Polycrystalline Wüstite Surface Observed by STM and LEED

Yohsuke MASAKI,¹⁾ Takashi WATANABE,¹⁾ Toru YAMASHITA,²⁾ Miyuki HAYASHI¹⁾ and Kazuhiro NAGATA¹⁾

1) Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552 Japan. 2) Mesaplexx Pty Ltd., 7 Clunies Ross Court, Eight Mile Plains QLD 4113, Australia.

(Received on September 10, 2008; accepted on October 20, 2008)

After annealing at 1273 K in UHV chamber to remove adsorbed molecule, the surface crystal structure and the composition of polycrystalline Fe_{1-x}O were analyzed at room temperature using STM, LEED and AES. The Fe_{1-x}O sample was prepared by oxidizing an polycrystalline electrolytic iron strip. The Fe_{1-x}O surface consists of facets, where many steps like zig-zag shape are arranged. The mesh-like structure, of which periodicity is about 0.8–1.3 nm, was observed on the terrace. The facets are (001) planes of Fe_{1-x}O , and the step direction is $\langle 110 \rangle$ by LEED measurement. The mesh-like structure is considered as the defect clusters derived from nonstoichiometry.

KEY WORDS: wüstite; polycrystal; surface structure; STM; LEED.

1. Introduction

On the reduction process of wüstite (Fe_{1-x}O) as one of the intermediate products in the iron making processes, Yamashita *et al.*¹⁾ has reported from the *in-situ* observation using a high temperature optical microscope that the reduction of Fe_{1-x}O on the surface consists of complicated mechanisms which depend on the partial pressure of CO and reaction temperature. They concluded that the elementary steps controlling the reaction near the surface, *e.g.* adsorption and diffusion of CO gas, depend on the partial pressure and temperature. In order to verify the controlling steps of the reaction on the surface, however, the *in-situ* observation of the reduction of the Fe_{1-x}O surface is required in a small scale of the nano order or atomic size. For the observation of the reaction on the surface in the nano order size, it is very important to clarify the atomic arrangements and defects on the surface in equilibrium.

The surface crystal structure of the Fe_{1-x}O film grown on the Pt and Ru substrates was studied using a scanning tunnelling microscope (STM) or a low energy electron diffraction (LEED).^{2–4)} After annealing the bulk Fe substrates in an oxygen atmosphere (10^{-8} – 10^{-9} atm), the $\text{Fe}_{1-x}\text{O}(001)-(1 \times 1)$ on $\text{Fe}(001)^{5–7)}$ and $\text{Fe}_{1-x}\text{O}(111)-p(2 \times 2)$ on $\text{Fe}(110)^{8)}$ were observed using LEED and Auger electron spectroscopy (AES) in the initial stage of oxidation. These surface structures may differ from the surface structure on the bulk Fe_{1-x}O . The Fe_{1-x}O films are so thin that the surface structures are affected by the strain caused by the misfit between the film and substrate. On the other hand, there are only limited reports on the surface crystal structure of bulk Fe_{1-x}O . Nagata *et al.*⁹⁾ have observed three types of polycrystalline Fe_{1-x}O surface with different concentration of Fe vacancy after annealing in ultra high vacuum (UHV) by STM. They found by the STM images that the Fe_{1-x}O surface consists of a mesh-like structure (surface super lat-

tices). However, those STM images may indicate electronic structures on the surface, that is, the density of states on Fermi level rather than atomic arrangements.

In this paper, the surface crystal structure and the composition of polycrystalline Fe_{1-x}O after annealing in UHV were analyzed at room temperature using LEED, AES as well as STM.

2. Experimental Procedure

2.1. Sample Preparation

The Fe_{1-x}O sample was prepared from the oxidation of an electrolytic iron strip (1 mm $\times$ 25 mm $\times$ 40 mm, 99.99% purity). The iron strip was suspended using a platinum wire in a SiC resistance furnace and equilibrated at 1473 K for 48 h in the flowing gas mixture of CO_2 (45 mL/min) and CO (45 mL/min) ($P_{\text{CO}_2}/P_{\text{CO}}=1$, which is in equilibrium with the oxygen partial pressure of 1.1×10^{-11} atm). This condition was chosen to produce $\text{Fe}_{0.92}\text{O}$ from FeO – Fe_2O_3 phase diagram.¹⁰⁾ The oxidized iron strip was then quenched to room temperature by dropping it to the bottom of the furnace and spraying argon gas onto it.

