

Structure and magnetism of Co-Cr thin films with an artificial superlattice structure

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(Received 1 August 1986; accepted for publication 15 October 1986)

Cobalt-chromium (Co-Cr) thin films deposited in an alternating multilayer structure by the magnetron sputtering method have an artificial superlattice hexagonal closed pack (hcp) structure with the *c*-axis normal to the film plane, where the *c*-plane of hcp-Co grows epitaxially on the (110) plane of the bcc-Cr. The film, composed of monatomic layers of Cr and then several atomic layers of Co in an alternating fashion, has an especially excellent hcp structure and shows a clearly separated spot pattern in reflection high-energy electron diffraction analysis. The artificial superlattice structure of the film is stable thermally to temperatures up to 500 °C. Small-angle x-ray diffraction analysis confirmed the layering of monatomic layers of Co and Cr, where the periodicity of layers was found to be about 5 Å. Transmission electron microscopic observation proved the artificially layered structure in these films. The films showed ferromagnetism over a wide Cr composition range, where the thickness ratio of Co and Cr layers was varied from 4/1 to 1/4. The perpendicular magnetization hysteresis loop was obtained in films with a Co layer thinner than about 12.5 Å for various thickness ratios of Co and Cr layers. It is concluded that the origins of the perpendicular magnetization in the Co-Cr films with artificial superlattice structures are the magnetocrystalline anisotropy and the shape anisotropy related to the columnar structure.

I. INTRODUCTION

The Co-Cr thin film is generally considered a good medium for perpendicular magnetic recording owing to its high perpendicular magnetic anisotropy.¹⁻⁹ Magnetic and crystallographic properties of Co-Cr thin films were studied on films prepared by various methods such as sputtering,¹⁻³ evaporation,⁴ and electroplating.⁵ Researchers pointed out that the perpendicular magnetic anisotropy in Co-Cr thin films was related to a hcp crystallographic structure with its *c* axis perpendicular to the film plane, where Cr was segregated near the grain boundaries. Magnetic properties and microstructures of Co-Cr films are strongly influenced by the preparing methods and substrate materials. Double-layer media such as Co-Cr/Fe-Ni, Co-Cr/Ta, and Co-Cr/Ti have been extensively studied for perpendicular magnetic recording applications.⁶⁻⁹

New materials with artificially layered structures have attracted much attention in many fields such as semiconductor,^{10,11} superconductor,^{12,13} and magnetic materials.¹⁴⁻²¹ Artificially layered films composed of monatomic or few atomic layers are of great interest as magnetic materials. The magnetic exchange interaction between constituent elements occurs only in a short atomic distance in these films. We reported a new class of amorphous Tb-Fe films with artificially layered structures prepared by alternate deposition of ultrathin layers of Tb and Fe, which exhibited large uniaxial anisotropy, high saturation magnetization, and high coercivity.^{20,21}

The present paper describes the formation of an artificial superlattice structure using two constituents with different crystal structures but the same atomic sizes, and the magnetic properties of the constituents divided in monatomic or few atomic layers. We made the layered structure in

Co-Cr films by a multisource dc-sputtering method. An artificially layered structure in these films was confirmed by transmission electron microscopy and small-angle x-ray diffraction analysis. The crystallographic properties of the films with artificial superlattice structures were studied by conventional x-ray diffraction analysis, cross-sectional transmission electron diffraction analysis, and reflection high-energy electron diffraction (RHEED) analysis at the film surface. This may be the first time that it has been possible to realize an artificial superlattice structure in magnetic materials.

II. EXPERIMENTAL PROCEDURES

Co-Cr thin films were deposited in an alternating multilayer structure onto glass substrates by a multisource dc-sputtering method. Sputtering was carried out at an argon pressure of 5×10^{-3} Torr after once bringing the chamber back to a pressure below 1×10^{-6} Torr. A 6-in.-diam Co target and a 5-in.-diam Cr target, both water cooled, were placed at opposite positions on a 125-mm-radius circle. The substrate holder, also water cooled and grounded electrically, was rotated at a speed of 3-120 rpm. Co and Cr were deposited in an alternating multilayer structure on the substrate. The spacing between the targets and the substrate was about 80 mm. The composition of the films was controlled by choosing appropriate deposition rates of Co and Cr, and the thicknesses of Co and Cr layers were controlled by varying both the individual deposition rate and the rotation speed of the substrate holder. The deposition rates of Co and Cr were determined by measuring the thicknesses of Co and Cr films deposited individually, divided by the deposition time. The composition of the films was determined by electron probe microanalysis (EPMA). The thickness of the

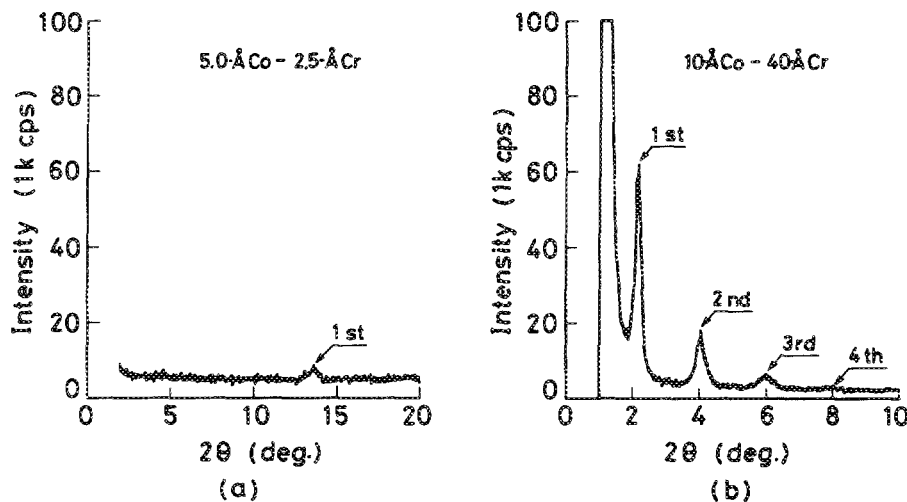


FIG. 1. Small-angle x-ray diffraction patterns for (a) the film with 5-Å Co and 2.5-Å Cr layers, and (b) the film with 10-Å Co and 40-Å Cr layers.

films was measured with a Taylor Hobson Talysurf.

Measurements of magnetic properties such as saturation magnetization M_s , coercivity H_c , and uniaxial anisotropy constant K_u , were made by using a vibrating sample magnetometer (VSM) and a torque magnetometer with an applied field of 20 kOe. Samples were placed in a vacuum or Ar gas atmosphere for measurements over a temperature range of 4–950 K.

Crystallographic structure of the films was examined by the standard x-ray diffraction with $\text{CoK}\alpha$ radiation. The layered structure of the films was studied using transmission electron microscopy (TEM) and small-angle x-ray diffraction analysis using $\text{CoK}\alpha$ radiation.

III. RESULTS AND DISCUSSIONS

A. Structure of Co-Cr films

1. Analysis of an artificially layered structure

Thick Co-Cr films (more than $1\ \mu\text{m}$) were prepared at room temperature, where the thickness ratios of Co and Cr layers were varied from 4/1 to 1/4 with periodicities varied from 5 to 200 Å. The deposition rates of Co and Cr were varied from 5 to 1.25 Å/s, and from 1.25 to 5 Å/s, respectively.

