電子および磁気構造の研究を対象としたFe-N原子層膜の研究

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Electronic and magnetic structures of iron-nitride atomic layers on Cu(001)

(Cu(001)基板上鉄窒化物原子層膜の電子・磁気構造の研究)

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Abstract

Iron nitride in iron-rich phases is known to possess rich ferromagnetism such as large saturation magnetization and high magnetic anisotropy, and thus expected to replace existing neodymium magnet as a rare-earth free alternate. The growth in a single phase has been a long-standing problem for iron nitride, which hinders a full characterization of intrinsic physical properties. Recently, the successful epitaxial growth of single-phase $\gamma'$-Fe$_4$N has been reported, and macroscopic properties of the system can be understood in terms of the strong hybridization between Fe and N states. Meanwhile, site-selective electronic and magnetic states as well as its interplay with structure/dimensionality of $\gamma'$-Fe$_4$N has remained elusive for lack of a detailed study in an atomic-layer limit.

In the present work, we establish a growth method and characterize the electronic/magnetic structures of $\gamma'$-Fe$_4$N atomic layers on Cu(001). First, we conduct detailed scanning tunneling microscopy (STM) measurements on the monolayer $\gamma'$-Fe$_4$N/Cu(001), to elucidate the nature of an Fe$_2$N plane in $\gamma'$-Fe$_4$N. The observed topographic images drastically change depending on a tip-surface distance unlike in pure transition-metal systems. This is attributed to a spatial variation in local density of states in a vacuum side, leading to the shift in an orbital character of the states dominantly detected by the tip with respect to the distance. More generally, this observation could be the first experimental demonstration of the orbital-selective tunneling process inherent in any STM measurements.

A large overlap between the Fe and N states possibly leads to the itinerant electronic states of the monolayer $\gamma'$-Fe$_4$N. This in fact renders the ferromagnetism of the sample sensitive to an atomic structure, namely, degree of surface lattice ordering as discussed in the next part. It turns out that an atomic point defect modulates the surrounding electronic structures in a large area, resulting in deterioration of the ideal sample ferromagnetism. This emphasizes the significant impact of a structural imperfection in an atomic scale on the entire physical properties of the system, which is previously overlooked in macroscopic observations on ferromagnet.

Finally, we report the growth of ordered multilayer $\gamma'$-Fe$_4$N on Cu(001). The strong two-dimensionality originating from the Fe-N hybridization enables a precise stacking of $\gamma'$-Fe$_4$N even in an atomic-layer limit, which makes it possible to scrutinize the layer-by-layer electronic and magnetic states realized in $\gamma'$-Fe$_4$N. The thickness dependence of the electronic structures and magnetic moments of the system has been investigated in detail, the origin of which is perfectly interpreted with the help of first-principle calculations.
Contents

1 Introduction 1

1.1 Background 1
1.1.1 Transition metal 1
1.1.2 3d transition metal nitride 2
1.1.3 Iron nitride $\gamma'$-$\text{Fe}_4\text{N}$ 2
1.2 Purpose of the present study 4

2 Experimental methods 7

2.1 X-ray absorption spectroscopy 7
2.2 X-ray magnetic circular dichroism 8
2.3 Scanning tunneling microscopy and spectroscopy 10
2.3.1 Theory of tunneling 10
2.3.2 Tersoff-Hamann model 10

3 Measurement systems 13

3.1 STM and preparation chamber 13
3.2 UVSOR BL 4B 14
3.3 Sample preparation 15
3.3.1 Substrate cleaning 15
3.3.2 Nitrogen bombardment 16
3.3.3 Iron deposition 16

4 Orbital-selective tunneling process observed in monolayer Fe$_2$N on Cu(001) 17

4.1 Introduction 17
4.2 Experiment 18
4.3 Results and Discussion 19
4.4 Conclusion 26

5 Impact of atomic defects on the macroscopic ferromagnetism of monolayer Fe$_2$N on Cu(001) 27
6 Thickness-dependent electronic and magnetic properties of $\gamma'$-Fe$_4$N multilayers on Cu(001) 29

Appendix
A Simulation of simple broadening for surface wave functions . . . . 31
B Estimated values of work function . . . . . . . . . . . . . . . . . . 34

Summary 35

Acknowledgments 37

References
Chapter 1

Introduction

1.1 Background

1.1.1 Transition metal

Transition metal (TM) exhibits rich physical properties originating from unpaired electrons in $d$ shells [1]. An elemental TM possesses a high crystallinity with either the body-centered cubic (bcc), face-centered cubic (fcc), or hexagonal close-packed (hcp) structure at room temperature (RT) and ambient pressure [2]. Compared with typical metals, TMs in a bulk form show fruitful properties such as high melting point and superconducting transition temperature, and a wide variety of magnetism [3–5]. The ground state of almost all the TMs is paramagnetic at ambient pressure. Meanwhile, Fe, Co, and Ni in the $3d$ group are known to show a spontaneous ferromagnetic ordering in an elemental form, with magnetic moments of a couple $\mu_B$/atom (where $\mu_B$ is Bohr magneton) and Curie temperature far above RT [6]. The robust ferromagnetism of $3d$ TMs, in addition to cheapness and abundance as resources, has attracted much interest in terms of both basic research and application. Furthermore, the nature of $d$ orbitals, represented by moderate localization and relatively small spin-orbit coupling compared to outer orbitals, renders physical properties of $d$-electron systems sensitive to surroundings, e.g. an atomic coordination, crystal field, or hybridization with the neighboring states [7]. This, in other words, makes it easy to tailor the electronic and magnetic properties by changing composition, combination, or dimension of the materials. In fact, lots of novel findings recently discovered in the field of magnetism are related to the spin-polarized nature of $3d$-TM-based ferromagnets: giant, tunneling, and colossal magnetoresistance effects [8–13], as well as large magnetic anisotropy of neodymium and $L1_0$-ordered magnets [14–17].
1.1.2 3d transition metal nitride

3d TMs tend to form a strong bonding to light elements with large electronegativity. It has been widely reported that the nitridation of 3d TMs not only improves chemical stability of the elements, but possibly adds another function to the system [18]. The theoretical observation anticipates that all the 3d TMs except for Cu and Zn can form relatively stable nitride in the composition of TM$_4$N with either a cubic or tetragonal crystal structure$^1$; the magnetism of the ground states ranges from nonmagnetic, ferrimagnetic, to ferromagnetic [19]. In particular, ferromagnetic TM$_4$N (TM = Mn, Fe, Co) has been under intense research because of the perpendicular magnetic anisotropy (Mn$_4$N) [20–22], high spin polarization and large saturation magnetization $M_s$ (Fe$_4$N, Co$_4$N) [23–26]. Further, these ferromagnetic TM$_4$N can be epitaxially grown on common substrates of LaAlO$_3$(001), MgO(001), or SrTiO$_3$(001) [22, 23, 27, 28]. Such a good epitaxy with the substrate possibly facilitates a precise control of the system dimension from a bulk, film to atomic-layer limit, in which the peculiar electronic and magnetic states are realized in 3d-TM-based ferromagnets [29–36].

