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Magnetic Hardening of Nano-thick $Sm_2Fe_{17}N_x$ Films Grown by Pulsed Laser Deposition

Choong Jin Yang and Jianmin Wu[1]

Electromagnetic Materials Lab., Research Institute of Industrial Science and Technology (RIST), P. O. Box 135, 790-330 Pohang, South Korea
[1]Dept. 2, Central Iron and Steel Research Institute, Beijing 100081, P. R. China

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$Sm_2Fe_{17}N_x$ film magnets were prepared using a Sm_2Fe_{17} target in a N_2 gas atmosphere using a Nd-YAG pulsed laser ablation technique. The effect of nitrogen pressure, deposition temperature, pulse 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 led to the formation of complete $Sm_2Fe_{17}N_x$ compound. Optimized magnetic properties with the nitrogenation temperature in the range 500-530 °C could be obtained by extending the nitrogenation time up to 4 hours. Relatively low coercivities of 400~600 Oe were found in $Sm_2Fe_{17}N_x$ films 50~100 nm thick, while a $4\pi M_s$ of 10~12 kG could be achieved. In-plane anisotropy, which was the basic goal in this study, was achieved by controlling the nitrogenation parameters.

1. Introduction

There has been a recent boom in research on permanent magnet films, due to their potential use in microelectromechanical system (MEMS) and sensor applications. The permanent magnetic properties of the film magnets are a major concern in material selection. Many 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 $Nd_2Fe_{14}B$/a-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 produced by laser ablation are reported. The effect of nitrogenation treatments 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, in-plane anisotropy must be induced in the nanoscale $Sm_2Fe_{17}N_x$ films for the anticipated applications in MEMS or sensors, including the application for a biasing permanent magnet layer for a spin valve head in a high density recording hard disk drive. Accordingly, our attention was focused on the high performance permanent magnetic properties in the regime where an in-plane anisotropy can be developed. 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 permits rapid deposition.

2. Experiment

Nano-thick magnetic films of SmFeN were deposited by a 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 composition Sm_2Fe_{17} was used. The target was made by plasma arc melting and was subjected to a homogenization treatment. The nanoscale films were deposited on SiO_2 glass at room temperature, and were annealed at 400~600 °C in a pressurized N_2 gas atmosphere with pressure up to 5 atm for 1 to 4 hours. During the nitrogenation an external magnetic field of 10 kG was applied paralled to the plane of the film samples which was intended to develop magnetic anisotropy during the formation of the nitride phase. The film thickness was controlled ranging over 50~200 nm by controlling the number of laser pulses at a pulse rate of 10 Hz. An 'α-Step' measurement device was used to measure the thickness of the films. X-ray diffraction analysis (Cu K_α) was used to identify the phases present, and the microstructure of films was characterized using high resolution TEM. A vibrating sample magnetometer was used to measure the magnetic properties of films in both the in-plane and perpendicular directions.

3. Results and Discussion

3.1. Magnetic phase transformation

The target used in this study was confirmed to consist of single phase Sm_2Fe_{17} with very small amount of α-Fe. Fig.

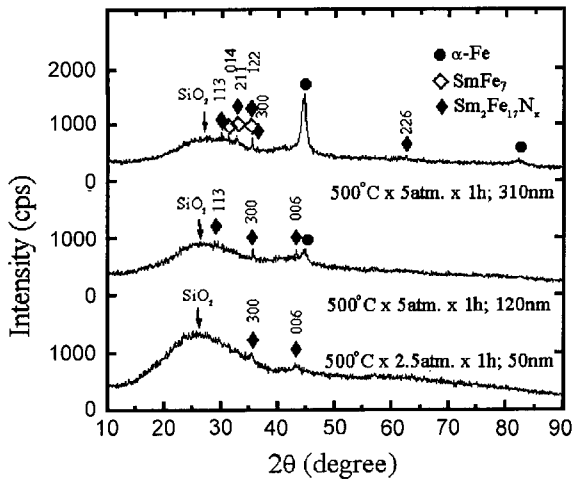

Fig. 1. X-ray diffraction patterns of $Sm_2Fe_{17}N_x$ film with different thickness.

