Fabrication of $L1_0$-FeNi films by denitriding FeNiN films

Keita Ito**, Masahiro Hayashida*, Masaki Mizuguchi**, Takashi Suemasu***, Hideto Yanagihara***, and Koki Takanashi**

*Institute for Materials Research, Tohoku Univ., 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
**Center for Spintronics Research Network, Tohoku Univ., 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
***Institute of Applied Physics, Univ. of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan

$L1_0$-FeNi films textured with the $c$ axis perpendicular to the film plane were successfully fabricated by denitriding FeNiN films. 20-nm-thick FeNiN films with two variants were epitaxially grown on SrTiO$_3$(001), MgAl$_2$O$_4$(001), and MgO(001) substrates by molecular beam epitaxy. Demagnetizing was performed by annealing at 300 °C for 4 h under an H$_2$ gas atmosphere. The epitaxial relationships were $L1_0$-FeNi[001]|| substrate[100] and $L1_0$-FeNi[010]|| substrate[100]. The uniaxial magnetic anisotropy energy ($K_u$) of the $L1_0$-FeNi film was estimated to be $4.4 \times 10^6$ erg/cm$^3$ at room temperature by magnetic torque measurement. This $K_u$ value corresponds to a degree of long range order of 0.4.

**Keywords:** $L1_0$-FeNi, FeNiN, denitriding, molecular beam epitaxy, uniaxial magnetic anisotropy energy

1. Introduction

According to an increasing demand of a permanent magnet for a motor of next-generation electric vehicles, ferromagnetic materials possessing large uniaxial magnetic anisotropy energy ($K_u$) and composed of earth abundant elements are required. We have focused on the $L1_0$-ordered FeNi alloy as a rare-earth- and noble metal-free high $K_u$ ferromagnetic material. $L1_0$-FeNi possesses face centered tetragonal structure with alternate stacking of Fe and Ni monatomic layers along the $c$ axis as shown in Fig. 1(a). Lattice constants are $a = 3.582$ Å and $c = 3.607$ Å; the $c/a$ ratio is 1.007. Saturation magnetization ($M_s$) is 1270 emu/cm$^3$ and the Curie temperature is higher than 550 °C. $K_u$ value was reported to be $1.3 \times 10^7$ erg/cm$^3$ in a bulk sample, and $7.0 \times 10^6$ erg/cm$^3$ in a film prepared by molecular beam epitaxy (MBE). We consider that these features of $L1_0$-FeNi are suitable for application to a permanent magnet. However, the order-disorder transition temperature of $L1_0$-FeNi is very low (320 °C), and it is difficult to form the $L1_0$ structure by a conventional annealing for FeNi alloys. Atomic diffusion of Fe and Ni is quite slow below 320 °C, and we need an astronomical long duration to obtain $L1_0$-ordered FeNi structure by simple annealing. The formation of bulk $L1_0$-FeNi was realized by several methods, promoting the atomic diffusion of Fe and Ni. For example, introduction of defects in FeNi alloys by neutron irradiation or electron bombardment followed by annealing with an external magnetic field, severe plastic deformation technique for FeNi powder, and annealing of rapidly quenched amorphous FeNiSiBPCu alloy. On the other hand, $L1_0$-FeNi films were prepared by alternate monatomic layer deposition using MBE or sputtering followed by annealing. Although a lot of studies on the formation of $L1_0$-FeNi were made, the degree of long range order $S$ or the volume fraction of $L1_0$-FeNi phase was not enough. Recently, however, the synthesis of polycrystalline $L1_0$-FeNi powder with large $S$ (0.71) has been achieved by nitrogen topotactic extraction from FeNiN powder. Figure 1(b) shows the crystal structure of FeNiN. FeNiN possesses a similar crystal structure to that of $L1_0$-FeNi, and thermodynamically stable ordered structure of FeN and Ni layers. Actually, the polycrystalline FeNiN powder with large $S$ was formed by a simple nitridation method for $L1_0$-FeNi (Fe and Ni are randomly located) powder using NH$_3$ gas. The $L1_0$-FeNi powder was formed by denitriding FeNiN by annealing under H$_2$ gas atmosphere. However, the evaluation of its $K_u$ value has never been performed because of polycrystalline powder. In this study, we have tried to grow epitaxial FeNiN films on SrTiO$_3$(STO)(001), MgAl$_2$O$_4$(MAO)(001), and MgO(001) substrates by molecular beam epitaxy (MBE), and fabricated $L1_0$-FeNi films with two variants by denitriding FeNiN films.

