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Giant Magnetization and Interface Reaction of Fe/MN (M=Al,Nb) Multilayered Thin Film

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Iron nitride with a giant magnetization was observed at the interface of multilayered Fe/AlN thin film prepared in rf-sputter deposition. The largest value of 233emu/g was in the film prepared at 100W. Interface reaction occurred between the α-Fe and thermally stable AlN layers to form metastable iron nitride during the deposition without substrate heating. The α-Fe slightly expanded in lattice and became smaller in crystallite sizes with the nitrogen incorporation. There expected to be an iron nitride interface reaction layer with nitrogen concentration gradient. Similar reaction occurred also in the α-Fe thin film sputter deposited on AlN ceramic substrate but it was not observed on Fe/metallic NbN multilayered thin film.

Key words: giant magnetization, multilayer, interface reaction, rf-sputter

1. INTRODUCTION

Possible giant magnetization has been proposed for α''-$Fe_{16}N_2$(1). Its single phase has not yet been prepared in bulk because of its metastable nature(2). It was very recently obtained by nitridation of α-Fe fine powder at 110℃ in ammonia flow but still had amorphous surface oxide(3). Interface reaction to form iron nitride was reported in multilayered Fe/AlN thin film deposited by rf-sputtering(4). There was a magnetic component in its Mössbauer spectrum with an internal magnetic field of 36T among several kinds of Fe sites(5). Its giant magnetization was confirmed in magnetic measurement of the multilayers prepared by sputter deposition at 100W(6). Free energy of formation values are very small in iron nitrides in comparison to −287kJ/mol for AlN(7). The interface reaction can not be explained by simple thermochemical estimation. In the present study, both multilayered Fe/AlN and Fe/NbN thin films were prepared by rf-sputter deposition to investigated the way to increase the amount of the giant magnetization component and the reaction mechanism.

2. EXPERIMENTAL

Multilayered thin films were prepared by rf-sputter deposition equipment JEOL JEH-430RS without substrate heating. Four kinds of film were fabricated by applying rf-power of 100 or 30W, respectively; $[Fe(500nm)/MN(500nm)]_1$, $[Fe(166nm)/MN(166nm)]_3$, $[Fe(62nm)/MN(62nm)]_8$, and $[Fe(31nm)/MN(31\ nm)]_{16}$ where M=Al, Nb. Fe and M targets were sputtered with Ar or N_2, respectively. Further experimental details have been published(6). α-Fe thin film itself was also formed on AlN ceramic substrate (Tokuyama, Shapal SH-15(F)). Formation of iron nitride was investigated by using x-ray diffraction and Mössbauer spectroscopy similarly to the previous studies(4,5). Vibrating sample magnetometer (BHV-5, Riken Denshi) was applied for magnetic measurement. Iron content in the multilayered film was determined by ICP (ICPS-8000, Shimadzu).

3. RESULTS AND DISCUSSION

(1) Fe/AlN multilayered thin films

Both α-Fe and AlN crystallized better in the multilayers deposited at 100W than those at 30W(8). X-ray diffraction lines were observed only for α-Fe on the both 8- and 16-times stacked multilayered film prepared at 30W. Lattice parameter and crystallite size were estimated for α-Fe as shown in Table 1. Diffraction lines for α-Fe gradually shifted to lower diffraction angle and became broader with increasing stacking number in 1 μm total thickness similarly to the previous observations(4,5). The lattice size was comparable to the JCPDS(6-696) value of 0.2866nm or slightly expanded. The expansion was larger on the films prepared at 30W than those at 100W. Both expansion and degradation in crystallinity of α-Fe can be explained by incorporation of nitrogen in the lattice. The multilayered films showed soft ferromagnetic behavior. Saturation magnetization values at room temperature are also summarized in Table 1. The largest value of 233emu/g was observed on $[Fe(500nm)/AlN(500nm)]_1$ prepared at 100W. It gradually decreased with increasing stacking number because of a formation of higher iron nitride in more amount. The values are larger for the films prepared at 100W than those at 30W because of the smaller nitrogen content in α-Fe lattice. The value of 233emu/g is much larger than 218emu/g for α-Fe and almost comparable to the theoretically expected value for α''-$Fe_{16}N_2$ with giant magnetization(9). Magnetization decreases with a nitrogen content in iron nitrides above $Fe_{16}N_2$ composition. It was measured in a temperature range up to 800K. It showed a reversible disproportionation of α''-$Fe_{16}N_2$ to a mixture of α-Fe and γ'-Fe_4N as reported for α''-$Fe_{16}N_2$(1). All these observations support that nitrogen content is larger in the interface iron nitride obtained at 30W than that at 100W and in more stacked multilayers.