1.1.3 Iron nitride $\gamma'$-Fe$_4$N

Figure 1.1: Basics of $\gamma'$-Fe$_4$N on Cu(001). (a) Bulk crystal structure of $\gamma'$-Fe$_4$N. A dotted parallelogram represents an Fe$_2$N plane. (b) Schema of $p4g(2 \times 2)$ surface reconstruction. From an unreconstructed $c(2 \times 2)$ coordination (dotted circles), each two of Fe atoms dimerizes in two perpendicular directions indicated by arrows. For (a) and (b), large (small) spheres represent Fe (N) atoms. (c) Atomically-resolved image (2.5 $\times$ 2.5 nm$^2$, sample bias $V_s = 0.25$ V, tunneling current $I = 45$ nA) of the surface-reconstructed Fe$_2$N plane. The dimerization of Fe atoms is indicated by encirclement. (d) LEED pattern with the $p4g(2 \times 2)$ symmetry, taken with the incident electron energy of 100 eV.

---

$^1$The metastability of TM$_4$N (TM = Cu, Zn) arises from the fully-occupied 3d shell of the TM elements.
1.1. Background

Among all the TM$_4$N, Fe$_4$N is theoretically expected to be most energetically stable with a so-called $\gamma'$-type crystal structure [19], in which one N atom occupies the center of the fcc Fe lattice as shown in Fig. 1.1(a). Due to a small lattice mismatch between the bulk crystals of $\gamma'$-Fe$_4$N (3.80 Å) and Cu(001) (3.62 Å) [37, 38], the $\gamma'$-Fe$_4$N can be epitaxially grown on metallic Cu(001). The topmost layer of the $\gamma'$-Fe$_4$N/Cu(001) is known to always consist of the Fe$_2$N plane in a bulk Fe$_4$N crystal structure [38–40]. Accordingly, the surface Fe$_2$N plane takes reconstruction to the $p4g(2 \times 2)$ coordination, in which the Fe atoms dimerize in two perpendicular directions as illustrated in Fig. 1.1(b). The $p4g(2 \times 2)$ coordination gains total energy in the ferromagnetic ground states, while the nonmagnetic ground states prefers the original $c(2 \times 2)$ coordination [38]. This surface reconstruction can be visualized directly by STM imaging as shown in Fig. 1.1(c), and the corresponding low energy electron diffraction (LEED) pattern of the surface is also observed [Fig. 1.1(d)].

Under the coordination shown in Fig. 1.1(a), two non-equivalent Fe sites FeI and FeII exist, those without and with a bonding to a N atom, respectively. The difference in the site results in the different electronic and magnetic states: FeI and FeII have an electron configuration of 3$d^7$4$s$ and 3$d^8$4$s$, as well as the magnetic moment of 3 $\mu_B$ and 2 $\mu_B$, respectively [37, 42]. The spin-polarized band calculation in Ref. 41 emphasizes the site dependence of the local density of states (DOS) as shown in Fig. 1.2. At the FeI site, the up-spin band is almost fully-occupied while contains some holes at the Fe FeII site. In contrast to nearly the same occupation into the up-spin band, the number of the down-spin electrons at the FeI and FeII sites are

Figure 1.2: Local DOS calculated for (a) FeI and (b) FeII sites of Fe$_4$N presented in Ref. 41. The Fermi energy is indicated by vertical arrows.
2.3 and 3.2, respectively. Therefore, the electrons occupied in the down-spin band is responsible for the inequality of the electronic population.

The previous experiments report $M_s$ of 2.3 $\mu_B$/atom for the bulk $\gamma'$-Fe$_4$N [42], comparable to that of 2.2 $\mu_B$/atom for a pristine bulk Fe [37]. The theoretical study points out almost full spin polarization around the Fermi energy $E_F$ [43], which has already been applied to magnetic tunneling junctions revealing large inverse tunnel magnetoresistance effect [26]. Thin films of the $\gamma'$-Fe$_4$N show an in-plane easy magnetization [44, 45] in contrast to metastable fcc Fe with a complex spin-spiral structure in the ground state [36, 46]. This difference in the magnetic structure apparently originates from the nitridation of the Fe atoms, which leads to a strong mixing between Fe and N states of the $\gamma'$-Fe$_4$N [19]. This hybridization turns out to be responsible for the unique electronic and magnetic states realized in the $\gamma'$-Fe$_4$N.

### 1.2 Purpose of the present study

In bulk and thick-film forms, $\gamma'$-Fe$_4$N samples with a high crystallinity can be obtained by molecular beam epitaxy [27] or an Fe deposition under a flux of N from a rf source [38, 39]. A good quality of the samples has made it possible to investigate macroscopic properties of the thick $\gamma'$-Fe$_4$N. On the other hand, for lack of a growth method for ordered $\gamma'$-Fe$_4$N atomic layers, the relationship between structure/dimensionality and the electronic/magnetic states has not been revealed so far in element- and site-selective manners.

In the present study, we succeed in fabricating well-ordered atomic layers of $\gamma'$-Fe$_4$N on a Cu(001) substrate, and conduct a full characterization of the physical properties by utilizing scanning tunneling microscopy/spectroscopy (STM/STS), x-ray absorption spectroscopy/magnetic circular dichroism (XAS/XMCD), and first-principles calculations. A complementary study from both microscopic and macroscopic points of views not only gives novel findings on the electronic and magnetic structures realized in the $\gamma'$-Fe$_4$N atomic layers on Cu(001), but fills the gap between past observations on the present system.

The previous STM works on the $\gamma'$-Fe$_4$N/Cu(001) report different topographic images with the $p4g(2 \times 2)$ [38] and $c(2 \times 2)$ [45] symmetry irrespective of the same surface structures confirmed by the LEED observations. This discrepancy between the images, possibly originating from the difference in the detected electronic structures, can be fully understood by the orbital-selective tunneling process in the STM measurement discussed in Chap. 4. As for the magnetism of the monolayer $\gamma'$-Fe$_4$N/Cu(001), the past XAS/XMCD study reports ferromagnetism with much small magnetic moments compared to the theoretical expectation [45]. The reason for the observed drop in the magnetic moments is clarified by atomically-
resolved STS observations in Chap. 5, which demonstrates the extensive impact of an atomic-scale disorder on the surrounding electronic structures. Finally, in Chap. 6, we present a new growth method to prepare the $\gamma'$-Fe$_4$N atomic layers on Cu(001), and discuss the origin of the thickness-dependent electronic and magnetic properties of the system.
2.1 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is a conventional technique utilizing the photon absorption and subsequent excitation of core electrons into unoccupied states. Combined with an energy-tunable light produced from synchrotron radiation source, this technique can extract detailed information on the sample electronic structures at specific absorption edges. The process of the photon absorption is dominated by the dipole transition, whose intensity \( I(\hbar\nu) \) is given by the following formula.

