Structural and magnetic properties of Fe-Al₂O₃ films prepared by helicon plasma sputtering

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Structural and magnetic properties of Fe-Al$_2$O$_3$ films
prepared by helicon plasma sputtering

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Abstract. Fe-Al$_2$O$_3$ films have been prepared by on-off deposition of Fe with continuous Al$_2$O$_3$ deposition, and also subsequently irradiated by 400 keV Ar ions for controlling of the structural and magnetic properties of the films. CEM spectra of the as-deposited films show the decrease in the average hyperfine fields ($H_{hf}$) with decreasing Fe/ Fe-Al$_2$O$_3$ volume ratio with keeping the $H_{hf}$ orientation parallel to the film plane. The decrease in $H_{hf}$ indicates the decrease of the Fe particle size and the in-plane orientation of $H_{hf}$ implies the non spherical shape of Fe particles in the film. On the other hand, 400 keV Ar ion irradiation induces the change from the superparamagnetic characteristics to the ferromagnetic one; the ferromagnetic peaks showing the random orientation of $H_{hf}$ appear and indicate the spherical growth of Fe particles in Al$_2$O$_3$ matrix.

1. Introduction
Nanocomposite materials like Fe-AlO films are very attractive in practical and basic fields because of appearance of new physical properties. Many preparation techniques (sputtering, ion implantation and sol-gel) are used to prepare nanocomposite materials [1-4]. The physical properties of nanocomposite materials are closely related to the size, shape and distribution of metal particles in insulating matrix. It has been reported that the film preparation by pulsed laser deposition and the process of ion beam irradiation after film preparation were suggested to control the properties of metal particles in insulating matrix [5, 6]. In this work, we deposited Fe-Al$_2$O$_3$ films with the open-close (on-off) operation of shutter in the front of helicon plasma magnetron cathode for film preparation [7], controlling the Fe contents in the film. Following the deposition, we did Ar ion irradiation for as-deposited film in order to modify the structural and magnetic properties of Fe particles in Fe-Al$_2$O$_3$ nanocomposite films.
2. Experimental

Fe-Al$_2$O$_3$ films were prepared on high resistive n-type (100) Si substrates by helicon plasma sputtering method in a base pressure lower than 1x10$^{-7}$ Torr and in 7x10$^{-4}$ Torr Ar gas pressure during depositions. The deposition rates of Fe and Al$_2$O$_3$ were 0.06 and 0.008 nm/sec, respectively. The Fe-Al$_2$O$_3$ film was formed by on-off deposition of Fe with continuous Al$_2$O$_3$ deposition. The composition and the thickness of Fe-Al$_2$O$_3$ film were controlled by the ratio of on-off Fe deposition and the total deposition time. In addition it is expected that the change in on-off time of Fe deposition affects the structural and magnetic properties of Fe-Al$_2$O$_3$ films. The measurement of conversion electron Mössbauer spectroscopy (CEMS) was done using a Mössbauer spectrometer with 740 MBq $^{57}$Co $\gamma$-ray source (Rh matrix), and conversion electrons were detected with a proportional counter flowed with He + 10 % methane mixture gas. The CEM spectra were analyzed by least square fitting assuming overlapped Lorentzian curves of singlet peak, doublet peaks and sextet peaks. The distribution of hyperfine field was assumed for broad widths of sextet peaks. The ratios of peak intensities for first, second and third peaks of sextet peaks were fixed as 3:x:1 where x was a free parameter. The structural and magnetic properties of the films were examined by x-ray diffraction (XRD) using CuK$_\alpha$ radiation and vibrating sample magnetometer (VSM) up to 1.5 T. The ion irradiation has been performed to the fluence of 5x10$^{16}$ ions/cm$^2$ by 400 keV Ar ions. The ion range of 400 keV Ar ions in Fe is calculated to be 182 nm by TRIM code. As the 3s (on)-12s (off) film (144 nm) is thinner than this ion range, the implanted Ar ions stop into Si substrate passing through Fe-Al$_2$O$_3$ film.

3. Results and discussion

Figure 1(a) and 1(b) are the CEM spectra of Fe-Al$_2$O$_3$ films prepared by on-off Fe deposition. The films were prepared on the condition of the same ratio between on- and off- Fe deposition time, 5s (on) -10s (off) and 3s (on) -6s (off) with the continuous Al$_2$O$_3$ deposition for 60 minutes. The CEM spectra show the overlapping of sextet peaks and singlet peak. Although not shown here, the magnetization curves of 5s-10s and 3s-6s films show partially superparamagnetic characteristics which corresponds to the single peak in the CEM spectra. The thicknesses of Fe layer corresponding to 5s or 3s deposition is within 0.3 nm. The thickness of Al$_2$O$_3$ by continuous deposition under Fe deposition is less than 0.12 nm. Therefore, it seems that Fe layer does not continuous and forms Fe particles in Al$_2$O$_3$ matrix. The average hyperfine fields ($H_{hfs}$) of figures 1(a) and 1(b) are 21.8 T and 18.2 T, respectively. From the values of $H_{hfs}$ in CEM spectra at room temperature below the superparamagnetic blocking temperature, the Fe particle size in Al$_2$O$_3$ matrix of 5s-10s and 3s-6s films can be estimated to be 2.9 nm and 2.6 nm ( assuming that magnetic anisotropy energy constant, K equals to 5x10$^5$ J/m$^3$ and particles are spherical.) [8]. Nevertheless, using Scherrer’s equation, the Fe particle sizes from the widths of Fe (110) peak in XRD patterns of 5s-10s and 3s-6s films are estimated to be 2.0 nm and 1.9 nm, respectively. As there is no difference in the particle sizes estimated from XRD patterns of the both films, the difference in the values of $H_{hfs}$ implies the structural change which results from the shape and distribution of Fe particles in 5s-10s and 3s-6s films.