The presence of a layered or compositionally modulated structure can be checked by x-ray diffraction since x-ray measurements are sensitive to a change in the scattering function and strain. X-ray reflection due to an artificial periodicity should be observed in the small-angle region if the films have a periodic structure resulting from the alternate deposition of Co and Cr. The positions of peaks are given by $2L \sin \theta = nZ$, where L is the periodicity, θ is the angle between the incident x-ray beam and the film plane, n (the order of the reflection) is an integer, and Z is the wavelength of the x ray. Peaks resulted from a modulated structure should appear on both sides of the main Bragg reflections of the constituents in the diffraction of a polycrystalline phase with a compositionally modulated structure. The satellite spacing corresponds to the periodicity.

For almost all films, except those with an extremely thin Co or Cr layer (thinner than 2.5 Å), a small-angle x-ray diffraction peak was observed and thus the regular periodicities

were confirmed. Figure 1(a) is the diffraction pattern of the film with 5-Å Co and 2.5-Å Cr layers. A small peak is observed at about 13.6° , leading to about 7.5 Å for periodic spacing calculated by using the Bragg formula. This periodic spacing is somewhat smaller than that estimated from the deposition thicknesses. A small-angle x-ray diffraction peak was also observed in a film with 2.5-Å Co and 5-Å Cr layers. However, the peak intensity of the film was weaker than that of the film with 5-Å Co and 2.5-Å Cr layers. The difference in intensities of small peaks observed between these films was also observed in the films with a large periodicity. If we assume that the metallic radius of Cr is about 1.25 Å since the metallic radii of Co and Fe, which are similar to Cr, are 1.25 and 1.27 Å, respectively, it is indicated that Cr is forming a monatomic layer in the film with 5-Å Co and 2.5-Å Cr layers and Co in the film with 2.5-Å Co and 5-Å Cr layers. It is plausible that Co and Cr are forming monatomic layers in the film with 2.5-Å Co and 2.5-Å Cr layers, in which only a very weak diffraction peak was observed at about 20.6° . These results suggest that the interdiffusion of Co and Cr at the interface between them could hardly occur during sputtering. On the other hand, we could not observe the diffraction peak in the films composed of a 1.25-Å Co layer and Cr layer thicker than 5 Å or a 1.25-Å Cr layer and Co layer thicker than 5 Å, in which the mixture of Co and Cr, i.e., compositional modulation, may occur when the deposition thickness of one of the layers is thinner than its atomic diameter.

Films with a small periodicity (less than 15 Å) show only the first-order reflection, and the intensity of the diffraction peak increases with increasing periodicity. If the periodicity is sufficiently large (more than 15 Å), high-order x-ray diffraction peaks are observed as shown in Fig. 1(b), which is the case for the film with 10-Å Co and 40-Å Cr layers. In a film composed of 40-Å Co and 10-Å Cr layers, high-order peaks are also observed. The intensity of peaks in this film was about one order stronger than that in the film with 10-Å Co and 40-Å Cr layers. The peak intensity of the films composed of a thicker Co layer than a Cr layer was always stronger than that of the films with reverse thicknesses of Co and Cr layers. It is likely that the difference in the peak intensity corresponds to the difference in the struc-

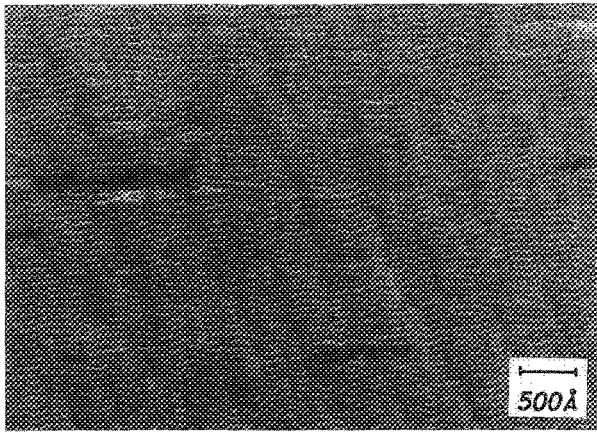


FIG. 2. Cross-sectional transmission electron micrograph of the film with 50-Å Co and 25-Å Cr layers.

tures of the films, since Co and Cr do not have a large difference in atomic size. These results indicate that small-angle x-ray diffraction is affected by not only the periodic thickness but also by the crystallographic structure of the layered films.

The direct observation of the layered structure was performed by means of transmission electron microscopy for films with various periodicities. Since the contrast originating between Co and Cr is not expected because they are quite similar materials, the observation was made on films with thin Co layers etched by aqua regia. Figure 2 shows the transmission electron micrograph of the cross section of a layered film for 50-Å Co and 25-Å Cr layers. The layered structure is clearly observed in this film. The periodic spacing is in agreement with the spacing estimated from the deposition thicknesses and the spacing determined by x-ray diffraction. The direct observation of the layered structure on films with small periodicity (less than 15 Å) has not been made because selective etching of Co layers could not be performed on these films.

2. Analysis of the crystallographic structure

The crystallographic structures of the Co-Cr films were mainly examined by standard x-ray diffraction with $\text{CoK}\alpha$ radiation in the range of $40^\circ < 2\theta < 60^\circ$, where Bragg peaks of (002) diffraction for hcp-Co, (110) diffraction for bcc-Cr, and (112) diffraction for σ -CoCr alloys should occur at about 52.5° , 52.0° , and 49.7° , respectively. The x-ray measurements were made on films with various periodicities and the thickness ratios of Co and Cr layers.

The x-ray diffraction pattern of the Co-Cr films depends on both the periodicity (i.e., periodic thickness) and the

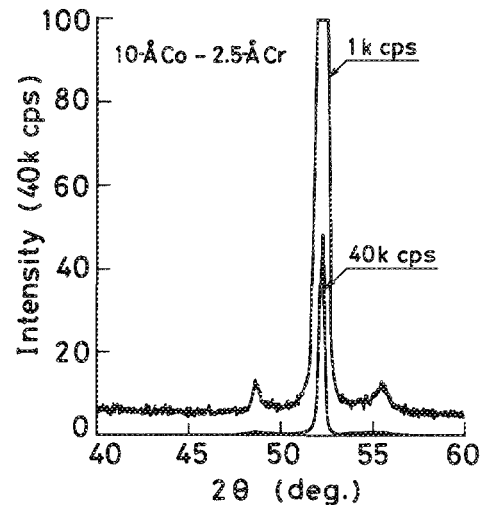


FIG. 3. X-ray diffraction pattern of the film with 10-Å Co and 2.5-Å Cr layers.

thickness ratio of Co and Cr layers. Films with a small periodicity (thinner than 20 Å) exhibit only one diffraction peak at about 52° while films with a large periodicity exhibit several small peaks in the range of 52 – 56° . Table I gives the typical results obtained in films with small or large periodicities for various thickness ratios of Co and Cr layers. Figure 3 is an x-ray diffraction pattern of a film with 10-Å Co and 2.5-Å Cr layers. The x-ray diffraction pattern measured in the low scale of intensity is also shown in order to study the modulation structure due to the interdiffusion of constituents. A large peak with an intensity of 19 kcps is observed at about 52.2° . The intensity is about one order stronger than that of (002) diffraction of hcp-Co, 0.2 kcps, and that of (110) diffraction of bcc-Cr, 1.1 kcps. This peak is identified as a (002) diffraction for the hcp structure. The d spacing is calculated to be 2.033 Å from the diffraction angle. This d spacing is somewhat larger than that of (002) of hcp-Co (2.023 Å), but smaller than that of (110) of bcc-Cr (2.039 Å). The interatomic distance of the $\langle 111 \rangle$ direction in bcc-Cr (2.498 Å) is nearly equal to that of $\langle 100 \rangle$ direction in hcp-Co (2.502 Å). It is likely, therefore, that the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions in the (110) plane of bcc-Cr are parallel to $\langle 100 \rangle$ and $\langle 010 \rangle$ directions in the c plane of hcp-Co, respectively, in the Co-Cr films deposited in an alternating multilayer structure. X-ray measurement results indicate that the Co-Cr films deposited in an alternating multilayer structure have a hcp crystallographic structure with its c axis perpendicular to the film plane, where the c plane of hcp-Co grows epitaxially on the (110) plane of bcc-Cr.

