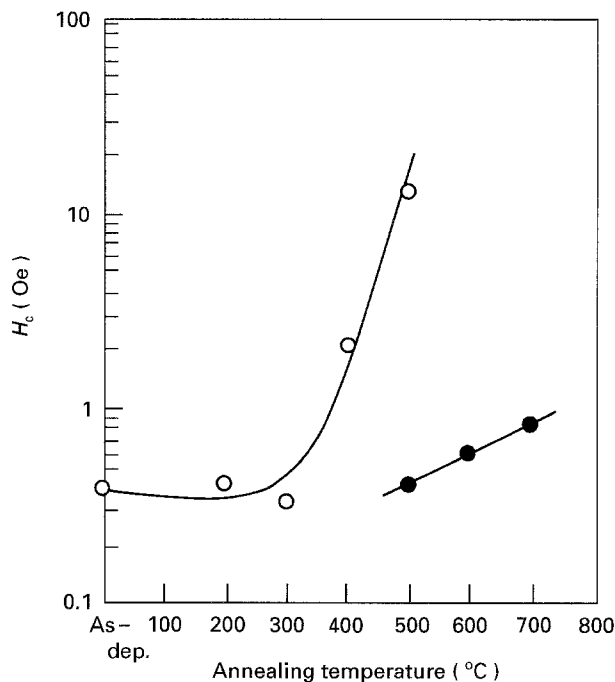


Figure 1 Coercive forces, $H_c$, at room temperature for the as-sputtered and annealed (1 h) (O) $Fe_{96}N_4$ and (●) $Fe_{85.6}Zr_{7.6}N_{6.8}$ films.
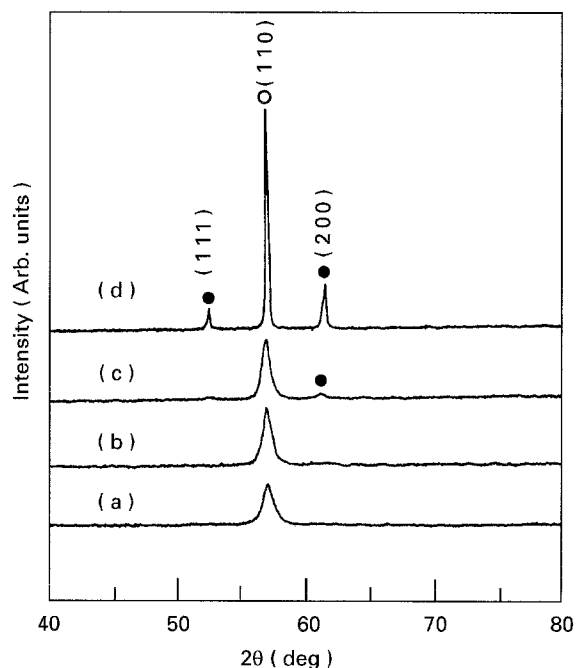


Figure 2 X-ray diffraction ($FeK_\alpha$) patterns at room temperature for the as-sputtered and annealed (1 h) $Fe_{96}N_4$ films. (a) As-sputtered, (b) 200 °C, (c) 300 °C, (d) 500 °C. (O) α-Fe, (●) γ'-$Fe_4N$.

γ'-$Fe_4N$ and on the grain size of α-Fe agree well with those reported by other authors [1–3]. The values of lattice constant, $a$, for α-Fe in the as-sputtered and annealed films were estimated. It was found that the value decreases gradually due to the annealing, from 0.2872 nm (as-sputtered film) to 0.2865 nm (film annealed at 500 °C). It is noted that the lattice constant of α-Fe in the film annealed at 500 °C is almost the same as that of pure α-Fe.

