Systematic study of surface magnetism in Si(111)–Fe system grown by solid phase epitaxy: In situ schematic magnetic phase diagram of Si(111)–Fe

Azusa N. Hattori a,⁎, Ken Hattori b, Keita Kataoka a,1, Emi Takematsu b, Akira Ishii b, Fumio Komori c, Hiroshi Daimon a

a Graduate School of Materials Science, Nara Institute of Science and Technology, Ikoma, Nara 630-0192, Japan
b Department of Applied Mathematics and Physics, Tottori University, Tottori 680-8552, Japan
c The Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan

⁎ Corresponding author. Present address: The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan.
E-mail address: a-hattori@sanken.osaka-u.ac.jp (A.N. Hattori).
1 Present address: Toyota Central Research and Development Laboratories, Inc., Nagakute, Aichi 480-1192, Japan.

Abstract
We have studied in situ structures and magnetic properties for several iron silicides grown on Si(111) 7 × 7 clean surfaces by the solid phase epitaxy (SPE) method: deposition of Fe at 40 K and subsequently annealing, and summarized almost all silicide phases depending on the deposition thickness and the annealing temperature as a “schematic magnetic phase diagram”. In the SPE growth, bcc-Fe(111)1√3–FeSi(111)1√3–1, bcc-Fe3Si(112)2√3–2, c-FeSi(111)√3–√3-R30°, β-FeSi2(101)√100 and polycrystalline phases are formed on Si(111)7 × 7 surfaces depending on Fe coverage (0.15–10.0 nm) and annealing temperature (470–1070 K). The structures and magnetic properties of all the above Fe silicide phases have been characterized by using in situ reflection high-energy electron diffraction, scanning tunneling microscopy, and surface magneto-optical Kerr effect. Bulk-unstable c-FeSi phases showed ferromagnetic property at 40 K and this ferromagnetism remained even after air exposure. For the c-FeSi(111)/Si(111) system, the large spin polarization was proposed at the Fe interface atoms in the B5-type interface structure between the c-FeSi(111) ultra-thin film and the Si(111) substrate by first-principle calculations.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction
Surfaces and interfaces become important factors increasingly in the device functions with a trend towards greater miniaturization (large-scale integration). The injection of a spin-polarized electric current from a ferromagnet into a semiconductor is one of the key techniques in spintronics research [1]. Even on the most common semiconductor substrate silicon, growth of the magnetic films with the quality required for efficient spin injectors has not been achieved up to now because the structures and physical properties of metal and/or metal silicides on Si substrates are much more complicated due to the complex hybridization reaction and intermixing of junctions, and these properties would be different from bulk phases. Interestingly, the surface and the interface can stabilize the bulk-unstable structures as the epitaxial ultra-thin films, for example c-FeSi [2] and B2-MnSi [3], and these metastable phases were predicted to be ferromagnetic [4–9].

Synthesis of iron-silicides on silicon substrates has attracted much attention in application for light-emitting devices utilizing the semiconducting β-FeSi2 phase [10] and for spintronic devices utilizing the ferromagnetic Fe3Si phase [11,12]. So far, the structure of Si(111)–Fe system has been systematically studied; in the Si(111)–Fe system, nine iron-silicide and iron phases (Fig. 1) were formed by solid phase epitaxy (SPE) method on Fe deposition thickness, ΘFe, and subsequent annealing temperature, Ta [13]. Among nine possible bulk phases, bcc-Fe (Fig. 1(a)), Fe3Si (Fig. 1(b)), c-FeSi (Fig. 1(d)), and β-FeSi2 (Fig. 1(f)) are stable at room temperature (RT), and α-FeSi2 (Fig. 1(e)) phase is bulk stable at high temperature (1210–1493 K) [14]. The c-FeSi (Fig. 1(c)) can be worthy of attention. The meta-stable c-FeSi hardly exists in bulk, however, the epitaxial c-FeSi(111) can be stabilized on the Si(111) surface by the lattice matching. This metastable phase can be appeared under limited conditions; single c-FeSi(111) film can grow with the film thickness below ~ 0.7 nm, i.e. 8–9 monolayers (ML) in previous reports [13,15–18]. Theoretical study shows that c-FeSi films on Si substrates have significant magnetic moments [4,5], however, they have not examined experimentally to our
knowledge. So far, there have been a few reports on the magnetic properties of ultra-thin Fe and/or Fe silicides films on Si surfaces [2,19–22], nor the obtained results are not in conformity with one another. Generally, the magnetic properties in ultrathin film are sensitively correlated with their surface and interface configurations [23]. Since the solid-phase reactions in the Fe/Si system are very sensitive to experimental conditions, the study of its magnetic behavior should involve simultaneous investigations under maintaining the phase composition. Thus, the magnetic properties for the initial stages of the Fe/Si interface are still poorly understood.

