

Room Temperature Growth of Magnetite Films on Arachic Acid Monomolecular Layers

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Mimicking the bacterial synthesis of magnetosomes, in which the functionalized surface of a cytoplasmic (lipid) membrane is considered to be stimulating the crystal growth of magnetite, we have successfully grown magnetite films at 30°C using an arachic acid monomolecular layer as a functionalized surface. The lipid monomolecular layer was spread on an aqueous solution of FeCl₂, which was oxidized by flowing a mixed gas, with ratio O₂/N₂=1/2000, on the surface of the lipid layer. Mössbauer and X-ray diffraction analyses revealed that the Fe₃O₄ films contain small amounts of ferric hydroxyl impurity phases of α-FeOOH and γ-FeOOH. This is because the oxygen partial pressure at the ferrite/aqueous interface changed as the film (through which the gas penetrated) increased in thickness. Methods to obtain single phase magnetite films are proposed.

Key words: Magnetite, Thin film, Monomolecular layer, Mössbauer spectroscopy

I. Introduction

Magnetotactic bacteria synthesize magnetosomes, or single crystals of magnetite (Fe₃O₄) encapsulated with a lipid layer at or below room temperature; Fukumori *et al.*¹⁾ proposed that the magnetosomes are synthesized on the cytoplasmic membrane, or a lipid membrane, which provides a functionalized interface to stimulate the nucleation and growth of ferrite. We, therefore, tried in this study to synthesize Fe₃O₄ films at room temperature on artificial monomolecular layers of a lipid by ferrite plating. Ferrite plating is a chemical method by which crystalline films of various spinel ferrites can be prepared from an aqueous solution, utilizing the oxidation reaction of Fe²⁺ to Fe³⁺ at 60~100°C.²⁾ Lowering the ferrite-plating temperature down to room temperature will allow us to fabricate various composites made of organic (mono)molecular layers and ferrite layers. The composites may be useful in biomedical applications and perhaps in studies of the physics of magnetism, for example studies of magnetic exchange coupling and spin tunneling between the ferrite layers intermediated by the organic molecular layers. Also, further research may give valuable information on the mechanism of bacterial ferrite synthesis; which is closely related to that of the ferrite plating.

In this study, we successfully synthesized magnetite films at 30°C by utilizing a lipid monomolecular layer spread on an aqueous solution of FeCl₂ as the functionalized interface which stimulates the ferrite growth. We think we are the first to have synthesized magnetite films at room temperature; to our knowledge, all previous reports on room-temperature growth of magnetite have resulted only in the

growth of powders.³⁾

II. Experimental

An aqueous solution (pH=6.6) of FeCl₂ (0.094 mol/l)+CH₃COONH₄ (0.13 mol/l; pH buffer) was contained in a glass vessel (500 ml), as shown in Fig. 1. After de-airating the aqueous solution by bubbling N₂ gas through it, we prepared an arachic acid (CH₃(CH₂)₁₈COOH) monomolecular layer on the surface of the aqueous solution by syringing a chloroform solution of the acid. The vessel was kept at 30°C in a water bath for 20 hrs or 5 hrs to grow solid films, flowing mixed gas of N₂ and air with the desired ratios of O₂/N₂=1/300~1/2000 on the surface of the monomolecular layer. The ferrite films precipitated on the solution surface were scooped up with filter papers, dried, and then subjected to scanning electron microscope (SEM) observation.

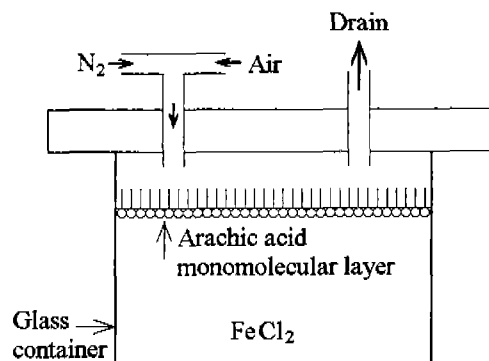


Fig. 1. Apparatus for growing magnetite films on arachic acid monomolecular layer spread on an aqueous solution of FeCl₂.

