Thickness Dependent Formation of Iron Silicides on Clean and Boron Modified Si(001) Surface

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Comparative study of solid phase epitaxy (SPE) of iron silicides on Si(001)2×1 and boron modified Si(001)4×2-B was conducted for iron coverage, which was varied from 0.6 to 11.3 monolayers (MLs). It was found that annealing of Fe film at 800°C leads to formation of islands of iron silicide, whose type depends on the Fe film thickness. Using reflection high energy electron diffraction method (RHEED) and atomic force microscopy (AFM), it was shown that at Fe coverage of less than 1 ML, the growth of ε-FeSi and α-FeSi2 islands occurs on Si(001)2×1 surface. Increase of Fe coverage up to ∼3 ML results in growth of three dimensional (3D) γ-FeSi2 islands, preferentially, as well as 2D islands of β-FeSi2. For iron film with thickness of 4-4.6 ML the complete transition to growth of β-FeSi2 islands was observed. It was found that in the case of the Si(001)4×2-B surface preferable growth of 3D γ-FeSi2 islands occurs starting from the coverage of 0.6 ML, while the transition to growth of β-FeSi2 islands takes place at Fe coverage of ∼6 ML. [DOI: 10.1380/ejssnt.2009.577]

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I. INTRODUCTION

Investigation of SPE grown films of iron silicides on the silicon surface with (001) orientation continues to attract considerable attention [1, 2]. So, recently, besides early proposed schematic phase diagrams [3, 4] a new one was obtained by Nakano with colleagues [5]. Data of these works evidence about formation of such silicides as α-, β-, γ-FeSi2 and ε-FeSi depending on coverage of deposited iron and annealing temperature of iron film. It was found [5] that annealing of thin iron film with thickness of less than 1 nm in the temperature range from ∼500 to 900°C leads to growth of both 2D and 3D silicide islands. The majority of these works were devoted to structural analysis of 2D silicide islands using STM and LEED [1, 5, 6], or such spectroscopic methods as XPS, UPS, EELS and AES [1, 3, 4]. On the other hand, there is not detailed information about crystalline structure of 3D silicide islands which begin to form on Si(001) surface at iron coverage of ∼1 ML (1 ML=6.8×1014at/cm² for Si(001)) [5].

In addition, it is of interest in the context of the one work to investigate the SPE of iron silicide islands on both clean Si(001)2×1 surface and the modified Si(001) one due to the presence of atoms of some chemical element. So, Park et al. [7] have shown that formation of Si(001) surface by Sb atoms results in decrease of the nucleation site density for Fe growth at room temperature (RT) and island density decrease on the modified surface in comparison with the clean Si(001)2×1. Similar decrease of chemical activity of Si(001) surface was observed in the case of H-termination that resulted in growth of polycrystalline Fe at room temperature [8]. Recently, Ivanchenko et al. [9] studied SPE growth of iron silicide islands on both clean Si(111)7×7 surface and boron modified Si(111)√3×√3-R30° in the temperature range of 400-700°C and submonolayer Fe coverage. It was found that on the √3×√3 surface the nucleation of 2D islands of direct band gap β-FeSi2 semiconductor mainly occurs. The √3×√3 surface was characterized by smaller density of structural defects and γ-phase islands. In the present work, for comparative study of SPE growth of iron silicide islands, besides clean Si(001)2×1 surface we also considered boron modified surface with 4×4 structure typical for silicon surface with (001) orientation. SPE growth was performed in temperature range of 20-800°C and iron coverage below 11.3 ML (0.9 nm for Fe).

