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Study on Atomic and Local Electronic Structures of $\text{Fe}_3\text{O}_4(001)$ Film Surfaces: Clean and Modified by Adsorbed H Atom

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for the Degree of Doctor of Philosophy

By

Satoshi Hiura

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Nanoelectronics Laboratory
Graduate School of Information Science and Technology
Hokkaido University
Sapporo, JAPAN

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I certify that I have read this dissertation and that in my opinion it is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Prof. K. Sueoka (Principal adviser)

Prof. Y. Takahashi

Prof. T. Uemura

Prof. A. Murayama

Approved by the University Committee on Graduate Studies

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Chapter 1

Introduction

1.1 Background

1.1.1 Spintronics

Electronic devices have widely advanced since the invention of the first transistor in 1947. The number of transistors can be doubled every two years. This well-known law is called “Moore’s law”. The transistor size has also scaled down following this law every year. As the transistor density has increased due to the shrinking in the size, processing speeds have increased. As a result, information technology has been rapidly advanced. Recently, however, following this Moore’s law is more difficult due to various issues, such as high static power caused by the leakage currents [1,2]. The static power arises mainly from the cache memory between the computing chip and main memory. It prevents computing from reaching high frequency and limits power efficiency, and thus the solutions to treat these issues are required. Development of novel electronic devices to replace conventional charge-based complementary metal-oxide-semiconductor circuits has attracted great attention.

Spintronics is an emerging field of electronics. This new discipline utilizes not only the charge of the electrons but also their quantum property called “spin”, as shown in Fig. 1.1. The Nobel Prize in Physics was awarded to Albert Fert *et al.* in 2007 for their discovery of the giant magnetoresistance effect, which is the cornerstone of spintronics. Since then, spintronic nanodevices, such as spin-valve and tunnel magnetoresistance (TMR) devices, were rapidly applied in hard disk drives. Nonvolatility is one of the most outstanding properties of spintronic

devices. Its property can power off the whole computing system in standby state. For example, spin transfer torque magnetic random access memory (STT-MRAM) can be a promising candidate for nonvolatile memories because of its fast speed and high density [3]. In addition, the endurance of memory cells is very crucial for the purpose of computing. Spintronics can provide nearly-infinite endurance to STT-MRAM. Therefore, developing spin-based functionalities for the nonvolatile solid-state memory and logic devices has been studied all over the world. A wide range of studies on new fundamental physics and characterization methods in spintronics have also been performed. These novel spintronic devices can realize extremely low power consumption in the near future electronics.

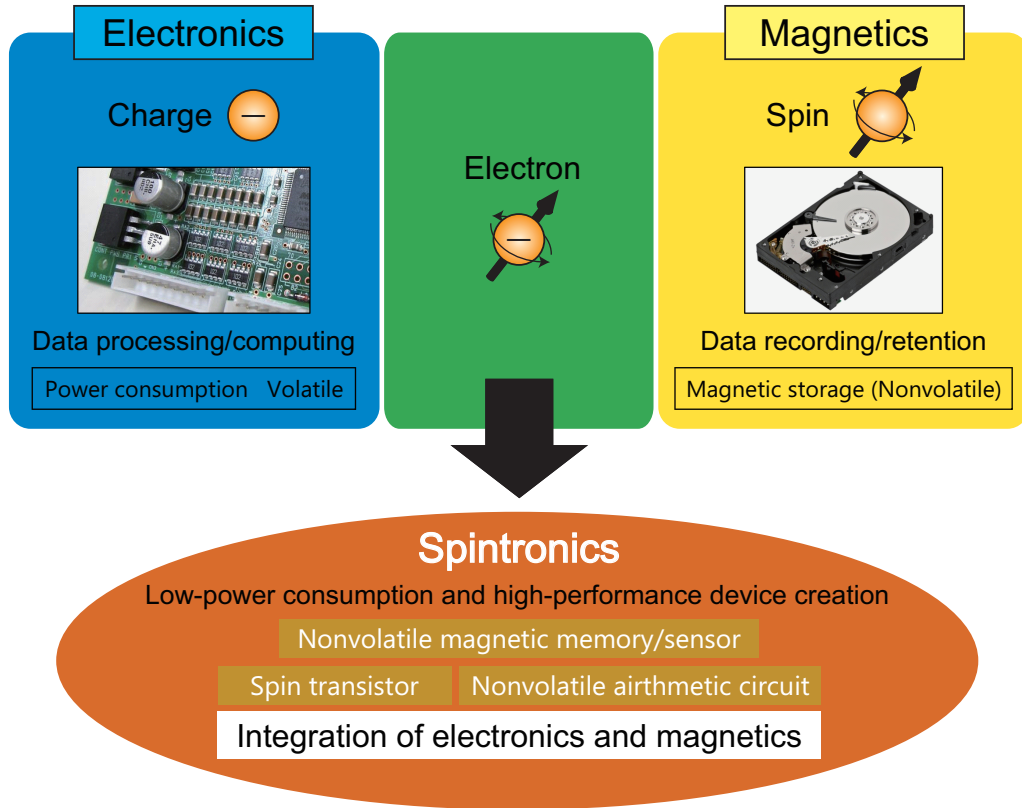


Figure 1.1 Concept of spintronics

1.1.2 Half-metallic material

In recent years, there has been a rapid increase in the interest toward the application of TMR devices with perpendicular magnetic anisotropy in spintronics, such as an STT-MRAM. This interest is driven by the several promises of this TMR device, such as high thermal and magnetic stabilities that will realize the extremely low dimensional and high reliability devices in more advanced spintronic applications. Until recently, TMR devices have been produced by sandwiching a thin insulating layer with ferromagnetic electrode layers. However, to obtain higher TMR values, more effective spin dependent scattering is required. Therefore, ferromagnetic materials with high electron-spin polarization are considered for spintronic device applications. TMR values are expected to follow Julliere's formula [4], $\text{TMR} = 2P_1P_2/(1-P_1P_2)$, where P_1 and P_2 are electron-spin polarizations of two ferromagnetic electrodes. Thus, finding and developing magnetic materials with higher electron-spin polarization is one the most important factor for spintronic field. The spin polarization is defined as the ratio of the density of states (DOS) of up-spin and down-spin electrons at the Fermi level, $P = (\text{DOS}_{\text{up}} - \text{DOS}_{\text{down}})/(\text{DOS}_{\text{up}} + \text{DOS}_{\text{down}})$. In paramagnetic materials, for example, the DOS of up-spin and down-spin electrons are equal, resulting in $P = 0\%$. On the other hand, since the DOS of up-spin and down-spins are different in ferromagnetic materials (see Fig. 1.2(a)), P values are 0–100%. The P values of Fe and Co are known to be about 50% [5]. If a material has a semiconducting energy gap in the minority band at the Fermi level and exhibits metallic behavior in the majority band, the DOS of the minority band is zero at the Fermi level. In this case, only up-spin electrons are present at the Fermi level, resulting in the P value of 100%. This type of material is called “half-metal” because it shows both metallic and semiconducting behaviors, as shown in Fig. 1.2(b).

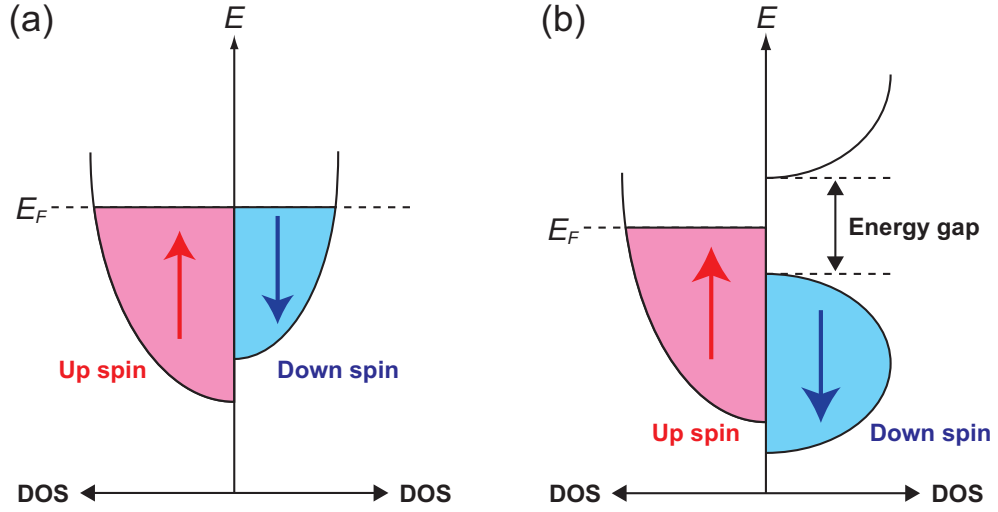


Figure 1.2 Density of states of ferromagnetic materials (a) and half-metallic materials (b).

1.1.3 Characteristics of magnetite (Fe_3O_4)

Magnetite (Fe_3O_4) is a magnetic iron oxide that has the unusual properties such as half-metallicity, high Curie temperature of 858 K and metal-insulator (Verwey) transition at around 120 K in the bulk [6–9]. Moreover, Fe_3O_4 is abundantly present in the earth and harmless to the human body. In the past decades, Fe_3O_4 has attracted great attention because of its potential applications in spintronic devices, catalyst, drug delivery and so on. Due to these outstanding properties, it is highly desirable to grow high-quality Fe_3O_4 films. The film growth has been performed using several deposition methods, such as molecular beam epitaxy [10–15], sputtering [16] and pulsed laser deposition [17,18]. Many research groups have succeeded in growing Fe_3O_4 films on various substrates (MgO , SrTiO_3 , MgAl_2O_4 , sapphire, and Si) [12,17,19–21]. However, these grown films have shown poor performances, such as decreased electrical conductivity [12], unsaturated magnetization [16,22] and low TMR values [23–26].

1.1.4 Disappearance of half-metallicity at the $\text{Fe}_3\text{O}_4(001)$ surface

As described above, the spin polarization value of electronic states is one of the most significant indices for spintronic devices. Recently, there is considerable interest in Fe_3O_4 due to its predicted half-metallic behavior in the bulk [6–8]. Consequently, Fe_3O_4 films can be candidates for highly spin-polarized electrodes for spintronic devices. However, the TMR values observed in Fe_3O_4 -based devices [23–26] and the spin injection efficiency obtained with a Fe_3O_4 electrode [27] have proved to be much lower than expected. These poor performances are correlated with the disruption of the half-metallic behavior at the material surface arising from the surface states [28] and the antiphase domain boundary defects in Fe_3O_4 films [16, 29]. Spin-polarized photoelectron spectroscopy (SPPES) measurements of a clean $\text{Fe}_3\text{O}_4(001)$ surface have shown that the surface spin-polarization at the Fermi level is -40% to -55% [30–32]. However, considering that the SPPES signal includes a significant contribution from the bulk, these spin-polarization values should be much lower at the surface. In fact, recent spin-polarized metastable de-excitation spectroscopy (SPMDS) measurements, which can be more sensitive to the topmost surface properties than SPPES, have demonstrated a less than -5% electron-spin polarization at the Fermi level of a clean $\text{Fe}_3\text{O}_4(001)$ surface [33–35]. To make this material useful for spintronic applications, developing an effective method of ensuring a surface electron-spin polarization close to that of the bulk is required.

1.1.5 Recovery of surface half-metallicity by hydrogen adsorption

Recent experimental and theoretical studies have revealed that the adsorption of hydrogen atoms on a clean $\text{Fe}_3\text{O}_4(001)$ surface significantly enhances the surface electron-spin polarization [28, 33–37]. SPMDS measurements have shown that the spin polarization value at the Fermi level is enhanced by atomic-H adsorption to at least $\sim 50\%$ at room temperature [33–35]. Density functional theory (DFT) calculations have also predicted that half-metallic behavior can be achieved through atomic-H adsorption [28, 34–37]. In addition, the adsorption of benzene molecules [33], carbon [38] and boron atoms [39] has been found to enhance the surface electron-spin polarization experimentally and theoretically. However, the detailed mechanism by which the surface electron-spin polarization is affected has not been revealed. Although theoretical predictions for the effect of hydrogen atoms on the surface local electronic/spin states are reported [28, 35, 37], there are no experimental reports of atomic-scale spectroscopic studies of an H-adsorbed $\text{Fe}_3\text{O}_4(001)$ surface. Moreover, the modifications of the surface local electronic and electron-spin properties induced by atomic-H adsorption have not been experimentally explored. However, evaluation of the changes of surface electronic properties at the atomic level is very crucial. This evaluation can advance our understanding of the interactions between adsorbates and $\text{Fe}_3\text{O}_4(001)$ topmost surface, and can contribute to an elucidation of the origin of the enhanced electron-spin polarization of $\text{Fe}_3\text{O}_4(001)$ surfaces.

1.2 Purpose

The broad purpose of this study is to elucidate the enhancement mechanism of $\text{Fe}_3\text{O}_4(001)$ surface electron-spin polarization. This mechanism can lead to avenue for realizing a half-metallic electronic state of $\text{Fe}_3\text{O}_4(001)$ surface and for interface engineering in Fe_3O_4 -based spintronic devices. The purpose of this work is to reveal the effect of hydrogen atoms on the surface atomic geometries and local electronic properties. To reveal these issues, atomic structures and iron electronic states of a clean $\text{Fe}_3\text{O}_4(001)$ surface were investigated by scanning tunneling microscopy/spectroscopy (STM/STS). Moreover, this work especially focused on modified iron atoms, whose electronic states are different from unmodified iron atoms by surface OH groups. The modifications of atomic geometries by hydrogen adsorption and the adsorption-site dependences for hydrogen atoms were investigated by STM results. The differences in the local electronic states between unmodified and modified iron atoms were also investigated by STS results obtained at these two types of iron sites. The origin of local electronic state modifications of surface iron atoms was discussed from comparing the results of this experimental work and previous theoretical ones. In addition, correlation between surface OH density and surface iron electronic states was investigated by STM/STS.

This doctoral thesis is organized as follows.

In chapter 1, the research background and purpose of this study are described.

In chapter 2, the schematic of ultra-high vacuum (UHV) surface science system used in this study, principles and measurement methods of STM/STS, and the principle and schematic of X-ray photoelectron spectroscopy (XPS) are explained. In addition, STM tip preparation and $\text{Fe}_3\text{O}_4(001)$ film growth are described.

In chapter 3, atomic structures and local electronic states of a clean $\text{Fe}_3\text{O}_4(001)$ surface are discussed by STM/STS results. First, surface termination and surface reconstructed structures are described using STM results. Next, the surface local electronic states of terraces and step edges are discussed by energy-gap values of

surface iron atoms, which are determined from STS spectra.

In chapter 4, subsurface electronic structures are discussed using STS and dI/dV mapping results. Periodic spatial modulation of local density of states was observed in these measurements. These experimental results clearly demonstrate that the subsurface Fe_B atoms show charge ordering of $\text{Fe}^{2+}\text{-Fe}^{2+}$ and $\text{Fe}^{3+}\text{-Fe}^{3+}$ dimers and this charge ordering is responsible for the $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction.

In chapter 5, atomic structures of $\text{H}/\text{Fe}_3\text{O}_4(001)$ surface are mainly discussed from STM results of the surface. First, the presence of surface OH groups of UHV-prepared $\text{Fe}_3\text{O}_4(001)$ films grown on $\text{MgO}(001)$ substrates is verified by XPS. Next, the origin of surface OH groups is investigated by STM measurements. Moreover, changes of surface atomic structure by surface OH groups and adsorption-site dependences for hydrogen atoms are discussed by STM results.

In chapter 6, local electronic states of $\text{H}/\text{Fe}_3\text{O}_4(001)$ surfaces are discussed by STM/STS and dI/dV mapping. First, effect of hydrogen atoms on the surface iron electronic states are investigated by STS and dI/dV mapping. The electron-transfer mechanism predicted to occur in this surface is discussed from comparing these experimental and previous theoretical results. Moreover, correlation between surface OH density and surface iron electronic states are discussed by atomic-scale STM/STS.

In chapter 7, the main results of this doctoral thesis are summarized.

Chapter 2

Experimental setup

2.1 UHV surface science system

Scanning tunneling microscopy/spectroscopy (STM/STS) and X-ray photoelectron spectroscopy (XPS) measurements were performed in an Omicron ultra-high vacuum (UHV) surface science system shown in Fig. 2.1. The UHV system was mainly composed of three chambers; load-lock chamber, preparation chamber and analysis chamber. Sample and tip exchange was done through the load-lock chamber. The vacuum of this chamber can be achieved below 5.0×10^{-7} Pa using a turbo molecular pump (TMP), a titanium sublimation pump (TSP) and bake out system.

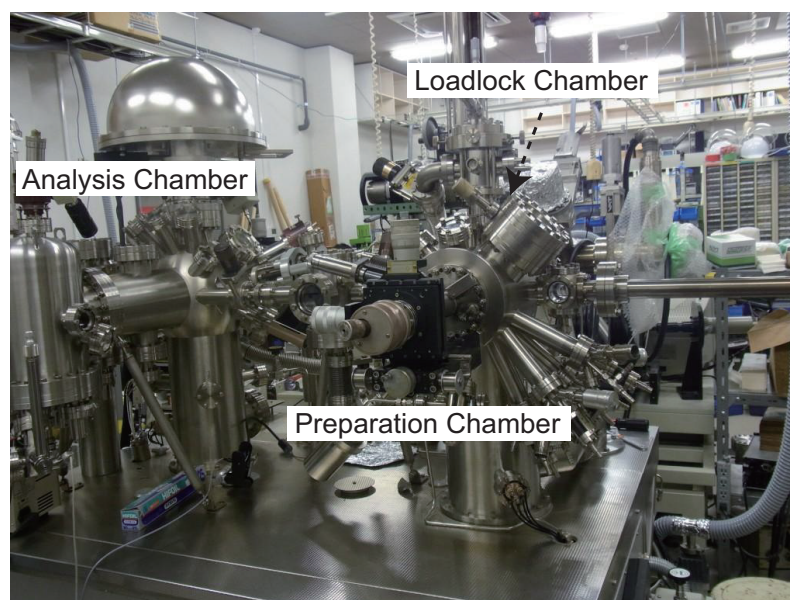


Figure 2.1 Omicron UHV surface science system

The preparation chamber was used for sample and tip preparation, equipped with facilities such as four electron-beam heating evaporators (Omicron EFM3), heating system of sample and tip, Ar ion sputtering system and reflection high energy electron diffraction (RHEED) system. The vacuum of this chamber was kept below 5.0×10^{-9} Pa by a combination of TMP, sputter ion pump (SIP) and TSP.

The analysis chamber was used for sample preparation and characterization, equipped with facilities such as one electron-beam heating evaporator (Omicron EFM3), sample heating system, low energy electron diffraction system, XPS system, Omicron UHV-STM system and Omicron variable temperature STM (VT-STM) system. STM/STS and XPS experiments were performed in the analysis chamber. STM/STS measurements were mainly done in the VT-STM system at room temperature. The vacuum of analysis chamber was also kept below 5.0×10^{-9} Pa by a combination of TMP, SIP and TSP. The schematic of $\text{Fe}_3\text{O}_4(001)$ film growth and measurement system is depicted in Fig. 2.2.

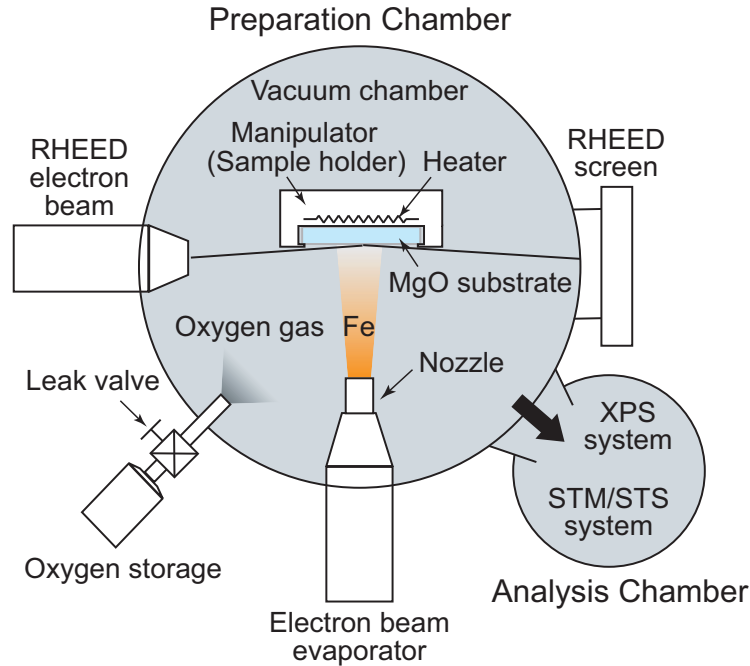


Figure 2.2 Growth and measurement system of $\text{Fe}_3\text{O}_4(001)$ film samples

2.2 Experimental methods

$\text{Fe}_3\text{O}_4(001)$ film samples were mainly characterized using STM, STS, differential tunneling conductance (dI/dV) mapping and XPS. The detail of each experimental method is explained below.

2.2.1 Scanning tunneling microscopy (STM)

STM was invented in the early 1980s by G. Binnig, H. Rohrer and co-workers at the IBM Zürich research laboratory [40]. The Nobel Prize in Physics was awarded to them in 1986 for their design of the STM. Since then it has become a fundamental technique in surface science field due to its ability to probe material surfaces in real space at the atomic scale. Among many experimental methods used for the investigation of material surface physics, STM is one of the most powerful tools that provide the geometric information of the surface with atomic resolution. The STM can also perform the local tunneling spectroscopy called STS, which can provide the density of states of atomic sites [41, 42], elementary excitation of phonon, magnon [43], plasmon and so on. These two features of STM/STS technique enable us to correlate the structural and electronic properties of a material surface at the atomic resolution [44]. Therefore, STM/STS methods have been widely used for the investigation of atomic-scale defects, adsorbed atoms/molecules [45, 46] and local physics phenomena at the surfaces. Recently, spin-polarized STM/STS methods using magnetic tips are used for the investigation of surface magnetism at the atomic scale [47–50].

