Spin Orientation of Iron Films Produced by Laser Deposition

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Iron films deposited on Al substrates were investigated using Mössbauer spectroscopy and scanning electron microscopy. It was found that the nuclear spin orientation of iron films produced by deposition of Fe atoms vaporized by resistive heating was perpendicular to the substrate surface, while that of films produced by laser deposition of Fe was parallel to the substrate surface. The droplets produced by laser deposition have a disk-like shape and perturb the spin orientation of the film.

Laser deposition is a very useful technique for producing thin films of various materials.[1] The laser-deposition process is complicated because of the high energies and fluxes involved. We reported previously that laser ablation of iron metal induces novel reactions which produce species that cannot be formed under normal conditions.[2,3] We also reported that laser-deposited iron films on Al or Si substrates form Fe/Al or Fe/Si reaction products at the interface between the iron films and substrate and that the nuclear-spin orientation of these films tends to be parallel to the substrate surface.[4,5] Mössbauer spectroscopy is very useful for investigating the magnetic properties and the spin orientation of iron-based materials; this is because the intensity ratio of sextet absorption in Mössbauer spectra provides direct information on the orientation of the nuclear spin.[6] Laser-evaporated Fe atoms have kinetic energies of several hundred eV, which is sufficiently energetic to cause the atoms to migrate on the substrate surface prior to crystallizing. Another characteristic of laser evaporation is that, depending on the condition of the target material, it not only evaporates atoms but also particles; these particles are referred to as "droplets". In this study, we produced relatively thick (900 nm) Fe films by resistive heating and laser deposition in order to investigate the formation mechanism of Fe films having spin orientation. Most previous studies in the literature focus on the nature of very thin films or the Fe monolayer,[7] and they discuss the deposition mechanism in terms of constant-rate deposition. The Fe/Al interface produced by pulsed laser deposition was studied using conversion electron Mössbauer spectroscopy,[8] and a nonmagnetic interface phase of FeAl was discovered. The main focus of this present study is the effect of the deposition method on the spin orientation of thick Fe films.

In order to vaporize ground-state Fe atoms, iron wire (ϕ0.5 mm × 30 cm, purity 99.5%, Nilaco Co.) was resistively heated using a current of 10 A in a vacuum. For laser evaporation, laser light from a YAG laser (NewWave, Tempest 10, wavelength 532 nm, pulse energy 100 mJ, pulse width 5 ns, repetition rate 2 Hz) was focused by a convex lens onto a block of enriched ^{57}Fe metal (purity 95%) in a vacuum chamber (10^{-5} Pa). Fe atoms were deposited on a polished 40-μm thick Al substrate at room temperature. It was estimated that a single shot of the pulsed laser light vaporized approximately 3×10^{-9} mol of iron atoms on the basis of the weight loss of the iron target. The deposition area was 5.3 cm^2, and the distance between the laser target (^{57}Fe metal) and the Al substrate was 22 mm. The thickness of the film was estimated by the weight gain after laser deposition, and from this estimate the yield for forming the film on the substrate was found to be approximately 20% of the evaporated Fe atoms. Mössbauer spectra of the Fe films on the substrates were obtained at room temperature in transmission geometry using a ^{57}Co/Rh source and a Wissel MDU1200 transducer. The isomer shifts were referred to α-Fe. The films were also examined by scanning electron microscopy (SEM) (Hitachi S-5000).

First, Fe atoms vaporized by resistive heating of Fe wire in a vacuum (10^{-4} Pa) were deposited onto an Al substrate at room temperature, producing a 920-nm-thick Fe film. A Mössbauer spectrum obtained at room temperature is shown in Figure 1a, and the parameters ($\delta = 0.00$ mm/s, $\Delta E_Q = 0.00$ mm/s, $\Gamma = 0.31$ mm/s, and $H = 330$ kOe) indicate that the film is pure α-Fe and does not contain any reaction products with the Al substrate. The intensity ratios of the sextet peaks were 3:0.50:1:1:0.50:3, which indicates that the nuclear spins of the iron film are oriented almost perpendicular to the substrate surface. A SEM image of the same film sample is shown in Figure 1b. The image shows a crack in the film; the cross section of the Fe film observed through the crack shows a rod-shape structure perpendicular to the substrate, and the ends of the rod-shape crystals produce a rough surface. The dark region in the SEM image is the smooth surface of the Al substrate. The α-Fe crystals grow perpendicular to the Al substrate surface, since the resistively vaporized Fe atoms do not have enough energy to migrate on the surface and crystallize horizontally.

Next, the Fe film containing droplets produced by laser deposition was investigated. When a metal target is irradiated by multiple laser pulses at a fixed position, a hole is produced, and the surface roughness increases, which in turn causes the number of droplets to increase. The laser ablation position on the target Fe metal was kept fixed during laser deposition in order to produce a large amount of droplets. A film having a thickness of 900 nm was produced using 108000 laser shots (Figure 2).

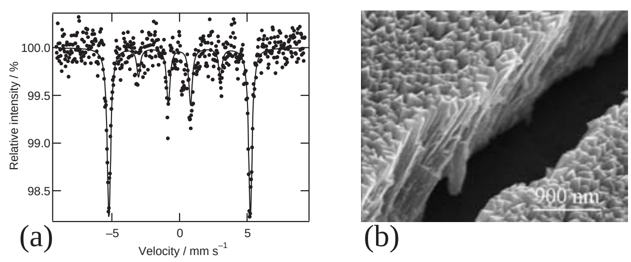

Figure 1. Mössbauer spectrum (a) and SEM image (b) of the Fe film produced by vaporization of resistively heated Fe wire on Al substrate. The Fe thickness is 920 nm.