The phase and the lattice parameter of the oxidized sample were determined by using the XRD technique (Rigaku Co. RINT-TTR-3C/PC) and confirmed to be Fe_{1-x}O . The lattice parameter of Fe_{1-x}O was calculated by means of the Nelson–Riley function, using diffraction peaks of (111), (200), (220), (311), (222), (400), (331) and (420). The density of the Fe_{1-x}O sample was determined by means of the Archimedeian method.

The Fe_{1-x}O sample was cut in pieces and polished with emery paper with several different grids and finally with diamond paste with a grain size of 0.5 μm . It was then rinsed in acetone using an ultrasonic bath for 30 min.

2.2. Observation of Surface

The surface of the Fe_{1-x}O sample was analyzed in an UHV chamber equipped with STM (Unisoku Co. USM-1100SX3) and LEED/AES optics (OCI Inc. BDL800IR). The Fe_{1-x}O sample was annealed to obtain the clean surface at 1273 K for 4 min under the total pressure of 1.3×10^{-6} Pa by passing a direct current through the sample. The temperature of the sample was measured by a two-color pyrometer through the quartz window of the chamber. After the sample was rapidly cooled down to room temperature, STM, LEED and AES analyses were performed. The tungsten tips were fabricated by electrochemical etching in an aqueous KOH. The tips were cleaned by electronic heat radiation in the UHV chamber (2.7×10^{-8} Pa) and were subsequently used for the STM observation. All STM data were obtained in the constant current mode. The incident electron beam for LEED was applied in perpendicular to the Fe_{1-x}O surface, and the images of the LEED patterns were obtained using a digital camera. 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 fixed in 2.7×10^{-8} and 5.3×10^{-9} Pa, respectively.

3. Results

3.1. Determination of x in Fe_{1-x}O Sample

The polycrystalline iron oxide samples had the grain size of about 2–4 mm and were confirmed to be wüstite (Fe_{1-x}O) by XRD. The non-stoichiometric number, x , in Fe_{1-x}O is calculated by the following equation¹¹⁾:

$$x = \frac{M_{\text{FeO}}}{M_{\text{Fe}}} \cdot \frac{d_{\text{cal}} - d_{\text{meas}}}{d_{\text{cal}}} = \frac{M_{\text{FeO}}}{M_{\text{Fe}}} \cdot M_{\text{V}} \dots \dots \dots (1)$$

where d_{cal} is the theoretical density that is derived from the lattice parameter, a_0 , d_{meas} is the observed density that is determined by the Archimedian method, M_{V} is the mass percent concentration of Fe vacancy, and M_i is molecular weight of component i . **Table 1** shows the results of the calculation, and x is 0.10. x is estimated to be 0.08 in case of $a_0 = 4.297$ Å, which is the obtained lattice parameter, from the relationship between x and lattice parameter.¹²⁾ It was concluded that x of the sample used in the present study is $\text{Fe}_{0.91}\text{O}$ (*i.e.* $x = 0.09 (\pm 0.01)$).

3.2. Polycrystalline $\text{Fe}_{0.91}\text{O}$ Surface after Annealing in UHV

3.2.1. AES Spectra of $\text{Fe}_{0.91}\text{O}$

Figure 1 shows the AES spectra of the $\text{Fe}_{0.91}\text{O}$ surface after annealing at 1273 K in UHV. All peaks are assigned to the Fe and O spectra. After the heat treatment at 1273 K in the UHV chamber, all contaminations were removed successfully to below the detection limit of the AES analyzer.

3.2.2. STM Image of $\text{Fe}_{0.91}\text{O}$

The STM image of the $\text{Fe}_{0.91}\text{O}$ surface is shown in **Fig. 2** and **Fig. 3**. Many steps with the zigzag shaped edges were formed on the surface after annealing in **Fig. 2**. The ob-

Table 1. Characterization of bulk Fe_{1-x}O .

$a_0 / \text{\AA}$	$d_{\text{cal}} / \text{g}\cdot\text{cm}^{-3}$	$d_{\text{meas}} / \text{g}\cdot\text{cm}^{-3}$	$M_{\text{V}} (\%)$	$1-x$
4.297	6.03	5.55	7.69	0.90

Fig. 1. AES spectra of $\text{Fe}_{0.91}\text{O}$ surface measured after annealing at 1273 K.