Two satellite peaks located about 3.5° apart from the

TABLE I. Results of x-ray measurements in the Co-Cr films with small or large periodicities for various thickness ratios of Co and Cr layers. The peak intensity of (002) diffraction of hcp-Co, $2\theta = 52.5^\circ$, is about 0.4 kcps and the peak intensity of (110) diffraction of bcc-Cr, $2\theta = 52.0^\circ$, about 1.1 kcps.

Ratio (Co/Cr)	4/1		2/1		1/1		1/2		1/4	
Thickness (Å)	10/2.5	50/12.5	5/2.5	50/25	2.5/2.5	50/50	2.5/5	25/50	2.5/10	12.5/50
Peak position	52.2°	54.6°	52.2°	54.3°	52.3°	52.4°	46.4°	53.2°	52.5°	52.7°
d spacing (Å)	2.033	1.950	2.033	1.960	2.029	2.026	2.270	1.997	2.022	2.015
Peak intensity (kcps)	19	1	27	0.2	0.2	0.2	0.2	0.3	1.4	1.4

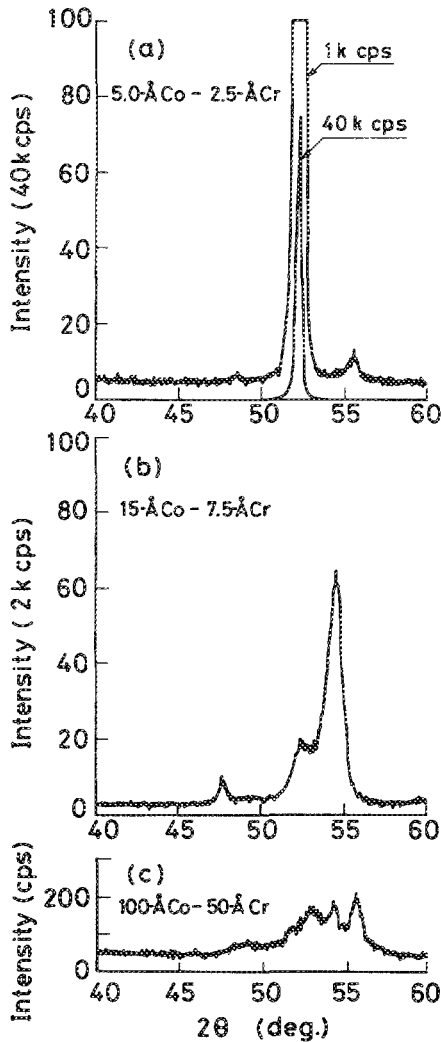


FIG. 4. Evolution of the experimental x-ray diffraction on the film with 5-Å Co and 2.5-Å Cr layers.

main peak are also shown in Fig. 3. Similar satellite peaks are also observed at the same position in a film with 5-Å Co and 2.5-Å Cr layers as shown in Fig. 4(a). The satellite peak was not observed in films with thickness ratios of 1/1, 1/2, and 1/4. These satellite peaks seem to occur not from the modulation structure but from another origin. These satellite peaks are so near to the main peak that they are observed at about the same positions even if the films are constructed with different thickness ratios. This suggestion is consistent with the result obtained by small-angle x-ray diffraction analysis. The origin of the satellite peaks is not clear.

The position and intensity of a (002) diffraction peak strongly depends on the periodicity in films with thickness ratios of 4/1, 2/1, and 1/1. The intensity of the main peak due to (002) diffraction decreases rapidly and, in turn, another peak appears with increasing periodicity as shown in Fig. 4. Figure 4 shows the evolution of the x-ray diffraction pattern for increasing periodicity (i.e., Co and Cr layer thicknesses) in the film with a thickness ratio of 2/1. Figure 4(a) is the diffraction pattern of the film with 5-Å Co and 2.5-Å Cr layers, where the main peak is located at about 52.2° with symmetrical satellite peaks 3.5° apart from the main peak. The *c*-axis orientation of the film is so excellent

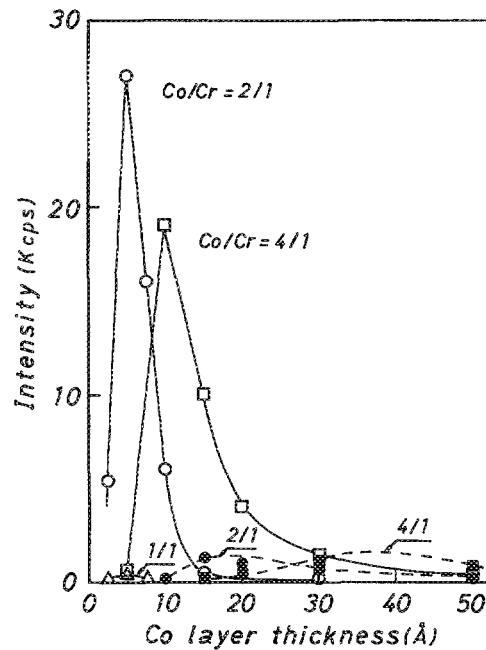


FIG. 5. Co thickness dependence of the peak position for the films with various thickness ratios of Co and Cr layers. The open marks and filled marks indicate the (002) diffraction peak and the new peak, respectively.

that the (002) peak intensity is about 27 kcps. In Fig. 4(b), which is the diffraction pattern of the film with 15-Å Co and 7.5-Å Cr layers, the intensity of (002) diffraction decreases to about 400 cps and another peak appears at about 54.5°. The intensity of this new peak reaches a maximum value of about 1.3 kcps at around a periodicity of 30 Å and decreases with increasing periodicity in a range of 30–100 Å. Films with large periodicities (thicker than 60 Å) show three small peaks as seen in Fig. 4(c), which is the x-ray diffraction pattern of the film with 100-Å Co and 50-Å Cr layers. The small peaks are observed at about 52.9°, 54.2°, and 55.5°. Films with the thickness ratio of 4/1 also exhibited a large periodicity dependence of the peak intensity of (002) diffraction. The small peaks in the films with large periodicities (thicker than 50 Å) were observed at various positions in a range of 49–56°. On the other hand, the periodicity dependence of the peak intensity of the (002) diffraction was small in the films with thickness ratios 1/1, 1/2, and 1/4. The small peaks in the films with large periodicities thicker than 50 Å were also observed at various positions in the range of 52–56°. The small peaks observed at about 52° and 53° in films with large periodicities for various thickness ratios of Co and Cr layers seem to be (110) diffraction of bcc-Cr and (002) diffraction of hcp-Co, respectively, because the intensities of these small peaks were somewhat larger than those of other peaks. Other small peaks were not identified. The films with large periodicities (i.e., thick Co and Cr layers) may not have an artificial superlattice structure but only an artificially layered structure, i.e., regular periodic stacking of thick Co and Cr layers. However, it seems that the structural coherence may exist only in the vicinity of interface between Co and Cr layers. Figure 5 shows the Co layer thickness dependence of the (002) peak and the new peak intensities for films with thickness ratios of 4/1, 2/1, and 1/1. The

