Three-dimensional elongated island of iron silicide grown on Si(001) surfaces by solid phase epitaxy

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Abstract. We observed three-dimensional (3D) elongated islands of iron silicide grown on Si(001) surfaces by solid phase epitaxy. Scanning tunneling microscopy images showed islands of narrow width (less than ≈3 nm) elongated to either Si[110] or Si[¯110] direction for 10–20 nm. Reflection high-energy electron diffraction patterns showed the transmission spots of the islands having reciprocal rods parallel to the surface, Si[ ¯110] and Si[110]. We proposed two possible crystal models, α-FeSi₂ and B2 (CsCl) FeSi, for the 3D elongated islands.

1. Introduction
The structures and the electronic properties of Fe silicides grown on Si surfaces have been widely studied for applications to Si-based device technology. In particular, the semiconducting β-FeSi₂ epitaxial phase has attracted much attention for optoelectronic devices [1]. Recently, ferromagnetic properties of some silicides have been reported [2]. For the fabrication of functional silicide films, growth at the initial stage is one of the key processes. So far, many authors have reported the initial growth of iron silicides on clean Si(111)7×7 surfaces by the simple growth process, solid phase epitaxy (SPE): annealing after deposition [3].

On the important substrate for the semiconductor industry, Si(001), however, only a few works [4, 5] have reported on the initial growth with atomically resolved scanning tunneling microscopy (STM). Raunau et al. [4] demonstrated the existence of rectangle-shape like islands (assigned to γ-FeSi₂(001)), c(2×2) islands (assigned to β-FeSi₂(100)), and islands with a rectangle surface unit (assigned to β-FeSi₂(001) or (010)), depending on deposition thickness and annealing temperature. Hajjar et al. [5] showed also two-dimensional c(2×2) islands, which they assigned to α-FeSi₂. Since various kinds of islands of iron silicides can co-exist on Si(001) substrates, we should take account of the growth conditions when we analyze properties of a surface area, including the different phases of islands with photoelectron spectroscopy, Auger electron spectroscopy and so on.

In this paper we present a new type of silicide islands, three-dimensional (3D) elongated island SPE-grown on Si(001), studied with STM, low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED). We also show the origin of 2×1 streaks observed in LEED and RHEED.
2. Experimental
The experiments were performed in two different ultra-high vacuum (UHV) systems; one [6, 7] is equipped with LEED optics and STM equipment, and the other [2] with RHEED equipment. Both systems have alumina-crucible evaporators cooled by water and thickness monitors. The base temperature of the sample stage in the former STM system was room temperature (RT), while that in the latter RHEED system was about 50 K (LT). Si(001) mirror-polished samples (Sb doped, 0.03 Ωcm) were degassed and flashed at ≈1250°C by direct-current heating for a few of tens times below 2-3×10⁻⁸ Pa, and showed clean Si(001)2×1 at RT and c(4×2) at LT. The iron (99.999%) was deposited on these clean surfaces at RT or LT until \( \theta_{Fe} = 1–2 \) monolayers (1 ML = \( 6.78 \times 10^{14} \text{cm}^{-2} \)) below 4×10⁻⁸ Pa and subsequently annealed at \( T_a = 200–800 \)°C for 10 min or 3.5 min, respectively, below 1×10⁻⁸ Pa. The RT surfaces were observed with LEED and STM in the current-imaging mode using a chemically etched W tip. The LT surfaces were observed with RHEED at the primary energy 15 keV.

