Growth of iron nitride thin films by molecular beam epitaxy

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Abstract—

Iron nitride films were grown by atomic-nitrogen-assisted molecular beam epitaxy. ZnS-type FeN (γ' -FeN) was synthesized with low Fe evaporation rates (≤ 0.2 Å/s) at low growth temperatures below 210°C whereas γ' -Fe₄N was synthesized with high Fe evaporation rates (≥ 1.0 Å/s) at 130-415°C. Our results indicate that the stabilization of ZnS-type FeN requires not only the fulfillment of thermodynamic constraints but also the control of a delicate balance of kinetically driven competition. The use of lattice-matched GaN(0001) substrates enables the growth of epitaxial films of ZnS-type FeN.

Key words:

A1. Crystal structure, A3. Molecular beam epitaxy, B1. Nitrides, B2. Magnetic materials

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1. INTRODUCTION

It is known that a wide variety of compounds exist in the binary Fe-N system: *e.g.*, α'' -Fe₁₆N₂, α' -Fe₈N, γ' -Fe₄N, ϵ -Fe₃N, ζ -Fe₂N, and γ'' -FeN [1]. Some of the Fe-rich phases (α'' -Fe₁₆N₂, γ' -Fe₄N) are attractive for their high magnetic moment [2]. Increasing the N/Fe ratio decreases the magnetic moment rapidly, which makes the compounds less interesting from a magnetic application point of view. Furthermore the difficulty in the synthesis of Fe-N increases markedly for the more N-rich phase. Accordingly, the N-rich region (N/Fe $\sim$ 1) in the Fe-N binary phase diagram was almost unexplored until the early 1990's. Indeed no bulk synthesis of FeN has yet been reported. The synthesis of FeN has so far relied on thin-film growth techniques such as sputtering [4-6], pulsed laser deposition [7], laser-nitriding [8], molecular beam epitaxy assisted by atomic nitrogen [8-10], etc.

Many transition-metal nitrides with the 1:1 stoichiometry adopt the NaCl structure, apart from small deviations from the ideal geometry such as small tetragonal distortions and such-like. In fact, the early members of 3d transition-metal nitrides, ScN to MnN, adopt the NaCl structure, and some (TiN, VN) are superconducting. In contrast, FeN and CoN both crystallize in the zinc-blend (ZnS) structure. The subsequent members, NiN and CuN, are theoretically predicted to adopt the ZnS structure although they have not hitherto been synthesized. The transition-metal nitrides possess a richness of structural and electric/magnetic properties and form an interesting family of compounds [11].

In early efforts, there have been reports of the existence of two compounds (two structural isomers) with an FeN stoichiometry: nonmagnetic γ'' -FeN with the ZnS structure and probably antiferromagnetic γ''' -FeN with the NaCl structure. In ZnS-type γ'' -FeN, each nitrogen atom is coordinated by four iron atoms at the corners of a regular tetrahedron whereas in NaCl-type γ''' -FeN, each nitrogen atom is coordinated by six iron atoms at the corners of a regular octahedron. The latter coordination is commonly seen in the Fe-N system (α'' -Fe₁₆N₂, α' -Fe₈N, γ' -Fe₄N, ϵ -Fe₃N, and ζ -Fe₂N). Hinomaru *et al.* carried out

^{57}Fe Mössbauer spectroscopy measurements for the films prepared by sputtering. They claimed that stoichiometric FeN_x ($x \approx 1.0$) formed in the ZnS phase whereas nitrogen-deficient FeN_x ($x \approx 0.6$) was a mixture of two phases having the ZnS and NaCl structures [12]. Later, however, Andrzejewsak *et al.* prepared the specimens by MBE and identified the structure of FeN_x ($x > 0.5$) as the ZnS structure with nitrogen vacancies [8]. This conclusion was reached by conversion electron Mössbauer spectroscopy. Furthermore, developments in MBE techniques have enabled the growth of single-crystalline single-phase films having the ZnS structure [9, 10], while the existence of the NaCl-type FeN remains elusive.

