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Articles

Mössbauer Investigation into the Reactions of Laser-evaporated Iron with Solid Oxygen at Low Temperatures

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Laser-evaporated iron was deposited onto solid oxygen at 20 K to produce stratified samples consisting of Fe and O_2 layers. The Mössbauer spectra of these samples were acquired in order to investigate their oxidation states and chemical properties. The reaction produced the trivalent iron oxide particles whose size varied depending on the amount of Fe atoms deposited on the solid oxygen. Samples which had smaller amounts of Fe produced smaller iron oxide particles having superparamagnetism. When the sample was annealed at 293 K, the size of the iron oxide particles became larger due to aggregation. The sample with the thickest Fe-layer (180 nm) had a pure α-Fe layer above the iron oxide layer, and the divalent iron oxide was formed after annealing at 293 K.

1. Introduction

Laser-ablation has been studied extensively and has been applied to many fields including the surface treatment of solids and the formation of thin films. Laser-evaporation is a very useful method for vaporizing various kinds of materials without causing radiant heating of surrounding materials. This makes it a convenient method for vaporizing materials near a cold head in a cryostat in order to study low-temperature reactions. We have previously reported reactions of laser-evaporated iron atoms with various reactant gases using a low temperature matrix isolation technique and Mössbauer spectroscopy.[1-4] The reactions of laser-evaporated iron atoms with oxygen produced FeO, $Fe(O_2)$, FeO_3, $(O_2)FeO_2$, and OFeO which are reaction products of the gas phase and are trapped in a low temperature Ar matrix.[5] We have also reported laser-deposition of Fe metal onto Al or Si substrates at various temperatures,[6] and the formation of Fe-Al alloy or Fe-Si compounds was observed at the boundary between the Fe-films and the Al or Si substrate. Laser-deposition of hematite or magnetite onto Al substrates produced iron oxide films whose composition varied depending on the substrate temperature.[7] Thereby laser-deposition has the possibility of producing functional films whose chemical compositions and physical properties can be controlled.

Here, we report the reactions of laser-evaporated Fe with solid oxygen at 20 K. While the experimental setup is very similar to that employed in our previous matrix-isolation studies,[5] in this study the Fe atoms and O_2 gas are introduced alternately to the cold substrate in order to investigate the reaction of Fe with solid oxygen rather than the gas-phase reactions. This study is also a useful cross reference for the ^{57}Mn in-beam Mössbauer study of solid oxygen,[8] although the densities of ^{57}Fe and ^{57}Mn atoms are very different. Furthermore the reactions of laser-evaporated Fe atoms with solid oxygen may potentially provide a new technique for producing iron oxide particles or films.

2. Experimental

The experimental setup is almost the same as that employed for our previous matrix-isolation studies.[5] Briefly, the second-harmonic laser light of a YAG laser pulse (Continuum Surelite, 532 nm, 200 mJ/pulse, 6 ns) was focused using a convex lens onto a ^{57}Fe metal target, and the iron atoms were laser-evaporated. One laser pulse evaporates 2×10^{-9} mol/pulse. The O_2 gas was introduced via an electric pulse valve onto the Al substrate (40 μm) that was cooled down to 20 K using a closed-cycle helium refrigerator (Iwatani Cryomini-D). The deposition area was 3.4 cm^2. The introduction of O_2 was accumulative, and the stratified sample consisting of O_2 layers and Fe layers was produced. The Mössbauer spectra of the sample were acquired using a ^{57}Co/Rh source in transmission geometry on a Wissel MDU1200 system.

3. Results and discussion

A schematic diagram of the stratified samples (**A, B, C, D**, and **E**) produced on the Al substrates at 20 K is shown in Figure 1. The thicknesses indicated in the figure are the equivalent values calculated from the amount of O_2 gas introduced and the amount of laser-evaporated ^{57}Fe atoms. For example, the sample **C** shown in Figure 1c consists of O_2 layers and Fe layers which have equivalent thicknesses of 1.7 μm and 11 nm, respectively. There were 25 such double layers in order that for there to be sufficient ^{57}Fe amounts to acquire a good Mössbauer spectrum; the corresponding Mössbauer spectrum, which was acquired at 20 K, is shown in Figure 2c. The actual boundaries of the O_2 and ^{57}Fe layers are not smooth as indicated in the Figure 1. The actual boundaries would be rough and reactions might occur on the boundaries.