**Fig. 1** Crystal structure of (a) $L1_0$-FeNi and (b) FeNiN.

2. Experiment

20 nm-thick FeNiN films were grown on STO(001), MAO(001), and MgO(001) substrates by MBE in an
ultra-high vacuum chamber supplying Fe, Ni, and radio-frequency (RF) N\textsubscript{2} plasma, simultaneously.\textsuperscript{15} The lattice mismatches in the \textit{c} plane between FeNiN and the substrates are 2.5 (STO), –0.98 (MAO), and –4.9 \% (MgO). Supply rates of Fe and Ni were controlled to get the equiatomic composition of Fe and Ni. The growth temperature, \textit{N}\textsubscript{2} gas flow rate, and RF input power were fixed to be 300 °C, 1.0 sccm, and 240 W, respectively. Then, denitrifying was performed by furnace annealing at 300 °C for 4 h under H\textsubscript{2} gas flow rate of 1 L/min at ambient pressure. Structure of the samples was characterized by out-of-plane (\(\omega-2\theta\)) and in-plane (\(\varphi-2\theta\)) x-ray diffraction (XRD) using Cu-K\alpha radiation. The thickness of the \textit{L1\textsubscript{0}}-FeNi layer was estimated by x-ray reflectometry (XRR). Magnetization curves were measured by vibrating sample magnetometer at room temperature (RT). Magnetic field was applied to in-plane or out-of-plane direction of the films. The \(K_u\) value was estimated by a magnetic torque (\(L\)) measurement with a 45°-torque method.\textsuperscript{16} Torque curves were measured at RT under the applied field in the range of 2 to 19 kOe by rotating the electromagnet clockwise and counterclockwise around the (010)-plane of the substrates.

3. Results and discussion

Figure 2(a) shows the \(\omega-2\theta\) XRD patterns of the FeNiN films. Only the diffraction peak of FeNiN 200 is observed, and the \textit{a} axes of FeNiN films are perpendicular to the film plane for all the substrates. Figures 2(b) and 2(c) show the \(\varphi-2\theta\chi\) XRD patterns of the same samples. The scattering vector (\(Q\)) was set to the [100] direction of the substrates. In Fig. 2(b), the peaks of FeNiN 020 and 002 are obtained. This means that the FeNiN films are epitaxially grown with two variants: the epitaxial relationships are FeNiN[001](100) || STO, MAO[100](001) and FeNiN[010](100) || STO, MAO, MgO[100](001), as shown schematically in Fig. 3. There are the two variants with the in-plane caxis of FeNiN intersecting at 90°. In Fig. 2(c), the super lattice peak of FeNiN 001 is clearly observed for all the samples. This is attributed to the long-range order of N atoms in the FeNiN films.\textsuperscript{15}

Figures 4(a) and 4(b) show the XRR patterns of the sample grown on the STO(001) substrate before and after the denitrifying process, respectively. The red and blue curves correspond to the experiments and the calculations based on the models shown in the right-hand figures, respectively. After denitrifying, the
calculated curve assuming the existence of the surface oxidation layer agrees well to the experiment. The total film thickness becomes thinner after denitriding. This is attributed to the shrink of the unit-cell volume associated with the change from FeNiN to $L1_0$-FeNi.

