C-3

Magnetic hardening of nano-thick $Sm_2Fe_{17}N_x$ films grown by a pulsed laser deposition

Choong Jin Yang, Sang Won Kim

Electromagnetic Materials Lab., Research Institute of Industrial Science and Technology(RIST), P. O. Box 135, 790-330 Pohang, South Korea,

Jianmin Wu

Dept.2, Central Iron and Steel Research Institute, Beijing 100081, P. R. China

Abstract

$Sm_2Fe_{17}N_x$ film magnets using a Sm_2Fe_{17} target were prepared at N_2 gas atmosphere using a Nd-YAG laser ablation technique. The effect of nitrogen pressure, deposition temperature, pulsation time and film thickness on the structure and magnetic properties of $Sm_2Fe_{17}N_x$ film were studied. Increasing the nitrogen pressure up to 5 atm. was confirmed to lead the formation of complete $Sm_2Fe_{17}N_x$ compound. Optimized magnetic properties with the nitrogenation temperature ranging over 500-530℃ could be obtained by extending the nitrogenation time up to 4 hours. Relatively low coercivities of 400~600 Oe were exhibited from the $Sm_2Fe_{17}N_x$ films having the thickness of 50~100 nm while $4\pi M_s$ of 10~12 kG could be achieved. In-plane anisotropic characteristic, which was the basic goal in this study, was achieved by controlling the nitrogenation parameters.

Key words: nanoscale films, laser ablation, permanent magnet, nitrogenation

1. Introduction

Recently the research on permanent magnet films has become a booming research activities and potential area due to their latent aims for microelectromechanical system(MEMS) and sensors applications. Accordingly the permanent magnetic properties of the film magnets are of a major concern in material selection. Lots of high-performance magnet films based on rare-earth transition compounds such as $SmCo_5$[1,2], $Sm(Co,M)_{7\sim8.5}$[3-5], $Nd_2Fe_{14}B$[6,7], $Nd(Fe,Ti)_{12}N_x$[8], $Sm_2Fe_{17}N_x$ [9~12], and also nanocomposite films such as $Nd_2Fe_{14}B/\alpha\text{-}Fe$ or Fe_3B [13~17], and $SmCo_5/Co$ [18] have been studied extensively.

In this work, the magnetic properties of nanoscaled $Sm_2Fe_{17}N_x$ films via laser ablation technique are reported. The effect of nitrogenation treatment such as N_2 gas pressure during laser deposition, substrate temperature, laser pulsation time, and the effect of film thickness on the microstructure and magnetic properties of $Sm_2Fe_{17}N_x$

films were studied. Most importantly the in-plane anisotropic characteristics must be induced in the nanoscale $Sm_2Fe_{17}N_x$ films taking into account the anticipated application for MEMS or sensors including the application for a biasing permanent magnet layer for a spin valve head of high density recording HDD. Accordingly the basic concern was focused on the high performance permanent magnetic properties in the regime where the in-plane anisotropic character exhibits. Since the target to be used is a rare earth compound single target, Nd-YAG laser pulsation was employed to make a high energy beam which will be convenient for a short time deposition.

2. Experiment

Nano-thick magnetic films of SmFeN were deposited by Nd:YAG laser ablation technique. The laser beam energy density used in this study was about 200 J/cm^2. For the ablation a single compound target of Sm_2Fe_{17} composition was used which was made by induction arc melting and subject to homogenization treatment. The nanoscale films on SiO_2 glass were deposited at room temperature at *400~600* °C followed by annealing treatment at pressurized N_2 gas atmosphere up to 5 atm. for 1~4 hours. During the nitrogenation an external magnetic field of 10 kG was applied along the in-plane direction of film samples. The thickness was controlled ranging over 50~200 nm by using the pulsation rate of 10 Hz. 'α-Step' measurement device was used to measure the thickness of films. X-ray diffraction analysis was used to identify the phase present, and the microstructure of films was characterized using a high resolution TEM. Vibrating sample magnetometer was used to measure the magnetic properties of films.

3. Results and discussion

3.1. Magnetic phase transformation

First of all, the composition of target used in this study was confirmed to be Sm_2Fe_{17} with an indication of possible presence of α-Fe. Fig.1 is X-ray diffraction spectra of $Sm_2Fe_{17}N_x$ films grown to a different thickness. The nitrogenation condition for each sample is denoted in the inset. No presence of α-Fe can be seen in the film of 50nm thick. However, the α-Fe tends to form with increasing the film thickness through 120 up to 310 nm. The magnetic phase present in the both 50 nm and 120 nm thick films was indexed perfectly to be of $Sm_2Fe_{17}N_x$ while the films of 310 nm thick indicated the presence of dual phases of Sm_2Fe_{17} and $SmFe_7$ without any clear evidence of $Sm_2Fe_{17}N_x$ formation. Indexing was not able to be clear considering that no nitorgenation took place. Anyway, the Sm_2Fe_{17} films thicker than 310 nm was shown to be very difficult to be magnetically hardened into $Sm_2Fe_{17}N_x$ at the nitrogenation temperature of 500 °C for 1 hour.

