Metastable iron carbide thin films produced by pulsed laser deposition of iron in methane atmosphere



Takumi Funabashi¹ · Yoshio Kobayashi^{2,3} · Yasuhiro Yamada¹

Published online: 26 November 2019 © Springer Nature Switzerland AG 2019

Abstract

Metastable iron carbide thin films (χ -Fe₅C₂ and o-Fe₇C₃) were produced by pulsed laser deposition of Fe in a CH₄ atmosphere, and their Mössbauer spectra and X-ray diffraction patterns were measured. Films consisting of amorphous Fe-C carbide were obtained when the substrate temperature was kept at 300 K during deposition, while crystalline films were produced for a substrate temperature of 573 K. The effect of CH₄ pressure was investigated. Films produced below 4.0 Pa consisted of a combination of χ -Fe₅C₂ and α -Fe, and single-phase carbide films were produced at higher pressure: pure χ -Fe₅C₂ and o-Fe₇C₃ films were produced at 4.0 and 6.0 Pa, respectively. At 13 Pa, a film was produced consisting of o-Fe₇C₃ and paramagnetic amorphous Fe-C containing a large amount of C atoms. The film produced at the highest pressure of 40 Pa consisted solely of paramagnetic amorphous Fe-C.

Keywords Iron carbide · Thin films · Pulsed laser deposition · Mössbauer spectroscopy

1 Introduction

Iron carbides have been extensively studied because of their various useful industrial applications, owing to their magnetic properties and catalytic activity [1-3]. Iron-based materials such

Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME2019), 1-6 September 2019, Dalian, China Edited by Tao Zhang, Junhu Wang and Xiaodong Wang

Takumi Funabashi 1318613@ed.tus.ac.jp

¹ Department of Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8602, Japan

- ² Graduate School of Informatics and Engineering, The University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan
- ³ Nishina Center for Accelerator-Based Science, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

as ferrite, austenite, martensite, and cementite (Fe₃C) are well understood, although Hägg carbide (Fe₅C₂) and Eckstrom-Adcock carbide (Fe₇C₃) are known as metastable iron carbides, and are not present in the Fe-C phase diagram [4–8]. Fe₅C₂ and Fe₇C₃ have Fischer-Tropsch catalytic activity [9]. These metastable iron carbides have been reported to be synthesized in nanoparticle form [10, 11]. The production of iron carbide films in a glow discharge containing Fe(CO)₅ and H₂ has been reported [12]. However, generally, it is hard to obtain pure metastable iron carbides without the coexistence of other iron carbides or iron oxides.

Pulsed laser deposition (PLD) is a very useful technique to produce films with controlled composition. Laser ablation of Fe metal produces a metal vapor consisting of Fe atoms having high translational energy. Unstable species produced in the gas phase are deposited on a substrate. When the substrate temperature is low, the deposited materials on the surface quench their energies rapidly to form amorphous phases. On the other hand, when the substrate temperature is high, the deposited materials diffuse on the surface to enhance nucleation and crystal formation. Using this technique, iron carbide species unobtainable under normal conditions can be synthesized. We have previously reported iron carbide films produced by PLD of Fe in a C_2H_2 atmosphere [13], where a mixture of iron carbides, Fe_3C , Fe_7C_3 , and paramagnetic amorphous Fe-C were produced. In this study, we employed CH₄ as the reactive gas to produce single-phase iron carbides, because CH₄ is less reactive than C_2H_2 and the C atom content can be more easily controlled.

2 Experimental

Pulsed laser light from a Nd:YAG laser (NewWave Research, TEMPEST 10; wavelength: 532 nm; pulse energy: 85 mJ; pulse duration: 5 ns; repetition rate: 10 Hz) was focused by a convex lens onto the target ⁵⁷Fe metal block. The CH₄ pressure was kept constant in a range between 0.5 and 40 Pa by controlling the flow rate and the exhaust speed of CH₄ gas during the deposition. The flow rate was controlled by a mass flow controller (Fujikin: FCST1005LC-4F2-F30-AR), and the exhaust speed was controlled by a butterfly valve attached to a



Fig. 1 XRD patterns of films produced by the PLD of Fe onto Al substrates at 573 K in methane atmosphere of (a) 4.0 Pa and (b) 6.0 Pa. Bars in the figure denote χ -Fe₅C₂ (PDF #04–014-4562), o-Fe₇C₃ (PDF #01–075-1499), and Al substrate (PDF#4–0787)