\[
I(\hbar\nu) = \sum_f |\langle f | T | i \rangle|^2 \delta(E_i - E_f - \hbar\nu),
\]

where \( \hbar\nu \) is a photon energy of the incident x-ray, \( T \) a dipole-transition operator, \(|i\rangle\) \((|f\rangle)\) the initial (final) state and the corresponding energy of the state, respectively. According to Eq. 2.1, it is clear that the transitions accompanied by a change of the angular momentum by \( \pm 1 \) can have a main contribution to \( I(\hbar\nu) \). Figure 2.1(a) represents an absorption process between the \( 2p \) and \( 3d \) states for \( 3d \) TMs. Due to the strong spin-orbit coupling originating from \( 2p \) holes created by the photon absorption, total spin and orbital angular momenta themselves are no longer good quantum numbers. Instead, the \( 2p \) states can be labeled with total angular momentum \( J = 1/2 \) and \( 3/2 \). Accordingly, an absorption spectrum reveals two major peaks at so-called \( L_{2,3} \) \((2p_{1/2,3/2} \rightarrow 3d) \) edges as shown in Fig. 2.1(b). The intensity of an experimental background can be expressed by a superposition of two arc-tangents in a common manner [47]. It should be noted that a XAS spectrum at the \( L_{2,3} \) edges reflects the electronic structures of the final \( 3d \) states in the vicinity of the \( E_F \), because the initial states in the \( 2p \) core level are well described by atomic orbitals. In the present study, the absorption spectroscopy is operated in the total-electron yield (TEY) mode, which detects drain current from the sample generated by irradiation of the incident soft x-ray. The TEY mode has the potential probing.
depth of \( \sim 5 \) nm from the surface, which is determined mainly by the mean free path in the energy range of the soft x-ray [48]. Therefore, the measurement in the TEY mode is quite surface-sensitive.

![Figure 2.1: Principle of XAS. (a) Schematic diagram of electron excitation from the 2\( p \) core levels to the 3\( d \) bands. (b) Typical absorption spectrum at the \( L_{2,3} \) edges of 3\( d \) TMs. A dotted line represents an absorption background.](image)

2.2 X-ray magnetic circular dichroism

Combined with circularly polarized x-ray, the information on the sample magnetism can be extracted from the XAS measurement. For ferromagnetic materials in which the 3\( d \)-band occupation differs depending on the spin channel, the photon absorption process varies with respect to the relative direction between the photon helicity and 3\( d \) majority spin, as shown in Fig. 2.2(a). This originates from that the right (left)-handed circularly polarized light has the angular momentum of +1 (-1), and then the transition obeys the selection rules. Two absorption spectra toward different circular polarization are distinguished as \( \mu_+ \) and \( \mu_- \), and those difference \( \mu_+ - \mu_- \) is defined as x-ray magnetic circular dichroism (XMCD). In Fig. 2.2(b), typical XAS and XMCD spectra at the \( L_{2,3} \) edges of 3\( d \) TMs are presented. The important is that this technique possesses an element specificity, which arises from an element-dependent energy range of absorption edges. Unlike conventional techniques for the characterization of magnetism, this allows us to extract a particular
magnetic component even when measuring a material composed of more than two magnetic elements. Further, by applying XMCD sum rules [49, 50] to the experimental XAS and XMCD spectra, we can separately estimate the quantitative values of the spin ($M_{\text{spin}}$) and orbital ($M_{\text{orb}}$) magnetic moments, according to the following equations.

$$M_{\text{orb}} = -\frac{4}{3} \int_{L_3+L_2} (\mu_+ - \mu_-) d\nu (10 - n_d), \quad (2.2)$$

$$M_{\text{spin}} + 7M_T = -\frac{6}{\int_{L_3+L_2} (\mu_+ + \mu_-) d\nu} \int_{L_3+L_2} (\mu_+ - \mu_-) d\nu (10 - n_d), \quad (2.3)$$

where integration is conducted with respect to the photon energy $h\nu$ over the $L_3$ and/or $L_2$ edges, and $n_d$ is the number of $3d$ electrons. The $M_T$ term is related to the magnetic dipole moment, which originates from the anisotropy of $M_{\text{spin}}$ [51] and can be neglected when the spectra are measured in the geometry at "magic angle" [52].
2.3 Scanning tunneling microscopy and spectroscopy

2.3.1 Theory of tunneling

The quantum mechanics allows the tunneling of electrons through a potential barrier, even when their energy is lower than the barrier height. The most simplified model is that the electrons pass through a one-dimensional potential barrier (height $V_0$, width $w$) as presented in Fig. 2.3. The electrons, coming from Region I and impinging on the potential barrier in Region II, can exist in Region III with a finite probability. A wave function of the electrons $\Psi(r)$, whose probability density to be located at a position $r$ corresponds to $|\Psi(r)|^2$, obeys the time-independent Schrödinger equation in a stationary limit [53]:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r) - E\right] \Psi(r) = 0 \quad (2.4)$$

$$V(r) = \begin{cases} V_0 & \text{(Region II)} \\ 0 & \text{(Region I, III)} \end{cases} \quad (2.5)$$

where $\hbar$ is the reduced Planck constant, $m$ the mass of the electron, $V(r)$ potential, and $E$ the energy of the electrons. A general solution of this equation is in the following form:

$$\Psi(r) = Ae^{ikr} + Be^{-ikr}, \text{ where } k = \sqrt{\frac{2m|V(r) - E|}{\hbar}}. \quad (2.6)$$

Under boundary conditions at the interface between the regions, the transmission probability $T$, in proportion to the tunneling current $I$, can be calculated as

$$T \propto e^{-2\kappa w}, \text{ where } \kappa = \sqrt{\frac{2m|V_0 - E|}{\hbar}}. \quad (2.7)$$

This fast dumping of $T$ through the potential barrier clearly leads to the sensitivity of the STM measurement to a tip-surface distance.