The STM principle is based on the quantum mechanical tunneling. In quantum mechanics, electrons can tunnel through the vacuum barrier between two conductors when positioned very close to each other, such as several nanometers. The tunneling phenomenon is originated from the wavelike properties of electrons, as illustrated in Fig. 2.3. Given that the vacuum barrier is one-dimensional, the solutions of the Schrödinger equation inside the vacuum barrier have the following form,

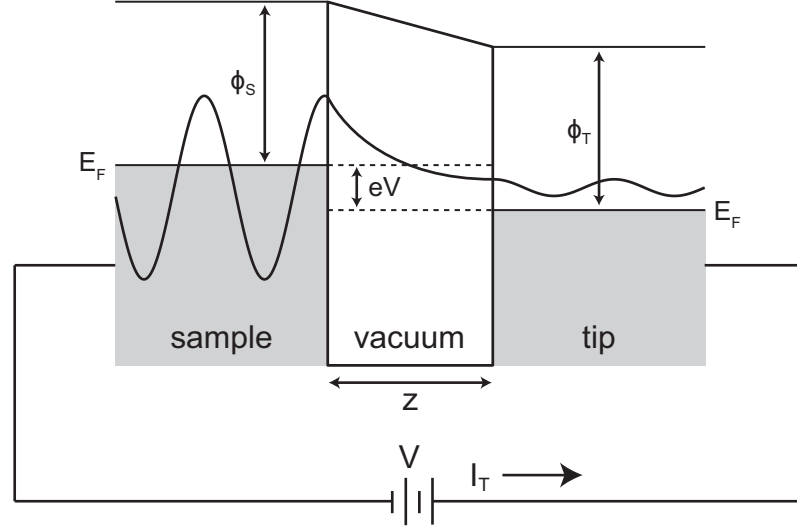


Figure 2.3 Quantum mechanical tunneling when a voltage V is applied between tip and sample.

$$\psi = e^{\pm\kappa z} \quad (2.1)$$

When tip and sample are positioned very close, their electron wave functions can overlap. The electron wave functions decay exponentially into the vacuum barrier with the inverse decay length κ given by,

$$\kappa = \frac{\sqrt{2m\phi}}{\hbar} \quad (2.2)$$

where m is the electron mass, and the tunneling barrier height ϕ is defined by,

$$\phi = \frac{\phi_S}{2} + \frac{\phi_T}{2} + \frac{eV}{2} - E \quad (2.3)$$

When a voltage V is applied between tip and sample, the overlap of the electron wave function leads to quantum mechanical tunneling and a current I will flow across the vacuum barrier. The tunneling current I is given by,

$$I \propto e^{-2\kappa z} \quad (2.4)$$

where z is the tip-sample distance. The tunneling current depends exponentially on the distance. If the distance is increased by 0.1 nm, the tunneling current is decreased by one order of magnitude and vice-versa. This exponential dependence of the tunneling current on the vacuum barrier width gives an unprecedentedly high vertical resolution.

Figure 2.4 shows a schematic of STM system. The STM can be operated in several modes. The most general measurement mode is the constant current mode. A feedback control continuously adjusts the tip height by a piezoelectric scanner to keep the constant current. By recording the voltage applied to the piezoelectric driver as a function of lateral position in order to keep the tunneling current constant,

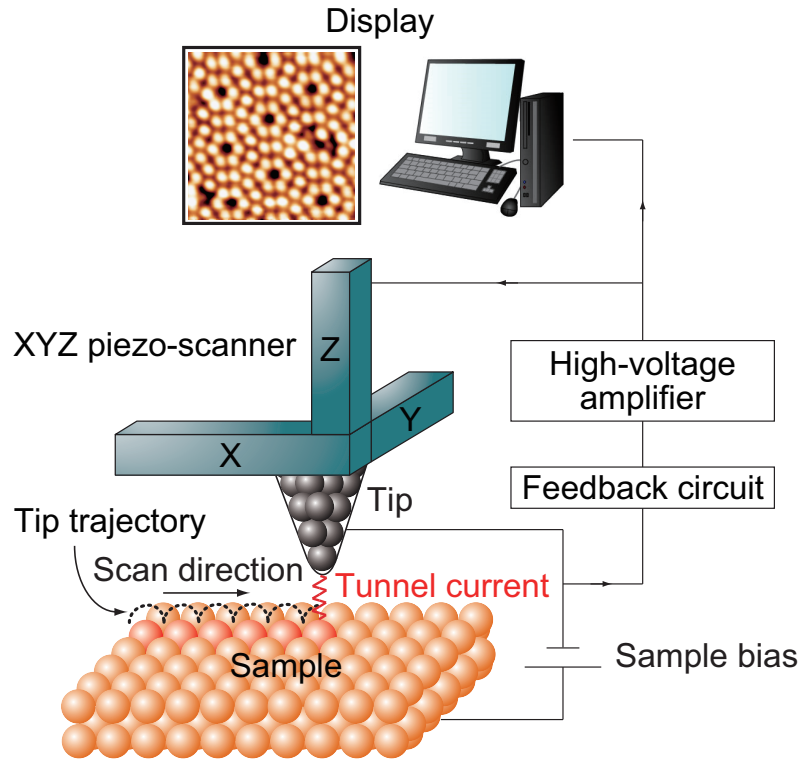


Figure 2.4 Schematic of STM system.

a topographic STM image can be acquired. The constant-current STM image is a convolution of topographical and electronic state effects, which means that properly speaking STM does not probe the atomic positions directly but the electron density of states.

By changing the voltage polarity, both occupied and unoccupied electronic states of the sample can be obtained with STM. When a positive voltage is applied to the sample, electrons tunnel from occupied states of the tip to unoccupied states of the sample. When a negative voltage is applied to the sample, electrons tunnel from occupied states of the sample to unoccupied states of the tip. This electron flow is illustrated in Fig. 2.5. Figure 2.6 shows an STM image of Si(111)(7×7) surface, in which the sample bias voltage is changed from +1.5 V (upper half) to -1.5 V (lower half) in the middle of scanning. The appearance of STM image is greatly different between the upper and the lower half. This difference is attributed to the access to unoccupied and occupied states of the surface. Positive bias voltage gives mainly the unoccupied states of adatoms (corner or center atoms), on the other hand negative bias voltage contributes more to occupied states of rest atoms [51].

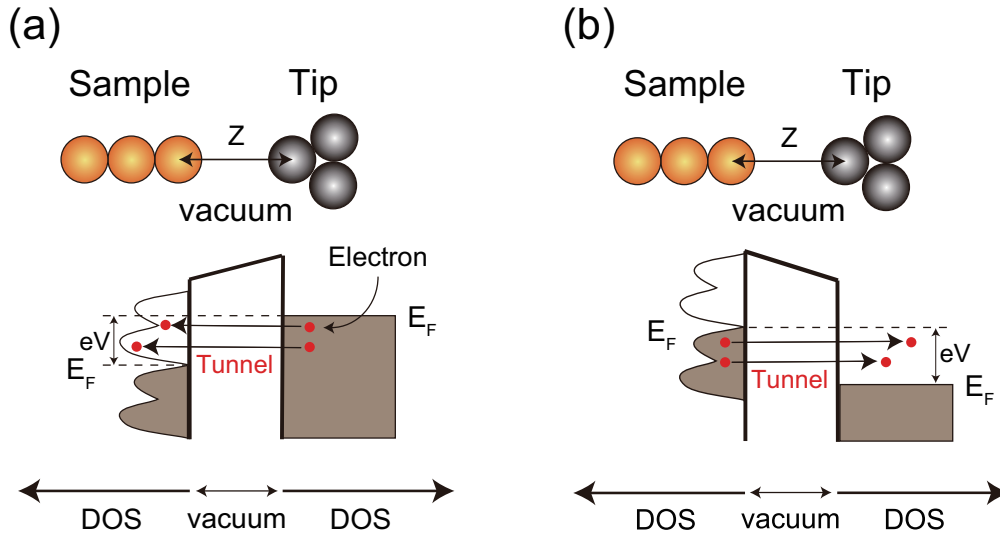


Figure 2.5 Quantum mechanical tunneling when a positive (a) or a negative (b) bias voltage is applied to the sample.

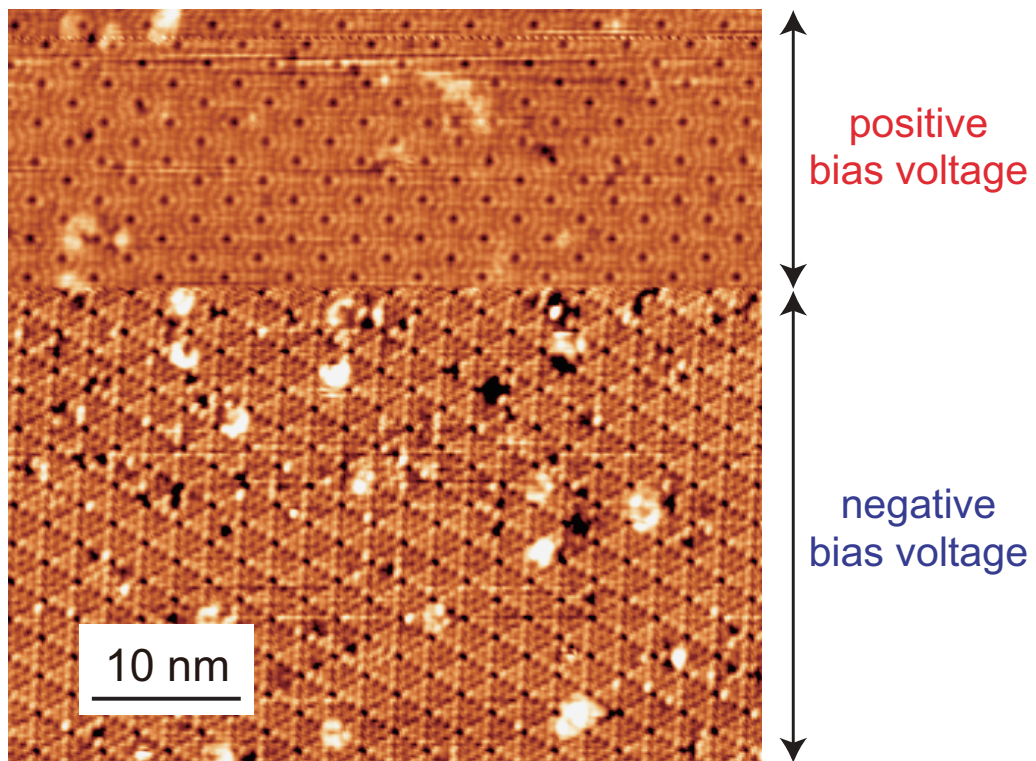


Figure 2.6 STM image of Si(111)(7×7) reconstructed surface. The polarity of the sample bias voltage is changed from +1.5 (upper half) to −1.5 V (lower half) in the middle of scanning over the surface.

2.2.2 Scanning tunneling spectroscopy (STS)

The STM can obtain not only topographic information but also local electronic density of states (LDOS) of a material surface using STS method. In this method, the feedback loop is turned off and the tip-sample distance is kept constant. Then a voltage sweep is performed and the tunneling current is recorded at each voltage point. The differential of this tunneling current is proportional to the LDOS in the particular point, see below. This spectroscopic signature of the LDOS gives a direct information about energy dependences of the LDOS, such as surface energy gap values.

The tunneling current I as a function of the bias voltage V applied between tip and sample can be expressed by,

$$I = \int_0^{eV} \rho_s(E) \rho_t(-eV + E) T(z, eV, E) dE \quad (2.5)$$

where ρ_s and ρ_t are DOS of sample and tip, respectively, and T is the transmission probability [52]. Keeping the ρ_t constant and taking the first derivative of (2.5) with respect to the bias voltage V ,

$$\frac{dI}{dV} \propto e \rho_t \rho_s(eV) T(z, eV, eV) + \int_0^{eV} \rho_s(E) \rho_t \frac{dT(z, eV, E)}{dV} dE \quad (2.6)$$

The constant ρ_t can be justified using a clean and metallic tip. The tunneling current is dominated by a single s state of the tip [53]. The first term in equation (2.6) is directly proportional to the sample DOS, and the second term contains the voltage dependence of the transmission probability. The transmission factor T monotonically increases with V and the contribution of the second term in (2.6) is a smoothly varying background. Since the increase is smooth and monotonic, dI/dV structures as a function of V can be assigned at an approximation to changes in the sample DOS via the first term. As a result, equation (2.6) shows that dI/dV curves give a direct information about the sample LDOS.

Figure 2.7(a) and (b) show a high-resolution STM image of Si(111)(7×7) surface and representative dI/dV spectra obtained on three types of Si sites shown in Fig. 2.7(a). These dI/dV spectra show higher occupied LDOS (in particular, near -1.0 eV) of rest atoms and higher unoccupied LDOS of adatoms. This dI/dV feature is reproduced by dI/dV mapping method, as described below.

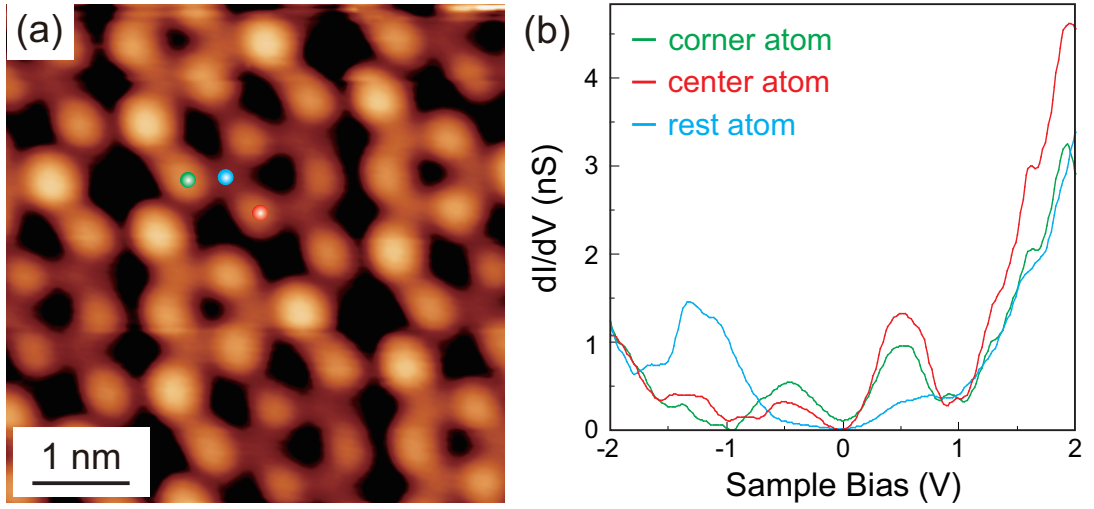


Figure 2.7 (a) STM image of Si(111)(7×7) surface. $V_S = -1.0$ V, $I_T = 0.3$ nA. (b) dI/dV spectra obtained on three types of Si sites.

2.2.3 Differential tunneling conductance (dI/dV) mapping

When STM users need to obtain only the spectroscopic contrast at a specific energy, dI/dV mapping method can be highly effective. This is a less time-consuming method to get access to the electronic properties of the whole scanning area of samples. In this method, the dI/dV signal at a specific bias voltage is recorded at each point of the scanning area using standard lock-in technique with a modulation of bias voltage, simultaneously regular constant-current STM images are obtained with closed feedback. Therefore, the topographic and the spectroscopic data can be obtained simultaneously with high spatial resolution in a short time, which permits a direct correlation of the topographic and the electronic properties at the atomic scale. However, different bias voltages generally stabilize the tip at different tip-sample distances, and thus comparing dI/dV images at different energies is so difficult. In this method, since the feedback loop is closed when recording the dI/dV signal, the modulation should be much faster than the response of the feedback loop so that a crosstalk between topographic image and dI/dV signal can be avoided. Figure 2.8(a) and (b) show STM and dI/dV images of Si(111)(7×7) surface obtained at a sample bias voltage of -1.0 V, respectively. By comparing these two images, the rest atoms are observed to be more brighter than the adatoms in the dI/dV image. Since the brightness in the dI/dV image reflects the LDOS intensity at a specific energy, this result clearly shows much higher LDOS at -1.0 eV of rest atoms than adatoms, which is in good agreement with the STS result shown in Fig. 2.7(b). Moreover, it can be seen from these results that the LDOS at -1.0 eV of rest atoms of unfaulted half is higher than that of faulted half. In this way, dI/dV mapping method is a powerful tool in surface science field due to the ability to obtain the spatial distribution of sample LDOS at the atomic level.

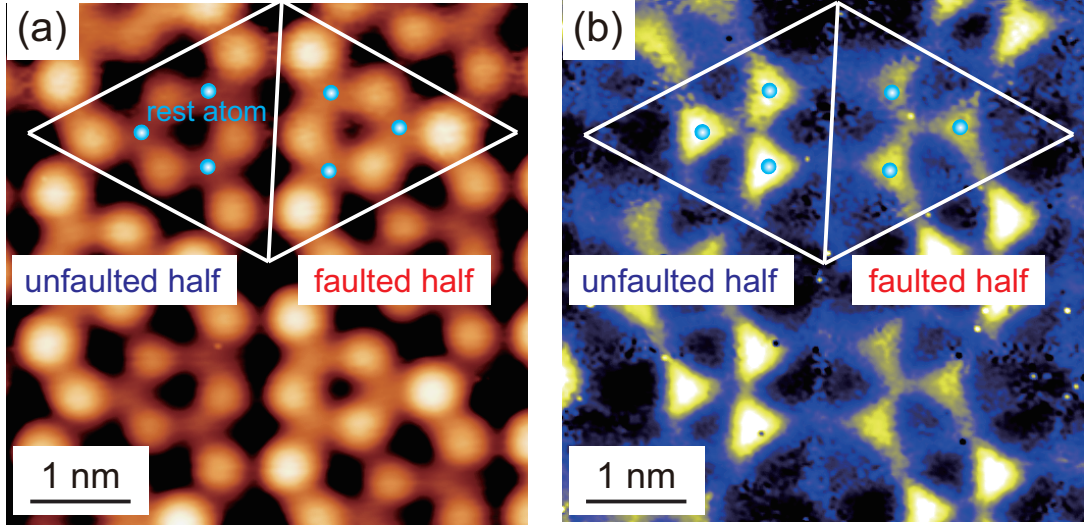


Figure 2.8 (a) STM image and (b) dI/dV image of Si(111)(7 $\times$ 7) surface. $V_S = -1.0$ V, $I_T = 0.3$ nA.

2.2.4 X-ray photoelectron spectroscopy (XPS)

XPS is one of the quantitative spectroscopic technique that measures the elemental composition and chemical state of a material in its as-grown state or after some surface treatments. XPS spectra are obtained by irradiating a material with a beam of X-rays (see Fig. 2.9) while simultaneously measuring the kinetic energy and the number of electrons that escape from the material surface at the depth of 1 to 5 nm. By utilizing angle-resolved XPS technique, chemical states of the topmost surface can also be obtained. Figure 2.10 shows a representative XPS spectrum of an as-grown $\text{Fe}_3\text{O}_4(001)$ film grown on the $\text{MgO}(001)$ substrate. The spectrum shows sharp peaks originated from Fe 2*p* and O 1*s* core levels, and shows that the grown films are mainly composed of iron and oxygen elements. This XPS technique also plays a significant role in investigating adsorbed atoms/molecules on the surface, such as carbon-based impurities. In this work, the presence of OH groups on UHV-prepared $\text{Fe}_3\text{O}_4(001)$ film surfaces was verified by XPS, and thus this knowledge obtained from this XPS technique became the basis of this study on H/ $\text{Fe}_3\text{O}_4(001)$ surface physics.

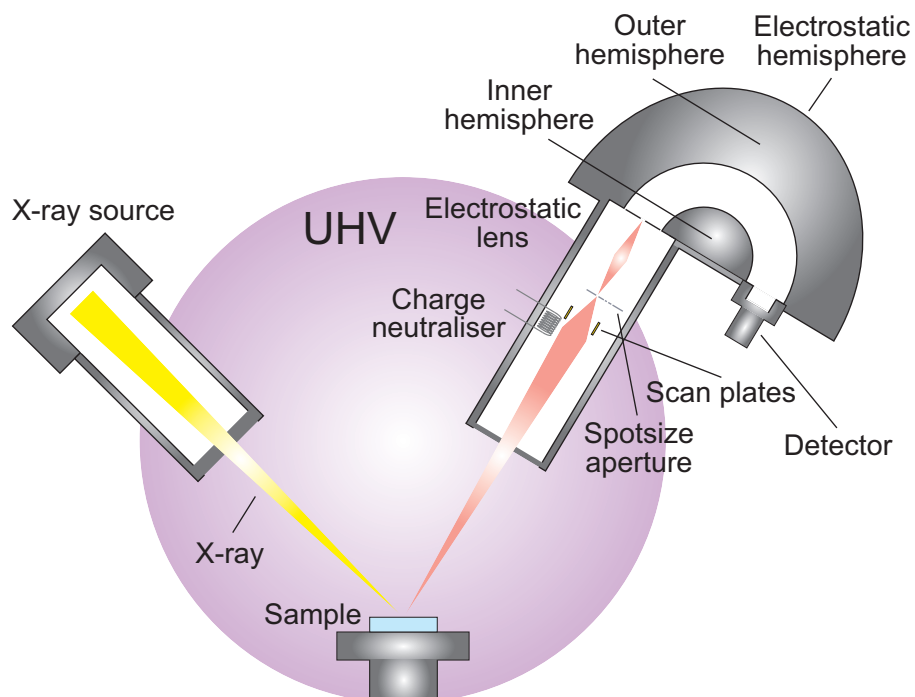


Figure 2.9 Schematic of XPS system.

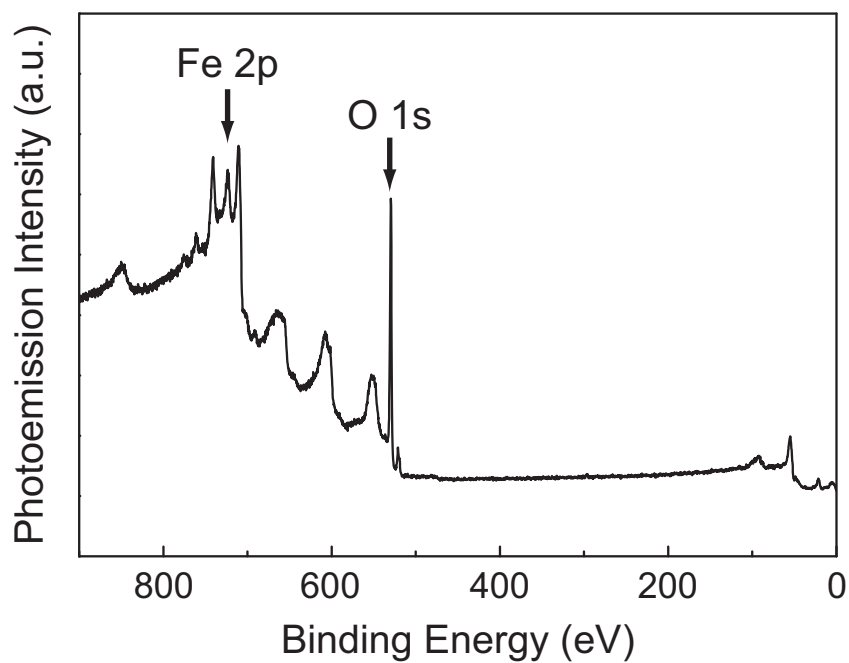
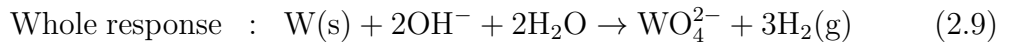
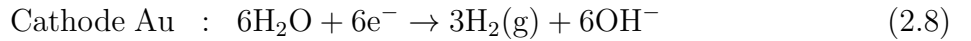


Figure 2.10 XPS spectrum of an as-grown $\text{Fe}_3\text{O}_4(001)$ film

2.3 Tip preparation

2.3.1 Tip fabrication

In STM, tunneling current depends strongly on both tip and sample electronic states. Therefore, the quality of a prepared STM tip is an important factor to obtain highly reproducible STM images and reliable STS spectra. A variety of methods to make a high-quality STM tip have ever been developed [45, 54–56] and each method has been refined [57–59]. Electrochemical etching has been widely used to make a sharp STM tip. In this work, this general method was used to make a sharp tip reproducibly. The chemical reaction process of this method is described below. Polycrystalline tungsten (W) wire was used as a tip material. Figure 2.11 shows a schematic of the tip etching system. As a first step, a W wire with a diameter of 0.30 mm was cut in ~ 2.0 cm length. After that the wire was ultrasonically cleaned in acetone for ten minutes. During etching, a W wire and a Pt wire behave as an anode and a cathode, respectively. A NaOH solution (2 mol/l) was used as a electrolyte. Applying the voltage between the anode and the cathode, the W wire was etched. The following chemical reaction occurs during etching [60, 61].