Fig. 2 Mössbauer spectra of films measured at (a) 293 K and (b) 3 K produced by PLD of Fe onto Al substrates at 573 K in 4.0 Pa methane atmosphere

diaphragm gauge and a pressure controller (VAT: Series 612). Laser-evaporated Fe atoms reacted with CH₄ in the gas phase and formed iron carbide films deposited onto Al substrates (target-substrate distance: 22 mm). A resistive heater was utilized to maintain the temperature of the substrate at 573 K. The amount of Fe atoms vaporized was estimated by weighing the target ⁵⁷Fe metal block before and after PLD. One laser ablation pulse produced 1.4×10^{-9} mol of Fe atoms, and the films were produced by accumulating 110,000 laser pulses. The thickness of the films was measured by weighing the film samples; the α -Fe equivalent thickness of the films in this study was 400 nm. Mössbauer spectra of the Fe-C films on the Al substrates at 293 K and 3 K were measured by transmission Mössbauer spectroscopy (⁵⁷Co/Rh source). X-ray diffraction patterns of the films were obtained using a RINT2500 diffractometer (RIGAKU, Cu-K α).

3 Results and discussion

Various iron carbide films were produced by varying the temperature of the Al substrates and the CH_4 pressure. A film sample was produced in a 4.0 Pa CH_4 atmosphere while the substrate

Temperature	Component	δ mm/s	Δ mm/s	H kOe	Г mm/s	Yields %
(a) 293 K	χ -Fe ₅ C ₂ (I)	0.25 (0)	0.02 (1)	219 (1)	0.40 (0)	39.9
	χ -Fe ₅ C ₂ (II)	0.16 (0)	0.05 (0)	182 (2)	0.40(0)	37.6
	χ -Fe ₅ C ₂ (III)	0.18(1)	0.06(1)	108 (4)	0.40(0)	22.5
(b) 3 K	χ -Fe ₅ C ₂ (I)	0.36(1)	0.08 (2)	257 (1)	0.50(1)	39.6
	χ -Fe ₅ C ₂ (II)	0.31 (1)	0.12(1)	220 (1)	0.50(1)	38.8
	χ -Fe ₅ C ₂ (III)	0.27 (1)	0.12 (2)	132 (1)	0.50(1)	21.6

Table 1 Mössbauer parameters of the spectra shown in Fig. 2



Fig. 3 Mössbauer spectra of films measured at (a) 293 K and (b) 3 K produced by PLD of Fe onto Al substrates at 573 K in 6.0 Pa methane atmosphere

temperature was kept at 300 K; the Mössbauer spectrum of the film showed a broad absorption (maximum at H=160 kOe), indicating that the films consisted of amorphous Fe-C. The energy of the Fe/C atoms deposited on the substrates at 300 K was not high enough to form crystalline films. Thus, in this study, the substrate temperature was increased at 573 K to enhance the diffusion and crystal growth of the deposited materials on the substrate.

The XRD pattern of the film produced in 4.0 Pa CH₄ was measured (Fig. 1a). The most intense peak corresponded to the Al substrate, and other peaks corresponded to those of χ -Fe₅C₂ (PDF #04–014-4562). However, XRD patterns are only representative of bulk phases with a long-range periodic structure.

A film was produced in a 4.0 Pa CH₄ atmosphere on an Al substrate (573 K), and the Mössbauer spectra of the film were measured at 293 K and 3 K (Fig. 2). The Mössbauer parameters are summarized in Table 1. Both spectra were fitted into a combination of three sextets: H=219, 182, and 108 kOe at 293 K, H=257, 220, and 132 kOe at 3 K, which corresponded to the three Fe atom sites in the χ -Fe₅C₂ lattice structure. The Mössbauer spectra

Temperature	Component	δ mm/s	Δ mm/s	H kOe	Г mm/s	Yields %
(a) 293 K	o-Fe ₇ C ₃ (I)	0.30 (1)	-0.33 (2)	220 (2)	0.36 (1)	15.9
	$o-Fe_7C_3$ (II)	0.25 (1)	0.05 (2)	216 (1)	0.36(1)	24.0
	o-Fe ₇ C ₃ (III)	0.21 (0)	-0.09(1)	188 (2)	0.36(1)	15.2
	$o-Fe_7C_3$ (IV)	0.21 (1)	0.19(1)	169 (1)	0.36(1)	29.4
	$o-Fe_7C_3$ (V)	0.19(1)	0.15 (2)	159 (1)	0.36(1)	15.5
(b) 3 K	$o-Fe_7C_3$ (I)	0.45 (1)	-0.05 (2)	241 (1)	0.43 (1)	16.3
	$o-Fe_7C_3$ (II)	0.40 (2)	0.03 (1)	236 (1)	0.43 (1)	23.6
	$o-Fe_7C_3$ (III)	0.30 (2)	-0.09(2)	203 (1)	0.43 (1)	16.2
	$o-Fe_7C_3$ (IV)	0.43 (1)	0.19 (2)	193 (2)	0.43 (1)	28.8
	o-Fe ₇ C ₃ (V)	0.32 (2)	0.15 (2)	183 (1)	0.43 (1)	15.1