The thickest Fe layer was 180 nm (sample **A**, Figure 1a) and the Mössbauer spectrum for this sample (Figure 2a) has two sets of sextets, which correspond to iron oxide and α-iron. The Mössbauer parameters of the iron/oxygen-stratified samples are summarized in Table 1. The iron oxide produced by these samples is trivalent Fe_2O_3 with hyperfine magnetic fields of 422 kOe. The Mössbauer parameters of this iron oxide do not correspond to those of commonly known trivalent iron oxides crystals such as hematite (α-Fe_2O_3) or maghemaite (γ-Fe_2O_3). Structures of iron hydroxides and iron oxides are closely related because their surrounding natures of Fe atoms with O atoms are similar. Among commonly known iron hydroxides lepidocrocite (γ-FeOOH) is reported to have a small magnetic hyperfine field (458 kOe at 4.2 K),[9] but the iron oxide produced in

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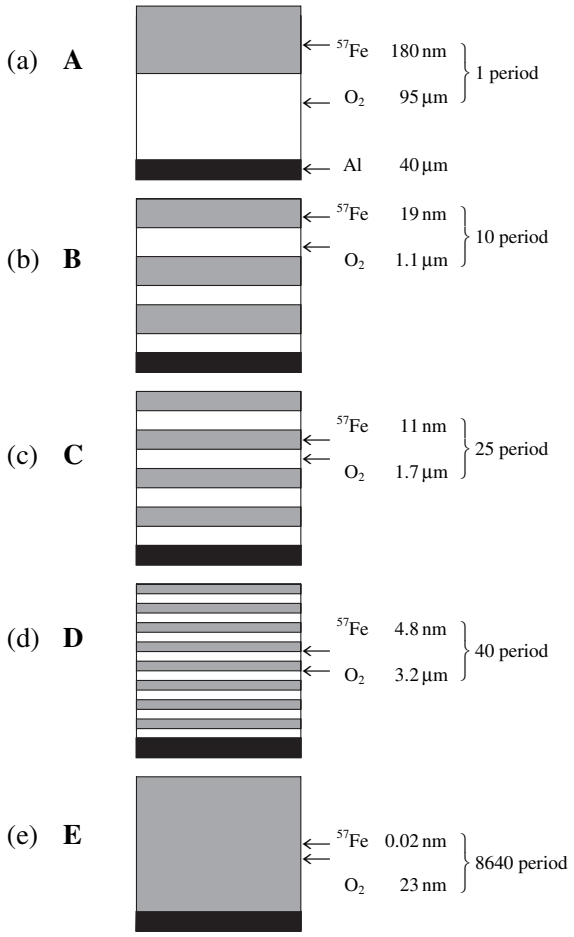

Figure 1. Schematic diagram of stratified samples (**A**, **B**, **C**, **D**, and **E**) consisting of ^{57}Fe and O_2 layers. The thicknesses indicated in the figure are the equivalent values calculated from the amount of ^{57}Fe and O_2 introduced.

