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Studies on NdFeB thin films over a wide composition range

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Abstract

The magnetic properties of NdFeB thin films have been studied over a wide range of composition. A detailed study on the effect of composition and other process parameters on the magnetic and structural properties of NdFeB thin films is also presented. An investigation into the effect of the substrate revealed that substrates containing oxygen may not be suitable for preparing these thin films. The coercive force as well as the microstructure of these films were found to depend on the thickness. The composition dependence of coercive force, saturation magnetization and the energy product ($B_r \times H_c$) are shown by three dimensional bar diagrams. High coercive force and high energy product were observed at Nd concentrations slightly higher than that of the stoichiometric composition.

Keywords: Annealing; $Nd_2Fe_{14}B$; Hard magnetic thin films; High energy product; High coercive force

1. Introduction

High coercive materials like $Nd_2Fe_{14}B$ are being studied extensively by the researchers since the last decade [1–6]. These materials, in the bulk form, have the highest ever commercial BH product and yet, various studies have been carried out to improve the BH product as well as the other physical properties of these materials. On the other hand, the investigations on these materials in the form of thin films are comparatively less. This is in spite of the fact that films with high B–H products are required for the Micro Electric Mechanical Systems (MEMS) of the future [7–16]. We have been carrying out studies on $Nd_2Fe_{14}B$ thin films in the recent past [17,18]. In this report, we present the study of magnetic properties of NdFeB thin films over a wide concentration range. This study is important as a study on the composition dependence of magnetic properties of NdFeB thin films is not available in the literature. Moreover, it is beneficial to investigate NdFeB thin films with less rare earth content and try out the possibility of forming the exchange spring magnets [19,20].

2. Experimental techniques

A facing targets sputtering system was used to deposit the films in this study. The facing targets were Fe metal of 99.9% purity. The composition of the films was varied by changing the number of Nd and B chips (99.9% purity) which were placed only on the bottom Fe target. The base pressure prior to sputtering was below 2×10^{-6} Torr. During sputtering, the sputter gas (Ar) pressure was maintained at 3×10^{-3} Torr. A dc power of about 150 W was applied and the deposition rate was found to be about 3000 Å h^{-1}. Presputtering was done for about 1 h to eliminate any oxidation that has occurred on the surface of the Nd chips. Thermally oxidised Si (shall be referred to as SiO_2/Si in further discussions) and metallic foils such as Ta and Mo were used as the substrates. The deposition condition of the substrate ranged from no heating to heating the substrates to 650°C. Thickness was measured with a surface profilometer. The magnetization data was obtained using a vibrating sample magnetometer (VSM). Composition was measured by electron probe micro-analysis (EPMA). X-ray diffraction (XRD) was used to identify the phases and SEM was used to observe the microstructure of the films.

3. Post-deposition annealing

For commercial production, it is desirable to deposit films at ambient temperatures and to do a post-deposition annealing to obtain the required phase. Therefore, as a first step, we attempted to deposit the films without substrate heating and to do post-deposition annealing to obtain $Nd_2Fe_{14}B$ phase.

Initially, 2000 Å thick films were deposited on SiO_2/Si

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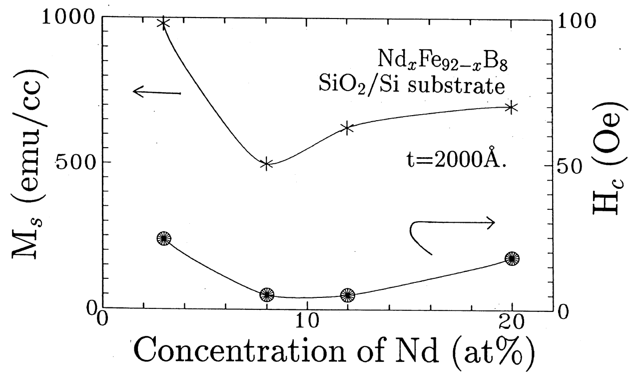

Fig. 1. The saturation magnetization and coercivity values of as-deposited $Nd_xFe_{92-x}B_8$ thin films.

substrates. The films with higher Nd and B concentration (more than 10 at. %) were found to be X-ray amorphous. However, the XRD of films with a low Nd and B concentration showed a peak corresponding to α-Fe indicating the presence of bcc-Fe phase. The films also exhibited soft magnetic properties with high saturation magnetization (M_s) and a low coercive force (H_c) as shown in Fig. 1.