In order to investigate the nitrogenation behavior in Sm_2Fe_{17}, a comparison of X-ray patterns for 50 nm thick films heat treated for 1 and 4 hours at N_2 atmosphere, respectively, was made as shown in Fig. 2. The N_2 gas pressure was also increased for the comparison. It can be noticed that the intensity of diffraction peaks from the identical plane increases with extending the duration of nitrogenation time. The relatively wide range of bump shown at low angle side in Fig. 2 was confirmed to be from SiO_2 glass substrate. Since the best magnetic properties of $Sm_2Fe_{17}N_x$ films were obtained around 500 °C in this study the following discussions are focused on only the samples nitrogenated at 500 °C. Particularly $Sm_2Fe_{17}N_x$ films treated at higher than 560 °C were found to decompose back into Sm_2Fe_{17} and α-Fe.

3.2. The effect of nitrogenation parameters on nano-thick $Sm_2Fe_{17}N_x$ films

The relationship between the magnetic properties of $Sm_2Fe_{17}N_x$ films along in-plane and nitrogen pressure under 500 °C × 1 hour nitrogenation condition is shown in Fig. 3. It is clearly shown that the saturation magnetization($4\pi M_s$) and coercivity(H_c) increase while the remanence($4\pi M_r$) decreases with increasing the N_2 gas pressure up to 2.5 atm. It shows that at a low N_2 pressure nitrogenation makes the saturation magnetization and coercivity increase rapidly. However, both the saturation, remanent magnetization, and the coercivities become almost invariant when the N_2 gas pressure is higher than 2.5atm. According to this result the influence of N_2 pressure, if the pressure is higher than a critical value, seems not to be effective on transformation from Sm_2Fe_{17} to $Sm_2Fe_{17}N_x$ at a certain nitrogenation treatment. Comparison of hysteresis curves for the samples treated at a different N_2 pressure was made, and shown in Fig. 4. As was expected anisotropy along in-plane direction is prominent. For the sample nitrogenated at 0.8 atm. of N_2 exhibits the character of soft magnetic phase. This is because Sm_2Fe_{17} phase seems not be transformed into $Sm_2Fe_{17}N_x$ yet. However, the other samples treated at 2.5 and 5 atm. of N_2, respectively, look almost identical hysteresis without changing the anisotropy by the N_2 pressure. Consequently M_r/M_s ratio was measured to be almost invariant.

The effect of film thickness on the magnetic properties along in-plane of the films transformed at 500 °C x 1 h x 5 atm. N_2 condition is shown in Fig.5. Both the saturation($4\pi M_s$) and remanence($4\pi M_r$) increase up to 13 and 12 kG, respectively, with increasing the film thickness, while the coercivity decreases continuously below 100 Oe when the thickness is more than 120 nm. This means that the Sm_2Fe_{17} films hardly transform into $Sm_2Fe_{17}N_x$ when the thickness is thicker than 120 nm. Above the thickness of 160 nm, the films were found to remain Sm_2Fe_{17} as shown in Fig. 6(a) and (b). Analyzing the results exhibited in Fig. 5 and 6, one can notice that the M_r/M_s ratio, which is denoted by the open circle's curve in Fig. 5, tend to increase with increasing the thickness. The ratio. This is because the films tend to remain as Sm_2Fe_{17} exhibiting a soft magnetic character. Also it would be very possible that the existing $Sm_2Fe_{17}N_x$ phase decomposes into Sm_2Fe_{17} + (α-Fe) as suggested in Fig. 1. Therefore the microstructure, i.e, texture of $Sm_2Fe_{17}N_x$ films could change with increasing the thickness which is a function of deposition time.