In this study, we show the magnetic properties of each phase with well-defined structure in the Si(111)–Fe system at typically 40 K. The in situ surface magneto-optical Kerr effect (SMOKE) was provided to evaluate the magnetic property. SMOKE measurement can allow us to obtain the qualitative magnetic information of each phase, i.e., ferromagnetic (FM) or not-FM (NFM) with monolayer sensitivity, even if the surface system consists of more than one phases [24]. In situ SMOKE measurements revealed that metastable c-FeSi films exhibit FM property, and other phases show similar magnetic properties to their bulk system. Surprisingly, the FM properties maintained even after exposure...
the ultra-thin films into ambient air. The c-FeSi films were investigated by ex situ superconducting quantum interference device (SQUID). The c-FeSi ultra-thin films showed clear super-paramagnetic properties and FM properties depending on the film thickness. In order to understand the origin of the ferromagnetism, the first-principle calculations were employed to find the stable atomic arrangements of c-FeSi/Si and their magnetic moments. The comparison with experimental results allow us to convince that the magnetic moments are generated by the c-FeSi(111)/Si(111) interface configurations.

2. Experiment and calculation

Various Fe silicides were prepared by the SPE method: deposition and subsequent annealing. Sample preparations by SPE were performed in an ultra-high vacuum (UHV) system [12] equipped with a He refrigerator for the sample stage, Fe evaporators with alumina crucibles, a quartz-crystal thickness monitor, reflection high-energy electron diffraction (RHEED), and SMOKE. The base pressure was less than $7 \times 10^{-9}$ Pa. Si(111) (5b-doped, 0.02 Ω cm) samples of $\sim 4 \times 26 \times 0.5$ mm$^2$ in size were degassed and flashed for a few tens of times by direct-current heating at $\sim 1520$ K below $5 \times 10^{-8}$ Pa. After the flashing clean Si(111)$7 \times 7$ reconstructed surfaces were confirmed using RHEED. Fe (99.997%) was deposited from 470 to 1070 K for typically 5 min. Some of phases are ferromagnetic (FM), while other phases are not FM (NFM) at 40 K.

Both RHEED and SMOKE measurements were carried out for all the samples after cooling to 40 K in situ. Maximum applied magnetic field was 600 Oe in both in-plane and out-of-plane directions. The magnets consist of three York-type solenoids; two are fixed for the in-plane direction, and another is movable for the out-of-plane direction combined with the two fixed solenoids. A sample can rotate in the azimuth direction for RHEED and in-plane/out-of-plane SMOKE measurements. Scanning tunneling microscopy (STM) measurements were done at 300 K individually to confirm the surface local structures [25]. For some samples, SMOKE measurements were performed after air-exposure; the samples prepared in UHV were expressed to the air atmosphere, and reintroduced into the UHV chamber. For the reintroduced samples, any additional treatments were not carried out. The quantitative magnetic measurements were performed using SQUID (Quantum Design, MPMSXL) for the air-exposed samples.

For the calculations, the slabs of three c-FeSi(111) bi-layers on two Si(111) bi-layers with various interfaces are assumed. The surface unit size was Si(111)$1 \times 1$. First-principles calculations were carried out using a simulation tool for atom technology (STATE)-Senri [26] for relaxed structures and magnetic moments, with density functional theory within generalized gradient approximation proposed by Perdew, Brucke, and Ernzerhof, and ultrasoft (Toulliver-Mavtins non-conserving) pseudo potentials for Fe, Si and H atoms. The wave functions were expanded by a plane wave set with a cut-off energy of 25 Ry. $8 \times 8 \times 1$ k-points were considered. All atoms except the bottom Si(111)$1 \times 1$ layer were relaxed until all residual force components are less than 0.05 eV/Å. The spin polarization was considered.