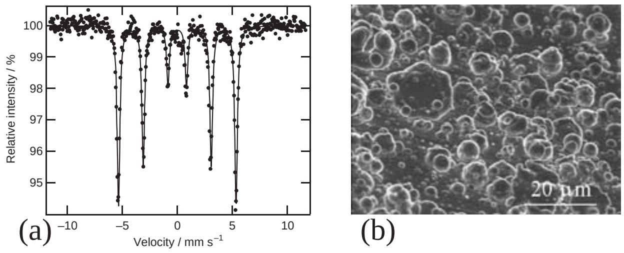

Figure 2. Mössbauer spectrum (a) and SEM image (b) of the Fe film containing droplets produced by laser deposition of ^{57}Fe on Al substrate. The Fe thickness is 900 nm.

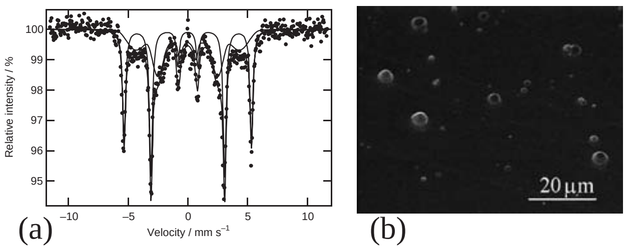

Figure 3. Mössbauer spectrum (a) and SEM image (b) of the Fe film containing few droplets produced by laser deposition of ^{57}Fe on Al substrate. The Fe thickness is 920 nm.

A SEM image of the film (Figure 2b) shows that a large number of droplets having diameters of 5–20 μm are present on the Al substrate. In the Mössbauer spectrum (Figure 2a), only the α-Fe component is evident, indicating that no reaction had occurred with the Al substrate. This suggests that the droplets do not migrate on the Al substrate because of their large size. The intensity ratios of the sextet absorption of α-Fe film were 3:2.3:1:1:2.3:3 indicating that the spin orientation of Fe is almost random. While the droplets form disk-like particles on the Al surface, magnetic shape anisotropy was not observed. This is because the roughness of the Fe film causes random spin orientation.

Iron films that did not contain droplets were produced by suppressing the production of droplets by continuously shifting the focal point of laser ablation on the iron targets. The thickness of the film was 920 nm, and the SEM image (Figure 3b) shows a smooth surface having few droplets. The Mössbauer spectrum (Figure 3a) has a sharp sextet as well as broad absorption. The Mössbauer parameters of the sextet are identical to those of pure α-Fe ($\delta = 0.00$ mm/s, $\Delta E_Q = 0.00$ mm/s, $\Gamma = 0.30$ mm/s, and $H = 330$ kOe) with the intensity ratios of 3:4:1:1:4:3 showing that the spin orientation of the iron atoms is parallel to the substrate surface. The broad absorption is attributed to the environment of the Fe atoms; in general, Fe atoms having a larger number of Fe neighbors have larger magnetic splittings. The Mössbauer spectra were fitted with a distribution of hyperfine splitting, and the distribution has a peak at 260 kOe. From the absorption area of the Mössbauer spectrum, 47% of the laser-deposited Fe atoms are estimated to migrate to the Al substrate, and the remainders of the Fe atoms (53%) produce α-Fe. The effect of the amount of Fe atoms on the composition of films were reported in our previous studies:[4] the reaction product of Fe–Al at the interface is dominant when a small number of Fe atoms are deposited, and α-Fe film is produced when the number of Fe atoms are increased.

The balance between growth and dissociation processes for a cluster on the substrate surface is governed by the total free energy of the cluster and the flux of the incident atoms. Pulsed laser deposition has several unique characteristics: a large number of vapor atoms are incident on the substrate at any one time, and the vapor consists of highly energetic atoms, clusters and particles. The particles (droplets) produced by laser deposition have a disk-like shape on the substrate. It might be thought that this anisotropy in particle shape is one of the causes of spin orientation; however, the film having the largest amount of droplets in this study had random spin orientation. Thus, it is considered that the crystal formation process of the Fe atoms is the origin of the parallel spin orientation of the laser-deposited Fe film. In pulsed laser deposition, the probability of incident atoms forming aggregates is high because of their high fluxes and arrival energies, and consequently the film grows parallel to the substrate surface. In this study, the deposition rate of resistively evaporated Fe was 1.2×10^{-7} mol/s, while that of laser-evaporated Fe was 6×10^{-4} mol/s if it is assumed that the plume produced by laser ablation has a duration of 1 μs. When the Fe vapor flux is high, the probability of Fe atoms migrating to the substrate surface is enhanced, and thus solid Fe is formed on the substrate surface in two dimensions, whereas when the flux and the energy of incident Fe atoms are low, Fe atoms are trapped on the previously produced solid Fe.

In this study, we have demonstrated that the spin orientation of Fe films can be controlled by employing different deposition methods. Resistively vaporized Fe forms films having spin orientations perpendicular to the Al substrate, while laser deposition of Fe on Al substrates produces α-Fe films having spin orientations parallel to the surface, although a portion of the Fe atoms migrates to the substrate. Laser-deposited Fe film having a large number of droplets prevents migration to the substrate resulting in a random spin orientation.

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