II. EXPERIMENTAL

The experiments were performed in an ultra-high vacuum MBE-system “Katun” equipped with 25 keV reflection high-energy electron diffraction (RHEED) apparatus, an electron gun to evaporate Si, and Knudsen cell to evaporate Fe. The base pressure of the MBE system was 1×10⁻¹⁰ Torr and it was kept below 5×10⁻⁹ Torr during iron evaporation. The substrate was heated radiatively by a Ta resistive heater situated behind the substrate. The p-type Si(001) wafers of 4.5 Ω·cm resistivity and 20×10×0.5 mm³ in size were used. The surface was protected by an ultrathin oxide layer prepared by a wet chemical treatment [10] before loading the substrate into the growth chamber. The protective oxide layer was removed by...
heating to 910°C for 10 min and the clean Si(001)2×1 surface was formed. Boron modified Si(001)4×4 surface \( (\theta_B=0.5\ \text{ML}) \) was formed by B\(_2\)O\(_3\) deposition on the clean Si(001)2×1 surface at the temperature of 750°C which is enough for 4×4 structure formation and oxygen desorption from the surface [11]. The deposition rate of iron was 0.6 ML/min. It was calibrated by monitoring of complete RHEED pattern transformation from \((7\times7)\) structure to \((2\times2)\) one at deposition of approximately 1 ML of iron on Si(111)7×7 surface at substrate temperature of 500°C [12]. The value of Fe deposition rate determined by this way may be underestimated. So, it was found in Ref. [13, 14] that Fe coverage necessary for \((2\times2)\) structure formation at SPE growth is equal to \(\sim 1.5\) ML. After Fe deposition on Si(001)2×1 surface at RT the sample was gradually heated up to 800°C with the rate of \(\sim 20^\circ\text{C}/\text{min}\) and kept at this temperature for 5 minutes. The structure and composition of the grown silicide films were determined from analysis of the RHEED patterns taken during sample heating. Theoretical patterns of transmission diffraction presented in this work for various iron silicides correspond to reciprocal-lattice cross sections perpendicular to direction of electron beam incidence. The morphology of the SPE grown films was observed by atomic force microscopy (AFM) after unloading samples from the vacuum chamber.

III. RESULTS AND DISCUSSION

A. SPE growth of iron silicides on Si(001)2×1 surface

1. SPE growth of iron silicides at Fe coverage of 0.6 ML

RT deposition of 0.6 ML of Fe on the Si(001)2×1 surface resulted in slight intensity decrease of \((0,1/2)\) streaks observed for \(2\times1\) structure (Fig. 1(a)). Such diffraction pattern was observed at heating of the substrate up to 420°C. At temperature of 420°C the intensity of background increased and additional diffuse spots located near \((0,1/2)\) streaks appeared. These spots are marked by upward arrows in Fig. 1(b). At 550°C typical for transmission diffraction pattern sharp spots appeared instead of the diffuse ones (Fig. 1(c)). At subsequent heating up to 800°C and annealing for 5 minutes we observed increase of sharpness and intensity of both the transmission spots and the \((0,1/2)\) streaks (Fig. 1(d)). Intensity of the transmission spots was larger at smallest glancing angles of electron beam but upon increase of the angle their intensity decreased and \((0,1/2)\) streaks became brighter. The origin of the transmission spots is related with growth of the 3D epitaxial islands on the Si(001)2×1 surface. Transmission electron diffraction for these islands is maximum for smallest glancing angles of electrons (close to 0°) whereas at large angles the maximum diffraction by flat Si(001)2×1 surface occurs. Analysis of RHEED patterns (Fig. 2(a) and Fig. 3(a)) obtained from Si(001) surface (Fig. 1(d)) at different angles shows the presence of the transmission spots from the 3D islands with two types of crystalline structure.

The diffraction spots of one type of the lattice marked by upward arrows in the RHEED pattern of Fig. 2(a) were observed well at a small angles that can be related with small height of islands. The spots are in accordance with theoretical transmission pattern in [112] direction for cubic lattice (B20 structure) of iron monosilicide \(\varepsilon\)-FeSi (Fig. 2(b)). The epitaxial relationships for \(\varepsilon\)-FeSi islands are \((111)_{\varepsilon}||[(111)_{\text{Si}}^\parallel (110)_{\text{Si}}]\). So, the filled squares in Fig. 2(b) correspond to the theoretical pattern of \(\varepsilon\)-FeSi where the matching face \((111)_{\varepsilon}\) is parallel to \((111)_{\text{Si}}\). However, one can see in Fig. 2(a) that spots marked by arrows have twins situated symmetrically relatively \([001]_{\text{Si}}\) axis passing through the \([000]\) spot (from the incident electron beam). The origin of the twins is connected with the transmission diffraction by \(\varepsilon\)-FeSi islands with the matching face \((111)_{\varepsilon}\) parallel to \((111)_{\text{Si}}\). Theoretical RHEED pattern for such islands is presented.