Fig. 2. Constant current STM image of $\text{Fe}_{0.91}\text{O}$ surface annealed at 1273 K for 4 min. 20.7 nm $\times$ 20.7 nm scanning range, 0.35 V sample bias, 0.14 nA tunneling current.

served minimum step height was 0.5 nm in the present study. The step height ranged in 0.5 nm and 1.5 nm. The mesh-like structure was observed on the terrace. The periodicity of each mesh was about 0.8–1.3 nm, which is 2 to 3 fold longer than the lattice parameter of wüstite. The depth of the mesh has been measured as *ca.* 0.05 nm, however, in fact it may be deeper because the apex of tips has curvature. Though most of the edges of the steps were zigzag in shape, linear edges were sometimes observed as shown in **Fig. 3**. The step height and the mesh-like structure on the terrace were the same as the crystals with the zigzag edges in **Fig. 2**.

3.2.3. LEED Analysis

The LEED patterns from the $\text{Fe}_{0.91}\text{O}$ surface after anneal-

Fig. 3. Constant current STM image of $\text{Fe}_{0.91}\text{O}$ surface annealed at 1273 K for 4 min on the other grain. (b) is magnified image of (a). (a) 119.4 nm $\times$ 119.4 nm scanning range, 0.33 V sample bias, 0.12 nA tunneling current. (b) 15.9 nm $\times$ 15.9 nm scanning range, 0.50 sample bias, 0.12 nA tunneling current.

ing is shown in **Fig. 4** with the different beam energies. When the beam energy increases, two subsets of the spots individually move toward certain spots as the Ewald sphere becomes larger. Consequently, two subsets of the diffraction images, as indicated as A and B in **Fig. 5**, were identified. The two spots which remained stationary throughout the experiment, whilst the other spots moved towards it, were labelled (00) for each set of diffraction pattern. Thus two sets of diffraction patterns appear to be superimposed in this figure. In other areas of the sample, more than 2 patterns were superimposed in the LEED patterns. In such cases, the incident electron beam might radiate several grains. The square lattice is the pattern from (001) plane of Fe_{1-x}O which has the rock-salt type crystal structure. Therefore the streaks were parallel to $\langle 110 \rangle$ direction of Fe_{1-x}O . No additional spots were observed except the basic reflection from (001) of the bulk wüstite.

4. Discussion

4.1. Facet Growth of Polycrystalline Fe_{1-x}O Surface by Annealing

The only basic reflection from (001) of bulk is obtained in the LEED patterns of the polycrystalline Fe_{1-x}O after annealing in UHV. The (001) facet was formed on the surface during the heat treatment. From the view point of electroneutrality, the (001) surface is the most stable structure in the case of rock-salt structure. Thus, each grain faces the (001) by forming the facet structure.

The streak in the LEED pattern is derived from the arrangement of parallel steps on the surface. When the

Fig. 4. Transition of LEED patterns of $\text{Fe}_{0.91}\text{O}$ surface obtained after annealing at 1273 K for 4 min with the change of incident electron energy of (a) 42.4 eV, (b) 61.1 eV and (c) 90.9 eV.

Fig. 5. Schematic illustration of LEED pattern determined specular reflection of A and B in **Fig. 4(a)**.

steps are parallel with varying widths, the electrons scattered from the same terrace are in phase, however, the scattering from separate terraces are out-of-phase. In such a case, the diffraction spots can be streaked.¹³⁾ In the present study, it is considered that the step direction in the STM image is the $\langle 110 \rangle$ because the streaks sit along the square diffraction pattern.

4.2. Long-period Structure on the Terrace of Fe_{1-x}O Surface

The periodicity of the ‘mesh-like’ structure on the terraces, which is shown in Figs. 2 and 3(b), was about 0.8–1.3 nm. Non-stoichiometric Fe_{1-x}O has Fe vacancies aggregating to make clusters consisting of the Fe vacancies, Fe³⁺ ions and O²⁻ ions.¹⁴⁾ The clusters are arrayed in lengths which are 2.5–2.7 times longer than the lattice parameter of the fundamental cell in a bulk.¹⁵⁾ The mesh-like structure may represent the density of states on the Fermi level of the defect clusters because the cluster periodicity is in agreement with the spacing of the ‘mesh’ in the STM image. At this stage it cannot be concluded that the mesh-like structure is a result of surface topography or due to the density of states. The AES spectra revealed that the Fe_{0.91}O surface consists of Fe and O atoms after annealing at 1273 K in UHV. The surface structures on the bulk of the metallic iron^{16,17)} and other compounds such as Fe₃O₄^{18–22)} and Fe₂O₃^{23–25)} have been investigated on the various crystallographic orientations. None of these reported structures are in agreement with the results obtained in this study. Consequently, the Fe_{0.91}O sample was not oxidized and reduced by annealing in UHV performed before the surface observation. The defects in Fe_{1-x}O derived from nonstoichiometry make clusters¹⁴⁾ and these clusters may be observed as a mesh-like structure in the STM images. No clear spots attributed to the super-lattice may be appeared in the LEED patterns owing to the overlap of the patterns from several grains and the streak from many steps on the surface as the background.