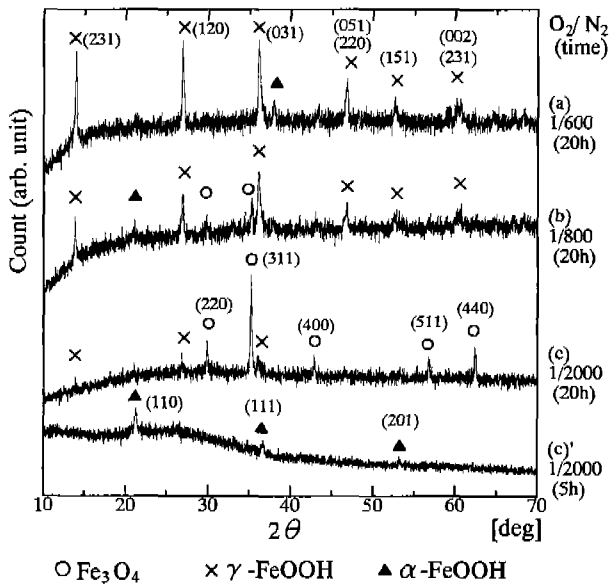


Fig. 2. X-ray diffraction diagrams for the films grown by flowing mixed gas with various ratios of O_2/N_2 for 20 hrs and 5 hrs.

The films were powdered and subjected to $CuK\alpha$ X-ray diffraction (XRD) analyses, to magnetic measurements using a vibrating sample magnetometer, and to Fe^{57} Mössbauer absorption measurements using a Co^{57} source. All the experiments were performed at room temperature.

III. Results and Discussion

Figs 2 (a)–(c) show the XRD patterns for the samples grown for 20 hrs. When $O_2/N_2=1/600$ ((a)) they consist of peaks due primarily to γ -FeOOH and slightly to α -FeOOH. Contribution from these hydroxides reduces and that from Fe_3O_4 increases as the gas ratio decreases to 1/800 ((b)). When $O_2/N_2=1/2000$ the diffraction peaks are primarily attributed to magnetite phase having slight impurity phases of α -FeOOH and γ -FeOOH. As shown in Fig. 2(c)', however, the layers grown for the shorter time or 5 hrs, at the same gas ratio $O_2/N_2=1/2000$ exhibit XRD peaks due only to α -FeOOH. This can be explained as follows. Because the oxidizing mixed gas penetrated the films as they grew, the supply rate of the gas, and therefore the oxygen partial pressure, in the aqueous solution decreased continuously with time. The films grown for a relatively short time (5 hrs, (c)) are therefore in a more oxidized state (primarily composed of α -FeOOH, a ferric hydroxide) than those grown for the longer time (20 hrs, (c)). The latter are primarily composed of magnetite, a ferric-ferrous intermediate oxide.

The Mössbauer spectra shown in Fig. 3 support this interpretation. The films grown for 20 hrs exhibit spectra primarily consist of a paramagnetic quadrupole doublet from γ -FeOOH, with a weak superimposed sextet from antiferromagnetic α -FeOOH when $O_2/N_2=1/600$ ((a)) and lines from α -FeOOH and Fe_3O_4 when $O_2/N_2=1/800$ ((b)). When $O_2/N_2=1/2000$ ((c)), on the other hand, the spectrum is primarily composed of a couple of sextets from magnetite, on which a sextet from α -FeOOH and a doublet from γ -FeOOH superimpose slightly. The spectrum from magnetite is compared in Fig. 4 with the spectrum obtained for the magnetite coating grown on polymer microspheres $\sim 0.25 \mu m$ in