In this article, we report the influence of growth parameters on the resultant phase formation in the Fe-N films prepared by atomic-nitrogen-assisted MBE. We found that not only the growth temperature (thermodynamic parameter) but also the growth rate (kinetic parameter) are critical in stabilizing ZnS-type FeN. We also report the transport properties of FeN films, on which only very limited information has been available. The resistivity of ZnS-type FeN films shows a metallic but complicated temperature dependence, which suggests the possible existence of some phase transition.

2. Experimental

Fe nitride films were grown in the customer-designed ultrahigh vacuum (UHV) MBE system with base pressure of $\sim 1 \times 10^{-9}$ Torr. Fe was evaporated from an e-beam source, while simultaneously exposing a substrate to a flux of atomic nitrogen generated by a radio-frequency (RF) plasma discharge source (ARIOS, IRFS-504). The atomic nitrogen source was operated with the input RF power of 200~400 W and N_2 flow rate of 0.7 sccm. The growth temperature (T_s) was varied from ambient to 500°C. It turned out that the evaporation rate of Fe (R_{Fe}) is a critical parameter deciding which phase forms, therefore the rate was varied in a fairly wide range from 0.05 to 1.0 Å/s. **The film thickness is estimated**

from the Fe deposition rate, assuming the sticking coefficient of Fe is 1.0, which may be reasonable at growth temperatures below 500°C.

The substrates used were mainly GaN(0001) and MgO(001). GaN(0001) was grown on sapphire(0001) by metalorganic vapor phase epitaxy (MOVPE) using the AlON buffer-layer technology [13]. GaN has the wurtzite structure (hexagonal) with the lattice constants of $a_0 = 3.189 \text{ \AA}$ and $c_0 = 5.185 \text{ \AA}$. The Ga-Ga distance is $3.189 \text{ \AA}$, which is close to the Fe-Fe distance ($3.046 \text{ \AA}$) in ZnS-type γ'' -FeN ($a_0 = 4.307 \text{ \AA}$). On GaN(0001), the epitaxial growth of γ'' -FeN(111) films is expected. On the other hand, MgO has the NaCl structure with $a_0 = 4.211 \text{ \AA}$, which is close to $a_0 = 4.307 \text{ \AA}$ of FeN. On MgO(001), the epitaxial growth of γ'' -FeN(001) films is expected (cube-on-cube epitaxial relationship). Our preliminary experiments for the growth of elemental iron films on oxide substrates indicated that reaction takes place between iron and oxygen in the substrates at T_s above 350°C. Nitriding of surfaces of oxide substrates before growth appears to suppress this reaction, at least, partially. The structure of the films was characterized by *in-situ* reflection high-energy electron diffraction (RHEED) and X-ray diffraction (XRD). The ω -2 θ (equivalently θ -2 θ) XRD scans were performed using Rigaku, Smart Lab with Cu K_α radiation, which is monochromatized by Ge(220) crystals. The resistivity-vs-temperature (ρ - T) characteristics of the films were measured by a standard four-probe method.

3. Results and Discussion

3-1. Low Fe evaporation rate

First we describe the results of the growth with low Fe evaporation rates ($R_{Fe} = 0.05 \sim 0.2 \text{ \AA/s}$). Figure 1(a) shows the XRD patterns of the Fe-N films grown with $R_{Fe} = 0.1 \text{ \AA/s}$ for 30 min on GaN(0001) at different growth temperatures from ambient to 250°C. The thickness estimated is $305 \text{ \AA}$. The input power for the RF atomic nitrogen source was optimized and set to 300 W. The (111) and (222) reflections from ZnS-type γ'' -FeN are