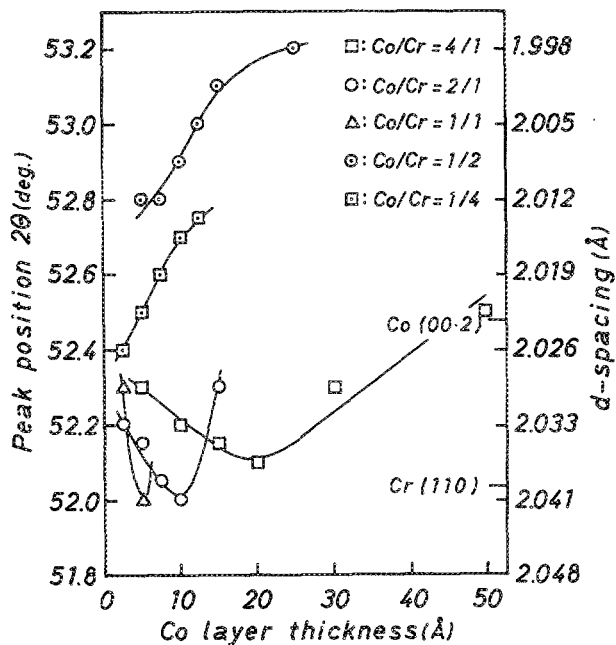


FIG. 6. Co layer thickness dependence of the peak position for the films with various thickness ratios of Co and Cr layers.

largest peak was obtained only in films with a 2.5-Å Cr layer among the many films that have various periodicities and thickness ratios.

The hcp-Co is piled up with *A* and *B* layers in an alternating fashion to the (001) direction and the bcc-Cr is also piled up with *a* and *b* layers in an alternating fashion to the (110) direction, where the basal planes, i.e., the first layers of Co and Cr, are denoted as *A* or *a* layers, respectively. The Co-Cr with a Co layer thickness of 5 Å and a Cr layer thickness of 2.5 Å may be piled up as follows:

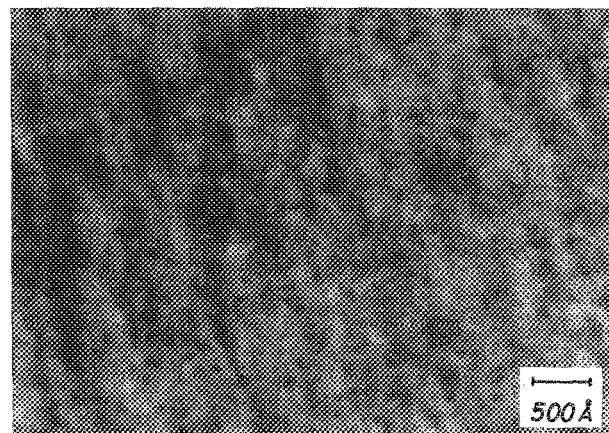
$$\cdots/a/B/A/b/A/B/a/B/A/b/A/B/a\cdots$$

a/A, *A/a*, *b/B*, and *B/b* stacks composed of Co and Cr may not occur because in these stacks the atoms in the second layer are placed directly over the atoms in the first layer. *a/B*, *A/b*, *b/A*, and *B/a* stacks composed of Co and Cr layers may be arranged as hcp or bcc stacks. If these stacks are hcp stacks, the Co-Cr films are composed of only the hcp structure. If these stacks are the bcc stack, the Co-Cr films are composed of the hcp structure and the bcc structure in an alternating fashion. The structure of the films with 10-Å Co and 2.5-Å Cr layers or 2.5-Å Co and 2.5-Å Cr layers can be explained using the same discussion. The films with 10-Å Co and 2.5-Å Cr layers and with 5-Å Co and 2.5-Å Cr layers exhibited strong intensities of 19 kcps and 27 kcps, respectively. Then, these films seemed to be composed mainly of the hcp structure, where the bcc stack composed of Co and Cr layers may have been deformed to the hcp stack. The film with 2.5-Å Co and 2.5-Å Cr layers, which exhibited only a very weak intensity of 0.2 kcps, seemed to be composed of both the hcp and bcc structures.

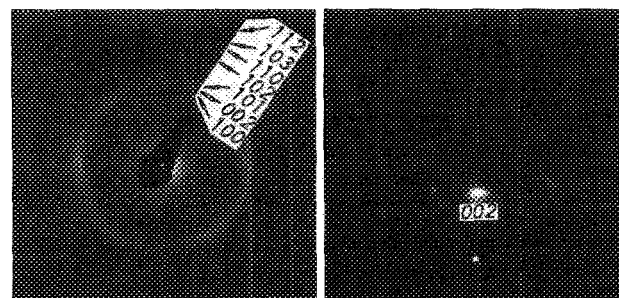
The films with 10-Å Co and 5-Å Cr layers may be piled up as follows:

$$\cdots/a/b/A/B/A/B/a/b/A/B/A/B/a/b/\cdots$$

The Co-Cr films with two atomic layers of Cr, 5 Å thick, may be composed of both the bcc stack and hcp stack, because *a/b* stacks of Cr layers and *A/B* stacks of Co layers are bcc and



(a)



(b)

(c)

FIG. 7. (a) Cross-sectional transmission electron micrograph, (b) electron diffraction pattern, and (c) reflection high-energy electron diffraction pattern of the film with 5-Å Co and 2.5-Å Cr layers.

hcp stacks, respectively, and *b/A* and *B/a* stacks of Co and Cr layers are bcc or hcp stacks, as mentioned previously. Films with a thick Cr layer (more than two atomic layers) is also composed of the bcc and hcp stack. The bcc stack in these films increases with increasing periodicity whether the films are composed of a Cr layer that is thicker or thinner than the Co layer. Figure 6 shows the Co layer thickness dependence of the (002) peak position for films with various thickness ratios. The *d* spacings corresponding to the peak positions of (002) of hcp-Co and of (110) of bcc-Cr are also shown in this figure. The smallest diffraction angles (i.e., the largest *d* spacing) in films with thickness ratios of 4/1, 2/1, and 1/1 are obtained in films with Cr layer thicknesses of 5 Å. These large *d* spacings seem to occur from the presence of a number of *a/b* stacks, i.e., a bcc stack with a large *d* spacing.

The crystallographic structure of the Co-Cr films was also studied by the cross-sectional transmission electron microscopy (TEM), high-energy electron diffraction (HEED) analysis, and reflection high-energy electron diffraction (RHEED) analysis. Figure 7(a) shows the transmission electron micrograph of a cross section of a film with 10-Å Co and 5-Å Cr layers. The layered structure and textured structure are not observed in the film. The cross-sectional diffraction pattern, shown in Fig. 7(b), is comprised of many spotty rings. These rings are identified as (100), (002), (101), etc., as indicated in the figure. The *d* spacing of (002) for the film is calculated to be 2.032 Å from the

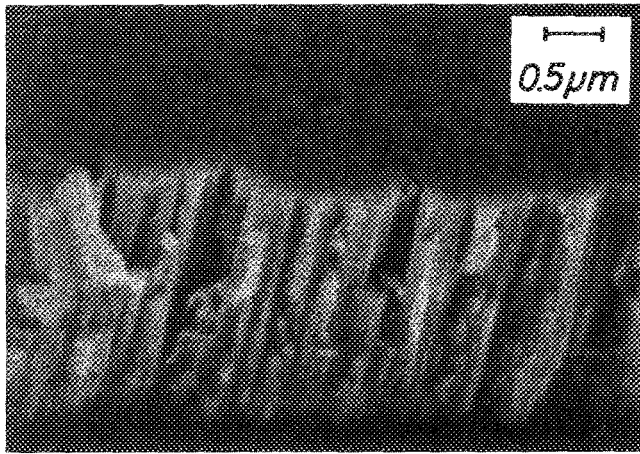


FIG. 8. Scanning electron micrograph of fractured surface of the film with 5-Å Co and 2.5-Å Cr layers.

distance of the diffraction ring, which is in good agreement with that determined by x-ray diffraction analysis (2.033 Å). The diffraction pattern indicates that the film is composed of textured grains but not randomly oriented grains and that the preferred orientation is still present. The *c*-axis dispersion can be measured from the width of the (002) reflection. The *c*-axis dispersion of a film with a small periodicity is narrower than that of a film with a large periodicity. This result is also consistent with that obtained in the x-ray diffraction analysis, where the films with small periodicities exhibit a (002) diffraction peak with a large intensity and a small half-width in comparison with the films with large periodicities.

