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Variety of iron silicides grown on Si(001) surfaces by solid phase epitaxy: Schematic phase diagram

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Abstract

We systematically studied the formation of various iron–silicide phases, grown on Si(001) surfaces by solid phase epitaxy, with scanning tunneling microscopy, low-energy electron diffraction and reflection high-energy electron diffraction. We found and studied the phases of c(2 × 2) islands, rectangle-like islands, elongated islands, layered islands, dome-like islands, eddy and cracked structures, and small clusters. A schematic phase diagram of these phases is successfully summarized against iron coverage at room temperature and subsequent annealing temperature.
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1. Introduction

Iron silicides grown on silicon substrates have attracted much attention because of the possibility of applying optical [1] and magnetic [2] functions to Si-based device technology. The structure of formed iron silicide depends on Si substrate and preparation recipe. Complex recipes to produce a certain epitaxial silicide, mainly β-FeSi$_2$ [3], have been described. Nevertheless, so far there is no well established schematic phase diagram for the formations of various silicides, even by a simple method, such as solid phase epitaxy (SPE): annealing after deposition, in a wide range of preparation conditions of deposition thickness and annealing temperature. Since plural silicides can co-exist on surfaces, local structure analyses such as scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) are the most powerful methods to study the silicide formation, in addition to averaged structure analyses such as

low-energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED), X-ray photoelectron diffraction (XPD), X-ray photoelectron spectroscopy (XPS), ultra-violet photoelectron spectroscopy (UPS), and so on. STM results have been reported for many studies of silicides grown by SPE on Si(111), but in restricted preparation conditions, and recently, progress has been made in establishing a schematic phase diagram [4]. For silicides on Si(001) there are few STM works [5–7] which have reported in very restricted conditions, and there is no detailed phase diagram, even though works using averaged structure analysis [8,9] have suggested rough phase diagrams.

In this paper, we report on what types of iron silicides are SPE-grown on Si(001) systematically in a wide range of preparation conditions, using STM, LEED and RHEED. From the analysis of islands, clusters or morphologies of forming silicides we present a schematic phase diagram for Si(001)-Fe.

2. Experimental

The main experiments were performed in an ultra-high vacuum (UHV) system equipped with LEED optics and

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STM equipment [10,11]. Si(001) mirror-polished samples (Sb doped, 0.03 Ω cm) were degassed and flashed at $\approx 1250\,°C$ by direct-current heating for a few tens of times below $2-3 \times 10^{-8}$ Pa, and showed clean Si(001)2 × 1 at room temperature (RT). Hereafter, we describe only 2 × 1 for both 2 × 1 and 1 × 2 domains. The iron (99.999%) was deposited on the clean surfaces at RT using alumina-crucible evaporators cooled by water below 4×10^{-8} Pa. The Fe coverages θ_{Fe} estimated by a thickness monitor were 1, 2, 4, 8, 10, 12.5 and 16 ML (1 ML = 6.78×10^{14} cm^{-2}). The deposition rate was typically 0.4 ML/min. The deposited samples were subsequently annealed at $T_a = 200-900\,°C$, increasing to a higher T_a for 10 min at each annealing below 1×10^{-8} Pa. After each step of annealing, the surfaces were observed at RT with LEED and STM in the current-imaging mode using a chemically etched W tip. The RHEED experiments were performed in a different UHV chamber; the detailed conditions were the same as described elsewhere [7].

3. Results and discussion

An obtained schematic phase diagram is shown in Fig. 1, where observed (θ_{Fe}, T_a) points with STM and LEED are marked by a circle and a point, respectively. We classified iron silicides into types A–G by reconstruction of island surfaces, shape of islands and characteristic structures, mainly from the STM results. The boundaries of the region of each type are drawn as close as possible to the middle between areas where observation of islands could be confirmed, or not confirmed, respectively. Since different types of silicides co-exist we should note the overlaps of regions of the different types. For instance, region **B** overlaps regions **A** and **E**, and region **D** overlaps region **E**. In addition, the phase diagram also shows the LEED

Fig. 2. STM images of an Fe deposited and annealed Si(001) surface at $\theta_{Fe} = 2$ ML and $T_a = 500\,°C$. The sample bias voltages are (a) $V_s = -1$ V and (b) $V_s = -1.2$ V. (a) includes the islands of the different types (A, B and E) and the 2 × 1 substrate (H). The inset shows the magnification of a type-A island surface with a c(2 × 2) eye-guide. (b) is a magnification of a typical rectangle-like island (B).

results; no spots appear at $\theta_{Fe} > \approx 3$ ML and $T_a < \approx 450\,°C$ while substrate 2 × 1 spots appear at $\theta_{Fe} < \approx 3$ ML or $T_a > \approx 450\,°C$. The 2 × 1 substrate can also co-exist with the silicides of types A–E.