Figures 5(a) and 5(b) show the $\omega 2\theta$ and $\varphi 2\theta\chi$ XRD patterns of the denitrided samples, respectively. The dashed lines indicate the peak position of $L1_0$-FeNi 002 and 200 expected from the lattice constants of bulk $L1_0$-FeNi. The diffraction around $2\theta = 52^\circ$ in Fig. 5(a) corresponds to $L1_0$-FeNi 200, and that around $2\theta\chi = 51^\circ$ in Fig. 5(b) is associated with $L1_0$-FeNi 002 and 020. The peak shift from the dashed lines indicates the tensile strain induced in the films by the larger lattice constants of substrates than that of $L1_0$-FeNi. Therefore, we can say that the epitaxial relationship between the $L1_0$-FeNi films and the substrates is maintained after the denitriding process as shown in Fig. 6:

$L1_0$-FeNi[001](100) $\parallel$ STO, MAO, MgO[100](001) and $L1_0$-FeNi[010](100) $\parallel$ STO, MAO, MgO[100](001).

Fig. 7(a) and 7(b) display the magnetization curves of the $L1_0$-FeNi films in the in-plane ([100]) and out-of-plane magnetic fields, respectively. $M_s$ of the samples are approximately 1100 emu/cm$^3$ for all the samples. For comparison an epitaxially grown Al-FeNi film was prepared on STO(001) and the magnetization curves were measured as shown by black ones in Figs. 7(a) and 7(b). In Fig. 7(a), the $L1_0$-FeNi films formed by denitriding show
larger coercive fields and smaller remanent magnetizations than those of the A1-FeNi film. This is attributed to the presence of the a-axis (magnetic hard axis) of L10-FeNi along to the in-plane direction of the denitrided samples, as shown in Fig. 6. Furthermore, in Fig. 7(b), the saturation fields of denitrided L10-FeNi films are larger than that of the A1-FeNi film. This is explained by the a-axis (magnetic hard axis) orientation of L10-FeNi perpendicular to the film plane in the denitrided samples. These results strongly suggest the formation of a-axis textured L10-FeNi films which have two variants with different c-axis directions from each other, showing uniaxial magnetic anisotropy for each. There is no significant difference in structure and magnetic properties of the denitrided samples grown on the three different substrates.

Figure 8 shows the torque curves of the L10-FeNi film on STO(001). The inset shows the geometry of the film sample and the magnetic field. \( \theta \) is the angle relative to the surface normal: \( \theta = 90^\circ \) and \( \theta = 0^\circ \) show that the magnetic field was applied in parallel to the in-plane and out-of-plane of the L10-FeNi film, respectively. The saw-tooth-like curves show that the magnetization is not saturated at 19 kOe. These curves exhibit two-foil symmetry because of \( K_u \) in the L10-FeNi film. Figure 9 shows the \( L \cdot (L/H)^2 \) plots using the averaging absolute values at \( \theta = 45^\circ, 135^\circ, 225^\circ, \) and 315\(^\circ\). The \( M_s \) and effective uniaxial magnetic anisotropy energy \( (K_u^{\text{eff}}) \) values were obtained from the intersections of the fitting lines with the vertical and horizontal axes, respectively. By considering the two variants of the sample, magnetic anisotropy energy \( (E_A) \) and \( L \) are expressed by equations (1) and (2), respectively.

\[
E_A = \frac{1}{2} (K_u + 2nM_s^2) \sin^2 \theta + 1/2 \cdot 2nM_s^2 \sin^2 \theta \quad (1)
\]

\[
L = -dE_A/d\theta = -(K_u/2 + 2nM_s^2) \sin 2\theta \quad (2)
\]

Here, it is noted that positive \( K_u \) means the easy magnetization axis in the in-plane direction. Using the equation \( K_u^{\text{eff}} = K_u/2 + 2nM_s^2 \), the \( K_u \) value is calculated to be \( 4.4 \times 10^6 \) erg/cm\(^2\) for L10-FeNi/STO(001). From the relationship between \( K_u \) and \( S \) reported for L10-FeNi films prepared by MBE,\(^6\) \( K_u \) of 4.4 \( \times \) \( 10^6 \) erg/cm\(^2\) corresponds to \( S \) of 0.4. This value is smaller than that of the L10-FeNi powder reported in ref. 13 (\( S = 0.71 \)). In our case, denitriding was performed at 300 °C, which is higher than that in ref. 13 (250 °C). We chose higher temperature to promote denitriding. However, this high temperature might have caused the deterioration of the L10 structure and the reduction of \( S \) and \( K_u \), when the N atoms were extracted from the FeNiN lattice. Further optimization of the denitriding conditions and the elucidation of the denitriding mechanism are required in order to obtain much larger \( S \) and \( K_u \) values.

