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Growth of Fe silicides on Si(111) surfaces from bcc-Fe to fine-polycrystal and $\beta$-FeSi$_2$ phases: Structure and magnetism

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Abstract

We studied the structure and magnetism of the bcc-Fe(111) phase to the fine-polycrystal and $\beta$-FeSi$_2$ phases in solid phase epitaxial growth of iron silicides on Si(111) surfaces. In the polycrystal phase displaying Debye rings in reflection high-energy electron diffraction, we found randomly-oriented bcc-Fe fine-crystals to be responsible for the phase, and obtained ferromagnetic hysteresis but the magnetization was small. In the polycrystal phase, other irons and silicides were sometimes included: epitaxially-grown bcc-Fe crystals with preferential orientation in different directions, and $\beta$-FeSi$_2$(101) or (110) layers. We show a growth scheme with annealing for structure and magnetism of these phases.

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1. Introduction

Iron silicides grown on silicon substrates have attracted much attention since semiconducting $\beta$-FeSi$_2$ became a candidate for near-infrared (≈1.5 μm) light-emitting devices [1]. Recently, the co-existence of ferromagnetic silicides and $\beta$-FeSi$_2$ layers on an Si(111) surface was reported [2,3] in a simple growth method, that is, solid phase epitaxy (SPE: annealing after deposition), suggesting a possibility to apply it to spintronic devices; for instance, spin-polarized carriers injected from ferromagnetic layers to luminescent layers induce circularly-polarized light-emission [4].

In SPE-grown Si(111)-Fe surfaces with >15 monolayers (ML) in initial Fe coverage, Kataoka et al. [5] have reported a changing of schematic phase from diffuse bcc-Fe[111] $\times$ 1 to fine-polycrystal and then to $\beta$-FeSi$_2$ with thermal annealing. Thus, studies on both structure and magnetism in these phases are interesting for fundamental science and application. In the polycrystal phase, where low-energy electron diffraction (LEED) shows no specific features and reflection high-energy electron diffraction (RHEED) shows Debye rings [5], $\epsilon$-FeSi [5] and Fe$_2$Si [3,6] have been suggested as candidates of constituent until now.

In this paper, we show that the polycrystal phase arises from randomly-oriented bcc-Fe fine crystals and is a ferromagnetic phase. When changing the phase from bcc-Fe(111) to polycrystal and $\beta$-FeSi$_2$, we also present RHEED and X-ray diffraction (XRD) results for structure and surface magneto-optic Kerr effect (SMOKE) and vibrating sample magnetometer (VSM) results for magnetism, and discuss the growing process of iron silicides on Si(111) surfaces, as shown in Fig. 1.

2. Experimental

Sample preparations and in-situ RHEED and SMOKE measurements were performed in an ultra-high vacuum (UHV) system equipped with an He refrigerator at the manipulator [2,3]. Si(111) mirror-polished samples (500 μm) were degassed and flashed at ≈1520 K by direct-current heating for a few tens of times below 2–3 $\times$ 10$^{-8}$ Pa, and were shown to be clear Si(111)$\{1\over 7\}$ $\times$ 7 RHEED patterns. The iron (99.997%) was deposited by in-situ RHEED (electron-beam energy 15 keV) and SMOKE (±600 Oe). Magnetization of some samples was measured by ex-
Fig. 1. Growing schemes of Fe silicides on Si(111) surfaces by annealing from bcc-Fe to fine-polyoriental and β-FeSi$_2$ phases.

situ VSM after coating of Au (3 nm) to reduce oxidation. Crystal quality of some samples at 300 K was measured by ex-situ XRD (Cu K$_\alpha$) with $\theta$–$2\theta$ scan mode.

