Thickenss-dependent electronic and magnetic properties of $\gamma'$-Fe$_4$N atomic layers on Cu(001)

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Growth, electronic and magnetic properties of $\gamma'$-Fe$_4$N atomic layers on Cu(001) are studied by scanning tunneling microscopy/spectroscopy and x-ray absorption spectroscopy/magnetic circular dichroism. A continuous film of ordered trilayer $\gamma'$-Fe$_4$N is obtained by Fe deposition under N$_2$ atmosphere onto monolayer Fe$_2$N/Cu(001), while the repetition of a bombardment with 0.5 keV N$^+$ ions during growth cycles results in imperfect bilayer $\gamma'$-Fe$_4$N. The increase in the sample thickness causes the change of the surface electronic structure, as well as the enhancement in the spin magnetic moment of Fe atoms reaching $\sim 1.4 \mu_B$/atom in the trilayer sample. The observed thickness-dependent properties of the system are well interpreted by layer-resolved density of states calculated using first principles, which demonstrates the strongly layer-dependent electronic states within each surface, subsurface, and interfacial plane of the $\gamma'$-Fe$_4$N atomic layers on Cu(001).

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I. INTRODUCTION

Iron nitrides, especially in iron-rich phases, have been under intense research due to the strong ferromagnetism and interest in its physical origin. The difficulty in obtaining a single phase has been a long-standing problem for ferromagnetic iron nitrides, to hinder fundamental understanding of intrinsic physical properties. Recently, the successful epitaxial growth of single-phase ferromagnetic $\gamma'$-Fe$_4$N has been reported on various substrates, which helps to comprehend a crucial role for the hybridization between Fe and N states in the ferromagnetism of $\gamma'$-Fe$_4$N. The robust Fe-N bonding also renders an Fe$_2$N layer strongly two-dimensional, which possibly facilitates a layer-by-layer stacking of $\gamma'$-Fe$_4$N on metals. This contrasts with the case of elemental 3$d$ transition metals (TMs) deposited on 3$d$ TM substrates, in which inevitable atom intermixing and exchange of constituents prevent the formation of ordered overlayers. Therefore, the investigation into the electronic and magnetic states of $\gamma'$-Fe$_4$N atomic layers can not only elucidate the layer-/site-selective electronic and magnetic states of $\gamma'$-Fe$_4$N, but unravel the origin of the strongly thickness-dependent physical properties in a thin-film limit of 3$d$ TM ferromagnets.

Here, we report two growth modes of $\gamma'$-Fe$_4$N/Cu(001) depending on preparation methods. The scanning tunneling microscopy/spectroscopy (STM/STS) observations indicated a successful growth of ordered trilayer $\gamma'$-Fe$_4$N, without extra nitrogen bombardment onto the existing structures. X-ray absorption spectroscopy/magnetic circular dichroism (XAS/XMCD) measurements revealed the thickness dependence of the magnetic moments of Fe atoms, the origin of which was well explained by the first-principles calculations. Based on an atomically-resolved structural characterization of the system, the layer-by-layer electronic and magnetic states of the $\gamma'$-Fe$_4$N atomic layers have been understood from both experimental and theoretical points of view.

II. METHODS

A clean Cu(001) surface was prepared by repetition of sputtering with Ar$^+$ ions and subsequent annealing at 820 K. Iron was deposited at room temperature (RT) in a preparation chamber under an ultrahigh vacuum (UHV) condition (< 1.0 $\times$ 10$^{-10}$ Torr), using an electron-bombardment-type evaporator (EFM, FOCUS) from a high-purity Fe rod (99.998 %). The STM measurements were performed at 77 K in UHV (< 3.0 $\times$ 10$^{-11}$ Torr) using electrochemically etched W tips. The differential conductance $dI/dV$ was recorded for STS using a lock-in technique with a bias-voltage modulation of 20 mV and 719 Hz. The XAS and XMCD measurements were performed at BL 4B of UVSOR-III in a total electron yield (TEY) mode. The degree of circular polarization was $\sim 65 \%$, and the x-ray propagation vector lay within the (110) plane of a Cu(001) substrate. All the XAS/XMCD spectra were recorded at $\sim 8$ K, with external magnetic field $B$ up to $\pm 5$ T applied parallel to the incident x-ray. The symmetry and quality of the surface were also checked by low energy electron diffraction (LEED) in each preparation chamber. First-principles calculations
were performed within the density functional theory in the local density approximation\textsuperscript{27}, using a self-consistent full-potential Green function method specially designed for surfaces and interfaces\textsuperscript{28,29}.