**Figure 1.** CEM spectra of Fe-Al$_2$O$_3$ films prepared by on-off Fe deposition, (a) 5s-10s and (b) 3s-6s.
In Table 1, the $H_{\text{hf}}$ of Fe-Al$_2$O$_3$ films decreases with decreasing volume ratio of Fe in the films. In addition, the intensity ratio of second/third -peaks does not change against the volume ratio of Fe. The value 4 in the peak ratio indicates that the $H_{\text{hf}}$ orients to the film plane. Therefore, the shape of the Fe particles in Fe-Al$_2$O$_3$ films seems to elongate in the film plane. It implies that the Fe particles dispersed in the as-deposited films still keep multi layer-like structure.

It is shown in Figure 2 that the CEM spectrum (2a) of 3s (on) -12s (off) films with the continuous Al$_2$O$_3$ deposition for 120 minutes has singlet peak and doublet peaks. Although not shown here, the magnetization curve of 3s-12s film shows the superparamagnetic characteristics, which corresponds to the singlet peak in the CEM spectrum. On the other hand, the CEM spectrum (2b) of 3s-12s film after 400 keV Ar ion irradiation to the fluence of 5x10$^{16}$ ions/cm$^2$ shows sextet peaks, doublet peaks and small singlet peak. The appearance of sextet peaks indicates the growth of Fe particles. As seen in table 1, the intensity ratio of second/third -peaks in the sextet peaks is 2.3; that is, the direction of magnetization of Fe particles in the film seems to be random. Consequently, the shape of Fe particles in the film after 400 keV Ar ion irradiation is indicated to be a sphere. Therefore, it is clear that the 400 keV Ar ion irradiation alters the size and shape of Fe particles in Al$_2$O$_3$ matrix.

**Table 1.** The Fe volume ratio, film thickness and hyperfine parameters of Fe-Al$_2$O$_3$ as-deposited films and the film after 400 keV Ar ion irradiation to the fluence of 5x10$^{16}$ ions/cm$^2$.

<table>
<thead>
<tr>
<th>Open (sec)-close (sec)</th>
<th>Nominal $x$ of Fe$_x$(Al$_2$O$<em>3$)$</em>{1-x}$</th>
<th>Nominal thickness (nm)</th>
<th>$H_{\text{hf}}$ (T)</th>
<th>Peak intensity ratio (2nd/3rd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-0</td>
<td>0.88</td>
<td>244.8</td>
<td>31.9</td>
<td>4</td>
</tr>
<tr>
<td>5-5</td>
<td>0.78</td>
<td>136.8</td>
<td>30.2</td>
<td>4</td>
</tr>
<tr>
<td>5-10</td>
<td>0.71</td>
<td>100.8</td>
<td>21.8</td>
<td>3.5</td>
</tr>
<tr>
<td>3-6</td>
<td>0.71</td>
<td>100.8</td>
<td>18.2</td>
<td>3.9</td>
</tr>
<tr>
<td>3-12</td>
<td>0.6</td>
<td>144</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-12 after irradiation</td>
<td>0.6</td>
<td>144</td>
<td>30.8</td>
<td>2.3</td>
</tr>
</tbody>
</table>

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![Figure 2](image-url) **Figure 2.** CEM spectra of Fe-Al$_2$O$_3$ films prepared by on-off Fe deposition, (a) 3s-12s before ion irradiation and (b) 3s-12s after ion irradiation. The shaded peaks are doublet peaks.
4. Conclusion
In conclusion, the CEM spectra of the nanocomposite Fe-Al$_2$O$_3$ films prepared by helicon plasma sputtering show that the decrease of the Fe particle size with decreasing Fe volume ratio judging from the values of $H_{hf}$, and the layer-like structure from the direction of $H_{hf}$ oriented to the film plane. On the other hand, 400 keV Ar ion irradiation to the superparamagnetic film induces the growth of spherical Fe particles in the films, which is indicated from the ratio of peak intensities of sextet peaks appeared by the ion irradiation.

References
[8] Morup S 1990 *Hyperfine Interactions* 60 959-74