1. Introduction

The characteristics of iron under aqueous solution is very interesting in order to study the corrosion processes because of its theoretical and industrial importance. The passive films formed on iron in aqueous solution have been investigated with ex situ and in situ techniques, e.g. X-ray photoelectron spectroscopy (XPS),1–5 Auger electron spectroscopy (AES),6–9 Mossbauer spectroscopy,1,10–13 secondary ion mass spectroscopy (SIMS),8,14,15 ellipsometry,16–21 surface enhanced Raman spectroscopy (SERS),22–27 light reflectance spectroscopy,28,29 X-ray absorption near-edge structure (XANES) study30 and scanning electrochemical microscopy (SECM),31 but more information is required for better understanding about the behavior of iron in aqueous solution.

Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) are powerful techniques for in situ studies of surfaces in electrochemical environment. Especially, the STM and AFM investigation at atomic scale with the electrochemical oxidation processes of a well-defined electrode surface of base metals, such as copper32,33 nickel34–36 and cobalt,37 is intriguing because it gives information about the epitaxial relationship between anodically formed oxide film and substrate.

A few STM and AFM observations about the oxidation and corrosion of iron in aqueous solution were performed previously. In situ electrochemical topological, not atomic resolution, STM and AFM studies were carried out in borate,38,39 citrate40 and alkaline41,42 solution. Ryan et al.43 succeeded in atomically resolved STM observation upon the anodic oxide layer formed on the sputtered thin iron film in borate solution. However, atomic resolution images of unoxidized bare Fe surfaces were not obtained both in air and in solution because of the stability of oxide layer. Therefore, it was not clarified how the orientation of the anodically formed oxide film is related to that of iron substrate.

In the present paper, we show in situ atomic resolution AFM images of a bare Fe(110) and an anodically formed oxide on Fe(110) in 0.05 M Na2SO4 aqueous solution under potential control. From these images, we discuss an epitaxial relationship between the anodically formed oxide layer and Fe(110) substrate.

2. Experimental

Fe(110) samples were prepared from a Fe single crystal rod (99.9%, Monocrystal). Orientation of the samples was verified within ±1° by Laue backscattering method. After mechanically polished, Fe samples were etched in 3%HF–97%H2O2 solution for 10 min in order to remove the damaged layers. In situ electrochemical AFM (EC-AFM) images are taken by Nanoscope E (Digital Instruments, Inc.). Figure 1 shows the cross section of EC-AFM cell. The potential of working electrode was controlled by a potentiostat and was referred to the reference electrode. The reference electrode used here was the Hg/Hg2SO4 electrode (0.65 V vs. normal hydrogen electrode; NHE), to which all potential shown in this paper were referred. The space surrounded by the working electrode, the cantilever mount and the O-ring
were filled with the electrolytes. The electrolytes used here were 0.05 M Na₂SO₄ (pH 5.6), which were prepared from Na₂SO₄ (Wako, Superior) and MilliQ-water. The electrolytes were deaerated with N₂ gas for more than 1 h before the experiments.

3. Results and Discussion

Figure 2 indicates a typical cyclic voltammogram (CV) for Fe(110) in 0.05 M Na₂SO₄ aqueous solution from 1.9 V to 0.7 V with sweep rate of 50 mV sec⁻¹. In the positive scan, there is an oxidation peak at 1.25 V (A₁), followed by the active region (A₂). This positive scan practically agrees with the anodic sweep voltammogram in neutral solution reported. Reversing the potential toward negative at 0.7 V, there is a cathodic peak at 1.4 V (C₁), which is the reduction of the peaks (A₁, A₂) and is followed by hydrogen evolution region (C₂). The peak (A₁) is considered to be due to one monolayer formation of Fe(OH)₂(0001) film on Fe(110) substrate according to the discussion below.

After setting the sample in EC-AFM, we tried to remove the effect of the oxide layer formed under air. First, we keep the potential at 2.5 V, where the unoxidized iron is stable according to the Pourbaix diagram, for 30 min, however, we didn’t succeed in the exposure of any well-ordered structures. As the next trial, we tried to scan the surface by the AFM cantilever continuously for 10 min while keeping the potential at −2.5 V and succeed in obtaining a good AFM image. In the filtered image (Fig. 3(b)) of image (a), we can recognize the spots which have two-fold symmetry with interatomic distance of 0.29 nm and 0.40 nm. This superlattice corresponds to the protuberances

![Fig. 1. Schematic model of the cross section of electrochemical AFM cell.](image)

![Fig. 2. Cyclic voltammogram for Fe(110) electrode in 0.05 M Na₂SO₄ aqueous solution from 1.9 V to 0.7 V with sweep rate of 50 mV sec⁻¹.](image)

![Fig. 3. (a) In situ atomic resolution EC-AFM image of Fe(110) obtained at −1.9 V in 0.05 M Na₂SO₄ aqueous solution after keeping the potential in hydrogen evolution region and removing the oxide layer off the iron surface by means of the AFM cantilever. (b) Filtered image of image (a). (c) Schematic model of the Fe(110)-(1×1) plane.](image)
by OH groups or Fe atoms on unreconstructed Fe(OH)$_2$(0001)–(1×1) (Fig. 5(a)), since the bulk structure of Fe(OH)$_2$ is known as shown in Fig. 5(b). On one hand, a charge of 0.174 mC cm$^{-2}$ is required to form a monolayer of Fe(OH)$_2$(0001) film. On the other hand, the charge consumption of peak (A$_1$) estimated from the CV shown in Fig. 2 was 0.260.05 mC cm$^{-2}$. If the effect of peak (A$_2$) was ignored at −1.2 V, the thickness of Fe(OH)$_2$(0001) film formed on Fe(110) electrode is estimated to be only one monolayer at −1.2 V.

After combining the Figs. 3 and 4, we found that the atomic rows along the [2110] direction of Fe(OH)$_2$(0001) surface were parallel with those along the [110] direction of Fe(110) surface as shown in Fig. 6. This Fe(OH)$_2$ (0001)//Fe(110) epitaxial system has small lattice constant misfit of 1.3% along [001] direction. Along [110] direction, there is large misfit of 19.3%, but the misfit between 5 times of the Fe(OH)$_2$ periodicity and 4 times that of the Fe(110) is less than 1%. Such a long-scale epitaxial relationship between the anodic oxide layers and the metal substrates was also observed in the case of the Cu$_2$O(111)//Cu(111), NiO(111) (or Ni(OH)$_2$(0001))/Ni(111) and Co(OH)$_2$(0001)//Co(0001).

4. Conclusion

A Fe(110) single crystal electrodes in 0.05 M Na$_2$SO$_4$ aqueous solution under potential control were investigated by in situ EC-AFM. Keeping the potential at −2.5 V and repeated scanning the surface with the AFM cantilever for 10 min yielded to remove the oxide layer off the iron surface and we observed an unreconstructed Fe(110)–(1×1) structure at −1.9 V in 0.05 M Na$_2$SO$_4$ aqueous solution. As far as we know, this is the first atomic image of bare Fe(110)–(1×1) obtained in solution. Fe(OH)$_2$(0001)–(1×1) structure of the anodic oxide layer on Fe(110) single crystal was observed at −1.2 V in 0.05 M Na$_2$SO$_4$ aqueous solution by in situ EC-AFM. We have found that the anodic oxide layer and Fe(110) substrate had an epitaxial relationship of Fe(OH)$_2$(0001)[2110]/Fe(110) [110] and that the misfit between the anodic oxide layer and Fe(110) substrate was less than 1.3%.

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