In order to crystallize the films and to obtain the $Nd_2Fe_{14}B$ phase, annealing was carried out at different temperatures at a pressure of 10^{-6} Torr. Annealing was done with a Kanthal heater and the annealing temperature was measured by a thermocouple which was in contact with the film.

The XRD pattern of the annealed samples indicated the formation of an α-Fe phase after annealing (Fig. 2). The formation of the α-Fe also led to an increase in the value of M_s. The VSM and XRD data did not give any indication of the formation of $Nd_2Fe_{14}B$ phase even after annealing at temperatures as high as 900°C.

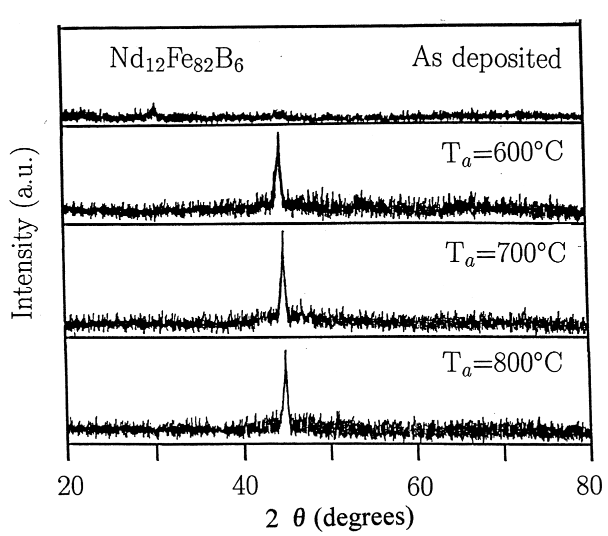

Fig. 2. XRD pattern of as-deposited and annealed $Nd_{12}Fe_{82}B_6$ thin films.

It was found that annealing temperatures higher than 900°C cannot be attained with our heater. However, in order to see if there is any possibility of formation of $Nd_2Fe_{14}B$ phase by annealing at higher temperatures, the films were prepared on Mo substrates. The Mo substrate itself was used as a resistive heater to heat the film. In this way, annealing temperatures as high as 1100°C (higher than the melting point of Nd) could be easily obtained. However, it was observed from the XRD and VSM data that the $Nd_2Fe_{14}B$ phase was not formed even at this temperature. Therefore, it was realized that post-deposition annealing would not be helpful to form $Nd_2Fe_{14}B$ phase. It is possible that when the films are annealed after deposition, the Nd has already reacted with the impurities. This can lead to a deficiency in the concentration of Nd and, therefore, the hard magnetic $Nd_2Fe_{14}B$ phase cannot be formed by post-deposition annealing [2]. Therefore, it was decided to use substrate heating during the deposition of NdFeB thin films.

4. Substrate heating

In order to see the effects of various parameters such as thickness of the films, substrate material, substrate temperature and so on, various studies were carried out. The thickness dependence of the films indicated that the coercive force increases up to 5000 Å beyond which it is almost constant. The microstructural studies also showed an increase in the grain size indicating the possibility of a correlation between the crystal growth and the increase of coercive force with an increase in thickness. Therefore, it was decided to deposit films with a thickness of about 6000 Å in all the films.

