Thermodynamic Stability of Iron Nitrides at Temperatures below 350 °C

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Although iron nitride coatings are applied for their good tribological properties, their thermodynamic stabilities are unknown in the temperature range in which they are used. We have investigated the ε and γ' nitride phases between 0 and 350 °C with ion implantation and find evidence that while the ε-Fe_2N_{1-x} with $(1-x) \geq \frac{2}{3}$ is stable, γ'-Fe_4N is not. At $T \leq 150\,°C$, ion irradiation converts γ'-Fe_4N into ε-Fe_2N_{1-x}, with $x = 0.5$. This ε nitride can then be transformed back into γ'-Fe_4N by annealing at temperatures of 150 °C and higher. Ion irradiation assists this process as well.

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There is little, if any, thermodynamic information available for most binary systems at temperatures below 350 °C, because potential phase transformations are often kinetically limited. However, ion beams can be used to overcome these kinetic limitations, allowing thermodynamic driving forces to be explored at relatively low temperatures. In this Letter we investigate phase stability near room temperature in the Fe-N system. The use of irradiation assisted phase transformations may also be applied to other important binary alloy systems such as Fe-C and Ni-Al, where the low temperature stability of technologically useful compounds is also not known.

The well known Fe-N system includes the ε-Fe_2N_{1-x} and γ'-Fe_4N phases [1]. The ε phase covers a wide range of N concentrations, ranging from 18 to 32 at.% N ($0.56 > x > 0$). The γ' phase, however, is a nearly stoichiometric line compound. These phases are commonly used as hard coatings, because of their good tribological and corrosion-resistant properties [2]. Usually, these nitrides are prepared from an ammonia-hydrogen mixture flowing over a hot iron substrate [3]. Another well-known method is solidification from the melt of an iron-nitrogen mixture. Both methods require temperatures above 350 °C. Thus, even though the Fe-N is one of the best known phase diagrams [4], nothing is known about the stability of these nitrides below ≈350 °C, the temperature range in which they are used.

Previous experiments using N ion implantation into Fe to form these nitrides have suggested that the γ' phase is in fact metastable with respect to α-Fe and ε nitrides at temperatures below 300 °C [5]. Thermodynamic calculations, based on an extrapolation from higher temperature data [6], point to the same direction [5]. This thermodynamically favored transformation would have to be kinetically limited in order to explain why decomposition of γ' at room temperature has not been observed before.

In this Letter we demonstrate the existence of a new critical point in the Fe-N system. Under ion irradiation, we observe a reversible phase transformation at 150 °C between γ' and ε, with the obtained ε at the same N composition as γ'. A consequence is that the eutectic $\gamma' \rightarrow \alpha$-Fe$+\varepsilon$ must occur at higher temperatures, although kinetics still inhibits this phase separation.

Methods for low temperature fabrication of uniform γ' layers on bulk Fe substrates were developed by Vredenberg *et al.* [5]. First, a low temperature ($\leq 100\,°C$) "preimplantation" of N is used to form ε precipitates around the N projected range. Annealing at temperatures $\geq 300\,°C$ results in the formation of a stoichiometric and continuous γ' layer. The thickness of this layer can be increased by higher energy N implantations at 300 °C ("hot implant") where the N comes to rest in the remaining Fe, diffuses [7] to the γ' layer, and is incorporated in the growing layer. Thus ion implantation enables the formation of stoichiometric pore-free ε and γ' layers. Since with conventional methods this is not possible, thermodynamic and tribological properties of the individual ε and γ' phases have not been determined so far.

In the present study, samples were used which consisted of γ' layers on top of Si substrates instead of bulk Fe, because N diffuses readily into bulk Fe even at low (≈150 °C) temperatures. Below 350 °C, Fe-N layers on Si substrates behave as two noninterfering thermodynamic systems. To prepare the samples, Fe (99.99 at.% purity) was deposited on a Si(111) crystal with the use of electron beam evaporation. Prior to deposition the native oxide was etched away with an HF solution. The evaporation was done at room temperature with a deposition rate of 0.9 ± 0.1 Å/sec to a thickness of 4300 Å. The pressure during deposition was 2×10^{-7} mbar. X-ray diffraction showed a polycrystalline Fe layer exhibiting a strong (110) texture.

Implantations of $^{15}N^+$ or $^{22}Ne^+$ were performed using a 1 MV Van de Graaff type implanter. An ion beam of approximately 100 μA (N_2^+ or Ne^+) and a few mm in width was rastered electrostatically to achieve laterally homogeneous implantations over the specimen surface. During implantation the specimens were attached to a copper block with silver paint to ensure good thermal contact. For low temperature implants, the copper block was cooled by connecting it to a liquid nitrogen cooled heat sink, such that the temperature of the specimens

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remained below ~50 °C. Hot implants up to 320 °C were achieved by heating the backside of the copper block by a hot filament. The temperature could by controlled within 10 °C, as monitored by both an optical pyrometer and a Cr-Al thermocouple. During implantation the pressure in the target chamber was below 2×10^{-7} mbar. Annealing of the specimens was performed in a vacuum furnace with a base pressure of $\leq 1\times10^{-7}$ mbar.