1 shows x-ray diffraction spectra of $Sm_2Fe_{17}N_x$ films grown to different thicknesses. The nitrogenation condition for each sample is shown in the inset. No α-Fe is detected in the 50 nm film. However, α-Fe tends to form with increasing film thickness through 120 up to 310 nm. The magnetic phase present in the both 50 nm and 120 nm thick films was perfectly indexed to be $Sm_2Fe_{17}N_x$, while the films of 310 nm thick indicated the presence of both $Sm_2Fe_{17}N_x$ and $SmFe_7$ with no clear evidence of Sm_2Fe_{17} formation. Indexing was not conclusive since the $Sm_2Fe_{17}N_x$ and $SmFe_7$ phases show almost identical reflecting planes, as shown in Table 1 and 2, respectively. However, the coercivities of films with thicknesses more than 200 nm always showed low values of less than 60 Oe. These results might be due not only to the incomplete nitrogenation from Sm_2Fe_{17} to $Sm_2Fe_{17}N_x$ but also to the presence of $SmFe_7$ as is suggested by the x-ray pattern in Fig. 1.

In order to investigate the nitrogenation behavior of Sm_2Fe_{17}, a comparison of x-ray patterns for 50 nm thick films heat treated for 1 and 4 hours under 2.5 atm N_2 atmosphere, respectively, was made as shown in Fig. 2. It can be noticed that the intensity of the diffraction peaks from the identical plane increases with the nitrogenation time. The transformation from Sm_2Fe_{17} to $Sm_2Fe_{17}N_x$ would take time to be completed which is indicated by the intensity of reflected peaks. Since the best magnetic properties of $Sm_2Fe_{17}N_x$ films were obtained after annealing around 500 °C in this study, the following discussion is focused only on the samples nitrogenated at 500 °C.

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 direation and N_2 pressure nitrogenated at 500 °C for 1 hour is shown in Fig. 3. It is clearly shown that the saturation magnetization ($4\pi M_s$) and

Table 1. X-ray diffraction data indexed to $Sm_2Fe_{17}N_x$ and α-Fe

No	X-ray diffraction Measurement Result			$Sm_2Fe_{17}N_3$ JCPDS Standard Card			α-Fe JCPDS Standard Card		
	d (Å)	2θ (degree)	I/I_0	hkl	D (Å)	I/I_0	hkl	d (Å)	I/I_0
1	3.0315	29.440	100	113	3.0360	29			
2	2.5253	35.520	86	300	2.5240	39			
3	2.0888	43.280	83	006	2.1090	28			
4	2.0214	44.880	87				110	2.0268	100

Table 2. X-ray diffraction data indexed to $SmFe_7$ and α-Fe

No	X-ray diffraction Measurement Result			$SmFe_7$ JCPDS Standard Card			α-Fe JCPDS Standard Card		
	d (Å)	2θ (degree)	I/I_0	hkl	D (Å)	I/I_0	hkl	d (Å)	I/I_0
1	2.9761	30.000	55	113	2.969	65			
2	2.8501	31.360	52	014	2.858	35			
3	2.7282	32.800	53	211	2.725	16			
4	2.5308	35.440	48	122	2.548	16			
5	2.4715	36.320	40	300	2.465	65			
6	2.1893	41.200	41						
7	2.0248	44.720	100				110	2.0268	100
8	1.8448	49.360	32						
9	1.5633	59.040	29						
10	1.4835	62.560	29	226	1.489	100			
11	1.1732	82.080	24				211	1.1702	30

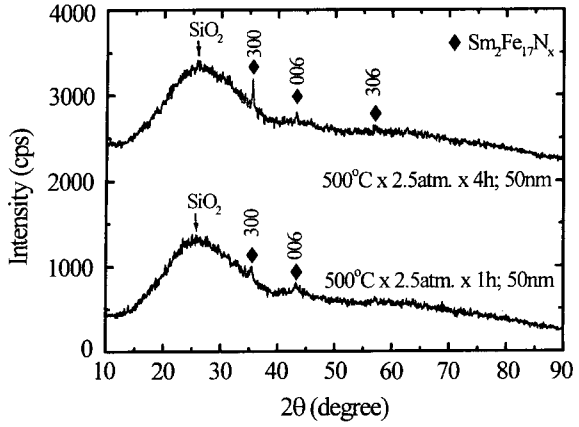

Fig. 2. X-ray diffraction patterns of $Sm_2Fe_{17}N_x$ films treated with different nitrogenation times.