The RHEED pattern of the film with a small periodicity exhibits many clearly divided spots, as seen in Fig. 7(c). The most intense spot was identified as a (002) reflection of hcp-Co, but other spots were not identified. These spots seem to originate from an interference between the diffractions from Co and Cr. The presence of spots in the diffraction pattern suggests that the film with a small periodicity is composed of not only a highly oriented textured structure but also of a columnar structure. This analysis is consistent with that obtained by x-ray measurement. On the other hand, the RHEED pattern of the film with a large periodicity exhibits some broad rings. The innermost ring is equivalent to the *d*

spacing of the (002) reflection of hcp-Co. The second and third rings are also identified as (110) and (200) reflections of hcp-Co, respectively. The films with a large periodicity, then, seem to be composed only of a textured structure. The preferred orientation of the textured grains is also present in these films.

Figure 8 shows a SEM observation of the fractured surface of a Co-Cr film with 10-Å Co and 5-Å Cr layers. Columnar grains elongated from the bottom to the top are clearly observed. This result indicates that the growth of the films is epitaxial and the Co-Cr film deposited in an alternating multilayer structure is composed of columns strongly aligned perpendicular to the film plane.

3. Annealing effect

The thermal stability of the Co-Cr films with an artificial superlattice structure was evaluated by measuring changes in both the peak intensity of the small-angle x-ray diffraction and the (002) diffraction before and after annealing. Annealing at 100–600 °C was performed for films with various periodicities and thickness ratios of Co and Cr layers.

A change in the peak intensity of the small-angle x-ray diffraction was not observed after annealing at temperatures lower than 300 °C. A decrease in peak intensity was observed after annealing at temperatures above 400 °C, but the artificial superlattice structure was still intact. Figure 9 shows the change in the small-angle x-ray diffraction peak of the film with 10.3-Å Co and 5-Å Cr layers before and after annealing at 400 °C for 20 h. The intensity of the first peak decreased and the second peak vanished after annealing, as seen in Fig. 9(b). The peak intensity decreased with increasing annealing temperature and time. The small-angle x-ray diffraction was not observed in all films after annealing at 600 °C for 5 h.

An increase in the peak intensity of (002) diffraction was observed in films with small periodicities (less than 20 Å) after annealing at temperatures lower than 500 °C. A decrease of peak intensity of (002) diffraction, on the other hand, was observed in films with large periodicities. A decrease in peak intensity only was observed in all films after annealing at temperatures higher than 500 °C. These results indicate that in films with small periodicities the interdiffusion of Co and Cr could hardly occur in comparison with

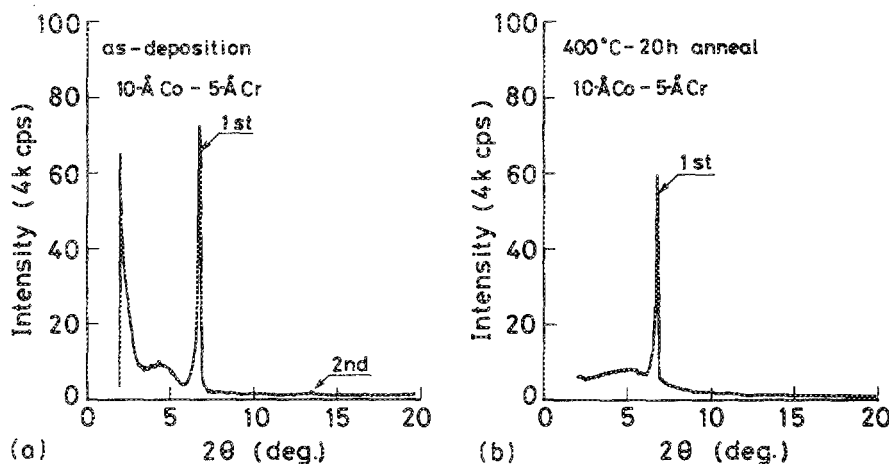


FIG. 9. Small-angle x-ray diffraction patterns of the film with 10-Å Co and 5-Å Cr layers; (a) as deposited, and (b) after annealing at 400 °C for 20 h.

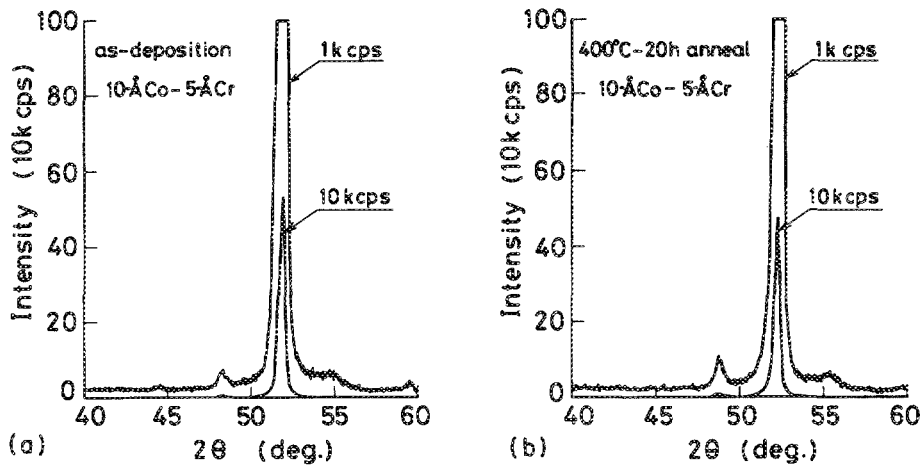


FIG. 10. X-ray diffraction patterns of the films with 10-Å Co and 5-Å Cr layers; (a) as-deposited, (b) after annealing at 400 °C for 20 h.

films with large periodicities. Figure 10 illustrates the change in the (002) diffraction peak of the film with 10.3-Å Co and 5-Å Cr layers before and after annealing at 400 °C for 20 h. The intensity of the (002) diffraction slightly increased and the peak position shifted from 52.0° to 52.2° by annealing, as seen in Figs. 10(a) and 10(b). The shifts of the peak position toward a higher angle due to thermal treatment were observed for almost all films. Figure 11 shows the changes in intensity and position of the (002) diffraction peak for the film with 5.3-Å Co and 2.5-Å Cr layers as a function of annealing temperature. This peculiar behavior on annealing can be attributed to a certain diffusion effect which causes a change in the structure from bcc to fcc stack at the interface of the Co and Cr layers. This behavior cannot be explained in terms of the interdiffusion between Co and Cr layers, since the diffraction peak for Co-Cr alloy is not observed at all.