The CEM spectra at room temperature for the as-sputtered and annealed (300 and 500 °C) films are
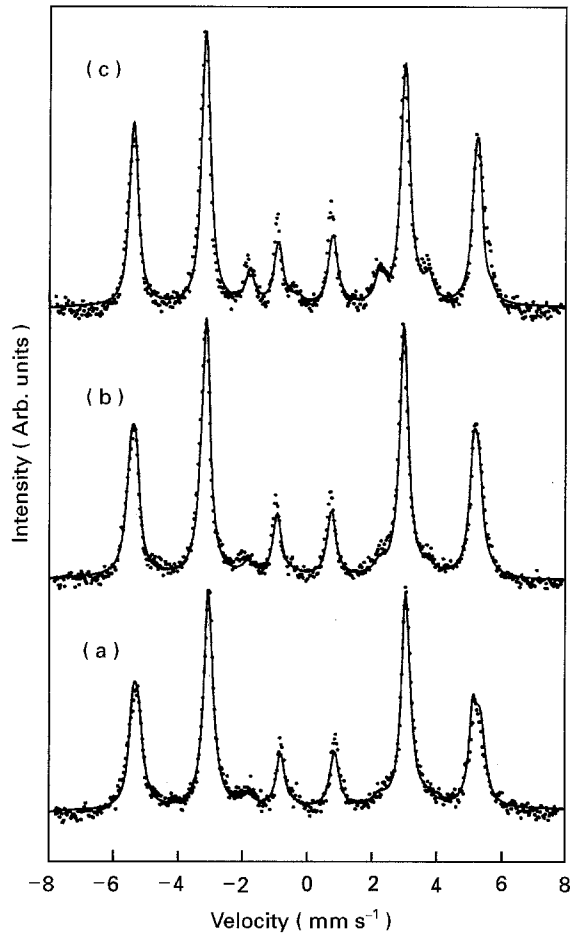
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Figure 3 Conversion electron Mössbauer spectra at room temperature for the as-sputtered and annealed (1 h) $Fe_{96}N_4$ films. (a) As-sputtered, (b) 300 °C, 1 h, (c) 500 °C, 1 h.
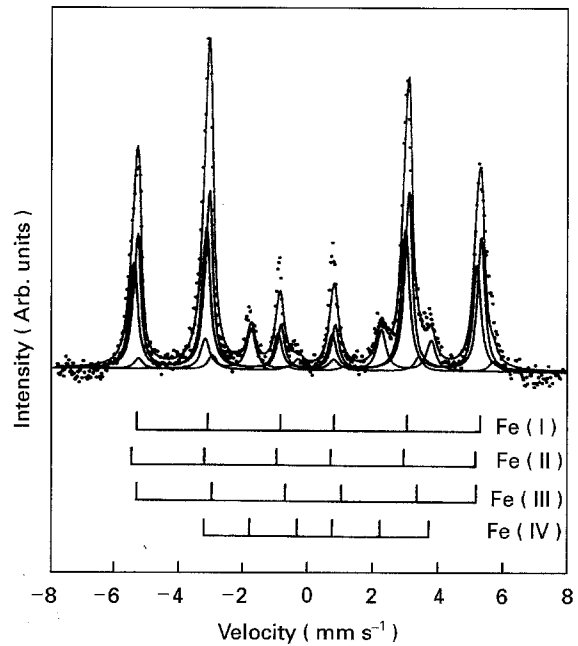


Figure 4 Conversion electron Mössbauer spectrum at room temperature for the $Fe_{96}N_4$ film annealed at 500 °C for 1 h.

TABLE I Internal magnetic fields, $H_i$, isomer shifts, IS, and intensities, $I$, for various iron sites for the $Fe_{96}N_4$ and $Fe_{85.6}Zr_{7.6}N_{6.8}$ annealed films. These values were obtained from CEM spectra at room temperature

| Film | Fe site | $H_i$(kOe) | IS(mm s$^{-1}$) | $I$(%) |
|---|---|---|---|---|
| $Fe_{96}N_4$ annealed 500 °C, 1 h | Fe(I) | 332 | − 0.024 | 44.7 |
| | Fe(II) | 331 | − 0.127 | 38.7 |
| | Fe(III) | 342 | 0.202 | 4.1 |
| | Fe(IV) | 217 | 0.254 | 12.5 |
| $Fe_{85.6}Zr_{7.6}N_{6.8}$ annealed 500 °C, 1 h | Fe(I) | 325 | 0.159 | 35.8 |
| | Fe(II) | 323 | 0.020 | 43.2 |
| | Fe(III) | 291 | − 0.023 | 21.0 |

