Surface analysis of Fe–Si–Al sputtered alloy films by conversion electron Mössbauer spectrometry

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Fe–Si–Al alloy films were deposited on silicon wafers heated to various temperatures by DC Ar sputtering and the microstructure of the films was analyzed by CEMS. As-prepared films on cooled substrate contained superparamagnetic components in addition to magnetic components. The fine grains included yielded a random orientation of magnetic spins in the films. The spin orientation became perpendicular to the surface by annealing the sputtered films at more than 773 K. The magnetic fields in sputtered films on a heated substrate were parallel to the surface.

1. Introduction

The Fe–Si–Al alloy with composition of Si: 9.62 wt%, Al: 5.38 wt% and Fe: balance (called sendust) shows excellent soft magnetic characteristics [1]. However, cast sendust alloy is mechanically hard and has poor workability. Therefore, this cast alloy has been pulverized using ball milling before making films. In the powdering process, the crystalline structure of the alloy became amorphous and disordered [2]. Si can substitute Al continuously in Fe–Si–Al alloy. The prepared sendust alloy deviates from the stoichiometric composition Fe3(Si, Al). We have

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studied the effect of particle size and shape on the magnetic properties of sendust powder by conversion electron Mössbauer spectrometry (CEMS) and transmission Mössbauer spectrometry (TMS) [3]. The disordered structure of the α type transforms to the ordered structure of the B2 and DO₃ type by annealing [4]. The unit cell of the DO₃ structure is divided into four face-centered cubic sublattices, in which two sites are distinguished. In a completely ordered DO₃ structure, one third of the Fe atoms occupy sites surrounded by eight Fe atoms as nearest neighbors (nn atoms), and two thirds of the Fe atoms occupy sites surrounded by four Fe and four (Si, Al) atoms as nn atoms [5]. The magnetic sites show hyperfine fields of about 31 and 20 T, respectively. A "gas atomization" technique produces homogeneous sendust powders. It was found that target disc made of homogeneous powder has good workability [6]. The present paper describes a CEMS study of sendust films, deposited on silicon wafers by sputtering the target disc and the effect of annealing and different substrate temperature on the sputtered films.

2. Experimental

85 wt% Fe–9.6 wt% Si–5.4 wt% Al (composition Fe₇₃.₇Si₁₆.₆Al₉.₇) powder was produced using a gas atomization technique at 6 atm Ar pressure. A steel capsule filled with the powder was evacuated, sealed by welding and hot pressed at 1473 K and about 60 kg/mm² in an extrusion press [6]. Using the target material of the extruded alloy, sendust films of 500 nm thickness were deposited on cooled or heated silicon wafers by DC Ar sputtering (Nichiden Anelba: SPF-332H, with Ar pressure: 2.4–2.0 Pa, distance between electrode and sample: 80 mm, rotation of cooled substrate: 10 rpm, DC sputtering power: 500 W). The composition of the as-sputtered films was 85.44 wt% Fe–9.68 wt% Si–4.88 wt% Al (Fe₇₄.₄Si₁₆.₈Al₈.₈), a little different from that of the target material.

As-deposited films were annealed for 2 h in an Ar atmosphere at various temperatures. CEM spectra were measured with a 370 MBq ⁵⁷Co(Rh) source at room temperature using a home-made proportional flow counter (He + 5% CH₄) [7]. The incident γ rays were perpendicular to the sample surface. X ray diffraction patterns and electron probe micro analytical data were observed to confirm the structure and the distribution of Al, Si and Fe in the grains. The (220) plane was oriented on the Si(111) substrate plane.

3. Results and discussion

The ordered DO₃ structure has two Fe sites: one surrounded by 4Fe and 4(Si, Al) as nn atoms and 6Fe as next nearest neighbors (nnn atoms) and the other by 8Fe as nn atoms and 6(Si, Al) as nnn atoms [8]. Therefore, the sputtered films were first fitted by two sextets, with 31 T (Fe environments of 8Fe as nn atoms and 6(Si, Al) as nnn atoms) and 20 T (Fe environments of 4Fe and 4(Si, Al) as nn atoms), and
further by adding several other sextets. The additional sextets belong to Fe sites with less or more than 4Fe and 4(Si, Al) as nn atoms or Fe sites with less than 8Fe as nn atoms, which will be caused by any deviation from the stoichiometric composition Fe3(Si, Al) or any disordering. The Mössbauer parameters obtained from a computer fit are listed in Table 1.

