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NMR Study on Compositional Inhomogeneity in Electroless-Deposited CoNiP Films for Perpendicular Magnetic Recording

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Compositional inhomogeneity in electroless-deposited CoNiP films with perpendicular magnetic anisotropy was examined using the spin echo ^{59}Co-NMR technique for the first time. The existence of a Co-rich component was observed which was thought to cause the formation of an hcp structure and produce high perpendicular coercivity, Hc(⊥). An increment in the Co-rich component by heat-treatment was also observed which might be an origin of the increase in Hc(⊥).

The electroless-deposited CoNiP films, previously developed by Osaka et al.,[1] exhibit perpendicular magnetic anisotropy, whose perpendicular coercivity, Hc(⊥), can be controlled up to 1500 Oe. The high Hc(⊥) film consists of c-axis perpendicularly oriented hcp crystallites,[3] although it has a Ni-rich composition in which only an fcc structure is stable in the case of bulk CoNi alloys.[2] It was also observed that the Hc(⊥) increases with heat treatment up to 350°C, whereas it decreases sharply at higher temperature treatments in which fcc structure is formed although the composition remains unchanged through the treatment.[4] These results suggest that the films are not in a compositionally homogeneous state.

The spin echo ^{59}Co-NMR technique is a powerful tool for analyzing compositional inhomogeneities in Co-based ferromagnetic materials. It has been used to prove compositional separation for evaporated or sputtered CoCr perpendicular magnetic recording media by Yoshida et al.,[5] Takei and Maeda,[6,7] and for CoCr-based longitudinal magnetic recording media by Maeda and Takei.[7,8] In the present study, we use this technique to observe compositional inhomogeneity in electroless-deposited CoNiP films.

Table 1 shows the composition and operating conditions for the baths from which the CoNiP films were electroless-deposited. Two kinds of film, A and B, were deposited from baths A and B, respectively. All the electroless-deposition was carried out without agitating the baths. Table 2 shows the profiles of 150nm-thick films A and B deposited onto polyimide substrates. Film compositions were determined with an inductively coupled argon plasma atomic emission spectrophotometer. Film A, with a low Hc(⊥) of 500 Oe, consists mainly of randomly-oriented fcc crystallites, while film B with a high Hc(⊥) of 1500 Oe, consists mainly of c-axis perpendicularly oriented hcp crystallites.[3] The spin echo NMR

measurements[6] were carried out at 4.2 K without applying an external field.

Previous studies on bulk CoNi alloys by Kobayashi et al.,[9] and by Takei and Maeda,[10] showed that the main peak resonance frequency of hcp Co decreases almost linearly from 225 MHz with an increase in Ni content. An NMR spectra simulation of sputtered CoNi films[10] indicated that the films were in a compositionally homogeneous state in which the Co and Ni were distributed randomly at the lattice sites. Figure 1 shows representative NMR spectra of films A and B (dotted lines), and of $Co_{35}Ni_{65}$ bulk alloy[10] (solid line). Although both films have almost the same average compositions as that of the bulk alloy specimen, the films

Table 1. Bath composition and operating conditions for electroless CoNiP films

Chemicals	Concentration / mol dm^{-3} Bath A	Bath B
$NaH_2PO_2 \cdot H_2O$	0.20	0.20
$(NH_4)_2SO_4$	0.50	0.50
$CH_2(COONa)_2 \cdot H_2O$	0.75	0.75
$C_2H_2(OH)_2(COONa)_2 \cdot 2H_2O$	0.20	0.20
$C_2H_3OH(COONa)_2 \cdot 1/2H_2O$	0.375	0.375
$CoSO_4 \cdot 7H_2O$	0.03	0.06
$NiSO_4 \cdot 6H_2O$	0.08	0.16
Bath temperature	80 °C	
pH (adjusted using NH_4OH)	9.5	

Table 2. Profiles of films A and B, deposited from baths A and B, respectively

	Film A	Film B
Composition [at%]	$Co_{31}Ni_{62}P_7$	$Co_{39}Ni_{55}P_6$
Ms [emu cc^{-1}]	550	600
Hc(⊥) [Oe]	500	1500
Hc(//) [Oe]	230	700
Crystal structure	fcc	hcp
Film thickness	150 nm	
Substrate	75 μm thick polyimide	

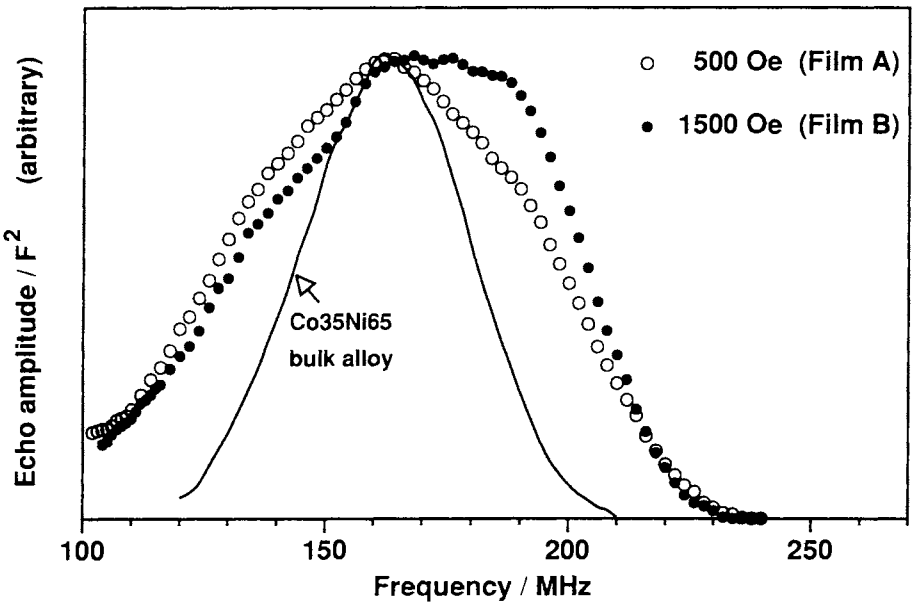

Fig. 1. NMR spectra of electroless-deposited CoNiP films A and B in as-deposited states (dotted lines), and of $Co_{35}Ni_{65}$ bulk alloy (solid line).