III. RESULTS AND DISCUSSION

A. Monolayer and bilayer-dot \( \gamma' \)-Fe\textsubscript{4}N

Monolayer Fe\textsubscript{2}N on Cu(001) was prepared prior to any growth of multilayer \( \gamma' \)-Fe\textsubscript{4}N by the following cycle: \( \text{N}^+ \) ion bombardment with an energy of 0.5 keV to a clean Cu(001) surface, subsequent Fe deposition at RT, and annealing at 600 K. Note that the monolayer Fe\textsubscript{2}N is identical to Fe\textsubscript{2}N on Cu(001) in a monolayer limit, and thus referred to as also "monolayer \( \gamma' \)-Fe\textsubscript{4}N" hereafter. A topographic image of the sample after one growth cycle is shown in Fig. 1(a). The monolayer \( \gamma' \)-Fe\textsubscript{4}N is formed on the Cu terraces at \( \sim 0.85 \) ML coverage. An atomically-resolved image of that surface displayed in Fig. 1(b) reveals a clear dimerization of the Fe atoms, typical of ordered \( \gamma' \)-Fe\textsubscript{4}N on Cu(001)\textsuperscript{30,31}. A LEED pattern of the surface is shown in Fig. 1(c), which exhibits sharp spots with the corresponding \( p4g(2 \times 2) \) symmetry. It is known that \( 30-33 \) the topmost layer of the \( \gamma' \)-Fe\textsubscript{4}N on Cu(001) always consists of the Fe\textsubscript{2}N plane in a bulk Fe\textsubscript{2}N crystal shown in Fig. 1(d). A schematic model of the monolayer \( \gamma' \)-Fe\textsubscript{4}N is given in Fig. 1(e), composed of a single Fe\textsubscript{2}N plane on Cu(001). Accordingly, the surface Fe\textsubscript{2}N plane takes reconstruction to the \( p4g(2 \times 2) \) coordination\textsuperscript{30}, in which the Fe atoms dimerize in two perpendicular directions as illustrated in Fig. 1(f).

After repeating the growth cycles, we found a new structure different from the monolayer \( \gamma' \)-Fe\textsubscript{4}N. Figure 2(a) displays the surface after two growth cycles in total, namely, another cycle of the \( \text{N}^+ \) ion bombardment, Fe deposition, and annealing onto the existing monolayer \( \gamma' \)-Fe\textsubscript{4}N surface. Then, the surface becomes mostly covered with the monolayer \( \gamma' \)-Fe\textsubscript{4}N, which contains a small number of bright dots. For a structural identification of these dots, we measured atomically-resolved topographic images and line profiles at different \( V_s \) as shown in Fig. 2(b) and 2(c). The dot structure imaged at \( V_s = -0.1 \) V reveals the dimerization of the Fe atoms.

FIG. 1. (Color online) Topography and atomic structure of the monolayer \( \gamma' \)-Fe\textsubscript{4}N on Cu(001). (a) Topographic image \( (100 \times 50 \) nm\textsuperscript{2}, sample bias \( V_s = +1.0 \) V, tunneling current \( I = 0.1 \) nA) of the monolayer \( \gamma' \)-Fe\textsubscript{4}N on Cu(001). White lines represent step edges of the Cu(001) terraces. Color contrast is enhanced within each terrace. (b) Close view \( (2.5 \times 2.5 \) nm\textsuperscript{2}, \( V_s = 0.25 \) V, \( I = 45 \) nA) of the surface Fe\textsubscript{2}N layer. The dimerization of Fe atoms is indicated by encirclement. (c) LEED pattern obtained with an incident electron energy of 100 eV. (d) Bulk crystal structure of \( \gamma' \)-Fe\textsubscript{4}N. A dotted parallelogram represents an Fe\textsubscript{2}N plane. (e) Atomic structure of the monolayer \( \gamma' \)-Fe\textsubscript{4}N on Cu(001). (f) Schema illustrating \( p4g(2 \times 2) \) reconstruction in the surface Fe\textsubscript{2}N layer of \( \gamma' \)-Fe\textsubscript{4}N. Arrows indicate the shift of the Fe atoms from an unreconstructed \( c(2 \times 2) \) coordination (dotted circles). For (d) to (f), large blue (yellow) and small red spheres represent Fe (Cu) and N atoms, respectively.