The etching reaction proceeds intensively at the interface between air and electrolyte, and thus the neck is formed at the interface as depicted in Fig. 2.11. As the etching reaction proceeds, the neck becomes too thin to sustain the weight of the W wire in the solution. As a result, the W wire in the solution drops off. To make a high-quality STM tip, keeping the stable interface of electrolyte without vibration is vital. However, the H_2 gas bubbles generated from the cathode usually make an unstable interface. Therefore, I used a glass tube coiled by the Pt wire and

put the W wire into the glass tube, as shown in Fig. 2.11. This system avoids the gas bubbles from disturbing the interface in the glass tube. It is also important to cut off the etching current immediately after the etching, because the current can make the tip blunt quickly [61]. For this reason, the differentiating circuit to cut off the current was utilized. The etching current decreases suddenly at the instant of the completing of the etching. The differentiator detects the sudden decrease in the current and then the electronic circuit immediately stop the current. After the etching, the etched W tip was rinsed in a hot distilled water to remove the residual NaOH on the tip. The curvature radius of the fabricated tips is estimated to be ranging from 20 to 50 nm. One of the scanning electron microscope (SEM) images of the W tip is shown in Fig. 2.12.

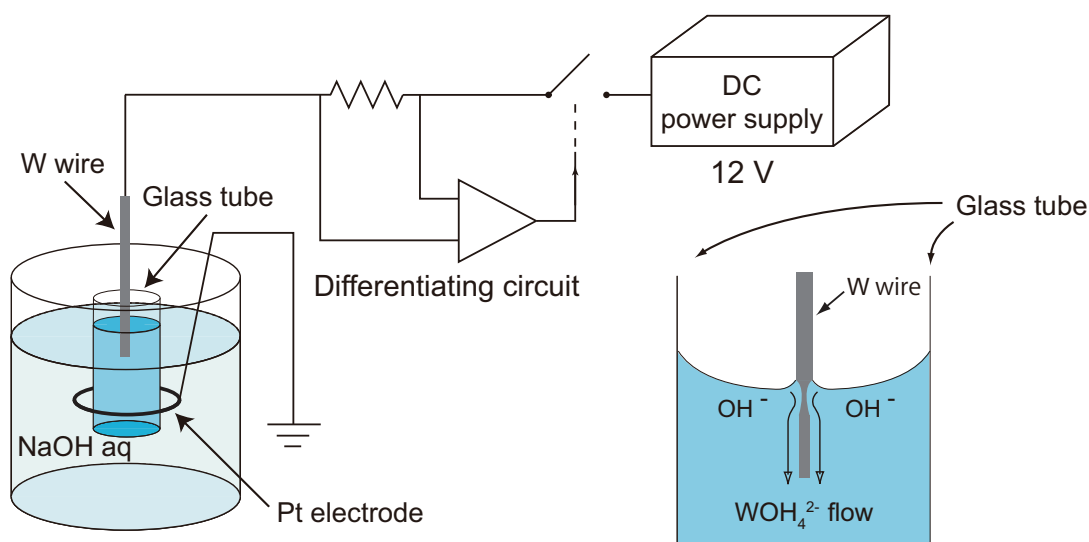


Figure 2.11 Schematic of tip etching system.

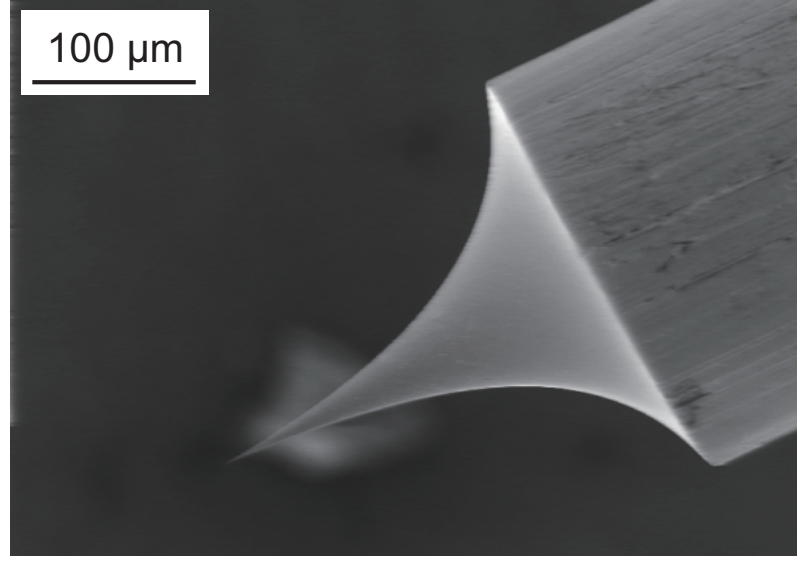


Figure 2.12 SEM image of the fabricated W tip.

2.3.2 Tip cleaning

Although a sharp STM tip can be made by the electrochemical etching method described above, the atomic composition and arrangement at the tip apex are the most important factor for electron tunneling process in STM. Therefore, the cleaning method to remove the nature oxide layer and contaminants at the tip apex is essential. Two types of cleaning methods were adopted in this work. The first cleaning method is electron bombardment heating method. In this method, a W tip is positioned in front of a W filament heated by direct current. Applying the voltage between the tip and the filament, thermal electrons are emitted from the filament to the W tip. As a result, the W tip is heated and its apex is cleaned. The second cleaning method is to scan a tip at high bias voltage. By scanning a tip over a clean Si(111)(7×7) surface at a sample bias voltage of -10 V to -5 V, the contaminants at the tip apex gradually fall down. An STM image of Si(111)(7×7) surface obtained before tip cleaning is shown in Fig. 2.13(a), in which the contaminants are clearly seen from place to place. Combining these two methods, the atomic-resolution STM images of Si(111)(7×7) surface could be reproducibly ob-

served, as shown in Fig. 2.13(b). In addition, the cleaned tip became more stable by the bias voltage sweeping, which is very important for STS measurements. Since the tip apex was unexpectedly and spontaneously contaminated during scanning over sample surfaces, negative voltage pulses (-10 V to -5 V) were also frequently performed for cleaning.

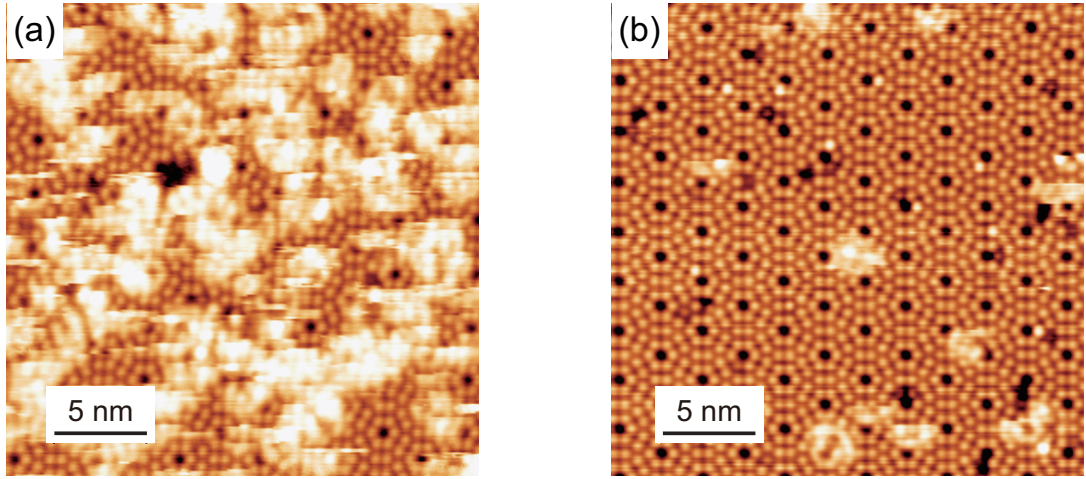


Figure 2.13 STM images of Si(111)(7×7) surface obtained before tip cleaning ($V_S = +2.0$ V, $I_T = 1.0$ nA) (a) and after tip cleaning ($V_S = +2.0$ V, $I_T = 0.5$ nA) (b).

2.4 Sample preparation

The $\text{Fe}_3\text{O}_4(001)$ film samples were epitaxially grown on $\text{MgO}(001)$ single-crystal substrates by electron-beam deposition of iron in the presence of oxygen [10, 11, 62–67]. $\text{MgO}(001)$ was used as the substrates because of its small lattice mismatch of $\sim 0.3\%$. A lattice constant of MgO and Fe_3O_4 is 0.4212 and 0.8397 nm, respectively. In this work, mechanically-polished and cleaved $\text{MgO}(001)$ substrates were used. After organic solvent cleaning, the $\text{MgO}(001)$ substrates were cleaned in UHV by heating at 573 K over 16 hours and then annealed at 1073 K for 1 hour in oxygen atmosphere (7.0×10^{-5} Pa). The RHEED pattern shown in Fig. 2.14(a) indicates the preparation of a clean $\text{MgO}(001)$ substrate surface. After that the iron deposition was performed using an electron-beam heating evaporator at a substrate temperature of 523 K. During the film formation, the oxygen pressure was set in the range from 7.0×10^{-5} to 1.0×10^{-4} Pa. The growth rate was 0.9 ML/min and the film thickness was 20 nm. After the deposition, the grown films were post-annealed at 523 K for 30 min in the same oxygen atmosphere to obtain an atomically-flat surface. The RHEED pattern shown in Fig. 2.14(b) indicates the well-known growth properties of $\text{Fe}_3\text{O}_4(001)$ films on $\text{MgO}(001)$ substrates, showing a $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction.

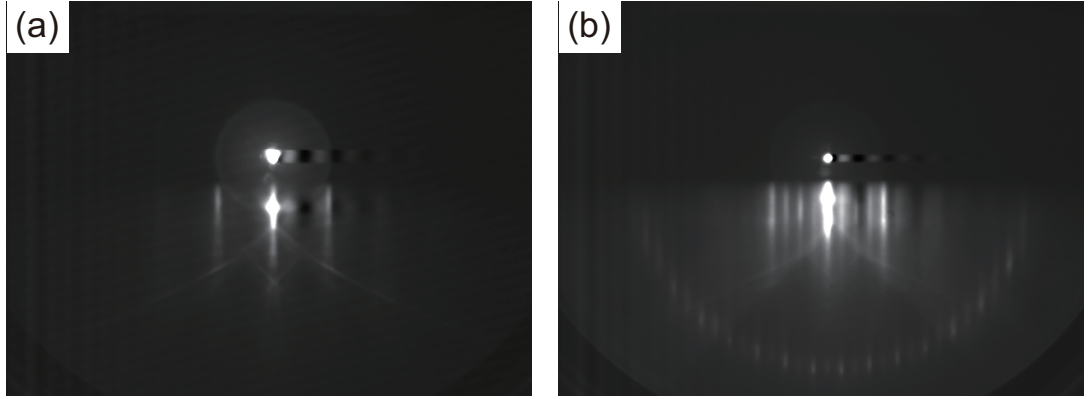


Figure 2.14 RHEED patterns taken from the $[100]$ direction. (a) $\text{MgO}(001)$ substrate after annealed in oxygen. (b) $\text{Fe}_3\text{O}_4(001)$ films epitaxially grown on $\text{MgO}(001)$ substrate

Chapter 3

Atomic structures and local electronic states of clean $\text{Fe}_3\text{O}_4(001)$ surface

In this chapter, atomic structures and local electronic states of a clean $\text{Fe}_3\text{O}_4(001)$ surface are mainly discussed by scanning tunneling microscopy/spectroscopy (STM/STS) results. First, surface termination and reconstruction are investigated by overview and high-resolution STM images of the surface. Next, the surface local electronic states are discussed by STS. Energy-gap values of surface iron atoms, which are determined from STS spectra, are especially focused on. The difference in the electronic states between iron atoms of terraces and those of step edges is also discussed.

3.1 Surface termination and reconstruction

Bulk Fe_3O_4 has a cubic inverse spinel structure. In the $[001]$ direction, A layers of tetrahedral iron atoms (Fe_A) and B layers containing octahedral iron (Fe_B) and oxygen atoms are stacked alternately as shown in Fig. 3.1. A B-terminated surface with the $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction has often been observed on the $\text{Fe}_3\text{O}_4(001)$ surface by STM [30, 68, 69], and theoretical prediction also shows the energetically-stable modified B-layer termination of $\text{Fe}_3\text{O}_4(001)$ surface [70, 71]. Several models have been proposed to explain the surface reconstruction on the basis of surface charge ordering [69], the presence of oxygen vacancies on the surface [68, 72], Jahn-Teller distorted bulk truncation [70] or subsurface cation vacancy structure [73].

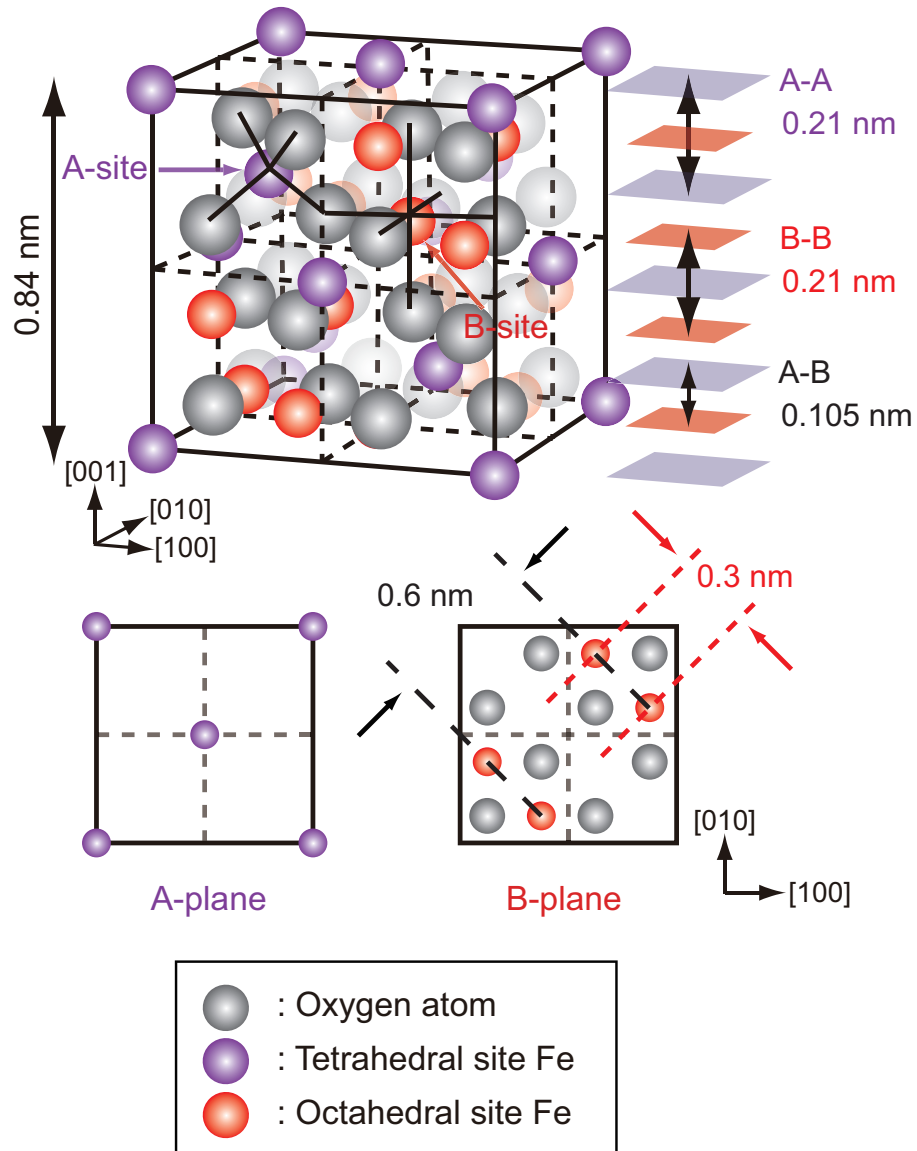


Figure 3.1 Cubic inverse spinel structure of Fe_3O_4 . Tetrahedral iron in the A-plane (Fe_A), octahedral iron (Fe_B) and oxygen atoms in the B-plane are indicated by purple, red and gray circles.

3.1.1 B-layer surface termination

An STM image of the $\text{Fe}_3\text{O}_4(001)$ film surface is shown in Fig. 3.2(a). Atomically-flat terraces can be seen in the STM image. The minimum step height is ~ 0.21 nm, as evident in the line profile in Fig. 3.2(b). This step height corresponds to the A-A or B-B layer separation distance of $\text{Fe}_3\text{O}_4(001)$. This STM result indicates that the surface is terminated by the A-plane or the B-plane without the coexistence of both layers. Moreover, a high-resolution STM image is shown in Fig. 3.3(a). As evident in the line profile AA in Fig. 3.3(b), the average distance between neighboring atoms within the rows is ~ 0.3 nm. Since this periodicity of the atoms correspond to that of the Fe_B atoms in the B-terminated $\text{Fe}_3\text{O}_4(001)$ surface, as shown in Fig. 3.1, the atoms observed in the STM images of $\text{Fe}_3\text{O}_4(001)$ surface should represent single Fe_B atoms in the B-plane.

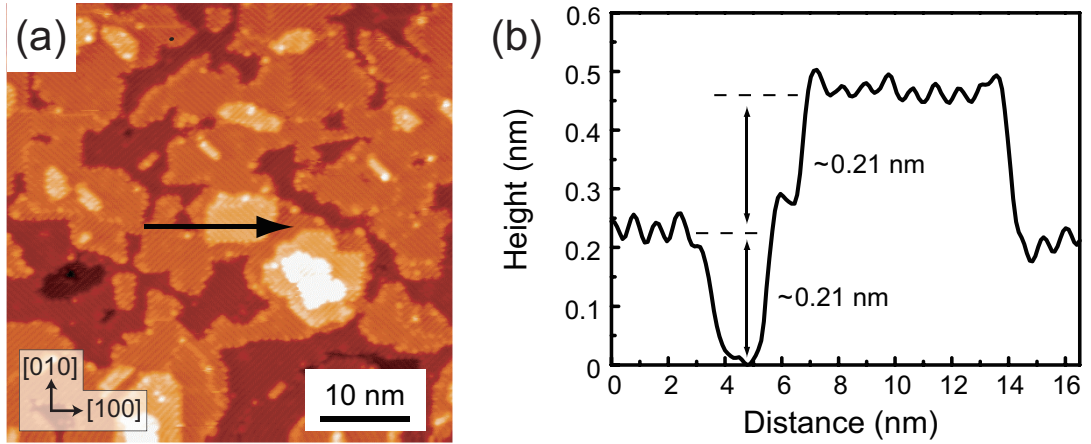


Figure 3.2 (a) Overview STM image of $\text{Fe}_3\text{O}_4(001)$ film surface. The feedback control set point was $V_S = +2.0$ V, $I_T = 1.0$ nA. Atomically-flat terraces exhibiting $[110]$ or $[1\bar{1}0]$ atomic rows can be seen. (b) Line profile taken along the black line in (a). The step height of ~ 0.21 nm is indicated.

3.1.2 $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction

As evident in the line profile AB in Fig. 3.3(b), the average distance between neighboring rows is ~ 0.6 nm. The STM image and line profile AB also indicate that the atoms within each row are slightly shifted along the direction perpendicular to the rows. This STM image and line profile clearly demonstrate the presence of narrow and wide sections, as depicted in the atomic arrangement model in Fig. 3.4. The narrow and wide sections are marked as “n” and “w”, respectively. These small displacements of the atoms perpendicular to the rows have been observed previously in density functional theory (DFT) and low energy electron diffraction analysis studies [30, 31, 70, 71]. These STM results are consistent with a Jahn–Teller distorted B-layer termination that is established to be energetically favorable over several oxygen chemical potentials [70, 71]. Surprisingly, recent studies of synthetic $\text{Fe}_3\text{O}_4(001)$ single crystal surfaces prepared by Ar ion sputtering followed by annealing in oxygen have shown that the stable surface termination comprises subsurface Fe_B cation

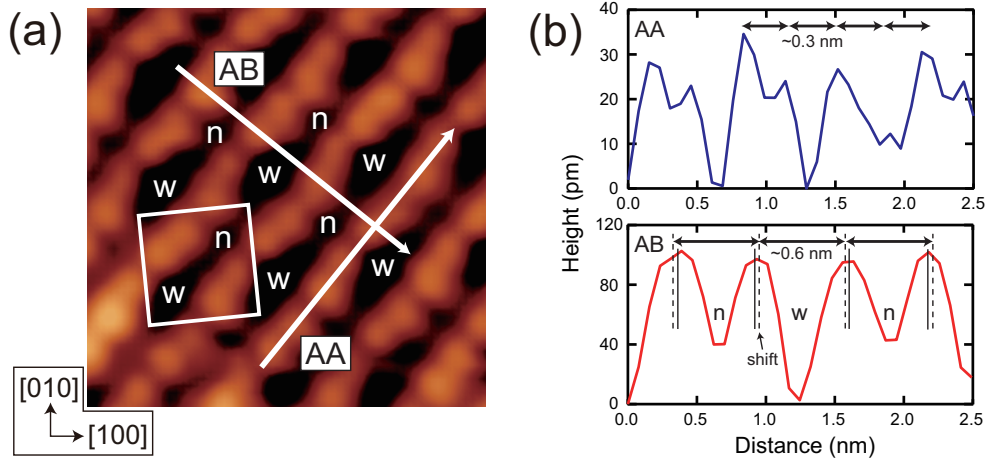


Figure 3.3 (a) High-resolution STM image ($3.5 \times 3.5 \text{ nm}^2$) of $\text{Fe}_3\text{O}_4(001)$ film surface. The feedback control set point was $V_S = +1.0 \text{ V}$, $I_T = 0.3 \text{ nA}$. The $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstructed unit cell is indicated by the white square. The narrow and wide sections are marked as “n” and “w”, respectively. (b) Line profiles corresponding to the lines AA and AB in (a).

vacancies and interstitials [73]. However, this study assumes a Jahn–Teller distorted B-layer termination without vacancies and interstitials because creating such vacancies using atomic layer-by-layer molecular beam epitaxy should be difficult. This distorted surface is stabilized by in-plane relaxations perpendicular to the atomic rows, as illustrated in Fig. 3.4. Following a previous STM report of $\text{Fe}_3\text{O}_4(001)$ surface [74], I define the two nonequivalent surface oxygen atoms formed by the distortion as O_N and O_W . The subscripts N and W included in these labels indicate that the O–O distances at the surface are shorter and longer than that in the bulk, respectively.