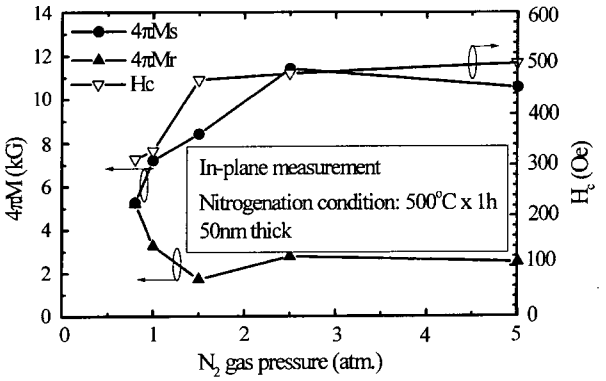

Fig. 3. Effect of N_2 gas pressure on the magnetic properties along in-plane of films.

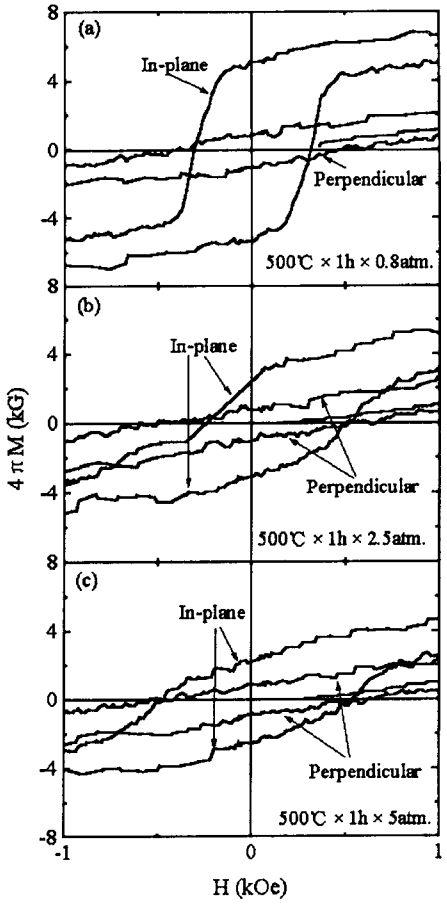

Fig. 4. Effect of N_2 pressure on the hysteresis loop in-plane and perpendicular to the films 50 nm thick.

coercivity (H_c) increase while the remanence ($4\pi M_r$) decreases with increasing N_2 gas pressure up to 2.5 atm. A low N_2 pressure, nitrogenation makes the saturation magnetization and coercivity increase rapidly. However, both the saturation, remanent magnetization, and the coercivity become almost constant when the N_2 gas pressure is higher than 2.5 atm. According to this result, the influence of N_2 pressure, above a critical value seems not to be effective in the transformation from Sm_2Fe_{17} to $Sm_2Fe_{17}N_x$ at 500°C. Comparison of hysteresis loops for samples treated at different N_2 pressures was made, as shown in Fig. 4. As was expected, anisotropy along in-plane direction is prominent. The sample nitrogenated at 0.8 atm of N_2 exhibits the character of a soft magnetic phase. This is because the Sm_2Fe_{17} phase seems not be transformed into $Sm_2Fe_{17}N_x$ yet. However, the samples treated at 2.5 and 5 atm of N_2 seem to show almost identical hysteresis. Consequently the M_r/M_s ratio was almost invariant.

The effect of film thickness on the magnetic properties along in-plane direction of the films processed at 500 °C for 1 hour under 5 atm of N_2 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 to values below

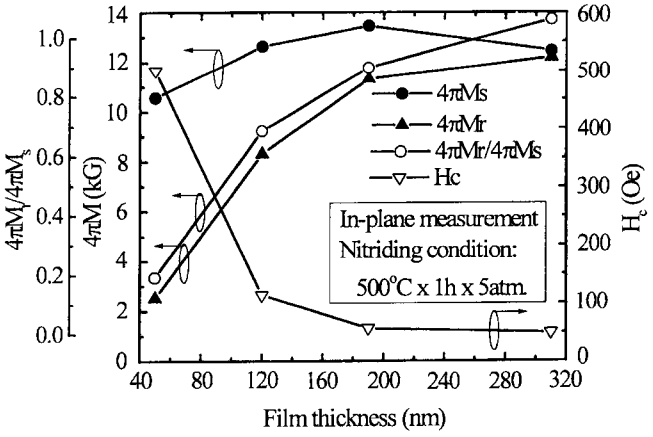

Fig. 5. Effect of film thickness on the in-plane magnetic properties.

