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LETTER TO THE EDITOR

The thermostability of the $Fe_{16}N_2$ phase deposited on a GaAs substrate by ion-beam-assisted deposition

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Abstract. An Fe–N film was deposited on a GaAs(100) substrate by ion-beam-assisted deposition at an N/Fe atomic arrival ratio of 0.12. The results from x-ray diffraction showed that the film consisted of the $Fe_{16}N_2$ phase. The results of an annealing experiment indicated that the $Fe_{16}N_2$ phase formed is stable after annealing at 150 °C. At 200 °C, the $Fe_{16}N_2$ started to decompose to α-Fe and γ'-Fe_4N, and it converted to α-Fe and γ'-Fe_4N completely at 300 °C. The magnetic properties of films annealed at different temperatures were also measured and the results are discussed.

Since the discovery of the giant magnetization of $Fe_{16}N_2$ by Kim and Takahashi [1], extensive research has been devoted to the investigation of the formation of the $Fe_{16}N_2$ phase and to the clarification of its magnetic properties. In recent work by the groups of Sugita and Nakajima [2–4], Fe–N films containing the $Fe_{16}N_2$ phase have been successfully formed by molecular beam epitaxy (MBE) and ion implantation. However, the $Fe_{16}N_2$ phase can only be formed at a thickness of several hundred ångströms by MBE. In the ion implantation process, the film thickness is also limited by the ion range. Therefore the amount of the $Fe_{16}N_2$ phase in the films prepared by the above methods is usually small. In this letter, we report the formation of an Fe–N film containing the $Fe_{16}N_2$ phase by ion-beam-assisted deposition and the thermostability of the $Fe_{16}N_2$ phase. The magnetic properties of the Fe–N film are also discussed. Other than the early work by Jack [5], the transformation of $Fe_{16}N_2$ by annealing has rarely been studied due to difficulties in the forming of $Fe_{16}N_2$, as is well known.

Experiments were performed in a high-vacuum system of ion-beam-assisted deposition. A base pressure of 8×10^{-5} Pa was achieved by using a cryogenic pump. A Kauffman ion source was used and its current density measured using a Faraday cup. The ion energy could vary from 2 to 30 keV. The partial pressure of N_2 gas (99.999%) was 5.0×10^{-3} Pa with the ion source operating. The evaporation of Fe (> 99.9%) was carried out using an electron gun. The deposition rate and film thickness were monitored using a thermal couple in contact with the back of the substrate. The N/Fe atomic arrival ratio at the substrate was obtained according to the evaporation rate and N-ion (N^+/N_2^+) current density during deposition. Table 1 lists the deposition conditions for the film. The annealing experiment was carried out in a vacuum system that had a base pressure of 1.1×10^{-4} Pa.

The structure of the films was analysed using x-ray diffraction (Cu Kα radiation). The saturation magnetization was measured using a vibrating-sample magnetometer (VSM) applying an external field of 10 kOe parallel to the film plane. The Fe contents of the

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Table 1. The preparation conditions of the film.

Base vacuum	$< 8 \times 10^{-5}$ Pa
N_2 pressure	5×10^{-3} Pa
Ion energy	5 keV
Ion current density	35–60 μA cm^{-2}
Deposition rate	2–3 Å s^{-1}
Film thickness	$\sim$ 3500 Å

films were measured as follows. First the films were completely dissolved into 10% HCl solution, then inductively coupled plasma atomic emission spectrometry (ICP AES) was used to measure the Fe content in the solution. The error in the measurement of Fe content by this method was less than 3%.

According to Jack [5], the $Fe_{16}N_2$ (α'') structure is essentially a nitrogen martensite, in which the nitrogen atoms are completely ordered. Thus, in some cases, the $Fe_{16}N_2$ phase can be identified by the superlattice diffraction of $Fe_{16}N_2$, which does not appear in nitrogen martensite (α') with the same N concentration in which the N atoms are disordered. Figure 1 shows the XRD pattern of an Fe–N film deposited on a GaAs substrate at an N/Fe atomic arrival ratio of 0.12. It can be seen that a strong diffraction line appears at 58.8° (2θ), corresponding to a d-spacing of 1.57 Å, which can be assigned as from $Fe_{16}N_2$(004) and α'(002). A weak line at about 28.5° (2θ) that only belongs to the superlattice diffraction line of $Fe_{16}N_2$(002) is also observed. Therefore, we can confirm that the $Fe_{16}N_2$ phase has been formed in the film. From the XRD pattern one can see that the intensity ratio I(004)/I(002) is about 10, which is comparable to the theoretical value for $Fe_{16}N_2$. Thus, it can be considered that the peak at 58.8° (2θ) is mainly from the $Fe_{16}N_2$ phase, i.e. the $Fe_{16}N_2$ phase is predominant and the quantity of α' phase is small.