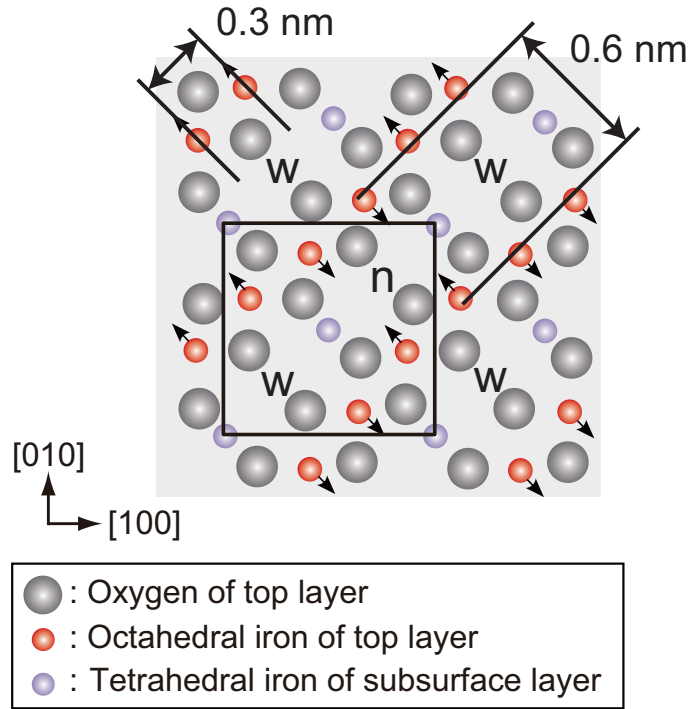


Figure 3.4 Model of the B-terminated surface structure of $\text{Fe}_3\text{O}_4(001)$. The black arrows indicate the directions of the displacements of octahedral iron atoms of the top layer. The $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstructed unit cell is indicated by the black square. The narrow and wide sections are marked as “n” and “w”, respectively.

3.2 Local electronic states of surface Fe atoms

Local electronic states of surface Fe_B atoms are discussed here. To investigate the local electronic states, I probed the local density of states (LDOS) of the Fe_B atoms situated at terraces by STS. Figure 3.5 shows normalized dI/dV spectrum numerically obtained from the $I(V)$ curves taken on surface Fe_B site. In this study, I followed the procedure proposed by Feenstra [75]. In this method, total conductance (I/V) data are convoluted with an exponential function, relying on the broadening width (ΔV) to remove the background noise near $V_\text{s} = 0$. The convolution step has no influence on the features of the spectra. In all cases $\Delta V = 0.6$ V was used according to the order of the energy-gap values of surface Fe_B atoms, which was determined by STS spectra, as discussed below. Normalized dI/dV spectra used here are found to provide a relatively direct measure of the surface LDOS [41, 52]. These methods also allow the detection of small LDOS near the Fermi level [52].

The STS spectrum in Fig. 3.5 shows pronounced increases for both $V_\text{s} < 0$ and $V_\text{s} > 0$. The onsets of the occupied and unoccupied states were determined by applying a linear extrapolation at the onset of the differential conductivity, as was previously performed [76, 77]. The onsets of the occupied and unoccupied states of the Fe_B atom are observed at -0.44 ± 0.01 and $+0.24 \pm 0.01$ eV, respectively. Thus, the energy-gap value near the Fermi level of the surface Fe_B atom is estimated to be 0.68 ± 0.01 eV. An energy gap in the range 0.4–0.8 eV has been confirmed regardless of the tip and sample used, and also on different Fe_B sites. The dispersion of the energy-gap values may be attributed to tip-induced band bending (TIBB) effect, the difference in W tip electronic states and a subtle influence from surrounding adsorbates. TIBB is an effect where some of the applied bias decreases in the sample instead of in the vacuum region, resulting in enlarged observed energy gaps [78, 79]. Anyway, surface Fe_B atoms of terraces show a semiconducting nature relative to the predicted half-metallic state of bulk Fe_3O_4 .

These observed energy-gap values of 0.4–0.8 eV are larger than the value of 0.2 eV reported in a previous STS study of a single crystalline $\text{Fe}_3\text{O}_4(001)$ surface [80].

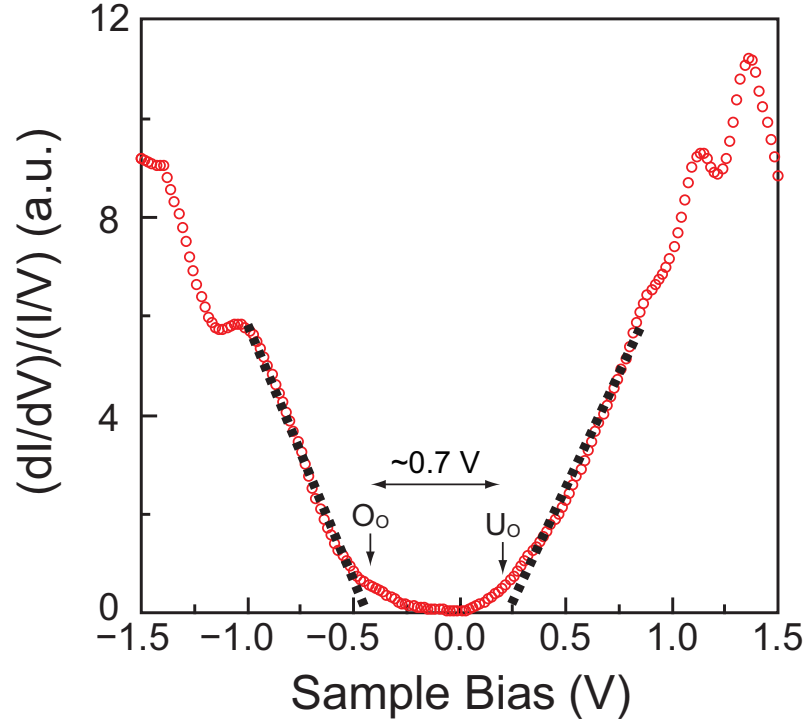


Figure 3.5 Normalized dI/dV spectrum numerically obtained from the $I(V)$ curves taken on surface Fe_B site situated at a terrace using the method proposed by Feenstra [75]. The onsets of the occupied and unoccupied states of the Fe_B atom were determined from linear extrapolations, indicated by the dashed lines, and are marked as O_O and U_O , respectively.

The previously reported value was obtained from averaged $I(V)$ curves taken over a specific area of the $\text{Fe}_3\text{O}_4(001)$ surface. Therefore, the value might include local electronic states of surface atoms other than Fe_B atoms. The $I(V)$ curves could also be taken near step edges. Such areas have more oxygen vacancies [80] and more adsorbates such as OH groups [65] than terraces, which can modify the surface local electronic properties due to coordinative unsaturation and excess charges, which could account for the observed changes in the $I(V)$ characteristics. Indeed, the STS spectrum measured at step edges shows a metallic-like behavior and the obtained energy-gap values were 0.1-0.2 eV, as shown in Fig. 3.6.

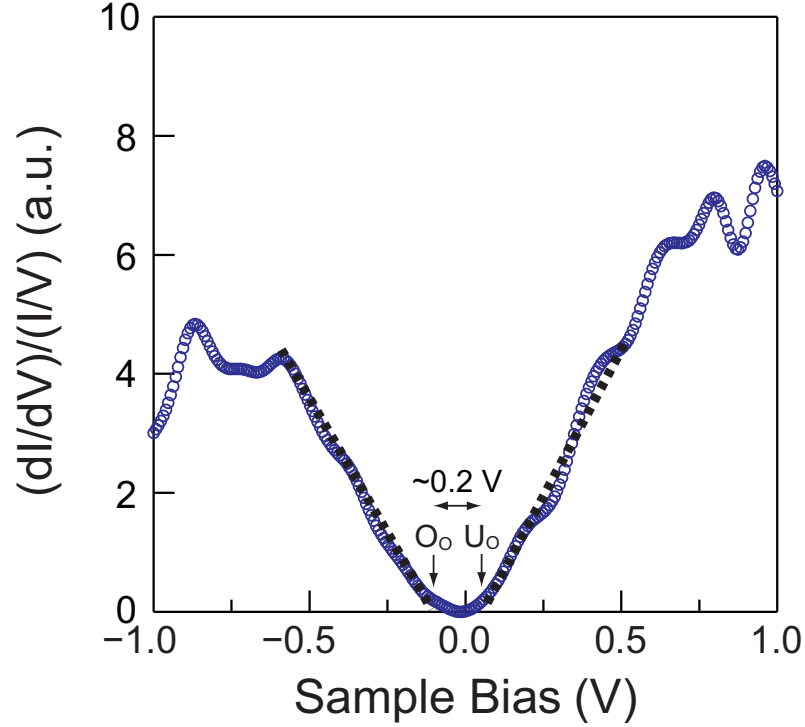


Figure 3.6 Normalized dI/dV spectrum numerically obtained from the $I(V)$ curves taken on surface Fe_B site situated at a step edge using the method proposed by Feenstra [75]. The onsets of the occupied and unoccupied states of the Fe_B atom were determined from linear extrapolations, indicated by the dashed lines, and are marked as O_O and U_O , respectively.

The observation of an energy gap of 0.68 eV for the surface Fe_B atom of terraces is consistent with the LDOS projected on the Fe_B 3d orbitals for the first surface layer, which has been obtained by DFT calculations [81]. Judging from the DFT results, occupied and unoccupied 3d states of surface Fe_B atoms are located below -0.4 eV and above $+0.2$ eV, respectively, suggesting an about 0.6 eV energy gap near the Fermi level. Since the surface Fe_B atom resides in an exclusively Fe^{3+} -like state due to the charge and orbital ordering of Fe^{2+} and Fe^{3+} in the subsurface layers, which is confirmed by DFT [37,81–84] and angle-resolved X-ray photoelectron spectroscopy [36, 84], the onset of the occupied states observed at -0.44 eV should arise from the occupation of 3d states corresponding to Fe^{3+} -like state.

3.3 Summary

Atomic structures and local electronic states of a clean $\text{Fe}_3\text{O}_4(001)$ surface were investigated by STM/STS measurements. The STM studies showed the well-known B-terminated surface with a $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction. The reconstructed (distorted) surface is stabilized by in-plane relaxations perpendicular to the atomic rows. The atomic-scale STS studies revealed that the surface Fe_B atoms of terraces show energy-gap values of 0.4–0.8 eV near the Fermi level. This STS result indicates a semiconducting nature relative to the predicted half-metallicity of bulk Fe_3O_4 . Moreover, surface local electronic states of step edges were found to be metallic-like with respect to a semiconducting nature of terraces, which can be due to the presence of more oxygen vacancies and more adsorbed atoms/molecules at step edges.

Chapter 4

Electronic structures of $\text{Fe}_3\text{O}_4(001)$ subsurface

The $\text{Fe}_3\text{O}_4(001)$ surface structure has been mainly studied by scanning tunneling microscopy (STM) and low energy electron diffraction [30, 31, 68]. Several research groups have observed individual Fe_B atoms and a $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction using STM, which revealed wave-like structures of the Fe_B rows, as depicted in Fig. 4.1(a) [30, 31, 62–66, 68]. Pentcheva *et al.* predicted the B-terminated surface structure on the basis of density functional theory (DFT) calculations [70, 71]. They also suggested that the $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction is a result of a Jahn–Teller distortion and that the surface shows a metallic nature. However, Jordan *et al.* reported a surface energy gap of ~ 0.2 eV on the basis of a scanning tunneling spectroscopy (STS) study [80], which indicates a semiconducting nature of the surface. In addition, this study shows the energy-gap value near the Fermi level of the surface Fe_B atoms to be ~ 0.7 eV. The reconstructed structure and the semiconducting nature of the surface have been proposed to be derived from the subsurface charge-ordered structures [81, 85, 86] or subsurface cation vacancy structures [73]. As described in the prior chapter, this study assumes a perfect Fe_3O_4 stoichiometry without cation vacancies, and thus the subsurface charge-ordered structures are focused on and are discussed by STM/STS results in this chapter.

4.1 Subsurface structure models

Two types of subsurface structure models, which are charge-ordered structure and cation vacancy structure, have been proposed to explain the $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction of Fe₃O₄(001) surface and its semiconducting nature. The detail of these two structure models is explained below.

4.1.1 Charge-ordered structure

Pentcheva *et al.* studied the Fe₃O₄(001) surface using a variety of methods and proposed that the $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction results from a lattice distortion [70]. After that Lodziana proposed that the reconstruction could be interpreted in terms of a surface Verwey transition using DFT calculations that account for the on-site Coulomb interaction of Fe *d* electrons, i.e., subsurface charge ordering is responsible for the $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction [81]. The proposed charge ordering structure shown in Fig. 4.1(a) opens a small band gap of 0.2 eV in DFT calculations, which is consistent with the STS results performed by Jordan *et al* [80].

4.1.2 Cation vacancy structure

The subsurface cation vacancy structure model of the $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction was proposed in 2014 [73]. In this model, the surface Fe_B-O layer remains stoichiometric, however is distorted by a rearrangement of the iron cations in the subsurface layers. Especially, an additional interstitial tetrahedral Fe atom (Fe_{int}) in the subsurface layer replaces two subsurface octahedral Fe_B atoms (see Fig. 4.1(b)), resulting in a net reduction of one iron atom per unit cell. The presence of Fe_{int} in the subsurface layer is predicted to block adsorption of metal adatoms. The DFT calculations also indicate that the subsurface cation vacancy structure is thermodynamically more stable than the previously proposed structures over the entire range of oxygen chemical potentials accessible in ultra-high vacuum [73]. The outermost

unit cell has an intermediate stoichiometry, $\text{Fe}_{11}\text{O}_{16}$ and the DFT calculations predict that the outermost unit cell contains Fe^{3+} cations only [73], which is consistent with angle-resolved X-ray photoelectron spectroscopy measurements [36, 84].

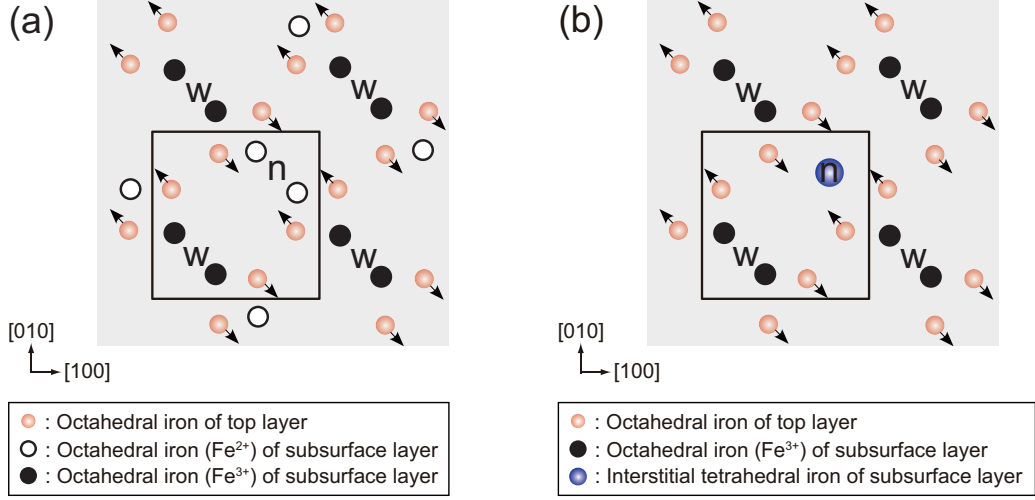


Figure 4.1 Model of the subsurface charge-ordered structure (a) and the subsurface cation vacancy structure (b) of $\text{Fe}_3\text{O}_4(001)$. The black arrows indicate the directions of the displacements of Fe_B atoms of the top layer. The $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstructed unit cell is indicated by the black square. The narrow and wide sections are marked as “n” and “w”, respectively.

4.2 Local electronic states at narrow/wide section of surface reconstruction

We performed STS measurements on the $\text{Fe}_3\text{O}_4(001)$ film surface to explore the subsurface electronic structures. Figure 4.2 shows two dI/dV spectra obtained at the previously described narrow and wide sections. These STS spectra were obtained with a z-offset of 300 pm toward the surface with respect to the original set point of +1.2 V and 0.3 nA so that the subsurface electronic states could be effectively detected. This STS result shows the higher local density of states (LDOS) just

below the Fermi level of the narrow section relative to the wide one. These dI/dV signals might include contributions from the surface Fe_B atoms, however all surface Fe_B atoms exclusively exhibited an Fe^{3+} charge state [36,66,84–86]. If the spectra included mainly the surface Fe_B LDOS, such a visible difference in the LDOS would not be observed. Therefore, the dI/dV spectra in Fig. 4.2 should include mainly the subsurface electronic states. The difference in the electronic states between the narrow and the wide sections is also discussed by dI/dV mapping results in the next section.

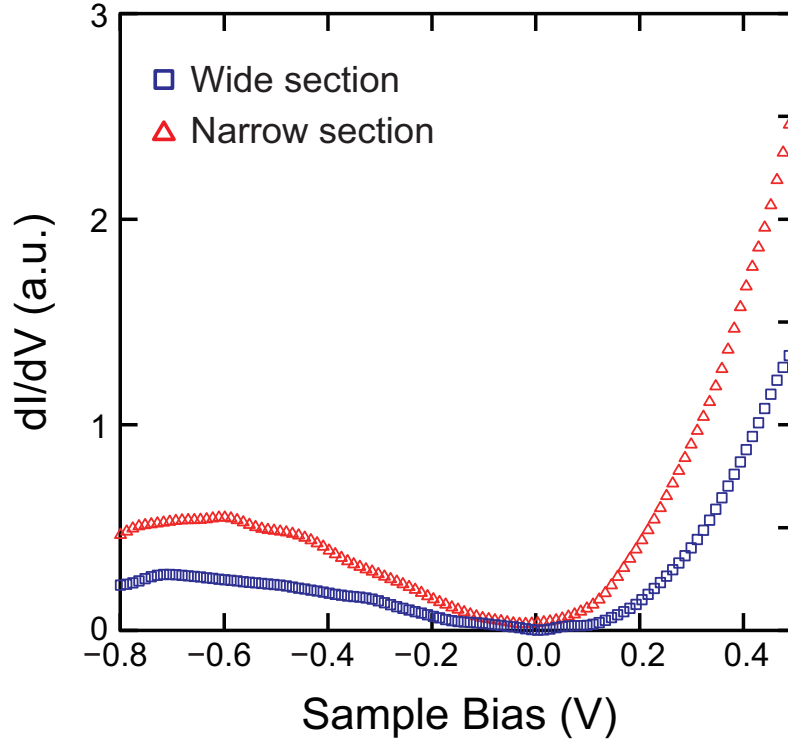


Figure 4.2 dI/dV spectra obtained at narrow and wide sections of the $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction perpendicular to the Fe_B rows. These spectra were obtained with a z-offset of 300 pm toward the surface with respect to the original set point of +1.2 V and 0.3 nA.

4.3 Periodic spatial modulation of local density of states

We also performed dI/dV mapping of the $\text{Fe}_3\text{O}_4(001)$ film surface to further elucidate the subsurface electronic structure. Figure 4.3(a) and (b) display a set of images acquired using the multipass scanning method described in chapter 6.1 [87]. The STM (Fig. 4.3(a)) and dI/dV (Fig. 4.3(b)) images were obtained at a sample bias voltage of +1.0 V and -0.4 V, respectively. Figure 4.3(c) shows cross-sectional line profiles of the STM and dI/dV images taken along the arrows marked as X and Y, respectively. The relative positions of the arrows are the same. In the STM image, the Fe_B rows are running along the [110] direction. However, the dI/dV image shows a periodical electronic structure that differs from that in the STM image. It comprises two different dI/dV peak intensities (high peak and low peak), as indicated by the line profile Y in Fig. 4.3(c). The line profile was taken along the [1-10] direction, i.e., the direction perpendicular to the Fe_B rows. This result indicates that the periodicities of high(low)-peak to high(low)-peak and high(low)-peak to low(high)-peak are ~ 1.2 and ~ 0.6 nm, respectively.

In the dI/dV image shown in Fig. 4.3(b), periodical patterns with a $(\sqrt{2} \times \sqrt{2})R45^\circ$ symmetry are clearly observed, as indicated by the white square. Two types of bright spots in the dI/dV image are observed between the Fe_B rows (see Fig. 4.3(a) and (b)). As evident in Fig. 4.3(c), the positions of high(low) dI/dV peaks correspond to those of the narrow(wide) section, which is in good agreement with the dI/dV spectra shown in Fig. 4.2. The observed dI/dV peaks are derived from the electronic states of surface oxygen atoms or subsurface Fe_B atoms according to the structure model shown in Fig. 4.1. Considering that DFT calculations have predicted that the LDOS of surface oxygen atoms is almost zero near the Fermi level [85] and that the LDOS at -0.4 eV of subsurface Fe^{2+} cations is much higher than that of subsurface Fe^{3+} cations [81,85], the high(low) dI/dV peak should indicate the presence of Fe^{2+} - Fe^{2+} (Fe^{3+} - Fe^{3+}) dimers in the subsurface layer. These experimental findings clearly demonstrate the presence of subsurface charge ordering, and the

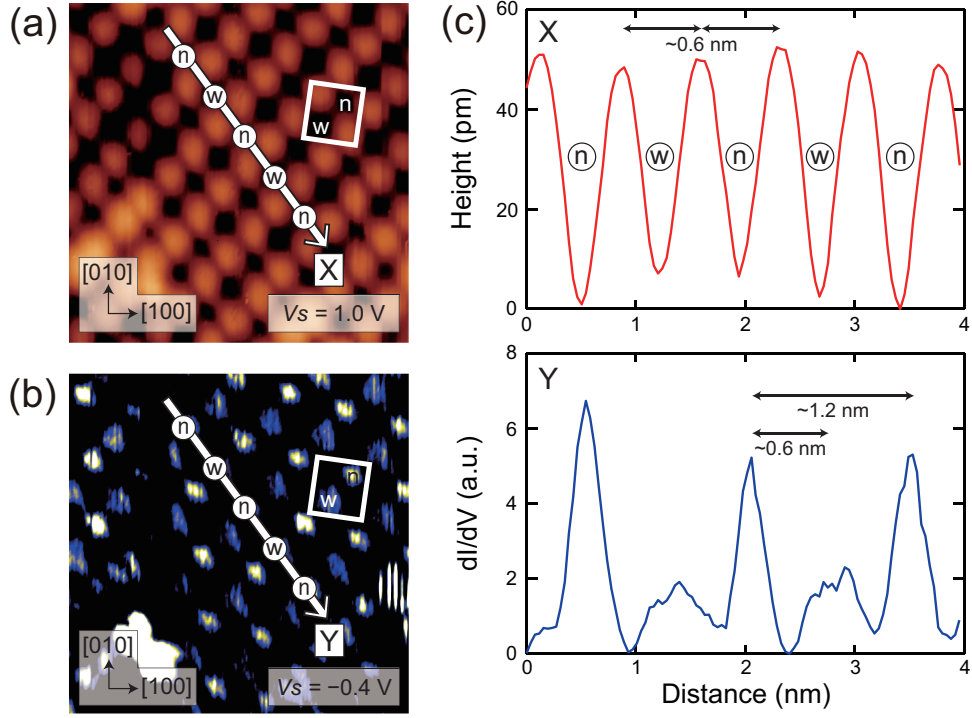


Figure 4.3 (a), (b) Two-pass scan images (5.0×5.0 nm²). First, an unoccupied-state STM image (a) was taken at a set point of +1.0 V and 0.3 nA. Second, a dI/dV image (b) was taken at a sample bias voltage of -0.4 V. The topography recorded in (a) was played with a z-offset of 100 pm toward the surface. The narrow and wide sections are marked as “n” and “w”, respectively. (c) Line profiles taken along the arrows marked as X and Y in (a) and (b), respectively.

subsurface charge-ordered electronic structure is sufficient to explain the $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction [81]. Moreover, these results indicate that a degree of electronic ordering on the $\text{Fe}_3\text{O}_4(001)$ surface observed in previously reported STM images [62,69] likely corresponds to that on the subsurface, as discussed in this doctoral thesis. Although the imaging mechanism of the subsurface electronic states has not been clarified completely, we suggest that the subsurface Fe_B atoms can be imaged on the basis of the insulating-like nature of the topmost $\text{Fe}_3\text{O}_4(001)$ surface, on which the energy gap of ~ 0.7 eV is present near the Fermi level [66]. Theoretical studies that directly compare the surface electronic states with the subsurface ones are required to further elucidate the imaging mechanism.

