High-coercivity Co-ferrite thin films on (100)-SiO₂ substrate

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Co-ferrite films were deposited on SiO₂ single-crystal substrates. The as-deposited films were amorphous. The crystallization required an annealing at 700 °C or higher. Magnetic properties were found to be strongly dependent on annealing temperature, annealing duration, and film thickness. A small film thickness can restrict the formation of large particles. A coercivity as high as 9.3 kOe was achieved in the 50 nm film after annealing at 900 °C for 15 min deposited on (100)-SiO₂ substrate. The high coercivity was associated with a nanostructure, lattice strain, and larger Raman shift with a relatively sharp peak. © 2004 American Institute of Physics. [DOI: 10.1063/1.1695438]
Our AFM study revealed a clear relationship between microstructure and coercivity. As shown in Fig. 2, the 20 nm film was not continuous and the microstructure was not uniform (since a few relatively large particles were visible). The 50 nm film possessed a uniform microstructure, as all particles were found in the range of 40–50 nm. Figure 3 gives HRTEM images of the 50 nm film after annealing at 900 °C for 2 h. Grains of 30–50 nm were observed under HRTEM. The grain size was in the same order of the particle size under AFM. In the 100 nm film, the average particle size under AFM was bigger (70–80 nm) and a few large particles were observed. The presence of the larger particles indicated the possibility of abnormal grain growth. When the film thickness was grown to 450 nm, the surface was fully covered with large particles and the microstructure was not uniform. This work showed that the microstructure is strongly dependent on the film thickness. When the film was too thick, large particles were formed immediately after crystallization. These results indicated that a thin film can restrict the formation of large particles. The decrease in coercivity with increasing film thickness was certainly associated with the formation of large particles.

In this work, we have studied magnetic properties as a function of annealing time at the optimized temperature (900 °C). A reduction in annealing time resulted in a further increase of coercivity. The high value of coercivity (9.3 kOe) was obtained after annealing for 15 min. This value is much higher than the coercivity of bulk Co-ferrite (below 1 kOe). This film possessed an in-plane anisotropy, as high coercivity and remanence were measured in plane, as shown in Fig. 4.

It is very interesting to investigate the coercivity mechanism. Except for a nanograin structure, the fitting of XRD peaks for thin films indicated the presence of strain. Strain in Co-ferrite thin films has been reported previously, and it may contribute to high coercivity. Raman spectroscopy is a powerful tool for the examination of strain.

Table 1 shows the Raman spectra of the tetrahedral site for Co-ferrite powder and the Co-ferrite films (50 nm and 450 nm, respectively, after annealing at 900 °C) together with the reference sample (Co-ferrite powder). There are two sites (octahedral and tetrahedral, as denoted as O and T sites) for 3d ions in the spinel structure. Because of a strong overlapping of the O-site peak with the peaks of SiO₂, only the peak of the T site is shown in Fig. 5. It can be seen that the T-site peak of the reference sample is broadened. The 450 nm Co-ferrite appeared sharper and a small blueshift was visible. For the 50 nm Co-ferrite, the sharper peak had a more obvious blueshift. As reported previously, lattice strain may result in a shift of the Raman peak. A blueshift in Co-ferrite films in this work was associated with the lattice strain observed in our XRD examinations.

As reported, diffusion anisotropy can be achieved in Co-ferrite, because spinel Co-ferrite may contain a relatively high density of vacancies and possess a relatively high diffusion rate of ions. In this work, we have performed magnetic annealing on a powder reference sample and Co-ferrite films. The reference powder sample possessed a relatively large diffusion anisotropy after a magnetic annealing at 300 °C. On the other hand, the 450 nm film only had a small magnetic anisotropy after magnetic annealing, while no sig-

![AFM images of Co-ferrite films after annealing at 900 °C for 2 h with different thicknesses: 20 nm (a), 50 nm (b), 100 nm (c), and 450 nm (d).](image)

### Table I. Magnetic properties of 100 nm films in the as-deposited state and after annealing at different temperatures for 2 h. (Coercivity \( H_{c,i} \), measured in the film plane—in plane; the remanence ratio \( \langle M_r / M_s \rangle_i \) in plane; coercivity \( H_{c,i} \), measured perpendicular to the plane—out of plane; remanence ratio \( \langle M_r / M_s \rangle_i \) out of plane; saturation magnetization \( M_s \); grain size determined from Scherrer’s formula.)

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>( H_{c,i} ) (kOe)</th>
<th>( \langle M_r / M_s \rangle_i )</th>
<th>( H_{c,i} ) (kOe)</th>
<th>( \langle M_r / M_s \rangle_i )</th>
<th>( M_s ) (emu/cm³)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.5</td>
<td>80.6%</td>
<td>1.8</td>
<td>61%</td>
<td>220</td>
<td>28.9</td>
</tr>
<tr>
<td>50</td>
<td>8.4</td>
<td>85%</td>
<td>2.0</td>
<td>60%</td>
<td>250</td>
<td>55.6</td>
</tr>
<tr>
<td>100</td>
<td>7.5</td>
<td>75%</td>
<td>6.1</td>
<td>65%</td>
<td>303</td>
<td>75.1</td>
</tr>
<tr>
<td>150</td>
<td>3.2</td>
<td>78%</td>
<td>3.1</td>
<td>66%</td>
<td>291</td>
<td>168.5</td>
</tr>
<tr>
<td>450</td>
<td>2.7</td>
<td>81.6%</td>
<td>2.4</td>
<td>69%</td>
<td>345</td>
<td>259.2</td>
</tr>
</tbody>
</table>

![FIG. 2.](image)
Significant magnetic anisotropy was observed in the 50 nm film after magnetic annealing. This result indicated that the ionic diffusion is strongly restricted in Co-ferrite films, particularly in thin films (~50 nm). These could be related with the sharpness of Raman peak ~15 and high coercivity in Co-ferrite thin films. The investigation will be continued in our future study.

As found in this work, thin Co-ferrite films deposited on a (100)-SiO$_2$ substrate possessed high values of coercivity accompanied by the presence of a relatively large lattice strain. Co-ferrite and SiO$_2$ have a relatively large difference in thermal coefficient. ~17 The relatively large lattice strain in Co-ferrite thin films was probably due to the difference in thermal coefficient, because the Co-ferrite phase was formed at a relatively high temperature (~900 °C). The presence of lattice strain may induce a large magnetic anisotropy and therefore lead to high coercivity. ~12,18 The lattice strain is expected to be reduced with increasing film thickness, while coercivity decreased with film thickness. The coercivity mechanism and the relationship with lattice strain need to be investigated further.

In conclusion, Co-ferrite thin films were deposited on SiO$_2$ single-crystal substrates. The influence of annealing temperature and film thickness on magnetic properties has been investigated. A coercivity of as high as 9.3 kOe was achieved in the 50 nm Co-ferrite film on a (100)-SiO$_2$ substrate after annealing at 900 °C for 15 min. This coercivity value is very high for Co-ferrite. The high coercivity is associated with nanograined structure and lattice strain, accompanied by a blueshift and sharper peak in the Raman spectrum.