3. Results and discussions

Fig. 2 shows a summarized schematic magnetic phase diagram at 40 K for Si(111)-Fe grown by SPE. The reproducibility of structures and magnetic properties was confirmed for all phases depending on $\Theta_{Fe}$ and $T_a$, therefore, we consider that this magnetic phase diagram is highly reliable. In SPE growth, Kataoka et al. reported that $\delta$-7 $\times$ 7, 1 $\times$ 1, and c-FeSi(111)$1 \times 1$ 2, 2 $\times$ 2, 4 $\times$ 4, and 3D-2 $\times$ 2 (α-FeSi$_2$), $\sqrt{3} \times \sqrt{3}$-R30$^\circ$, β-FeSi$_2$, and fine polycrystal phases form on the Si(111) surface depending on $\Theta_{Fe}$ and $T_a [13]$. The as-deposited 1 $\times$ 1 phase ($\Theta_{Fe} = 0.15$–0.6 nm) is assigned to Fe(111) [13]. For 1 $\times$ 1 ($\Theta_{Fe} = 0.15$–0.60 nm and $T_a = 470$–620 K), 2 $\times$ 2 ($\Theta_{Fe} = 0.15$–1.30 nm and $T_a = 620$–770 K), c(4 $\times$ 8) ($\Theta_{Fe} = 0.09$–0.45 nm and $T_a = 470$–620 K) phases are identified as c-FeSi(111) [18,15,16,27]. The surface structure difference has been proposed due to crystal structure difference in islands or nano-films with some Si adatoms and Fe vacancies distributions. $\sqrt{3} \times \sqrt{3}$-R30$^\circ$ (3, hereafter) phase ($\Theta_{Fe} = 0.24$–1.30 nm and $T_a = 670$–970 K) has been proposed as epitaxial ε-FeSi(111) [28–31]. Three dimensional (3D)-2 $\times$ 2 phase appeared at $\Theta_{Fe} = 0.15$–1.30 nm and $T_a = 870$–1070 K is assigned to the α-FeSi$_2$(112) [13]. For thicker region, bcc-Fe(111) ($\Theta_{Fe} > 0.6$ nm and $T_a = 670$ K), Fe$_3$Si fine polycrystals ($\Theta_{Fe} > 0.6$ nm and $T_a = 670$–770 K), and β-FeSi$_2$(101)$\parallel$(110) ($\Theta_{Fe} > 0.6$ nm and $T_a > 770$ K) appeared [13,12,13].

Among nine phases we found that c-FeSi, α-FeSi$_2$, and β-FeSi$_2$ are NFM, and the other phases have FM properties at 40 K. It should be noted that the relationship between $\Theta_{Fe}$ (nm) and the film thickness in average for Fe(111): $\Theta_{Fe}^{FM}$ and c-FeSi(111): $\Theta_{Fe}^{FM}$ (ML) is $\Theta_{Fe}^{FM} = \Theta_{Fe}^{FM}(0.092)$ (ML) and $\Theta_{Fe}^{FM} = \Theta_{Fe}(0.092 \times 2)$ (ML), respectively [33].

3.1. As-grown 1 $\times$ 1 phase: Fe(111)$1 \times 1$

At deposition, a 1 $\times$ 1 RHEED pattern (Fig. 3(a)) was observed in the region with a thickness of $\Theta_{Fe}^{FM}$ below 5.6 ML corresponding to Fe(111)$1 \times 1$ [13]. The STM image of this phase (Fig. 3(b)) showed a great number of clusters on the surface. The small clusters play a role as the nucleation centers for bcc-Fe growth, and above 5.6 ML, 3D bcc-Fe(111) islands form [12,13,13]. Fig. 3(c) and (d) shows the SMOKE results (red curves) of the 4.3 ML Fe(111)$1 \times 1$ sample. A square shape hysteresis loop appeared in the out-of-plane direction (Fig. 3(d)), and non-hysteresis curves in in-plane directions (Fig. 3(e)). Similar STM and SMOKE results were observed in the range of $\Theta_{Fe}^{FM} = 1.6$–7.6 ML. SMOKE results show that these small Fe clusters are FM with easy axis of out-of-plane. Although bulk α-Fe is FM with an easy axis of [100]$_{Fe}$ and a hard axis of [111]$_{Fe}$ [34],