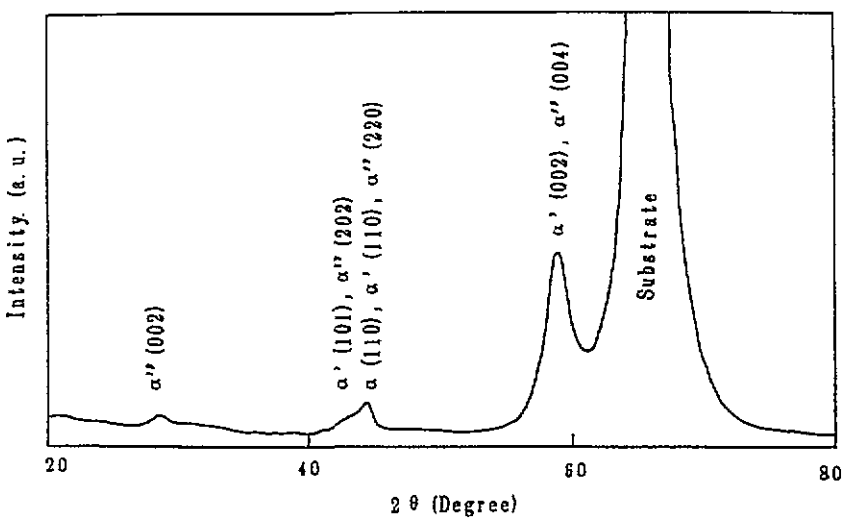

Figure 1. The XRD pattern of the Fe–N film: α, α-Fe; α', N martensite; α'', $Fe_{16}N_2$.

In order to investigate the thermostability of the $Fe_{16}N_2$ phase, the sample was divided into several plates, which were annealed in vacuum from 150 °C to 500 °C. For the film

annealed at 150 °C, no new line was found in the XRD pattern compared with that for the film before annealing, and the intensities of the $Fe_{16}N_2$ lines were also not increased, which indicates that the film is stable at 150 °C and a short annealing time at low temperature has little influence on the crystallites of $Fe_{16}N_2$. However, for a higher annealing temperature, it is observed that the phases in the films have changed. Figure 2 shows the XRD patterns of the films annealed from 200 °C to 500 °C. From figure 2(a) we can see that diffraction lines from γ'-Fe_4N appear in the pattern. According to the studies by Jack [5], the $Fe_{16}N_2$ is an intermediate phase, which first forms from N martensite and gradually decomposes to α-Fe and γ'-Fe_4N. Thus, it can be assumed that $Fe_{16}N_2$ has started to decompose to α-Fe and γ'-Fe_4N at 200 °C, but most of the $Fe_{16}N_2$ still remains in the film after annealing for 2 h. With further increase of annealing temperature, more $Fe_{16}N_2$ phase will transform to α-Fe and γ'-Fe_4N. From figure 2(c) we can see that the $Fe_{16}N_2$ phase has converted to α-Fe and γ'-Fe_4N completely after annealing at 300 °C. The XRD pattern of the film after annealing at 400 °C shows sharper γ'-Fe_4N lines, which indicates larger crystallites of γ'-Fe_4N. When the temperature reaches 500 °C, since the film has reacted with the GaAs substrate, many lines are observed in addition to the one for α-Fe and γ'-Fe_4N.