observed with no impurity peak in the films grown at T_s from 90 to 210°C whereas almost no peak is observed in the film grown at $T_s = 250^\circ\text{C}$. The result indicates that the single-phase FeN(111) films with the ZnS structure are grown on GaN(0001) at T_s from 90 to 210°C. For comparison, the XRD patterns of the Fe-N films grown on MgO(001) are shown in Fig. 1(b). The films are crystallized in the ZnS structure in the range of T_s from 130 to 210°C and in $\zeta\text{-Fe}_2\text{N}$ at $T_s = 250^\circ\text{C}$. As mentioned in §2, the cube-on-cube epitaxial relationship is expected for ZnS-type FeN films on MgO. Against this expectation, the films on MgO are a mixture of FeN(001) and FeN(111) grains. At a first look, only the (111) and tiny (222) reflections appear to be present in the XRD patterns (Fig. 1(b)). However, the enlarged view of the XRD pattern near $\theta \approx 40^\circ$ (Fig. 1(c)) clearly reveals the presence of the (002) reflection of FeN in the tail of the intense (002) reflection of an MgO substrate. The observed (integrated) intensity ratio of (002) : (111) is about 1 : 1 for the film grown at $T_s = 170^\circ\text{C}$. According to the experimental powder XRD pattern of FeN by Suzuki *et al.* [4], the intensity ratio, (002) : (111), is 29 : 100. By correcting the observed intensities of the (002) and (111) reflections by this ratio, the volume ratio of the (001) oriented portion to (111) oriented one in the films is 3~4. Namely, the films grown on MgO(001) are dominantly FeN(001) but with a certain amount of FeN(111).

In Fig. 2(a) and 2(b), the peak intensity and the d value of the (111) reflection of the ZnS-type FeN films on both of GaN and MgO are plotted against T_s . The former indicates that the optimum growth temperature for ZnS-type FeN is 130-170°C. With regard to the latter, the d value is slightly smaller in the films on GaN than on MgO. This may be explained by epitaxial strain. It has been reported [10] that FeN thin films (~ 150 Å) on GaN are distorted by in-plane tensile epitaxial strain (3.189 Å for the Ga-Ga distance versus 3.046 Å for the Fe-Fe distance) and that, accordingly, the out-of-plane lattice constant becomes shorter than the value reported for thick FeN films prepared by sputtering [4]. On the other hand, the lattice constant of the films on MgO is close to the reported value, indicating that

the strain is mostly relaxed [footnote#1].

Figure 3 shows the corresponding ρ - T data of these films. Only the ρ - T curves of the films on GaN are plotted since the behavior is essentially identical for films on two substrates. The films grown at T_s from 130 to 170°C have the lowest resistivity. The ρ - T curve is concave at $T > \sim 150$ K and convex at $T < \sim 150$ K with an inflection point at ~ 150 K. This inflection point may suggest the existence of some phase transition. Figure 2(c) and 2(d) are a summary of the ρ - T data: (c) $\rho(300\text{ K})$ and (d) residual resistivity ratio (RRR) plotted as a function of T_s . The RRR is defined as $\rho(300\text{ K})/\rho(4.2\text{ K})$ and a measure of metallicity. The $\rho(300\text{ K})$ is the lowest and the RRR is the largest in the same range of T_s as the crystallinity is the highest (Fig. 2(a)). The trend implies that higher crystallinity provides more metallic films.

As mentioned before, the evaporation rate of Fe is a critical parameter for stabilizing the ZnS phase of FeN. Figure 4 shows the XRD patterns of the films grown on MgO at $T_s = 170^\circ\text{C}$ with different R_{Fe} from 0.05 to 1.0 Å/s. The deposition time is 30 min for $R_{\text{Fe}} = 0.05\text{--}0.2$ Å/s, 15 min for 0.4 Å/s, and 5 min for 1.0 Å/s [footnote#2]. As seen in this figure, the ZnS phase forms for $R_{\text{Fe}} = 0.05 \sim 0.2$ Å/s whereas the γ' -Fe₄N forms for $R_{\text{Fe}} = 1.0$ Å/s. The film grown with $R_{\text{Fe}} = 0.4$ Å/s showed no XRD peak. The result indicates that low growth rate is prerequisite for stabilizing ZnS-type FeN.

