Nonstoichiometric Wüstite (001) Surface Exposing Defect Clusters

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The (001) surface of nonstoichiometric wüstite (Fe0.94O) grown by the floating zone technique was investigated using STM, LEED and AES. Two distinctive structures, i.e., the dents arrangement and the FeO(001)–c(4×2) reconstructed structure coexist on the terrace after annealing at 1 073 K in the ultrahigh vacuum (UHV) system. On the other hand, the only dents exist after annealing at 1 273 K. The dent is the Fe vacancy pair in the rocksalt-type FeO(001)–(1×1) matrix, which is the exposed P' phase of the defect cluster due to nonstoichiometry.

KEY WORDS: iron oxide; wüstite; Fe1−xO; nonstoichiometry; vacancy; defect cluster; scanning tunneling microscopy.

1. Introduction

Wüstite (Fe1−xO) is one of the phases of iron oxides and nonstoichiometric compound which is stable above 833 K.1) The measure of the deviation from stoichiometry, x, widely ranges from 0.05 to 0.15 depending on the temperature and the oxygen partial pressure. Fe1−xO can also exist as a metastable phase at room temperature by quenching from the high temperatures where Fe1−xO exists in the equilibrium state. The crystal structure of the bulk form of Fe1−xO is the rocksalt type structure. The surface structures on the bulk of the metallic iron2,3) and other iron oxides such as Fe3O49–11) have been investigated on the various crystallographic orientations. However, there are only limited reports on the surface of the bulk Fe1−xO. The surface crystal structures of the Fe1−xO(111) films grown on the Pt and Ru substrates were studied using a scanning tunnelling microscope (STM) and a low energy electron diffraction (LEED).12–14) After annealing the bulk Fe substrates in an oxygen atmosphere (10−3–10−4 Pa), the Fe1−xO(001)–(1×1) oxide layer on the Fe(001) substrate15–17) and Fe1−xO(111)–p(2×2) on the Fe(110) substrate18) were observed using LEED and Auger electron spectroscopy (AES) in the initial stage of iron oxidation. Lopes et al. have grown Fe1−xO(001) film on Ag(001) and have indicated from the I–V curve obtained by the LEED measurement that the Fe1−xO(001) surface has the small rumpling with the oxygen ions extending toward the vacuum.19) The effect of the nonstoichiometry, i.e., Fe vacancies on the surface, has not been referred in the above reports despite the fact that the stoichiometric FeO (x=0) cannot exist in the equilibrium state.11) These surface structures may differ from those on the bulk Fe1−xO. To understand the surface structures of the bulk Fe1−xO and the configuration of the Fe vacancies on the surface is very important for the industrial applications such as iron making in which the reduction reaction of iron ore proceeds on the surface, and Fe vacancies are the carriers of the surface diffusion in the reaction.

In this paper, the single-crystalline Fe0.94O(001) surface was analyzed at room temperature using LEED, AES and STM after annealing in the ultrahigh vacuum (UHV) system. The reason the authors have chosen the (001) surface is that the (001) surface is the most stable structure in the rock-salt type structure such as Fe1−xO, as clearly understood from the view point of its electroneutrality. In fact, the authors have previously observed the polycrystalline Fe1−xO surface using LEED, and have found that the (001) facet is only formed on the surface.20) The STM imaging can be performed at room temperature because the electrical resistivity of the bulk Fe1−xO is about 0.1 Ω cm at room temperature though Fe1−xO is an insulator with the band gap of 2.4 eV.21)