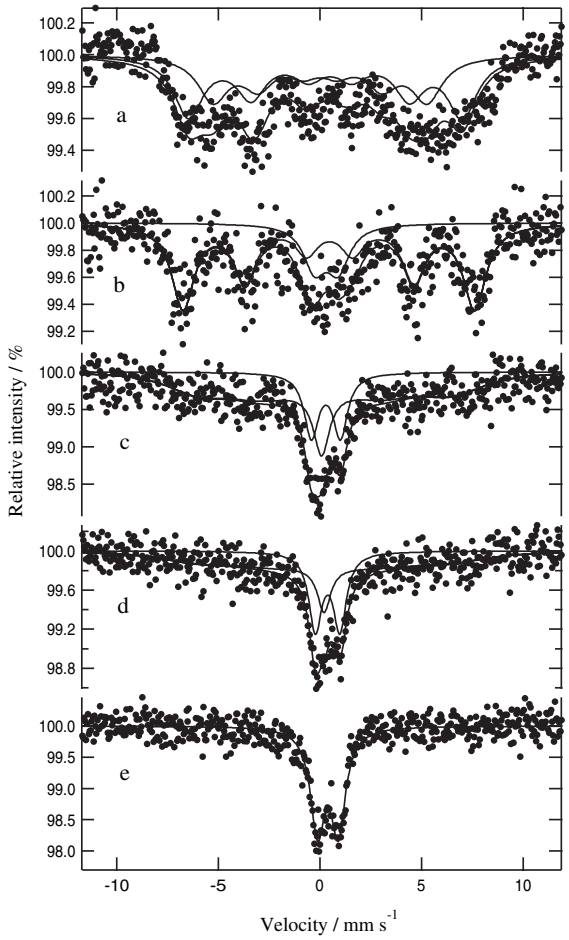

Figure 2. Mössbauer spectra of Fe/O_2 stratified samples (**A**, **B**, **C**, **D**, and **E**) at 20 K. The equivalent thicknesses of ^{57}Fe/O_2 layers are (a) 180 nm/95 μm (**A**), (b) 19 nm/1.1 μm (**B**), (c) 11 nm/1.7 μm (**C**), (d) 4.8 nm/3.2 μm (**D**), and (e) 0.02 nm/23 nm (**E**).

this study has an even smaller magnetic hyperfine field. This small hyperfine magnetic field (422 kOe) may be attributed to large defects in its crystal structure or to small particle size. ^{57}Fe reacted with O_2 to form iron oxides at the interface of the ^{57}Fe and O_2 layers, and the ^{57}Fe atoms that did not react with O_2 were deposited to form an α-Fe (H = 330 kOe) layer on top of the iron oxide layer. From the area intensities of the Mössbauer spectrum, the thicknesses of iron oxide (Fe_2O_3) and the pure iron (α-Fe) layers are calculated to be 70 and 110 nm, respectively.

The sample **B** with ^{57}Fe layers having an equivalent thickness of 19 nm (Figure 1b and Figure 2b) does not show the sextet absorption of α-Fe, instead doublet absorption was observed, which was assigned to superparamagnetic fine iron oxide particles. In addition, the sextet of iron oxide (Fe_2O_3) was observed. The amount of ^{57}Fe atoms introduced was not enough to form large Fe_2O_3 particles, and hence the Fe_2O_3 layer was too thin to stabilize the unreacted ^{57}Fe layer. The sample **C** having thinner ^{57}Fe layers (Figure 1c) has doublet absorption and a broad absorption exhibiting relaxation. The small size of the iron oxide particle gives a relaxation spectrum because of superparamagnetism. Although the particle size may have a size distribution, the relaxation spectrum is fitted by assuming it has a single relaxation time using Wickman's formula described in Reference 10; the relaxation time estimated by this method is 3.5 ns. The spectrum **D** shown in Figure 2d is also fitted by two components: a doublet and a relaxation component. The relaxation time of the superparamagnetic component is 2.6 ns, which is a narrower absorption than that estimated for the spectrum shown in Figure 2c. The spectrum shown in Figure 2e (sample **E**) is fitted by one doublet absorption without any magnetic hyperfine components. The doublet absorptions (for Figures 2b, c, d, and e) have almost identical Mössbauer parameters, and the area intensities become larger as the ^{57}Fe layers become thinner. This doublet component may be attributed to fine particles of Fe_2O_3 or to an amorphous component which is too small to have a magnetic hyperfine structure even at 20 K. We have previously investigated the Mössbauer spectra of an iron oxide species isolated in a low-temperature Ar matrix,[5] and the Fe(O_2) had similar Mössbauer parameters (δ = 0.35 mm/s and ΔE_Q = 0.96 mm/s) to that of the doublet (δ = 0.40 mm/s and ΔE_Q = 1.02 mm/s) observed in this study. But the infrared spectrum of the sample acquired under the same conditions did not show any absorption bands corresponding to Fe(O_2) (979 cm^{-1}), and this species may not stabilize after the deposition of Fe atoms on the solid oxygen. Therefore we assigned the doublet to very small-sized oxide particles Fe_2O_3. The Mössbauer parameters for the doublet are in agreement with the parameters reported for superparamagnetic γ-Fe_2O_3 particles reported in Reference 11 (δ = 0.35 mm/s and ΔE_Q = 0.72 mm/s). Mössbauer parameters of ε-Fe_2O_3 particles reported in literature[12] are not in agreement with our experimental results. The larger ΔE_Q value of the observed doublet is due to the inhomogeneity of the size and crystallinity of the iron oxide Fe_2O_3 particles.