Rutherford backscattering spectrometry (RBS) was used to measure the N concentration profiles after implantation and annealing. Spectra were taken with 2 MeV He^+ ions at normal incidence and with a scattering angle of 165°. Phase identification of the implanted specimens was done via x-ray diffraction (XRD) at the Technical University Delft, using a Siemens ω diffractometer, Cu $K\alpha$ radiation, and a graphite monochromator in the diffracted beam.

Figure 1 shows RBS spectra of an Fe layer on Si before N implantation, after the preimplantation, and after the hot implantation. The dashed line shows the Fe and Si signals before implantation. The deposited Fe layer is approximately 4300 Å thick. After preimplantation of 100 keV N to a dose of $3.2\times10^{17}/\mathrm{cm}^2$ (solid line), the dip in the Fe signal comes from a near Gaussian distribution of N centered around the projected range of 0.1 μm. The peak concentration of nitrogen is 31 at.%, calculated using the method of Yin [8]. The signal from N may also be seen on top of the Si substrate signal, near a backscattered energy of 0.6 MeV. The specimen was then heated to 300 °C and implanted with 450 keV N^+ to an additional dose of $5.5\times10^{17}\ \mathrm{N\,cm}^{-2}$. The dash-dotted line in Fig. 1 shows the RBS spectrum of this sample. The average N concentration of $(20\pm0.3)\%$, as evaluated using the computer code RUMP [9], is also shown. This is exactly the concentration of γ'-Fe_4N. Only at the interface with the Si is the iron signal a little higher, indicating that there is still some pure iron left. XRD measurements confirm that γ'-Fe_4N and α-Fe are the only phases present after hot implantation.

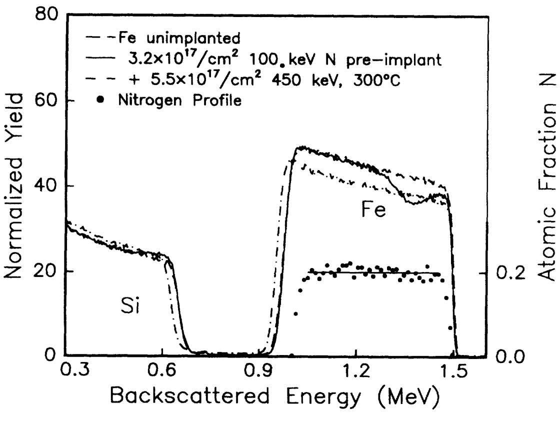

FIG. 1. RBS spectra of an unimplanted Fe layer on a Si substrate (dashed line), after a 100 keV implant of 3.2×10^{17} N/cm^2 at 100 °C (solid line), and after a subsequent 450 keV implant of 5.5×10^{17} N/cm^2 at 300 °C (dash-dotted line). By subtracting the latter spectrum from the unimplanted, the indicated nitrogen profile is obtained.

No changes were observed in the XRD of these γ' layers after subsequent anneals at temperatures between 200 and 300 °C for times ranging from 24 to 200 h. Although this apparently indicates that the proposed $\gamma'\rightarrow\varepsilon+\alpha$ eutectic decomposition does not occur, kinetic factors may still limit the transformation rate, making the γ' metastable. One difficulty may be nucleating the new phases. To overcome this, we performed an additional implant of 3×10^{17} 250 keV N/cm^2 at 300 °C to nucleate ε (with 27 ± 1 at.% N) in the layer (α already existed). Still γ' did not decompose at any anneal temperatures below 300 °C. However, the diffusivity of N in iron nitrides is very low [10] while the Fe self-diffusion is almost negligible (nitrides exhibit extremely low diffusivity and because of this they are used as diffusion barriers). Therefore, the eutectic transformation, requiring separation into N-rich (ε-nitride) and N-poor (α-Fe) phases, may be extremely difficult to achieve under purely thermal conditions.