2. Experimental

2.1. Sample Preparation

Powder mixtures of Fe (99.9% purity) and Fe2O3 (99.99% purity) corresponding to a Fe0.94O stoichiometry of the protoxide were pressed and formed into a rod (12 mm in diameter and 40 mm in length). It was sintered in vacuum at 1373 K for over 20 h and then rapidly cooled at room temperature. The single crystal of Fe1−xO was grown from the sintered rod in an optical floating zone furnace (Canon Machinery Inc., Desktop Single Crystal Growth) in a flow of pure argon (99.99% purity) deoxidized by zirco-
nium sponge heated at 1 073 K. The (001) orientation of the single crystal was analysed using the X-ray pole figure (Rigaku Co. RINT-TTR-3C/PC & MPA-2000) and cut into pieces of 1 mm in thickness. The Fe1\textsubscript{x}/H11002 samples on a Pt foil were placed in a SiC electrical resistance furnace and equilibrated at 1 473 K for 48 h in a flow of a CO–CO\textsubscript{2} mixture (P\textsubscript{CO2}/P\textsubscript{CO}/H11005 = 0.38, which is equivalent to the oxygen partial pressure of 1.6×10\textsuperscript{-7} Pa). This condition was chosen to produce Fe\textsubscript{0.94}O in accordance with the FeO–Fe\textsubscript{2}O\textsubscript{3} phase diagram.\textsuperscript{1)} The Fe1\textsubscript{x}/H11002 samples were then quenched to room temperature.

The annealed samples were subjected to the powder XRD technique (Rigaku Co. RINT -TTR-3C/PC) to confirm the phase purity of Fe1\textsubscript{x}/H11002 and to determine the lattice parameter. The lattice parameter of Fe\textsubscript{1–x}/H11002 was calculated by means of the Nelson–Riley function using diffraction peaks of (111), (200), (220), (311), (222), (400), (331) and (420).

The Fe1\textsubscript{x}/H11002 samples were polished using several diamond pastes with different grain sizes and the final polishing was performed using a paste with 0.5 \textmu m grains and were then rinsed in acetone using an ultrasonic bath for 30 min. They were clamped onto a Mo holder and loaded into the UHV chamber.

### 2.2. Surface Observation

The surface of the Fe\textsubscript{1–x}O samples were analyzed in an UHV chamber equipped with STM (Unisoku Co. USM-1100SX3) and LEED/AES optics (OCI Inc. BDL800IR). In order to obtain a clean surface for observation, there are two possible methods: (1) to fracture the sample in vacuo to obtain a cleaved surface, and (2) to anneal the sample in vacuo to evaporate the adsorbed matter from the surface. In the present study, the method (2) was adopted because the high resolution could not be achieved for the method (1). When a Fe\textsubscript{1–x}O single crystal was fractured in vacuo, the obtained cleaved surface had a high density of steps and the area of terraces was not large enough to observe the surface structure with high resolution. For the method (2), however, the oxygen potential during annealing might affect the lattice defect concentration. To reduce the annealing effect, the annealing time was shortened as much as possible. The Fe\textsubscript{1–x}O samples were annealed at 1 073 K (±10 K) or 1 273 K (±10 K) for various durations (3–30 min) under the total pressure of 1.3×10\textsuperscript{-9} Pa by passing a direct current through the samples. The temperature of the samples was measured by a two-color pyrometer through the quartz window of the chamber. After the samples were rapidly cooled down to room temperature, STM, LEED and AES analyses were performed. The tungsten tips for the STM observation were fabricated by electrochemical etching in an aqueous KOH. All STM data were obtained in the constant current mode. The same electron gun and the optical system were utilized for AES as well as LEED. The retarding field analyzer (RFA) was used for analyzing the electron energies. The total pressures during LEED and STM measurements were 2.7×10\textsuperscript{-8} and 5.3×10\textsuperscript{-9} Pa, respectively.

### 3. Results

#### 3.1. Chemical Composition of Fe\textsubscript{1–x}O Sample

The XRD measurements have revealed that the single-crystalline samples have the single phase of wüstite (Fe\textsubscript{1–x}O) with the lattice parameter of 4.305 Å. This lattice parameter corresponds to x = 0.06 in Fe\textsubscript{1–x}O.\textsuperscript{22)} As a consequence, the chemical composition of the sample used in the present study is Fe\textsubscript{0.94}O.

**Figure 1** shows the AES spectra of the Fe\textsubscript{0.94}O(001) surface measured after annealing at 1 073 K or 1 273 K.