To study the effect of thickness of the films, i.e, the variation of texture, the films of 50 nm thick treated at 500 °C x 2.5 atm. of N_2 were analyzed by varying the nitrogenation time, and the results are shown in Fig. 7. Before the nitrogenation take place, the $4\pi M_s$ of soft magnetic Sm_2Fe_{17} films shows much lower value around 9 kG, and $4\pi M_r$ is rather low about 5.5 kG where the squareness must be high due to its soft magnetic character. Once the nitrogenation goes on the $4\pi M_s$ enhances due to the formation of $Sm_2Fe_{17}N_x$, and the $4\pi M_r$ tend to decrease slowly due to the magnetic hardening. This analogy can be rationalized also in terms of the abrupt increase from 1.5 kOe to 9 kOe of coercivity right after the nitrogenation takes place. However, the maximized $4\pi M_s$ and H_c tend to drop after 1 hour without a prominent variation in $4\pi M_r$. This means that a significant textural change start to take place with a prolonged nitrogenation. To investigate the change of texture in detail, a comparison was made between in-plane and perpendicular measurement of the films nitrogenated at 500 °C x 2.5 atm. N_2 for 2h, 4h and virgin Sm_2Fe_{17} sample, respectively, and the results are shown in Fig. 8. Virgin Sm_2Fe_{17} films, which initially showed in-plane anisotropies, tend to change their texture by extending the duration of nitrogenation time as shown in Fig. 8(b) and (c). By the prolonged time of N_2 treatment the hysteresis curves measured in-plane direction tend to lie down while the curves measured along perpendicular direction tend to show a strong coercive force which is definitely due to the change of texture. Fig. 9 shows the variation of coercivity measured along both the in-plane and perpendicular directions. Up to the thickness of 80 nm, coercivities along in-plane direction were measured to be superior to those of perpendicular direction. However, this result was reversed with increasing the thickness of films due to the textural change, and the out-of plane anisotropy becomes prominent. Fig. 10 shows the typical nano-scaled microstructure of films nitrogenated at 500 °C for 4 hours at N_2 pressure of 2.5 atm. Basically (0001) $Sm_2Fe_{17}N_x$ grains are shown to be prominent. However, (0110) $Sm_2Fe_{17}N_x$ and (001) Fe grains are also shown to be present around the area focused at center region.

4. Summary

$Sm_2Fe_{17}N_x$ film magnets using a Sm_2Fe_{17} single target was possible to be grown by laser ablation technique. The effect of nitrogen pressure and deposition temperature, were found to be very influential on the performance of nitrogenation of Sm_2Fe_{17} films into $Sm_2Fe_{17}N_x$. Besides the deposition time, i.e., the film thickness was confirmed to be decisive on the anisotropic texture of $Sm_2Fe_{17}N_x$ films. By controlling the N_2 pressure from 1~4 atm. and nitriding temperature about 500~530 °C, an in-plane anisotropy was obtainable from the films up to 80 nm thick. However, the in-plane anisotropy changes to out-of-plane due to the textural change for the thicker films. $Sm_2Fe_{17}N_x$ films with $4\pi M_s$ of 13 kG, $4\pi M_r$ of 12 kG, and coercivty(H_c) of 550 Oe were obtained by the optimized nitrogenation treatment. However, H_c of 550 Oe seems to be still low compared to that of bulk $Sm_2Fe_{17}N_3$ compound. One of the reasons for those low values was found to be the oxidation of films during the laser ablation of Sm_2Fe_{17} films, which was very difficult to avoid.

Acknowledgement

The authors would like to thank for the supports from The Research Center for Advanced Magnetic Materials at Chunnagm National University under Contract No. of 2000D004, and from The Korean Ministry of Science & Technology under contract No. of 99E006 to carry out the present study.

References

[1] F. J. Cadieu, T. D. Cheung, S. H. Aly, L. Wickramasekara and R. C. Pirich, IEEE Trans. on Magn. Mag-19 (1983) 2038
[2] F. J. Cadieu, R. Rain, T. Theodoropoulos and Li Chen, J. Appl. Phys. 85 (1999) 5895
[3] H. Hegde, S. U. Jen, K. Chen and F. J. Cadieu, J. Appl. Phys. 73 (1993) 5926
[4] V. Neu and S. A. Shaheen, J. Appl. Phys. 86 (1999) 7006
[5] F. J. Cadieu, H. Hegde and K. Chen, IEEE Trans. on Magn. 25 (1989) 3788
[6] Choong Jin Yang, Sang Won Kim and Jong Seog Kang, J. Appl. Phys. 83 (1998) 6620
[7] J. L. Tsai, E. Y. Huang, T. S. Chin and S. K. Chen, IEEE Trans. on Magn. 33 (1997) 3646
[8] A. Navarathna, H. Hegde, R. Rani, K. Chen, and F. J. Cadieu, IEEE Trans. on Magn. 29 (1993) 2812
[9] P. W. Jang, D. Wang and W. D. Doyle, J. Appl. Phys. 81 (1997) 4664
[10] D. Wang, G. C. Hadjipanayis and D. J. Sellmyer, IEEE Trans. on Magn. 28 (1992) 2590
[11] R. Rnai, H. Hegde, A. Navarathna and F. J. Cadieu, J. Appl. Phys. 73 (1993) 6023
[12] Jae Man Song, Hiroyuki Sadakata, Masaki Nakano, Yasuhisa Kanai, Hirotoshi Fukunaga and Jae Gui Koh, IEEE Trans. on Magn. 35 (1999) 3052
[13] Choong Jin Yang and Song Won Kim, J. Magn. Magn. Mater. 202 (1999) 311
[14] Choong Jin Yang and Eon Byung Park, J. Magn. Magn. Mater. 168 (1997) 278
[15] Choong Jin Yang and Eon Byung Park, J. Magn. Magn. Mater. 166 (1997) 243
[16] Youhui Gao, Jinghan Zhu, Yuqing Weng, Eon Byung Park and Choong Jin Yang, J. Magn. Magn. Mater. 191 (1999) 146
[17] Youhui Gao, Jinghan Zhu, Choong Jin Yang and Eon Byung Park, J. Magn. Magn. Mater. 186 (1998) 97
[18] J. P. Liu, R. Skomski and D. J. Sellmyer, J. Appl. Phys. 85 (1999) 4812