4.1. Effect of substrate material and substrate temperature

In order to choose the substrate in which the $Nd_2Fe_{14}B$ phase can be formed with better properties, films were deposited on SiO_2/Si and Ta substrates. In Fig. 3 the XRD data of NdFeB films deposited on SiO_2/Si and Ta substrates are shown. In the case of films on a SiO_2/Si substrate, the presence of NdO peaks is quite intense though there are peaks corresponding to $Nd_2Fe_{14}B$ phase. However, the films deposited on Ta substrate do not show the presence of NdO. They, in contrast, show several $Nd_2Fe_{14}B$ peaks. In the case of SiO_2/Si substrate, it is possible that, at high substrate temperatures, Nd interacts with the oxygen present in the substrate and forms NdO phase. This could lead to a deficiency in the Nd concentration. Therefore, it is difficult to form the required $Nd_2Fe_{14}B$ phase with the SiO_2/Si substrates.

This effect was also reflected in the shape of M–H loops (Fig. 4). While the M–H loops of the films prepared on Ta substrates indicated a hard magnetic phase with a high

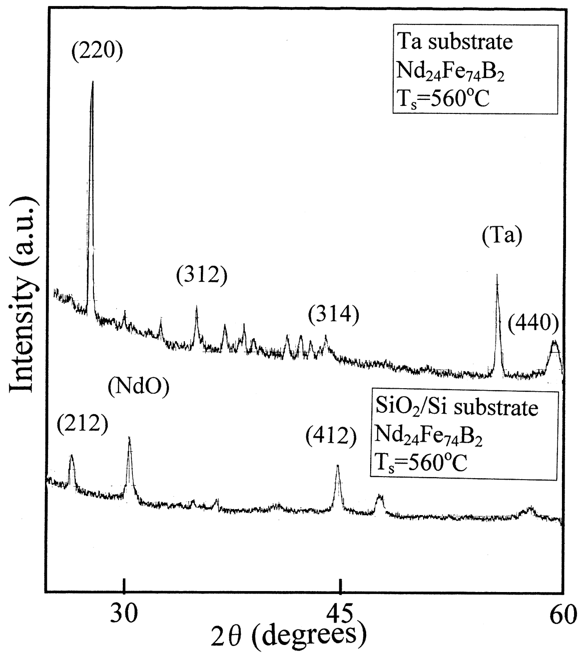

Fig. 3. XRD pattern of $Nd_{24}Fe_{74}B_2$ thin films on a Ta substrate and on a SiO_2/Si substrate.

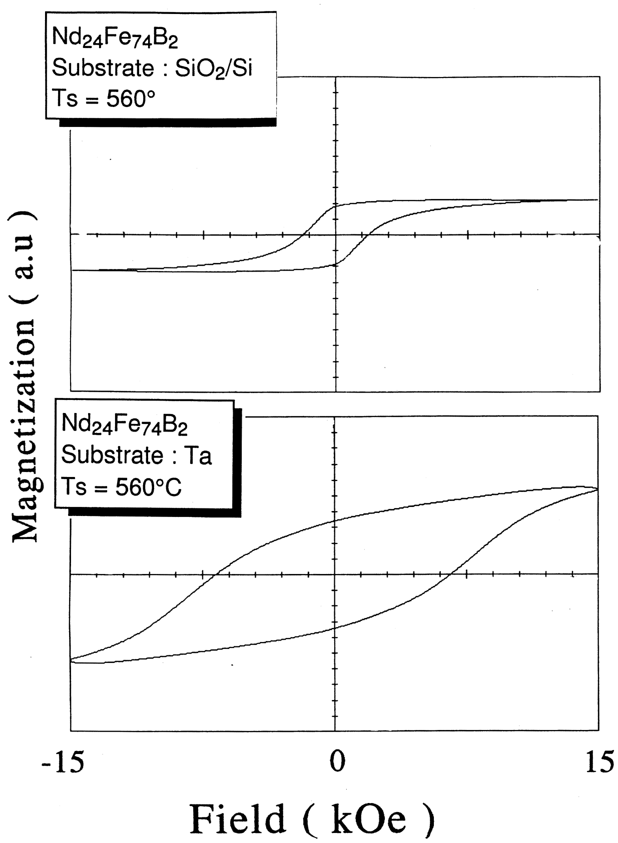

Fig. 4. M–H loops of $Nd_{24}Fe_{74}B_2$ thin films deposited on a Ta substrate and on a SiO_2/Si substrate.