FIG. 2. (Color online) Topography of the bilayer \( \gamma' \)-Fe\textsubscript{4}N dot on Cu(001). (a) Topographic image \( (120 \times 60 \) nm\textsuperscript{2}, \( V_s = -0.1 \) V, \( I = 0.1 \) nA) of the monolayer (darker area) and dot-like bilayer \( \gamma' \)-Fe\textsubscript{4}N on Cu(001). White lines represent step edges of the Cu(001) terraces. Color contrast is enhanced within each terrace. (b,c) Upper panels: Atomically-resolved topographic images \( (7 \times 3 \) nm\textsuperscript{2}, \( I = 2.0 \) nA) taken at (b) \( V_s = -0.1 \) V and (c) +0.1 V. Lower panels: Height profiles measured along lines indicated in the upper panels. (d) Proposed atomic structure of the bilayer-dot \( \gamma' \)-Fe\textsubscript{4}N on Cu(001). Large blue (yellow) and small red spheres correspond to Fe (Cu) and N atoms, respectively.
as the monolayer $\gamma'$-Fe$_4$N surface. This indicates that the topmost part of the dot consists of the reconstructed Fe$_2$N. At positive $V_s$ of +0.1 V, in contrast, the dot is recognized as a single protrusion both in the topographic image and line profile, while the surrounding monolayer $\gamma'$-Fe$_4$N still shows the Fe dimerization. This implies the different electronic structure of the dot compared to the monolayer $\gamma'$-Fe$_4$N, which comes from the difference in a subsurface atomic structure.

The observed height difference between the dot and the monolayer $\gamma$'-Fe$_4$N ranges from 4 to 10 pm depending on $V_s$. These values are in the same order of a lattice mismatch between the bulk crystals of the $\gamma'$-Fe$_4$N/Cu(001) (380 pm) and Cu(001) (362 pm)\(^\text{30}\), but an order of magnitude smaller than the lattice constant of the $\gamma'$-Fe$_4$N/Cu(001). This suggests that the topmost layer of the dot is not located above the monolayer $\gamma'$-Fe$_4$N surface, but shares the Fe$_2$N plane with. Furthermore, the bright dot is composed of only four pairs of the Fe dimer as imaged in Fig. 2(b), indicating that the difference in the atomic and/or electronic structures is restricted within a small area. Considering the above, it is most plausible that one Fe atom is embedded just under the surface N atom at the dot center, and thus a bilayer $\gamma'$-Fe$_4$N dot is formed as schematically shown in Fig. 2(d). This structure corresponds to a minimum unit of the bilayer $\gamma'$-Fe$_4$N on Cu(001).

This bilayer dot formed clusters by a further repetition of the growth cycles. Figure 3(a) shows an enlarged view of the iron-nitride surface after two growth cycles. The coverage of the dot is estimated to be \(\sim 5\%\) of the entire surface. Another growth cycle onto this surface led to an increase in a dot density up to \(\sim 40\%\), as shown in Fig. 3(b). However, further repetitions of the cycles resulted in neither a considerable increase in the dot density nor the formation of a continuous bilayer film. This can be attributed to an inevitable sputtering effect in every growth cycle: an additional N\(^+\) ion bombardment to the existing surface not only implanted N\(^+\) ions but also sputtered the surface, which caused the loss of the iron nitrides already formed at the surface, as well as the increase in the surface roughness.

To compensate this loss of surface Fe atoms by the sputtering effect, we also tried to increase the amount of deposited Fe per cycle. Nonetheless, the number of Fe atoms, which remained at the surface after annealing, did not increase possibly because of the thermal metastability of Fe/Cu systems\(^\text{34-37}\). The isolated Fe atoms without any bonding to N atoms were easily diffused and embedded into the Cu substrate during the annealing process. As a result, only the imperfect bilayer $\gamma'$-Fe$_4$N was obtained through this method.

### B. Trilayer $\gamma'$-Fe$_4$N film

Multilayer $\gamma'$-Fe$_4$N films were obtained by the following procedure. First, the monolayer $\gamma'$-Fe$_4$N was prepared on Cu(001) as above. Then, 2 ML Fe was deposited under N$_2$ atmosphere (5.0x10^{-8} Torr)\(^\text{38}\) at RT, and the sample was annealed at 600 K. Figures 4(a) and 4(b) show topographic images after two and three above mentioned cycles, respectively. In the images, the coverage of new bright area, different from the imperfect bilayer dot, monotonously increases with repeating the cycles. A close view of that new surface is displayed in Fig. 4(c), revealing the dimerized (or even c(2x2)-like dot) structures. Because a LEED pattern shown in the inset of Fig. 4(c) exhibits the $p4g(2x2)$ symmetry without extra spots, the topmost layer of this surface is composed of the reconstructed Fe$_2$N plane\(^\text{31}\). Therefore, these observations suggest that the new area would consist of $\gamma'$-Fe$_4$N other than both of the monolayer and bilayer dot.

