

Effect of Pt Buffer on Magnetic Property of Fe₄N Thin Film Deposited by Atmospheric Pressure Halide CVD Method

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Polycrystalline Fe₄N thin films were prepared by AP-HCVD from the starting materials of FeCl₃ and NH₃. The effect of Pt buffer layer on Si(100) substrate was examined. It was clarified that coexistence of the second phases such as Fe₃N and α-Fe was detected on Pt buffer layer. The sample was deposited on 10 nm-thick Pt buffered Si(100) substrate. It was considered that the introduction of Pt buffer layer affected to the coverage and uniformity of the film.

Key words: Fe₄N, AP-HCVD, Pt-buffer layer, thin film, Si substrate

1. INTRODUCTION

Various iron nitrides such as γ'-Fe₄N (cubic), ζ-Fe₂N (orthorhombic), ε-Fe₂N (hexagonal), ε-Fe₃N (hexagonal) and α''-Fe₁₆N₂ (body centered cubic) are known [1]. All of these iron nitrides are interstitial compounds. It is also known that several iron nitrides such as γ'-Fe₄N and α''-Fe₁₆N₂ have high saturation magnetization [2]. Crystal system and saturation magnetization for several iron nitrides were shown as Table 1. Among these iron nitride, Fe₄N is promising due to its mechanical strength and high oxidation resistance [3]. Crystal structure of Fe₄N is shown in Figure 1. In this work, preparation of Fe₄N thin films on Si(100) substrate by atmospheric pressure halide CVD (AP-CVD) was examined. In this work, the effect of Pt buffer later on the crystal growth and magnetic property of Fe₄N was examined.

2. EXPERIMENTAL

Figure 2 shows schematic drawing of the AP-CVD equipment used in this work. The equipment is made of silica glass and composed of a reactor, a substrate rod, a substrate folder and a boat in which raw material (FeCl₃ is charged). In the reactor, carrier gas (N₂), counter gas (N₂) and blower gas (NH₃+N₂) were provided. The size of the reactor is 1,010 mm long and φ22 mm in internal diameter. The reactor is covered with two electric furnaces; one is used to evaporate raw material (FeCl₃) and another is used to deposit iron nitride films. Growth conditions of Fe₄N were summarized in Table 2. In this work, the films were deposited on Si(100) substrate with natural oxide and Si(100) substrates covered with 10 and 70 nm-thick Pt buffer layers. The films were characterized by x-ray diffraction, scanning electron microscopy (SEM) and vibration sample magnetometer (VSM).

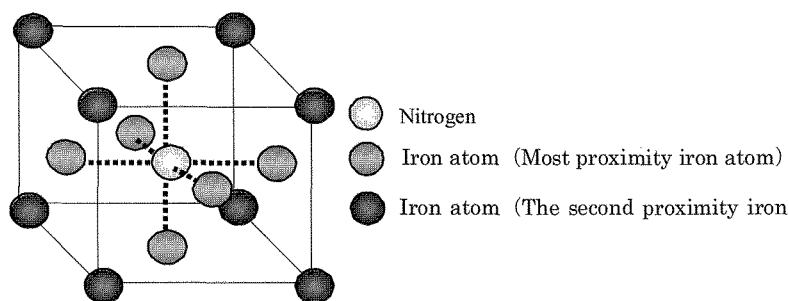


Figure 1. Crystal structure of Fe₄N.

Table 1. Cryst

al system and saturation magnetization for several iron nitrides.

Composition	Crystal structure	Saturation magnetization (emu/g)
ζ-Fe ₂ N	Orthorhombic	-
ε-Fe ₃ N	Hexagonal	138
γ'-Fe ₄ N	Cubic	182
α''-Fe ₁₆ N ₂	Breast conserving therapy	240