XPS depth profile has showed possible co-presence of metallic Al in AlN with the iron nitride at the interface of multilayered Fe/AlN thin film. It was confirmed in Al K-edge XANES. The spectra were measured on several kinds of multilayered samples using AlN powder and Al metal foil as their references at the BL-7A in UVSOR of Institute for Molecular Science in Okazaki with 750MeV electrons. The multilayers prepared at 100W showed EXAFS fine structure characteristic for AlN as represented in Fig.1. The fine structure was almost lost in $[Fe(31nm)/AlN(31nm)]_{16}$ multilayered film prepared at 30W as in the Al metal foil reference. The interface reaction was assumed to occur following the equation; $xFe + yAlN \rightarrow Fe_xN_y + yAl$. AlN supplied its nitrogen to α-Fe lattice at the interface forming iron nitride with a

Table 1 Lattice parameter a[1], crystallite size t[2] and saturation magnetization σ for Fe in the $[Fe/AlN]_n$ multilayers prepared at 30W and 100W.

RF-power	30W			100W		
n	a /nm	t /nm	σ /emu•g^{-1}	a /nm	t /nm	σ /emu•g^{-1}
1	0.2862	9.35	217	0.2866	13.87	233
3	0.2870	9.15	216	0.2865	13.87	224
8	0.2875	6.72	211	0.2872	7.29	218
16	0.2890	2.56	167	0.2872	9.05	217

1) Calculated using 110 and 211 lines by least squared method. The value is 0.2866nm for α-Fe in JCPDS 6-696.

2) Calculated using 110 diffraction line by Scherrer's equation.

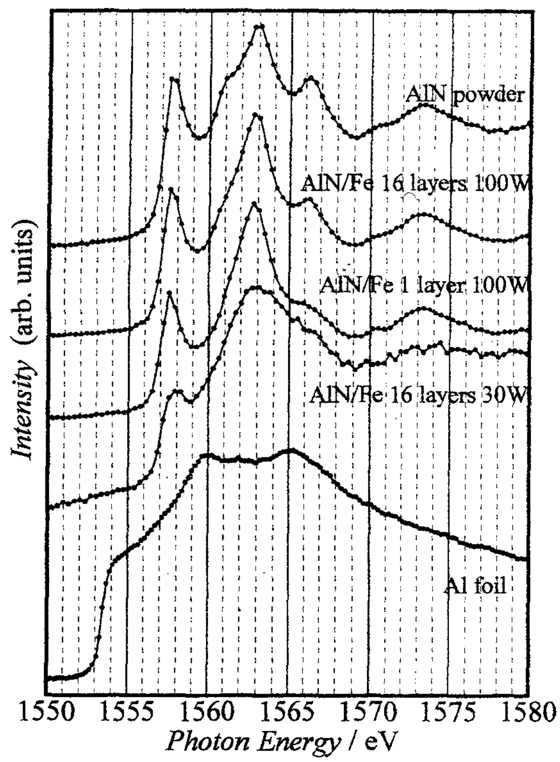

Fig.1 Al K-edge XANES spectra for Fe/AlN thin films, Al metal and AlN powder.

small amount of metallic Al. A reverse reaction of the AlN disproportionation was accelerated at 100W to form the giant magnetization α''-$Fe_{16}N_2$.

(2) α-Fe thin film on AlN ceramic substrate

α-Fe thin film of 200nm thickness was deposited on AlN ceramic substrate by rf- sputtering in 100W. Its x-ray diffraction showed the peak broadening of α-Fe similarly to the Fe/AlN multilayers. The sudden magnetization decrease was found out at about 530K in its temperature dependence as depicted in Fig.2. It corresponds to the disproportionation of α''-$Fe_{16}N_2$ observed in the multilayered thin film. The magnetization again decreased abruptly above 680K because of an oxidation of the film with an atmosphere in the measurement. The temperature dependence was not reversible because of the oxidation.