shown in Fig. 3. The CEM spectrum for the as-sputtered film is mainly composed of six broad peaks. In all the spectra, small peaks are observed at velocities of around − 2,2 and 4 mm s$^{-1}$. It is clear that the intensities of those peaks increase with increasing annealing temperature. First, we tried to fit the spectra by considering three kinds of iron sites, because the XRD patterns shown in Fig. 2 indicate the presence of at least two kinds of iron compounds, i.e. α-Fe and γ'-Fe$_4$N. It should be pointed out that there are two kinds of iron sites in γ'-Fe$_4$N [8, 11, 12]. But the quality of the fit was poor. All the spectra were fitted by a sum of four kinds of six-line hyperfine splittings with Lorentzian profiles with fairly good quality. The CEM spectrum for the film annealed at 500 °C is shown again in Fig. 4, as a typical example. The Mössbauer parameters obtained, i.e. internal magnetic fields, $H_i$, isomer shifts, IS, and intensities, $I$, for four iron sites in this film are summarized in Table I. The Fe(I) and Fe(II) sites, having $H_i$ values of 332 and 331 kOe, were assigned to different iron sites in α-Fe, because these $H_i$ values are almost the same as the value of $H_i = 333$ kOe in pure α-Fe, and the other Fe(III) and Fe(IV) sites, having $H_i$ values of 342 and 217 kOe, correspond to iron sites in γ'-Fe$_4$N [8]. Frazer [11] reported that the magnetic moments of two different iron sites in γ'-Fe$_4$N are 3 $\mu_B$ for the corner iron atom and 2 $\mu_B$ for the face centred iron

atom in a cubic unit cell. The ratio of $H_i$ for different iron sites obtained from the CEM spectrum, i.e. $342/217 = 1.58$, is very consistent with the ratio of magnetic moment in γ'-Fe$_4$N reported by Frazer, i.e. $3/2 = 1.5$. The intensity ratio of Fe(IV) /Fe(III) is 3.05, and this value agrees well with the ideal population ratio, i.e. 1/3, in γ'-Fe$_4$N. The values of isomer shift for Fe(III) and Fe(IV) sites are very close to those reported by Lo et al. [8].

The values of $H_i$ for Fe(I) and Fe(II) sites in as-sputtered and annealed films are shown in Fig. 5, indicating the gradual increase in $H_i$ with annealing temperature. The values of the intensity of four iron sites for as-sputtered and annealed films are shown in Fig. 6. It is seen that the intensities of Fe(III) and Fe(IV) sites in the film annealed at 500°C are larger than those in other as-sputtered and annealed films. This means that the formation of γ'-Fe$_4$N occurs significantly at 500 °C. From the composition of the films and the intensity of iron sites corresponding to γ'-Fe$_4$N, we can estimate what proportion of nitrogen
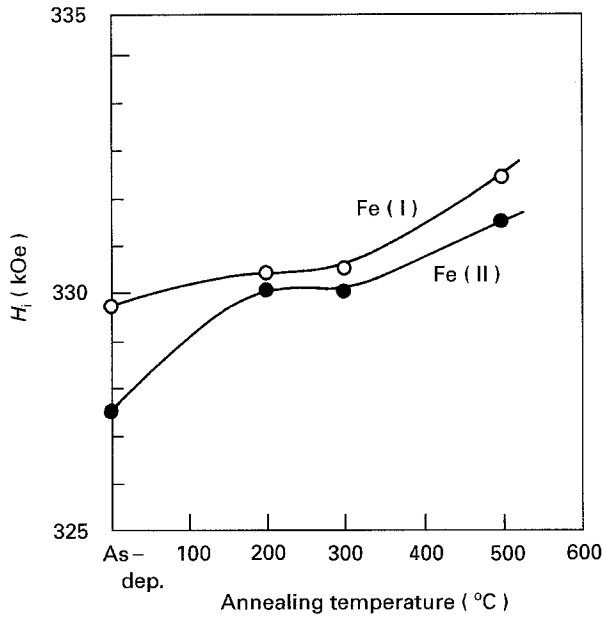
*Figure 5* Internal magnetic fields, $H_i$, of the iron sites in α-Fe present in the as-sputtered and annealed (1 h) $Fe_{96}N_4$ films.
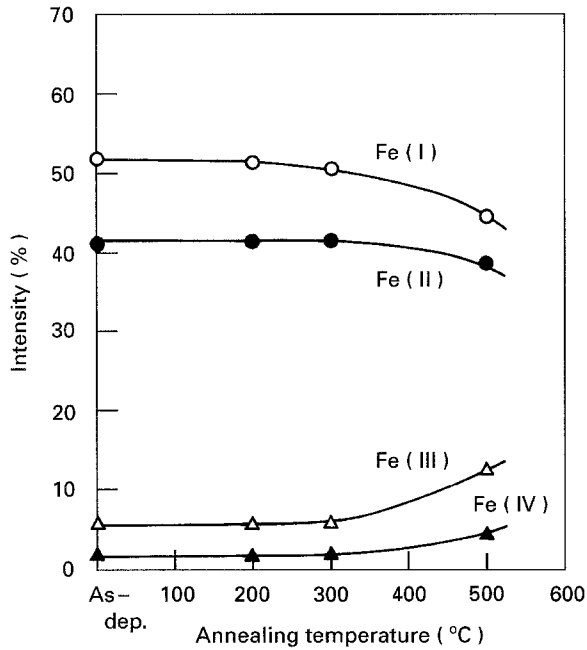