One of the typical silicides which has been studied [5,6] is the c(2 × 2) island. It was observed at $\theta_{Fe} = 2$ and 4 ML and $T_a \geqslant \approx 500\,°C$ (region **A** in Fig. 1). Fig. 2a and b show STM images obtained at $\theta_{Fe} = 2$ ML and $T_a = 500\,°C$. The c(2 × 2) islands are labeled A in Fig. 2a. The inset of Fig. 2a shows the magnification of a c(2 × 2) island with an eye guide of the c(2 × 2) unit cell. Almost all c(2 × 2) islands in region **A** in Fig. 1 have substrate dips around the islands[1] [5] and two-dimensional (2D) flat structures without any stacking layers [6]. Since the 2D c(2 × 2) islands co-exist with the 2 × 1 substrate, LEED patterns are superimpositions of c(2 × 2) and 2 × 1 (and 1 × 2) domains, which resemble p(2 × 2). Although the previous LEED [8] and STM [5] studies suggested a p(2 × 2) structure, our LEED intensity vs. primary energy E_p curves of equivalent $(\frac{1}{2}, 1)$ spots showed no significant difference for the clean and the c(2 × 2)-silicide surfaces, indicating the main part of the $(\frac{1}{2}, 1)$ spots on the silicide surfaces arises from the 2 × 1 substrate. Moreover, the intensity of $(\frac{1}{2}, \frac{1}{2})$ LEED spots compared to that of the $(\frac{1}{2}, 1)$ spots at certain E_p depends on the preparation conditions and showed maximum at $\theta_{Fe} = 4$ ML and $T_a = 500-600\,°C$.

The previous STS measurements [5] on the c(2 × 2) island showed semiconducting behavior and suggested β-FeSi$_2$-(100)[010]||Si(001)⟨110⟩, while the UPS and XPD study [6] suggested metallic α-FeSi$_2$(001)[110]||Si(001)⟨110⟩. The STM image of the latter surface (Fig. 5 in Ref. [6]),
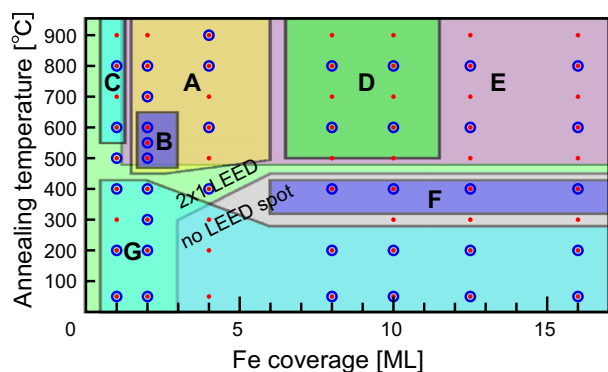

Fig. 1. Schematic phase diagram of iron silicides SPE-grown on Si(001)2 × 1 surfaces, as functions of Fe coverage θ_{Fe} and subsequent annealing temperature T_a, from STM (○) and LEED (·) results. Silicide types (A) 2D c(2 × 2) islands, (B) rectangle-like islands, (C) 3D elongated islands, (D) 3D layered islands, (E) 3D dome-like islands, (F) eddy and cracked structures, and (G) small clusters were observed in the regions denoted by the same bold characters. Note co-existence of the different silicide types: B with A and E, and D with E.
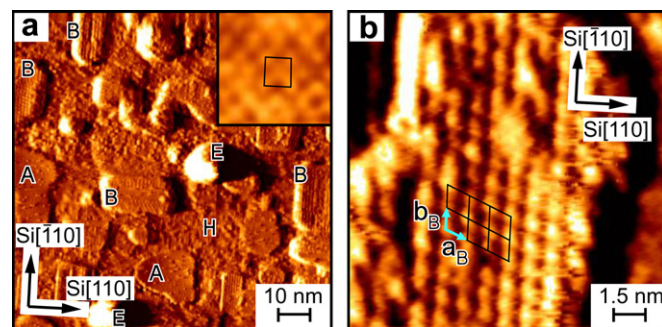
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[1] Ref. [5] showed a c(2 × 2) island at $\theta_{Fe} = 0.5$ ML, calibrated by Auger electron spectroscopy. We consider that this thickness value was underestimated after comparison with our results estimated by a thickness monitor. Actually, Ref. [6] reported the islands at $\theta_{Fe} = 3$ ML. In the same manner, $\theta_{Fe} = 3$ ML where β-FeSi$_2$(001) forms in Ref. [5] would be underestimated.