**Figure 2** shows the STM image of the Fe\textsubscript{0.94}O(001) surface after annealing at 1 073 K for 17 min taken at sample bias 0.35 V, tunneling current 0.08 nA. (b) Line profile between A and B in (a).
after annealing at 1073 K in UHV, where many steps with the zigzag shaped edges along [110] direction are observed. It is found that the step height varies in the range between 0.2 nm and 1.0 nm. Two structures, which are indicated as $\alpha$ and $\beta$ in Fig. 2, coexist on the terrace. Higher resolution zooms of the $\alpha$ and $\beta$ structures are shown in Figs. 3(a), 3(b) and 3(c), respectively. The $\alpha$ structure is the rhombic lattice. The low and dark dots at a positive sample bias in Fig. 3(a) correspond to the high and bright ones at a negative sample bias in Fig. 3(b). The $\beta$ structure shown in Fig. 3(c) is the distorted arrangement consisting of the dark parts, the detail of which is described in the next subsection. The LEED pattern from the Fe$_{0.94}$O(001) surface after annealing at 1073 K is shown in Fig. 4. The FeO(001)–c(4×2) structure overlaps in Fig. 4, which is at a 90° angle to the c(4×2). Consequently, the $\alpha$ structure is FeO(001)–c(4×2). The ratio of the areas between the $\alpha$ and $\beta$ does not depend on the annealing time.

3.3. Fe$_{0.94}$O(001) Surface after Annealing at 1273 K

The STM image of the Fe$_{0.94}$O(001) surface after annealing at 1273 K in UHV is shown in Fig. 5. The steps have the same geometry as that of the steps in the sample annealed at 1073 K, that is the zigzag shaped edges along [110] direction. The step height varies in the range between 0.2 nm and 1.5 nm. Figures 6(a) and 6(b) show the STM images on the terrace of the Fe$_{0.94}$O(001) surface after annealing at 1273 K for 3 min at (a) positive and (b) negative sample biases. The observed areas are identical between the positive and negative sample biases. Only the same structure as the $\beta$ in Fig. 3(c) exists on the terrace. In Fig. 6(a),
many dark parts can be observed beside the bright dots aligned along (110) direction. The shapes of the dark parts are the corn shape at a positive sample bias and the rectangle shape at a negative sample bias. The corn and rectangle shapes are randomly aligned along either [110] or [1¯10] direction. The dark parts are observed as a concave at both positive and negative sample biases, and thus it is concluded that the dark parts are dents.

Figure 7 shows the fast Fourier-transformed (FFT) image of Fig. 6(a). There are four sharp spots located at the four corners of a square and the vague square inside them. The spots and square are associated with the bright lattice and the arrangement of the dents in Fig. 6(a), respectively. Thus, it is found that the arrangement of the dents is highly distorted from a regular crystal structure. The LEED pattern from the Fe0.94O(001) surface after annealing at 1 273 K is shown in Fig. 8. The FeO(001)–(1×1) pattern and the weak satellite streaked along the [100] direction around each basic reflection from FeO(001)–(1×1) in Fig. 8 is interpreted as the reflection from the arrangement of the defect clusters due to non-stoichiometry. In the bulk Fe1-xO, the Fe vacancies aggregate and make the defect clusters based on the 4 : 1 units shown in Fig. 9(a), where 4 is the number of Fe2+ vacancies and 1 is the number of tetrahedral Fe3+ interstitials to maintain electro-neutrality. The defect clusters are arrayed in the rocksalt-type FeO matrix with longer period than the lattice parameter of the fundamental cell.

4. Discussion

It has been found that the surface structure obtained in the present study is different from those of the bulk metallic iron and other iron oxides such as Fe3O4 and Fe2O3, which have been investigated on the various crystallographic orientations. Therefore, the composition of observed surface remains Fe1-xO, and is not changed to Fe or other iron oxides by annealing. The square-shaped satellites along the [100] direction around each basic reflection from FeO(001)–(1×1) in Fig. 8 is interpreted as the reflection from the arrangement of the defect clusters due to non-stoichiometry. In the bulk Fe1-xO, the Fe vacancies aggregate and make the defect clusters based on the 4 : 1 units shown in Fig. 9(a), where 4 is the number of Fe2+ vacancies and 1 is the number of tetrahedral Fe3+ interstitials to maintain electro-neutrality. The defect clusters are arrayed in the rocksalt-type FeO matrix with longer period than the lattice parameter of the fundamental cell.
ment of the defect clusters is classified into $P'$ and $P''$ phases which are incommensurate and commensurate with the rocksalt structure, respectively. Welberry et al. have reported that the $P'$ phase is the highly distorted lattices in which the unit cell angles and lengths vary, and the average spacing is $2.7a_0 \times 2.7a_0 \times 2.7a_0$ ($a_0$ is the lattice parameter of the rocksalt-type FeO).\textsuperscript{25,26} The weak and diffused satellite spots have been observed around the basic reflection from Fe$_{1-x}$O in the X-ray diffraction pattern of the $P'$ phase. This is consistent with the LEED pattern from the $\beta$ structure in Fig. 8. The dent in the $\beta$ structure corresponds to the defect cluster in the $P'$ phase having highly distorted lattices because the satellite configuration in the LEED pattern is consistent with the vague square from the arrangement of the dents in the FFT image of Fig. 7. Also, the bright dots arrangement in Fig. 6(a) is interpreted as the Fe or O sublattice in FeO(001)–(1×1).