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 indicated in Fig. 6(a) and (b). Analyzing the results exhibited in Fig. 5 and 6, one can notice that the $4\pi M_r/4\pi M_s$ ratio, which is denoted by the open circles curve in Fig. 5, tends to increase with increasing the thickness. This is because the films tend to remain as Sm_2Fe_{17},

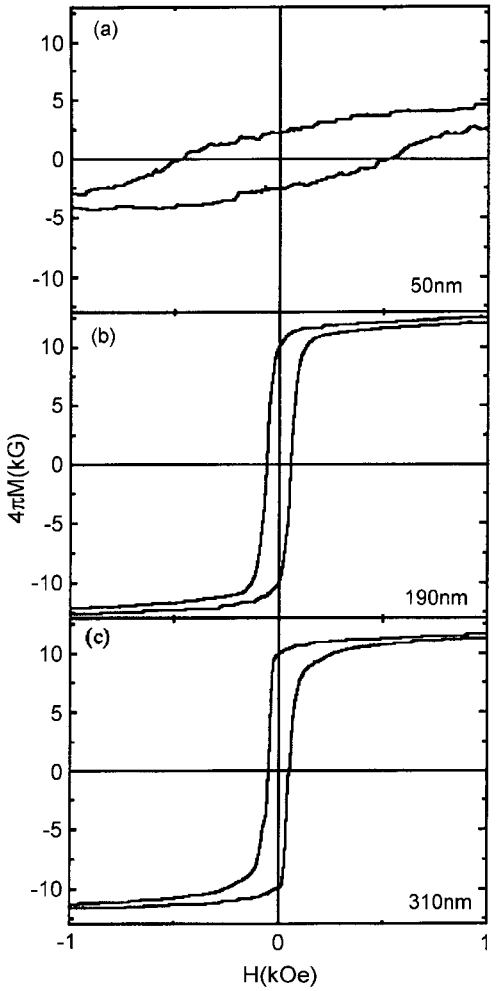

Fig. 6. Effect of film thickness on the in-plane hysteresis loop of films nitrogenated at 500 °C for 1 hr under 5 atm N_2.

exhibiting a soft magnetic character.

The microstructure, or more precisely the crystallographic texture, of $Sm_2Fe_{17}N_x$ films could be dependent upon the thickness of films, which is also a function of deposition time. To study the effect of film thickness, i.e, the variation of texture, the films of 50 nm thick were treated at 500 °C under 2.5 atm of N_2 for various time periods, and the results are shown in Fig. 7. Before the nitrogenation takes place, $4\pi M_s$ of the soft magnetic Sm_2Fe_{17} films shows a value around 9 kG, and $4\pi M_r$ is rather low at about 5.5 kG, where as the squareness should be high due to the soft magnetic character. Once nitrogenation occurs, the value of $4\pi M_s$ increases due to the formation of $Sm_2Fe_{17}N_x$, and $4\pi M_r$ tends to decrease slowly due to the magnetic hardening. The coercivity increases abruptly from 100 Oe to 450 Oe after nitrogenation takes place. However, the high values of $4\pi M_s$ and H_c tend to drop after 1 hour, with as substrantial variation in $4\pi M_r$. This means that texlural change occurs with prolonged nitrogenation. To investigate the change of texture in detail, a comparison was made between in-plane and perpendicular measurement of films nitrogenated at 500 °C under 2.5 atm of N_2 for 2h and 4h,