In order to determine the structure of this newly obtained $\gamma'$-Fe$_4$N, a typical height profile of the surface was recorded as shown in Fig. 4(d). It is clear that the new structure is higher than both the Cu surface and the surface including the monolayer/dot-like bilayer $\gamma'$-Fe$_4$N. This suggests that the new area is composed of $\gamma'$-Fe$_4$N thicker than bilayer. Quantitative information on the thickness of the new structure could be obtained from Fe L (2p \(\rightarrow\) 3d) edge jump spectra shown in Fig. 4(e), whose intensity is roughly proportional to the amount of surface/subsurface Fe atoms. The sample prepared in the same procedure as that shown in Fig. 4(b) reveals an edge jump value of 0.32, while the monolayer $\gamma'$-Fe$_4$N 0.12\(^\text{39}\). Considering that the new area occupies \(\sim 60\%\) of the entire surface as deduced from Fig. 4(b), the thickness of this $\gamma'$-Fe$_4$N must be less than quadrilayer to meet the experimental edge jump value of 0.32 (See Appendix A). Hence, the newly obtained structure is identified as a trilayer $\gamma'$-Fe$_4$N film. An atomic structure expected for the trilayer $\gamma'$-Fe$_4$N on Cu(001) is presented in Fig. 4(f). The growth without any ion bombardment to the monolayer surface possibly stabilizes the subsurface pure Fe layer, which could promote the formation of the trilayer $\gamma'$-Fe$_4$N film in a
obtained in a continuous film form. This implies that an
study, only the monolayer and trilayer
ion bombardment with a relatively
trilayer
γ
N structures during the repetition of the growth
cycles. The reported different electronic/magnetic states
ions successfully avoids extra damage to the existing
Cu(001), by the N
40
low energy of 0.15 kV
γ
layer-by-layer growth of the
γ
large area.
Finally, let us mention another growth method of
the γ'-Fe4N film on Cu(001). We previously report a possible
Fe deposition under N2 atmosphere and subsequent annealing onto the monolayer γ'-Fe4N on Cu(001). The setpoint is I = 0.1 nA, Vc = -0.1 V for (a) and -0.05 V for (b). White lines indicate step edges of the Cu terraces. Color contrast is enhanced within each terrace. (c) Atomically-resolved topographic image (4×4 nm2, I = 5.0 nA, Vc = -0.1 V) of the trilayer γ'-Fe4N surface. An inset represents a LEED pattern of the sample shown in (b), obtained with an incident electron energy of 100 eV. (d) Height profile measured along the line indicated in (b). (e) XAS edge jump spectra of the trilayer (solid) and monolayer (dotted) samples at the Fe and Cu L edges. The intensity is normalized to the Cu edge jump. (f) Atomic model expected for the trilayer γ'-Fe4N on Cu(001). Blue (yellow) large and red small spheres represent Fe (Cu) and N atoms, respectively.

Fe2N-layer termination would be preferable through the present methods, possibly due to the metastability of an interface between Cu and pure Fe layers.34–37

FIG. 4. (Color online) Topography of the trilayer γ'-Fe4N film on Cu(001). Topographic images (100×100 nm2) after (a) two and (b) three cycles of the Fe deposition under N2 atmosphere and subsequent annealing onto the monolayer γ'-Fe4N on Cu(001). The setpoint is I = 0.1 nA, Vc = -0.1 V for (a) and -0.05 V for (b). White lines indicate step edges of the Cu terraces. Color contrast is enhanced within each terrace. (c) Atomically-resolved topographic image (4×4 nm2, I = 5.0 nA, Vc = -0.1 V) of the trilayer γ'-Fe4N surface. An inset represents a LEED pattern of the sample shown in (b), obtained with an incident electron energy of 100 eV. (d) Height profile measured along the line indicated in (b). (e) XAS edge jump spectra of the trilayer (solid) and monolayer (dotted) samples at the Fe and Cu L edges. The intensity is normalized to the Cu edge jump. (f) Atomic model expected for the trilayer γ'-Fe4N on Cu(001). Blue (yellow) large and red small spheres represent Fe (Cu) and N atoms, respectively.

large area.

FIG. 5. (Color online) Surface electronic structures of the γ'-Fe4N on Cu(001). Experimental dI/dV spectra recorded above the trilayer (solid) and monolayer (dotted) γ'-Fe4N surfaces are presented. The dI/dV intensity is arbitrary. A STM tip was stabilized at Vc = +1.0 V, I = 3.0 and 7.0 nA for the trilayer and monolayer surfaces, respectively. Gray lines are guide to the eye.