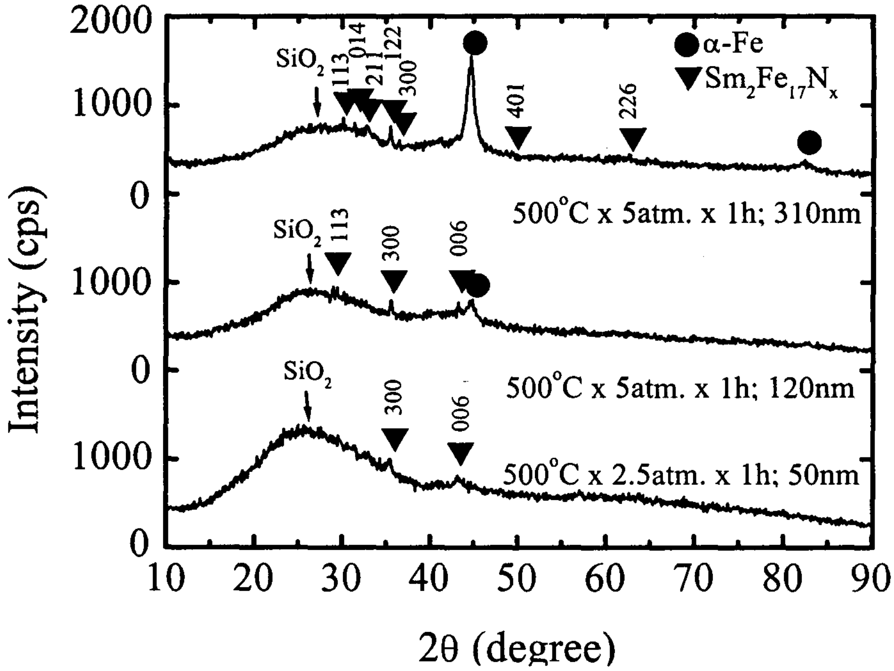

Fig.1 X-ray diffraction pattern of $Sm_2Fe_{17}N_x$ film of different thickness

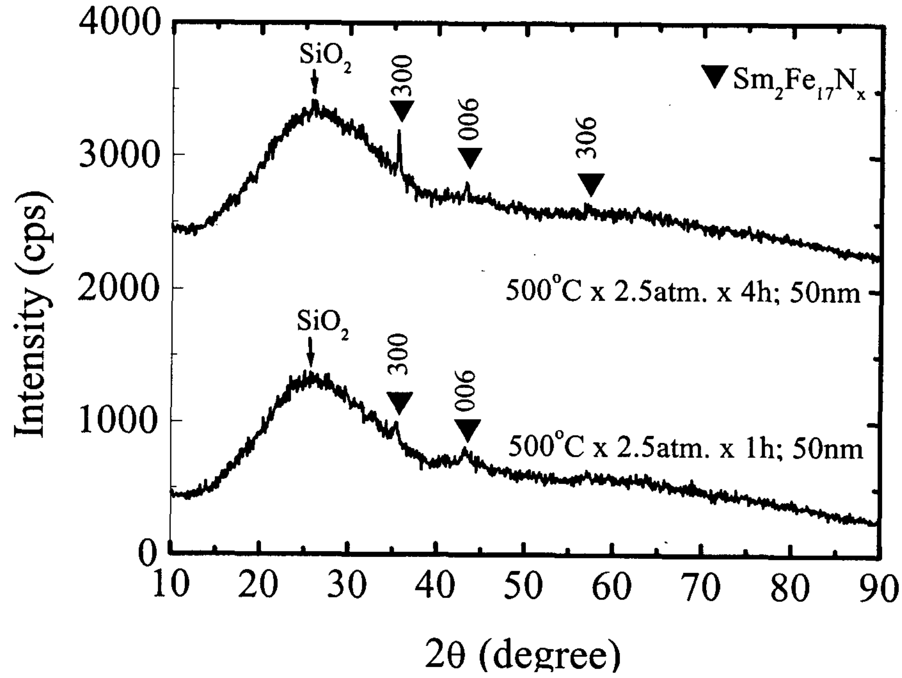

Fig.2 X-ray diffraction pattern of $Sm_2Fe_{17}N_x$ films treated at different nitrogenation time