4. Summary

We have succeeded in growing a-axis textured FeNiN films with the two variants on STO(001), MAO(001), and MgO(001) substrates by MBE, and forming L10-FeNi films by denitriding them. The \( K_u \) of the L10-FeNi film is estimated to be 4.4 \( \times \) \( 10^6 \) erg/cm\(^2\) at RT, and the \( S \) is expected to be approximately 0.4. In order to get higher \( S \) and \( K_u \), as a next step, the optimization of the growth conditions and denitriding conditions of the FeNiN films are required.

Acknowledgements This work was supported in part by the Elements Strategy Initiative Center for Magnetic Materials (ESICMM) under the outsourcing project of Ministry of Education, Culture, Sports, Science and Technology, Japan. The XRD measurements were carried out at the Cooperative Research and Development Center for Advanced Materials, IMR, Tohoku University. The magnetic torque curve measurements were performed with the help of T. Sekido, the University of Tsukuba. We thank S. Goto and H. Kura, DENSO CORPORATION, for fruitful discussion about the denitriding process.

References

1) K. Takanashi, M. Mizuguchi, T. Kojima, and T. Y. Tashiro: J. Phys. D: Appl. Phys., 50, 483002 (2017).
2) M. Kotsugi, H. Maruyama, N. Ishimatsu, N. Kawamura, M.
Suzuki, M., Mizumaki, K., Osaka, T., Matsumoto, T., Ohkochi, and T. Ohtsuki: *J. Phys.: Condens. Matter*, **26**, 064206 (2014).

3) J. Paullevé, A. Chamberod, K. Krebs, and A. Bourret: *J. Appl. Phys.*, **39**, 989 (1968).

4) T. Nagata and M. Funaki: *Mem. Natl Inst. Polar Res. Spec.*, **46**, 245 (1987).

5) P. Wasilewski: *Phys. Earth Plan. Inter.*, **52**, 150 (1988).

6) L. Néel, J. Paullevé, R. Pauthenet, J. Laugier, and D. Dutremp: *J. Appl. Phys.*, **35**, 873 (1964).

7) T. Kojima, M. Mizuguchi, T. Koganezawa, K. Osaka, M. Kotsugi, and K. Takanashi: *Jpn. J. Appl. Phys.*, **51**, 010204 (2012).

8) K. B. Reuter, D. B. Williams, and J. I. Goldstein: *Met. Trans. A*, **20**, 711 (1989).

9) S. Lee, K. Edalati, H. Iwaoka, Z. Horita, T. Ohtsuki, T. Ohkochi, M. Kotsugi, T. Kojima, M. Mizuguchi, and K. Takanashi: *Phil. Mag. Lett.*, **94**, 639 (2014).

10) A. Makino, P. Sharma, K. Sato, A. Takeuchi Y. Zhang, and K. Takenaka: *Sci. Rep.*, **6**, 16627 (2015).

11) T. Y. Tashiro, M. Mizuguchi, T. Kojima, T. Koganezawa, M. Kotsugi, T. Ohtsuki, K. Sato, T. Konno, and K. Takanashi: *J. Alloys Compd.*, **750**, 164 (2018).

12) A. Frisk, B. Lindgren, S. D. Pappas, E. Johansson, and G. Andersson: *J. Phys.: Condens. Matter.*, **28**, 406002 (2016).

13) S. Goto, H. Kura, E. Watanabe, Y. Hayashi, Y. Yanagihara, Y. Shimada, M. Mizuguchi, K. Takanashi, and E. Kita: *Sci. Rep.*, **7**, 13216 (2017).

14) R. J. Arnott and A. Wold: *J. Phys. Chem. Solids*, **15**, 152 (1960).

15) F. Takata, K. Ito, and T. Suemasu: *Jpn. J. Appl. Phys.*, **57**, 058004 (2018).

16) H. Miyajima, K. Sato, and T. Mizoguchi: *J. Appl. Phys.*, **47**, 4669 (1976).

**Received Jan. 18, 2019; Accepted Apr. 16, 2019**