3. Results and Discussion
Figure 1(a) shows a typical STM image of the surfaces for \( \theta_{Fe} = 1.0 \) ML and \( T_a = 600 \)°C. The sample bias voltage was -1.0 V and the tunneling current was 0.3 nA. We can see elongated islands with two different grown directions, Si[110] and Si[\bar{1}10], and with ≈10–20 nm in length and ≈3 nm in width. In this figure we should note the ghost of the islands, which often appears when the island shape is sharper than the tip apex. The tip used was a standard one since such ghosts were not observed with the same tip on other surfaces prepared under different conditions, for instance, at lower \( T_a \). Thus, figure 1(a) shows us the formation of high and cliffy 3D islands with a narrower width than ≈3 nm. We could not estimate the height of the islands in STM because they are the current images. Such 3D elongated islands were observed in STM at \( (\theta_{Fe} \text{ (ML)}, T_a \text{ (°C)}) = (1.0, 600), (1.0, 800) \) and \( (2.0, 800) \), but not at \( (1.0, 200), (1.0, 400), (2.0, 200), (2.0, 400) \) and \( (2.0, 600) \).

![Figure 1](image)

**Figure 1.** (a) An STM image of 3D elongated islands on Si(001), and corresponding RHEED patterns with (b) Si[1\bar{1}0] and (c) Si[100] incidences. Transmission spots (e.g. \( O' \), \( A-D \)) arising from the islands are seen additionally with the substrate Si(001)2×1 (and 1×2) spots. Also 2×1 (and 1×2) streaks are seen (e.g. arrows).
Figure 2. A schematic of a part of the reciprocal lattice. The reciprocal lattice of the 3D elongated islands is shown by black and white rods parallel to the surface, Si[110] and Si[110] directions, respectively.

Figure 3. Crystal models for the 3D elongated islands: (a) α-FeSi$_2$ and (b) B2 (CsCl) FeSi. Solid and open circles present Fe and Si atoms, respectively. Open squares are substrate Si atoms.

The LEED patterns for the surfaces (figure 1(a)) showed 2×1 (and 1×2) spots with 2×1 (and 1×2) streaks. Hereafter we describe only 2×1 for both domains. The 2×1 streaks imply that the Si(001) substrate between the 3D elongated islands appears in the 2×1 reconstruction with many defects which induce poor ordering toward the dimer-row (×1) directions. Actually, we observed STM images of the 2×1 substrates with defects, of which density was higher than that of the clean surfaces, and LEED patterns with 2×1 streaks in wide conditions for preparation.

Figures 1(b) and (c) show RHEED patterns in Si[110] and Si[100] electron-incidences, respectively, for $\theta_{Fe} = 2.0$ ML and $T_a = 600^\circ$C. Transmission spots, for instance, labeled by $O'$ and $A-D$, are seen with 2×1 spots and 2×1 streak curves (some of them are indicated by arrows). We can see also faint p(2×2) and c(4×2) spots, indicating that a smaller part of the substrate reconstructs into p(2×2) or c(4×2) at LT, but the greater part is 2×1 with defects (2×1 spots and streaks) as described above.

Since the transmission spots were observed at $(\theta_{Fe}$ (ML), $T_a$ (°C)) = (1.5, 550) and (2.0, 600) but not at (2.0, 230) and (2.0, 440), we can identify the transmission spots as those from the 3D elongated islands (figure 1(a)). At $\theta_{Fe} = 2.0$ ML and $T_a = 600^\circ$C where the transmission spots appeared in RHEED, we did not observe the 3D elongated islands in STM. Slightly different observation conditions between the STM and the RHEED results could arise from the difference of the preparation: base temperature, annealing time and so on, in the two different UHV systems.

From the analysis of azimuth-scanning RHEED patterns, we can draw a schematic reciprocal lattice, as shown in figure 2. Here, $a^*_{ab}$ is the reciprocal-lattice length of the Si(001)1×1 surface-unit length, $a_b = 0.384$ nm. Thick solid lines parallel to the Si[001] direction represent the 1×1 surface rods. The hatched planes represent the 2×1 streak planes. For instance, the intersection of the streak planes (arrows) with the Ewalt sphere appear as the streak curves (arrows in figure 1(b)).