![Fig. 2. The in situ schematic structure and magnetism diagram of SPE-grown Si(111)-Fe surfaces. The Si(111)$7 \times 7$ surface deposited with Fe at 40 K was subsequently annealed for 5 min. Some of phases are ferromagnetic (FM), while other phases are not FM (NFM) at 40 K.](image-url)
Fe(111) samples have easy axis lying in the out-of-plane direction. For the magnetic properties about the Fe deposited Si(111) surface, Nazir et al. reported that the magnetic easy axis lies in the out-of-plane direction at 100 K among 2.8–4.6 ML by ex-situ SMOKE [20]. Our SMOKE results are roughly in agreement with their results, although the sample shows out-of-plane ferromagnetism among $\Theta_{Fe}^{film}=1.6$–7.6 ML in our experiments. Above 7.6 ML, the samples showed the in-plane magnetic easy axis. The transformation of easy axis from out-of-plane to in-plane direction around $\Theta_{Fe}^{film} \sim 7.6$ ML should be caused by shape magnetic anisotropy [35,36]. STM images showed the reduction of surface morphology with increasing film thickness. We consider that at the thinner region pseudomorphic Fe grows with an in-plane film strain on the Si substrate, and strain relaxation around 7 ML thickness triggers the transformation of structure and magnetic easy axis.

3.2. Ferromagnetism in c-FeSi(111)

The c-FeSi(111) phases are formed by annealing at $T_a=470$–800 K. Depending on $T_a$ and $\Theta_{Fe}$, their surface orderings changed from $1 \times 1$ to $2 \times 2$ and/or $c(4 \times 8)$. Fig. 4 shows typical RHEED patterns and STM images for the c-FeSi(111) samples with $1 \times 1$, $2 \times 2$, and $c(4 \times 8)$ surface-orderings. Single $2 \times 2$ phase can be formed in the region of $\Theta_{Fe}^{film}=2.2$–4.3 ML and $T_a=620$–700 K. Out of these $\Theta_{Fe}^{film}$ and $T_a$ regions, $c(4 \times 8)$ and/or $\sqrt{3}$ phases coexist. The STM image for c-FeSi(111) $1 \times 1$ (Fig. 4(d)) shows rough surface, which is considerably different from that of the as-deposited sample in Fig. 3(b). Fig. 4(e) and (f) showed that the $2 \times 2$ and $c(4 \times 8)$ structure covers the surface forming the wide terraces, respectively. The atomic-resolved images of the $2 \times 2$ and $c(4 \times 8)$ arrangements [13] on the terraces were observed (not shown). Fig. 5 shows in situ Kerr loops for the $\Theta_{Fe}^{film}=8.7$ ML c-FeSi(111) $1 \times 1$ sample at 40 K. The no-square hysteresis loops appeared in the in-plane direction (Fig. 5(a)) while a hysteresis loop did not appear in out-of-plane (Fig. 5(c)). It should be noted that the applied magnetic field was not sufficient to saturate Kerr intensity, thus, the observed Kerr loops were “minor loops”. Those results show that c-FeSi(111) $1 \times 1$ has FM property at 40 K. The c-FeSi (111) $1 \times 1$ samples exhibited hysteresis loops with the $\Theta_{Fe}^{film}$ of 3.9–9.8 ML. The change of the remanence in Kerr loops, $\Delta I_r$, with increasing the thickness is plotted in Fig. 5(c). Above 7 ML, $\Delta I_r$ value decreased. The similar Kerr loops were observed in both $2 \times 2$ and $c(4 \times 8)$ samples. In $2 \times 2$ samples, however, the reduction of $\Delta I_r$ value started at around 5 ML. Fig. 6(a) shows a typical RHEED pattern for the coexistence of the $2 \times 2$ (red arrows) and $\sqrt{3}$ (blue arrows) phases on the sample with $\Theta_{Fe}=0.4$ nm and $T_a=700$ K. There was a tendency for $\Delta I_r$ values decreasing as the ratio of $\sqrt{3}$ [37] increases (Fig. 6(b)). Because the magnetic property of c-FeSi has been attributed to NFM property of c-FeSi.