B. Magnetic properties of Co-Cr films

1. Magnetic properties versus periodicity

The saturation magnetization of the sputtered Co-Cr films is larger than that of the bulk Co-Cr alloy for the same Cr compositions. Zero magnetization is observed in the bulk alloy at about 25 at. % Cr (Ref. 22) and in sputtered film at about 30 at. % Cr.^{1,2} It is pointed out that a large value of saturation magnetization of a sputtered film, in comparison

with the bulk alloys, may be attributed to a segregation of chromium at the grain boundaries, and that the shape anisotropy relating to the columnar structure may be the main source of anisotropy in sputtered Co-Cr films. The Co-Cr films studied in this work have an artificial superlattice structure, i.e., the periodic stacking of layers of constituents as mentioned in the previous section. The Co-Cr films with an artificial superlattice structure are expected to exhibit magnetic properties different from those of the Co-Cr films without an artificial superlattice structure studied earlier.

Magnetic measurements were made on the films with various periodicities and various thickness ratios of Co and Cr layers. The results show that almost all films exhibit ferromagnetism with a strong dependence on both the periodicity and thickness ratio of Co and Cr layers [except those with extremely thin Co layers (less than 5 Å)] for thickness ratios of 1/1, 1/2, and 1/4. The results of magnetic measurements are shown in Fig. 12, where saturation magnetization M_s is plotted as a function of Co layer thickness. Films with a thin Co layer (less than 5 Å) for thickness ratios of 1/1, 1/2, and 1/4 exhibit very small magnetization, but films with the

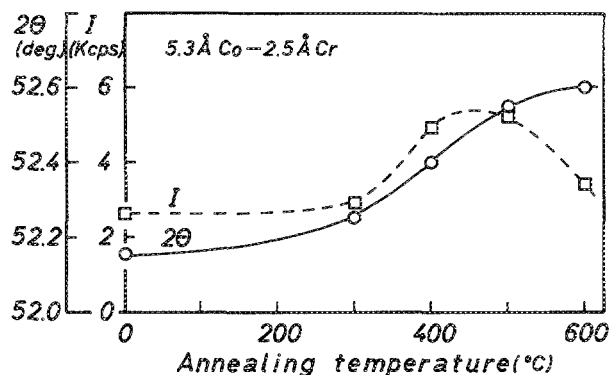


FIG. 11. Changes of peak position and intensity for the (002) diffraction due to thermal treatments at various temperatures.

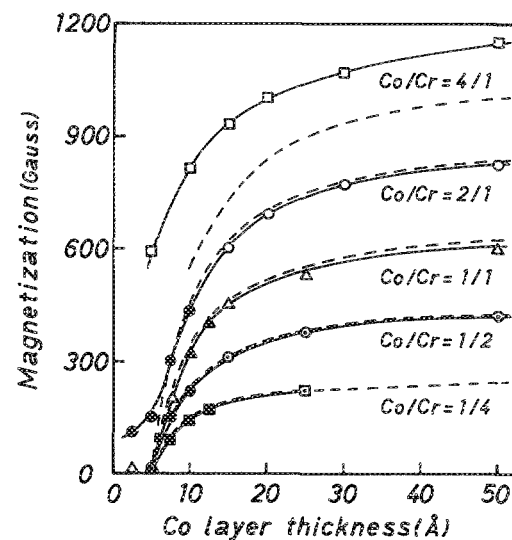


FIG. 12. Co layer thickness dependence of the saturation magnetization for the Co-Cr films with various thickness ratios of Co and Cr layers. The dotted lines are calculated values. The filled mark shows the films with the perpendicular magnetization hysteresis loop.

same thickness of the Co layer for thickness ratios of 4/1 and 2/1 exhibit large magnetization. The Co-Cr films with thickness ratios of 1/1, 1/2, and 1/4 are composed of a monatomic or a two-atomic layer of Co divided by one or several atomic layers of Cr. On the other hand, Co layers are separated by a monatomic layer of Cr in films with thickness ratios of 2/1 and 4/1. These results suggest that the Co layer that is in contact with a Cr layer and/or is separated from the other Co layer by two or more atomic layers is nonmagnetic. Hosoi *et al.*¹⁶ reported from the Mössbauer study that the Fe atoms in the monatomic layer sandwiched with Sb layers had no local magnetic moment. Liebermann *et al.*²³ measured the magnetization of Fe, Co, and Ni thin films, which were electrodeposited on Cu, Ag, or Au substrates, and concluded that the first or second layers facing the substrate metals were nonmagnetic. Gradmann²⁴ reported from the torque measurement of single-crystalline films of the Fe-Ni alloy that coating the Fe-Ni alloy films with Cu or Ag made no magnetic effect and coating with Mn or C produced one or two nonmagnetic layers. These results should support the present result.

It is a very crude assumption to divide the magnetism into two parts, nonmagnetic magnetization and bulk magnetization. The magnetizations of many films, except those films with a thickness ratio of 4/1 and 5-Å Co and 2.5-Å Cr layers, can be well explained if we assume that only the first Co layers paired with a Cr layer at the interface between Co and Cr have a small magnetization and that the Co layers located apart from the interface have a bulk magnetization M_b of 1400 G. The effective magnetization M_{eff} is given by $M_{\text{eff}} = M_b (N_{\text{eff}}/N_t)$, where M_b is the bulk magnetization of Co, N_{eff} is the number of Co layers not in contact with the Cr layer, and N_t is the total number of Co and Cr layers. The magnetization calculated under this assumption is also shown by the dotted lines in Fig. 12. The films with thickness ratios of 4/1 and with 5-Å Co and 2.5-Å Cr layers show a large discrepancy between the experimentally obtained magnetization and the magnetization calculated under this assumption. The magnetizations for films with 10-Å Co and 2.5-Å Cr layers and 5-Å Co and 2.5-Å Cr layers are expected to be about 840 and 470 G, respectively, if we assume that only the one layer among the Co layers that was in contact with the Cr layer lost the magnetization. This assumption can explain the magnetization for films with Cr layers thicker than 5 Å, i.e., two-atomic layer. The experimental value is in good agreement with the calculated value in the film with 10-Å Co and 2.5-Å Cr layers, but the experimental value is smaller than that calculated in the film with 5-Å Co and 2.5-Å Cr layers. The films with large periodicity for a thickness ratio of 4/1 exhibit a large discrepancy between the experimentally obtained magnetization and the magnetization calculated under these assumptions. The results indicate that the Co layer in films with a thickness ratio of 4/1 has a large magnetization. The Co and Cr lattices at the interface between Co and Cr layers might be deformed to a considerable extent in the Co-Cr films with an artificial superlattice structure because of the structural coherence between Co and Cr layers. The small or zero magnetization of the first Co layers seems to originate from the lattice de-

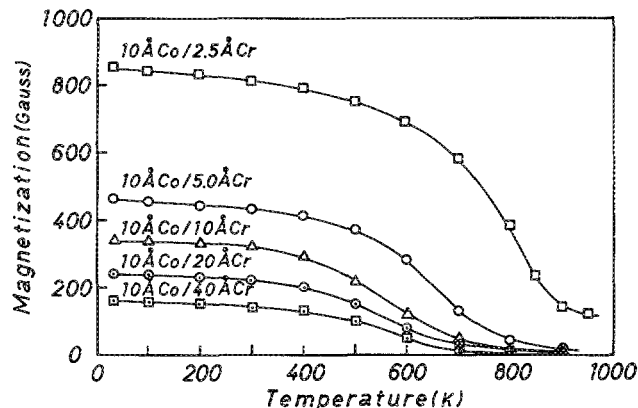


FIG. 13. Temperature dependence of saturation magnetization M_s in Co-Cr films with 10-Å Co layer thickness for various thickness ratios.

formation, antiferromagnetic coupling with Cr atoms, and/or covalent bonding with Cr atoms.