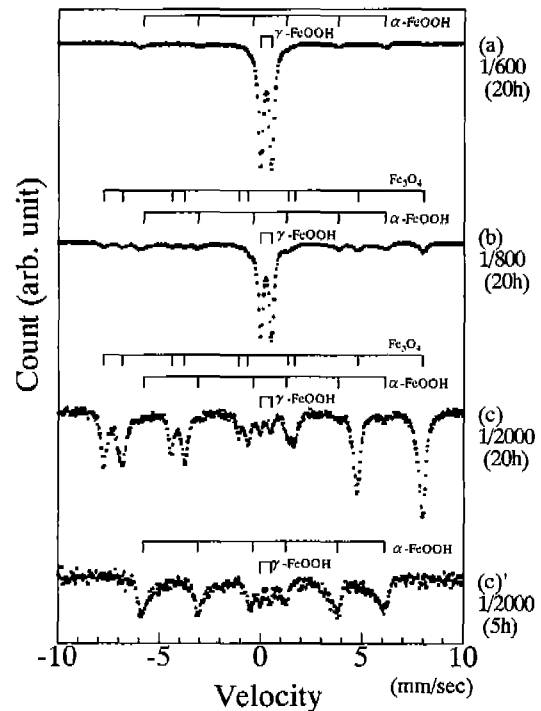


Fig. 3. Fe^{57} Mössbauer spectra for the films grown by flowing mixed gas with various ratios of O_2/N_2 for 20 hrs and 5 hrs.

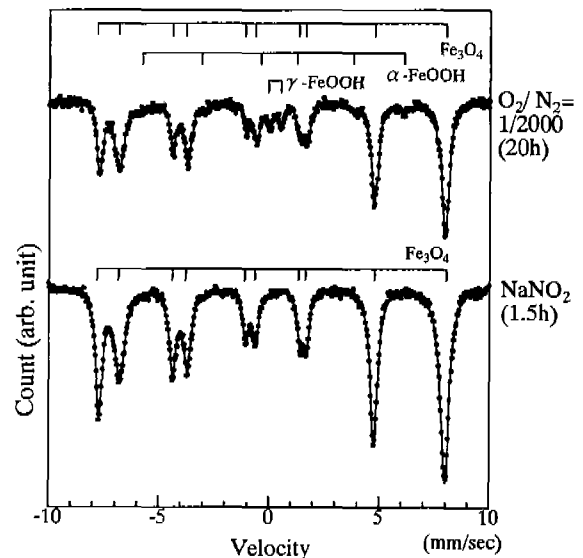


Fig. 4. Mössbauer spectra for the magnetite film grown in this study ($T=30^\circ C$, $O_2/N_2=1/2000$, for 20 hrs) and magnetite-coating formed on polymer microspheres ($T=70^\circ C$, using $NaNO_2$ as an oxidizing agent, for 1.5 hrs). Least-square fitted lines are drawn.

$N_2=1/2000$ ((c)), on the other hand, the spectrum is primarily composed of a couple of sextets from magnetite, on which a sextet from α -FeOOH and a doublet from γ -FeOOH superimpose slightly. The spectrum from magnetite is compared in Fig. 4 with the spectrum obtained for the magnetite coating grown on polymer microspheres $\sim 0.25 \mu m$ in

Table 1. Intensity Ratio $R = \text{Fe}^{2.5+}/\text{Fe}^{3+}$ of Magnetite Subspectra and Solubility x in $(\text{Fe}_3\text{O}_4)_{1-x}(\gamma\text{Fe}_2\text{O}_3)_x$. Calculated from R , for the Samples Prepared in this and Previous⁴ Studies.

| | Oxidizing reagent | Growth temperature | Intensity ratio $\text{Fe}^{2.5+}/\text{Fe}^{3+}$ | Solubility x |
|----------------|-------------------|--------------------|---|----------------|
| This study | O_2 | 30°C | 1.59 | 0.08 |
| Previous study | NaNO_2 | 70°C | 1.16 | 0.19 |

diameter at 70°C by the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ oxidation, using NaNO_2 as an oxidizing reagent; this does not show the superimposed impurity spectra.⁴ Ascribing the wider and narrower sextets to Fe^{3+} ions and $\text{Fe}^{2.5+}$ (intermediate valence state due to fast electron exchange on the octahedral sites),⁵ respectively, and taking into account the impurity lines from the hydroxyl phases, the spectra were least-square fitted as shown in Fig. 4. From the area ratio of the Fe^{3+} and $\text{Fe}^{2.5+}$ subspectra, the solubility x in $(\text{Fe}_3\text{O}_4)_{1-x}(\gamma\text{Fe}_2\text{O}_3)_x$ was calculated for the magnetite samples assuming $f(\text{Fe}^{2.5+})/f(\text{Fe}^{3+}) = 0.94$ (f : recoilless fraction).^{5,6} As given in Table 1 we obtained for the present sample ($T = 30^\circ\text{C}$) $x = 0.08$, which was smaller than $x = 0.22$ obtained for the previous sample ($T = 70^\circ\text{C}$).