C. Electronic and magnetic properties of γ'-Fe4N atomic layers

The surface electronic structures of γ'-Fe4N showed large dependence on the sample thickness. Figure 5 displays experimental dI/dV spectra measured on the surfaces of the trilayer and monolayer γ'-Fe4N. The peaks located at Vc = +0.20, +0.55, and +0.80 V, mainly originating from the unoccupied states in the down-spin band characteristic of Fe local density of states (LDOS), are observed for both the trilayer and monolayer surfaces. A significant difference between the spectra is a dominant peak located around Vc = -50 mV observed only for the trilayer surface. This peak possibly originates from the LDOS peak located around E - E_F = -0.2 eV, calculated for the Fe atoms not bonded to N atoms in the subsurface Fe layer [corresponding site of Fe4 shown in Fig. 7(b)]. Because of the d_{3z^2-r^2} orbital character, this peak could be dominantly detected in the STS spectrum for the trilayer surface. Thus, the appearance of this additional peak could support the different subsurface structure of the trilayer sample, especially, the existence of the subsurface Fe layer proposed above.

The entire electronic and magnetic properties of the sample, including both surface and subsurface information, were investigated by using XAS and XMCD techniques at the Fe L_{2,3} (2p_{1/2,3/2} \rightarrow 3d) absorption edges. Figure 6(a) shows XAS (µ+, µ-) and XMCD (µ+ - µ-) spectra under B = ±5 T of the trilayer and monolayer samples in the grazing (θ = 55°) and normal
incidence ($\theta = 0^\circ$). Here, $\mu_+ (\mu_-)$ denotes a x-ray absorption spectrum with the photon helicity parallel (antiparallel) to the Fe 3d majority spin, and an incident angle $\theta$ is defined as that between the sample normal and incident x-ray. The trilayer (monolayer) sample was prepared in the same procedure as that shown in Fig. 4(b) [Fig. 1(a)]. It is clear that the XMCD intensity is larger in the trilayer one, indicating an enhancement of magnetic moments with increasing thickness.

For a further quantitative analysis on the magnetic moments, we applied XMCD sum rules\textsuperscript{41,42} to the obtained spectra and estimated spin ($M_{\text{spin}}$) and orbital ($M_{\text{orb}}$) magnetic moments separately. Note that the average number of $3d$ holes ($n_{\text{hole}}$) of 3.2 was used in the sum-rule analysis, which was estimated by comparing the area of the experimental XAS spectra with that of a reference spectrum of bcc Fe/Cu(001) ($n_{\text{hole}} = 3.4$)\textsuperscript{43}. The thickness dependence of the $M_{\text{spin}}$ and $M_{\text{orb}}$ values is summarized in Fig. 6(b). The value of $M_{\text{spin}}$ increases monotonously with increasing the Fe $L$-edge jump value, namely, an average sample thickness, and finally saturates at $\sim 1.4 \mu_B/\text{atom}$ in the trilayer sample (corresponding edge jump value of 0.32). The change in $M_{\text{orb}}$ is not so systematic relative to $M_{\text{spin}}$, however, the $M_{\text{orb}}$ values seem to be enhanced in the grazing incidence. This implies an in-plane easy magnetization of the $\gamma'$-Fe$_4$N atomic layers on Cu(001), also consistent with the previous reports on the $\gamma'$-Fe$_4$N thin films on Cu(001)\textsuperscript{8,40}. Figure 6(c) shows magnetization curves of the monolayer sample, whose intensity corresponds to the $L_3$-peak XAS intensity normalized to the $L_2$ one. The curve recorded in the normal incidence shows negligible remanent magnetization. On the other hand, that in the grazing one draws a rectangular hysteresis loop, which confirms the in-plane easy magnetization. The coercivity of the monolayer sample is estimated to be $\sim 0.05$ T at 8.0 K, larger than $\sim 0.01$ T for 5 ML Fe/Cu(001)\textsuperscript{21}, $\sim 1$ mT for 5 ML Fe/GaAs(100)-(4×6)\textsuperscript{44} and the 30 nm thick $\gamma'$-Fe$_4$N film\textsuperscript{8} at RT.

### D. Theoretical analysis on the electronic and magnetic states of $\gamma'$-Fe$_4$N atomic layers on Cu(001)

The observed thickness dependence of the magnetic moments can be well understood with a help of first-principles calculations. Figures 7(a) and 7(b) show layer-resolved DOS of the monolayer and trilayer $\gamma'$-Fe$_4$N on Cu(001), respectively. Here, non-equivalent Fe sites in each layer are distinguished by different numbering.