4.4 Summary

STM/STS measurements of $\text{Fe}_3\text{O}_4(001)$ film surfaces were performed to investigate the surface atomic structures and the subsurface electronic structures. Individual Fe_B atoms and a B-terminated surface structure with a $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction were observed by STM, as mainly described in the prior chapter. The observed surface structure corresponds to the theoretical model reported by Pentcheva *et al.* [70, 71] and to previous STM results [30, 31, 68]. The obtained STS spectra and dI/dV image demonstrated the presence of charge ordering in the $\text{Fe}_3\text{O}_4(001)$ subsurface layer. The charge-ordered electronic structure with two alternating types of LDOS exhibits a $(\sqrt{2} \times \sqrt{2})R45^\circ$ symmetry and is consistent with the structure model of subsurface charge ordering [81, 85]. These experimental findings clearly demonstrate that the subsurface Fe_B atoms show charge ordering of $\text{Fe}^{2+}\text{-Fe}^{2+}$ and $\text{Fe}^{3+}\text{-Fe}^{3+}$ dimers and this charge ordering is responsible for the $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction.

Chapter 5

Atomic structures of H/Fe₃O₄(001) surface

Scanning tunneling microscopy (STM) studies of H/Fe₃O₄(001) surface are mainly discussed in this chapter. First, the presence of surface OH groups on ultra-high vacuum (UHV)-prepared Fe₃O₄(001) film is verified by X-ray photoelectron spectroscopy (XPS) measurements. Next, the origin of surface OH groups is investigated by STM measurements. Moreover, changes of surface atomic structure by surface OH groups and adsorption-site dependences for hydrogen atoms are discussed by STM results.

5.1 Surface OH groups on UHV-prepared Fe₃O₄(001) film

An overview STM image of the as-grown Fe₃O₄(001) film surface is shown in Fig. 5.1. This result represents the formation of an atomically flat surface. STM images of the unoccupied surface states show Fe_B atomic rows running along the [110] or [1-10] direction [64–67]. Here, several bright protrusions (BPs) situated at Fe_B sites are clearly observed within the atomic rows. The area enclosed by the green oval contains some BPs, whereas that enclosed by the red oval contains none. This difference in the apparent height indicates that the local electronic states of the Fe_B atoms are significantly modified. Since STM images alone cannot explain the reason for the observed modified electronic states, the surface chemical states were

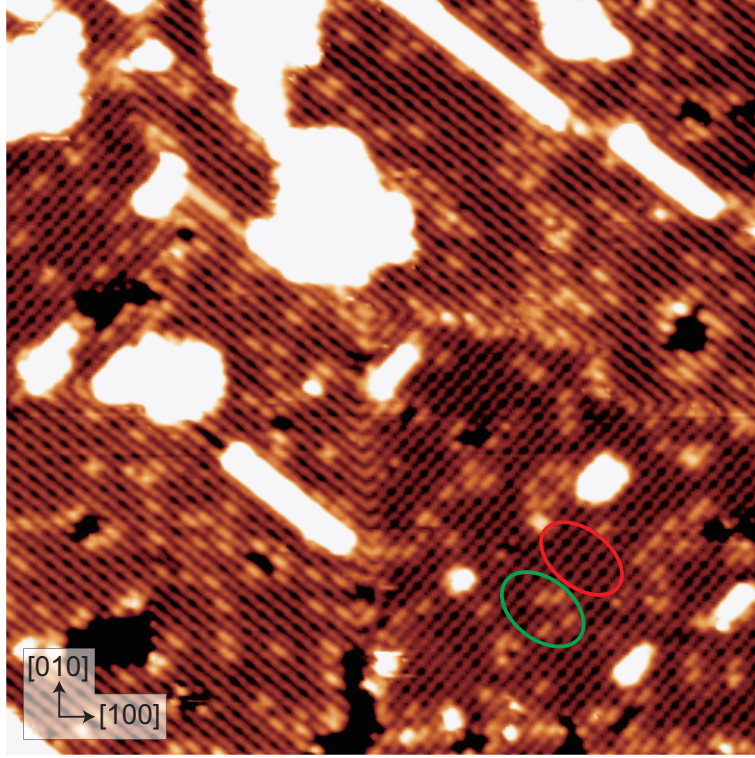


Figure 5.1 Overview STM image ($40 \times 40 \text{ nm}^2$) of the as-grown Fe₃O₄(001) film surface. The feedback control set point was $V_S = +1.2 \text{ V}$, $I_T = 0.3 \text{ nA}$. The red and green ovals enclose regions containing Fe(C) and some Fe(H) atoms, respectively.

investigated by XPS in detail [66]. The obtained XPS spectra showed two distinct features. A small peak at a binding energy (BE) of 284.6 eV and a slight asymmetry in the O1s peak representing tailing toward the high BE side were observed. The small peak at 284.6 eV is attributed to nonoxygenated carbon on the surface, as previously reported [88]. The surface atomic concentration of C was estimated to be $\sim 0.5\%$. Since many BPs were observed in the large-scale STM images as shown in Fig. 5.1, the BPs cannot be attributed to carbon-based impurities. Figure 5.2 shows the Shirley background-subtracted O1s XPS spectrum that is fitted with two components using mixed Lorentzian-Gaussian curves. The first and more intense component peak located at 530.0 eV is assigned to the oxygen in Fe₃O₄ [88]. The

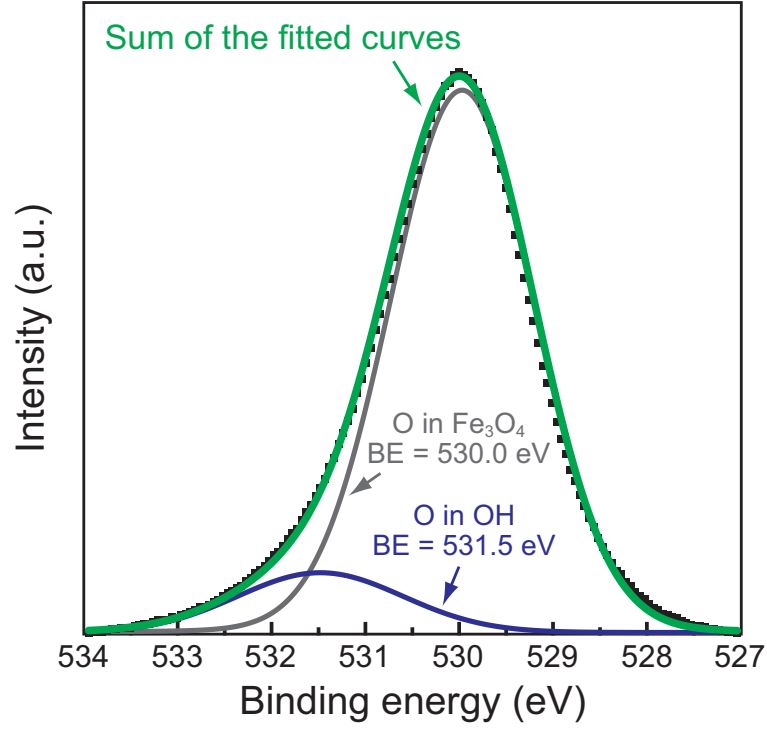


Figure 5.2 Shirley background-subtracted O1s XPS spectrum (Mg $K\alpha$ photons) from the Fe₃O₄(001) film surface. The spectrum is decomposed into two components, as discussed in the text.

other small component peak at 531.5 eV is strictly attributed to the oxygen in the OH group [89], because the concentration of carbonyl groups, whose oxygen BE resides in the same energy region, are negligible due to the low concentration of C mentioned above. Therefore, the fitting results indicate that OH groups are present on the UHV-prepared Fe₃O₄(001) film surface [66].

Henceforth, I refer to the BPs observed in the STM images as Fe(H) and, otherwise, as Fe(C), which are Fe_B atoms residing in a clean (Jahn–Teller distorted) B-layer surface. Figure 5.3 shows a high-resolution STM image of an area containing both Fe(C) and Fe(H) atoms, in which two adjacent Fe_B atoms are observed as BPs. The previous STM studies of atomic-H [36] or disassociated-H₂O [74] adsorbed Fe₃O₄(001) surfaces performed by Parkinson *et al.* have revealed that surface OH

groups, which are formed by hydrogen bonding to O_N sites, modify the local electronic states in the neighboring two Fe_B atomic pairs, as depicted by the atomic arrangement model shown in Fig. 5.3. Therefore, the BPs observed in the STM images of UHV-prepared Fe₃O₄(001) film surfaces can be attributed to surface OH groups. The typical H coverage of the as-grown Fe₃O₄(001) film surface is 0.12 ML, where 1 ML = 1 adsorbate per $(\sqrt{2} \times \sqrt{2})R45^\circ$ unit cell, based on the proposed model for atomic-H adsorption.

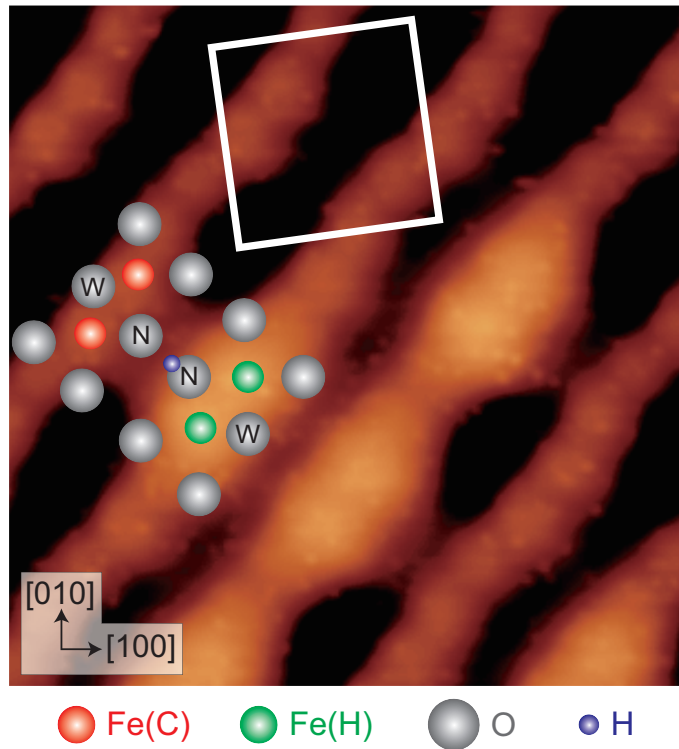


Figure 5.3 High-resolution STM image ($3.0 \times 3.0 \text{ nm}^2$) of an area containing both Fe(C) and Fe(H) atoms, with an overlaid atomic arrangement model. The feedback control set point was $V_S = +1.2 \text{ V}$, $I_T = 0.3 \text{ nA}$. The white square represents the $(\sqrt{2} \times \sqrt{2})R45^\circ$ unit cell. The red, green, gray, and blue circles represent Fe(C), Fe(H), O, and H atoms, respectively.

5.2 Origin of surface OH groups

The origin of surface OH groups was explored by STM measurements. Figure 5.4 shows the variation of the number of BPs observed in $40 \times 40 \text{ nm}^2$ STM images of a single sample surface as a function of the holding time at UHV, t_k . In this work, BPs observed in the proximity of surface defects such as step edges, and those larger bright cluster-like protrusions are not counted because these protrusions might be oxygen vacancies where extra electrons are trapped or carbon impurities originating from UHV residual gases. This results show an approximately linear increase in the number of BPs over time, indicating that surface OH groups are derived from UHV residual gases. This tendency was also observed in other samples. In fact, the presence of both cations and anions on metal oxide surfaces tends to promote the dissociative adsorption of H₂O [82, 83]. Thermodynamic calculations of the Fe₃O₄(001) surface have also demonstrated the high stability of surface OH groups in an UHV environment [37]. Therefore, the surface OH groups can be speculated to arise from dissociative adsorption of UHV residual gases such as H₂O and H₂. In this regard note that from Fig. 5.4, the number of BPs at $t_k = 0$ is estimated to be 150. This indicates the presence of OH groups on the surface, even prior to the onset of STM measurements, which may stem from the lower vacuum of the UHV transfer system connecting the preparation and the analysis chambers, or from impurities contained in the introduced oxygen gas. In addition, I followed the variation of the O1s XPS spectrum as a function of t_k , however visible changes showing the increasing surface OH groups with t_k were not observed. This nonobservation of the changes can be due to the XPS detection limit including also the bulk chemical structures.

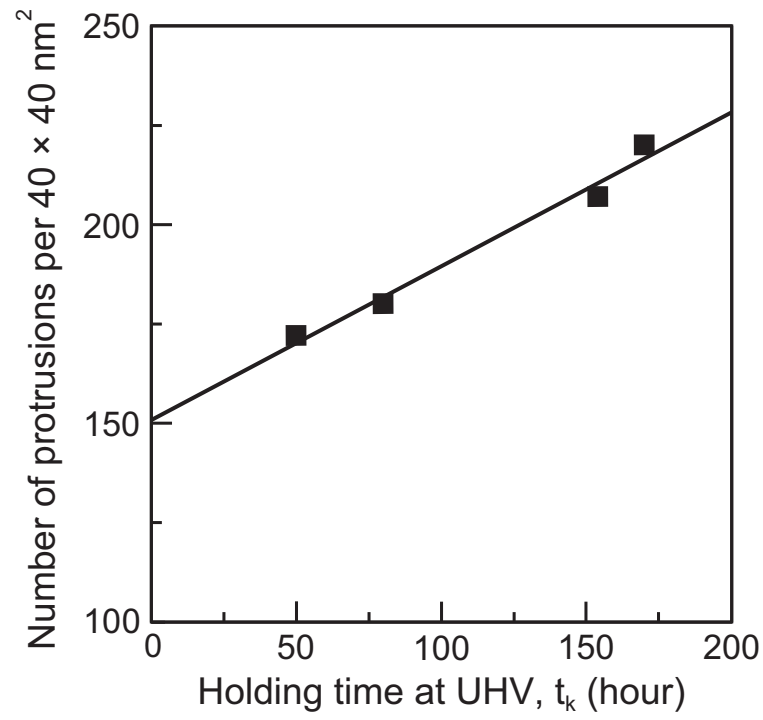


Figure 5.4 Variation of the number of BPs observed in $40 \times 40 \text{ nm}^2$ STM images of a single sample surface as a function of the holding time at UHV, t_k . The straight line indicates an approximately linear relation.

5.3 Atomic structure relaxation by hydrogen adsorption

Figure 5.5(a) also shows a high-resolution STM image of the area containing both Fe(C) and Fe(H) atoms. It clearly shows that the configuration of Fe(C) rows is wavy, on the other hand the Fe(H) rows are straight. Density functional theory (DFT) calculations and STM experiments have demonstrated that Fe_B rows of a clean Fe₃O₄(001) surface show wave-like structures [30, 31, 69–71]. However, STM measurements of an H-adsorbed Fe₃O₄(001) surface have revealed that the configuration of surface atomic rows turns to straight by hydrogen adsorption [36]. This STM result shown in Fig. 5.5(a) corresponds to the previous reports. Figure 5.5(b) shows a cross-sectional line profile taken along the white solid line shown in Fig. 5.5(a). It shows not only the distances between two Fe(C) atoms along the perpendicular direction to surface atomic rows but also the distances between two Fe(H) atoms along the direction. The former distances consist of two different values, 0.56 nm and 0.64 nm. Wavy rows observed in STM images are attributed to such in-plane relaxations perpendicular to atomic rows direction for surface Fe_B atoms, as described in chapter 3.1. On the other hand, the latter distances have a single value, 0.60 nm. This value corresponds to the distance between two Fe_B atoms along the direction in the bulk, indicating that atomic positions of Fe(H) atoms are consistent with ones of bulk Fe_B atoms. Furthermore, it demonstrates that the configuration of Fe(H) rows is straight similar to the bulk Fe_B rows, because atomic displacements induced by OH groups are expected to occur at two surface Fe_B atoms adjacent to them. This STM result showing adsorbed-H induced changes of surface atomic geometries agrees well with the previous DFT results [36], which have shown that the surface atoms relax back to bulk-terminated positions following hydrogen adsorption. A clean Fe₃O₄(001) surface has the $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction as shown in Fig. 5.5(a), however low energy electron diffraction and DFT studies of an H-adsorbed Fe₃O₄(001) surface have revealed that the surface exhibits (1×1) symmetry same as the bulk [28, 33, 35, 36].

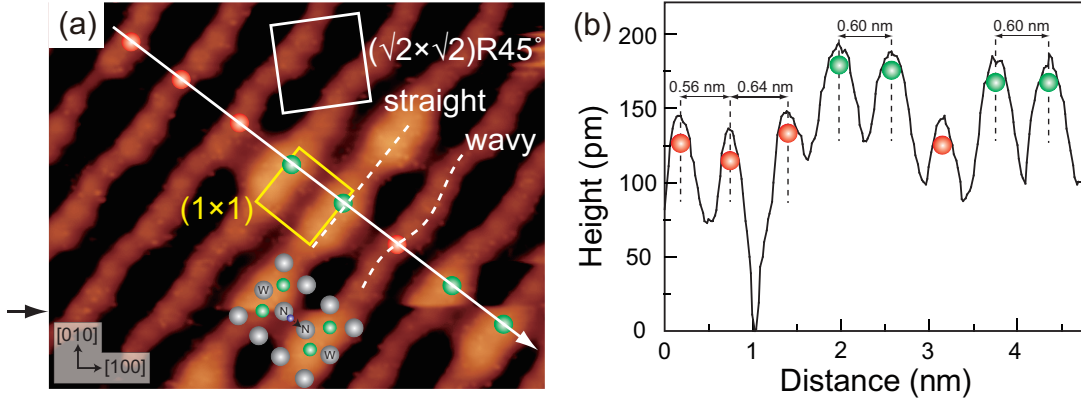


Figure 5.5 (a) High-resolution STM image ($3.5 \times 4.5 \text{ nm}^2$) of the area containing both Fe(C) and Fe(H) atoms, and the atomic arrangement models. The feedback control set point was $V_S = +1.2 \text{ V}$, $I_T = 0.3 \text{ nA}$. The white and yellow squares show the $(\sqrt{2} \times \sqrt{2})R45^\circ$ and the (1×1) symmetry, respectively. The white wavy and straight dashed lines show Fe(C) and Fe(H) rows, respectively. The outside black arrow shows the line position of discontinuity for BPs. The inside black arrow shows the direction of hydrogen hopping. (b) Cross-sectional line profile taken along the white solid line shown in (a). The color coding of the ions corresponds to the one in Fig. 5.3.

An interesting phenomenon has often been observed during scanning over the surface such that the BPs jump into a neighboring row as shown in the bottom part of Fig. 5.5(a). The STM image discontinuously changes at the line position indicated by the outside black arrow. In the STM image, the tip scanned the surface from the top to the bottom and the left to the right. This type of switching phenomenon of BPs has also been reported by the previous STM studies of an H-adsorbed Fe₃O₄(001) surface [36]. The hydrogen atom adsorbed on an O_N site tends to hop into the neighboring O_N site. In this STM measurement, the same things were happened as indicated by the atomic arrangement model shown in Fig. 5.5(a). This hopping phenomenon did not depend on the scanning direction and was frequently observed. I could identify more than one hopped site in nearly every measurement (wide area scan: $40 \times 40 \text{ nm}^2$ to $50 \times 50 \text{ nm}^2$). These facts indicate that hydrogen atom should be bonded to an O_N site not an O_W site, and hops into a neighboring O_N site rather than a neighboring O_W site.

5.4 Adsorption-site dependences for H atoms

Recent DFT study of Fe₃O₄(001) surfaces with one hydrogen atom per unit cell showed that the neighboring O_N sites are not equivalent for hydrogen adsorption [37]. According to the DFT study, adsorption energies for these O_N sites are different by 0.05 eV. To distinguish these two types of O_N sites I label them as O_{N1} and O_{N2}. In the surface atomic arrangement model depicted in Fig. 5.6(a), these oxygen sites within [110] atomic rows are marked as “N1” and “N2”, respectively. Since the DFT result indicates that one of these sites is preferable for hydrogen to be adsorbed, I have expected that STM images should reflect this difference. As seen in the high-resolution STM image shown in Fig. 5.6(a), the H-adsorbed O_{N1} and O_{N2} sites are both identified. Therefore, I investigated the numbers of H-adsorbed sites for their O_N atoms using larger-scale STM images (40 × 40 nm² to 50 × 50 nm²) such as Fig. 5.6(b). Checking more than 1000 BPs within [110] atomic rows observed in the STM images of single sample surface, the histogram for the emergence at their O_N sites was obtained. The histogram shown in Fig. 5.6(c) suggests that there is no obvious difference for the emergence between these sites.