To examine the origin of ferromagnetism in c-FeSi, we studied the dependence of FM property upon the annealing duration. Fig. 7 shows the annealing time dependence of $\Delta I_r$ (solid square) for the 5.4 ML c-FeSi(111) $2 \times 2$ samples. There was no tendency that $\Delta I_r$ decreases with the annealing time, instead, $\Delta I_r$ became a little bigger. We confirmed the unchanged $2 \times 2$ ordering, non-existence of other phases and maintenance surface morphology for the long time annealed samples by RHEED and STM. Moreover, FM property remained after the air exposure (open square in Fig. 7).
Fig. 4. Typical RHEED images for (a) $\Theta_{\text{film FeSi}} = 8.7$ ML c-FeSi(111)\(1 \times 1\) sample, (b) 3.3 ML c-FeSi(111)\(2 \times 2\) sample, and (c) 8.7 ML c-FeSi(111)c\((4 \times 8)\) sample. In (b) and (c), $2 \times 2$ (red arrows) and $c(4 \times 8)$ (blue arrows) surface reconstruction spots are seen. The electron incident direction was at $\frac{1}{2} \{11\}$. Corresponding STM images for (d) c-FeSi(111)\(1 \times 1\) sample ($V_s = 1$ V, $I_t = 0.20$ nA), (e) c-FeSi(111)\(2 \times 2\) sample ($V_s = 1$ V, $I_t = 0.25$ nA) and (f) c-FeSi(111)c\((4 \times 8)\) ($V_s = 1$ V, $I_t = 0.25$ nA). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

Fig. 5. In situ Kerr loops at 40 K for $\Theta_{\text{film FeSi}} = 8.7$ ML c-FeSi(111)\(1 \times 1\) sample in (a) the in-plane [11\(\bar{2}\)] and (b) the out-of-plane [11\(\bar{1}\)] directions. (c) The thickness dependence of the remanence intensity, $\Delta \gamma$, at 40 K for the c-FeSi(111)\(1 \times 1\) samples, at $T_a = 500$ K.

Fig. 6. (a) A typical RHEED image and Kerr loop for 0.40 nm-Fe deposited on the Si(111) surface ($\Theta_{\text{film FeSi}} = 8.7$ ML) annealed at 700 K. The electron incident direction was at [11\(\bar{2}\)]. Some of the $2 \times 2$ peaks and $\sqrt{3} \times \sqrt{3}$ peaks are indicated by red and blue arrows, respectively. (b) $\Theta_{\text{film FeSi}}$ dependence of $\Delta \gamma$ (left) and the ratio of certain RHEED spots for $\sqrt{3} \times \sqrt{3}/2 \times 2$ (right) at 40 K. Here, $T_a$ was $\sim 700$ K. $\Delta \gamma$ and $\sqrt{3} \times \sqrt{3}/2$ ratio are represented by red squares and blue circles, respectively. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)
The surface structure was completely damaged after the air exposure; the \( \frac{2}{2} \text{C}_2 \) and \( \frac{4}{2} \text{C}_2 \) reconstruction super-spots as shown in Fig. 4(b) and (c), respectively, were vanished on RHEED patterns. The slight reduction of \( \Delta I_r \), implying FM dissipation was observed, however, FM properties were able to be captured by \textit{ex situ} SQUID.