The sample **A** shown in Figure 2a, which had the α-Fe layer, was annealed in order to investigate how its composition changed upon heating. The temperature of the sample was increased to room temperature (293 K), and O_2 molecules were vaporized and evacuated, while iron species, which have a low vapor pressure, remained on the Al substrate. The Mössbauer spectrum acquired at room temperature (Figure 3a) shows a

TABLE 1: Mösbauer parameters of iron/oxygen stratified samples at 20 K

Sample	Temperature (K)	Component	δ (mm/s)	ΔE_Q (mm/s)	H (kOe)	Γ(mm/s)	relaxation time (ns)	Area intensity (%)
A	20	α-Fe sextet	0.00 0.39(5)	0.00 –0.24(8)	330 422(3)	1.83(20) 1.77(13)		57 43
B	20	doublet sextet	0.30(7) 0.43(3)	1.11(11) –0.04(5)	426(2)	0.32(2) 1.29(5)		21 79
C	20	doublet relaxation	0.28(3) 0.17(9)	1.45(6) 0.22(17)	422	0.86(12) 0.16(6)	3.5(4)	25 75
D	20	doublet relaxation	0.37(2) 0.16(18)	1.20(4) –0.06(36)	430(26)	0.76(9) 0.15(7)	2.6(6)	37 63
E	20	doublet	0.40(1)	1.02(2)		0.86(3)		100
A	293	relaxation	0.77(7)	1.10(15)	270(46)	0.42(5)	0.7(2)	100
A after annealing	20	doublet relaxation	0.70(2) 0.77	0.86(4) 1.10	270	0.50(5) 0.96(15)	2.7(3)	14 86
B	293	doublet	0.33(1)	0.97(2)		0.49(3)		100
B after annealing	20	sextet	0.44(2)	0.01(5)	432(2)	1.07(6)		100

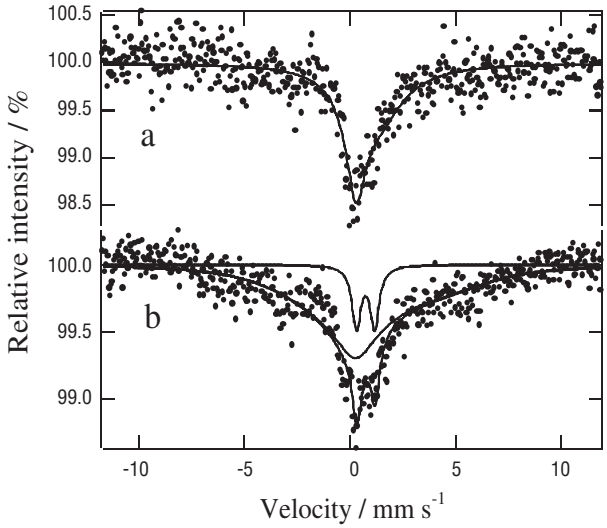

Figure 3. Mössbauer spectra of Fe/O_2 stratified sample **A** ($^{57}Fe/O_2$ = 180 nm/95 μm) observed at 293 K (a) and 20 K (b).

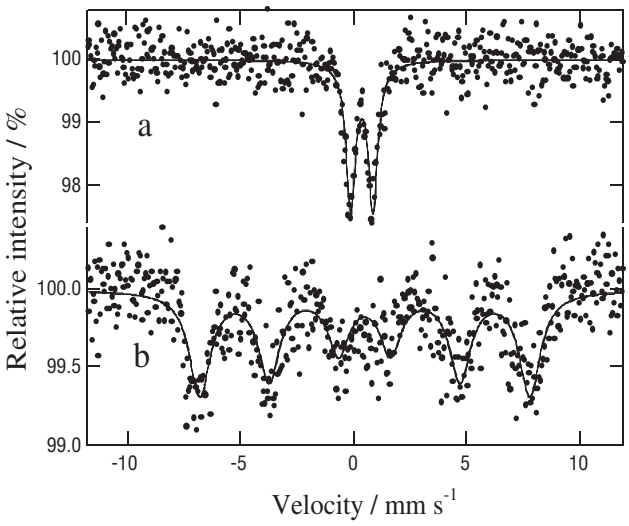

Figure 4. Mössbauer spectra of Fe/O_2 stratified sample **B** ($^{57}Fe/O_2$ = 19 nm/1.1 μm) observed at 293 K (a) and 20 K (b).