Stearns [5] showed that the hyperfine field on Fe sites with 8Fe as nn atoms in Fe–Si alloys decreases by about 4.5 T if a Fe atom on 8Fe sites as nn atoms is replaced by a Si atom. Arita et al. [8] introduced the relation between the hyperfine fields (H_in) and the number of the nn Si atoms, considering the influence of the nnn Si configuration: \( H_{\text{in}} = 32.1 - 1.184(\text{nn Si})^{1.668} - 0.14(\text{nnn Si}) \). Therefore, two additional sextets with hyperfine fields of about 28 and 25 T correspond to two kinds of Fe sites surrounded by 6Fe2(Si, Al) and 5Fe3(Si, Al) as nn atoms, respectively.

Miyazaki et al. [9] have decomposed the sextet peaks of Fe site surrounded by 4Fe4(Si, Al) as nn atoms into two magnetic components on the base of the binomial distribution model, with respect to the ratio of Al and Si atoms. The isomer shift (IS) increases slightly by an increase in Al content [10] and the isomer shift of the Fe site surrounded by 4Fe4Al atoms is high (0.28 mm/s) [11]. However, the sextet peaks of Fe sites surrounded by 4Fe4(Si, Al) could not be easily decomposed into two components. Figs. 1 and 2 show CEM spectra of the as-sputtered film and the films annealed at 673, 773, 873 and 973 K for 2 h. In these films, the hyperfine distributions were different from those of an ideal DO3 ordered structure. Two paramagnetic doublets were observed in addition to four magnetic sextets. The former was considered to be superparamagnetic peaks of small crystalline grains with a size calculated to be about 11 nm from the peak width of X-ray diffraction patterns. The doublet with IS = 0.23 mm/s and QS = 0.92 mm/s was attributed to Fe atoms surrounded by Si and Al atoms, such as 4Fe4(Si, Al), and the other, with

<table>
<thead>
<tr>
<th>Fe sites (Fe environments as nn atoms)</th>
<th>( H_{\text{in}} ) (T)</th>
<th>Isomer shift (mm/s)</th>
<th>Quadrupole splitting (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 8Fe</td>
<td>30.7 ± 1.0</td>
<td>0.06 ± 0.02</td>
<td>-0.01 ± 0.05</td>
</tr>
<tr>
<td>(b) A6</td>
<td>28.2 ± 1.0</td>
<td>0.052 ± 0.03</td>
<td>0.06 ± 0.13</td>
</tr>
<tr>
<td>6Fe2(Si, Al)</td>
<td>24.5 ± 0.4</td>
<td>0.17 ± 0.03</td>
<td>-0.02 ± 0.08</td>
</tr>
<tr>
<td>(c) A5</td>
<td>20.0 ± 0.4</td>
<td>0.24 ± 0.01</td>
<td>0.06 ± 0.07</td>
</tr>
<tr>
<td>(d) A4</td>
<td>superparamagnetism</td>
<td>0.23 ± 0.04</td>
<td>0.92 ± 0.09</td>
</tr>
<tr>
<td>(e) SP1</td>
<td>superparamagnetism</td>
<td>0.10 ± 0.04</td>
<td>1.38 ± 0.07</td>
</tr>
</tbody>
</table>

Table 1
Average Mössbauer parameters of Fe–Si–Al alloy films prepared by Ar DC sputtering.
Fig. 1. CEM spectra of (a) as sputtered Fe–Si–Al film and (b) the annealed film at 673 K for 2 h.

IS = 0.10 mm/s and QS = 1.38 mm/s, to Fe atoms surrounded by a few Si and Al atoms such as 8Fe0(Si, Al) and 6Fe2(Si, Al) since the isomer shift is close to that of the magnetic sextets. The intensity of these doublets decreased by annealing.