To overcome any atomic mobility problems, we used a high energy Ne^+ beam to induce radiation enhanced diffusion. The ion energies (0.9 or 1 MeV) were chosen so that the Ne comes to rest in the Si substrate, and the doses, ranging between 3×10^{15} and $1\times10^{17}/\mathrm{cm}^2$, were high enough to displace every atom in the nitride layer at least once, as estimated using TRIM'89 [11]. Figure 2

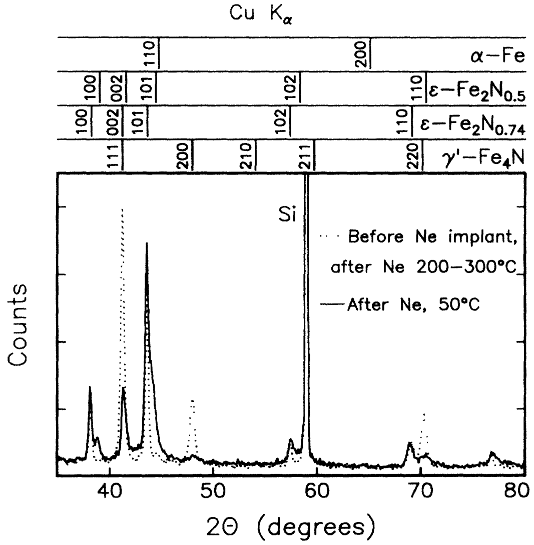

FIG. 2. The x-ray diffractograms of a $\gamma'+\varepsilon$ layer before and after 1 MeV Ne irradiations. The spectra after 300 °C and 200 °C (2×10^{16} Ne/cm^2) are identical to the spectrum before implantation, and are all represented by the dotted line. After 8×10^{16} Ne/cm^2 at 50 °C (solid line), nearly all of the γ' phase converted to ε-$Fe_2N_{0.5}$.

shows XRD diffractograms after Ne irradiation of the layer, which contained both γ' and ε, at substrate temperatures of 300, 200, and 50 °C (for comparison, the spectrum before irradiation is also presented). The spectra after irradiation at substrate temperatures of 300 and 200 °C do not display significant differences from the unimplanted case, and all three are represented by the dotted curve. However, after irradiation at 50 °C to a dose of $1\times10^{17}/\text{cm}^2$ (the solid curve) the spectrum has changed significantly. All γ' peaks are reduced and the ε peaks (with 27 ± 1 at.% N) all show a shoulder on the higher angle side. These shoulders are due to ε phases with a lower N concentration of about 20 ± 1 at.% N (Fe_2N_{1-x}, with $x=0.5$). Note also that α peaks are not observed. Thus γ' is unstable at 50 °C under ion irradiation, and converts into ε-Fe_2N_{1-x}, with $x=0.5$.

These results can be compared with a calculated free energy diagram. In Fig. 3 the Gibbs free energy curves of the phases under discussion are depicted, calculated for a temperature of 50 °C according to Ref. [4]. The atomic fraction of the ε phase with the lowest energy, which is slightly temperature dependent, is 0.31 at 50 °C. Note that the minimum in free energy for the γ' phase is actually at an atomic fraction of 0.196 instead of 0.2. It can be seen that γ'-Fe_4N is unstable against α and ε with 31 at.% (arrow 2). We do not observe this transformation. The predicted eutectoid transformation of γ' into ε and α requires long range diffusion inside the nitride layer, which is likely to be inhibited at these relatively low temperatures. The observed transformation is γ' into ε-Fe_2N_{1-x} ($x=0.5$). This transformation can be explained by the calculations (arrow 1 in Fig. 3), and can proceed in the absence of long range diffusion. According to the calculations γ' will become unstable with respect to ε-Fe_2N_{1-x} (with $x=0.5$, i.e., the same N composition as γ') at temperatures below 125 °C.

We still must demonstrate that this phenomenon is a thermodynamically induced phase transition, rather than being caused solely by radiation effects. Therefore, we have started with a pure γ' layer on Si and performed various irradiations at different temperatures. Figure 4 shows XRD spectra, centered on the $\gamma'(200)$ peak, from such a series. The original spectrum is shown in Fig. 4(a); irradiations at temperatures ≥ 200 °C result in no changes. However, after irradiation at 150 °C for a fluence of 1×10^{17} Ne/cm^2 the integrated intensity of the γ' peak has decreased by $(20\pm1)\%$ [Fig. 4(b)]. Lower irradiation temperatures result in faster disappearance of the γ'. After irradiation at 50 °C of 1×10^{17} N/cm^2 all γ' has disappeared [Fig. 4(c)], and only ε with a composition of 20 ± 1 at.% N remains (Fig. 2). More importantly, this transformation is *reversible*: Implanting the ε-$Fe_2N_{0.5}$ layer at 150 °C with 1.5×10^{16} Ne/cm^2 results in the reappearance of some γ'-Fe_4N [Fig. 4(d)]. Thus γ' can be grown at the same temperature as it can be destroyed. This excludes radiation damage accumulation as the responsible mechanism. At higher temperatures this