To the best of our knowledge, there are no reports with respect to the electronic structure of the Fe$_{1-x}$O(001) surface. On the other hand, because Fe$_{1-x}$O, NiO and CoO are all 3$d$-transition-metal monoxide forming rocksalt-type structure and have the similar physical properties to each other,\textsuperscript{27} the electronic structure of the Fe$_{1-x}$O surface is considered to be the same as those of the NiO and CoO (001)–(1×1) surfaces, which have been already investigated.\textsuperscript{28–30} In the STM images, the metal and oxygen sites have been observed at positive and negative sample biases, respectively, because the empty and filled states predominantly consist of the metal 3$d$ and oxygen 2$p$ orbitals, respectively, which is the same as that in the bulk. Consequently, it is considered that Fig. 6(a) shows the empty-state STM image where the bright dots correspond to the Fe sublattice with 3$d$ orbitals in the atomic order of FeO(001)–(1×1). In the same manner, Fig. 6(b) may show the filled-state STM image where the bright region correspond to the O sublattice with 2$p$ orbitals though the atomic resolution could not be obtained in Fig. 6(b). By taking into account the observed dent size, it is considered that a black dent correspond to two Fe vacancies in Fig. 9(a). The difference of the dent shape between positive and negative sample biases can be represented by Figs. 9(b) and 9(c). The corn shape consisting of the Fe sublattice and the rectangle shape consisting of the O sublattice around the Fe vacancy pair are observed as the empty- and filled-state images, respectively. Consequently, it is concluded that the $\beta$ structure is the arrangement of the Fe vacancy pairs in the rocksalt-type FeO(001)–(1×1) matrix, which is the exposed $P'$ phase of the defect cluster.

Contrary to the $\beta$ structure, the c(4×2) structure ($\alpha$ structure) might be the reconstructed structure, which have no Fe vacancies. The dark and bright dots in the c(4×2) structure observed at positive and negative sample biases, respectively, are considered to be the site of the occupied state though the detailed position of the atoms in the c(4×2) structure cannot be determined in the present results. As described before, the phase transformation from the $\alpha$ to the $\beta$ is an irreversible process though the definite transformation temperature has not been measured. Consequently, the c(4×2) structure is the metastable phase, and the most stable structure of the Fe$_{0.94}$O(001) surface is the $\beta$ structure.

5. Conclusion

After annealing in UHV, the Fe$_{0.94}$O(001) surface was investigated at room temperature using STM, LEED and AES. Two distinctive structures, the dents arrangement and the FeO(001)–c(4×2) reconstructed structure, coexist on the terrace after annealing at 1073 K, however, only dents arrangement is observed after annealing at 1273 K. The dent is the Fe vacancy pair in the rocksalt-type FeO(001)–(1×1) matrix, which is the exposed $P'$ phase of the defect cluster.