Table 2 gives the spectrum parameters and the area ratios determined for all the samples. The parameters obtained for Fe_3O_4 , $\alpha\text{-FeOOH}$ and $\gamma\text{-FeOOH}$ agree with the values given in the literature⁷ within experimental error.

The Mössbauer spectrum (Fig. 3 (c')) of the film grown for 5hr at $\text{O}_2/\text{N}_2 = 1/2000$ consists primarily (88%) of sextet from $\alpha\text{-FeOOH}$ on which a weak (12%) doublet contribution from

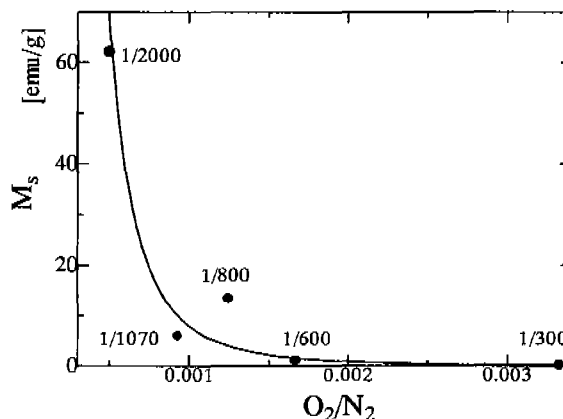


Fig. 5. Saturation magnetization for the films grown by flowing for 20 hrs mixed gases having various values of O_2/N_2 ratio, which is taken as the horizontal axis.

$\gamma\text{-FeOOH}$ superimposes. The weak phase of $\gamma\text{-FeOOH}$ is not observed in the XRD pattern (Fig. 2 (c')). This is because Mössbauer analysis is more sensitive to weak impurity phases than XRD analysis, especially when the samples available for the measurements are of very small amount as in this study.

Fig. 5 shows that the saturation magnetization in the films grown for 20 hrs increases as O_2/N_2 is decreased, reaching 62 emu/gr (about 67% of that reported for bulk Fe_3O_4) when $\text{O}_2/\text{N}_2 = 1/2000$. This agrees with the observation by the XRD and Mössbauer analyses that the ferrimagnetic component of Fe_3O_4 increased while antiferromagnetic and paramagnetic components of $\alpha\text{-FeOOH}$ and $\gamma\text{-FeOOH}$,

Table 2. Mössbauer Spectrum Parameters for the Films Grown for 20 h, or 5 h, in the Mix Gas with Various Values of O_2/N_2 Ratio. Row (d) Gives Parameters for the Magnetite-coating Formed on Polymer Microspheres Prepared by Ultrasound Enhanced Ferrite Plating⁴

| O_2/N_2 (Growth time) | Crystal phase | δ^a (mm/sec) | ΔE^b (mm/sec) | H_{hr}^c (kOe) | Area ratio (%) | |
|--|-------------------------------|------------------------|--------------------------|---------------------|-------------------|----|
| (a) 1/600 | $\alpha\text{-FeOOH}$ | 0.37 | -0.27 | 368 | 14 | |
| (20 h) | $\gamma\text{-FeOOH}$ | 0.37 | 0.54 | - | 86 | |
| (b) 1/800 | $\text{Fe}_3\text{O}_4(2.5+)$ | 0.66 | 0.00 | 459 | 18 | |
| (20 h) | $\text{Fe}_3\text{O}_4(3+)$ | 0.28 | -0.02 | 488 | | |
| | $\alpha\text{-FeOOH}$ | 0.37 | -0.26 | 370 | 23 | |
| | $\gamma\text{-FeOOH}$ | 0.37 | 0.53 | - | 59 | |
| (c) 1/200 | $\text{Fe}_3\text{O}_4(2.5+)$ | 0.66 | 0.00 | 457 | 83 | 51 |
| (20 h) | $\text{Fe}_3\text{O}_4(3+)$ | 0.27 | -0.01 | 487 | | 32 |
| | $\alpha\text{-FeOOH}$ | 0.40 | -0.30 | 371 | 12 | |
| | $\gamma\text{-FeOOH}$ | 0.38 | 0.50 | - | 5 | |
| (c') 1/2000 | $\alpha\text{-FeOOH}$ | 0.36 | -0.24 | 362 | 88 | |
| (5 h) | $\gamma\text{-FeOOH}$ | 0.35 | 0.55 | - | 12 | |
| (d) NaNO_2 | $\text{Fe}_3\text{O}_4(2.5+)$ | 0.66 | 0.02 | 455 | | 53 |
| (1.5 h) | $\text{Fe}_3\text{O}_4(3+)$ | 0.29 | -0.02 | 487 | | 47 |