*Figure 7* Percentage of nitrogen used for the formation of $\gamma'$-$Fe_4N$ in as-sputtered and annealed (1 h) $Fe_{96}N_4$ films.



*Figure 6* Intensities of the Fe(I) and Fe(II) sites in α-Fe and Fe(III) and Fe(IV) sites in $\gamma'$-$Fe_4N$ present in the as-sputtered and annealed (1 h) $Fe_{96}N_4$ films.



*Figure 8* Possible interstitial sites of nitrogen in α-Fe. (O) Fe, (●) N, (O) octahedral site, (T) tetrahedral site. The figure is taken from [14].

present in the films participates in the formation of $\gamma'$-$Fe_4N$. The results are shown in Fig. 7. It is seen that about 40% nitrogen participates in the formation of $\gamma'$-$Fe_4N$ for the as-sputtered and annealed (200 and 300 °C) films. On the other hand, in the films annealed at 500 °C, almost all the nitrogen present in the films is used for the formation of $\gamma'$-$Fe_4N$. This is very consistent with the value of $H_i$ for the Fe(I) and Fe(II) sites in the film annealed at 500 °C being almost the same as that for the iron site corresponding to pure α-Fe, as given in Table I.

In the present CEM study, one of the most important results is information on the incorporation of nitrogen into α-Fe. As described above, almost all the nitrogen in the film annealed at 500 °C is used for the
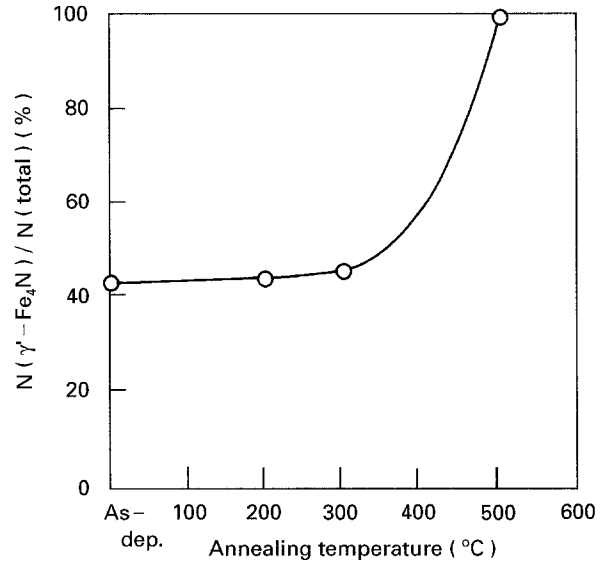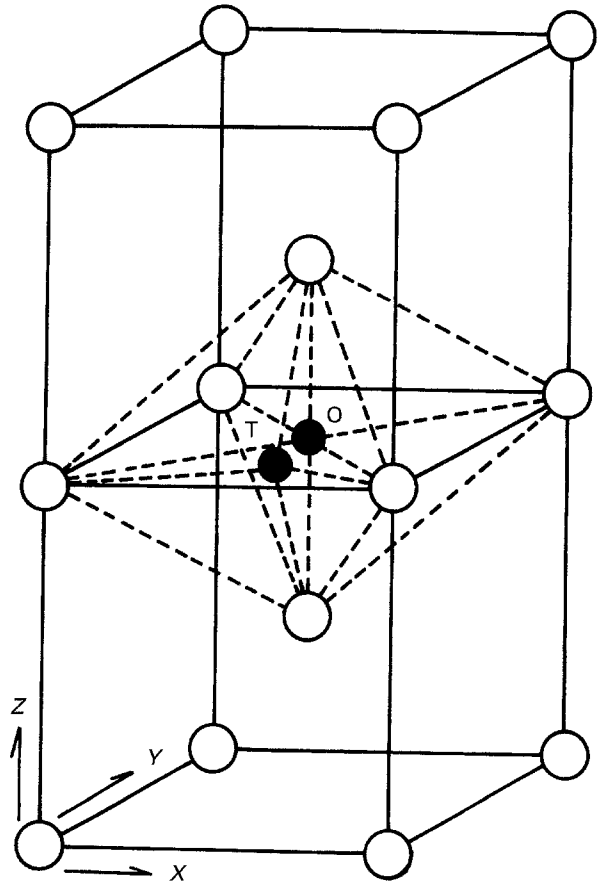
formation of $\gamma'$-$Fe_4N$. In the as-sputtered and annealed (200 and 300 °C) films, however, some nitrogen, i.e. about 60%, is still present in α-Fe. From the atomic radius of nitrogen (0.092 nm), it is considered that nitrogen atoms can occupy interstitial positions in α-Fe [13]. Two inequivalent sites, i.e. octahedral and tetrahedral sites, would be possible as interstitial positions of nitrogen in α-Fe, [14], as shown in Fig. 8. The existence of two inequivalent nitrogen sites in