From the RHEED analysis, we found that the trajectories of the transmission spots form
reciprocal rods parallel to the surface, Si[110] and Si[110] directions, as shown by black and white rods, respectively, in figure 2. For instance, transmission spots O’ and A–D in figures 1(b) and (c) correspond to points around O’ and A–D in figure 2, respectively. We can also recognize the reciprocal rods from the transmission spots located far from the reciprocal lattice origin. The two kinds of reciprocal rods (black and white rods in figure 2) imply the existence of 3D islands grown in two directions. For instance, the islands having the black rods elongate in the ordered Si[110] direction and are narrow in the disordered Si[110] direction. For the ordering directions, Si[001] and Si[110], the spot profiles showed a crystalline domain size of >10 nm.

We propose two possible crystal models from the reciprocal rods: α-FeSi2 and B2 (CsCl) FeSi in figures 3(a) and (b), respectively. Here, solid and open circles present Fe and Si atoms, respectively. Open squares are Si(001)1×1 substrate atoms, of which relative position to the crystals is tentative. The reciprocal lattices of both structures are the same, when the crystal units shown in figure 3 are arranged orderly in Si[001] and Si[110] and disorderly in Si[110]. Other structures of iron silicides cannot satisfy the obtained reciprocal lattice.

Although the α-FeSi2 bulk phase is stable only at high temperature (937–1220°C), the existence of this phase at RT has been reported for iron silicides grown on (anchored to) Si(111) substrates [8]. The lattice mismatches to Si[110] and Si[110] are -1% and +34%, respectively (figure 3). The B2 FeSi phase is unstable in bulk, however this phase has been also suggested for some silicides grown on Si(111) substrates [9]. The lattice mismatches to Si[110] and Si[110] are 0% and -29%, respectively.

The smaller mismatch to Si[110] and the larger mismatch to Si[110] can explain the ordered and elongated growth to Si[110] and the disordered and narrow width along Si[110], respectively, for both models. The rod profiles in RHEED and the island size in STM suggest that the island forms with a crystalline domain of 10–20 nm along elongated Si[110] and of >10 nm along surface-normal Si[001]. The growth to Si[110] by the crystals is hard, resulting in a width narrower than ≈3 nm.

4. Conclusions
We observed 3D elongated islands of iron silicide grown on Si(001) surfaces by SPE method using STM, LEED and RHEED. STM images showed 3D islands elongated to either Si[110] or Si[110] for 10–20 nm and with a narrow width (less than ≈3 nm). RHEED patterns showed the transmission spots indicating reciprocal rods parallel to the surface, Si[110] and Si[110], arising from the 3D elongated islands. We proposed two possible crystals, α-FeSi2[110]|110 || Si(001)|110| and B2 FeSi[110]|110 || Si(001)|110|, for the Si[110]-elongated islands. The lattice mismatches of the both crystal models explain the growth (ordered in >10 nm) and the non-growth (disordered) directions. The Si(001) substrate between the islands shows dimer rows with many defects resulting in the 2×1 streaks in the diffraction.

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References
[1] For example, Leong D, Harry M, Reeson K J and Homewood K P 1997 Nature 387 686-8
[2] Hattori A N, Hattori K and Daimon H (submitted to this J. Phys.: Conf. Ser.)
[3] For example, Lifshits V G, Saranin A A and Zotov A V 1994 Surface Phases on Silicon (Chichester: John Wiley & Sons)
[4] Raunau W, Niehues H and Comsa G 1993 Surf. Sci. 284 L375-83
[5] Hajjar S, Garreau G, Pelletier S, Bertoncini P, Wetzel P, Gewinner G, Imhoff M and Pirri C 2003 Surf. Sci. 532-535 940-45
[6] Hattori K, Nishimura T, Kataoka K, Shimamoto Y and Daimon H 2004 *Thin Solid Films* **464-465** 5-9
[7] Nishimura T, Hattori K and Daimon H *Surf. Rev. Lett.* (in press)
[8] Jedrecy N, Waldhauer A, Sauvage-Simkin M, Pinchaux R and Zheng Y 1994 *Phys. Rev.* B **49** 4725-30
[9] Walter S, Bandorf R, Weiss W, Heinz K, Starke U, Strass M, Bockstedte M and Pankratov 2003 *Phys. Rev.* B **67** 085413