EFFECT OF INTRODUCED GASES ON MAGNETIC PROPERTIES OF VACUUM DEPOSITED Co-Cr FILMS

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ABSTRACT Investigated is the effect of Ar, N₂, O₂, CH₄ and H₂O on magnetic properties of Co-Cr films prepared with a web-coater type evaporating system. In introducing any of these gases, $H_{k\text{eff}}$ decreases with increasing gas flow rate. With the introduction of O₂ or H₂O, H_c decreases and M_s increases, while the introduction of the other gases, H₂ and CH₄ are almost constant. In the vacuum deposition of Co-Cr films, N₂ and CH₄ are as inert as Ar is, and they scatter evaporating Co and Cr atoms. O₂ is active enough to react selectively with Cr, and deteriorates the magnetic properties. H₂O decomposes to oxygen and hydrogen during the deposition.

INTRODUCTION

Co-Cr films are prepared mainly by means of sputtering and vacuum deposition, in which atmosphere is one of the most influential factors on magnetic properties of the films.

Various effect of impurity gases on magnetic properties and microstructure of Co-Cr films have been reported [1]-[4].

However, the effect of gases on Co-Cr films prepared at high deposition rate has not been studied, though these films are most promising from the industrial point of view.

In this paper, an experimental study is reported on the effect of introduced gases on magnetic properties of Co-Cr films which are deposited directly on polymer substrates at high rate with continuous vacuum deposition.

EXPERIMENTAL

As shown in Fig. 1, the polymer substrates transported around a cylindrical can were treated with ion beam, following which Co-Cr films were deposited on the treated substrates. The substrates used were polyimide films of 10 μm in thickness.

The diameter of the can was 40 cm. The ion beam was generated with a Kaufman type ion source, the grid diameter of which was 8 cm. The ion source ionized Ar introduced at flow rate of 20 cc/min. The Co-Cr films deposited on the substrates treated with the ion beam have the reproduced voltage as high as that of the Co-Cr films with a

Fig. 1 Schematic illustration of the web-coater type evaporating system.

Ti underlayer [5]. The evaporation source was a 270 degrees deflection type electron beam evaporator.

Gases, except for H_2O , were introduced near the mask (Fig. 1), and the gas flow rate was controlled with gas flow meters. The total pressure and the partial pressure of the gas were measured with an ionization vacuum gauge and a quadrupole mass filter, respectively. Introduced gases were Ar, N_2 , O_2 and CH_4 . Before the deposition, the substrates were degassed thoroughly, since polymer substrates had contained H_2O [6], [7]. The degassing was done by transporting the substrates around the heated can in the vacuum chamber.

H_2O was not introduced from the outside of the chamber. The partial pressure of H_2O during the deposition was varied by changing the can temperature during the degassing of the substrates. Because the residual H_2O in the substrates was discharged by contact of the substrates with the heated can just before the deposition.

Hysteresis loops were measured with a vibrating sample magnetometer (VSM). Perpendicular anisotropy field, H_{keff} , was estimated from the in-plane hysteresis loop. Orientation of c-axis, $\Delta\theta_{50}$, was estimated from an X-ray rocking curve of hcp(002).

RESULTS AND DISCUSSION

Effect of Gases

Conditions of the degassing and the deposition are shown in Table 1. When Ar was introduced at the rate of 0.5 l/min, the increase of pressure in the chamber was 3×10^{-5} Torr.

Fig. 2 shows the gas flow rate dependence of perpendicular coercive force, $H_{c(v)}$, in-plane coercive force, $H_{c(i)}$, anisotropy field, H_{keff} , and orientation of c-axis, $\Delta\theta_{50}$. With increasing Ar, N_2 or CH_4 , $H_{c(i)}$ and $\Delta\theta_{50}$ increased, H_{keff} decreased and $H_{c(v)}$ was nearly constant. On the other hand, with the introduction of

O_2 , $H_{c(v)}$, $H_{c(i)}$ and H_{keff} decreased and $\Delta\theta_{50}$ increased.

Saturation magnetization, M_s , of the Co-Cr films increased by about 100 emu/cc with introducing O_2 at the rate of 0.5 l/min, while the introduction of the other gases did not change the value of M_s which was about 450 emu/cc.

Fig. 3 shows the scanning electron microscope (SEM) views of the surface and the cross-section of the Co-Cr films. The films shown in (a) and (b) were prepared with the introduction of N_2 and O_2 at the rate of 0.5 l/min, respectively. The surface shown in (a) was rougher than that shown in (b). In comparison with the cross-section shown in (b), that shown in (a) had a clearer columnar structure.

Fig. 4 shows the spectra of X-ray photoelectron spectroscopy (XPS) on $Cr(2p_{1/2})$, $Cr(2p_{3/2})$ and $Co(2p_{3/2})$ in the Co-Cr films. These analyses were performed at 0.04 μm in depth from the surface of the films. For the film (a) prepared with N_2 , Co and Cr had the same profiles as those of the reference film (c) prepared without the introduction of gases. It was supposed that there was no nitride in the vacuum deposited Co-Cr films. For the film (b) prepared with O_2 , Cr was combined with O_2 , but no peak of Co-oxide could be observed.

In this experiment, Ar, N_2 and CH_4 had the same tendency of the effect on the magnetic properties of the vacuum deposited Co-Cr films. N_2 and CH_4 were as inert as

Table 1 Conditions of the degassing and the deposition in the experiment on the effect of gases.