REFERENCES

1) A. Muan and E. F. Osborn: Phase Equilibria Among Oxides in Steel-making, Addison-Wesley, Massachusetts, (1965), 28.
2) H. Tamura, Y. Yamada and T. Mizoguchi: \textit{CAMP-ISIJ}, 20 (2007), 1248.
3) T. K. Yamada, H. Tamura, M. Shishido, T. Irisawa and T. Mizoguchi: \textit{Surf. Sci.}, 603 (2009), 315.
4) S. F. Ceballos, G. Mariotto, K. Jordan, S. Murphy, C. Seoighe and I. V. Shvets: \textit{Surf. Sci.}, 548 (2004), 106.
5) R. Jansen, V. A. M. Brabers and H. van Kempen: \textit{Surf. Sci.}, 328 (1995), 237.
6) Y. Oda, S. Mizuno, S. Todo, E. Torikai and K. Hayakawa: \textit{Jpn. J. Appl. Phys.}, 37 (1998), 4518.
7) A. R. Lennie, N. G. Condon, F. M. Leiblse, P. W. Murray, G. Thornton and D. J. Vaughan: \textit{Phys. Rev. B}, 53 (1996), 10244.
8) N. G. Condon, F. M. Leiblse, T. M. Parker, A. R. Lennie, D. J. Vaughan and G. Thornton: \textit{Phys. Rev. B}, 55 (1997), 15885.
9) N. G. Condon, P. W. Murray, F. M. Leiblse, G. Thornton, A. R. Lennie and D. J. Vaughan: \textit{Surf. Sci.}, 310 (1994), L609.
10) N. G. Condon, F. M. Leiblse, A. R. Lennie, P. W. Murray, D. J. Vaughan and G. Thornton: \textit{Phys. Rev. Lett.}, 75 (1995), 1961.
11) N. G. Condon, F. M. Leiblse, A. R. Lennie, P. W. Murray, T. K. Parker, D. J. Vaughan and G. Thornton: \textit{Surf. Sci.}, 397 (1998), 278.
12) Y. J. Kim, C. Westphal, R. X. Yuzunza, Z. Wang, H. C. Galloway, M. Salmeron, M. A. Van Hove and C. S. Fadley: \textit{Surf. Sci.}, 416 (1998), 68.
13) S. Shaikhutdinov, M. Ritter and W. Weiss: \textit{Phys. Rev. B}, 62 (2000), 7535.
14) G. Ketteler and W. Ranke: \textit{J. Phys. Chem.}, B107 (2003), 4320.
15) C. Leygraf and S. Ekelund: \textit{Surf. Sci.}, 40 (1973), 609.
16) G. W. Simmons and D. J. Dywer: \textit{Surf. Sci.}, 48 (1975), 373.
17) A. J. Pignocco and G. E. Pellissier: \textit{J Electrochem Soc.}, 112 (1965), 1188.
18) D. Cappus, M. Habel, E. Neuhaus, M. Heber, F. Rohr and H.-J. Freund: \textit{Surf. Sci.}, 337 (1995), 268.
19) E. L. Lopes, G. J. P. Abreu, R. Paniago, E. A. Soares, V. E. de Carvalho and H.-D. Pflannes: \textit{Surf. Sci.}, 601 (2007), 1239.
20) Y. Masaki, T. Watanabe, T. Yamashita, M. Hayashi and K. Nagata: \textit{ISIJ Int.}, 49 (2009), 74.
21) H. K. Bowen, D. Adler and B. H. Auker: \textit{J Solid State Chem.}, 12 (1975), 355.
22) L. von Bogdandy and H. J. Engell: The Reduction of Iron Ores: Scientific Basis and Technology, Springer-Verlag, Berlin, (1971), 29.
23) L. Minervini and R. W. Grimes: \textit{J. Phys. Chem. Solids}, 60 (1999), 235.
24) C. Lebrton and L. W. Hobbs: \textit{Radiat. Eff.}, 74 (1983), 227.
25) T. R. Welberry and A. G. Christy: \textit{J. Solid State Chem.}, 117 (1995), 398.
26) T. R. Welberry and A. G. Christy: \textit{Phys. Chem. Miner.}, 24 (1997), 24.
27) V. S. Mandel: \textit{J. Cryst. Growth}, 174 (1997), 346.
28) M. R. Castell, P. L. Wincott, N. G. Concon, C. Muggelberg, G. Thornton, S. L. Dudarev, A. P. Sutton and G. A. D. Briggs: \textit{Phys. Rev. B}, 55 (1997), 7859.
29) S. L. Dudarev, A. I. Liechtenstein, M. R. Castell, G. A. D. Briggs and A. P. Sutton: \textit{Phys. Rev. B}, 56 (1997), 4900.
30) M. R. Castell, S. L. Dudarev, G. A. D. Briggs and A. P. Sutton: \textit{Phys. Rev. B}, 59 (1999), 7342.