(3) Fe/NbN multilayered thin films

The interface reaction in Fe/AlN system can be explained by assuming the excitation of bonding

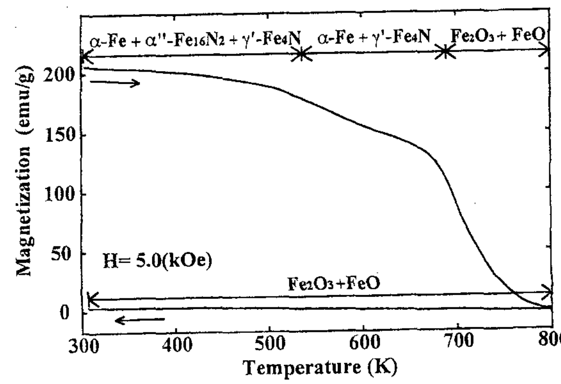

Fig.2 Temperature dependence of magnetization for rf-sputter deposited α-Fe thin film on AlN ceramic substrate.

electron in AlN with a negative electron affinity during the deposition(10,11). The excited electron to the conduction band is spontaneously irradiated from AlN because its energy level is located above the vacuum level. The liberated electron is transferred to the α-Fe layer to take the nitrogen released from the AlN layer in Fe/AlN junction. Metallic NbN is different from the semiconducting AlN in the electronic state. Multilayered samples were prepared in Fe/NbN system in a similar way to the Fe/AlN films. X-ray diffraction showed that δ-NbN deposited in very bad crystallinity with some nitrogen deficiency because of the low deposition temperature. Low temperature phase γ-NbN also coexisted in the films prepared at 30W. α-Fe crystallized in slightly expanded lattices from the literature value of 0.2866nm as represented in Table 2. There was no systematic lattice expansion with the multilayer structure as observed in Fe/AlN multilayer. Its crystallite size decreased with the increasing number of stacking because of the thinner single layer thickness. Mössbauer spectra were measured in conversion electron method. Its signal/noise ratio was much reduced in Fe/NbN in comparison to Fe/AlN because of the larger γ-ray scattering effect of Nb in the top covering layer. The $[Fe(31nm)/NbN(31nm)]_{16}$ prepared at 100W showed the most well resolved spectrum as shown in

Table 2 Lattice parameter a and crystallite size t in the $[Fe/NbN]_n$ multilayers prepared at 30W and 100W.

RF-power	30W		100W	
n	a /nm	t /nm	a /nm	t /nm
1	0.2876	16.9	0.2870	19.4
3	0.2867	13.3	0.2868	16.6
8	0.2882	9.5	0.2871	13.6
16	0.2884	9.2	0.2868	11.2

Fig.3 because of its thinnest top NbN layer. The nitrogen amount in the interface iron nitride should be the largest in multilayer configuration of $[Fe(31nm)/NbN(31nm)]_{16}$ among the Fe/NbN multilayers, if a similar interface reaction occurs in Fe/NbN to Fe/AlN. However, there was only a spectrum for α-Fe in the observation for the $[Fe(31nm)/NbN(31 nm)]_{16}$ multilayer prepared at 100W. Spectrum resolution was worse in other samples but there was no sign to show a presence of other kind of Fe site. Interface iron nitride was not formed in the rf-sputter deposited Fe/metallic NbN multilayered thin film.

4. CONCLUSION

Interface reaction occurred to form iron nitride with giant magnetization in rf-sputter deposited Fe/AlN multilayered thin film as well as α-Fe thin film deposited on AlN ceramic substrate. It was not observed on Fe/NbN multilayered thin film.

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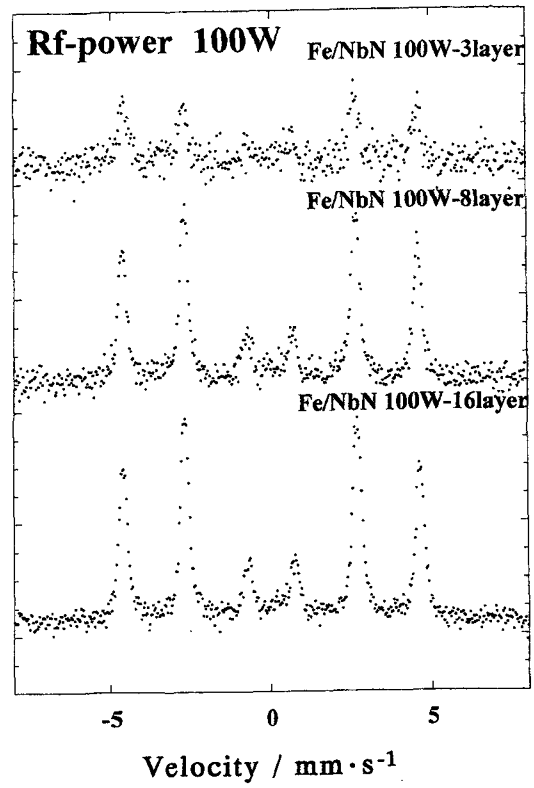

Fig.3 Mössbauer spectra for Fe/NbN multilayered thin films prepared at 100W.

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