3. Results and discussion

The bcc-Fe(111) $1 \times 1$ phase appears at $T_{\text{Fe}} = 5$ nm and $T_a \sim 620$ K, according to Kataoka et al. [5] where a unity ML corresponds to 0.092 nm of Fe. Fig. 2(a) shows a RHEED pattern of an Si(111) surface deposited with Fe of 5 nm without annealing (sample 1). The electron-beam incidence-direction is $[10\overline{1}]_\text{Si}$ and the direct beam is seen at 000$_\text{Fe}$. The scale bar $a_\text{Fe}$ corresponds to the unit length of an Si(111) $1 \times 1$ surface in the reciprocal lattice space; the unit length of $1 \times 1$ in real space is $a_\text{Fe} = 0.384$ nm. Clearly transmission spots are seen and we can assign them to reciprocal lattice points of bcc-Fe, as noted as $12\overline{1}T_{\text{Fe}}$, in reference to $a_\text{Fe}$. The RHEED pattern shows that bcc-Fe(111) $1/2<121/C_{2}$ is parallel to Si(111),$[\overline{1}1\overline{2}]$. Previous studies [5,7,8] also reported the epitaxial growth of bcc-Fe in these orientations. The size of the epitaxial bcc-Fe fine-particles displaying the transmission spots is less than the mean free path (~15 nm) of the incident electron beam. The estimated crystalline size is ~1 nm full width at half maximum for in-plane and out-of-plane directions from the spot profile. Since the previous scanning tunneling microscopy (STM) study reported randomly-shaped small grains (5–20 nm) under similar conditions [5], we consider that the grains consist of aggregated small (~1 nm) bcc-Fe(111) epitaxial islands (Fig. 1(a)).

Fig. 2(b) and (c) show SMOKE hysteresis loops of this sample at ~40 K: Kerr intensity as a function of the applied magnetic field toward in-plane $[10\overline{1}]_\text{Fe}$ and out-of-plane $[11\overline{2}]_\text{Fe}$ directions, respectively. In the other in-plane direction (e.g., $[11\overline{2}]_\text{Fe}$) loops similar to Fig. 2(b) were observed. Ferromagnetic loops from bcc-Fe can been observed. Ferromagnetic loops from bcc-Fe can been observed. For rings in this figure, we should distinguish Debye rings and Newton rings (NR) due to the direct-beam fluorescence; the former is suppressed below the shadow edge while the latter has the same intensity. We can see a Debye ring passing a $101\overline{1}T_{\text{Fe}}$ spot.
and a faint Debye ring passing a 121$_{Fe}$ spot. Thus we assign them to 110$_{Fe}$ and 211$_{Fe}$ Debye rings, respectively. Next we prepared another sample (sample 3) with almost the same growth condition. For sample 3 we obtained different transmission patterns but the same Fe Debye rings, as shown in Fig. 3(b) at $1/11^2_2/C_{138}^{Si}$ incidence. We can see several spots on the 110$_{Fe}$ and 211$_{Fe}$ Debye rings, indicating bcc-Fe transmission spots. For instance, 101$_{Fe2}$ and 121$_{Fe2}$ spots are attributed to the epitaxial islands with bcc-Fe(111) $11/2^{10}_{1}/C_{138}^{Si}$. Similarly the spots with subscript notations, Fe1 and Fe4, are attributed to those with bcc-FeSi$_2$(101) and (110) surfaces, respectively, parallel to Si(111) $11/2^{10}_{1}/C_{138}^{Si}$.

For the spots with Fe3, bcc-FeSi$_2$(121) $110_{Si}$. RHEED patterns at $110_{Fe}$, $T_a$ and annealing duration imply that the formation process is very transient and is influenced by uncontrollable factors. Sometimes we observed the co-existence of randomly-oriented bcc-Fe polycrystals and b-FeSi$_2$(101) or (110) surfaces in the polycrystal phase. Fig. 3(c) shows an RHEED pattern of an Si(111) surface at $110_{Fe}$ = 5 nm and $T_a$ = 770 K for 200 min (sample 5) at $112_{Si}^{Si}$ incidence. Some spots (e.g., 121$_{Fe-2}$) are attributed to

and a faint Debye ring passing a 121$_{Fe}$ spot. Thus we assign them to 110$_{Fe}$ and 211$_{Fe}$ Debye rings, respectively. Next we prepared another sample (sample 3) with almost the same growth condition. For sample 3 we obtained different transmission patterns but the same Fe Debye rings, as shown in Fig. 3(b) at [112$^{Si}_3$] incidence. We can see several spots on the 110$_{Fe}$ and 211$_{Fe}$ Debye rings, indicating bcc-Fe transmission spots. For instance, 101$_{Fe2}$ and 121$_{Fe2}$ spots are attributed to the epitaxial islands with bcc-Fe(111) $[111]_1^{Si}||[111]_1^{Fe}$, $[111]_1^{Ti}||[111]_1^{Si}$. Similarly the spots with subscript notations, Fe1 and Fe4, are attributed to those with bcc-FeSi$_2$(101) and (110) surfaces, respectively. For the spots with Fe3, bcc-Fe(121) $[111]_3^{Si}$. RHEED patterns at $10^{Si}_3$ incidence showed the same Debye rings and transmission spots attributed to epitaxial Fe islands.