FIG. 1: RHEED pattern from the Si(001)2×1 surface along [110] direction (at an electron beam incident angle of 1°): after deposition of 0.6 ML of Fe at RT (a); at heating of the Fe layer up to 420°C (b) and 550°C (c); after annealing at 800°C for 5 minutes (d).

FIG. 2: The RHEED pattern from the surface shown in Fig. 1(d) at a small glancing angle of \(\sim 0.3^\circ\) (a), and the theoretical transmission pattern for the cubic \(\varepsilon\)-FeSi lattice (B20 structure) in [112] direction (b) with \((111)_{\varepsilon}||[(111)_{\text{Si}}^\parallel (110)_{\text{Si}}]\) (solid squares) and with \((111)_{\varepsilon}^\parallel [(111)_{\text{Si}}]\) (open squares).
in Fig. 2(b) as open squares. Since [111]$^\text{Si}$ and [111]$^\text{Si}$ axes have the same angle with [001]$^\text{Si}$ axis ($\sim$54°), the RHEED pattern looks mirror-like relative to [001]$^\text{Si}$ axis.

It was also reported in Ref. [4,5] about formation of ε-phase of FeSi for the Fe coverage exceeding 3.5 ML in temperature range of 350-450°C. However, we have not found any information about epitaxial growth of this silicide on Si(001) for Fe layer thickness of 1 ML. On the other hand, formation of ε-crystallites was often observed in experiments devoted to Fe deposition onto hot silicon surface. So, it was shown in Ref. [15] where Fe was deposited on Si(001) surface at 500°C and in Ref. [16] where ε-crystallites were grown by RF magnetron sputtering of Fe at temperature higher than 700°C. Growth of ε-FeSi islands was also observed for Fe deposition on the Si(110) surface [17]. It was established the epitaxial relationships for islands were the same as in our work. Such epitaxial orientation for which cubic lattice is rotated 30° about [111]$^\text{Si}$ axis is characteristic for SPE growth of a continuous ε-FeSi film on Si(111) surface [18, 19]. At a small Fe coverage deposited on Si(001) surface these epitaxial relationships for lattice of ε-FeSi islands remain the same.

Diffraction spots for crystalline lattice of another type were well seen both at small and large electron beam incidence angles (more than 3°). These spots are marked by upward arrows in the RHEED pattern shown in Fig. 3(a). Position of the marked spots is in accordance with the theoretical transmission diffraction pattern (Fig. 3(b)) for the tetragonal lattice of α-FeSi$_2$ in [110]$^\alpha$ direction where the matching face (111)$^\alpha$ is parallel to (001)$^\text{Si}$. So, bright spots marked by upward arrows in Fig. 3(a) correspond to spots with indices (113), (112) and (111) depicted as solid circles in the theoretical pattern (Fig. 3(b)). The presence of twins for these spots located symmetrically relative to (001)$^\text{Si}$ axis (Fig. 3(a)) is connected with growth of α-FeSi$_2$ islands, whose lattice is rotated by 180° in (001)$^\text{Si}$ plane. In other words, there are two epitaxial orientations of α-FeSi$_2$ islands with the matching face (111)$^\alpha$||[001]$^\text{Si}$; [110]$^\alpha$||[110]$^\text{Si}$ and [110]$^\alpha$||[110]$^\text{Si}$. In Figure 3(b) spots for rotated α-FeSi$_2$ islands are marked by open circles.