2.3.2 Tersoff-Hamann model

To extract the information on the electronic structures of the sample surface from the STM measurement, it is convenient to make some assumption on the tip state. Within the first-order perturbation theory, $I$ is expressed as follows [54]:

$$I = \frac{2\pi e}{\hbar} \sum_{\mu, \nu} |f(E_\mu)| \{1 - f(E_\nu + eV_s)\} - f(E_\nu + eV_s) \{1 - f(E_\mu)\}$$

$$\times |M_{\mu\nu}|^2 \delta(E_\mu - E_\nu), \quad (2.8)$$
2.3. Scanning tunneling microscopy and spectroscopy

Figure 2.3: Tunneling through the potential. The decay of the electron wave function $\Psi$ via the potential barrier is illustrated.

where $f(E)$ is the Fermi distribution function, $E_{\mu,\nu}$ the energies for wave functions $\Psi_{\mu,\nu}$ of two electrodes, $V_s$ bias applied between electrodes. Note that, in the actual STM measurement, one of the electrode corresponds to the tip and the other the sample surface. $M_{\mu,\nu}$ is the tunneling matrix element determined from an overlap between the wave functions $\Psi_{\mu}$ and $\Psi_{\nu}$. According to the Bardeen’s theory [55], its numerical expression is

$$M_{\mu,\nu} = -\frac{\hbar^2}{2m} \int dS \cdot (\Psi_{\mu}^{*} \nabla \Psi_{\nu} - \Psi_{\nu} \nabla \Psi_{\mu}^{*}) , \quad (2.9)$$

where integral is over any surface within the barrier region. Tersoff and Hamann assumed $s$-type wave functions for the tip, and then $M_{\mu,\nu}$ becomes simply a function of local density of states (LDOS) of the sample [56, 57]. In a low $V_s$ limit, $I$ can be a reduced expression of

$$I \propto \int_{0}^{eV_s} \rho_s(r_0, E) \rho_t(\pm eV_s \pm E) dE , \quad (2.10)$$

where $\rho_s(r_0, E)$ corresponds to the DOS at the position of the tip center $r_0$, and $\rho_t$ the DOS of the tip. Here, all the energies are measured with respect to the $E_F$. This relationship tells that the sample LDOS integrated to the measurement voltage can be a counterpart of what measured in the STM. Under the WKB approximation [58], the following expression can be obtained:

$$I \propto \int_{0}^{eV_s} \rho_t(\pm eV_s \mp eV_s) \rho_s(E) \cdot T \quad (2.11)$$

$$T \approx \exp \left[ -2(s + R) \sqrt{\frac{2m}{\hbar}} \left( \frac{\Phi_s + \Phi_t}{2} + \frac{eV_s}{2} - E \right) \right] . \quad (2.12)$$
where $s$ is distance of nearest approach, $R$ radius of curvature for a tip apex, and $\Phi_s (\Phi_t)$ a work function of the sample (tip). Within a common approximation of a constant DOS for the tip, the differential conductance $dI/dV_s$ reflects the sample LDOS.

![Diagram](image.png)

Figure 2.4: Simplified model for the tip. (a) Tip assumed in the Tersoff-Hamann model. The center of the tip, radius of curvature, and nearest approach are labelled with $r_0$, $R$, and $s$, respectively. (b) Tunneling model in the STM measurement assuming the constant LDOS of the tip.
Chapter 3

Measurement systems

3.1 STM and preparation chamber

STM measurements were performed under ultrahigh vacuum (UHV) condition ($< 3.0 \times 10^{-11}$ Torr) using Scienta Omicron STM equipped with cryostat, operated at 4 K with LHe cooling [Fig. 3.1(a)] and 77 K with LN$_2$ one [Fig. 3.1(b)]. A good UHV condition could be achieved by a basic pumping with rotary and turbomolecular pumps, in combination with ion and titanium-sublimation pumps for a further improvement in pressure. All the processes needed for a sample preparation including a surface cleaning, nitrogen bombardment, iron deposition and subsequent annealing were conducted in the UHV preparation chamber ($< 1.0 \times 10^{-10}$ Torr).
Torr). The sample grown in the preparation chamber was transferred into the STM chamber without breaking UHV (namely, *in-situ* measurement). A sharp tip, made of tungsten wire and chemically etched with sodium hydroxide solution, was used for the STM measurement. The tip apex was cleaned by sputtering with Ar$^+$ ions and heated by electron bombardment to obtain an acute and stable tip configuration. For the STS measurement, the differential conductance $dI/dV$ was recorded using a conventional lock-in technique with a bias-voltage modulation of several tens mV and 700-900 Hz.

### 3.2 UVSOR BL 4B

For the element-specific XAS/XMCD measurements, an energy-tunable x-ray emitted from a synchrotron light source is indispensable. Here, all the synchrotron-based measurements were performed using BL 4B at Ultra Violet Synchrotron Orbital Radiation (UVSOR)-III, the facility of the Institute for Molecular Science, Okazaki, Japan. This beamline can acquire a high energy resolution of $E/\Delta E > 5000$ in the soft x-ray range, by adopting a varied-line-spacing plane grating monochromator (VLS-PGM) based on the Hetrick-type design [59, 60] as shown in Fig. 3.2. The degree of circular polarization was $\sim 65\%$ during our experiments, determined by measuring reference ferromagnetic samples. The x-ray propagation vector lay within the (110) plane of the Cu(001) substrate. A XMCD chamber installed at BL 4B is presented in Fig. 3.3. The main measurement system is equipped with a split multifilamentary NbTi superconducting magnet [61]. Magnetic field $B$ up to $\pm 5$ T can be applied to the sample in the direction parallel to an incident x-ray. By
rotating the sample manipulator, we could perform the XMCD measurement in any incidence at an angle $\theta$, where $\theta$ is defined as the angle between the sample normal and incident x-ray. For the investigation of magnetic anisotropy, the spectra were recorded mainly in the normal ($\theta = 0^\circ$) and grazing ($\theta = 55^\circ$) incidence. The latter corresponds to the measurement at the magic angle discussed above [52]. The sample was prepared in the UHV preparation chamber connected to the measurement chamber [Fig. 3.3(a)]. An all-in-one sample manipulator is equipped in the preparation chamber, at which all the preparation and characterization can be done without extra transferring. During the annealing of the sample, temperature was monitored with a thermocouple located close to the substrate. The sample surface could be characterized using any of LEED, reflection high-energy electron diffraction, and Auger electron spectroscopy. All the measurements were performed at $\sim 8$ K with a LHe cooling.

Figure 3.3: XMCD measurement system in BL 4B at UVSOR. Schema (a) and actual view (b) of the system are presented [61].

### 3.3 Sample preparation

#### 3.3.1 Substrate cleaning

A clean surface of the Cu(001) substrate was prepared in the following steps: First, a single crystal of Cu(001) was chemically etched in a mixed solution of methanol and nitric acid. The cleaned single crystal was mounted on a molybdenum sample holder, fixed with tantalum wires as shown in Fig. 3.4. After introducing the sample
inside the UHV preparation chamber, the cycles of sputtering with Ar$^+$ ions and subsequent annealing at 800 K were repeated several times. The cleanness of the Cu surface was finally checked by a direct imaging with STM, as well as the sharp spots observed in a LEED pattern.

3.3.2 Nitrogen bombardment

Nitrogen ions, with an energy of 0.5 keV, were implanted to the surface by means of bombardment using a commercial ion gun (ULVAC-PHI). The bombardment was conducted under a pressure of $\sim 2.0 \times 10^{-5}$ Torr, typically for 15 min. The ion current could be measured through electrodes touching to the sample holder, so that the amount of the implanted nitrogen ions was checked to be enough to saturate the Cu surface.