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α-Fe would result in two inequivalent iron sites having different internal magnetic fields and isomer shifts. If so, from the intensities of the two inequivalent iron sites shown in Fig. 6, it is considered that the populations of nitrogen in octahedral and tetrahedral sites are almost the same. It is expected that the iron atoms corresponding to tetrahedral nitrogen atoms, Fe(T), would have a value of $H_i$ smaller than that of iron atoms corresponding to octahedral nitrogen atoms, Fe(O). That is, the Fe(O) and Fe(T) sites would correspond to the Fe(I) and Fe(II) sites given in Table I, respectively.

It is known that the activation energies for diffusion of interstitial atoms in α-Fe, such as carbon and nitrogen are much smaller than those of substitutional atoms in α-Fe such as silicon [13]. The diffusion coefficients, $D$, of interstitial atoms are large compared with those of substitutional atoms, e.g. $D = 6 \times 10^{-8}$ cm$^2$ s$^{-1}$ at 500 °C for nitrogen in α-Fe and $D = 1.2 \times 10^{-14}$ cm$^2$ s$^{-1}$ at 500 °C for silicon in α-Fe [13]. In other words, interstitial nitrogens in α-Fe tend to leave easily with increasing temperature. This could be the reason why, in the Fe–N films annealed at 500 °C, nitrogen is not incorporated into α-Fe. Because the diameter of α-Fe particles is closely related to the formation of $\gamma'$-Fe$_4$N, it is clear that the growth rate of α-Fe is severely controlled by the amount of interstitial nitrogen in α-Fe.

## 3.2. Fe$_{85.6}$Zr$_{7.6}$N$_{6.8}$ film

The composition of r.f.-sputtered Fe–Zr–N films was Fe$_{85.6}$Zr$_{7.6}$N$_{6.8}$ (at %). The values of $H_c$ for annealed (500–700 °C) films are shown in Fig. 1. The values are below 1 Oe for all the films, indicating that the addition of zirconium atoms to binary Fe–N films is effective in depressing deterioration of soft magnetic properties, even for annealing at high temperatures (above 500 °C). These results are very consistent with those reported by Terunuma et al. [3].

It was found from the XRD patterns (not shown here) at room temperature for the annealed films that the films consist of α-Fe and ZrN. The presence of $\gamma'$-Fe$_4$N is not detected unlike the case of Fe–N films. The mean diameters of α-Fe particles in the annealed films, which were estimated from the full-width at half-maximum of the (2 2 0) peak, are about 5 nm, and are independent of annealing temperature. The results clearly indicate that the prominent grain growth of α-Fe does not occur in Fe–Zr–N films. These results are in good agreement with those reported previously by other authors [3, 15].