Fig. 8(a) shows magnetization as a function of magnetic field: the \( M-H \) curve of the 4.6 ML c-FeSi\([111]2 \times 2 \) sample at 50 K, obtained by SQUID. A 5.0 ML c-FeSi\([111]1 \times 1 \) sample also showed similar \( M-H \) curves. These samples exhibited superparamagnetic (SPM)-like behavior (no hysteresis loop). On the other hand, a thicker c-FeSi\([111]2 \times 2 \) sample with \( \Theta_{\text{film}} = 6.5 \) ML indicated FM behavior (open hysteresis loop), as shown in Fig. 9(a) and (b) which are \( M-H \) curves at 5 K and 100 K, respectively. c-FeSi \( \frac{1}{2} \times 1 \) and \( \frac{2}{2} \times 2 \) samples with \( \Theta_{\text{film}} = 7.6 \) ML also showed similar FM \( M-H \) curves. In Fig. 8(a) one may think paramagnetic for these \( M-H \) curves, however, compared with calculated Curie paramagnetic curve (Fig. 8(a) inset), the sample had a precipitous slope which is \( 10^3 \) times bigger than theoretical paramagnetic values, assuming that all deposited Fe atoms have individual magnetic moments. In general, superparamagnetism \([39-41]\) lacks of hysteresis in the magnetization curve. The theoretical treatments developed for ordinary paramagnetism can be expressed by the Langevin function \( \text{L(x)} = \coth(x) - 1/x \), where \( x = \mu H/k_B T \) \([39]\). Fig. 8(b) is \( M \) vs. \( H/T \) plots at 20 K (squares), 30 K (triangle), and 50 K (circle) for the c-FeSi\([111]2 \times 2 \) sample. The curves can be fitted by one Langevin function curve, which is a signature of superparamagnetism. Assuming the absence of interactions between particles, we can estimate the average value of the effective magnetic moment \( \mu \) \([42]\) to yield \( \mu \approx 4 \times 10^{-18} \) emu. For a 6.5 ML c-FeSi sample, the spontaneous
magnetization, $M_s$ at 5 K was estimated by the interception of the linearly extrapolated $M$ near the saturation region at $H=0$: $M_s \sim 7 \times 10^{-7}$ emu (Fig. 9(a)). When $M_s$ value is counted to the magnetic moments in the $1 \times 1$ unit cell, the magnetic moments in the $1 \times 1$ unit correspond to $\sim 1.2\mu_B$.

3.3. Origin of ferromagnetism in c-FeSi(111)/Si(111)

There have been no experimental reports about c-FeSi magnetic properties because c-FeSi is unstable in bulk phase, thus, the origin of FM in c-FeSi(111) is unclear. There are four possibilities of the origin of ferromagnetism in the c-FeSi(111)/Si(111) system related to (1) c-FeSi bulk, (2) surface structure of c-FeSi(111), (3) the interface structure between c-FeSi(111) and Si(111), and (4) extrinsic FM impurities. As mentioned before, we can exclude possibilities (2) and (4) by the air-exposure and annealing duration dependence (Fig. 7), respectively. The different easy-axis direction of c-FeSi (Fig. 5) from that of bcc-Fe (Fig. 3) also excludes the extrinsic FM-Fe impurity. The first-principles calculations with spin-polarization showed that bulk c-FeSi has truly small local magnetic moments of $\sim 0.01\mu_B$, which is consistent with previous theoretical report [6]. This denies possibility (1). Therefore, we propose the origin of FM in c-FeSi(111)/Si(111) would be their interface arrangement; the c-FeSi(111)/Si(111) system has “interface ferromagnetism”.

So far, eight different atomic configurations at the interface c-FeSi(111)/Si(111) have been modeled [15,43]. They can be classified by (i) the coordination of the Fe atom nearest to the interface (4-, 5-, 7-, and 8-fold) and (ii) the stacking sequence of silicide layers relative to the substrate (unfaulted A-type and faulted B-type). In particular, B5 [15] and B8 [15,43] were proposed to be relatively stable interface configurations. Our first-principle calculations involving spin-polarization show that B5 is most stable interface configurations, and c-FeSi with B5 interface has significant magnetic moments ($2.2 \mu_B/1 \times 1$ unit). In the c-FeSi, one bilayer is defined as a pair of 1-ML Fe and 1-ML Si [43], and Si termination is preferred as the outermost atomic layer [5,15]. For 6 layer c-FeSi with B5 interface, 6L-B5 model as shown in Fig. 9(c), the Fe atoms at the nearest to the interface (Fe 1) have the biggest magnetic moment ($1.6 \mu_B/1 \times 1$ unit) and Fe 3 atoms have 0.8 $\mu_B/1 \times 1$ unit. Any other atoms have no significant magnetic moments. These results strongly support that c-FeSi(111)/Si(111) would have the interface ferromagnetism.