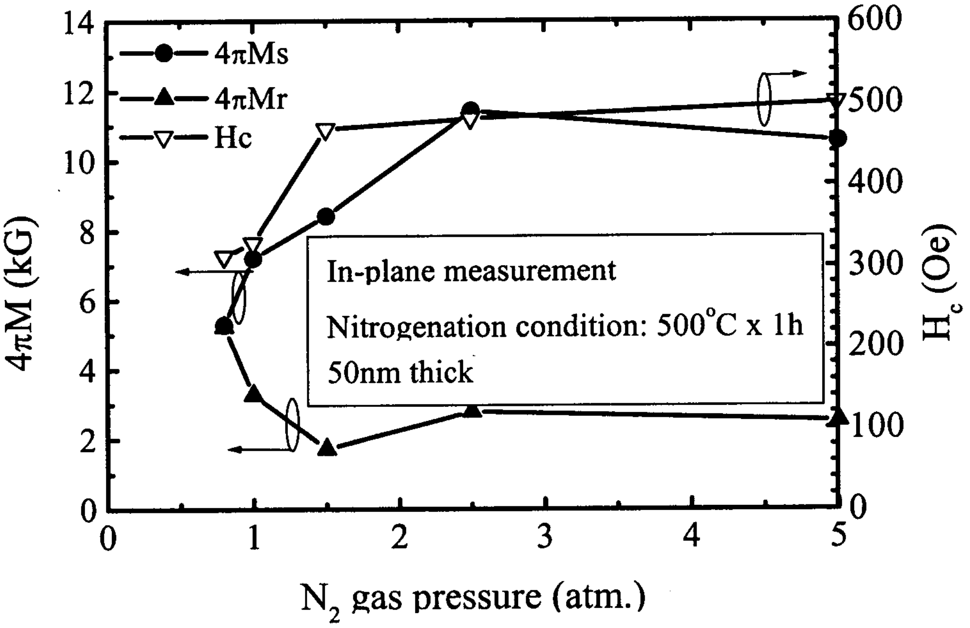

Fig.3 Effect of N_2 gas pressure on the magnetic properties along in-plane of films

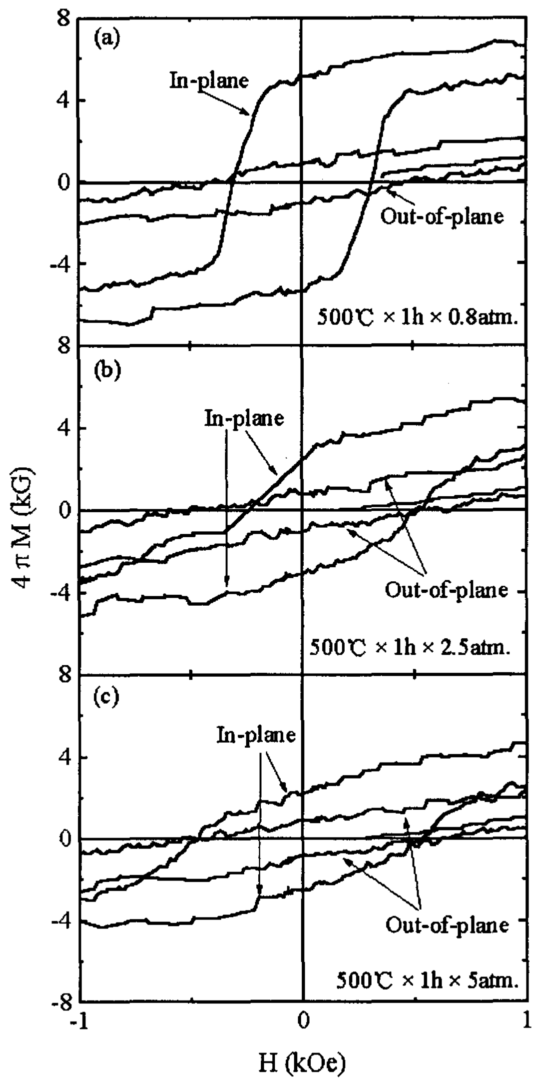

Fig.4. Effect of N_2 pressure on the hysteresis curve along in-plane and out-of-plane of films with 50 nm thick