In Fig. 3(a) and (b), the Fe Debye rings indicate random orientations of fine bcc-Fe polycrystals (Fig. 1(b)), while the transmission spots indicate the survival or growth of the epitaxial Fe islands with some preferential orientations (Fig. 1(c)). The different transmission spots appeared at the same $\Theta_{Fe}$, $T_a$ and annealing duration imply that the formation process is very transient and is influenced by uncontrollable factors. Sometimes we observed the co-existence of randomly-oriented bcc-Fe polycrystals and b-FeSi$_2$(101) or (110) surfaces (Fig. 1(c)) in addition to the epitaxial Fe islands with some preferential orientations. Fig. 4 shows an ex-situ 0–20 XRD pattern of sample 4 prepared in the same manner as samples 2 and 3 ($\Theta_{Fe}$ = 5 nm, $T_a$ = 670 K, 5 min). We can identify the XRD peaks as randomly-oriented bcc-Fe polycrystals, b-FeSi$_2$(101) or (110) surfaces [11], and an Si(111) substrate. The broad b-FeSi$_2$ peaks would reflect the small crystalline size in the [111]$_{Si}$ direction and/or the distribution of distorted b-FeSi$_2$ domains. In RHEED we sometimes also confirmed b-FeSi$_2$(101) or (110) surface-spots in the polycrystal phase. Fig. 3(c) shows an RHEED pattern of an Si(111) surface at $110_{Fe}$ = 5 nm and $T_a$ = 770 K for 200 min (sample 5) at [112]$_{Si}^{Si}$ incidence. Some spots (e.g., 121$_{Fe-2}$) are attributed to
epitaxial bcc-Fe islands like Fig. 3(b). The other spots are attributed to \(\beta\)-FeSi\(_2\)(101) or (110) surfaces (as shown in Fig. 3(d), presented later). The 110\(_{\text{Si}}\) Debye rings become very faint but exist. For another sample (\(\Theta_{\text{Fe}} = 5\,\text{nm}, \, T_a = 770\,\text{K}, \, 5\,\text{min}\)), RHEED showed only faint Fe Debye rings (Fig. 1(d)). In the polycrystal phase, we emphasize that the other phases can co-exist (by uncontrollable factors) possibly under non-equilibrium conditions\([5]\), but there is a tendency of decreasing bcc-Fe polycrystals with increasing \(T_a\) and annealing duration. The previous STM study\([5]\) reported a rough surface with \(\sim 10\,\text{nm-grains and no periodic structure in atomic scale in the polycrystal phase.}

All samples displaying Fe Debye rings in RHEED showed ferromagnetic hysteresis loops in SMOKE. Fig. 5(a) shows a hysteresis loop of sample 3 applied at in-plane [10\(\bar{1}\)\(\text{Si}\)] magnetic field: obviously a ferromagnetic minor loop. The loop at in-plane [\(1\bar{1}2\)\(\text{Si}\)] was similar to Fig. 5(a). After the Au deposition (3 nm) we obtained similar hysteresis loops in SMOKE. Fig. 5(b) shows an ex-situ VSM hysteresis loop of this Au-coated sample applied at in-plane direction at 300 K; the diamagnetic component of the Si substrate is subtracted. The small coercive force (\(\sim 50\,\text{Oe}\)) was measured after applying high magnetic field (1500 Oe). Fig. 5(a) and (b) suggests that more than 600 Oe in magnetic field was required to remove the magnetic domain walls at first, and that magnetization directions can easily change once the magnetization domains are combined. Since the film area was 4.0 mm \(\times\) 15 mm, the expected saturation magnetization is \(5.0 \times 10^{-4}\,\text{emu}\), assuming that all deposited Fe atoms form a bcc-Fe film. The obtained saturation value is, however, \(\sim 2 \times 10^{-4}\,\text{emu}\), less than half of the expected value. This suggests that more than half of the deposited Fe atoms react with Si substrate atoms, forming silicides with less magnetization in sample 3. As mentioned above, the density of bcc-Fe polycrystals decreases with thermal annealing. For other samples displaying Fe Debye rings, sometimes it was hard to obtain ferromagnetic hysteresis loops in ex-situ VSM, probably due to less sensitivity compared with in-situ SMOKE; SMOKE showed ferromagnetic minor loops for the samples, with and/or without Au-coat, even after air exposure.