The difference of magnetic properties between SPM and FM depending on the film thickness mainly would arise from the air-exposure effects on the interface structures. The inert property of the c-FeSi(111)/Si(111) interface and the reactive property of the island edges were reported [44]. The oxidation would begin at surface edges and reach to the interface between c-FeSi(111) and Si(111). A little reduction of FM elements after the air-exposure for 1 h (Fig. 7) may be caused by the partial breaking interface configuration due to progress oxidation at surface terrace edges. Applying a simple volume conversion model, the 5.0 ML c-FeSi (Fig. 8) is expected to consist of $\sim 50\%$ of the 4L and $\sim 50\%$ of the 6L while 6.5 ML c-FeSi (Fig. 9) consists of $\sim 80\%$ 6L and $\sim 20\%$ 8L. The magnetic ordering process depends on magnetic domain size. With decreasing domain, i.e., particle size, the magnetic anisotropy energy per particle responsible for holding the magnetic moment along certain directions becomes comparable to the thermal energy, and leads to superparamagnetism [40,41]. The SQUID results showed magnetic properties involving the degradation due to the degree of damage (destruction) for the interface structures after air-exposure. STM showed that the 6.5 ML c-FeSi had wider terraces and less island edges compared with the 5.0 ML sample. The thicker 6.5 ML sample might prevent the oxidation precession, and maintain its FM interface. Indeed, the obvious degradation of ferromagnetism was observed on the 400 hours air exposed 6.5 ML c-FeSi sample. While the underlying mechanism of the proposed interface ferromagnetism needs to be confirmed, our proposed interface FM can adequately explain...
the observed results. These findings are anticipated to lead to further experimental and theoretical studies in exploring novel emergent ferromagnetism while potentially leading to new functionalities in, not only Fe/Si system, but any material where the interface configuration plays an important role in inducing properties.

4. Conclusion

In conclusion, the overall view on the magnetic properties of Fe silicides grown by SPE on the Si(111) surface have been revealed in this paper. We suggest the interface ferromagnetism for bulk-unstable c-FeSi(111) on the Si(111) system. Here, two different magnetic properties: super paramagnetic and ferromagnetic were observed depending on film thickness. While the underlying mechanism of the interface ferromagnetism needs to be confirmed, these findings are anticipated to lead to further experimental and theoretical studies in exploring novel emergent ferromagnetism while potentially leading to new functionalities and opening the possibility for their utilization in spintronics applications.

Acknowledgment

The SQUID measurements were performed using facilities of the Institute for Solid State Physics, the University of Tokyo.

References

[25] We confirmed the structure and magnetism have not depended on the Si (111)–7 x 7 surface temperatures during deposition: at either 40 K or 300 K, the growth condition of Fe(111) and Tm was the same.
[33] A unity monolayer: ML is defined as 0.092 nm which corresponds to the surface atomic density of an unreconstructed Si(111) phase: 7.3 x 10¹⁴ atoms/cm². Thus, the thickness of Fe(111)/1 x 1 at ΘFe = 0.4 nm represents ΘFe/0.4 = 0.092 ≈ 4.3 ML. In the case of the c-FeSi(111), consisting of Fe and Si layers, 1 ML of Fe(111) deposition corresponds to 2 layers of c-FeSi(111), the thickness of Fe(111)/1 x 1 at ΘFe = 0.4 nm represents ΘFe/0.4 = 0.092 ≈ 2–8.7 ML.
[38] C.P. Bean, J.D. Livingston, J. Appl. Phys. 30 (1959) S120.