Degassing	Can Temperature	320 °C
	Contact Time (Sub. and Can)	5 sec
	Pressure of Background	20 mTorr
Deposition	Can Temperature	250 °C
	Deposition Rate	0.4 μm /sec
	Thickness	0.3 μm
	Pressure of Background	5×10^{-6} Torr

Fig. 2 The gas flow rate dependence of $H_c(v)$, $H_c(i)$, H_{keff} and $\Delta\Theta_{50}$ of the Co-Cr films prepared with the introduction of Ar (a), N_2 (b), O_2 (c) and CH_4 (d).

Fig. 3 SEM views of the surface and the cross-section of the Co-Cr films prepared with the introduction of N_2 (a) and O_2 (b).

Ar. These gases only scattered evaporating Co and Cr atoms. The scatter disordered the orientation of c-axis, resulting in the decrease of H_{keff} and the increase of $H_c(i)$. And the scatter made the columnar structure clearer because of the self shadowing effect.

O_2 had different effect from Ar, N_2

Fig. 4 The XPS spectra of Cr and Co in the Co-Cr films prepared with the introduction of N_2 (a), O_2 (b) and reference (c).

and CH_4 . O_2 combined selectively with Cr, which caused of the decrease of H_c and the increase of M_s . It had been supposed that Cr weakened the intercolumnar magnetic coupling by the segregation of Cr near the grain boundaries and Cr reduced M_s of Co-Cr alloy by filling 3d energy band of Co with electrons of Cr. Oxidation of Cr was

considered to take from these functions of Cr mentioned above, resulting in the decrease of H_c and the increase of M_s .

Effect of Water

The polymer substrates contained various gases. Table 2 shows a composition

Table 2 Composition in pressure of discharged gases during the degassing.

Gas	H ₂	H ₂ O	N ₂	O ₂	CO ₂
P _p /P _t	0.02	0.94	0.02	<0.01	<0.01

Table 3 Conditions of the degassing and the deposition in the experiment on the effect of water.

Degassing	Can Temperature	25-320 °C
	Contact Time (Sub. and Can)	5 sec
	Pressure of Background	20 mTorr
Deposition	Can Temperature	250 °C
	Deposition Rate	0.4 $\mu\text{m}/\text{sec}$
	Thickness	0.25 μm
	Pressure of Background	5×10^{-6} Torr

in pressure of discharged gases during the degassing. In Table 2, P_p and P_t are partial pressure of each gas and total pressure of gases discharged, respectively. H₂O was the most part of content among gases discharged during the degassing. The partial pressure of H₂O during the deposition was varied by changing the can temperature during the degassing of the substrates. Table 3 shows the conditions of the degassing and the deposition.

Fig. 5 shows the content of H₂O and H₂ in the vacuum chamber when the substrates ran which were degassed at various can temperature. $I(\text{H}_2\text{O})$ and $I(\text{H}_2)$ are the ion currents of H₂O and H₂, respectively. The ion currents were measured with the quadrupole mass filter. Degassing temperature is the can temperature during the degassing. In Fig. 5 (a), the substrates ran around the can in the same conditions as those of the deposition except that the electron beam for evaporator was off. The lower degassing temperature, the more H₂O discharged during the deposition. In this case, O₂ was $1.0-1.3 \times 10^{-8}$ A constantly at all range of the

Fig. 5 The degassing temperature dependence of H₂O and H₂ content in the course of running the substrates without the deposition (a) and during the deposition (b).

degassing temperature. Fig. 5 (b) shows the content of H_2O and H_2 during the deposition. H_2O decreased to 10^{-8} A from 10^{-7} A, on the other hand H_2 increased to 10^{-7} A from 10^{-8} A. H_2O increased considerably, as the degassing temperature was below about 200°C . The ion currents of O_2 was less than 10^{-10} A through the range of the degassing temperature.

Fig. 6 shows the degassing temperature dependence of $H_{C(v)}$, $H_{C(i)}$, H_{keff} and $\Delta\theta_{50}$ of the Co-Cr films. The magnetic properties and the orientation of c-axis were constant when the degassing temperature was above 200°C . Below 200°C , with the degassing temperature lowering, $H_{C(v)}$, $H_{C(i)}$ and H_{keff} decreased, and $\Delta\theta_{50}$ increased. These changes of the properties corresponded to the increase of the content of H_2O discharged.

The effect of H_2O on the magnetic properties of the Co-Cr films was much the same as that of O_2 . It was obvious that H_2O decomposed to hydrogen and oxygen during the deposition, because H_2 increased to about ten times and H_2O decreased to about a tenth part. O_2 decreased during the deposition, because O_2 combined selec-

tively with Cr. M_s of the Co-Cr films increased by about 30 emu/cc, as the degassing temperature was from 200°C down to 25°C .

The cause of the decomposition of H_2O was inferred as follows. H_2O molecules collided with the electrons from the electron gun for the evaporator or evaporating Co and Cr atoms. Oxygen atoms combined with evaporating Cr, and were deposited together with other evaporating atoms on the substrates.

SUMMARY

Investigated was the effect of gases on the magnetic properties of the Co-Cr films deposited at high rate directly on the polymer substrates with the continuous vacuum deposition. The results were following.

N_2 and CH_4 were as inert as Ar, and such inert gases only scattered the evaporating atoms. The scatter did not only disorder the orientation of C-axis, but also made the columnar structure clearer because of the self shadowing effect.

O_2 was combined selectively with Cr, and the oxidation took from the functions of Cr in the Co-Cr films.

H_2O had much the same effect as O_2 , since H_2O decomposed to oxygen and hydrogen during the deposition.

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