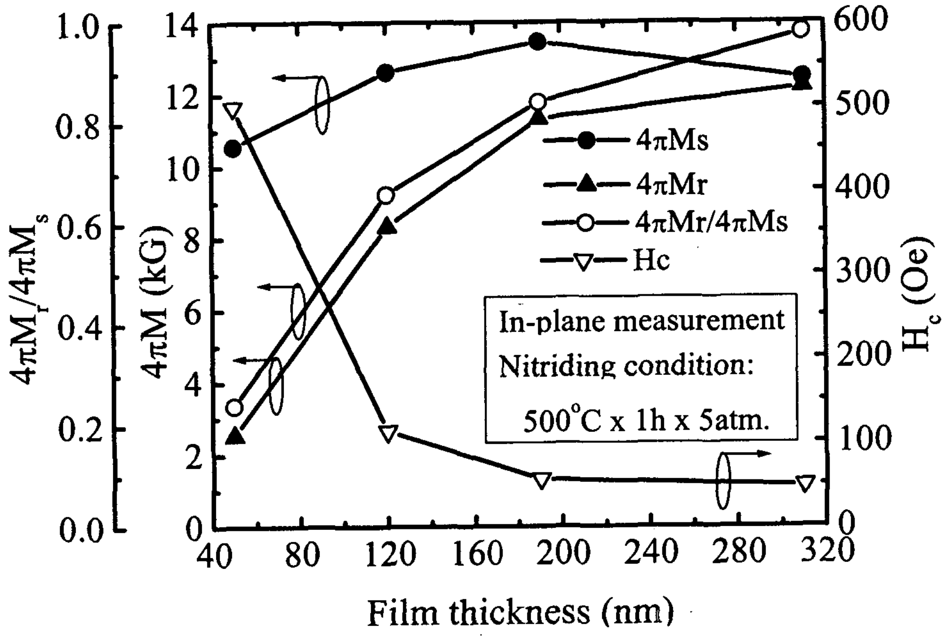

Fig.5 Effect of film thickness on the magnetic properties along in-plane of films

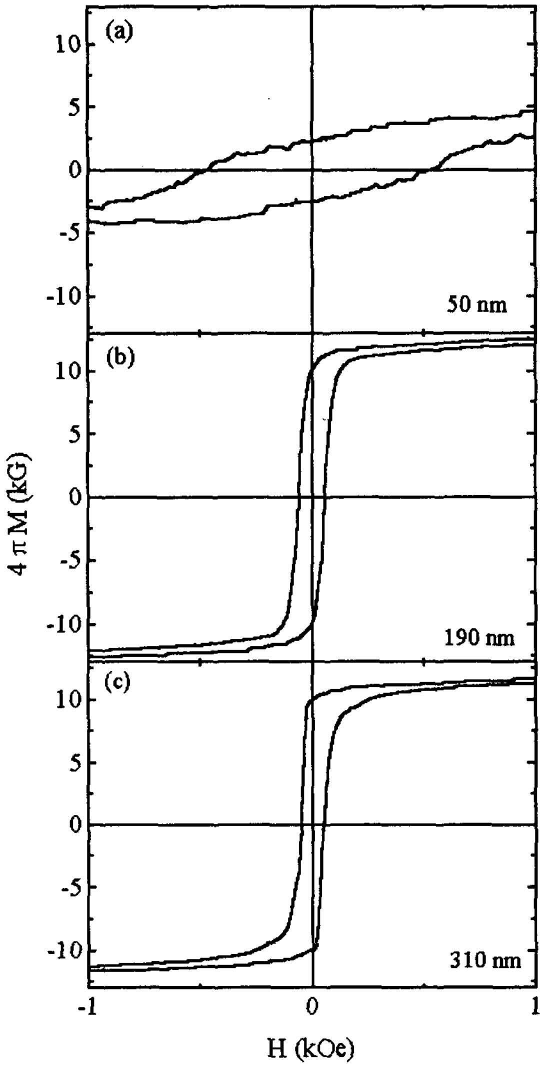

Fig.6 Effect of film thickness on the hysteresis curve along in-plane of films nitrogenated at 500¡ æfor 1 hr at 5 atm. N_2