Also we have found spots with weak intensity that are marked by downward arrows in the experimental RHEED pattern (Fig. 3(a)). These spots can correspond to α-FeSi$_2$ as well with the matching face (110)$^\alpha$ parallel to (001)$^\text{Si}$ with [001]$^\text{Si}$ ||[110]$^\text{Si}$. So, theoretical transmission pattern for α-FeSi$_2$ in [001]$^\alpha$ direction is depicted as open rhombuses with indices marked by asterisks. Experimentally observed spots marked by downward arrows in Fig. 3(a) correspond to the (020)*, (110)* and (120)* spots. On the other hand, the same transmission pattern may be observed in [001] for fluorite γ-FeSi$_2$(110) lattice, whose (220), (200), (040), (220), (400) spots practically coincide with position of spots for tetragonal α-FeSi$_2$(110) lattice: (110)*, (111)*, (010)*, (100)*, (020)*, (110)*, (200)*. Similar diffraction pattern was observed at electron diffraction by iron silicide nanocrystallites grown at Fe deposition on Si(001) surface at 550°C and following annealing at 800°C [15]. Spots depicted as rhombuses can be also explained by reciprocal lattice points of Fe$_3$Si or c-FeSi with CsCl-structure [20]. So, the position of (110)* and (100)* spots can be associated with reciprocal lattice points (110) and (100) for c-FeSi, and (220) and (200) for Fe$_3$Si. However, our analysis shows that the theoretical values of reciprocal distances $d_{220}$ for Fe$_3$Si and $d_{110}$ for c-FeSi (equal to 0.50 and 0.51 Å$^{-1}$) are smaller than the experimental value (0.52 Å$^{-1}$).

AFM image of surface (Fig. 4) obtained after annealing at 800°C shows the presence of silicide islands with a height of 2-11 nm and a total density of $\sim$2×10^6 cm$^{-2}$. Some encircled islands in Fig. 4 have elongated (or rectangular) shape. These islands we explain by α-FeSi$_2$(111) ones, which have elongated shape in [110]$^\text{Si}$ direction as
it was shown by Homma et al. [21] using TEM. Actually, diffraction spots in Fig. 4(a) in Ref. [21] well correspond to those (solid circles) in Fig. 3(b). After annealing of Fe layer with thickness of 1 ML, Nakano et al. [5] using STM have shown formation of only 3D elongated islands. These islands were accounted for \(\alpha\text{-FeSi}_2\) with matching face (110) parallel to (001)\(\gamma\). It can be proposed that at Fe coverage increase up to 1 ML, the 3D elongated \(\alpha\text{-FeSi}_2\)/\(\gamma\text{-FeSi}_2\) islands begin to grow, preferentially.

2. **SPE growth of iron silicides at Fe coverage of 2.9 ML**

Deposition of iron layer with thickness of 2.9 ML resulted in strong intensity decrease of \((0,1/2)\) streaks (Fig. 5(a)). At substrate heating up to \(\sim 400^\circ\mathrm{C}\) transmission spots appeared which were quite elongated (Fig. 5(b)). At temperature of \(650^\circ\mathrm{C}\) brightness and sharpness of these spots reached maximum value that evidences about enlargement of grown 3D islands (Fig. 5(c)). These spots marked by upward and downward arrows in RHEED pattern of Figure 5(c) were appeared due to transmission diffraction by 3D \(\alpha\text{-FeSi}_2\)\(\gamma\) and \(\alpha\text{-FeSi}_2\)\(\gamma\) islands. Except for bright \(\alpha\)-phase transmission diffraction spots we have also found a transmission spots with weak intensity, which were not observed for coverage of 0.6 ML. The substrate heating higher than \(\sim 700^\circ\mathrm{C}\) caused complete disappearance of \(\alpha\)-phase spots. RHEED pattern from surface obtained after annealing at \(800^\circ\mathrm{C}\) for 5 minutes (Fig. 5(d)) have shown bright streaks from \(2\times1\) surface structure and weak transmission spots from \(\gamma\text{-FeSi}_2\) 3D islands.