Table 2 Mössbauer parameters of the spectra shown in Fig. 3



Fig. 4 Room-temperature Mössbauer spectra of films produced by PLD of Fe onto Al substrates at 573 K in methane atmosphere of (a) 0.5 Pa, (b) 1.0 Pa, and (c) 2.0 Pa

of powder χ -Fe₅C₂ samples produced by carburizing iron metal or Fe₂O₃ in a mixture of CO (30%) + H₂ (70%) at 400 °C were reported in the literature [14], and the Mössbauer parameters of the three sextets observed in the present study are in agreement with the values reported in that study. The occupation ratio of Fe atoms in the χ -Fe₅C₂ lattice is reported to be Fe ₁: Fe _{II}: Fe _{II} = 2: 2: 1 [15], and the area intensity ratio of the three sextets in this study perfectly corresponded to the occupation ratio of a χ -Fe₅C₂ crystal. This result indicated that a pure, highly crystalline χ -Fe₅C₂ film was obtained in this study.

Pressure	Component	δ mm/s	Δ mm/s	H kOe	Γ mm/s	Yields %
(a) 0.5 Pa	χ -Fe ₅ C ₂ (I)	0.22 (0)	0.04 (1)	221 (0)	0.52 (1)	35.7
	χ -Fe ₅ C ₂ (II)	0.16(1)	0.05 (1)	177 (1)	0.52 (1)	33.7
	χ -Fe ₅ C ₂ (III)	0.17 (1)	0.08 (1)	111 (0)	0.52 (1)	20.1
	α-Fe	0.00 (0)	0.00 (0)	330 (0)	0.40(1)	10.5
(b) 1.0 Pa	χ -Fe ₅ C ₂ (I)	0.22 (0)	0.02(1)	219 (2)	0.46 (0)	38.2
	χ -Fe ₅ C ₂ (II)	0.16 (0)	0.04 (0)	181 (0)	0.46 (0)	36.1
	χ -Fe ₅ C ₂ (III)	0.18(1)	0.06(1)	109 (4)	0.46 (0)	21.5
	α-Fe	0.00 (0)	0.00 (0)	330 (0)	0.40(1)	4.2
(c) 2.0 Pa	χ -Fe ₅ C ₂ (I)	0.23 (4)	0.03 (1)	219 (2)	0.41 (1)	38.8
	χ -Fe ₅ C ₂ (II)	0.16 (2)	0.04 (1)	181 (0)	0.41 (1)	36.6
	χ -Fe ₅ C ₂ (III)	0.16(1)	0.06(1)	110 (3)	0.41 (1)	21.8
	α-Fe	0.00 (0)	0.00 (0)	330 (0)	0.40 (1)	2.8

Table 3 Mössbauer parameters of the spectra shown in Fig. 4



Fig. 5 Room-temperature Mössbauer spectra of films produced by PLD of Fe onto Al substrates at 573 K in methane atmosphere of (a) 13 Pa, and (b) 40 Pa

To increase the amount of C atoms supplied in the reaction, films were produced in a 6.0 Pa CH₄ atmosphere. The XRD pattern of the film (Fig. 1b) exhibited the peaks of o-Fe₇C₃ (PDF #01–075-1499). The Mössbauer spectra of the film measured at 293 K and 3 K are shown in Fig. 3, and the parameters are summarized in Table 2. The spectrum was fitted into a combination of five sextets: H = 220, 216, 188, 169, and 159 kOe at 293 K, and H = 241, 236, 203, 193, and 183 kOe at 3 K. Though the Mössbauer spectrum of o-Fe₇C₃ has yet to be reported, the Mössbauer parameters of o-Fe₇C₃ were predicted on the basis of DFT with GGA-PBEsol [16]. The calculated parameters for o-Fe₇C₃ were almost the same as those of the spectrum measured at 3 K in this work. The Fe atoms in o-Fe₇C₃ occupy five different lattice sites, with occupation ratio of Fe ₁: Fe _{II}: Fe _{II}: Fe _{IV}: Fe _V = 1: 2: 1: 2: 1. The area intensity ratio of the five sextets in the spectra also had the same ratio, which suggested that a pure, crystalline o-Fe₇C₃ film was obtained.