3-2. High Fe evaporation rate

Next we describe the results of the growth with a high Fe evaporation rate ($R_{\text{Fe}} = 1.0$ Å/s). Figure 5(a) shows the XRD patterns of the Fe-N films grown for 5 min on MgO(001) at different growth temperatures from ambient to 500°C. The thickness estimated is 464 Å. The films are crystallized in γ' -Fe₄N with the (001) plane parallel to the substrate surface at T_s from 130 to 415°C, and show sharper and stronger XRD peaks for higher T_s . The films grown at T_s below 130°C show no XRD peak whereas the film grown at $T_s = 500^\circ\text{C}$ is

elemental Fe containing no nitrogen, indicating that γ' -Fe₄N is not stable at $T_s = 500^\circ\text{C}$ [14]. It should be emphasized again that ZnS-type FeN has never formed with high R_{Fe} ($\geq 1.0 \text{ \AA/s}$) even by lowering T_s down to 30°C , judging from both of the XRD patterns and ρ - T curves. Instead some reflections from hexagonal ϵ -Fe₃N ($a_0 = 4.7080 \text{ \AA}$, $c_0 = 4.3885 \text{ \AA}$, see Fig. 5(c), [15]) was discernible by lowering T_s , although the intensity was small, in the films grown on substrates such as LaAlO₃(001), YAlO₃(001), *etc.* other than MgO [footnote#3].

The crystal structure of γ' -Fe₄N is cubic and can be viewed as the face-centered cubic (fcc) lattice of Fe with interstitial N at the body-center position (see Fig. 5(c)). This is the simplest structure among the Fe-N binary system. The lattice constant, $a_0 = 3.795 \text{ \AA}$, of γ' -Fe₄N should be compared with $3.45 \text{ \AA}$ for fcc γ -Fe, which is an unstable phase at ambient temperature (the stable phase at ambient temperature is bcc α -Fe with $a_0 = 2.87 \text{ \AA}$). Interstitial nitrogen in γ' -Fe₄N expands the fcc lattice by 10% in a_0 and reduces the $3d$ - $3d$ overlap, thereby stabilizing a ferromagnetic state with a Curie temperature of 767 K. This is one of the reasons why iron and nitrogen look like a promising combination for magnetic applications [1].

Figure 5(b) shows the corresponding ρ - T data of these films. The ρ - T curves of γ' -Fe₄N films have prominent convex curvature. Figure 6 is a summary of the results: (a) intensity of the (002) reflection, (b) d value of the (002) reflection, (c) $\rho(300 \text{ K})$, and (d) RRR. The best crystallinity of films was attained at $T_s = 415^\circ\text{C}$, which is just below the decomposition temperature ($\leq 500^\circ\text{C}$). This trend in the growth of Fe₄N films appears to correspond to the Hammond-Bormann law in the growth of oxide films, which claims that proximity to the equilibrium decomposition line may be favorable for *in-situ* film growth [16]. At $T_s = 415^\circ\text{C}$, the electrical conductivity is also optimized. The RRR value reaches 33, which is substantially higher than ~ 10 for epitaxial films grown by dc reactive sputtering [17] or ~ 3 for polycrystalline films grown by dc reactive facing-target sputtering [18]. The high RRR value, namely low residual resistivity of the Fe₄N films grown by reactive coevaporation

implies high crystallinity and/or low density of defects such as nitrogen vacancies.