The \(\beta\)-FeSi\(_2\) phase dominates at \(\Theta_{\text{Fe}} = 5\,\text{nm}\) and \(T_a > 820\,\text{K}\)\([5]\); LEED patterns show \(c(4 \times 2)\) spots of three domains\([5,12,13]\), the unit of which corresponds to half the size of \(\beta\)-FeSi\(_2\)(101) or (110) in the \(a\) axis direction. The LEED spots are streaky toward (1\(\bar{1}2\)\(\text{Si}\)) due to the crystalline domain size restriction induced by the lattice mismatch. Fig. 3(d) shows an RHEED pattern of an Si(111) surface at \(\Theta_{\text{Fe}} = 5\,\text{nm}\) and \(T_a = 870\,\text{K}\) for 5 min (sample 6) at [1\(\bar{1}2\)\(\text{Si}\)] incidence. All spots are attributed to \(c(4 \times 2)\) (some expected spot positions are marked by circles for eye guide), indicating the formation of \(\beta\)-FeSi\(_2\)(101) or (110) surfaces. Although RHEED and LEED display only \(c(4 \times 2)\) spots in the \(\beta\)-FeSi\(_2\) phase, STM shows a variety of locally-reconstructed \(\beta\)-FeSi\(_2\) surfaces\([5]\). For magnetism of sample 6, we obtained ferromagnetic minor hysteresis loops in (sensitive) SMOKE but no ferromagnetic hysteresis in VSM. For a further-annealed sample (\(\Theta_{\text{Fe}} = 5\,\text{nm}, \, T_a = 870\,\text{K}, \, 200\,\text{min}\)) displaying a \(c(4 \times 2)\) pattern (\(\beta\)-FeSi\(_2\)), we obtained no ferromagnetic hysteresis in both SMOKE and VSM. Since \(\beta\)-FeSi\(_2\) crystal is paramagnetic, these results imply that ferromagnetic species (might be bcc-Fe clusters, for instance) with small density (not detected by RHEED and LEED) are removed and transformed to \(\beta\)-FeSi\(_2\) by further thermal annealing (Fig. 1(f)).

4. Conclusion

We studied structure and magnetism of the bcc-Fe phase, the polycrystal and \(\beta\)-FeSi\(_2\) phases in annealing of the Si(111)-Fe SPE system (\(\Theta_{\text{Fe}} = 5\,\text{nm}\)), using RHEED, XRD, SMOKE and VSM. In the bcc-Fe(111) phase where epitaxial Fe(111)|\(\text{Z}\)\(\text{T}\)\(_n\)\(\text{Si}(111)|\(\text{Z}\)\(\text{i}\), an Fe thin film consisting of Fe islands indicated the ferromagnetic easy axis of almost in-plane direction. Annealing in the bcc-Fe(111) phase (\(T_a < 620\,\text{K}\)) led to an increase in the coercive force. When \(T_a > 820\,\text{K}\), Debye rings, indicating the polycrystal phase, started to appear in RHEED. We found that randomly-oriented bcc-Fe fine-crystals are responsible for the polycrystal phase. The polycrystal phase was metastable and easily changed to other structures, for instance, epitaxially-grown (preferentially oriented) bcc-Fe crystals in different orientations and \(\beta\)-FeSi\(_2\)(101) or (110) layers by uncontrollable factors. Though the polycrystal phase is ferromagnetic, the magnetization value was smaller than expected from the deposition quantity, suggesting reduction of the net volume of bcc-Fe by the reaction with substrate Si. For the initial saturation of the magnetization it was suggested to require higher magnetic field than that after saturation. In the \(\beta\)-FeSi\(_2\) phase at \(T_a > 820\,\text{K}\), further annealing removed (randomly-oriented) ferromagnetic bcc-Fe crystals and the surface was covered by \(\beta\)-FeSi\(_2\)(101) or (110) layers (displaying \(c(4 \times 2)\) spots).

Acknowledgments

The authors thank Dr. Kodama and Prof. Hosoiito for VSM, and Katao for XRD in NAIST. This work was partially supported by the Murata Science Foundation.

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