Soft Magnetic Properties of Co-Cr-O Granular Films

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Excellent soft magnetic properties have been achieved for Co-Cr-O granular films with nanoscaled grains of Co distributed in the amorphous intergranular regions of Cr₂O₃. A rapid decrease in coercivity has been observed with decreasing the volume fraction of Co. This rapid decrease in coercivity is attributed to the reduction in size $D$ of Co grains, and follows the $D^6$-power law of the random anisotropy model for nanocrystalline materials. The minimum coercivity value of 0.39 Oe is obtained at 75.5 volume \% of Co without post annealing. The saturation magnetization, in-plane anisotropy field, FMR frequency, and permeability at 1 GHz are 11.8 kG, 80 Oe, 2.94 GHz, and 141, respectively. Hence, Co-Cr-O granular films can be used in the high frequency devices operated over 2 GHz.

**Key words:** granular structure, soft magnetic material, thin film, nanocrystalline, magnetic anisotropy, ferromagnetic resonance

1. Introduction

In the past several years, there has been increasing interest in soft magnetic properties of granular films from both fundamental and practical standpoints. The granular soft magnetic films are composed of two regions of nanoscaled ferromagnetic grains and amorphous intergrains. The most attractive feature of this granular film is that they exhibit soft magnetic properties despite including nanocrystals with high magnetic anisotropy which usually causes a degradation of the soft magnetic properties of the films. The mechanism is currently understood by the random anisotropy model for nanocrystalline materials quantitatively \(^1\). Other essential characteristics such as in-plane anisotropy and magnetic losses at very high frequencies have also been investigated intensively to date \(^2\)-\(^3\).

On the other hand, from a viewpoint of practical applications operated over 100 MHz such as micro inductors \(^4\), noise filters, and micro sensors \(^5\), less magnetic loss is required for the magnetic films. The granular films are attractive because the electrical resistivities $\rho$ are very high compared to those of conventional amorphous alloy films. Up to now, iron-based granular films with excellent properties have been developed. For example, soft magnetic properties of Fe-M-N \(^6\)-\(^7\) and Fe-M-O \(^8\)-\(^9\) films have been reported, where $M$ are materials such as B, Hf, Zr, Al, rare-earth metal, etc. In these films, owing to very high $\rho$ of 300-1000 $\mu\Omega$cm, the magnetic loss relating to the eddy current is less than that in the amorphous soft magnetic films below several hundred MHz. Moreover, in recent years, the operation at much higher frequency has been required for the magnetic devices. For this purpose, some researchers have successfully achieved higher ferromagnetic resonance (FMR) frequency in Co-Al-O films, preserving the high $\rho$ \(^10\). As a result, the operation frequency has been extended up to GHz region.

In these granular systems, the interaction between Co grains through the intergrains is considered to be important for the soft magnetic property. Hence, we expected further improved properties by using other material. Under such situations, we were interested in the intergranular regions including 3d transition metal, and therefore studied Co-Cr-O granular films composed of intergranular regions including Cr \(^11\).

In the present work, we describe the magnetic properties of the Co-Cr-O granular films which are cosputtered using Co and Cr$_2$O$_3$ targets, and then discuss the essential correlation between the volume fraction of cobalt and the coercivity. We also explain the effect of additional elements briefly.

2. Experimental method

The Co-Cr-O thin films were deposited on glass and silicon (100) substrates in a magnetron sputtering system with a base pressure of 4 - 8 x 10$^{-7}$ Torr. The Co and Cr$_2$O$_3$ targets were sputtered simultaneously in an Ar atmosphere of 3.0 x 10$^{-5}$ Torr. In order to change the composition of the samples, the deposition rate of Cr$_2$O$_3$ was varied over a wide range from 0 to 10 nm/min, while that of Co was kept constant at 16 nm/min. The thicknesses of films were 550 nm for all the samples. In order to induce uniaxial magnetic anisotropy, the films were deposited in the presence of static in-plane magnetic field of 100 - 150 Oe. The substrate temperatures were below 50 degree during the deposition.