The CEM spectrum at room temperature for the film annealed at 500 °C for 1 h is shown in Fig. 9, as a typical example. Similar CEM spectra were obtained for other annealed (600 and 700 °C) films. All the spectra were fitted by a sum of three kinds of six-line hyperfine splittings with fairly good quality. The Mössbauer parameters obtained for the film annealed at 500 °C are summarized in Table I. It is seen that all the iron sites (I), (II) and (III), have values of $H_i$ smaller than that (333 kOe) of the iron site in α-Fe, implying that some nitrogen or zirconium is incorporated into
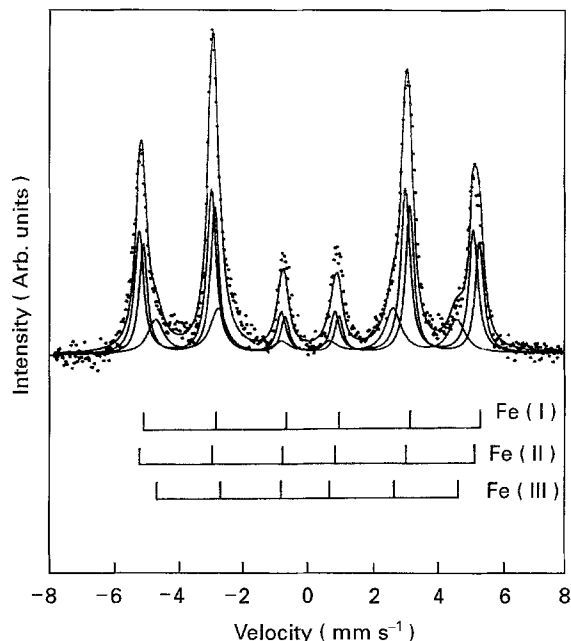


Figure 9 Conversion electron Mössbauer spectrum at room temperature for the Fe$_{85.6}$Zr$_{7.6}$N$_{6.8}$ film annealed at 500 °C for 1 h.
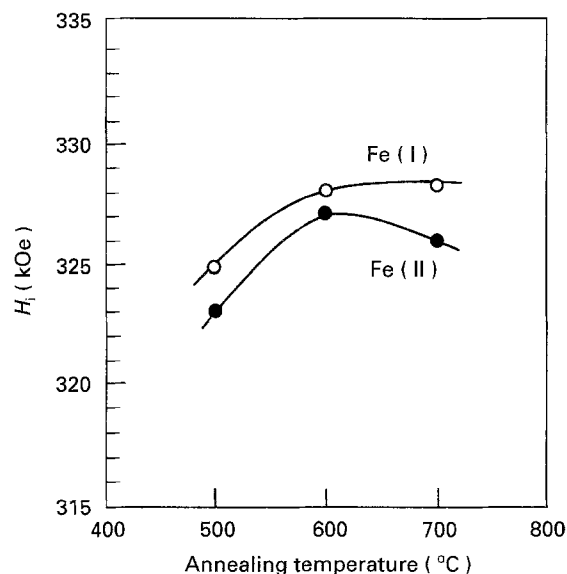


Figure 10 Internal magnetic fields, $H_i$, of the iron sites in α-Fe present in the annealed (1 h) Fe$_{85.6}$Zr$_{7.6}$N$_{6.8}$ films.

α-Fe interstitially or substitutionally. In particular, it is noted that the value of $H_i$ of Fe(III) site is very small, i.e. $H_i = 290$ kOe. The values of $H_i$ for Fe(I) and Fe(II) sites and the intensities of all iron sites in the annealed films are shown in Figs 10 and 11, respectively, as a function of annealing temperature. The values of $H_i$ of Fe(I) and Fe(II) sites tend to increase with increasing annealing temperature. The intensity of the Fe(III) site having the smallest value of $H_i$ decreases rapidly. On the other hand, the intensities of the other iron sites (I) and (II) increases gradually.