3.3.3 Iron deposition

Iron was deposited at room temperature (RT) from a high-purity Fe rod (99.998 %) using an EFM evaporator (FOCUS). Thermal electrons emitted from a tungsten filament inside the evaporator were designed to focus on an Fe rod apex, and heated Fe started to be evaporated with a finite flux monitored by the electronics. The deposition rate was almost the same during every deposition, estimated to be $\sim 0.2$ ML/min. Note that monolayer was defined with respect to the density of surface Cu atoms of the Cu(001) crystal.
Chapter 4

Orbital-selective tunneling process observed in monolayer Fe$_2$N on Cu(001)

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4.1 Introduction

Scanning tunneling microscopy (STM) is one of the most powerful tools to investigate surface topographic and electronic structures with an atomic resolution. Surface nanostructures are often discussed based on the topographic image. However, its image contrast mainly reflects the electron tunneling processes between the STM tip and the surface orbitals at each position, i.e., local electronic states [57]. As a consequence, the image does not always correspond to the real surface morphology [62, 63]. Systematic changes of the image contrast as a function of the sample-bias voltage $V_s$ have been widely interpreted in terms of energy-dependent electronic structures [64–66]. The STM tip-surface distance $d$ is the alternative for the image change. The strength of the STM tip-sample interaction changes at different $d$, which can occasionally cause the image variation [67, 68]. The $d$-dependent image change can be also expected for the surface consisted of several orbitals with different decay length of the wave function into the vacuum, e.g. compound systems. In such systems, the image change could be induced by the shift of the dominant surface orbital contributing to the tunneling process at different $d$, while a certain surface state usually dominates throughout the vacuum region for elemental systems.
The importance of this orbital selective tunneling process on the $d$-dependent images was suggested for O/Ru(0001), O/Fe(001) and the rutile TiO$_2$(011)-(2×1) surfaces [70–73]. However, the lack of the strong experimental evidence reinforced by the solid theory still complicates to achieve a common understanding of the impact of the orbital selectivity on the $d$-dependent imaging.

In this chapter, we also advocate the importance of an in-depth $d$-dependent STM imaging and spectroscopy to fully characterize the orbital selective tunneling as the origin of the topographic image changes. A monatomic layer of iron nitride (Fe$_2$N) on Cu(001) with the ferromagnetic Fe$_4$N stoichiometry [38, 45] is chosen so as to highlight the role of the orbital selectivity. Due to the strong bonding between Fe and N atoms typical for the nitride compounds [74, 75], we expect hybridization-induced non-negligible contributions of $s/p$ orbitals relative to $3d$ orbitals in the local density of states (LDOS), and the robust surface structure against the tip-induced effect, which meets the purposes of this study.

We here show that the topographic image of the Fe$_2$N layer changed from a dimerized atomic image reflecting the atomic surface structure to a square lattice of atomic-size dots with increasing $d$. Corresponding systematic $d$ dependence of the tunneling spectra implied the shift in the dominant electronic states contributing to the tunneling process. Combining with the LDOS calculations by first principles, we have attributed these to the change of the dominant orbitals detected by the STM tip from the Fe $3d$ states to the $s/p$ states with increasing the tip-surface distance. The results resolve the discrepancy for the topographic images of the previous STM studies between the $p4g$($2\times2$) structure for thick films and the $c$($2\times2$) one for atomic-layer films [38, 45].

### 4.2 Experiment

Monatomic-layer iron nitrides were prepared in ultrahigh vacuum (UHV) with a base pressure of better than $1.0 \times 10^{-10}$ Torr in the following process. First, a clean surface of Cu(001) was obtained by several cycles of sputtering with Ar$^+$ ions and subsequent annealing at 820 K. Then, N$^+$ ions with an energy of 0.5 keV were bombarded to the clean surface and submonolayer Fe was subsequently deposited at room temperature (RT). After annealing at 570 K, well-ordered iron nitrides were obtained on the surface. The surface structure was confirmed by LEED at RT, and STM at 77 K. For the scanning tunneling spectroscopy, the differential conductance $dI/dV$ was recorded using a lock-in technique with a bias-voltage modulation of 20 mV and 719 Hz.
4.3 Results and Discussion

Figure 4.1: (a) Large scale topographic image at $V_s = 100$ mV, $I = 5$ nA. (b) LEED pattern obtained with an incident electron energy of 100 eV. (c) Close view of a topographic image for the Fe$_2$N islands revealing a dimerization of Fe atoms ($V_s = 50$ mV, $I = 5$ nA). The dimerization is indicated by encirclement.

A large-scale topographic image of the surface is shown in Fig. 4.1(a). Iron-nitride islands of several tens of nanometers in diameter are formed on the Cu(001) surface. A LEED pattern of the same surface shown in Fig. 4.1(b) exhibits the $p4g(2 \times 2)$ symmetry identical to that of the previous studies [38, 45]. A close view of the STM image shows a dimerized structure as shown in Fig. 4.1(c), which agrees with the LEED pattern. This STM image is similar to that reported by Gallego et al. for the thick Fe$_4$N film [38]. It has been known that, irrespective of the film thickness, the topmost layer of Fe$_4$N films consists of an Fe$_2$N single layer [38, 45]. In the surface layer, N atoms occupy the hollow sites of an Fe sublattice. Due to the surface reconstruction, Fe positions are different from those of an ideal Fe$_2$N layer of the Fe$_4$N crystal; the Fe atoms are dimerized in the two perpendicular directions, which results in the decrease of the lattice constant compared to the bulk [38, 45]. This surface reconstruction did occur in the films of any thickness as confirmed by LEED. Thus, it still remains unclear why the STM image of the atomic-layer films showed the $c(2 \times 2)$-like symmetry despite the $p4g(2 \times 2)$ LEED pattern [45].

To explore the origin of this discrepancy in the previous studies, we first investigated the tunneling-current ($I$) dependence of the STM images by fixing $V_s$ at 0.25 V. Figure 4.2(a) shows a series of the images with varying $I$ from 0.1 to 45 nA. At $I = 45$ nA, the image consists of distinct Fe dimers. With the decrease of $I$, the
Figure 4.2: Current dependence of STM images. (a) Topographic images taken at $V_s = 0.25 \text{ V}$ with varying $I$ from 0.1, 3.0, 10 to 45 nA. (b) Line profiles at $V_s = 0.25 \text{ V}$, measured along lines indicated in (a). From the top to the bottom, $I$ varies as follows: 45, 40, 35, 30, 28, 25, 22, 20, 18, 15, 12, 11, 10, 9.0, 8.0, 7.0, 5.0, 3.0, 2.0, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1 nA, respectively. Empty circles indicate peak positions extracted from one Fe dimer.
split of the Fe dimers gradually becomes ambiguous and turns into one elongated structure, similar to that reported by Gallego et al. [38]. Finally at $I = 0.1$ nA, the image consists of broad dots, like that reported by Takagi et al. [45]. Comparing the structural model with the images for $I \geq 3.0$ nA, we specify that the dots at 0.1 nA are located at the hollow sites of the Fe sublattice with no N atom.