The structural and compositional characterization and the measurements of the electromagnetic properties were performed for the samples without any post annealing. The direct current resistivity was measured by the four-probe method. The structure was analyzed by transmission electron microscopy (TEM) and X-ray diffractometry (XRD) with CuK$\alpha$ radiation. The composition and chemical bonding were analyzed by X-ray photoelectron spectroscopy (XPS) using a MgK$\alpha$ X-ray source. Saturation magnetization $4\pi M_s$, coercivity $H_c$, and in-plane magnetic anisotropy field $H_k$ were measured by vibrating sample magnetometer (VSM). The complex permeability ($\mu = \mu' - j\mu''$) below 100 MHz was measured by the commercial permeance meter (Ryowa Electronics Inc.) \(^12\) together with HP4194A impedance analyzer and that from 100 MHz to 1 GHz was measured by the parallel
line method\textsuperscript{13} using HP8510C network analyzer. For the latter measurement, the measurement fixture was carefully designed to set its resonance frequency above 3.5 GHz.

3. Results and discussions

3.1 Film structure

In the present paper, we use a nominal volume fraction of Co to denote the composition of the samples. Figure 1 shows Co2p3/2 and Cr2p3/2 spectra of XPS for the Co-Cr-O film including 75.5 volume \% of Co. In the spectra, only the peaks owing to the metallic Co and Cr-O bond are observed, while peaks of Co-O, Co-Cr bonds and metallic Cr are not detected. The results of the XPS spectra are same for all the samples. It is also confirmed that the target composition of Cr$_2$O$_3$ is preserved in the films.

Figure 2 shows a typical X-ray diffraction pattern for the Co-Cr-O film of 75.5 volume \% of Co. The film shows broad diffraction peaks corresponding to fcc (111) and hcp (100), (002), (101) of Co, which is characteristic to the present Co-Cr-O films. The fcc and hcp peaks are decomposed by numerical fitting assuming a Gaussian distribution of these diffraction peaks after eliminating diffraction of CuK$\alpha_2$\textsuperscript{14}. As a result, the average size of fcc-Co ($D_{fcc}$) evaluated from FWHM using the Scherrer's formula\textsuperscript{15}, is larger than that of hcp-Co ($D_{hcp}$). The $D_{fcc}$ is estimated to be 4 nm. On the other hand, diffraction peaks relating to the crystallites of Cr$_2$O$_3$ are not observed. A (110) peak of Cr at 2$\theta$ = 44.39 \degree is negligible, which is consistent with the result of XPS.

We have also performed an observation of the microstructure. Figure 3 is a TEM image of the sample of 75.5 volume \% of Co. Several lattice images of 4-5 nm in size and a typical granular structure is observed, in which nanoscaled granular (dark area) and amorphous intergranular (bright area) region are included. The shape and size of the grains are not uniform. Since a clear separation between grains is not observed, we consider that a lot of nanoscaled grains are in contact with each other, combining with the resistivity characteristics as discussed in §3.2. Consequently, in our samples, nanoscaled metallic Co grains of 4 nm in average diameter

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{XPS spectra of the film with 75.5 volume \% of Co (Co77Cr9O14).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig2.png}
\caption{X-ray diffraction pattern of the film of 75.5 volume \% of Co (Co77Cr9O14).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig3.png}
\caption{A TEM image of 75.5 volume \% Co (Co 77Cr9O14) film.}
\end{figure}
are distributed in the amorphous intergranular region of Cr$_2$O$_3$.

In referring to the formation of granular structure of Co-M-O systems, Ohnuma et al. suggested that the difference of the heat of formation between Co-O and M-O should be large to realize an excellent microstructure. In the present Co-Cr-O system, the heats of formation of Co-O (Co$_3$O$_4$) and Cr-O (Cr$_2$O$_3$) are 887 J/mol and 1141 J/mol, respectively. Though the difference between these two is quite small compared to the Co-Al-O case, a good granular structure has been achieved in the present Co-Cr-O system.