The Mössbauer spectra of the films produced in 0.5, 1.0, and 2.0 Pa CH₄ atmosphere were measured at 293 K (Fig. 4), and the Mössbauer parameters are summarized in Table 3. These films consisted of a combination of χ -Fe₅C₂ and α -Fe, showing the three characteristic sets of sextets of χ -Fe₅C₂ and one sextet of α -Fe (H= 330 kOe). The yield of α -Fe was relatively large in the film produced at low CH₄ pressure. In order to have all the evaporated Fe atoms react with C atoms supplied by CH₄ to form χ -Fe₅C₂, at least 0.7 Pa of CH₄ is calculated to be

Pressure	Component	δ mm/s	Δ mm/s	H kOe	Γ mm/s	Yields %
(a) 13 Pa	o-Fe ₇ C ₃ (I) o-Fe ₇ C ₃ (II) o-Fe ₇ C ₃ (III) o-Fe ₇ C ₃ (IV) o-Fe ₇ C ₃ (V) amorphous Fe-C	$\begin{array}{c} 0.28 (1) \\ 0.26 (1) \\ 0.22 (2) \\ 0.20 (1) \\ 0.21 (2) \\ 0.40 (2) \end{array}$	$\begin{array}{c} -0.31 (2) \\ 0.03 (1) \\ -0.09 (0) \\ 0.21 (1) \\ 0.10 (2) \\ 1.11 (1) \end{array}$	221 (1) 217 (0) 188 (1) 169 (1) 160 (2)	0.38 (1) 0.38 (1) 0.38 (1) 0.38 (1) 0.38 (1) 0.38 (1) 0.70 (1)	11.7 19.3 10.7 19.3 12.0 27.0
(b) 40 Pa	amorphous Fe-C	0.40 (1)	1.11 (1)		1.10 (3)	100

 Table 4
 Mössbauer parameters of the spectra shown in Fig. 5

required, assuming that the evaporated Fe atoms react with the CH₄ molecules in the space between the point of laser ablation and the deposition area on the substrate: one laser pulse produces 1.4×10^{-9} mol of Fe, the deposition area was 400 mm², and the distance between substrate and target was 22 mm. However, the experimental result indicated that 0.7 Pa of CH₄ did not supply enough carbon atoms, and that pressure above 4.0 Pa of CH₄ was necessary for the production of χ -Fe₅C₂ without the presence of unreacted α -Fe impurity.

The Mössbauer spectra of the films produced in 13 Pa and 40 Pa CH₄ atmospheres were measured at 293 K (Fig. 5), and the Mössbauer parameters are summarized in Table 4. When the film was produced at 13 Pa (Fig. 5a), the Mössbauer spectrum showed a combination of o-Fe₇C₃ (H=221, 217, 188, 169, 160 kOe) and an extra doublet (δ =0.40 mm/s, Δ =1.11 mm/ s); the doublet was assigned to paramagnetic amorphous Fe-C, containing a large amount of C atoms [17]. For the film produced at the highest pressure of 40 Pa (Fig. 5b), only the doublet (δ =0.40 mm/s, Δ =1.11 mm/s) of amorphous Fe-C was obtained. The excess supply of carbon atoms under high pressure caused the production of amorphous Fe-C.

Unreacted α -Fe was present as a contaminant when the pressure of CH₄ below 4.0 Pa, whereas amorphous Fe-C was the contaminant when the pressure was over 6.0 Pa. Pure χ -Fe₅C₂ and o-Fe₇C₃ were obtained only at 4.0 and 6.0 Pa, respectively.

4 Conclusion

Iron carbide films with various compositions were produced by pulsed laser deposition of Fe in a CH₄ atmosphere. Both gas-phase and surface reactions governed the composition of the iron carbide films, and the surface reaction was enhanced by increasing the substrate temperature. The gas-phase reactions were controlled by varying the CH₄ pressure. Pure χ -Fe₅C₂ was obtained at 4.0 Pa, and pure o-Fe₇C₃ was obtained at 6.0 Pa. These metastable iron carbide films without impurity phases might provide useful materials for catalytic applications.