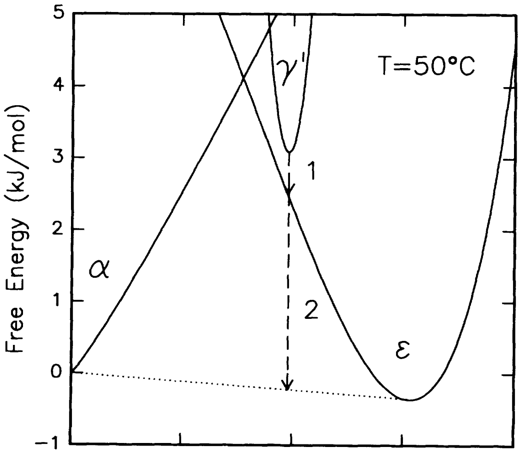

FIG. 3. Gibbs free energies of the α, ε, and γ' phases at 50 °C calculated according to Ref. [4]. Arrow 2 depicts the predicted eutectic phase transformation of $\gamma\rightarrow\alpha+\varepsilon$. Arrow 1 depicts the observed $\gamma'\rightarrow\varepsilon$-$Fe_2N_{1-x}$ ($x=0.5$) transformation.

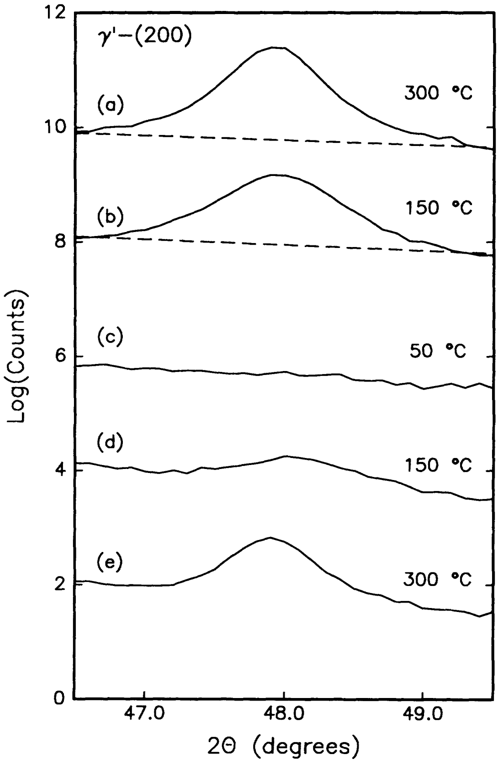

FIG. 4. Part of the x-ray spectra showing the γ'-(200). (a) After the production of γ' with N implantation at 300 °C, and after subsequent Ne irradiation at ≥ 200 °C. (b) After $1\times10^{17}/\text{cm}^2$ 1 MeV Ne$^+$ at 150 °C. (c) After $1\times10^{17}/\text{cm}^2$ 1 MeV Ne$^+$ at 50 °C. (d) After $1.5\times10^{16}/\text{cm}^2$ 1 MeV Ne$^+$ at 150 °C. (e) After $1\times10^{17}/\text{cm}^2$ 1 MeV Ne$^+$ at 300 °C.

transformation proceeds more rapidly until the γ' layer is fully recovered [Fig. 4(e) shows the spectrum after $1\times10^{17}/\text{cm}^2$ at 300 °C]. Furthermore, ε-Fe_2N_{1-x} (with $x=0.5$) can also be transformed back into γ'-Fe_4N during purely thermal anneals at temperatures $\geq 150\,°\text{C}$. The reversibility of the $\gamma'\leftrightarrow\varepsilon$ transition and the occurrence of the ion-assisted and purely thermal $\varepsilon\rightarrow\gamma'$ transition at the same temperature are strong evidence that this phase transition is determined by equilibrium thermodynamic factors. Although the ion beam is necessary for $\gamma'\rightarrow\varepsilon$, it only helps to overcome kinetic barriers to the phase transition.

In conclusion, the stability of two iron nitrides has been investigated in the temperature region in which they are used as hard coatings; ε-Fe_2N_{1-x} with $(1-x)\geq\frac{2}{3}$ is found to be stable in the whole temperature region and γ'-Fe_4N is not. According to thermodynamic calculations γ'-Fe_4N becomes a stable phase above 310 °C, which is consistent with experiment. However, the predicted eutectoid transformation $\gamma'\rightarrow\varepsilon+\alpha$ below 310 °C is not observed, presumably because of kinetic limitations. The γ'-Fe_4N phase remains stable upon thermal annealing $\leq 300\,°\text{C}$, whereas it is unstable under ion irradiation at temperatures $\leq 150\,°\text{C}$ and converts to ε-Fe_2N_{1-x} (with $x=0.5$). The γ' phase starts to grow back at temperatures of 150 °C and higher. Anneal temperatures above 300 °C are needed to fully convert the layer into γ'-Fe_4N. An ion beam stimulates the transformation rate from γ' into ε below 150 °C and from ε into γ' at higher temperatures. This irradiation assisted transformation may also have application to other important binary systems.

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