### 3.2 Electric and magnetic properties

Figure 4 shows a dependence of dc resistivity $\rho$ on the volume fraction of Co. The $\rho$ steeply increases with decreasing the volume fraction of Co. The values of $\rho$ are 330 $\mu$Ωcm around 75.5 volume % of Co, where the films exhibit excellent soft ferromagnetic properties as discussed below. These $\rho$ values are more or less low compared to those of the films reported previously 8)-10), which is due to the less oxygen atoms in the Co-Cr-O films.

Figure 5 shows $M-H$ curves of (a) 77.2 volume % of Co, (b) 75.5 volume % of Co, and (c) 70.7 volume % of Co. It is found that uniaxial anisotropy becomes notable in the film below 77.2 volume % of Co. Remarkably, the coercivity steeply changes according to the volume fraction of Co within a range from 77.2 to 70.7 %. Among them, the sample of 75.5 volume % of Co exhibits the smallest coercivity $H_c$ and a large uniaxial anisotropy field, $H_k$. The $4\pi M_s$, easy axis coercivity, $H_{ce}$, and $H_k$ are 11.8 kG, 0.39 Oe and 80 Oe, respectively. Because of the large $H_k$ and high $4\pi M_s$, a very high FMR frequency is expected in the film as discussed below.

Figure 6(a) shows a dependence of coercivity on the Co volume fraction. This is reproducible at 75.5 % since the size of the error bar is less than the diameter of the open circle when we deposited three different samples at a same sputtering condition. In the present system, it is remarkable that the coercivity strongly depends on the volume fraction of Co. The minimum coercivity is smaller by three orders of magnitude than that of pure Co film. As shown in Table 1, the films including Co of 73.8 - 75.5 volume % have coercivities less than 2 Oe. The minimum value of 0.39 Oe is one order of magnitude smaller than that of Co-Al-O. On the contrary, the coercivity in hard axis ($H_{ch}$) is 1.8 Oe. From a theoretical viewpoint of the magnetization rotation process in a film having a uniaxial anisotropy, $H_{ce}$ has to be larger than $H_{ch}$ 16). Therefore, the reason for the larger $H_{ch}$ is likely to be due to the magnetic anisotropy dispersion in the film. Actually, these coercivities have been improved by post-annealing in a static magnetic field.

Figure 6(b) shows a dependence of the fractional saturation magnetization on the volume fraction of Co. Here, the fractional saturation magnetization is defined as the ratio of the total saturation magnetizations of the samples to the volume fraction of Co $(M_s/N_{Co})$. The fractional saturation magnetizations is almost constant at 15.7 kG for the samples of volume fraction of Co equal to or larger than 75.5 %. This result suggests that the Co grains in the Co-Cr-O films contain the same magnetization as that of pure Co film, probably remaining a strong ferromagnetic coupling between Co grains. On the other hand, below 75.5 volume % of Co, the fractional magnetizations begin to decrease with decreasing the volume fraction of Co, while the coercivity begins to increase. Hence, excellent soft magnetic properties are dominated by the nanoscaled Co grains having the same magnetizations as that of pure Co film, and the minimum coercivity appears near the boundary where magnetizations of Co grains begin to decrease.

We discuss the rapid change in coercivity of the present Co-Cr-O system. In referring to the mechanism of the soft magnetic properties of the granular films, it is understood by the random anisotropy model, which was originally analyzed by Alben et al. 17) and was discussed...
in a nanocrystalline system by Herzer. The basic model is as follows: strongly and ferromagnetically coupled grains of size $D$ with magneto-crystalline anisotropies $K_I$ are oriented at random. In the case of very small grains less than ferromagnetic exchange length $L_{ex}$, the randomized magneto-crystalline anisotropy of each Co grain is effectively canceled within the range of $L_{ex}$ in the entire film.

$$L_{ex} = \sqrt{A/K}$$  \hspace{1cm} (1)

where $A$ is the exchange stiffness and $<K>$ is the mean fluctuation amplitude of the anisotropy energy. This theory suggests that the coercivity $H_c$ is proportional to the 6th power of $D$ in the case that $<K>$ dominates the macroscopic uniaxial anisotropy $K_u$. This $D^6$-power law was confirmed experimentally in nanocrystalline Fe-Cu-Nb-Si-B within a range of $D$ from 10 to 50 nm.