The intensity ratio analysis of the sextets (I1,6 : I2,5 : I3,4 = 3 : 2 : 1) proved that the magnetic moments in a layer of about 100 nm thickness were oriented at random. Fine grains contained in the sputtered films were considered to contribute to the decrease of anisotropic magnetism at the surface, that is, to random orientation. It was found that the magnetic fields were reoriented from random to normal to the surface at temperatures above 773 K, as shown in fig. 3 (a). The average composition of the films when annealed up to 873 K did not change much, but the Si concentration increased by more than a factor 2.5 when annealing at 973 K for 2 h and cubic FeSi compound was produced, although the Al concentration did not change in the film. Since the FeSi structure grows from the interface between sendust films and Si wafers by the incorporation of Si atoms into the films, the columnar structure may exist nearly perpendicular to the substrate. The spin orientation of the annealed sendust films is considered to be along the normal to the surface.
Fig. 2. CEM spectra of Fe–S–Al films on Si wafer, prepared by Ar DC sputtering at room temperature and annealed for 2 h at (a) 773 K, (b) 873 K and (c) 973 K.

because the magnetic moment lies on a cone. The relation between the columnar structure and spin orientation was reconfirmed by TEM observation of Fe–Co thin films [12]. The annealing temperature dependence of hyperfine fields and the intensity ratio are shown in figs. 4 and 5, respectively. The hyperfine fields of each component did not change, but the intensity ratio of components changed considerably by annealing. The component with hyperfine field of 19.7 T came mainly from a Fe site in cubic FeSi produced at high temperature. In the temperature range between 675 and 875 K, the intensity ratio of Fe environments of 8Fe and 4Fe4(Si, Al) as nn atoms deviated strongly from that (1 : 2) of DO3 structure. It is suggested that a phase separation occurs with the incorporation of Si while
Fig. 3. Relation between peak ratio \((P_{2,5}/P_{1,6})\) of magnetic sextets and preparation temperatures.
(a) Effect of annealing temperature after deposition, (b) effect of substrate temperature under deposition.

Fig. 4. Effect of annealing temperatures after deposition on magnetic hyperfine fields in sendust film. Next nearest neighbours: (a) 8Fe, (b) 6Fe2(Si, Al), (c) 5Fe3(Si, Al), (d) 4Fe4(Si, Al).

Fig. 5. Relative intensities of Fe components in sendust annealed films.
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annealing. A doublet of Fe$^{3+}$ was produced by the reaction with residual oxygen in the Ar atmosphere.

Fe–Si–Al films were further deposited on Si wafers heated to 573, 673, 723, 773, and 873 K. CEM spectra of these films are shown in fig. 6. The directions of spins in almost all Fe–Al–Si films formed on the heated substrate were parallel to the surface as shown in fig. 3 (b). Components (A5 and A6) due to Fe environments of 5Fe3(Si, Al) and 6Fe2(Si, Al) as nn atoms were observed in addition to the

![Fig. 6. CEM spectra of Fe–Si–Al films sputtered on Si wafer heated at (a) 573 K, (b) 673 K, (c) 723 K and (d) 873 K.](image-url)
main components due to Fe environments of 8Fe0(Si, Al) and 4Fe4(Si, Al) in all CEM spectra. The hyperfine fields and the intensity ratio of each component are shown in figs. 7 and 8, respectively. With the increase of the substrate temperature, the hyperfine fields increased a little, and the intensity of the A6 component decreased, but the intensity of the A5 component increased again at 873 K. X-ray diffraction peaks corresponding to superlattice diffraction were not clearly seen, but (220) and (222) peaks in body centered cubic (bcc) structure were observed. A perfectly ordered DO3 structure was not present in these films. The film deposited on the substrate heated at 773 K gave the lowest coercive force and highest effective permeability in these films. When the film prepared on the substrate heated to 673 K was further annealed at 773 K for 2 h, the A5 component decreased but
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the whole spectrum did not change much by annealing. A large amount of A5 and A6 components were included in this film compared with the as-sputtered film on the substrate heated to 773 K. Noort reported that the A5 and A6 components increase at the transient layers of the sendust films formed on Si wafer [13]. Therefore, the heating of the substrate during sputtering is more effective than the annealing after deposition. Annealing at 773 K for 1 h resulted in an improved DO3 structure of sendust in films formed on glass substrated by RF sputtering [9]. The difference between DC sputtering and RF sputtering suggests that it is more important to control the microstructure and elemental deviation of the initially formed films rather than the successive annealing.

4. Conclusion

Films of Fe–Si–Al alloy were prepared by DC sputtering. Fine grains included in the sputtered films lead to a random orientation of magnetic moments. The substrate affects the spin orientation of Fe–Si–Al films at high temperature. In order to fabricate good sendust films, it is important to control the initial composition of as sputtered films and to prevent the influence of the substrate. Heating the substrate during sputtering was found to be more effective for sendust films than annealing after deposition. The analysis of magnetic hyperfine fields and spin orientation proves to be a sophisticated way to differentiate between the quality of various sendust films.

References