The important results for the magnetic state of α-Fe in the Fe–Zr–N films are as follows. One is that the value of $H_i$ of iron atoms is much smaller than that of iron atoms in pure α-Fe. The other is that there are three inequivalent iron sites, even though only α-Fe
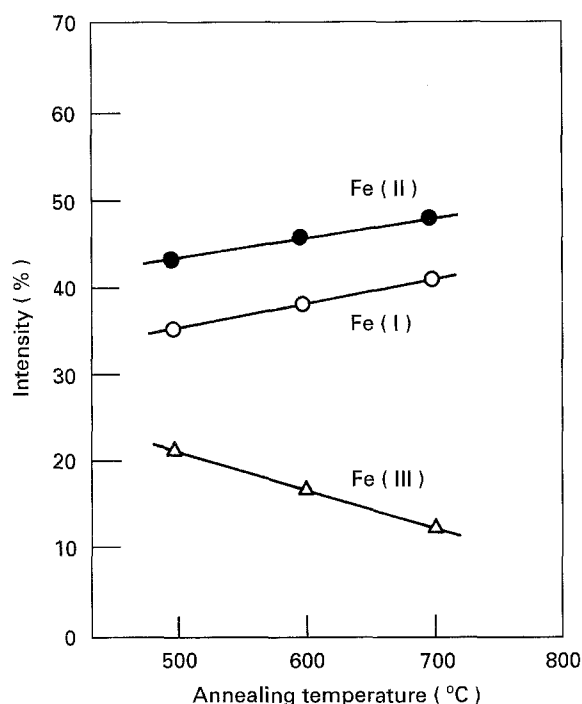
*Figure 11* Intensities of the Fe(I), Fe(II) and Fe(III) sites in α-Fe present in the annealed (1 h) $Fe_{85.6}Zr_{7.6}N_{6.8}$ films.

## 4. Conclusion

$Fe_{96}N_4$ and $Fe_{85.6}Zr_{7.6}N_{6.8}$ thin films were prepared using an r.f. sputtering method, and the magnetic state of α-Fe and the behaviour of nitrogen and zirconium during annealing were studied with a conversion electron Mössbauer spectroscopy for $^{57}$Fe. The crystalline phases present in Fe–N films were α-Fe and γ'-Fe$_4$N, and those in Fe–Zr–N films were α-Fe and ZrN. In the Fe–N films annealed below 300 °C, about 60% nitrogen was incorporated interstitially into α-Fe. In the Fe–N film annealed at 500 °C, almost all the nitrogen was used for the formation of γ'-Fe$_4$N. The displacement of nitrogen from α-Fe to γ'-Fe$_4$N led the grain growth of α-Fe particles and the increase in coercive force. In the Fe–Zr–N films, even if the films were annealed at 500–700 °C, some zirconium and nitrogen was still incorporated into α-Fe. The substitutional zirconium in α-Fe depressed the grain growth of α-Fe particles.

## Acknowledgements

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phase is detected in the XRD patterns as a magnetic iron compound. From the results obtained in the Fe–N films, it would be reasonable to conclude that the Fe(I) and Fe(II) sites, having values of $H_i$ larger than $H_i = 320$ kOe (Table I) correspond to the iron atoms around interstitially incorporated nitrogen atoms. Even in the films annealed at 600 and 700 °C, the highest value of $H_i$ is Fe(I) = 328 kOe, indicating that nitrogen atoms are still incorporated in those films. On the other hand, the iron site having a value of $H_i$ of around 290 kOe would correspond to the iron atoms around zirconium atoms. Because the atomic radius of zirconium atoms (0.148 nm) is larger than iron atoms (0.126 nm), it is expected that zirconium atoms would substitutionally occupy α-Fe. If so, such substitutional zirconium atoms would interact chemically with iron atoms, leading to a decrease in the saturation magnetic flux density of α-Fe, i.e. the decrease in $H_i$ of iron atoms in α-Fe.

Unfortunately, the diffusion behaviour of zirconium in α-Fe has not been reported so far. Compared with the diffusion coefficient of nitrogen in α-Fe, however, it is considered that the diffusion coefficient of zirconium would be considerably smaller. The small values of $H_i$ of iron atoms in the Fe–Zr–N annealed films (Table I) strongly support the above model. The large intensity (21%) of Fe(III) sites indicates that even in the film annealed at 700 °C, a considerable amount of zirconium is still incorporated into α-Fe. It is clear that the incorporation of zirconium is intrinsic for the depression of grain growth of α-Fe.