^a: Isomer shift relative to iron, ^b: quadrupole splitting, ^c: hyperfine field.

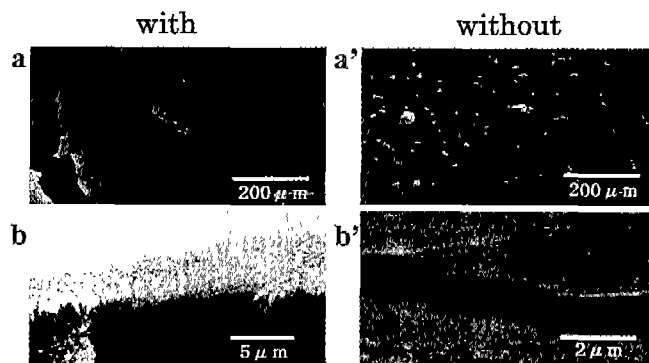


Fig. 6. SEM observations of the surfaces ((a) and (a')) and the cross sections ((b) and (b')) of the magnetite films grown by flowing the mixed gas with $O_2/N_2=1/2000$ for 20 hrs. The films were precipitated on the arachic acid monomolecular layer ((a) and (b)) and on the bare surface of $FeCl_2$ aqueous solution without the monomolecular layer ((a') and (b')).

respectively, decreased with decreasing O_2/N_2 .

As shown in SEM photographs of Fig. 6, the arachic acid monomolecular layer greatly accelerates the crystal growth of magnetite. When $O_2/N_2=1/2000$, we obtained on the monomolecular layer a thick ($\sim 5 \mu m$) film ((a)) having a smooth surface ((a')). On the other hand, a very thin ($\sim 0.2 \mu m$) layer (b) with a rough, partly-broken surface (b') was obtained on the bare surface of the aqueous solution when the arachic acid monomolecular layer is absent.

The deposition rate of the layer is 230 nm/h when deposited on the monomolecular layer, which decreased to 10 nm/h when deposits on the bare surface of the aqueous solution. However, the crystallographic and magnetic properties of the layers deposited with and without the lipid layer do not change appreciably, as revealed by the XRD and Mössbauer measurements.

IV. Conclusions

Our main results are summarized as follows:

1. The functionalized surface of the arachic acid monomolecular layer facilitates magnetite film formation at $30^\circ C$;
2. The monomolecular layer not only accelerates the growth rate (from 10 nm/h without the surface layer to 250 nm/h), but also improves the smoothness of the surface;
3. Magnetite films with slight hydroxyl impurity phases of α and γ -FeOOH grown when the $FeCl_2$ solution is oxidized for 20 hrs by a mixed gas with the ratio $O_2/N_2=1/2000$. How-

ever, the films in the initial stage of the growth consist of hydroxides α -FeOOH and γ -FeOOH. This is because the oxygen partial pressure at the ferrite/aqueous interface changes as the films increase in thickness with time.

In order to obtain films of single-phase magnetite, we must change the O_2/N_2 ratio in synchrony with the film growth. An alternate way is to replace the monomolecular layer spread on the aqueous surface by that deposited on a solid substrate using the Langmuir-Blodgett method, and to then pour into the aqueous solution a mixed gas with that fixed value of O_2/N_2 which is required for magnetite synthesis.

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