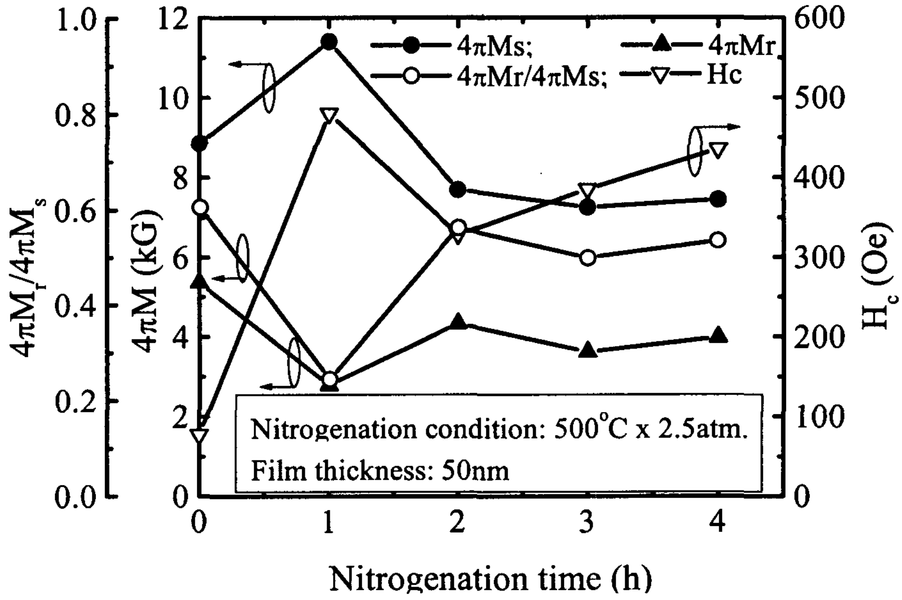

Fig.7 Effect of nitrogenation time on the magnetic properties along in-plane of films.

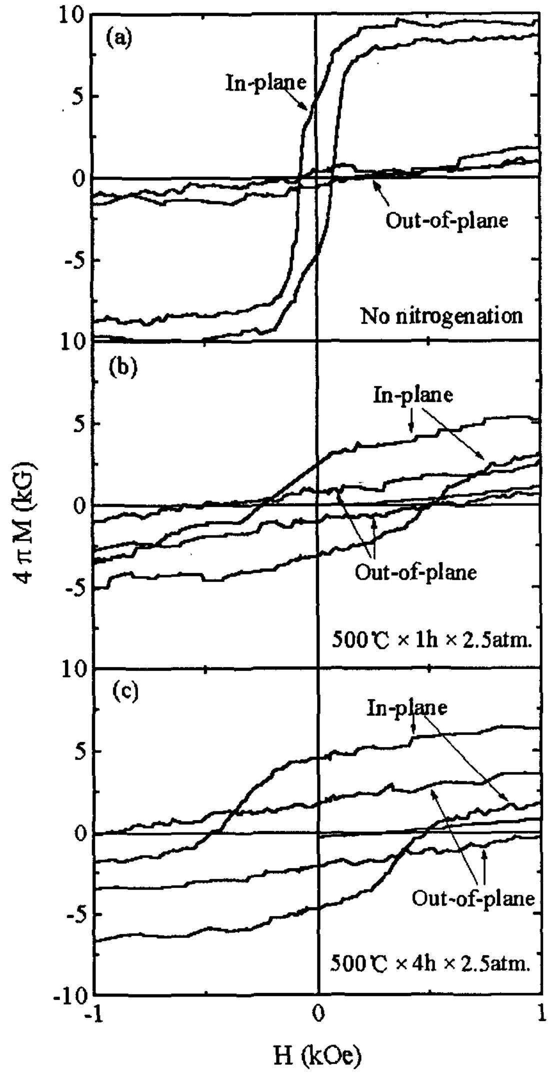

Fig.8 Effect of nitrogenation time on the hysteresis curve along in-plane and out-of-plane of films of 50 nm