For a further grasp of the STM-image change induced by $I$, we extracted line profiles along the Fe dimer for various $I$ values from 0.1 to 45 nA, as shown in Fig. 4.2(b). One can see that a gradual transformation from a double-peak structure to a single-peak one occurs at around $I = 3.0$ nA with decreasing $I$. The separation between the two protrusions is almost saturated at $I \geq 20$ nA, and its maximum reaches to 2.23 Å. This length is a little smaller than the reported distance between the dimerized surface Fe atoms of the Fe$_2$N layer, 2.83 Å of the monatomic-layer Fe$_4$N determined by LEED $I$-$V$ [45] and 2.73 Å of the thick Fe$_4$N film calculated by first principles [38].

It should be noted that the observed $I$ dependence of the Fe-dimer image differs from what generally expected for adjacent two protrusions in the STM observation. A protrusion in the image tends to be broader with increasing $d$ as long as the tip state keeps overlapping the identical states at the surface. Namely, in the present case, the width of the single dot for $I < 3$ nA could be broader than the separation of the two protrusions at higher $I$ if we assumed that the same states at the surface was detected in the entire $I$ range. However, this is not the case in the present observations.

To understand the role of the electronic states for the change of STM images, we performed extensive first-principles calculations of the surface LDOS for the monatomic Fe$_2$N layer on Cu(001) using a self-consistent Green function method within the density functional theory (DFT), specially designed for semi-infinite layered systems [72]. Figure 4.3(a) shows the total, spin- and elementally-resolved LDOS of the Fe$_2$N surface. Besides large contribution of minority spin states originating from Fe, N majority spin states also contribute to the total LDOS near the Fermi energy ($E_F$) at the surface. Typical $dI/dV$ spectra recorded above the Fe$_2$N and Cu(001) are shown in Fig. 4.3(b). In contrast to the Cu spectrum with only minor features, the Fe$_2$N spectrum shows several peaks located at $V_s = -0.35$, -0.15, 0.17, 0.52, and 0.79 V, respectively, which well correspond to the peaks of the calculated total LDOS shown in Fig. 4.3(a). Note that, possibly due to the tip condition, the fine structures at the occupied states in the calculation are not so obvious in the

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1 See also Fig. 4.5 and related discussion on the charge distributions calculated at different distances.

2 This threshold slightly changes depending on the tip condition.

3 This could be attributed to the difference between an exact atomic position and a projected LDOS distribution of the Fe dimer at each setpoint.

4 See Appendix A for a numerical simulation of simple broadening of the charge density.
Figure 4.3: (a) Spin-resolved LDOS of single-layer Fe$_2$N on Cu(001). Fe and N states are separately shown. (b) $dI/dV$ spectra of Fe$_2$N (solid) and bare Cu (dotted). The STM tip was stabilized at $I = 30$ nA and $V_s = 1$ V. (c) Threshold $d_c$ for the image change. Empty circles indicate parameter sets when the shift in the image from the dimerized to the dot structure occurred. Lines fitted freely to the experimental data with assuming the constant $d$ (solid), $E$ (dot-dashed), $V_s$ (fine-dashed), $P$ (rough-dashed) or $I$ (dashed) in Eq. (4.1) are also indicated. (d) Distant-dependent $dI/dV$ spectra measured at $d = 4.2$, 3.4, and 2.9 Å from the bottom to the top. Dashed curves indicate a tunneling background obtained by a Tersoff-Hamann approximation.
4.3. Results and Discussion

The experimental \(dI/dV\) spectrum. Thus, hereafter we focus on the unoccupied states (positive sample bias) near the \(E_F\).

In the STM measurement, local atomic structures and/or electronic properties of the surface can be modified by the experimental parameters such as \(I\), \(V_s\), \(d\), the local Joule heating \(P = V_s \times I\), and the electric field \(E = V_s/d\) [76]. To elucidate which parameter is crucial to induce the transformation of the STM image in the present study, we have taken the images in various combinations of \(I\) and \(V_s\).

Here, we determine \(I_c\) and \(d_c\), which denote the critical tunneling current and tipsample distance that the image transforms from the dimerized to the dot structure, respectively. The \(d_c\) was evaluated from \(I_c\) at each \(V_s\) by applying Simmons’ rule [77]

\[
d_c = -\frac{\hbar}{2\sqrt{2m\Phi}} \ln \left( \frac{R_0 I_c}{V_s} \right),
\]

(4.1)

where \(m\) is the electron mass, \(\Phi\) an average work function of the tip and the sample, and \(R_0\) the resistance for a single-atomic point contact of 12.9 k\(\Omega\) [78]. An average \(\Phi\) value of 5.5 eV, obtained from the fitting of several experimental \(I-d\) curves is used in the evaluation\(^5\). Figure 4.3(c) shows a plot of \(d_c\) as a function of \(V_s\) (empty circles). The nearly constant \(d_c\) values of 3.3 Å (solid line) are found, suggesting that \(I_c\) increases (decreases) at higher (lower) \(V_s\), and the image change is entirely caused by \(d\). None of \(E\), \(V_s\), \(P\) and \(I\) can be a threshold for the image change. Therefore, we can conclude that the observed image change is triggered by the tip-surface distance\(^6\).

It has been known that the decay length of the wave function strongly depends on an orbital character, i.e., the 3\(d\) states decay into the vacuum faster than the \(s/p\) states [79]. The different decay lengths between the \(d\) and \(s/p\) states were previously investigated and confirmed in terms of the spin polarization [80, 81]. Thus, the states detected by the tip with smaller distance could have more Fe 3\(d\) character.

To confirm this, we measured \(dI/dV\) spectra with various \(d\) values as shown in Fig. 4.3(d). Here, the tip was fixed at \(V_s = 0.1\) V, and all the spectra are normalized to the intensity at \(V_s = -0.1\) V. Note that the corresponding STM images at \(d = 2.9, 3.4\) and 4.2 Å consist of the distinct, blurred dimerized structures and the dot structure, respectively. At \(d = 2.9\) Å, the background contribution is small and the peak around 0.2 V is mainly attributed to the Fe 3\(d\) state, in comparison with the theoretical calculations (see Fig. 4.3(a). A detailed orbital assignment is discussed below). However, one can clearly see that the contribution of an integrated background signal monotonously increases as the tip becomes far. It should

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\(^5\)See Appendix B for the nearly constant \(\Phi\) values with respect to the tip-surface distance.