I also performed the same investigations concerning two types of O_N sites within [1-10] atomic rows. Although each of these O_N sites is equivalent to either O_{N1} site or O_{N2} site, the correspondence is unclear due to antiphase domain boundaries defects introduced in the Fe₃O₄(001) films [64]. Therefore, I label them as O_{N3} and O_{N4} (not O_{N1} and O_{N2}). In the surface atomic arrangement model depicted in the inset of Fig. 5.6(b), these oxygen sites are marked as “N3” and “N4”, respectively. The histogram for the emergence at their O_N sites shows the similar results to the former. These experimental results show no clear adsorption-site dependences between O_N sites. Thus, I revealed that two types of O_N sites of a Fe₃O₄(001) surface are almost equivalent for hydrogen adsorption. Although statistical analyses of hydrogen hopping frequency are not yet sufficient, there seems no clear difference in the hopping between N1 → N2 and N2 → N1 or N3 → N4 and N4 → N3. The hydrogen coverage on the as-grown Fe₃O₄(001) films surface is estimated to be 0.12

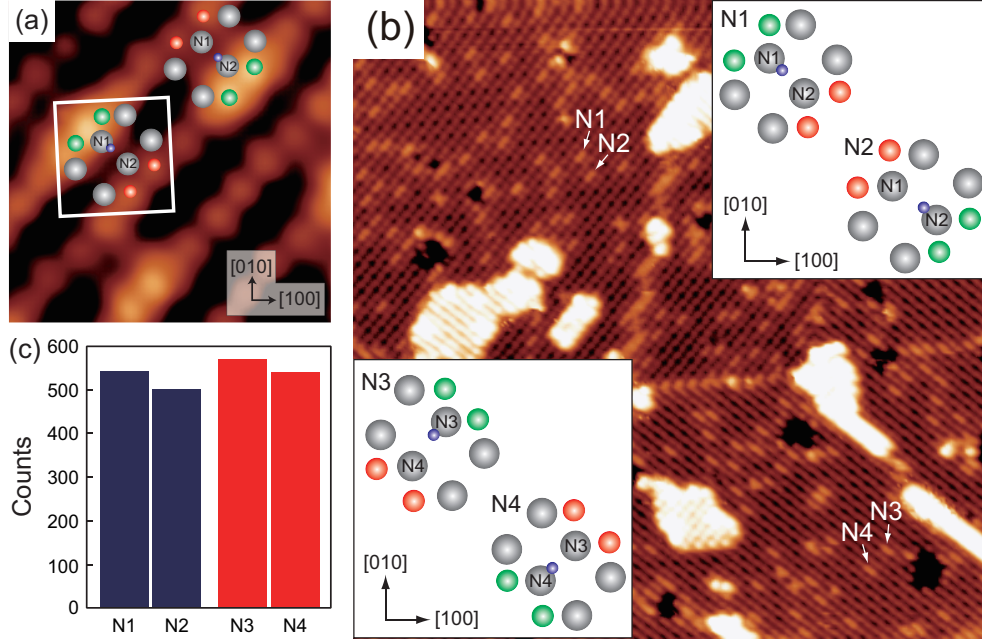


Figure 5.6 (a) High-resolution STM image ($2.5 \times 2.5 \text{ nm}^2$) and the atomic arrangement models. The feedback control set point was $V_S = +1.2 \text{ V}$, $I_T = 0.3 \text{ nA}$. The white square shows the $(\sqrt{2} \times \sqrt{2})R45^\circ$ symmetry. (b) Overview STM image ($40 \times 40 \text{ nm}^2$) of the as-grown $\text{Fe}_3\text{O}_4(001)$ film surface. The feedback control set point was $V_S = +1.2 \text{ V}$, $I_T = 0.3 \text{ nA}$. N1 and N2 or N3 and N4 in the inset show different hydrogen-adsorption patterns for $[110]$ or $[1\bar{1}0]$ atomic rows. N1 to N4 inside the STM image correspond to their patterns. (c) Histogram showing adsorption number counted from STM images for each adsorption-site, i.e., N1 to N4.

ML, i.e., 12% of the O_N sites are occupied. This study shows the priorities of H-adsorbed sites at low hydrogen coverage, however there have also been no reports on relations between hydrogen coverage and adsorption-site dependence. Moreover, these results obtained at room temperature are somewhat different from the previous theoretical prediction [37]. Further STM investigations of $\text{Fe}_3\text{O}_4(001)$ surfaces with varying hydrogen coverages and at varying temperatures are required to give newer experimental insights into an H-adsorbed $\text{Fe}_3\text{O}_4(001)$ surface.

5.5 Summary

Atomic structures of H/Fe₃O₄(001) surfaces were mainly investigated by STM measurements. It was demonstrated using XPS and STM that the bright protrusions observed in the STM images of UHV-prepared Fe₃O₄(001) film surfaces can be attributed to surface OH groups. STM studies revealed that the number of OH groups increase with increasing UHV holding time of sample, which indicates that the OH groups are derived from UHV residual gases. The STM studies also showed that surface Fe_B atoms relax toward the bulk-terminated positions following hydrogen adsorption. I also investigated adsorption-site dependences for hydrogen atoms, and revealed that there is no obvious dependence between two types of O_N sites of a Jahn-Teller distorted Fe₃O₄(001) surface, which is different from the previous theoretical prediction.

Chapter 6

Local electronic states of H/Fe₃O₄(001) surface

In this chapter, local electronic states of H/Fe₃O₄(001) surfaces are mainly discussed by scanning tunneling microscopy/spectroscopy (STM/STS) results. First, effect of hydrogen atoms on the surface iron electronic states are investigated by STS and dI/dV mapping. The electron-transfer phenomenon predicted to occur in this surface is discussed from comparing these experimental and previous theoretical results. Moreover, correlation between surface OH density and surface iron electronic states are discussed by atomic-scale STM/STS results.

6.1 Effect of H atoms on the surface Fe electronic states

To investigate the effect of adsorbed H atoms on the local electronic states of surface Fe_B atoms, I probed the local density of states (LDOS) of unmodified iron (Fe(C)) and modified iron (Fe(H)) atoms by STS. Figure 6.1 shows normalized dI/dV spectra numerically obtained from the $I(V)$ curves taken on Fe_B sites. The red and green curves indicate the representative spectra obtained on Fe(C) and Fe(H) sites within the same scan frame, respectively. As discussed in chapter 3.2, Fe(C) atoms are Fe³⁺ cations, showing a semiconducting nature. The energy-gap values of these Fe(C) atoms are 0.4–0.8 eV. Both curves show pronounced increases of the LDOS around at –0.4 and +0.2 eV. However, an additional occupied state is observed just

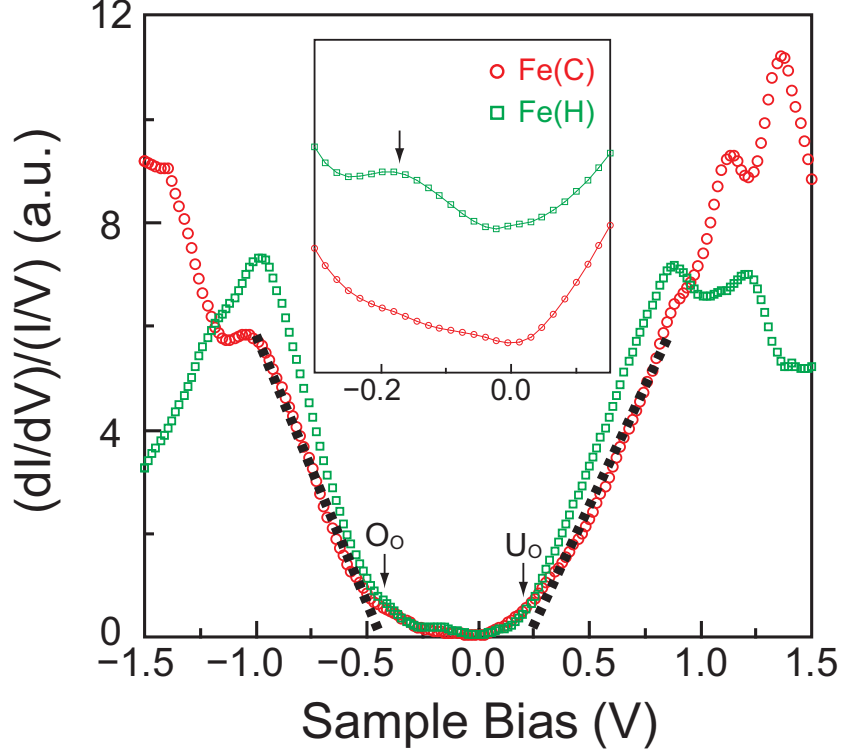


Figure 6.1 Normalized dI/dV spectra numerically obtained from the $I(V)$ curves taken on Fe_B sites using the Feenstra's method [75]. The red and green curves show the spectra obtained on Fe(C) and Fe(H) sites, respectively. The result of Fe(C) site is equal to the one shown in Fig. 3.5. The inset shows the region around $V_s = 0$, in which the curves are offset vertically for clarity. The arrow in the inset denotes the position of the small peak observed in the green curve.

below the Fermi level only in the green curve, as distinguished by the arrow in the inset.

Next, the additional occupied state described above is discussed. The occupied states are reproducibly observed on different Fe(H) sites, although the small differences in the energy position and in the density reside. In Fe₃O₄, features near the Fermi level originate from $3d$ - $3d$ transitions at the Fe_B ions with Fe²⁺ state [36]. Therefore, the additional occupied state can be attributed to the occupation of the $3d$ states for Fe²⁺ ions, which indicates that Fe(H) atoms exist in Fe²⁺-like state

whereas Fe(C) atoms exist in Fe³⁺-like state. In fact, recent DFT results of H-adsorbed Fe₃O₄(001) surfaces have shown the existence of Fe_B 3*d* states just below the Fermi level, corresponding to Fe²⁺-like state [37]. In addition, occupied states just below the Fermi level provide an evidence of the reduced energy gaps near the Fermi level of Fe(H) atoms. This result indicates that atomic-H adsorption on a clean Fe₃O₄(001) surface changes the local electronic states of the surface Fe_B atoms from a semiconducting to a metallic-like nature. These STS results are in good agreement with the results of other studies of H-saturated Fe₃O₄(001) surfaces, such as the results of angle-resolved X-ray photoelectron spectroscopy [36], which showed an increased proportion of Fe²⁺ ions on the surface relative to the clean surface, and those of spin-summed metastable de-excitation spectroscopy [33] and ultraviolet photoelectron spectroscopy [36], which showed a dramatic increase in emission just below the Fermi level by atomic-H adsorption.

dI/dV mapping was also performed to further ascertain the occupied state just below the Fermi level of Fe(H) atoms using the multipass scanning method shown in Fig. 6.2 [87]. Figure 6.3(a) and (b) show a high-resolution STM and dI/dV images of the Fe₃O₄(001) surface obtained using this method, respectively. A general dI/dV

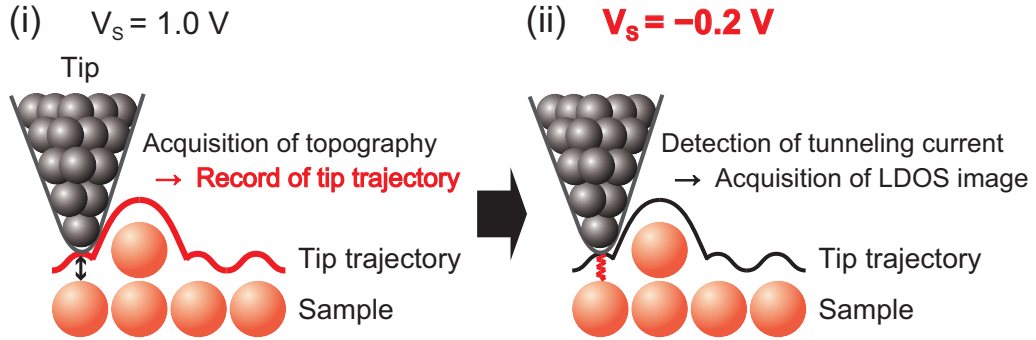


Figure 6.2 Schematic of multipass scanning method used in this study. (i) At a sample bias voltage of +1.0 V, surface topography is measured and recorded in the first pass using a constant-current mode. (ii) In the second pass, at a sample bias voltage of -0.2 V, LDOS image is obtained by detecting a tunneling current using the recorded tip trajectory in the first pass. (iii) The procedure (i)–(ii) is performed in all lines of the scanning area.

mapping using a constant-current mode can lead to tip crashes on the surface due to the lack of LDOS near the Fermi level [68]. In this multipass scanning method, surface topography was measured in the first pass. During the second pass, the acquired topographic trace was used to obtain a dI/dV image at a specific sample bias voltage. The distance offset for the second pass was 150 pm toward the surface with respect to the topography measured during the first pass. The STM (Fig. 6.3(a)) and dI/dV (Fig. 6.3(b)) images were obtained at a sample bias voltage of +1.0 V and -0.2 V, respectively. Comparison of these two images clearly shows the higher LDOS at -0.2 eV of Fe(H) than Fe(C) atoms, which is in good agreement with the STS result shown in Fig. 6.1.

These differences in the local electronic states between Fe(C) and Fe(H) atoms can be explained by the electron-transfer phenomenon. A differential charge density map of the H-adsorbed Fe₃O₄(001) surface at the topmost (001) plane has predicted that electrons are donated from hydrogen to surface oxygen atoms and then redistributed toward the neighboring Fe_B atoms due to the saturation of oxygen dangling bonds

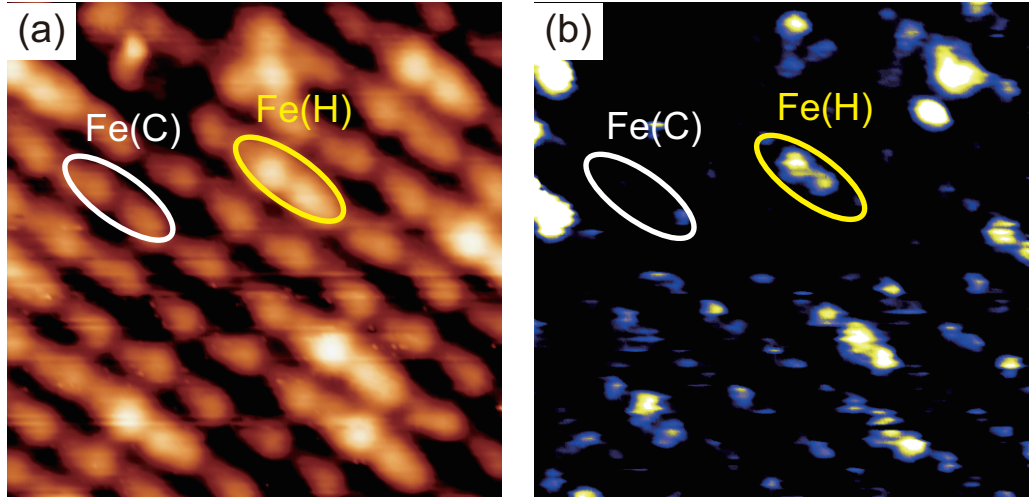


Figure 6.3 (a), (b) Two-pass scan images ($5.0 \times 5.0 \text{ nm}^2$). First, an unoccupied-state STM image (a) was taken at a set point of +1.0 V and 0.3 nA. Second, a dI/dV image (b) was taken at a bias voltage of -0.2 V. The topography recorded in (a) was played with a z-offset of 150 pm toward the surface.

through OH bonding [28]. Consequently, adsorbed-H and neighboring Fe_B atoms should behave as electron-donor and electron-trapping sites, respectively, in analogy with H and Ti atoms on the hydroxylated TiO₂ surface [90]. Judging from DFT results [28], two Fe_B atoms with an OH group neighbor are expected to gain spin-down electrons just below the Fermi level. Since occupied states just below the Fermi level of Fe(H) atoms are clearly resolved by this STS measurement, this electron-transfer phenomenon is expected to occur in this Fe₃O₄(001) film surface, as illustrated in Fig. 6.4. Therefore, the additional occupied state can be attributed to the gain of spin-down electrons from the neighboring H atoms. I expect that electron transfer from hydrogen atoms to a clean Fe₃O₄(001) surface can enhance the surface electron-spin polarization. Recent theoretical works have reported that the adsorption of carbon atoms [38] and boron atoms [39] can also be an effective method of surface modification for achieving a half-metallic Fe₃O₄(001) surface. This enhancement in the surface electron-spin polarization is also predicted to be related to an electron-transfer phenomenon. To reveal the mechanism of these enhancements in greater detail, further evaluation of the effect of adsorbed atoms on the surface local electron-spin states by spin-polarized STM/STS, such as the relations between adsorption structures and electron-spin polarization, is required.

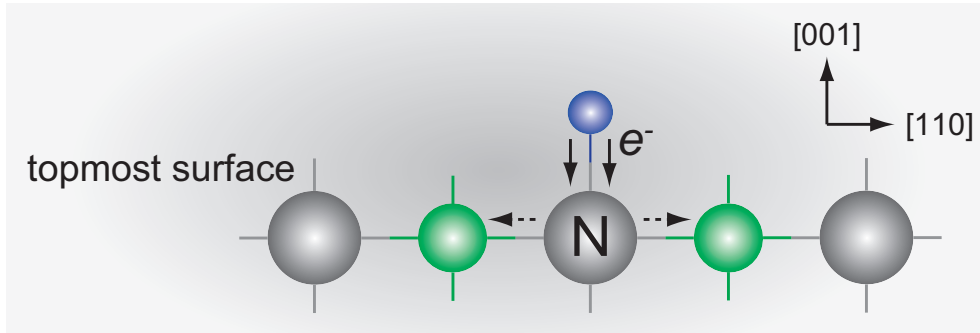


Figure 6.4 Schematic of electron transfer occurred in H/Fe₃O₄(001) surface. The color coding of the ions corresponds to the one shown in Fig. 5.3. The arrows indicate the directions of electron flow.

6.2 Correlation between OH density and surface Fe electronic states

Figure 6.5 shows an overview STM image of the as-grown Fe₃O₄(001) film surface, where Fe_B rows are running along the [110] or [1-10] direction on the larger terrace [64–66]. Many bright protrusions (BPs) situated at Fe_B sites are observed from place to place, as indicated in the yellow oval. As described above, the observed BPs are Fe(H) atoms whose local electronic states are significantly modified by surface OH groups [36, 65, 66, 74], compared to Fe(C) atoms residing in a clean Fe₃O₄(001) surface. Figure 6.6(a) shows a high-resolution STM image of an area

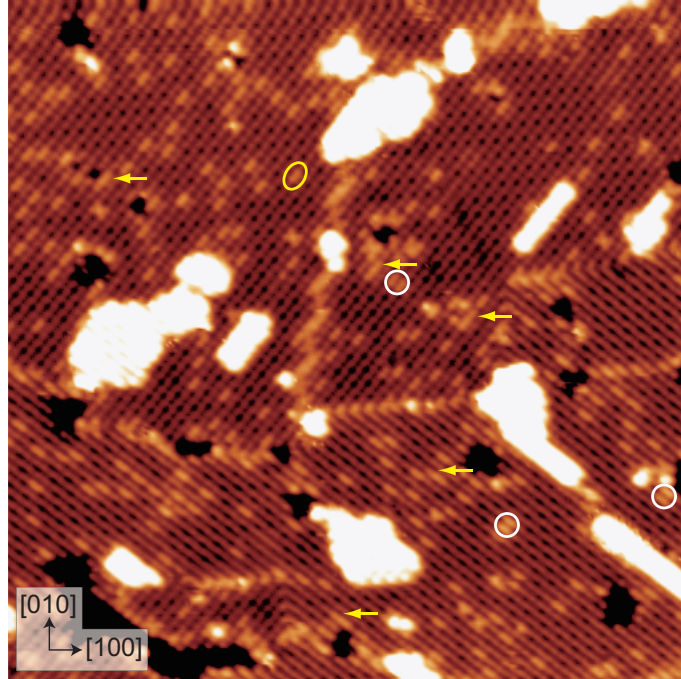


Figure 6.5 Overview STM image ($40 \times 40 \text{ nm}^2$) of the as-grown Fe₃O₄(001) film surface. The feedback control set point was $V_S = +1.2 \text{ V}$, $I_T = 0.3 \text{ nA}$. The yellow oval encloses a representative BP (SBP) which corresponds to paired Fe(H) atoms. The yellow arrows show the exceptional BPs (LBPs) whose length along the atomic rows is longer than SBPs. The white circles enclose the SBPs adjacently arranged perpendicular to the atomic rows.

containing a representative BP, in which two adjacent Fe(H) atoms are observed as BPs. It is theoretically predicted that hydrogen atoms strongly tilt from an initial on-top position, resulting in OH bonds between hydrogen atoms and O_N atoms of the opposite rows [37, 38]. The strong tilt of the OH bonds nearly parallel to the surface is closely associated with the frequently observed jumping of BPs between neighboring O_N sites, which correspond to hopping of hydrogen atoms between them, as discussed in the prior chapter [36]. Judging from the STM images, hydrogen atoms can not be bonded to O_W sites due to the nonobservation of jumping of BPs between neighboring O_W sites [65].

Another type of BPs can also be seen from Fig. 6.5, as indicated in the yellow arrows. Figure 6.6(b) shows a high-resolution STM image of the area containing such a BP, in which the BP is longer than that shown in Fig. 6.6(a). Henceforth, I refer to the shorter and the longer BP as “SBP” and “LBP”, respectively. These types of BPs

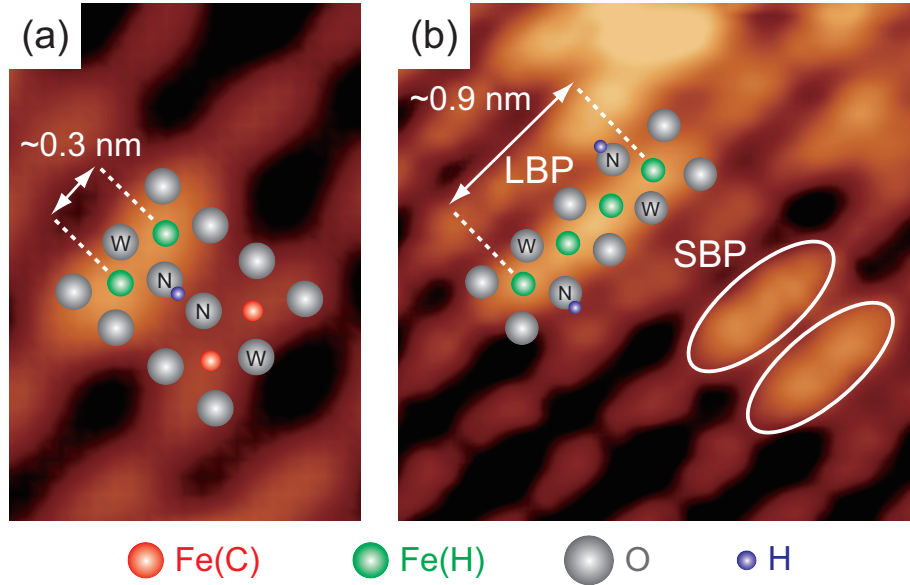


Figure 6.6 (a) High-resolution STM image ($2.4 \times 1.6 \text{ nm}^2$) of an area containing a SBP and the atomic arrangement model. (b) High-resolution STM image ($3.0 \times 3.0 \text{ nm}^2$) of an area containing one LBP and two SBPs, and the atomic arrangement model. The feedback control set point was $V_S = +1.2 \text{ V}$, $I_T = 0.3 \text{ nA}$.

longer than LBPs were not observed in the STM images. The LBPs are extremely uncommon with respect to the SBPs, resulting in only 5–10 LBPs compared to more than 160 SBPs observed in nearly every STM measurement (wide area scan: $40 \times 40 \text{ nm}^2$ to $50 \times 50 \text{ nm}^2$) [67]. This tendency is also visible on the Fe₃O₄(001) surface with a nearly saturated OH coverage (ca. 5% LBPs relative to SBPs) [74]. This low proportion of LBPs can be attributed to the adsorption structure. The LBP consists of four Fe(H) atoms with two OH groups neighbor, as shown in Fig. 6.6(b). Both of two adjacent O_N sites along the atomic rows are occupied by hydrogen atoms, whereas for SBPs either O_N site is occupied [67]. As a result, LBPs are energetically less favorable than SBPs due to the stronger OH–OH electrostatic repulsion at the shorter distance between the nearest OH groups, corresponding to much less emergence in the STM images. DFT results also indicate the enhanced instability of the surface with increasing OH coverages due to the OH–OH repulsion, therefore maximized OH–OH distance that reduces it is preferable [37]. Here, note that the SBPs adjacently arranged perpendicular to the atomic rows are observed in the STM images, as enclosed by the white circles in Fig. 6.5 or the white ovals in Fig. 6.6(b). This adsorption configuration can also be energetically unfavorable due to the OH–OH repulsion, resulting in infrequent cases observed in the STM images (not more than 10 cases observed in the $40 \times 40 \text{ nm}^2$ STM images) [67].