Chromium is the antiferromagnetic material with a Néel temperature of 311 K. The antiferromagnetism of Cr is a consequence of its particular Fermi surface in the bcc structure. It is pointed out by Mitsui and Tomizuka²⁵ that the Néel temperature of chromium decreases linearly with pressure. It is likely that compressive stress acts on the Co layers and tensile stress acts on the Cr layers at the interface between Co and Cr layers, because there is a small mismatch between Co and Cr lattices even if the (001) plane of the hcp-Co is epitaxially grown on the (110) plane of the bcc-Cr. The Néel temperature of Cr is expected to shift toward a high temperature in Co-Cr films with an artificial superlattice structure depending on the tensile stress, which may be varied in accordance with periodicity and thickness ratio of the Co and Cr layers.

Figure 13 shows a temperature dependence of the magnetization of the films with a 10-Å Co layer for various thickness ratios of the Co and Cr layers. These films exhibit a gradual decrease in the magnetization to 400 K and then a sharp decrease at above 400 K. The change of magnetization is reversible to a thermal treatment below 700 K, but irreversible to a thermal treatment above 700 K. The decrease in the magnetization above 700 K is originated from the interdiffusion of constituents. The result of the x-ray diffraction

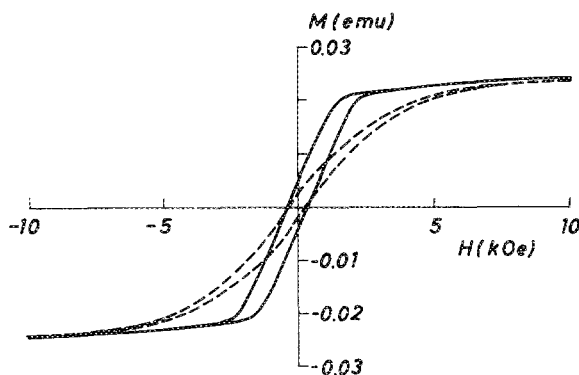


FIG. 14. Magnetic hysteresis loops of the Co-Cr films with 5-Å Co and 2.5-Å Cr layers. The solid and dotted lines indicate perpendicular and in-plane hysteresis loops, respectively.

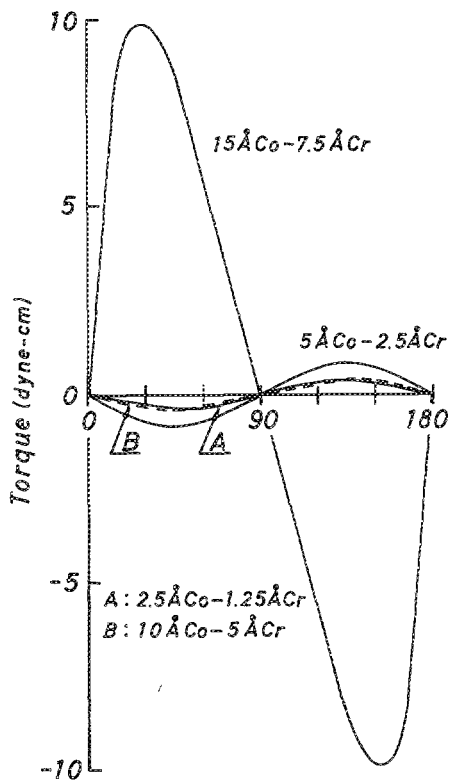


FIG. 15. Variation of torque curves for the Co-Cr films with a thickness ratio of 2/1.

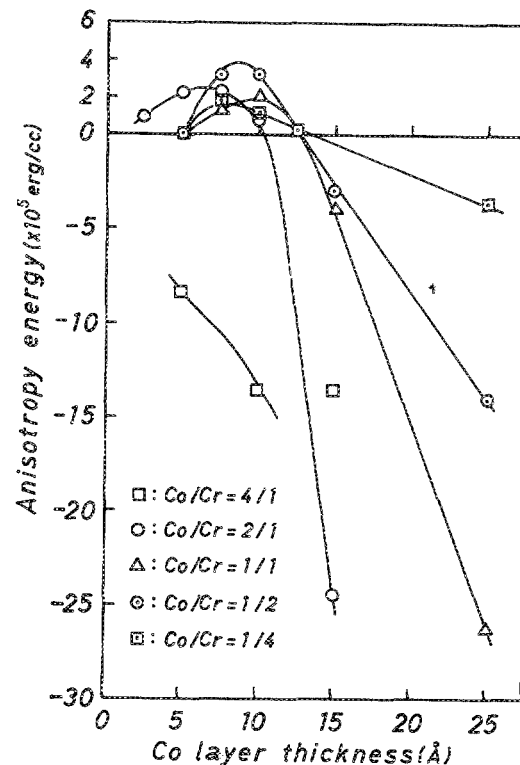


FIG. 16. Co layer thickness dependence of anisotropy energy K_u for Co-Cr films with various thickness ratios of Co and Cr.

measurement on films annealed at high temperatures above 800 K support this discussion, where a decrease in the intensity and the shift of the position for a (002) diffraction peak were observed. The temperature dependence of the magnetization suggests that the small magnetization of the Co layer at the interface originates from the antiferromagnetic coupling with the Cr layer. The decrease in magnetization in the temperature range 300–500 K is caused by the depression of the Néel temperature with rising temperature. Cobalt is a ferromagnetic material with the Curie temperature of about 1400 K. If the lattice deformation is the main origin of the small magnetization of Co, then the increase in magnetization is expected due to the relief of strain at high temperatures above 400 K. If the covalent bonding with Cr is the main origin of the small magnetization of Co, the large decrease in magnetization in the temperature range 400–700 K is not expected due to the existence of covalent bonding at any temperature.

The perpendicular magnetization films were obtained over all thickness ratios from 4/1 to 1/4. Figure 14 shows the perpendicular and in-plane magnetization hysteresis loops for a film with 5-Å Co and 2.5-Å Cr layers. The perpendicular magnetization films confirmed by the hysteresis loop measurement were also indicated by a filled mark in Fig. 12. The coercivities of these films were from several hundred to 700 Oe. These values are somewhat smaller than those reported earlier.¹⁻³ The superior perpendicular magnetization hysteresis loops, as shown in Fig. 14, were obtained in films with saturation magnetizations smaller than 300 G. This result suggests that the uniaxial anisotropies of these films are less than about 6×10^5 erg/cm³. The condition for perpen-

dicular magnetization is given by $K_u > 2\pi M_s^2$, where K_u is the anisotropy constant and M_s is the saturation magnetization.