coercive force, the M–H loops of films on SiO_2/Si substrates show a comparatively lesser coercive force. There have been reports on NdFeB films prepared on Al_2O_3 or quartz substrates [9,11]. Surprisingly, the formation of NdO phase has not been reported by the previous workers. However, we feel that substrates that provides oxygen atoms on heating are not suitable for the preparation of NdFeB thin films.

In order to find out the temperature at which the $Nd_2Fe_{14}B$ phase can be formed, films were deposited at different substrate temperatures. Films were deposited on Ta substrates and the thickness of all the films were maintained at 6000 Å. It was found from the magnetization and XRD data that a substrate temperature of 560°C is suitable for the formation of $Nd_2Fe_{14}B$.

4.2. Composition dependence

To study the composition dependence, we used the optimized parameters from the previous discussion. We used a Ta substrate and deposited 6000 Å thick films at a substrate temperature of about 560°C. The M–H loops were measured with a maximum field of 15 kOe applied in and perpendicular to the film plane. In Fig. 5 the XRD patterns of $Nd_2Fe_{98-x}B_2$ films are shown. The XRD shows peaks corresponding to α-Fe for lower Nd concentrations. However, at higher Nd concentrations, the peaks corresponding to $Nd_2Fe_{14}B$ are dominant. In Fig. 6 the M–H loops of $Nd_xFe_{98-x}B_2$ films are shown.

It can be seen that, at lower Nd concentrations, the M–H loop is narrow with a coercive force as low as 1.5 kOe. Whereas, further increase in the concentration of Nd leads to an increase in the coercive force. Therefore, it is clear that, at lower compositions, the presence of soft phases like α-Fe is more and so, the coercive force is less. However, for higher concentrations of Nd, $Nd_2Fe_{14}B$ phase increases.

In Fig. 7 the coercive force of NdFeB films for various compositions is shown. It can be seen that the coercive force increases with the increase in the Nd concentration as well as B concentration. It is interesting to note that films with composition close to the stoichiometric composition do not show the highest coercive force. However, it has been reported in bulk $Nd_2Fe_{14}B$ that the coercive force, depends on various parameters such as the grain size [14], atomic scale alignment at the grain boundary [14], the presence of other phases at the grain boundary [16], Nd dispersion and oxygen pickup [5] and so on. Therefore, in addition to composition, it is possible that any of these parameters would play a role in determining the coercive force of these films too.

In Fig. 8 the saturation magnetization (M_s) (at 15 kOe) of films of various Nd and B concentrations is shown. The M_s of the films does not show so much variation with the composition of the films as does the coercive force. However, films with less Nd content show a larger M_s.