On the other hand, when $<K>$ is smaller than $K_u$, $H_c$ is proportional to $D^3$ (for example, kinds of amorphous alloy film). Therefore, we compare the experimental results of the present Co-Cr-O films with this theory. Figure 7 shows a dependence of average grain size $D_{fcc}$ on the volume fraction of Co. All the grain sizes of the Co-Cr-O films are below 10 nm. The grain size decreases with decreasing volume fraction of Co, of which tendency is similar to that of coercivity observed in Fig. 6(a). Thus, the rapid decrease in coercivity is considered to be attributed to the reduction in size of the Co grains. Figure 8 shows a relation between $H_c$ and $D_{fcc}$ of the Co-Cr-O films. The relationship between $H_c$ and $D_{hcp}$ also shows similar tendency. The open and solid circles represent $Hce$ and $Hch$ of 79.0 - 75.5 volume % of Co, respectively, where Co grains contain the same magnetization as that of pure Co. On the other hand, the open and solid triangles correspond to $Hce$ and $Hch$ below 75.5 %, respectively. It is remarkable that coercivities are almost proportional to $D_{fcc}$ over 73.8 volume %. In the Co-Cr-O system, $Ku$ (7.6 x $10^4$ erg/cm$^3$) estimated by VSM is considerably large because of its large $Hk$ of 80 Oe. However, the tendency is similar to that in the case of $<K>$ > $K_u$. This is because of the presence of nanocrystalline Co with a large crystalline anisotropy $4.0 \times 10^6$ erg/cm$^3$, for single crystals) in the film. Thus, the appearance of soft magnetic properties in the Co-Cr-O film is explained by the random anisotropy model as well as the Fe-Cu-Nb-Si-B system.

On the contrary, below 75.5 volume %, the increase in coercivity with decreasing Co fraction may be caused by the gradual decrease in ferromagnetic coupling resulting in a gradual deviation from the random anisotropy model. The magnetism will probably

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**Table 1 Properties of the Co-Cr-O films**

<table>
<thead>
<tr>
<th>Composition</th>
<th>$H_c$ (Oe)</th>
<th>$4\pi M_s$ (kG)</th>
<th>$\rho$ ($\mu$Oe/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(volume % of Co) (at. %)</td>
<td>Easy Axis</td>
<td>Hard Axis</td>
<td></td>
</tr>
<tr>
<td>77.2 Co80Cr8O12</td>
<td>17.0</td>
<td>24.6</td>
<td>11.9</td>
</tr>
<tr>
<td>75.5 Co77Cr9O14</td>
<td>0.39</td>
<td>1.8</td>
<td>11.8</td>
</tr>
<tr>
<td>73.8 Co74Cr11O16</td>
<td>1.7</td>
<td>10.2</td>
<td>11.4</td>
</tr>
</tbody>
</table>

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**Fig. 6** Dependence of (a) coercivity and (b) fractional magnetization of Co on the volume fraction of Co.

**Fig. 7** Dependence of coercivity on the average grain size of fcc-Co in Co-Cr-O granular films. The open circles correspond to the films in which Co grains are strongly coupled (equal to or more than 73.8 volume % of Co).
approach to a superparamagnetic state with further
decrease in volume fraction of Co.