4. Summary

High-quality thin films of ZnS-type FeN (γ'' -FeN) and γ' -Fe₄N were grown by atomic-nitrogen-assisted MBE. It requires not only low temperatures (below 170°C) but also low Fe evaporation rates (≤ 0.2 Å/s) to stabilize the ZnS phase of FeN. This indicates that thermodynamics as well as kinetics are critical for stabilizing ZnS-type FeN. Our finding may provide a clue for the synthesis of NiN and CuN, which are yet to be synthesized. The optimum growth temperature for γ'' -FeN is 130-170°C. FeN films grow on GaN(0001) with FeN(111)//GaN(0001) whereas they grow on MgO(001) with FeN(001)//MgO(001) as the major orientation but with FeN(111)/MgO(001) as the minor orientation. High Fe evaporation rates (1 Å/s) stabilizes γ' -Fe₄N. The optimum growth temperature for γ' -Fe₄N is 415°C, at which a RRR value as high as 33 was obtained.

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Footnote

[#1] In Fig. 2(b), only the $d(111)$ values from the (111) reflection of the films are included.

The d value evaluated from the (002) reflection, although not very accurate due to the severe interference by the intense substrate reflection, is 2.151 Å, which is also in a good agreement with the reported value ($a_0/2 = 2.1535$) [4].

[#2] The thickness of the film grown with each R_{Fe} is different: 153, 306, 612, 612, and 510 Å for the deposition with $R_{Fe} = 0.05, 0.1, 0.2, 0.4$, and 1.0 Å/s, respectively.

[#3] The (11 $\bar{2}$ 1) reflection ($2\theta = 43.7^\circ$) of hexagonal ϵ -Fe₃N was observed on cubic

LaAlO₃, YAlO₃, and SrTiO₃ substrates. In the case of the films on MgO, the (11 $\bar{2}$ 1) reflection from ϵ -Fe₃N may be buried in the tail of a huge substrate (002) peak.

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Figure captions

Figure 1. XRD patterns of the Fe-N films grown with $R_{\text{Fe}} = 0.1 \text{ \AA/s}$ on (a) GaN(0001) and (b) MgO substrates at different T_s . The enlarged view near $\theta \approx 40^\circ$ for the film grown at $T_s = 170^\circ\text{C}$ in (b) is shown in (c), which clearly reveals the presence of the (002) reflection of FeN. The component of the (002) reflection of FeN was extracted as shown in (c), which was performed by subtracting a Lorentzian fit (broken line) for the tail of the (002) reflection of MgO from the experimental curve.

Figure 2. Summary of the structural and transport properties of the Fe-N films grown with $R_{\text{Fe}} = 0.1 \text{ \AA/s}$ on GaN(0001) (solid circles) and MgO(001) (crosses) as a function of T_s : (a) intensity of the (111) reflection, (b) d value of the (111) reflection, (c) $\rho(300 \text{ K})$, and (d) RRR. The dash-and-dot line in (b) represents the d value for the thick films prepared by sputtering in ref. 4.

Figure 3. Resistivity versus temperature for the Fe-N films grown with $R_{\text{Fe}} = 0.1 \text{ \AA/s}$ on GaN(0001) at different T_s .

Figure 4. XRD patterns of the Fe-N films grown on MgO(0001) substrates at $T_s = 170^\circ\text{C}$ with different R_{Fe} .

Figure 5. (a) XRD patterns and (b) ρ - T curves of the Fe-N films grown with $R_{\text{Fe}} = 1.0 \text{ \AA/s}$ on MgO(001) substrates at different T_s . The crystal structures of typical compounds in the Fe-N system are illustrated in (c).

Figure 6. Summary of the structural and transport properties of the Fe-N films grown with $R_{\text{Fe}} = 1.0 \text{ \AA/s}$ on MgO(001) as a function of T_s : (a) intensity of the (002) reflection, (b) d value of

the (002) reflection, (c) ρ (300 K), and (d) RRR. The dash-and-dot line in (b) represents the d value for bulk samples of γ' -Fe₄N. The data points indicated by (●) are for the films decomposed to elemental Fe. The gray line indicates the optimum growth temperature for γ' -Fe₄N.

Figure 1

(a)

(b)

(c)

Figure 2

Figure 3

Figure 4

Figure 5(a), (b)

(a)

(b)

Figure 5(c)

Figure 6