exhibit broad spectra, indicating that they are in an inhomogeneous state. In particular, the spectrum of film B has a shoulder in the higher frequency region around 185 MHz, which corresponds approximately to that of $Co_{60}Ni_{40}$ alloy with a richer Co composition. It is therefore assumed that there is greater compositional inhomogeneity in film B than that in Film A, resulting in the high Hc(⊥).

In order to study the compositional inhomogeneity of film B with the higher Hc(⊥) further, the heat-change behavior in its NMR spectrum was investigated. The specimen films were deposited from bath B onto 8 μm-thick copper foil and were cut into three pieces. Then two of the pieces were heat-treated at 2×10^{-3} Pa for 60 min at temperature of 350 °C or 500 °C. The profiles of these films are summarized in Table 3. The difference in average compositions of the films deposited from bath B onto copper foil and polyimide substrate comes from the difference in the catalyzing process.[4] The 350 °C treatment increases the Hc(⊥), while the 500 °C treatment decreases the Hc(⊥) sharply, and the crystal structure changes to an fcc structure.

Table 3. Magnetic properties of CoNiP film heat-treated at various temperatures

Treatment temperature / °C		as-deposited	350	500
Composition [at%]			$Co_{47}Ni_{47}P_6$	
Ms	[emu cc^{-1}]	670	680	680
Hc(⊥)	[Oe]	1500	2800	300
Hc(//)	[Oe]	800	1400	150
Crystal structure		hcp	hcp	fcc
Film thickness			150 nm	
Substrate			8 μm thick copper	

Figure 2 shows representative NMR spectra of the as-deposited and heat-treated films. The as-deposited film shows a broad spectrum, which is similar to that of film B shown in Fig. 1, although the peak has shifted slightly toward the higher frequency region due to the higher average Co content of the film. Thus the film also has compositional inhomogeneity in the as-deposited state. The peak at 185 MHz grows higher with the 350 °C heat-treatment, suggesting that the treatment causes the inhomogeneity to increase. On the other hand, the 500 °C treatment shifts the peak toward the lower frequency region. At the same time, the line width of the spectrum decreases, indicating that the higher temperature treatment changes the film into a homogeneous state. As described above, the compositional distribution changes considerably with heat treatment. This change in the compositional distribution corresponds to the changes in magnetic and structural properties shown in Table 3. As compositional inhomogeneity progresses the Hc(⊥) increases, whereas the homogeneous state resulting from the high-temperature treatment lowers the Hc(⊥) and changes the crystal structure from hcp to fcc which is the equilibrium state for CoNi alloy with the same average composition.

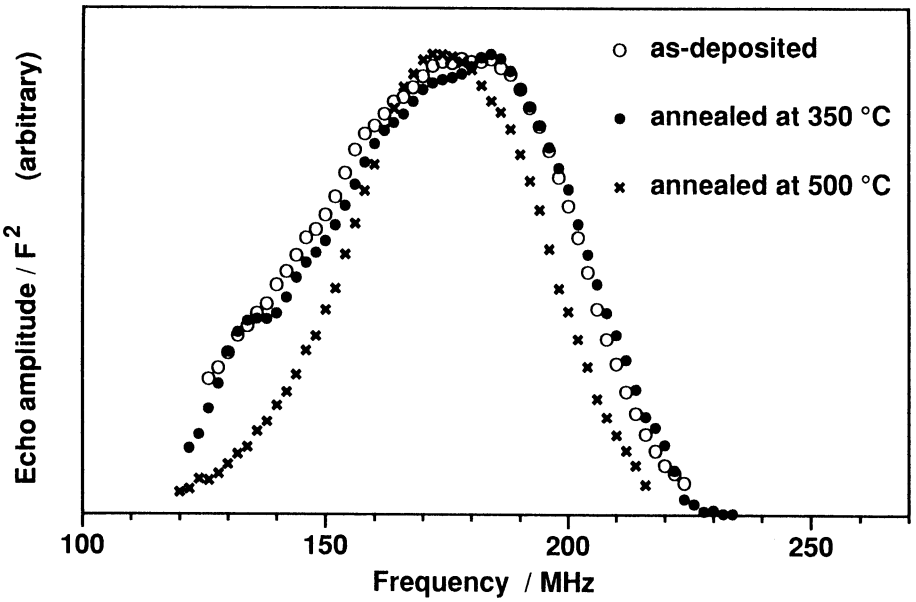

Fig. 2. NMR spectra of electroless-deposited CoNiP film; as-deposited, and heat-treated at 350 °C and 500 °C.

In summary, compositional inhomogeneities in electroless-deposited CoNiP films have been observed for the first time using the NMR technique, and the existence of Co-rich components in the films was confirmed. There was a strong indication that this compositional inhomogeneity plays an important role in forming an hcp structure in film with a Ni-rich composition, and in attaining a high Hc(⊥). The NMR technique combined with conventional methods such as electron microscopy and magnetometry is expected to broaden the field of microstructural studies on electroless-deposited films for perpendicular magnetic recording.

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