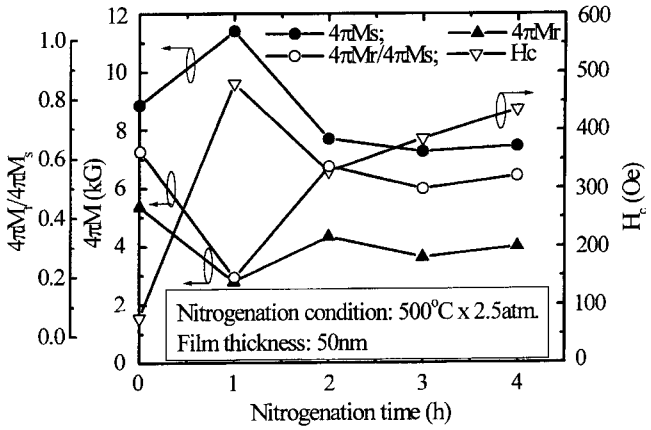

Fig. 7. Effect of nitrogenation time on the magnetic properties along in-plane of films.

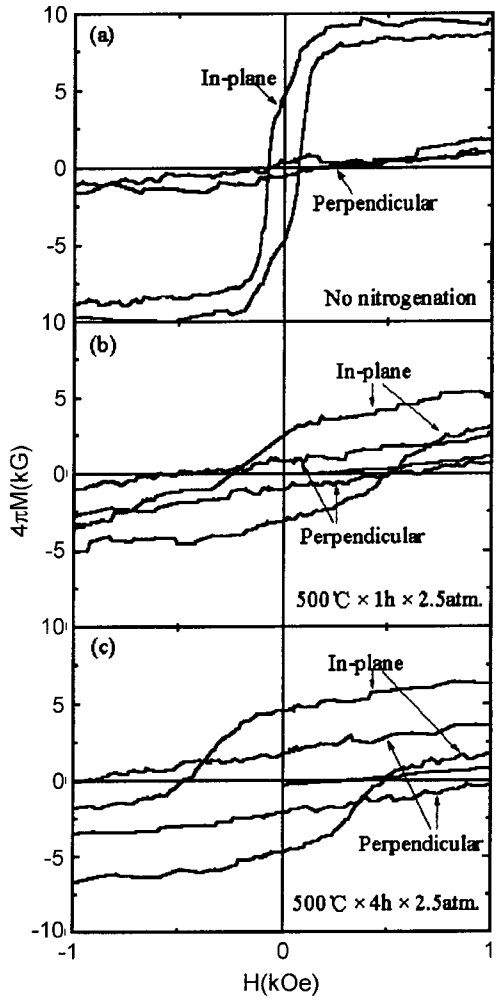

Fig. 8. Effect of nitrogenation time on the hysteresis lopp in-plane and perpendicular to 50 nm films.

and a virgin Sm_2Fe_{17} sample, respectively, and the results are shown in Fig. 8. The virgin Sm_2Fe_{17} films, which initially showed in-plane anisotropy, tend to change their texture during nitrogenation, as shown in Fig. 8(b) and (c). with prolonged time of N_2 treatment the hysteresis curves measured in-plane tend to decrease in magnitade while the

curves measured in the perpendicular direction tend to show a large coercive field which is partly due to the change of texture. If Fig. 2 is examined carefully, the reflected intensity of the (003) plane is seen to become prominent after a prolonged nitrogenation time of 4 hours. Accordingly there must be some textural change with the duration of nitrogenation.

Fig. 9 shows the variation of coercivity measured along both in-plane and perpendicular to the film. Up to a thickness of 80 nm, coercivities along in-plane were larger than those in the perpendicular direction. However, this result was reversed with increasing film thickness due to the textural change, and the out-of plane anisotropy becomes prominent. Note that an external magnetic field was applied in-plane during the nitrogenation process to influence the magnetic anisotropy of the films. Of course applying an external field of 10 kG in the paramagnetic range of the $Sm_2Fe_{17}N_x$ phase is expected be ineffective. The magnetic anisotropy of films in the range up to 80 nm thick favored in-plane magnetization, as defermined by repeated experiments.