\(^6\)The observed LEED pattern agrees with the STM image at short \(d\). Therefore, the tip-sample interaction is excluded as the origin of the image change in the present case.
be noted that an exponential background signal is mainly due to the tunneling processes between the tip states and the sample s/p states [58, 79]. Therefore, a series of the d-dependent dI/dV spectra well supports our interpretation on the observed d-dependent change of the STM image. Namely, at short d, the tunneling process through the Fe 3d states dominates that through the s/p states, and it results in the STM image of the dimerized structure.

We have further studied the decay of orbital-resolved LDOS into the vacuum by first-principles calculations to understand the tunneling process in detail. In Figs. 4.4(a) and 4.4(b), we extract dominant orbitals contributing to the total LDOS near the $E_F$. At the surface, the LDOS mainly consists of the Fe 3d states and the s/p states are minute as shown in Fig. 4.4(a). It means that, at a short tip-surface distance, the possible states dominantly detected by the STM tip are $3d_{z^2-r^2}$, $3d_{xy}$ and $3d_{yz}$. Another intriguing is that among 3d states, the $d_{xy}$ state shows no clear LDOS around $E - E_F = 0.2$ eV. This indicates a strong hybridization between Fe and N atoms, which leads to delocalization of the $d_{xy}$ state while the other 3d states relatively remain localized.

The situation drastically changed in the vacuum layer 4 Å above the surface.

Figure 4.4: Total and orbital-resolved LDOS of (a) surface and (b) vacuum (4 Å above the surface) layers. The states with negligible intensity in this energy range are not shown here. In the vacuum layer, LDOS cannot be separated into each atomic component due to a strong orbital mixing between Fe and N.
4.3. Results and Discussion

Figure 4.5: Charge distributions calculated at different distances. (a) Unreconstructed \(c(2 \times 2)\) surface model used for the calculation. Large (small) spheres correspond to the surface Fe (N) atoms. (b,c) Charge distribution at \(d = 1.8\) \(\text{Å}\) (b) and \(d = 6.5\) \(\text{Å}\) (c).

In Fig. 4.4(b), one can see that the contributions of isotropic \(s\) and out-of-plane-oriented \(p_z\) overwhelm those of \(3d\) except for \(3d_{3z^2-r^2}\). This is clearly due to the longer decay lengths of the \(s/p\) states than the \(d\) states. Such large \(s/p\) contributions relative to the \(3d\) ones and thus the tip-surface distance dependence of the STM image have not been expected in elemental \(3d\) systems, where the surface states mainly of \(d_{3z^2-r^2}\) character slowly decay into the vacuum [69]. The considerable enhancement of the \(s/p\) contribution in the present case is caused by strong hybridization of N \(s/p\) states with Fe \(s, p, d\) states, which is characteristic of compound systems.

Finally, we confirm how this shift in the \(s/p\) and \(d\) contributions at different distances shows up in a spatial distribution of the charge density using DFT. Figure 4.5 shows the calculated charge distributions of states at the energy \(E = E_F + 0.25\) eV, corresponding to our experimental \(V_s\) of 0.25 V. It should be noted that an energy resolved charge distribution can be associated with STM topographic images within the Tersoff-Hamann model [57]. An unreconstructed \(c(2 \times 2)\) surface shown in Fig. 4.5(a) was used in the calculation for simplicity, instead of the reconstructed \(p4g(2 \times 2)\) one. Thus obtained charge distributions at \(d = 1.8\) \(\text{Å}\) and 6.5 \(\text{Å}\) are shown in Fig. 4.5(b) and 4.5(c), respectively\(^7\). At a shorter distance of 1.8 \(\text{Å}\), the charge intensity is high on top of the Fe atoms, because of a large contribution of the Fe \(3d\) states. This is consistent with that the surface Fe atoms were distinctly imaged at higher \(I_s\) [see Fig. 4.2(a)]. In the case of \(d = 6.5\) \(\text{Å}\), in contrast, the intensity maxima locate above the hollow site of the Fe sublattice without N atoms. This originates from the dominance of states with \(s/p\) characters at larger distances, and

\(^7\)Note that the distances of the calculation cannot be directly compared with the experiments since DFT has less accuracy for reproducing the surface excess charge.
well reproduces the experimental $I$ dependence of the STM images.

### 4.4 Conclusion

In summary, we have performed the comprehensive STM work to elucidate the origin of the image changes for the monatomic-layer iron nitride on Cu(001). Systematic $d$-dependent STM imaging and spectroscopy reveal that the observed image change is attributed to the orbital-dependent decay length of the wave function at the surface. The validity of the experimental results is confirmed by the first-principles calculations, which successfully reproduce that the STM image is dominated by the Fe 3$d$ states at short distance whereas by the $s/p$ states at long distance. Since the orbital-selective tunneling process is inherent in any STM measurements, the atomic morphology based on the topographic image should be carefully discussed, especially in the compound systems.
Chapter 5

Impact of atomic defects on the macroscopic ferromagnetism of monolayer Fe$_2$N on Cu(001)

The contents of this chapter will be published elsewhere within five years, and thus not open to the public in the abbreviated version.
Chapter 6

Thickness-dependent electronic and magnetic properties of $\gamma'$-Fe$_4$N multilayers on Cu(001)

The contents of this chapter will be published elsewhere within five years, and thus not open to the public in the abbreviated version.
Appendix

A Simulation of simple broadening for surface wave functions

In the STM observation, two adjacent objects imaged at short tip-surface distance usually appear to be broader structures when the tip is sufficiently far from the surface. This is due to simple broadening of LDOS distribution, accompanied by the decay of the surface wave functions. Here, we check the possibility that the observed tunneling-current dependence of the line profiles can be explained by this kind of simple broadening. As a first approximation, we use a summation of Gaussian functions \( f_G \) to reproduce six peaks observed in the line profiles at higher \( I \). A numerical expression \( f_{\text{profile}} \) is given in the following form,

\[
f_{\text{profile}}(x, x_h, \sigma_h, x_l, \sigma_l) = A_h \{ f_G(x, x_h, \sigma_h) + f_G(x, -x_h, \sigma_h) \\
+ f_G(x, 2x_l - x_h, \sigma_h) + f_G(x, -2x_l + x_h, \sigma_h) \} \\
+ A_l \{ f_G(x, x_l, \sigma_l) + f_G(x, -x_l, \sigma_l) \},
\]

where \( f_G(x, x_0, \sigma) = \frac{1}{\sqrt{2\pi \sigma^2}} \exp \left[ -\frac{(x - x_0)^2}{2\sigma^2} \right] \),\( x_h \) (\( x_l \)), \( \sigma_h \) (\( \sigma_l \)) and \( A_h \) (\( A_l \)) are a center position, standard deviation and normalization coefficient of the Gaussian functions corresponding to four higher- (two lower-) intensity peaks in the line profiles, respectively. First, to analyze the charge distribution without considerable decay, the experimental line profile at \( I = 45 \) nA is fitted to Eq. (6.1). Thus simulated profile (solid line) is shown in the top panel of Fig. 6.1(a), well reproducing the experimental one (open circles). Note that all the profiles in Fig. 6.1(a) are normalized to the peak intensity, and dashed (dot-dashed) curves correspond to the first four (last two) terms in Eq. (6.1). Parameters extracted from the fitting are summarized in Table 6.1. Hereafter, for considering the decay of the surface wave functions at longer distances, only \( \sigma_h \) and \( \sigma_l \) are increased to the same extent, with \( x_h \) and \( x_l \) fixed. In Fig. 6.1(a), one can see that sharp peaks, recognized in the top panel, gradually become blunt with a broadening of the Gaussian functions, and finally form almost one broad structure at the center.
Table 6.1: Results of the fitting for the experimental line profile at $I = 45$ nA.