References

- Xu, K., Sun, B., Lin, J., Wen, W., Pei, Y., Yan, S., Qiao, M., Zhang, X., Zong, B.: ε-Iron carbide as a low-temperature Fischer–Tropsch synthesis catalyst. Nat. Commun. 5, 1–8 (2015)
- Yang, C., Zhao, H., Ma, D.: Fe₅C₂ Nanoparticles: A Facile Bromide-Induced Synthesis and as an Active Phase for Fischer–Tropsch Synthesis. J. Am. Chem. Soc. 134, 15814–15821 (2012)
- 3. de Smit, E., Cinquini, F., Beale, A.M., Safonova, O.V., van Beek, W., Sautet, P., Weckhuysen, B.M.: Stability and Reactivity of $\epsilon - \chi - \theta$ Iron Carbide Catalyst Phases in Fischer–Tropsch Synthesis: Controlling μ_{C} . J. Am. Chem. Soc. **132**, 14928–14941 (2010)
- Chipman, J.: Thermodynamics and phase diagram of the Fe-C system. Metall. Mater. Trans. B Process Metall. Mater. Process. Sci. 3, 55–64 (1972)
- Abhaya, K.: Datye, Yaming Jin, Linda Mansker, R. Thato Motjope, T. Humphrey Dlamini, Neil J. Coville: the nature of the active phase in iron Fischer-Tropsch catalysts. Stud. Surf. Sci. Catal. 130, 1139–1144 (2000)
- Prescher, C., Dubrovinsky, L., Bykova, E., Kupenko, I., Glazyrin, K., Kantor, A., McCammon, C., Mookherjee, M., Nakajima, Y., Miyajima, N., Sinmyo, R., Cerantola, V., Dubrovinskaia, N., Prakapenka, V., Ruffer, R., Chumakov, A., Hanfland, M.: High Poisson's ratio of Earth's inner core explained by carbon alloying. Nat. Geosci. 8, 220–223 (2015)
- Lee, B.J.: A modified embedded-atom method interatomic potential for the Fe–C system. Acta Mater. 54, 701–711 (2006)
- Cusenza, S., Schaaf, P.: Formation and characterization of NaCl-type FeC. Mater. Lett. 63, 1445–1447 (2009)

- Datye, A.K., Jin, Y., Mansker, L., Motjope, R.T., Dlamini, T.H., Coville, N.J.: The nature of the active phase in iron Fischer-Tropsch catalysts. Stud. Surf. Sci. Catal. 130, 1139–1144 (2000)
- Yao, S., Yang, C., Zhao, H., Li, S., Wen, J.L., Hu, G., Li, W., Hou, Y., Ma, D.: Reconstruction of the Wet Chemical Synthesis Process: The Case of Fe₅C₂ Nanoparticles. J. Phys. Chem. C. **121**, 5154–5160 (2017)
- Baskakov, A.O., Lyubutin, I.S., Starchikov, S.S., Davydov, V.A., Kulikova, L.F., Egorova, T.B., Agafonov, V.N.: Mechanism of Transformation of Ferrocene into Carbon-Encapsulated Iron Carbide Nanoparticles at High Pressures and Temperatures. Inorg. Chem. 57, 14895–14903 (2018)
- Siriwardane, H., Pringle, O.A., Newkirk, J.W., James, W.J.: Microstructure of thin iron carbide films prepared in a glow discharge. Thin Solid Films. 279, 155–161 (1996)
- Yamada, Y., Yoshida, H., Kouno, K., Kobayashi, Y.: Iron carbide films produced by laser deposition. J. Phys. Conf. Ser. 217, 012096 (2010)
- Le Caer, G., Dubois, J.M., Senateur, J.P.: Etude par spectrométrie Mössbauer des carbures de Fer Fe₃C et Fe₅C₂. J. Solid State Chem. 19, 19–28 (1976)
- Bernas, H., Campbell, I.A.: Electronic exchange and the Mössbauer effect in iron-based interstitial compounds. J. Phys. Chem. Solids Pergamon Press. 28, 17–24 (1967)
- Liu, X., Zhao, S., Meng, Y., Peng, Q., Dearden, A.K., Huo, C., Yang, Y., Li, Y., Wen, X.: Mössbauer spectroscopy of Iron carbides: from prediction to experimental confirmation. Sci. Rep. 6, 26184 (2016)
- Yamada, Y., Yoshida, H., Kobayashi, Y.: Laser deposition of iron on graphite substrates. Hyperfine Interact. 198, 55–59 (2010)

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.