5. Conclusion

The surface of the polycrystalline Fe_{0.91}O after annealing at 1273 K in UHV was observed using STM, LEED and AES. The (001) facet is formed, and many steps like zigzag shape in parallel with <110> is arranged on the Fe_{0.91}O surface. The mesh-like superstructure, which is considered as the arrangement of the defect clusters, exists on the terrace with period of about 0.8–1.3 nm.

REFERENCES

- 1) T. Yamashita, T. Nakada and K. Nagata: *Metall. Mater. Trans. B*, **38** (2007), 185.
- 2) Y. J. Kim, C. Westphal, R. X. Ynzunza, Z. Wang, H. C. Galloway, M. Salmeron, M. A. Van Hove and C. S. Fadley: *Surf. Sci.*, **416** (1998), 68.
- 3) S. Shaikhutdinov, M. Ritter and W. Weiss: *Phys. Rev.*, **B62** (2000), 7535.
- 4) G. Ketteler and W. Ranke: *J. Phys. Chem.*, **B107** (2003), 4320.
- 5) C. Leygraf and S. Ekelund: *Surf. Sci.*, **40** (1973), 609.
- 6) G. W. Simmons and D. J. Dwyer: *Surf. Sci.*, **48** (1975), 373.
- 7) A. J. Pignocco and G. E. Pellissier: *J. Electrochem. Soc.*, **112** (1965), 1188.
- 8) D. Cappus, M. Haßel, E. Neuhaus, M. Heber, F. Rohr and H.-J. Freund: *Surf. Sci.*, **337** (1995), 268.
- 9) K. Nagata and K. Kitamura: Collected Abstracts of the 1999 Autumn Meeting of the Japan Inst. Metals, (2004), 232.
- 10) A. Muan and E. F. Osborn: Phase Equilibria among Oxides in Steel-making, Addison-Wesley, Massachusetts, (1965), 28.
- 11) K. Nagata and K. Goto: *Bull. Jpn. Inst. Met.*, **26** (1987), 32.
- 12) L. von Bogdandy and H. J. Engell: The Reduction of Iron Ores, Springer-Verlag, Berlin, (1971), 29.
- 13) M. Henzler: *Appl. Phys.*, **9** (1976), 11.
- 14) F. Koch and J. B. Cohen: *Acta Cryst.*, **B25** (1969), 275.
- 15) P. J. Manenc: *J. Phys. Radium*, **24** (1963), 447.
- 16) H. Tamura, T. Yamada and T. Mizoguchi: *CAMP-ISIJ*, **20** (2007), 1248.
- 17) T. Yamada, H. Tamura, T. Irisawa and T. Mizoguchi: *CAMP-ISIJ*, **20** (2007), 1247.
- 18) S. F. Ceballos, G. Mariotto, K. Jordan, S. Murphy, C. Seoighe and I. V. Shvets: *Surf. Sci.*, **548** (2004), 106.
- 19) R. Jansen, V. A. M. Brabers and H. van Kempen: *Surf. Sci.*, **328** (1995), 237.
- 20) Y. Oda, S. Mizuno, S. Todo, E. Torikai and K. Hayakawa: *Jpn. J. Appl. Phys.*, **37** (1998), 4518.
- 21) A. R. Lennie, N. G. Condon, F. M. Leibsle, P. W. Murray, T. M. Parker, G. Thornton and D. J. Vaughan: *Phys. Rev.*, **B53** (1996), 10244.
- 22) N. G. Condon, F. M. Leibsle, T. M. Parker, A. R. Lennie, D. J. Vaughan and G. Thornton: *Phys. Rev.*, **B55** (1997), 15885.
- 23) N. G. Condon, P. W. Murray, F. M. Leibsle, G. Thornton, A. R. Lennie and D. J. Vaughan: *Surf. Sci.*, **310** (1994), L609.
- 24) N. G. Condon, F. M. Leibsle, A. R. Lennie, P. W. Murray, D. J. Vaughan and G. Thornton: *Phys. Rev. Lett.*, **75** (1995), 1961.
- 25) N. G. Condon, F. M. Leibsle, A. R. Lennie, P. W. Murray, T. K. Parker, D. J. Vaughan and G. Thornton: *Surf. Sci.*, **397** (1998), 278.