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**TABLE I.** Calculated atomic magnetic moments of the Fe atoms at each site (in units of $\mu_B$/atom). The site notation is the same as that used in Fig. 7.

|         | Surface Fe$_2$N | Fe2 | Subsurface Fe | Fe3 | Interfacial Fe$_2$N |
|---------|-----------------|-----|--------------|-----|---------------------|
| Monolayer | 1.1             | 1.1 | -            | -   | -                   |
| Trilayer | 1.8             | 1.8 | 2.0          | 3.0 | 0.62                | 0.62               |
In particular, the Fe atoms at the Fe3 (Fe4) site in the trilayer γ’-Fe4N correspond to those with (without) a bond to N atoms \(^{45}\). In Table I, calculated values of an atomic magnetic moment \(M_{\text{atom}}\), corresponding to \(M_{\text{spin}} + M_{\text{orb}}\) along the easy magnetization direction, are also listed. In the monolayer case, the calculated \(M_{\text{atom}}\) is 1.1 \(\mu_B/\text{atom}\), which is in perfect agreement with the experimental value. This supports an ideal atomic structure of our monolayer sample.

Interestingly, the value of \(M_{\text{atom}}\) for the Fe atoms in the monolayer γ’-Fe4N is more than 1.5 times smaller than that in the topmost layer of the trilayer one (1.83 \(\mu_B/\text{atom}\)). In comparison with the DOS shown at the top of Fig. 7(a), the impact of the hybridization with the Cu states on the Fe DOS can be seen in Fig. 7(a): First, the DOS in the up-spin band, especially with \(d_{3z^2-r^2}\) and \(d_{xz}\) orbitals, becomes to have a tail toward a higher-energy side across the \(E_F\). This change deviates the 3d electrons in the up-spin band from a fully-occupied nature. Moreover, the spin asymmetry of the occupied 3d electrons, the difference between the electron occupation into each spin band normalized by the sum of them, reduces especially for the DOS with \(d_{3z^2-r^2}\) and \(d_{xz}\) orbitals. These changes could decrease \(M_{\text{spin}}\) of the Fe atoms. Note that the similar reduction in the magnetic moments of 3d TMs due to the hybridization with Cu states is reported, for example, in Ref. 46 and 47.

Then, by comparing two different Fe2N interfaces with the Cu substrate, it turns out that \(M_{\text{atom}}\) of the monolayer γ’-Fe4N (1.1 \(\mu_B/\text{atom}\)) is almost twice compared to that of the trilayer one (0.62 \(\mu_B/\text{atom}\)). In the monolayer case, the Fe2N layer faces to a vacuum and the Fe atoms are under reduced atomic coordination. This results in the narrower band width, and thus the DOS intensity increases in the vicinity of \(E_F\). Accordingly, a larger exchange splitting can be possible and the spin asymmetry of the occupied 3d electrons increases as shown in Fig. 7(a), compared to the interfacial Fe2N layer of the trilayer γ’-Fe4N [bottom panel of Fig. 7(b)]. This leads to larger magnetic moments at the surface. As a result, the competition between the enhancement at the surface and the decrease at the interface would make \(M_{\text{atom}}\) values quite layer-sensitive.

In the subsurface Fe layer of the trilayer γ’-Fe4N, the value of \(M_{\text{atom}}\) becomes largest due to the bulk coordination of the Fe atoms. Especially the Fe atoms not bonded to the N ones possess \(M_{\text{atom}}\) of 3.0 \(\mu_B/\text{atom}\), which is comparable to the values of Fe atoms at the same site in the bulk γ’-Fe4N\(^2\). Consequently, by averaging the layer-by-layer \(M_{\text{atom}}\) values of the trilayer γ’-Fe4N, the total magnetic moment detected in the XMCD measurement is expected to be 1.7 \(\mu_B/\text{Fe}\), with the electron escape depth taken into account (See Appendix A). Considering the composition expected to the trilayer sample, this value can well explain the experimental one of \(\sim 1.5 \mu_B/\text{Fe}\).

The theory also demonstrates the direction of an easy magnetization axis. The in-plane easy magnetization of our γ’-Fe4N samples was confirmed by the magnetization curves as well as the incidence dependence of the \(M_{\text{orb}}\) value. In contrast, the pristine ultrathin Fe films, which form either fct or fcc structures on Cu(001), show uncompensated out-of-plane spins over a few surface layers\(^{24,48}\). This shift of magnetic anisotropy by nitridation can be understood from the orbital-resolved Fe DOS shown in Figs. 7(a) and 7(b). Unlike the pure Fe/Cu(001) system\(^9\), the occupation of 3d electrons in states with out-of-plane-oriented orbitals (\(d_{yz}, d_{xy}, d_{3z^2-r^2}\)) is considerably larger than that with in-plane-oriented ones (\(d_{xy}, d_{x^2-y^2}\)). This could make \(M_{\text{orb}}\) prefer to align within a film plane, resulting in the in-plane magnetization of the system\(^6\).