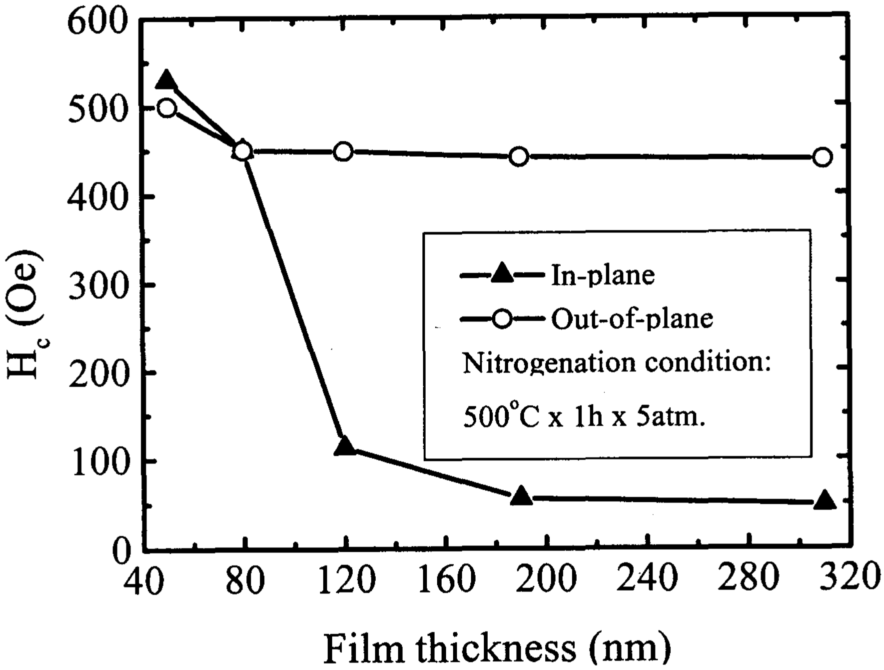

Fig. 9 Effect of film thickness on the coercivity along in-plane and out-of-plane

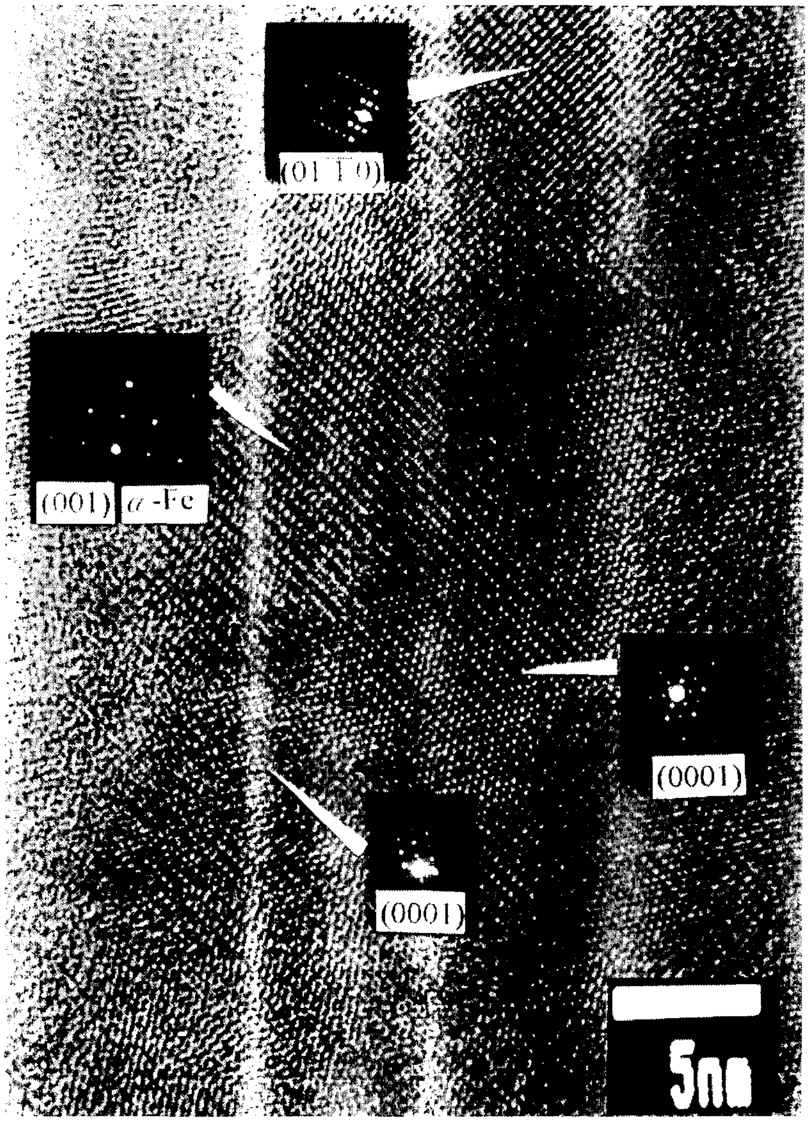

Fig. 10 Typical MicrosTructure of Nano-Thick $Sm_2Fe_{17}N_x$ films Nitrogenated at Optimized Condition.