Figure 6.6(b) also shows the central Fe(H) atoms within the LBP have a slightly increased apparent height compared to those within the SBPs (ca. 15 pm), which reflects the differences in the local electronic states between them [67]. I now turn to discuss the differences in the local electronic states between Fe(H) atoms within SBPs (Fe(H1)) and central Fe(H) atoms within LBPs (Fe(H2)). To investigate this difference, I probed the LDOS of these two types of Fe(H) atoms by STS. Figure 6.7(a) shows a high-resolution STM image of an area containing both Fe(H) atoms in which the STS measurements were performed. The green and blue curves in Fig. 6.7(b) show the normalized dI/dV spectra obtained on Fe(H1) and Fe(H2) site indicated in Fig. 6.7(a), respectively. Figure 6.7(b) also shows the normalized dI/dV spectrum taken on a Fe(C) site situated far from OH groups [66]. The normalized

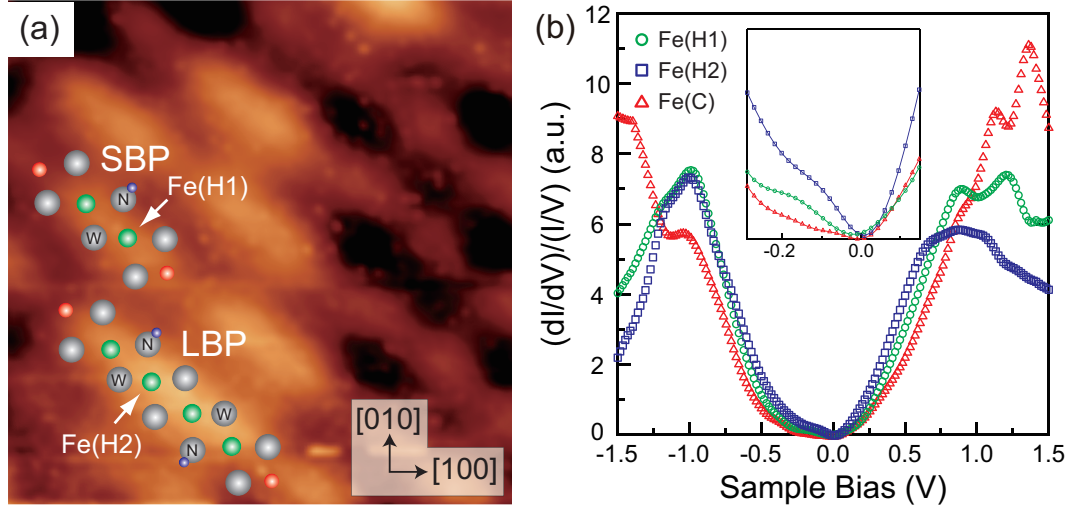


Figure 6.7 (a) High-resolution STM image ($3.0 \times 3.0 \text{ nm}^2$) of an area containing Fe(H1) and Fe(H2) atoms, and the atomic arrangement model. The feedback control set point was $V_S = +1.2 \text{ V}$, $I_T = 0.3 \text{ nA}$. (b) Normalized dI/dV spectra obtained on two Fe_B sites indicated in panel (a) and on a Fe(C) site [66]. The normalized dI/dV spectra were numerically obtained from the $I(V)$ curves using the Feenstra's method [75]. The inset shows the region around $V_s = 0$.

dI/dV spectra were numerically obtained from the $I(V)$ curves using the method proposed by Feenstra [75]. The three $I(V)$ curves intersect the imaging set point at $\{+1.2 \text{ V}, 0.3 \text{ nA}\}$ (data not shown), i.e., it is certain that there is no variation of the tip-sample distance during the STS measurements. Pronounced peaks around at $V_s = -1.0 \text{ V}$ are clearly observed in all three spectra, as shown in Fig. 6.7(b). These peaks can be attributed to the occupation of $3d$ states for Fe^{3+} ions [66]. However, the two spectra obtained on Fe(H1) and Fe(H2) sites also show additional small peaks just below $V_s = 0$, whereas this peak is not observed in the spectrum of the Fe(C) site (see the inset). As discussed in chapter 6.1, the observed peaks are attributed to the occupation of $3d$ states for Fe^{2+} ions, and this difference in the local electronic states between Fe(C) and Fe(H) atoms can be explained by the electron-transfer phenomenon described above [66]. This phenomenon is expected to occur in this $\text{Fe}_3\text{O}_4(001)$ surface, giving rise to the observed peaks just below V_s

= 0 of two spectra obtained on Fe(H1) and Fe(H2) sites.

Figure 6.7(b) also shows an enhanced intensity of the peak of the Fe(H2) site with respect to that of the Fe(H1) site, which means the higher LDOS just below the E_F of Fe(H2) atoms relative to Fe(H1) [67]. As described above, given that the modifications of Fe_B electronic states are induced mainly by surface OH groups, this STS result demonstrates that Fe(H2) atoms receive more contributions from OH groups than Fe(H1). Since Fe(H2) atoms are surrounded by two neighboring OH groups within the atomic rows relative to Fe(H1) with an OH group neighbor, as depicted in the atomic arrangement model in Fig. 6.7(a), one should consider Fe(H2) atoms gain more electrons from hydrogen atoms than Fe(H1) [67]. The gain of more electrons can be speculated to lead to the enhanced LDOS just below the E_F . This enhanced LDOS with increasing neighboring OH groups can also be closely associated with the previous experimental reports, which show the enhanced electron-spin polarization of Fe₃O₄(001) surfaces with increasing H coverages [33–35]. Since electronic states near the E_F of Fe_B atoms are dominated by spin-down electronic states [30,69,80], the enhanced LDOS just below the E_F would be due to the gain of more spin-down electrons from hydrogen atoms. Therefore, the experimental observations of the enhanced electron-spin polarization near the E_F of Fe₃O₄(001) surfaces with increasing hydrogen coverages [33–35] should be derived from the increase of half-metallic-like Fe_B atoms, which is induced by the increase of O_N sites occupied by hydrogen atoms. These results indicate that the saturation of O_N sites by hydrogen atoms can change all surface Fe_B atoms from a semiconducting to a half-metallic nature. In addition, these experimental findings have significant implications for understanding the correlation between hydrogen coverages and Fe_B electronic states. These STS results obtained on Fe(H1), Fe(H2) and Fe(C) sites have revealed that surface OH density is a factor for determining the LDOS just below the Fermi level of surface Fe_B atoms [67].

6.3 Summary

STM/STS measurements and dI/dV mapping of H/Fe₃O₄(001) surfaces were performed to investigate the surface local electronic states. STS results obtained on two types of Fe_B sites, one with neighboring OH groups and the other without, indicated that adsorbed-H atoms can modify the LDOS around the Fermi level of neighboring Fe_B atoms. The energy-gap value of these Fe_B atoms is reduced because of the occupation of $3d$ states just below the Fermi level, corresponding to Fe²⁺-like state. These modifications of local electronic states can be due to the gain of electrons from neighboring hydrogen atoms. These results indicate that adsorbate-induced modifications in the electronic and electron-spin properties of the topmost surface will play a significant role in designing interfaces for spintronic devices, which require high electron-spin polarization.

In addition, correlation between surface OH density and surface Fe_B electronic states were also investigated by STM/STS. Two types of BPs with different lengths along the atomic rows are observed in the STM images. The shorter BP consists of two Fe_B atoms with one OH group neighbor, on the other hand, the longer BP consists of four Fe_B atoms with two OH groups neighbor. The latter adsorption configuration where the OH–OH distance is shorter gives rise to much less emergence in STM images, presumably due to the stronger OH–OH electrostatic repulsion. In addition, the STS results evince the higher LDOS just below the Fermi level of surface Fe_B atoms with increasing neighboring OH groups. These experimental findings indicate that the LDOS just below the Fermi level of surface Fe_B atoms can be tuned by varying surface OH densities.

Chapter 7

Summary

This research work produced following six important results and knowledges.

1. Scanning tunneling microscopy (STM) studies of a clean $\text{Fe}_3\text{O}_4(001)$ surface showed the B-terminated surface with a $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction, which is in agreement with the previous works. Scanning tunneling spectroscopy (STS) studies of the surface revealed its energy gaps of 0.4–0.8 eV, indicating a semiconducting nature relative to the predicted half-metallic one of bulk Fe_3O_4 . Moreover, it was found that the surface local electronic states of step edges show a metallic-like nature with respect to a semiconducting one of terraces, which can be due to the presence of more oxygen vacancies and more adsorbates.
2. $\text{Fe}_3\text{O}_4(001)$ subsurface electronic structures were investigated by STM/STS and differential tunneling conductance (dI/dV) mapping. The STS results showed the higher local density of states (LDOS) just below the Fermi level of narrow sections than wide ones of the surface reconstruction perpendicular to the Fe_B rows. The dI/dV map clearly showed charge-ordered electronic structures and reproduced the STS results. These observed structures were consistent with a subsurface charge-ordering model of $\text{Fe}^{2+}\text{-Fe}^{2+}$ and $\text{Fe}^{3+}\text{-Fe}^{3+}$ dimers, as proposed in previous density functional theory studies. These experimental findings reveal the origin of the $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction to be the subsurface charge-ordered electronic structures.
3. It was demonstrated by X-ray photoelectron spectroscopy and STM that the bright protrusions (BPs) observed in the STM images of ultra-high vacuum

(UHV)-prepared $\text{Fe}_3\text{O}_4(001)$ film surfaces can be due to surface OH groups. In addition, the number of OH groups was found to increase with increasing UHV holding time of $\text{Fe}_3\text{O}_4(001)$ film samples, which indicates that the OH groups are derived from UHV residual gases.

4. STM studies of $\text{H}/\text{Fe}_3\text{O}_4(001)$ surfaces have revealed that surface Fe_B atoms relax toward the bulk-terminated positions by OH groups formed between hydrogen and surface O_N atoms. Moreover, adsorption-site dependences for hydrogen atoms were investigated by STM measurements in detail, and two types of surface O_N sites were found to be almost equivalent for hydrogen adsorption, which is different from the previous theoretical prediction.
5. Effect of hydrogen atoms on the surface Fe_B electronic states were investigated by STS and dI/dV mapping. The STS spectra measured on Fe_B sites with and without neighboring OH groups, and dI/dV map have indicated that adsorbed hydrogen and their neighboring Fe_B atoms behave as electron-donor and electron-trapping sites, respectively. This electron-transfer phenomenon changes the Fe_B atoms from a semiconducting to a metallic-like nature. These local electronic state modifications are related to the occupation of Fe $3d$ states just below the Fermi level, corresponding to Fe^{2+} -like state. The orbital occupation can be explained by the gain of electrons from the hydrogen atoms.
6. Correlation between surface OH density and Fe_B electronic states were investigated by STM/STS. Two types of BPs, whose lengths along the atomic rows are different, are observed in the STM images. The shorter and longer BPs consist of Fe_B atoms with one and with two OH groups neighbor, respectively. In addition, STS studies show the higher LDOS just below the Fermi level of Fe_B atoms with increasing neighboring OH groups. The variation can be derived from the difference in the gain of electrons from hydrogen atoms, which is due to the difference in the number of neighboring OH groups. These STM/STS results reveal that surface OH density is a factor for determining the LDOS just below the Fermi level of surface Fe_B atoms.

References

- [1] N. S. Kim, T. Austin, D. Baauw, T. Mudge, K. Flautner, J. S. Hu, M. J. Irwin, M. Kandemir, and V. Narayanan. Leakage current: Moore's law meets static power. *Computer*, Vol. 36, No. 12, pp. 68–75, 2003.
- [2] Y. Zhang, W. Zhao, J. O. Klein, W. Kang, D. Querlioz, Y. Zhang, D. Ravelosona, and C. Chappert. Spintronics for low-power computing. *2014 Design, Automation Test in Europe Conference Exhibition (DATE)*, pp. 1–6, 2014.
- [3] K. Tsuchida, T. Inaba, K. Fujita, Y. Ueda, T. Shimizu, Y. Asao, T. Kajiyama, M. Iwayama, K. Sugiura, S. Ikegawa, T. Kishi, T. Kai, M. Amano, N. Shimomura, H. Yoda, and Y. Watanabe. A 64Mb MRAM with clamped-reference and adequate-reference schemes. *2010 IEEE International Solid-State Circuits Conference (ISSCC)*, pp. 258–259, 2010.
- [4] M. Julliere. Tunneling between ferromagnetic films. *Phys. Lett. A*, Vol. 54, No. 3, pp. 225–226, 1975.
- [5] P. M. Tedrow and R. Meservey. Spin Polarization of Electrons Tunneling from Films of Fe, Co, Ni, and Gd. *Phys. Rev. B*, Vol. 7, pp. 318–326, 1973.
- [6] A. Yanase and K. Siratori. Band Structure in the High Temperature Phase of Fe_3O_4 . *J. Phys. Soc. Jpn.*, Vol. 53, No. 1, pp. 312–317, 1984.
- [7] Z. Zhang and S. Satpathy. Electron states, magnetism, and the Verwey transition in magnetite. *Phys. Rev. B*, Vol. 44, pp. 13319–13331, 1991.

- [8] A. Yanase and N. Hamada. Electronic Structure in High Temperature Phase of Fe_3O_4 . *J. Phys. Soc. Jpn.*, Vol. 68, No. 5, pp. 1607–1613, 1999.
- [9] E. J. W. Verwey. Electronic conduction of magnetite (Fe_3O_4) and its transition point at low temperatures. *Nature*, Vol. 144, No. 3642, pp. 327–328, 1939.
- [10] A. Subagyo and K. Sueoka. Defect-Induced Charge Freezing on Epitaxial $\text{Fe}_3\text{O}_4(001)$ Film Surfaces Studied by Spin-Polarized Scanning Tunneling Microscopy. *Jpn. J. Appl. Phys.*, Vol. 44, No. 7S, p. 5447, 2005.
- [11] A. Subagyo and K. Sueoka. Spin-polarized scanning tunneling microscopy study on charge ordering of reconstructed $\text{Fe}_3\text{O}_4(001)$ film surfaces. *Jpn. J. Appl. Phys.*, Vol. 45, No. 3B, pp. 2255–2258, 2006.
- [12] W. Eerenstein, T. T. M. Palstra, T. Hibma, and S. Celotto. Origin of the increased resistivity in epitaxial Fe_3O_4 films. *Phys. Rev. B*, Vol. 66, No. 20, 2002.
- [13] W. Eerenstein, T. T. M. Palstra, S. S. Saxena, and T. Hibma. Spin-Polarized Transport across Sharp Antiferromagnetic Boundaries. *Phys. Rev. Lett.*, Vol. 88, p. 247204, 2002.
- [14] W. Eerenstein, T. T. M. Palstra, T. Hibma, and S. Celotto. Diffusive motion of antiphase domain boundaries in Fe_3O_4 films. *Phys. Rev. B*, Vol. 68, p. 014428, 2003.
- [15] A. V. Ramos, J.-B. Moussy, M.-J. Guittet, A. M. Bataille, M. Gautier-Soyer, M. Viret, C. Gatel, P. Bayle-Guillemaud, and E. Snoeck. Magnetotransport properties of Fe_3O_4 epitaxial thin films: Thickness effects driven by antiphase boundaries. *J. Appl. Phys.*, Vol. 100, No. 10, p. 103902, 2006.
- [16] D. T. Margulies, F. T. Parker, M. L. Rudee, F. E. Spada, J. N. Chapman, P. R. Aitchison, and A. E. Berkowitz. Origin of the Anomalous Magnetic Behavior in Single Crystal Fe_3O_4 Films. *Phys. Rev. Lett.*, Vol. 79, pp. 5162–5165, 1997.

- [17] G. Q. Gong, A. Gupta, G. Xiao, W. Qian, and V. P. Dravid. Magnetoresistance and magnetic properties of epitaxial magnetite thin films. *Phys. Rev. B*, Vol. 56, pp. 5096–5099, 1997.
- [18] A. Hamie, Y. Dumont, E. Popova, A. Fouchet, B. Warot-Fonrose, C. Gatel, E. Chikoidze, J. Scola, B. Berini, and N. Keller. Investigation of high quality magnetite thin films grown on $\text{SrTiO}_3(001)$ substrates by pulsed laser deposition. *Thin Solid Films*, Vol. 525, No. 0, pp. 115–120, 2012.
- [19] F. C. Voogt, T. T. M. Palstra, L. Niesen, O. C. Rogojanu, M. A. James, and T. Hibma. Superparamagnetic behavior of structural domains in epitaxial ultrathin magnetite films. *Phys. Rev. B*, Vol. 57, pp. R8107–R8110, 1998.
- [20] S. B. Ogale, K. Ghosh, R. P. Sharma, R. L. Greene, R. Ramesh, and T. Venkatesan. Magnetotransport anisotropy effects in epitaxial magnetite Fe_3O_4 thin films. *Phys. Rev. B*, Vol. 57, pp. 7823–7828, 1998.
- [21] D. Reisinger, P. Majewski, M. Opel, L. Alff, and R. Gross. Hall effect, magnetization, and conductivity of Fe_3O_4 epitaxial thin films. *Appl. Phys. Lett.*, Vol. 85, No. 21, 2004.
- [22] D. T. Margulies, F. T. Parker, F. E. Spada, R. S. Goldman, J. Li, R. Sinclair, and A. E. Berkowitz. Anomalous moment and anisotropy behavior in Fe_3O_4 films. *Phys. Rev. B*, Vol. 53, pp. 9175–9187, 1996.
- [23] G. Hu and Y. Suzuki. Negative Spin Polarization of Fe_3O_4 in Magnetite/Manganite-Based Junctions. *Phys. Rev. Lett.*, Vol. 89, p. 276601, 2002.
- [24] W. Kim, K. Kawaguchi, N. Koshizaki, M. Sohma, and T. Matsumoto. Fabrication and magnetoresistance of tunnel junctions using half-metallic Fe_3O_4 . *J. Appl. Phys.*, Vol. 93, No. 10, pp. 8032–8034, 2003.
- [25] T. Kado. Large room-temperature inverse magnetoresistance in tunnel junctions with a Fe_3O_4 electrode. *Appl. Phys. Lett.*, Vol. 92, No. 9, 2008.

- [26] M. Opel. Spintronic oxides grown by laser-MBE. *J. Phys. D: Appl. Phys.*, Vol. 45, No. 3, p. 033001, 2012.
- [27] T. Taniyama, T. Mori, K. Watanabe, E. Wada, M. Itoh, and H. Yanagihara. Optically spin oriented electron transmission across fully epitaxial $\text{Fe}_3\text{O}_4/\text{GaAs}(001)$ interfaces. *J. Appl. Phys.*, Vol. 103, No. 7, 2008.
- [28] X. Sun, M. Kurahashi, A. Pratt, and Y. Yamauchi. First-principles study of atomic hydrogen adsorption on $\text{Fe}_3\text{O}_4(100)$. *Surf. Sci.*, Vol. 605, No. 1112, pp. 1067–1073, 2011.
- [29] K. P. McKenna, F. Hofer, D. Gilks, V. K. Lazarov, C. Chen, Z. Wang, and Y. Ikuhara. Atomic-scale structure and properties of highly stable antiphase boundary defects in Fe_3O_4 . *Nat. Commun.*, Vol. 5, , 2014.
- [30] M. Fonin, R. Pentcheva, Y. S. Dedkov, M. Sperlich, D. Vyalikh, M. Scheffler, U. Rudiger, and G. Guntherodt. Surface electronic structure of the $\text{Fe}_3\text{O}_4(100)$: Evidence of a half-metal to metal transition. *Phys. Rev. B*, Vol. 72, No. 10, 2005.
- [31] M. Fonin, Y. S. Dedkov, R. Pentcheva, U. Ruediger, and G. Guentherodt. Magnetite: a search for the half-metallic state. *J. Phys.: Condens. Matter*, Vol. 19, No. 31, 2007.
- [32] J. G. Tobin, S. A. Morton, S. W. Yu, G. D. Waddill, I. K. Schuller, and S. A. Chambers. Spin resolved photoelectron spectroscopy of Fe_3O_4 : the case against half-metallicity. *J. Phys.: Condens. Matter*, Vol. 19, No. 31, p. 315218, 2007.
- [33] A. Pratt, M. Kurahashi, X. Sun, and Y. Yamauchi. Adsorbate-induced spin-polarization enhancement of $\text{Fe}_3\text{O}_4(001)$. *J. Phys. D: Appl. Phys.*, Vol. 44, No. 6, p. 064010, 2011.
- [34] A. Pratt, M. Kurahashi, X. Sun, D. Gilks, and Y. Yamauchi. Direct observation of a positive spin polarization at the (111) surface of magnetite. *Phys. Rev. B*, Vol. 85, p. 180409, 2012.