IV. SUMMARY

In conclusion, we have conducted a detailed study on the growth, electronic and magnetic properties of the γ’-Fe4N atomic layers on Cu(001). The ordered trilayer film of γ’-Fe4N can be prepared by the Fe deposition under N\(_2\) atmosphere onto the existing monolayer surface. On the other hand, the repetition of the growth cycles including the high-energy N\(^+\) ion implantation resulted in the imperfect bilayer γ’-Fe4N. The STM and STS observations revealed the change in the surface topography and electronic structures with increasing the sample thickness. The XAS and XMCD measurements also showed the thickness dependence of the spectra, and the corresponding evolution of the \(M_{\text{spin}}\) values. All the thickness dependence of the electronic and magnetic properties is well explained by the layer-resolved DOS calculated using the first principles. Structural perfection of the system makes it possible to fully comprehend the layer-by-layer electronic/magnetic states of the γ’-Fe4N atomic layers.

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Appendix A: Conversion of XAS edge jump values to the thickness of $\gamma$-Fe$_4$N

The escape probability of electrons from inside a sample to a vacuum depends on the depth at which the electrons are excited. For a numerical interpretation of the XAS edge jump, the following factors should be mainly considered in principle: the penetration length of an incident x-ray ($\lambda_x$) and electron escape depth ($\lambda_e$), both energy-dependent. In the case of a few atomic layers of 3d transition metals, the attenuation of the incident x-ray intensity is almost negligible because $\lambda_e$ is orders of magnitude longer than the sample thickness. Therefore, in the present case, only the electron escape probability at the depth $z$ from the surface, namely, a factor of $\exp(-z/\lambda_e)$ is taken into account. As for the $\lambda_e$ value of Fe, 17 Å was tentatively assumed in our analysis, which is experimentally determined for Fe thin films. Then, based on the experimental Fe (N) edge jump values of 0.12 (0.015), those for the full-coverage dot-like bilayer, trilayer, and quadlayer $\gamma$-Fe$_4$N on Cu(001) are calculated as summarized in Table II.

| Fe edge jump          | Experiment Calculation | N edge jump          | Experiment Calculation |
|-----------------------|------------------------|----------------------|------------------------|
| Monolayer             | 0.12 (exp.)            | 0.015 (exp.)         |
| Bilayer dot           | -                      | 0.19                 | -                      |
| Trilayer              | 0.32                   | 0.40                 | 0.032                  |
| Quadlayer             | -                      | 0.57                 | 0.034                  |