<table>
<thead>
<tr>
<th>$x_h$ (Å)</th>
<th>$\sigma_h$ (Å)</th>
<th>$x_1$ (Å)</th>
<th>$\sigma_1$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.60</td>
<td>3.4</td>
<td>0.41</td>
</tr>
</tbody>
</table>

as shown in the bottom. A series of broadened line profiles is shown in the left of Fig. 6.1(b), in comparison with the current dependence of the experimental ones (the same in the manuscript). It is obvious that an increase in the $\sigma$ value renders the simulated profiles deviated from the experimental ones, in terms of the width of the peak structures and relative peak intensities. Note that these discrepancy cannot be compensated even if different decay speeds are assumed for the Gaussian functions with $\sigma_h$ and those with $\sigma_1$. Therefore, the simple broadening of the surface wave functions can be ruled out from a possible reason for the observed image change.
Figure 6.1: Demonstration of simple broadening of the charge density. (a) Simulated line profiles (solid) with \((\sigma_h, \sigma_i) = (0.60, 0.41), (0.70, 0.52), (0.80, 0.61), \) and \((1.1, 0.90), \) from the top to the bottom, respectively. Each profile is decomposed into four (two) equal Gaussian functions indicated by dashed (dot-dashed) curves. Open circles in the top panel correspond to the experimental line profiles at \(I = 45\) nA. (b) Simulated (experimental) line profiles are shown in the left (right). From the top to the bottom, \(\sigma (I)\) values become large (low).
B Estimated values of work function

Table 6.2: Values of work function $\Phi$ estimated for various pairs of $I$ and $V_s$. Corresponding $d$ values are also shown.

<table>
<thead>
<tr>
<th>$I$ (nA)</th>
<th>45</th>
<th>30</th>
<th>20</th>
<th>3.0</th>
<th>1.0</th>
<th>0.5</th>
<th>0.5</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_s$ (V)</td>
<td>0.25</td>
<td>0.4</td>
<td>0.5</td>
<td>0.2</td>
<td>0.2</td>
<td>0.25</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>$d$ (Å)</td>
<td>2.6</td>
<td>2.9</td>
<td>3.2</td>
<td>3.6</td>
<td>4.0</td>
<td>4.4</td>
<td>4.8</td>
<td>5.1</td>
</tr>
<tr>
<td>$\Phi$ (eV)</td>
<td>5.52</td>
<td>5.42</td>
<td>5.43</td>
<td>5.61</td>
<td>5.57</td>
<td>5.52</td>
<td>5.41</td>
<td>5.56</td>
</tr>
</tbody>
</table>

All the measured $I$-$z$ curves could be fitted to a single exponential function following Simmons’ rule [77]. In Table 6.2, we summarize values of the work function $\Phi$ estimated from the fitting of several experimental $I$-$z$ curves. No systematic change of the $\Phi$ value is observed depending on the combination of $I$ and $V_s$, and also on $d$. As a result, a small variation in $\Phi$ allowed us to assume the constant $\Phi$ for the estimation of $d$. 
Summary

In conclusion, we have investigated electronic and magnetic structures of the $\gamma'$-Fe$_4$N atomic layers on Cu(001). The important findings are summarized in the following.

1. **Surface electronic structures of the monolayer $\gamma'$-Fe$_4$N/Cu(001)**
   Due to the large hybridization between the Fe and N states in the $\gamma'$-Fe$_4$N, the decay of the states at the surface into the vacuum strongly depends on the orbital character. This contrasts with the case of elemental 3$d$ systems in which the surface states with particular orbitals dominate the vacuum, and thus no variation is expected for topographic images. The first experimental demonstration of the orbital-selective tunneling process in STM also links the two different images previously reported for the surface with the same symmetry [38, 45].

2. **Ferromagnetism of the monolayer**
   Not mentioned in the abbreviated version.

3. **Thickness dependence of the electronic/magnetic properties**
   Not mentioned in the abbreviated version.

Overall, the atomically-resolved observation on the sample atomic structure turns out to be indispensable for investigating the physical properties intrinsic to the $\gamma'$-Fe$_4$N atomic layers. The present study demonstrates a close interplay between the microscopic atomic structure and the electronic/magnetic properties of the system, by combining the complementary multiple methods.

The new observations here can also be a guide to the future experiments. The variation in the STM topographic images depending on the tip-surface distance was considered negligible so far. However, the present results establish the importance of the tip-surface distance as a measurement parameter, to be taken into account especially in the STM measurements on multielement/complex surfaces. Utilizing the orbital-dependent decay length could then pave the new way to experimentally identify the orbital character of the states decaying into the vacuum by detailed STM/STS experiments. It is also revealed that, for the systems with itinerant electronic states, the defect in an atomic level largely affects the surrounding electronic
structures. The impact of the atomic-scale disorder on the thin-film ferromagnetism was previously underestimated, but the characterization from both microscopic and macroscopic points of views would be necessary for the quantitative discussion on ferromagnetism particularly in an atomic-layer limit.

Finally, we briefly mention future prospects. The $\gamma'$-Fe$_4$N/Cu(001) is a unique monolayer 3$d$ ferromagnet on a metallic substrate and has a robust structure toward external perturbations such as the tip-induced force, oxidization, or contamination. That means, the present system will be a good template to investigate an intrinsic interaction between an adsorbate and ferromagnetic substrate; in particular, comparing the results with those on a common monolayer insulator of Cu$_2$N/Cu(001) with similar $c(2 \times 2)$ symmetry [82, 83], the role of a ferromagnetic interaction on physical properties including magnetic anisotropy, life time of magnetization, or Kondo effect could be understood. Furthermore, spin-polarized STM measurements [84] would give the additional information on the electronic and magnetic structures of the $\gamma'$-Fe$_4$N/Cu(001): the orbital-selective tunneling process possibly shows clear difference with respect to the spin channel, and the spin polarization around the atomic defect could inform the in-plane spin-dependent decay length of the ferromagnetic interaction.
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Yukio Takahashi
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