- [35] M. Kurahashi, X. Sun, and Y. Yamauchi. Recovery of the half-metallicity of an $\text{Fe}_3\text{O}_4(100)$ surface by atomic hydrogen adsorption. *Phys. Rev. B*, Vol. 81, p. 193402, 2010.
- [36] G. S. Parkinson, N. Mulakaluri, Y. Losovyj, P. Jacobson, R. Pentcheva, and U. Diebold. Semiconductor-half metal transition at the $\text{Fe}_3\text{O}_4(001)$ surface upon hydrogen adsorption. *Phys. Rev. B*, Vol. 82, No. 12, 2010.
- [37] N. Mulakaluri and R. Pentcheva. Hydrogen Adsorption and Site-Selective Reduction of the $\text{Fe}_3\text{O}_4(001)$ Surface: Insights From First Principles. *J. Phys. Chem. C*, Vol. 116, No. 31, pp. 16447–16453, 2012.
- [38] X. Sun, S. D. Li, B. Wang, M. Kurahashi, A. Pratt, and Y. Yamauchi. Significant variation of surface spin polarization through group IV atom (C, Si, Ge, Sn) adsorption on $\text{Fe}_3\text{O}_4(100)$. *Phys. Chem. Chem. Phys.*, Vol. 16, pp. 95–102, 2014.
- [39] X. Sun, A. Pratt, and Y. Yamauchi. Half-metallicity induced by boron adsorption on an $\text{Fe}_3\text{O}_4(001)$ surface. *Phys. Chem. Chem. Phys.*, Vol. 17, pp. 15386–15391, 2015.
- [40] G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel. Surface Studies by Scanning Tunneling Microscopy. *Phys. Rev. Lett.*, Vol. 49, p. 57, 1982.
- [41] J. A. Stroscio, R. M. Feenstra, and A. P. Fein. Electronic structure of the $\text{Si}(111)2\times 1$ surface by scanning tunneling microscopy. *Phys. Rev. Lett.*, Vol. 57, pp. 2579–2582, 1986.
- [42] R. M. Feenstra, J. A. Stroscio, and A. P. Fein. Tunneling spectroscopy of the $\text{Si}(111)2\times 1$ surface. *Surf. Sci.*, Vol. 181, pp. 295–306, 1987.
- [43] T. Balashov, A. F. Takacs, W. Wulfhekel, and J. Kirschner. Magnon Excitation with Spin-Polarized Scanning Tunneling Microscopy. *Phys. Rev. Lett.*, Vol. 97, p. 187201, 2006.

- [44] G. Binnig, H. Rohrer, C. Gerber, and E. Weibel. Spin-polarized electron microscopy. *Helv. Phys. Acta*, Vol. 55, p. 726, 1982.
- [45] J. A. Stroscio, R. M. Feenstra, and A. P. Fein. Local state density and long-range screening of adsorbed oxygen atoms on the GaAs(110) surface. *Phys. Rev. Lett.*, Vol. 58, pp. 1668–1671, 1987.
- [46] P. Martensson and R. M. Feenstra. Geometric and electronic structure of antimony on the GaAs(110) surface studied by scanning tunneling microscopy. *Phys. Rev. Lett.*, Vol. 39, pp. 7744–7753, 1989.
- [47] R. Wiesendanger, H. J. Güntherodt, G. Güntherodt, G. J. Gambion, and R. Ruf. Observation of vacuum tunneling of spin-polarized electrons with the scanning tunneling microscope. *Phys. Rev. Lett.*, Vol. 65, pp. 247–250, 1990.
- [48] R. Wiesendanger, I. V. Shvets, D. Bürgler, G. Tarrch, H. J. Güntherodt, J. M. D. Coey, and S. Gräser. Topographic and Magnetic-Sensitive Scanning Tunneling Microscope Study of Magnetite. *Science*, Vol. 255, pp. 583–586, 1992.
- [49] M. Bode, M. Getzlaff, and R. Wiesendanger. Spin-Polarized Vacuum Tunneling into the Exchange-Split Surface State of Gd(0001). *Phys. Rev. Lett.*, Vol. 81, pp. 4256–4259, 1998.
- [50] M. Bode, M. Getzlaff, and R. Wiesendanger. Quantitative aspects of spin-polarized scanning tunneling spectroscopy of Gd(0001). *J. Vac. Sci. Technol. A*, Vol. 17, pp. 2228–2232, 1999.
- [51] Ph. Avouris and R. Wolkow. Atom-resolved surface chemistry studied by scanning tunneling microscopy and spectroscopy. *Phys. Rev. B*, Vol. 39, , 1989.
- [52] N. D. Lang. Spectroscopy of single atoms in the scanning tunneling microscope. *Phys. Rev. B*, Vol. 34, pp. 5947–5950, 1986.

- [53] J. Tersoff and D. R. Hamann. Theory of the scanning tunneling microscope. *Phys. Rev. B*, Vol. 31, pp. 805–813, 1985.
- [54] D. K. Biegelsen, F. A. Ponce, J. C. Tramontana, and S. M. Koch. Ion milled tips for scanning tunneling microscopy. *Appl. Phys. Lett.*, Vol. 50, No. 11, 1987.
- [55] P. J. Bryant, H. S. Kim, Y. C. Zheng, and R. Yang. Technique for shaping scanning tunneling microscope tips. *Rev. Sci. Instrum.*, Vol. 58, No. 6, 1987.
- [56] G. W. Stupian and M. S. Leung. A scanning tunneling microscope based on a motorized micrometer. *Rev. Sci. Instrum.*, Vol. 60, No. 2, 1989.
- [57] I. Ekvall, E. Wahlström, D. Claesson, H. Olin, and E. Olsson. Preparation and characterization of electrochemically etched W tips for STM. *Meas. Sci. Technol.*, Vol. 10, No. 1, p. 11, 1999.
- [58] D. Kim and H. Ahn. Etching voltage control technique for electrochemical fabrication of scanning probe microscope tips. *Rev. Sci. Instrum.*, Vol. 73, No. 3, 2002.
- [59] Y. Nakamura, Y. Mera, and K. Maeda. A reproducible method to fabricate atomically sharp tips for scanning tunneling microscopy. *Rev. Sci. Instrum.*, Vol. 70, No. 8, 1999.
- [60] C. J. Chen. Introduction to Scanning Tunneling Microscopy. *Oxford University Press*, 1993.
- [61] J. P. Ibe, P. P. Bey, S. L. Brandow, R. A. Brizzolara, N. A. Burnham, D. P. DiLella, K. P. Lee, C. R. K. Marrian, and R. J. Colton. On the electrochemical etching of tips for scanning tunneling microscopy. *J. Vac. Sci. Technol. A*, Vol. 8, No. 4, 1990.
- [62] A. Subagyo, K. Sueoka, and K. Mukasa. Reconstruction and charge ordering of epitaxial $\text{Fe}_3\text{O}_4(001)$ films. *J. Magn. Magn. Mater.*, Vol. 290-291, pp. 1037–1039, 2005.

- [63] A. Subagyo, Y. Sasaki, H. Oka, and K. Sueoka. Inhomogeneous surface electronic properties and charge ordering in epitaxial Fe_3O_4 films On $\text{MgO}(001)$. *Phys. Status Solidi B*, Vol. 244, No. 12, pp. 4482–4485, 2007.
- [64] A. Ikeuchi, S. Hiura, T. Mizuno, E. Kaji, A. Subagyo, and K. Sueoka. Atomically Resolved Observations of Antiphase Domain Boundaries in Epitaxial Fe_3O_4 Films on $\text{MgO}(001)$ by Scanning Tunneling Microscopy. *Jpn. J. Appl. Phys.*, Vol. 51, No. 8S3, p. 08KB02, 2012.
- [65] S. Hiura, A. Ikeuchi, S. Shirini, A. Subagyo, and K. Sueoka. Scanning Tunneling Microscopy Study of an Altered $\text{Fe}_3\text{O}_4(001)$ Thin Films Surface by Hydrogen Adsorption. *e-J. Surf. Sci. Nanotechnol.*, Vol. 12, p. 26, 2014.
- [66] S. Hiura, A. Ikeuchi, S. Shirini, A. Subagyo, and K. Sueoka. Effect of adsorbed H atoms on the Fe electronic states of $\text{Fe}_3\text{O}_4(001)$ film surfaces. *Phys. Rev. B*, Vol. 91, p. 205411, 2015.
- [67] S. Hiura, A. Ikeuchi, S. Shirini, A. Subagyo, and K. Sueoka. Correlation between OH density and Fe electronic states of $\text{H}/\text{Fe}_3\text{O}_4(001)$ film surfaces studied by scanning tunneling microscopy/spectroscopy. *Jpn. J. Appl. Phys.*, Vol. 54, No. 8S2, p. 08LB02, 2015.
- [68] B. Stanka, W. Hebenstreit, U. Diebold, and S. A. Chambers. Surface reconstruction of $\text{Fe}_3\text{O}_4(001)$. *Surf. Sci.*, Vol. 448, No. 1, pp. 49–63, 2000.
- [69] I. V. Shvets, G. Mariotto, K. Jordan, N. Berdunov, R. Kantor, and S. Murphy. Long-range charge order on the $\text{Fe}_3\text{O}_4(001)$ surface. *Phys. Rev. B*, Vol. 70, No. 15, 2004.
- [70] R. Pentcheva, F. Wendler, H. Meyerheim, W. Moritz, N. Jedrecy, and M. Scheffler. Jahn-Teller stabilization of a “polar” metal oxide surface: $\text{Fe}_3\text{O}_4(001)$. *Phys. Rev. Lett.*, Vol. 94, No. 12, 2005.

-
- [71] R. Pentcheva, W. Moritz, J. Rundgren, S. Frank, D. Schrupp, and M. Scheffler. A combined DFT/LEED-approach for complex oxide surface structure determination: $\text{Fe}_3\text{O}_4(001)$. *Surf. Sci.*, Vol. 602, No. 7, pp. 1299–1305, 2008.
- [72] F. C. Voogt, T. Fujii, P. J. M. Smulders, L. Niesen, M. A. James, and T. Hibma. NO_2 -assisted molecular-beam epitaxy of Fe_3O_4 , $\text{Fe}_{3-\delta}\text{O}_4$, and $\gamma\text{-Fe}_2\text{O}_3$ thin films on $\text{MgO}(100)$. *Phys. Rev. B*, Vol. 60, No. 15, pp. 11193–11206, 1999.
- [73] R. Bliem, E. McDermott, P. Ferstl, M. Setvin, O. Gamba, J. Pavelec, M. A. Schneider, M. Schmid, U. Diebold, P. Blaha, L. Hammer, and G. S. Parkinson. Subsurface cation vacancy stabilization of the magnetite (001) surface. *Science*, Vol. 346, No. 6214, pp. 1215–1218, 2014.
- [74] G. S. Parkinson, Z. Novotny, P. Jacobson, M. Schmid, and U. Diebold. Room Temperature Water Splitting at the Surface of Magnetite. *J. Am. Chem. Soc.*, Vol. 133, No. 32, pp. 12650–12655, 2011.
- [75] R. M. Feenstra. Tunneling spectroscopy of the (110) surface of direct-gap III-V semiconductors. *Phys. Rev. B*, Vol. 50, p. 4561, 1994.
- [76] M. Hjort, J. Wallentin, R. Timm, A. A. Zakharov, U. Håkanson, J. N. Andersen, E. Lundgren, L. Samuelson, M. T. Borgström, and A. Mikkelsen. Surface Chemistry, Structure, and Electronic Properties from Microns to the Atomic Scale of Axially Doped Semiconductor Nanowires. *ACS Nano*, Vol. 6, No. 11, pp. 9679–9689, 2012.
- [77] H. J. Liu, J. H. G. Owen, and K. Miki. Degenerate electronic structure of reconstructed $\text{MnSi}_{1.7}$ nanowires on $\text{Si}(001)$. *J. Phys.: Condens. Matter*, Vol. 24, No. 9, p. 095005, 2012.
- [78] M. Hjort, S. Lehmann, J. Knutsson, A. A. Zakharov, Y. A. Du, S. Sakong, R. Timm, G. Nylund, E. Lundgren, P. Kratzer, K. A. Dick, and A. Mikkelsen. Electronic and Structural Differences between Wurtzite and Zinc Blende InAs

- Nanowire Surfaces: Experiment and Theory. *ACS Nano*, Vol. 8, No. 12, pp. 12346–12355, 2014.
- [79] R. M. Feenstra, Y. Dong, M. P. Semtsiv, and W. T. Masselink. Influence of tip-induced band bending on tunnelling spectra of semiconductor surfaces. *Nanotechnology*, Vol. 18, No. 4, p. 044015, 2007.
- [80] K. Jordan, A. Cazacu, G. Manai, S. F. Ceballos, S. Murphy, and I. V. Shvets. Scanning tunneling spectroscopy study of the electronic structure of Fe_3O_4 surfaces. *Phys. Rev. B*, Vol. 74, No. 8, AUG 2006.
- [81] Z. Lodziana. Surface verwey transition in magnetite. *Phys. Rev. Lett.*, Vol. 99, No. 20, 2007.
- [82] N. Mulakaluri, R. Pentcheva, M. Wieland, W. Moritz, and M. Scheffler. Partial Dissociation of Water on $\text{Fe}_3\text{O}_4(001)$: Adsorbate Induced Charge and Orbital Order. *Phys. Rev. Lett.*, Vol. 103, p. 176102, 2009.
- [83] N. Mulakaluri, R. Pentcheva, and M. Scheffler. Coverage-Dependent Adsorption Mode of Water on $\text{Fe}_3\text{O}_4(001)$: Insights from First Principles Calculations. *J. Phys. Chem. C*, Vol. 114, No. 25, pp. 11148–11156, 2010.
- [84] Z. Novotny, N. Mulakaluri, Z. Edes, M. Schmid, R. Pentcheva, U. Diebold, and G. S. Parkinson. Probing the surface phase diagram of $\text{Fe}_3\text{O}_4(001)$ towards the Fe-rich limit: Evidence for progressive reduction of the surface. *Phys. Rev. B*, Vol. 87, p. 195410, 2013.
- [85] I. Bernal-Villamil and S. Gallego. Charge order at magnetite $\text{Fe}_3\text{O}_4(001)$: surface and Verwey phase transitions. *J. Phys.: Condens. Matter*, Vol. 27, No. 1, p. 012001, 2015.
- [86] G. S. Parkinson, T. A. Manz, Z. Novotný, P. T. Sprunger, R. L. Kurtz, M. Schmid, D. S. Sholl, and U. Diebold. Antiphase domain boundaries at the $\text{Fe}_3\text{O}_4(001)$ surface. *Phys. Rev. B*, Vol. 85, p. 195450, 2012.

- [87] N. Ishida, M. Jo, T. Mano, Y. Sakuma, T. Noda, and D. Fujita. Direct visualization of the N impurity state in dilute GaNAs using scanning tunneling microscopy. *Nanoscale*, Vol. 7, pp. 16773–16780, 2015.
- [88] V. Chandra, J. Park, Y. Chun, J. W. Lee, I. Hwang, and K. S. Kim. Water-Dispersible Magnetite-Reduced Graphene Oxide Composites for Arsenic Removal. *ACS Nano*, Vol. 4, No. 7, pp. 3979–3986, 2010.
- [89] T. Kendelewicz, P. Liu, C. S. Doyle, G. E. Brown Jr., E. J. Nelson, and S. A. Chambers. Reaction of water with the (100) and (111) surfaces of Fe_3O_4 . *Surf. Sci.*, Vol. 453, No. 13, pp. 32–46, 2000.
- [90] M. Setvin, X. Hao, B. Daniel, J. Pavelec, Z. Novotny, G. S. Parkinson, M. Schmid, G. Kresse, C. Franchini, and U. Diebold. Charge Trapping at the Step Edges of TiO_2 Anatase (101). *Angew. Chem. Int. Ed.*, Vol. 53, No. 18, pp. 4714–4716, 2014.

Publication List

- (1) A. Ikeuchi, S. Hiura, T. Mizuno, E. Kaji, A. Subagyo, and K. Sueoka: “Atomically Resolved Observations of Antiphase Domain Boundaries in Epitaxial Fe_3O_4 Films on $\text{MgO}(001)$ by Scanning Tunneling Microscopy”, *Jpn. J. Appl. Phys.* 51, 08KB02 (2012).
- (2) T. Mizuno, H. Hosoi, A. Subagyo, S. Oishi, A. Ikeuchi, S. Hiura, and K. Sueoka: “Noncontact Atomic Force Microscopy Observation of $\text{Fe}_3\text{O}_4(001)$ Surface”, *Jpn. J. Appl. Phys.* 51, 08KB03 (2012).
- (3) S. Hiura, A. Ikeuchi, S. Shirini, A. Subagyo, and K. Sueoka: “Scanning Tunneling Microscopy Study of an Altered $\text{Fe}_3\text{O}_4(001)$ Thin Films Surface by Hydrogen Adsorption”, *e-J. Surf. Sci. Nanotech.* 12, 26 (2014).
- (4) S. Hiura, A. Ikeuchi, S. Shirini, A. Subagyo, and K. Sueoka: “Effect of adsorbed H atoms on the Fe electronic states of $\text{Fe}_3\text{O}_4(001)$ film surfaces”, *Phys. Rev. B* 91, 205411 (2015).
- (5) S. Hiura, A. Ikeuchi, S. Shirini, A. Subagyo, and K. Sueoka: “Correlation between OH density and Fe electronic states of $\text{H}/\text{Fe}_3\text{O}_4(001)$ film surfaces studied by scanning tunneling microscopy/spectroscopy”, *Jpn. J. Appl. Phys.* 54, 08LB02 (2015).
- (6) S. Hiura, A. Ikeuchi, M. Jochi, R. Yamazaki, S. Takahashi, A. Subagyo, and K. Sueoka: “Direct observation of subsurface charge ordering in $\text{Fe}_3\text{O}_4(001)$ by scanning tunneling microscopy/spectroscopy”, to be submitted.
- (6) S. Hiura, M. Jochi, R. Yamazaki, S. Takahashi, A. Subagyo, and K. Sueoka:

“Direct visualization of the occupied states near the Fermi level in H/Fe₃O₄(001) surface using scanning tunneling microscopy”, in preparation.

International Conference

- (1) Y. Okabe, S. Hiura, A. Ikeuchi, A. Subagyo, and K. Sueoka: “Origin of negative differential conductance observed on Cs adsorbed InAs(110) surfaces”, International Scanning Probe Microscopy Conference (ISPM 2011), p.86, P14, Munich, Germany, June, 2011.
- (2) S. Hiura, A. Ikeuchi, A. Subagyo, and K. Sueoka: “Difference in electronic states between clean and modified $\text{Fe}_3\text{O}_4(001)$ thin film surfaces”, The 20th International Colloquium on Scanning Probe Microscopy (ICSPM20), S3-53, p.91, Naha, Japan, December, 2012.
- (3) S. Hiura, A. Ikeuchi, A. Subagyo, and K. Sueoka: “Change of electronic states induced by hydrogen adsorption in $\text{Fe}_3\text{O}_4(001)$ thin films surface”, The 12th Asia Pacific Physics Conference (APPC12), A1-PWe-10, p.223, Chiba, Japan, July, 2013.
- (4) S. Hiura, A. Ikeuchi, A. Subagyo, and K. Sueoka: “STM/STS studies of modified magnetite thin films surface on $\text{MgO}(001)$ substrate”, International Conference on Nanoscience and Technology (ICN+T 2013), SS-P1-17, p.83, Paris, France, September, 2013.
- (5) S. Hiura, A. Ikeuchi, S. Shirini, A. Subagyo, and K. Sueoka: “Structural and Electronic Properties of a Modified $\text{Fe}_3\text{O}_4(001)$ Films Surface”, 12th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-12) & 21th International colloquium on Scanning Probe Microscopy (ICSPM21), 7PN-111, p.190, Tsukuba, Japan, November, 2013.
- (6) S. Hiura, A. Ikeuchi, A. Subagyo, and K. Sueoka: “Atomic structures and local electronic properties of modified $\text{Fe}_3\text{O}_4(001)$ film surfaces”, The 59th Annual

Magnetism and Magnetic Materials (MMM) Conference, GU-07, p.261, Hawaii, USA, November, 2014.

- (7) S. Hiura, A. Ikeuchi, A. Subagyo, and K. Sueoka: “Effect of adsorbed-H atoms on Fe atoms in $\text{Fe}_3\text{O}_4(001)$ film surfaces”, 22nd International Colloquium on Scanning Probe Microscopy (ICSPM22), S4-7, p.45, Atagawa, Japan, December, 2014.
- (8) S. Hiura, M. Jochi, A. Subagyo, and K. Sueoka: “Scanning tunneling microscopy /spectroscopy study of magnetite film surface: Effect of hydrogen atoms on the surface structural and electronic properties”, JSPS workshop on Japan-Sweden frontiers in spin and photon functionalities of semiconductor nanostructures, Jozankei, Japan, August, 2016.
- (9) S. Hiura, R. Yamazaki, M. Jochi, S. Takahashi, A. Subagyo, and K. Sueoka: “Scanning Tunneling Spectroscopy Study of $\text{H}/\text{Fe}_3\text{O}_4(001)$ Surface”, 24th International Colloquium on Scanning Probe Microscopy (ICSPM24), accepted for presentation.

Domestic Conference

- (1) 樋浦諭志, 岡部泰志, 池内昭朗, Agus Subagyo, 末岡和久: “Cs/InAs(110) 表面に見られる微分コンダクタンスの探針依存性”, 第 72 回応用物理学会秋季学術講演会, 30a-ZC-5, 山形, 2011 年 8 月.
- (2) 樋浦諭志, 池内昭朗, Agus Subagyo, 末岡和久: “Fe₃O₄(001) 薄膜表面に見られる吸着構造の STM/STS 測定”, 第 73 回応用物理学会秋季学術講演会, 11a-PA3-1, 松山, 2012 年 9 月.
- (3) S. Hiura, A. Ikeuchi, A. Subagyo, and K. Sueoka: “STM/STS measurements of a modified epitaxial grown Fe₃O₄(001) films surface”, 第 11 回スピントロニクス入門セミナー・若手研究会, P11, 札幌, 2012 年 12 月.
- (4) 樋浦諭志, 池内昭朗, シリニ・ソライヤ, スバギョ・アグス, 末岡和久: “表面修飾された Fe₃O₄(001) 薄膜表面の STM/STS 測定”, 第 37 回日本磁気学会学術講演会, 5pD-1, 札幌, 2013 年 9 月.
- (5) 樋浦諭志, 池内昭朗, Shirini Soraya, Subagyo Agus, 末岡和久: “吸着水素により誘起された Fe₃O₄(001) 表面の局所電子状態測定”, 平成 25 年度日本表面科学会東北・北海道支部学術講演会, P-06, 仙台, 2014 年 3 月.
- (6) 樋浦諭志, 池内昭朗, Shirini Soraya, Subagyo Agus: “Fe₃O₄(001) 薄膜表面における吸着水素により誘起された鉄イオン還元”, 第 61 回応用物理学会春季学術講演会, 18p-PG9-4, 相模原, 2014 年 3 月.
- (7) 樋浦諭志, 池内昭朗, Subagyo Agus, 末岡和久: “水素吸着による Fe₃O₄(001) 表面の局所電子状態変化の研究”, 第 75 回応用物理学会秋季学術講演会, 18p-PA8-2, 札幌, 2014 年 9 月.
- (8) 樋浦諭志, 池内昭朗, Shirini Soraya, 城地雅史, Subagyo Agus, 末岡和久: “STM/STS による水素吸着 Fe₃O₄(001) 薄膜表面の局所電子状態測定”, 第 76 回応用物理学

会秋季学術講演会, 16a-2U-5, 名古屋, 2015 年 9 月.

- (9) 樋浦諭志, 山崎陸, 城地雅史, 高橋聡太郎, Subagyo Agus, 末岡和久: “H/Fe₃O₄(001) 表面におけるフェルミ準位直下の局所状態密度測定”, 第 63 回応用物理学会春季学術講演会, 21p-H113-1, 東京, 2016 年 3 月.