Recently, there have been many research reports on the effects of high magnetic fields about 10 Tesla applied to Fe-based alloy steel [19, 20]. This externally applied field along a certain direction facilitated the textural formation of ultra fine (about 1 μm) ferrite grains along the field direction. The mechanism was explained to be due to the reduction in diffusion speed of Fe atoms in the range of increased magnetic transformation temperature from ferrite(α) to austenite(γ)s by the applied magnetic field. Accordingly, we believe that the in-plane anisotropy induced by the applied field in films up to 80 nm thick was caused by the same effect. As shown in Fig. 9, taking into account the abrupt drop of the coercivity with increasing the film thickness, the induced anisotropy might be due to the applied magnetic field, not by the shape anisotropy. Fig. 10 shows the typical nano-scaled microstructure of films nitrogenated at 500 °C

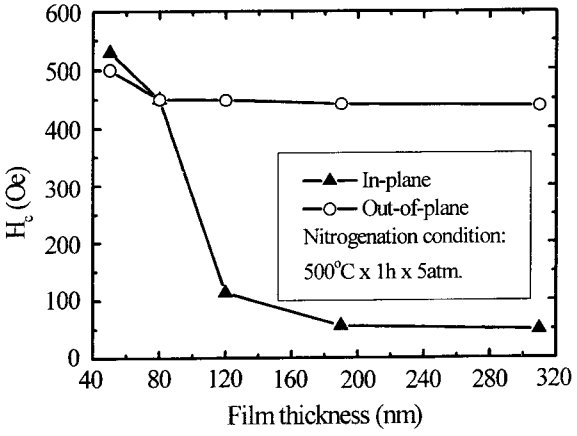

Fig. 9. Effect of film thickness on the coercivity in-plane and perpendicular to the film.

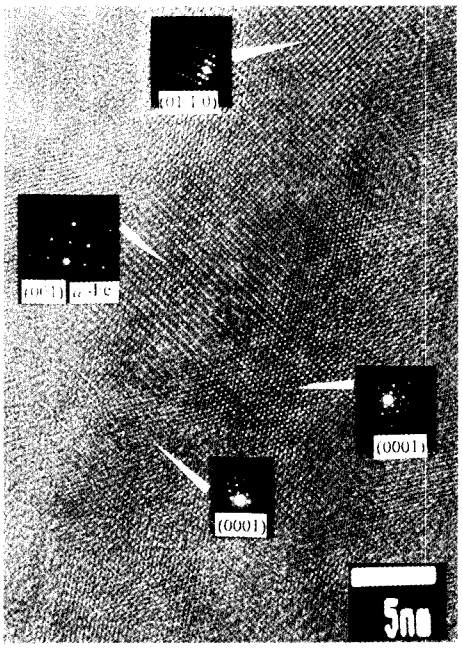

Fig. 10. Typical high resolution TEM microscope of the sample nitrogenated at 500 °C for 4 hours under 2.5 atm of N_2.

for 4 hours under N_2 pressure of 2.5 atm. Basically (001) $Sm_2Fe_{17}N_x$ grains are shown to be prominent as was suggested in Fig. 2 and Fig. 9. However, (010) $Sm_2Fe_{17}N_x$ and (001) Fe grains are also shown to be present around the center region.

Summary

$Sm_2Fe_{17}N_x$ film magnets were grown by a laser ablation technique using a single Sm_2Fe_{17} target. Nitrogen pressure and deposition temperature were found to be very influential on the nitrogenation of Sm_2Fe_{17} films into $Sm_2Fe_{17}N_x$. In addition, the deposition time (i.e., the film thickness) was shown to be decisive on the development of anisotropic texture in $Sm_2Fe_{17}N_x$ films. By controlling the N_2 pressure from 1 to 4 atm and the nitriding temperature at about 500~530 °C, an in-plane anisotropy was obtainable in the films up to 80 nm thick with the aide of an externally applied magnetic field. However, the in-plane anisotropy changes to out-of-plane due to the textural change in thicker films. $Sm_2Fe_{17}N_x$ films with $4\pi M_s$ of 13 kG, $4\pi M_r$ of 12 kG, or coercivity (H_c) of 550 Oe were obtained by an optimized nitrogenation treatment although not all three values could be obtained in the same sample. However, an H_c of 550 Oe is still low compared to that of bulk $Sm_2Fe_{17}N_3$. One of the reasons for the 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. Also the presence of $SmFe_7$ phase, which was not clearly distinguished from the $Sm_2Fe_{17}N_x$ phase, might also be a reason why the films exhibited relatively low values of coercivity.

Acknowledgement

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