Figure 6(a) shows RHEED pattern taken at a small glancing angle of electrons from surface obtained after annealing at \(800^\circ\mathrm{C}\). Two groups of transmission spots were found in the RHEED diffraction pattern that marked by upward and downward arrows. Nodes of network drawn with solid lines in Fig. 6(b) describe position of spots marked by downward arrows. It was found that the position of nodes is in good accordance with theoretical transmission pattern in [110] direction (solid circles) for cubic CuF\(_2\) (fluorite structure) lattice of \(\gamma\text{-FeSi}_2\) (with lattice constant 5.39\(\AA\)). If the cubic lattice of \(\gamma\text{-FeSi}_2\) has epitaxial orientation as the cubic lattice of silicon (i.e. [111]\(\gamma\)\([111]_{\text{Si}}\) and [001]\(\gamma\)\([001]_{\text{Si}}\)) the position of \(\gamma\text{-FeSi}_2\) spots would coincide with the position of open circles in Fig. 6(b) marked by indices with asterisks. However, the origin of experimental spots marked by downward arrows can be explained when the matching face of \(\gamma\text{-FeSi}_2\) is parallel Si(111) and the \(\gamma\)-phase lattice is rotated on \(180^\circ\) about [111] axis (i.e. [110]\(\gamma\)\([110]_{\text{Si}}\)). So, as seen in Fig. 6(b), solid circles with (111) and (220) indices are mirror images of corresponding open circles with (111)\(^*\) and (220)\(^*\) indices relatively [111]\(\gamma\)-axis.

The maximum difference between positions of network nodes (experimental spots) and solid circles (theoretical spots of \(\gamma\text{-FeSi}_2\)) is observed in [001]\(\gamma\) direction (Fig. 6(b)) that evidences about lattice tension of 3D \(\gamma\text{-FeSi}_2\) islands.
along this direction. So, found difference between experimental (2.79 Å) and theoretical (2.70 Å) values of interlayer distance \(d_{001}\) for \(\gamma\)-FeSi\(_2\) lattice is ~3.3%. This tension may be connected with \(\gamma\)-FeSi\(_2\) lattice rotation, as said above, at which \(001\)\(^{\text{Si}}\) and \(001\)\(^{\gamma}\) directions do not coincide (Fig. 6(b)).

The presence of twins relatively \(001\)\(^{\text{Si}}\) axis for spots marked by downward arrows can be explained by 3D \(\gamma\)-FeSi\(_2\) islands with matching face \(111\)\(^{\gamma}\) parallel to \(111\)\(^{\text{Si}}\). As since \(111\)\(^{\text{Si}}\) and \(111\)\(^{\gamma}\) planes are positioned symmetrically relative to \(001\)\(^{\text{Si}}\) axis, spots marked by downward arrows have mirror image relatively this axis.

Second group of spots marked by upward arrows in Fig. 6(a) can be described by theoretical transmission pattern for \(\gamma\)-FeSi\(_2\) in \(110\) direction (Fig. 6(c)). However, these spots are connected with diffraction by islands with matching face \(\gamma\)-FeSi\(_2\)(110) parallel to Si(001). Solid squares with (331), (220), (331) and (440) indices in Fig. 6(c) correspond to spots marked in Fig. 6(a). It was found the origin of theoretical diffraction pattern does not coincide with the position of incident beam marked as (000). This fact may be explained by second diffraction (by \(\gamma\)-FeSi\(_2\)(110) islands) of electron beam changed primary direction of propagation [22].

In AFM image of the surface obtained after Fe layer annealing at 800°C for 5 minutes (Fig. 7) we have discovered two types of islands with total density \(1.2 \times 10^{10}\) cm\(^{-2}\). Some islands (type A) are 3D ones with height of more than 3.5 nm while another islands (type B) are 2D ones with height of ~1 nm as one can see from the height profile in Fig. 7(b). High islands are connected with \(\gamma\)-phase the presence of which is corroborated by transmission spots in RHEED pattern (Fig. 6(a)). On the other hand, it was found the RHEED pattern in [100] direction (inset of Fig. 7(a)) shows additional \((1/2,1/2)\) streaks with weak intensity, which are connected with type B islands having 2D structure with \((2 \times 2)\) or \((c2 \times 2)\) symmetry. The portion of high islands is ~25%. It is worth to note that after annealing of 1.7 ML of Fe deposited on Si(001)\(\times\)\(1\) surface we observed the growth of 3D \(\gamma\)-FeSi\(_2\) islands, preferentially.