broad absorption, which is assigned to superparamagnetic iron oxide species having very small particle sizes. While the iron oxide particles may have a distribution of particle sizes and relaxation times, it is very difficult to fit the acquired relaxation spectrum by taking the size distribution of the iron oxide particles into account. Therefore the spectrum was fitted assuming a single relaxation time. The fitted result is shown in Figure 3a and the parameters obtained are given in Table 1; it has a large δ value (0.77 mm/s) which is assigned to Fe(II) species. The magnetic hyperfine field was small (H = 270 kOe) which is in good agreement with the small hyperfine field of Fe(II) species. The right shoulder of the absorption was attributed to the ΔE_Q (1.10 mm/s) of the absorption with relaxation. The temperature of the sample **A** was then reduced to 20 K again. The Mössbauer spectrum at 20 K (Figure 3b) had a broader absorption with a longer relaxation time than that observed at room temperature (Figure 3a). The spectrum was fitted assuming that the broad component had the same δ, ΔE_Q, and H values as those of Figure 3a, and it also had a doublet component. The relaxation time became longer (2.7 ns) and the doublet (δ = 0.70 mm/s and ΔE_Q = 0.86 mm/s) has the Mössbauer parameters assigned to a Fe(II) species. The spectrum acquired at 20 K did not have a component due to α-Fe and it reacted with O_2 to form iron oxide when the temperature was increased. Although iron oxide Fe_2O_3 with magnetic hyperfine splitting was observed at 20 K before increasing the temperature (Figure 2a), the Mössbauer spectrum observed after annealing (Figure 3b) had a shorter relaxation time because of the smaller particle size, indicating that the Fe_2O_3 particles did not aggregate to form larger particles on annealing. The divalent iron oxide FeO was produced by the reaction of pure Fe with O_2 and by the reduction of trivalent iron oxide Fe_2O_3 with pure Fe.

Next, we annealed the sample **B** shown in Figure 2b to investigate the thermal reactions of a sample not having pure α-Fe. When the temperature of the sample **B** was increased to room temperature 293 K, the solid O_2 layers evaporated and only the iron oxide remained on the Al substrate as large particles. The Mössbauer spectrum acquired at room temperature (Figure 4a) had only one doublet, which was assigned to the Fe_2O_3 particles which exhibit superparamagnetism at high temperatures. The isomer shift (δ = 0.33 mm/s) of this doublet is that of trivalent iron oxide Fe_2O_3 while it has a relatively large quadruple splitting (ΔE_Q = 0.97 mm/s) value. This sample **B** was again cooled to 20 K (Figure 4b), and the Mössbauer spectrum acquired at this temperature had a sextet absorption. The chemical composition or particle size may be the same as that for the sample in Figure 4a, and the only differences observed

were due to the different temperatures at which the Mössbauer spectra were acquired. Comparing the spectra of the samples **B** before (Figure 2b) and after annealing (Figure 4b), the doublet component disappeared and the component due to iron oxide Fe_2O_3 with magnetic hyperfine splitting increased. On annealing the sample **B** (Figure 2b) and subliming the solid oxygen, the iron oxide particles aggregate to form larger Fe_2O_3 particles which have magnetic hyperfine splitting at 20 K, although their size was not large enough to exhibit magnetism at room-temperature. Reduction of trivalent iron oxide Fe_2O_3 to form divalent iron oxide FeO was not observed because there was no pure α-Fe layer in this sample.

Laser-deposition of Fe onto solid oxygen at 20 K produced iron oxide Fe_2O_3 particles, and the species obtained by matrix-isolation studies were not found even at low temperatures (20 K). The Fe_2O_3 layer was formed up to thicknesses of 70 nm, and it had a small hyperfine magnetic field in the range 420 – 430 kOe. Laser-deposition of Fe onto solid O_2 may provide a new method to produce small Fe_2O_3 particles.

4. Conclusion

Laser-evaporated Fe was deposited onto solid oxygen at 20 K. Samples having thinner Fe layers produced smaller particles of trivalent iron oxide Fe_2O_3. The measured Mössbauer parameters for Fe_2O_3 particles do not correspond to those for known iron oxide crystals, and they may have a large number of defects. When the temperature of the sample was increased to 297 K, aggregation of the Fe_2O_3 particles to form larger particles was observed. When there was a large amount of laser-deposited Fe present, a layer of pure α-Fe formed on the Fe_2O_3 layer. On annealing the sample at 293 K, reduction of the trivalent oxide Fe_2O_3 to the divalent iron oxide FeO was observed due to the reduction reaction with pure Fe. It was demonstrated that laser deposition of Fe onto solid oxygen produces particles of iron oxide having a novel structure, and that the particle size was determined by the amount of Fe deposited.

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