1. J. Coey and P. Smith, J. Magn. Magn. Mater. 200, 405 (1999).
2. B. C. Frazer, Phys. Rev. 112, 751 (1958).
3. J. M. D. Coey, J. Appl. Phys. 76, 6632 (1994).
4. M. Komuro, Y. Kozono, M. Hanazono, and Y. Sugita, J. Appl. Phys. 67, 5126 (1990).
5. C. Ortiz, G. Dumpich, and A. H. Morrish, Appl. Phys. Lett. 65, 2737 (1994).
6. S. Atiq, H.-S. Ko, S. A. Siddiqi, and S.-C. Shin, Appl. Phys. Lett. 92, 222507 (2008).
7. D. M. Borsa, S. Grachev, D. O. Boerma, and J. W. J. Krussemakers, Appl. Phys. Lett. 79, 994 (2001).
8. J. M. Gallego, S. Y. Grachev, D. M. Borsa, D. O. Boerma, D. Ėcija, and R. Miranda, Phys. Rev. B 70, 115417 (2004).
9. K. Ito, G. H. Lee, K. Harada, M. Suzuno, T. Suemasu, Y. Takeda, Y. Saitoh, M. Ye, A. Kimura, and H. Akinaga, Appl. Phys. Lett. 98, 102507 (2011).
10. K. R. Nikolaev, I. N. Krivorotov, E. D. Dahlberg, V. A. Vas'ko, S. Urazhdin, R. Lolee, and W. P. Pratt, Appl. Phys. Lett. 82, 4534 (2003).
11. S. Kokado, N. Fujima, K. Harigaya, H. Shimizu, and A. Sakuma, Phys. Rev. B 73, 172410 (2006).
12. K. Ito, K. Toko, Y. Takeda, Y. Saitoh, T. Oguchi, T. Suemasu, and A. Kimura, J. Appl. Phys. 117, 193906 (2015).
13. C.-M. Fang, R. S. Koster, W.-F. Li, and M. A. van Huis, RSC Adv. 4, 7885 (2014).
14. S. H. Kim, K. S. Lee, H. G. Min, J. Seo, S. C. Hong, T. H. Rho, and J.-S. Kim, Phys. Rev. B 55, 7904 (1997).
15. F. Nouverté, U. May, M. Bamming, A. Rampe, U. Korte, G. Gäntherodt, R. Pentecheva, and M. Scheffler, Phys. Rev. B 60, 14382 (1999).
16. P. Torelli, F. Sirotti, and P. Ballone, Phys. Rev. B 68, 205413 (2003).
17. P. Srivastava, N. Haack, H. Wende, R. Chauvistre, and K. Baberschke, Phys. Rev. B 56, R4398 (1997).
18. M. Farle, W. Platow, A. N. Anisimov, P. Poulopoulos, and K. Baberschke, Phys. Rev. B 56, 5100 (1997).
19. M. Farle, B. Mirwald-Schulz, A. N. Anisimov, W. Platow, and K. Baberschke, Phys. Rev. B 55, 3708 (1997).
20. B. Schulz and K. Baberschke, Phys. Rev. B 50, 13467 (1994).
21. D. Li, M. Freitag, J. Pearson, Z. Q. Qiu, and S. D. Bader, Phys. Rev. Lett. 72, 3112 (1994).
22. M. Straub, R. Vollmer, and J. Kirschner, Phys. Rev. Lett. 77, 743 (1996).
23. W. Weber, A. Bischof, R. Allenspach, C. H. Back, J. Fassbender, U. May, B. Schirmer, R. M. Jungblut, G. Güntherodt, and B. Hillebrands, Phys. Rev. B 54, 4075 (1996).
24. H. L. Meyerheim, J.-M. Tonnerre, L. Sandratskii, H. C. N. Tolentino, M. Przybylski, Y. Gabi, F. Yildiz, X. L. Fu, E. Bontempi, S. Grenier, and J. Kirschner, Phys. Rev. Lett. 103, 267202 (2009).
25. T. Gejo, Y. Takagi, T. Hatsu, M. Nagasono, H. Oji, N. Kosugi, and E. Shigemasa, Chem. Phys. 289, 15 (2003).
26. T. Nakagawa, Y. Takagi, Y. Matsumoto, and T. Yokoyama, Jpn. J. Appl. Phys. 47, 2132 (2008).
27. J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
28. M. Lüders, A. Ernst, W. M. Temmerman, Z. Sztok, and P. J. Durham, J. Phys.: Condens. Matter 13, 8587 (2001).
29. M. Geilhufe, S. Achilles, M. A. Köbis, M. Arnold, I. Mertig, W. Hergert, and A. Ernst, J. Phys.: Condens. Matter 27, 435202 (2015).
30. J. M. Gallego, D. O. Boerma, R. Miranda, and F. Ynduráin, Phys. Rev. Lett. 95, 136102 (2005).
31. Y. Takahashi, T. Miyamachi, K. Ienaga, N. Kawamura, A. Ernst, and F. Komori, Phys. Rev. Lett. 116, 056802 (2016).
32. J. M. Gallego, S. Y. Grachev, M. C. G. Passeggi, F. Sacharovitz, D. Ecija, R. Miranda, and D. O. Boerma, Phys. Rev. B 69, 121404 (2004).
33. C. Navio, J. Alvarez, M. J. Capitan, D. Ecija, J. M. Gallego, F. Yndurain, and R. Miranda, Phys. Rev. B 75, 6632 (2007).
We checked the ionization of nitrogen molecules/atoms without bombardment using an ion gun. The ion flux monitored for the Fe evaporator increased in proportion to the rise in the N\textsubscript{2} pressure, far below the parameters at which Fe started to be evaporated. This indicates the ionization of the N\textsubscript{2} molecules and/or N atoms around the evaporator possibly by thermal electrons created inside it. Then, the N\textsuperscript{+} and N\textsubscript{2}\textsuperscript{+} ions could reach to the surface together with the evaporated Fe atoms, or iron nitride was already formed before landing.

The amount of the Fe atoms detected in the edge-jump spectra was smaller than that expected from the initially deposited ones. This implies that a certain amount of Fe atoms, not participating in forming any $\gamma'$-Fe\textsubscript{4}N structures, was embedded into the Cu substrate during annealing, at least several nms (probing depth in the TEY mode) below the surface.
Fig. 7. (Color online) Layer-by-layer electronic states of the γ′-Fe₄N atomic layers on Cu(001). Calculated layer-resolved DOS projected to each 3d orbital of the (a) monolayer and (b) trilayer γ′-Fe₄N on Cu(001). The DOS in the up-(down-) spin band is shown at upper (lower) panels. Note that the states with $d_{yz}$ and $d_{zx}$ orbitals are degenerated for the Fe3 and Fe4 sites in (b).