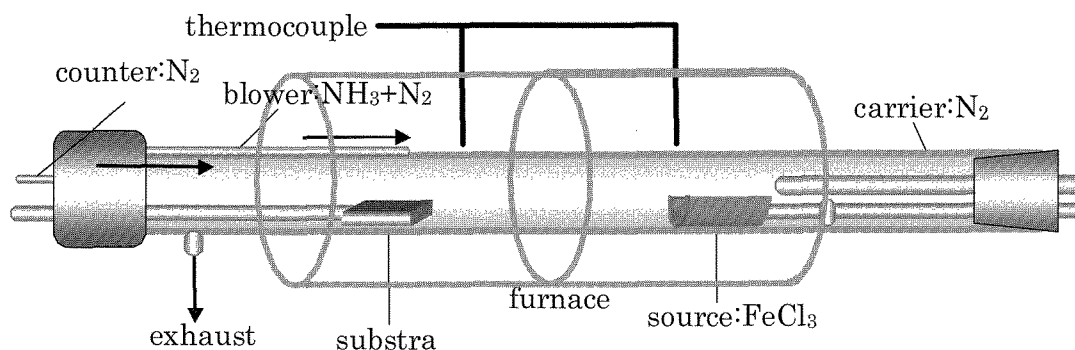
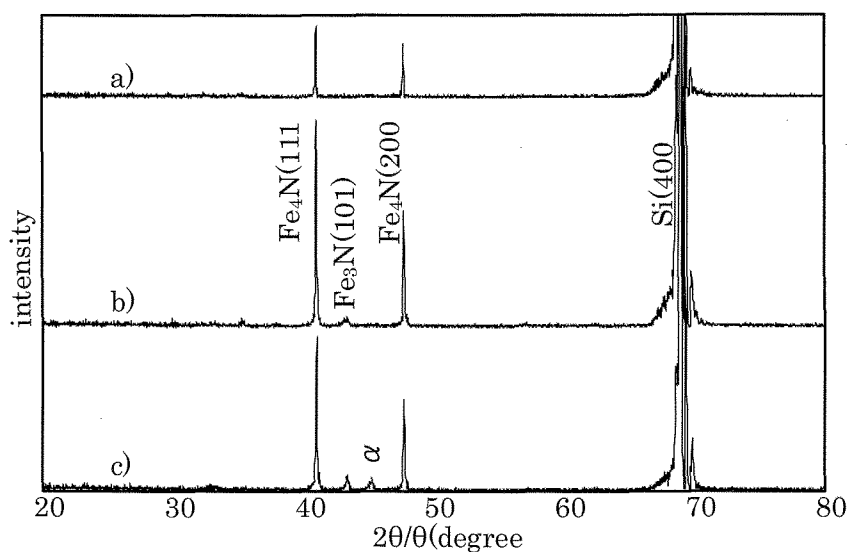


Figure 2. Schematic drawing of the AP-CVD equipment.

Figure 3. XRD patterns of Fe₄N thin films on Pt buffered Si substrate.

a) Si(100) without Pt, b) Si(100) with 10 nm-thick Pt, c) Si(100) with 70 nm-thick Pt.

Table 2. Growth conditions of Fe₄N.

Source	FeCl ₃ , NH ₃
Substrate	Pt-coated Si(100)
Substrate place	Under NH ₃ blow
Pt thickness [nm]	0, 10, 70
FeCl ₃ partial pressure [atm]	7.63×10^{-6}
NH ₃ partial pressure [atm]	1.42×10^{-1}
Growth temperature [°C]	600
V/VIII	1.87×10^4
Carrier gas	N ₂
Growth time [min]	30
Total flow rate [sccm]	900

3. RESULTS AND DISCUSSION

Figure 3 shows XRD patterns of the deposited films on (a) Si(100) substrate without Pt buffer layer, (b) and (c) Si(100) substrate with 10 and 70 nm-thick Pt buffer layers, respectively. This figure indicates that polycrystalline phase-pure Fe₄N thin film was deposited on Si(100) without Pt buffer layer. On the other hand, trace Fe₃N was detected for the film deposited on 10 and 70 nm-thick Pt buffer layer. On 70 nm-thick Pt, α-Fe was also detected. The α-Fe would be caused by the reduction of Fe₄N by H₂ that is derived by the decomposition of NH₃ due to the catalytic action of Pt.

Figures 4 and 5 show SEM photographs of surface and cross section of the films, respectively. These figures indicate that the films were granular and the surface is significantly rough. It is also observed that the grain size of Fe₄N film deposited on Pt buffer layer is smaller than that deposited on Si(100) without Pt buffer layer. This tendency agreed well with the crystallite diameter measured by the Scherrer's equation as shown in Table 3.