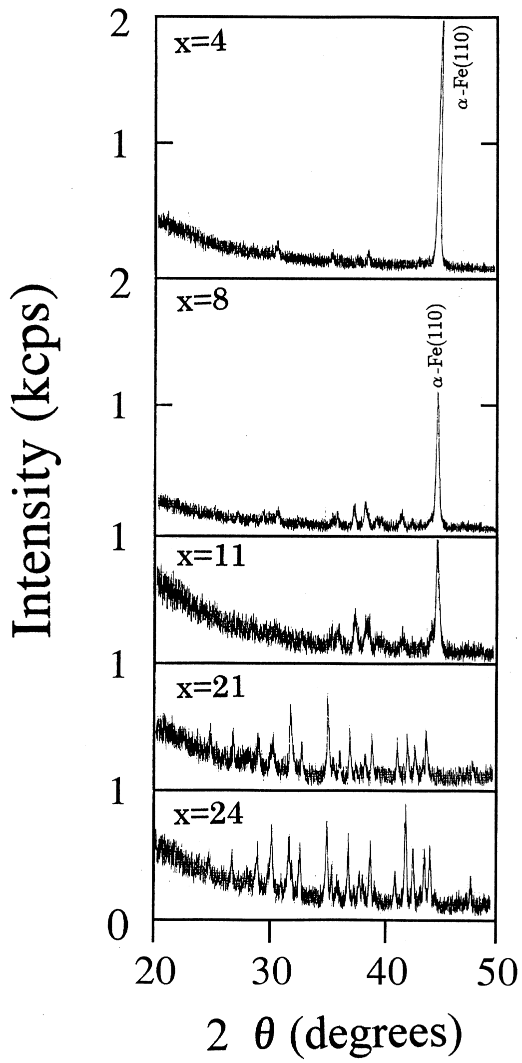

Fig. 5. XRD of $Nd_xFe_{98-x}B_2$ thin films for various values of *x*.

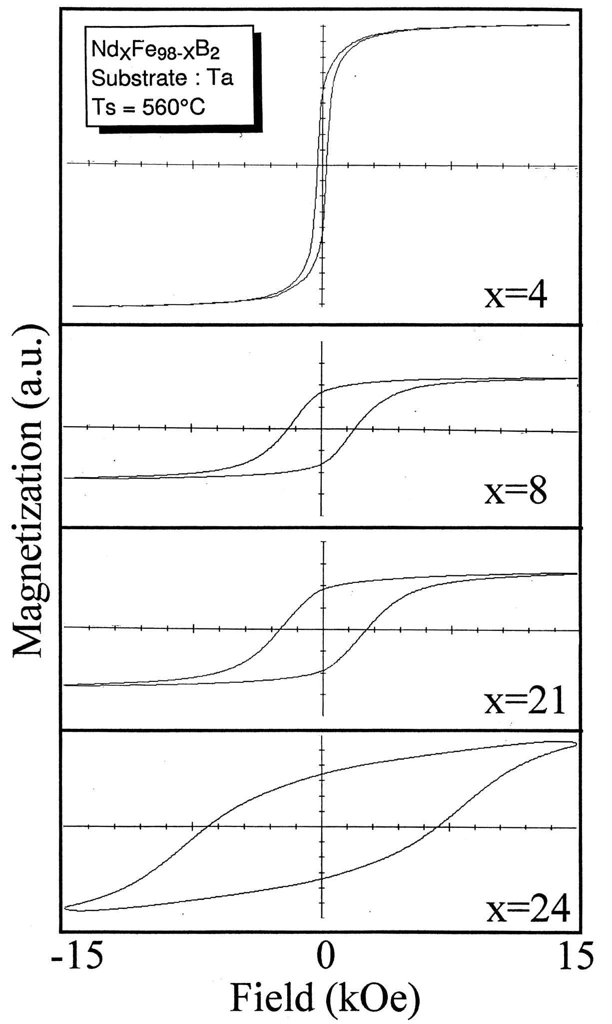

Fig. 6. M–H loops of $Nd_xFe_{98-x}B_2$ thin films for various values of *x*.

This is expected because Fe has a larger magnetic moment, and therefore, films with higher Fe are expected to have high M_s.

It is useful to know about the energy product of these films. For the sake of simplicity, we have calculated the product of remanent magnetic flux density ($B_r = 4\pi M_r$, where M_r is the remanent magnetization) and the coercive force (H_c) for various films (Fig. 9). It can be seen from the figure that the product is high for films with high Nd concentrations. However, the energy product also depends on the orientation and Nd dispersion etc. [5]. In our films too, the films that showed a perpendicular orientation ($Nd_{18}Fe_{78}B_4$) showed higher $B_r \times H_c$.