Torque measurements were also made on all films with various periodicities and various thickness ratios of Co and Cr layers. External magnetic fields as large as 20 kOe were applied normal to the film plane and rotated about an axis parallel to the film plane. The anisotropy of the Co-Cr films is described by a single anisotropy constant, i.e., the uniaxial anisotropy constant K_u , given as $K_u = K_1 - 2\pi M_s^2$ by the perpendicular magnetic anisotropy energy K_1 and the saturation magnetization M_s . The torque can be written as $L(\theta) = -K_u \sin(2\theta)$, where θ is the angle between the magnetization and the direction normal to the film plane. In our experiment, then, the magnetization is normal to the film plane if K_u is positive, and the magnetization is in the plane of the film if K_u is negative. The torque curves showed a negative slope at $-\theta^\circ$ for films with anisotropies perpendicular to the film plane ($K_u > 0$) and a positive slope for films with anisotropies in the plane of the film ($K_u < 0$). Figure 15 shows the torque curves for films with a thickness ratio of 2/1. The torque was independent of the external fields (stronger than 14 kOe) except those with extremely thick Co layers. This result indicates that the external field is stronger than an anisotropy field H_a , $H_a = 2K_u/M_s$. The anisotropy constant K_u was determined from the maximum values of the torque curves.²⁶ The values of the anisotropy constant for Co-Cr films with various thickness ratios are shown in Fig. 16 as a function of Co layer thickness. The films with Co layers thinner than 10 Å have positive anisotropy constants while films thicker than 12.5 Å have negative

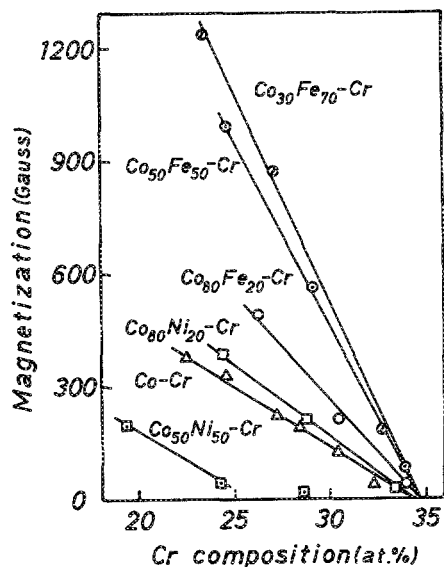


FIG. 17. Cr composition dependence of saturation magnetization M_s for Co-Cr, CoFe-Cr, and CoNi-Cr films, which are composed of constant Cr layer thicknesses of 2.5 Å.

anisotropy constants. This result is consistent with the measurements of magnetization hysteresis loops. The films with Co layers thicker than 12.5 Å exhibited the in-plane magnetization hysteresis loops. The Co-Cr films studied in this work are composed of columns aligned perpendicularly to the film plane, but have no segregation of chromium at grain boundaries. It is concluded that the uniaxial anisotropy of the Co-Cr films with an artificial superlattice structure arises from the magnetocrystalline anisotropy and the shape anisotropy relating to the columnar structure.

2. Magnetic properties versus composition

The study of the composition dependence of magnetic properties was also made on Co-Cr, CoFe-Cr, and CoNi-Cr films in Cr composition ranging from 19 to 36 at. %. CoFe-Cr and CoNi-Cr films were prepared using Co-Fe and Co-Ni alloy targets, respectively. The thickness of Cr layers in the films was kept constant at about 2.5 Å while the thickness of the Co, CoFe, or CoNi layers was varied, because the films with a layer thickness of about 2.5 Å had a superior crystallographic orientation and exhibited excellent perpendicular magnetization hysteresis loops, as mentioned in the previous section. The composition of the films was varied by changing the deposition rate of Co or Co alloys and keeping the deposition rate of Cr fixed.

The presence of the layered structure in CoFe-Cr and CoNi-Cr films was also confirmed by small-angle x-ray diffraction analysis. The crystallographic structure of these films was examined by the standard x-ray diffraction analysis. CoFe-Cr and CoNi-Cr films, as well as the Co-Cr films, also have the hcp structure. The intensity of the (002) diffraction of these films was somewhat weaker than that for the Co-Cr films, even with the same thicknesses of constituents.

Figure 17 shows the saturation magnetization of the

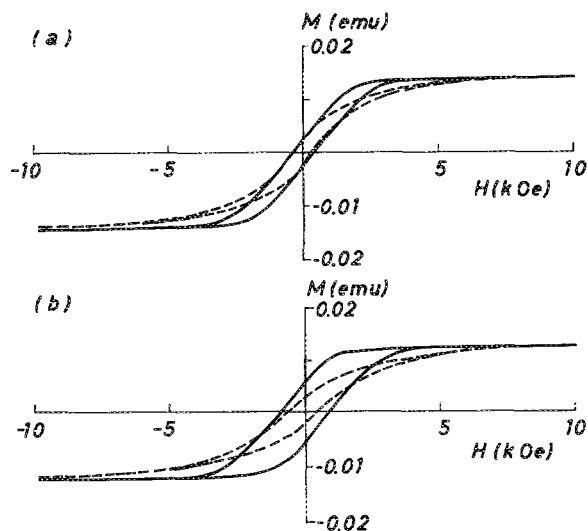


FIG. 18. Change of the magnetic hysteresis loop of the Co-Cr film after annealing at 500 °C for 5 h; (a) as-deposited, (b) after annealing. The solid and dotted lines indicate the perpendicular and in-plane hysteresis loop, respectively.

films as a function of the Cr composition. The saturation magnetization of the films decreases monotonically with increasing Cr composition and reaches to zero magnetization at about 35 at. % Cr. The Cr composition dependence of the saturation magnetization of our films with monatomic layer of Cr is similar to that reported earlier.¹⁻³ The values of the saturation magnetization are larger than their reported values for any given composition.

Long-term thermal stability of magnetic properties of the Co-Cr films with an artificial superlattice structure is a fundamental prerequisite to their practical use for perpendicular magnetic recording. The Co-Cr were isothermally annealed at temperatures 200–600 °C in an Ar atmosphere without an external magnetic field to study changes in magnetic properties by heat treatment. The results of the magnetic measurements after annealing showed that almost all the films exhibited an increase in coercivity and a small decrease in magnetization. The changes of these values were strongly dependent on the annealing conditions. Figure 18 shows hysteresis loops of the film with a Cr composition of 27.2 at. % before and after annealing at 500 °C for 5 h. Almost all films, except those with thickness ratios of 4/1, exhibited zero magnetization when the films were annealed at temperatures higher than 500 °C. The peculiar behavior, such as the decrease in the magnetization and/or the increase in coercivity, on annealing at temperatures lower than 500 °C can be attributed to a certain diffusion effect which causes a change in the structure from bcc to hcp stack at the interfaces of the Co and Cr layers. The zero magnetization observed at annealing at a high temperature, on the other hand, originated from the interdiffusion between Co and Cr layers.

IV. CONCLUSION

It is demonstrated that the Co-Cr films deposited in an alternating multilayer structure have an artificial superlat-

tice structure of hexagonal closed pack (hcp structure) with the c -axis normal to the film plane, where the c plane of the hcp-Co grows epitaxially on the (110) plane of the bcc-Cr. The films exhibit ferromagnetism over a wide periodicity range and thickness ratios of Co and Cr layers. The Co layer in contact with the Cr layer exhibits only small magnetization. The perpendicular magnetization hysteresis loops were observed over a wide periodicity range and thickness ratios of Co and Cr layers. It is concluded that the origins of the perpendicular magnetization are the magnetocrystalline anisotropy and the shape anisotropy related to the columnar structure.

The artificial superlattice structure is stable to thermal treatments at temperatures up to 500 °C. The interdiffusion of Co and Cr in each layer is observed after heat treatments at temperatures higher than 500 °C.

ACKNOWLEDGMENTS

I would like to thank Dr. M. Morizono, Dr. S. Miyaoka, and Dr. Y. Makino for continued encouragement and many helpful discussions during the course of this work. I also would like to thank Y. Sato, Y. Kondou, and H. Masuya for electron probe microanalysis and electron microscopic observation.

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