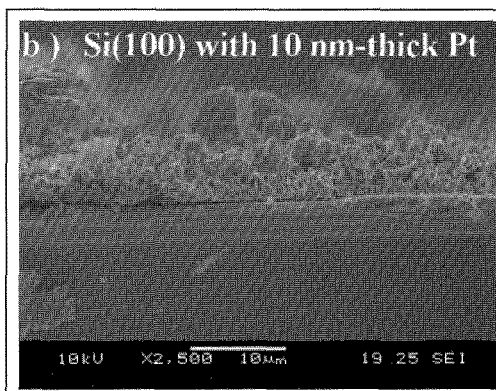
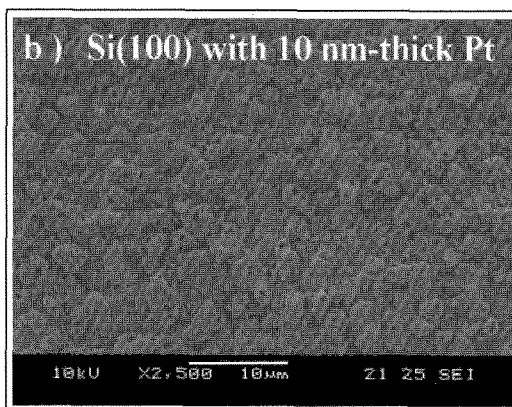
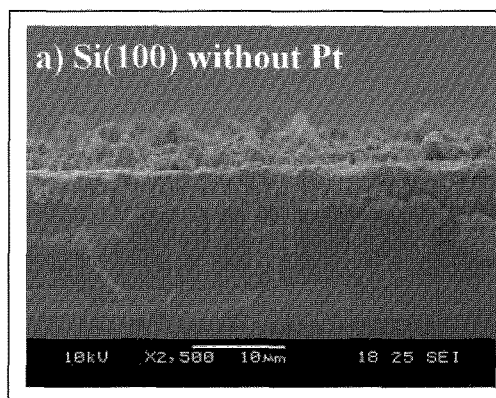
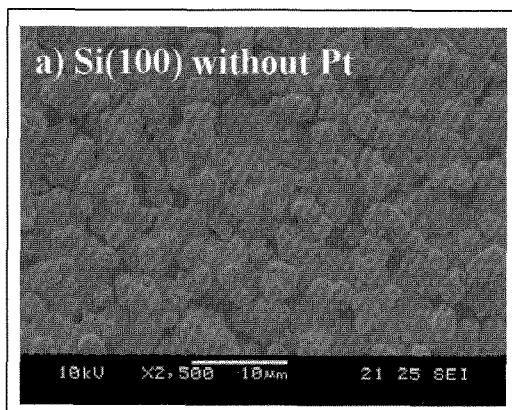


Fig 4. Surface SEM images of Fe₄N thin films on Pt buffered Si substrate

a) Si(100) without Pt, b) Si(100) with 10 nm-thick Pt.

Figure 5. Cross-section SEM images of Fe₄N thin films on Pt buffered Si substrate

a) Si(100) without Pt, b) Si(100) with 10 nm-thick Pt.

Table.3. Crystalline size of Fe₄N thin film on the basis of Scherrer's equation.

Sample	Particle diameter (nm)
Si(100) without Pt	146
Si(100) with 10 nm-thick Pt	106

Table.4. Saturation magnetization and coercive force of Fe₄N thin film.

Sample	Saturation magnetization (emu)	Coercive force (Oe)
Si(100) without Pt	0.238	81
Si(100) with 10 nm-thick Pt	0.390	52

Figures 6 and 7 show M-H curves of Fe₄N films deposited on Si(100) without and with Pt buffer layers, respectively. Saturation magnetization and coercive force were shown in Table 4. Since it was difficult to estimate the thickness of the film, saturation magnetization is not normalized as emu/g. However, from the shape of M-H curves, it can be mentioned that coercive force of Fe₄N deposited on Pt is smaller than that deposited on Si. By comparison with figure 3, it

would be considered that the difference of magnetic property, especially coercive force, is derived by the difference of crystallinity.

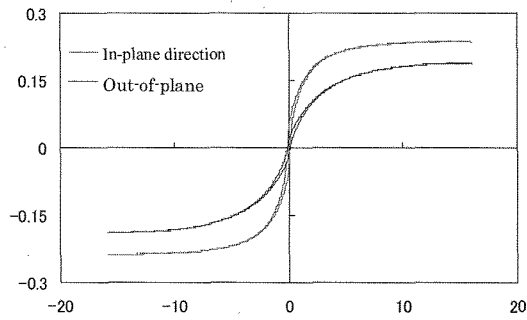


Fig. 6 M-H curves of Fe₄N thin film deposited on Si(100) substrate without Pt buffer layer.

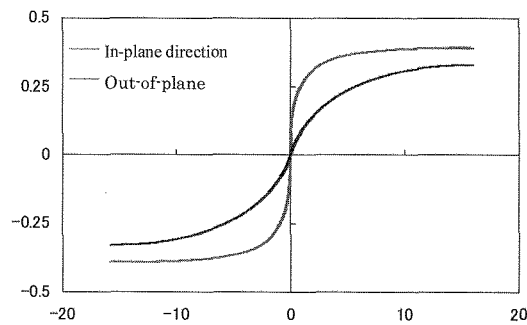


Fig. 7. M-H curves of Fe₄N thin film deposited on Si(100) substrate with 10 nm-thick Pt buffer layer.

4. REFERENCES

- [1] Satoshi Okamoto et al., Journal of Magnetism and Magnetic Materials 208 (2000) 102) 114
- [2] Y. Takahashi et al, Journal of Magnetism and Magnetic Materials 210 (2000) 333-340
- [3] Tadashi Takahashi et al, Solid State Sciences 6 (2004) 97-99

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