5. Conclusions

- A detailed investigation on the effect of composition and various processing parameters on the formation of $Nd_2Fe_{14}B$ in thin films was made. The study indicated

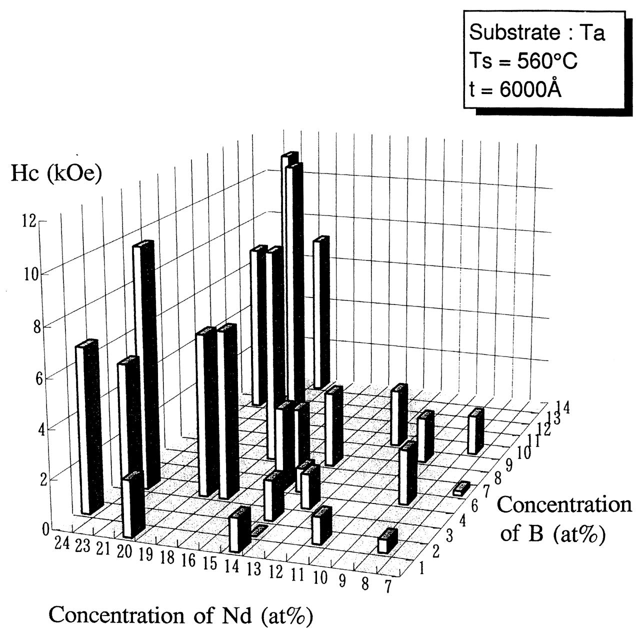

Fig. 7. The dependence of coercive force on the concentration.

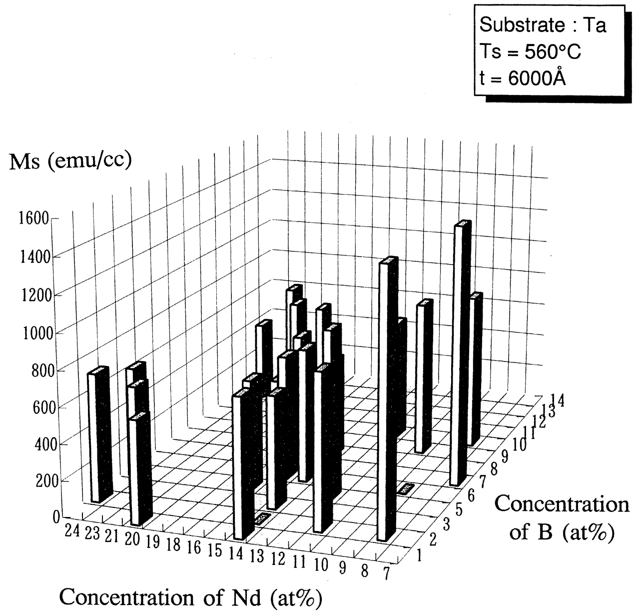

Fig. 8. The dependence of saturation magnetization on the concentration of Nd and B.

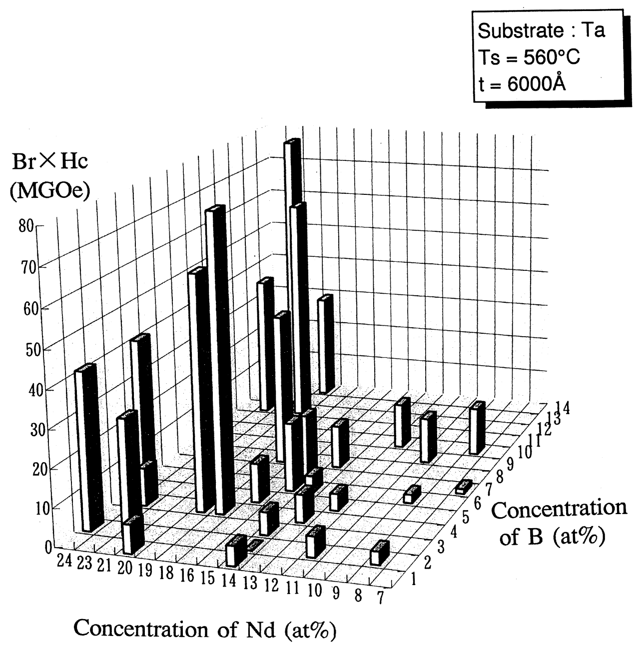

Fig. 9. The dependence of the product of remanent flux density and coercivity ($B_r \times H_c$) on the concentration of Nd and B.