Figure 9 shows a dependence of hard-axis complex
permeability \( \mu = \mu' - j\mu'' \) on frequency for the film of 75.5
volume % of Co. The open and solid circles represent the
real and imaginary part of the measured permeability,
respectively. The real part of measured permeability
remains constant at \( \mu' = 141 \) below 1 GHz. On the other
hand, the imaginary part is \( \mu'' = 1 \) below 300 MHz and
then increases with frequency. The solid and dotted lines
represent calculated \( \mu' \) and \( \mu'' \), respectively, by using the
solution of Landau-Lifshitz equations taking account of
the coherent spin rotation as follows 19)-20):

\[
\mu = \frac{4\pi M_s \omega^2 - \omega^2} {H_k^2 \left( \omega^2 - \omega^2 + j4\pi\lambda\omega \right)} 
\]

(2)

\[
\omega^2 = 4\pi M_s H_k^2
\]

(3)

where, \( \omega_0 \) is FMR frequency, \( \gamma \) is gyromagnetic constant
(here, \( 2.34 \times 10^5 \) m/As), and \( \lambda \) is relaxation frequency.

The calculated permeability agrees well with the
measured ones. This indicates that the domain wall
motion is eliminated because of the operation at a very
high frequency. Furthermore, since the Co-Cr-O film has
a large \( 4\pi M_s \) and \( H_k \), a high FMR frequency of 2.94 GHz
has been achieved. The skin depth of the film is
estimated at 1.4 \( \mu \)m at 2.9 GHz and eddy current loss is
negligible in this frequency region because of the large \( \rho \).
In consequence, it is expected that the real permeability \( \mu' \)
remains constant up to 2 GHz so that the present Co-Cr-O
system is applicable to the high frequency devices
operated around 2 GHz.

As for the effect of additional elements on the
magnetism of the Co-Cr-O granular films, we briefly
describe it below. It has been believed for several years
that only Ni, Pd and Pt enhance \( H_k \) and \( H_c \) of the granular
films 10). However, we found that other 4d or 5d
elements also enhance \( H_k \) of the granular soft magnetic
films. Figure 10 shows a typical \( M-H \) curve of
Co\(_{65}\)Ir\(_{12}\)Cr\(_{11}\)O\(_{12}\) granular film which includes
nanoscaled hcp+fcc Co grains of 7.5 nm in average size
and amorphous intergrains. It shows a very large \( H_k \)
of 130 Oe compared to that of the Co-Cr-O film. As a
result, the FMR frequency has been improved up to 3.4
GHz and the measured \( \mu' \) is 77 at 1 GHz. A similar effect
was also observed by additives of Rh, Ag and Au 21).
These additional elements are effective to expand the
operation range of the granular soft magnetic
films. The mechanism of the enhancement of the large
\( H_k \) and low \( H_c \) has to be clarified in the future.

4. Conclusions

Soft magnetic properties of the Co-Cr-O granular
crystals prepared by codeposition of Co and Cr\(_2\)O\(_3\) are
investigated. In the resulting films, nanoscaled Co grains
are distributed in the amorphous intergranular regions of

![Fig. 9 Dependence of hard-axis complex permeability \( \mu = \mu' - j\mu'' \) on frequency for the film of 75.5 volume % of Co. The solid and dotted lines denote the calculated \( \mu' \) and \( \mu'' \), respectively.](image)

![Fig. 8 Dependence of average grain size of fcc-Co on the volume fraction of Co in the Co-Cr-O granular films.](image)

![Fig. 10 M-H curve of the Co\(_{65}\)Ir\(_{12}\)Cr\(_{11}\)O\(_{12}\) granular film.](image)
Cr$_2$O$_3$. A drastic change in coercivity is observed depending on the volume fraction of Co. This drastic decrease in coercivity with decreasing Co fraction follows the $D^6$-power law of the random anisotropy model for nanocrystalline materials. The excellent soft magnetic property has been achieved at 75.5 volume % of Co. The $4\pi M_s$ of 11.8 kG, $H_k$ of 80 Oe, and $H_C$ of 0.39 Oe are obtained. The dc resistivity is 326 $\mu$Ocm. The real part of the permeability remains constant at 141 up to 1 GHz and the FMR frequency is 2.94 GHz. The Co-Cr-O granular films can be used in the high frequency devices operated around 2 GHz. We have also found that additional elements such as Ir enhance $H_k$ of the granular soft magnetic film, resulting in the improvement of FMR frequency.

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References