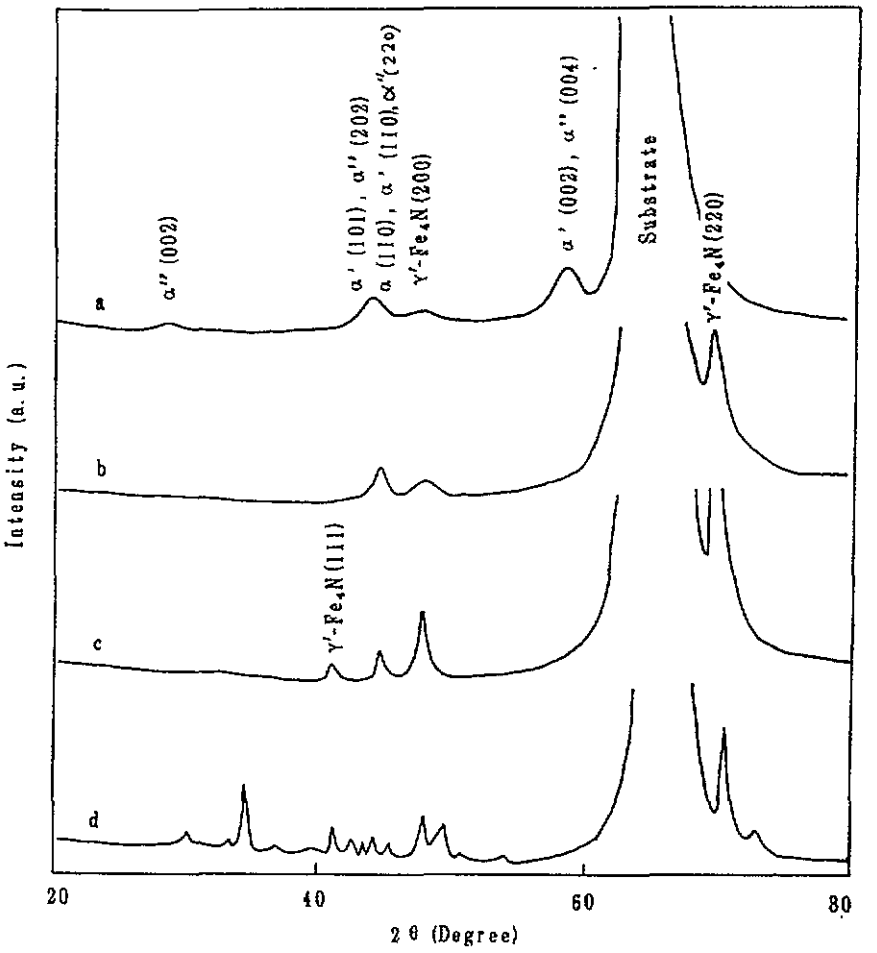

Figure 2. XRD patterns of the films after annealing at different temperatures.

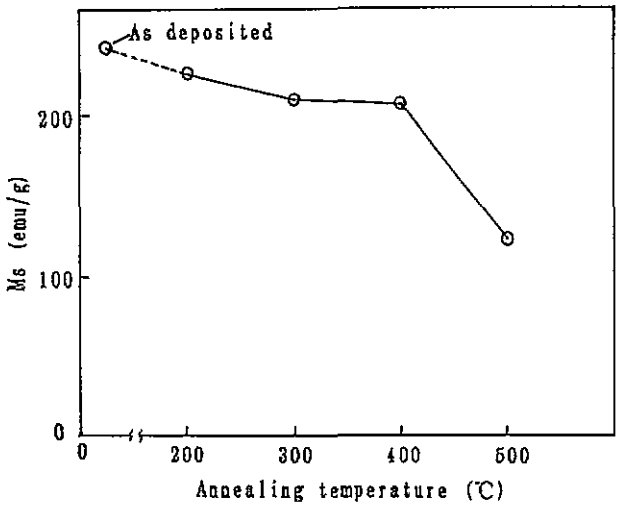

Figure 3. The dependence of the saturation magnetization (M_s) of the films on the annealing temperature.

The change of the phase composition causes the change in magnetic properties of the films. Figure 3 shows the variation of saturation magnetization (M_s) with annealing temperature. It can be seen that the M_s of the film before annealing is 237 emu g^{-1}, which is significantly larger than that of bulk Fe (210 emu g^{-1}). Since it is difficult to calculate exactly the fraction of the $Fe_{16}N_2$ phase in the film from its XRD pattern, the M_s-value of the $Fe_{16}N_2$ cannot be established. However, a rough estimation from XRD intensities indicates that the fraction of $Fe_{16}N_2$ phase in the film is over 55 vol%; the M_s-value of the $Fe_{16}N_2$ formed in our experiment seems less than that reported by Kim and Takahashi [1].

M_s-values of the films after annealing at 300 °C and 400 °C are about 200 emu g^{-1}; this value is between the M_s-values of α-Fe and γ'-Fe_4N since the films consist of these two phases. For the film annealed at 500 °C, the M_s-value of the film decreases and drops to 120 emu g^{-1} due to the occurrence of a reaction between the GaAs substrate and the film.

In summary, it is possible to form an Fe–N film containing the $Fe_{16}N_2$ phase by ion-beam-assisted deposition. The $Fe_{16}N_2$ was stable at 150 °C and started to transform into α-Fe and γ'-Fe_4N at 200 °C. After annealing at 300 °C for 2 h the $Fe_{16}N_2$ converted completely to α-Fe and γ'-Fe_4N. Although the M_s-value of the Fe–N film containing $Fe_{16}N_2$ is significantly higher than that of α-Fe, the M_s of $Fe_{16}N_2$ seems less than that reported. An accurate measurement of $Fe_{16}N_2$ in the film is necessary to determine its M_s-value. This part of the work is in progress.

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