that post-deposition annealing is not very helpful in the synthesis of $Nd_2Fe_{14}B$ thin films.

- It was found that substrates such as quartz glass or SiO_2/Si that may contain oxygen are not suitable for the synthesis of these films. On the other hand, metallic substrates such as Ta or Mo yield better properties.
- The coercive force and the grain size of these films increase correlated with the thickness.
- Coercive force and the energy product of these films were found to be obtained at concentrations of Nd and B slightly higher than the stoichiometric composition.

References

[1] G.C. Hadjipanayis, R.C. Hazelton, K.R. Lawless, Appl. Phys. Lett. 43 (1983) 797.
[2] J.J. Croat, J.F. Herbst, R.W. Lee, F.E. Pinkerton, J. Appl. Phys. 55 (1984) 2078.
[3] M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto, Y. Matsuura, J. Appl. Phys. 55 (1984) 2083.
[4] Y. Matsuura, S. Hirosawa, H. Yamamoto, S. Fujimura, M. Sagawa, K. Osamura, Jpn. J. Appl. Phys. 24(8) (1985) L635.
[5] M. Sagawa, H. Nagata, O. Itatani, T. Watanabe, Proceedings of the 2nd International Workshop on Materials Science, Hanoi, 1995, p. 635.
[6] A.S. Kim, F.E. Camp, H.H. Stadelmaier, J. Appl. Phys. 76(10) (1994) 6265.
[7] M. Munakata, M. Yagi, J. Mag. Soc. Jpn. 18(5) (1994) 911.
[8] K.D. Aylesworth, Z.R. Zhao, D.J. Sellmyer, G.C. Hadjipanayis, J. Appl. Phys. 64 (1988) 5742.
[9] H. Aoyama, Y. Honkura, J. Mag. Soc. Jpn. 20(2) (1996) 237.
[10] Ya.L. Linetsky, N.Y. Kornilov, J. Mater. Engg. Performance 4(2) (1995) 188.
[11] F.J. Cadieu, T.D. Cheung, L. Wickramasekara, N. Kamprath, IEEE Trans. Mag. MAG-22 (1986) 752.
[12] S. Yamashita, J. Yamasaki, M. Ikeda, N. Iwabuchi, J. Appl. Phys. 70(10) (1991) 6627.
[13] S. Yamashita, J. Yamasaki, M. Ikeda, N. Iwabuchi, J. Mag. Soc. Jpn. 15 (1991) 241.
[14] Y. Tsubokawa, S. Hirosawa, R. Shimizu, Jpn. J. Appl. Phys. 29(12) (1990) 2737.
[15] G.B. Clemente, J.E. Keem, J.P. Bradley, J. Appl. Phys. 64(10) (1988) 5299.
[16] G.C. Hadjipanayis, Y.F. Tao, K.R. Lawless, IEEE Trans. Mag. MAG-22 (1986) 1845.
[17] S.N. Piramanayagam, M. Matsumoto, A. Morisako, S. Takei, J. Mag. Soc. Japan 21 (1997) 417.
[18] S.N. Piramanayagam, M. Matsumoto, A. Morisako, S. Takei, IEEE Trans. Mag 33 (1997) 3643.
[19] E.F. Kneller, R. Hawig, IEEE Trans. Mag. 27(4) (1991) 3588.
[20] R. Skomski, J. Appl. Phys. 76(10) (1994) 7059.