Thus, results of the experiments reveal that at increase of Fe coverage up to 2.9 ML the high-temperature annealing leads to preferable of 2D silicide islands. Disappearance of \(\alpha\)-FeSi\(_2\) transmission spots at substrate heating up to 800°C may be explained by the island density decrease. It is possible at Fe coverage of 2.9 ML substrate heating leads to formation of few in number \(\alpha\)-FeSi\(_2\) islands, which coalesce at temperature higher than 700°C (Fig. 5(c,d)). At that the island density decreases to a value that is insufficient for RHEED pattern formation. It is interesting that Nakano et al. [5] have also observed by STM \(\alpha\)-FeSi\(_2\)(110) islands in temperature range of 450-650°C (region B in phase diagram). These islands were two-dimensional and had rectangle-like shape. On the other hand, disappearance of \(\alpha\)-FeSi\(_2\) spots can be connected with a phase transition. As it was said above spots in Fig. 5(c) marked by downward arrows can be explained by formation not only \(\alpha\)-FeSi\(_2\)(110) but also \(\gamma\)-FeSi\(_2\)(110) islands. In this case, disappearance of \(\gamma\)-FeSi\(_2\)(110) spots at temperature higher than 700°C can be connected with phase transition from \(\gamma\)- to \(\beta\)-phase. For instance, such transition was displayed for embedded in Si lattice \(\gamma\)-nanocrystals at substrate temperature of ~700°C [23], and for 3D \(\gamma\)-islands on Si(110) surface at 730°C [17].

Formation of \(\gamma\)-phase was earlier observed in the form of both epitaxial islands at Fe deposition on Si surface with (001) [15] and with (110) [17] orientation and coherent precipitates embedded in silicon at Fe implantation [23, 24]. It was also shown [23] that the matching face \(\gamma\)-FeSi\(_2\)(111) is parallel to Si(111) and there is rotation of \(\gamma\)-phase lattice on 180° about [111] axis. Although Behar et al. [23] have shown for precipitates complete transition from \(\gamma\) to \(\beta\)-phase at annealing the investigation of thermal stability of \(\gamma\)-FeSi\(_2\) islands on Si(001) surface needs further consideration.

3. SPE growth of iron silicides at Fe coverage of 4 ML

After deposition of 4 ML of Fe (0,1/2) streaks were not observed in RHEED pattern (Fig. 8(a)). Substrate heating up to ~400°C resulted in appearance of intensive elongated streaks located in position of (0,1) silicon streaks and weak elongated (0,1/2) streaks (Fig. 8(b)). Weak transmission spots from \(\gamma\)-FeSi\(_2\) islands were also seen. The substrate heating up to 650°C leads to both the sharpness increase of transmission spots and the elongation decrease of (0,1) streaks (Fig. 8(c)). (0,1/2) streaks became brighter and sharper. After annealing at 800°C transmission spots disappeared while streaks became bright (Fig. 8(d)).

Figure 9 demonstrates AFM image of this surface. It was found that the surface is mainly covered by type B islands with the density of \(3.7 \times 10^{10}\) cm\(^{-2}\). The increase in quantity of these islands as compared with 2.9 ML Fe coverage (Fig. 7) is accompanied by the intensity increase.
FIG. 8: The RHEED pattern of the Si(001)2×1 surface in [110] \textsuperscript{Si} direction (at an electron beam glancing angle of 1\degree): after deposition of 4 ML of Fe at RT (a); at subsequent heating up to 400\degree C (b) and 650\degree C (c); after annealing at 800\degree C for 5 minutes (d).

FIG. 9: The AFM image of the Si(001)2×1 surface obtained after deposition of 4 ML of Fe at RT and subsequent annealing at 800\degree C for 5 minutes. The inset shows the RHEED pattern in [100] \textsuperscript{Si} direction.

FIG. 10: The RHEED pattern of the Si(001)2×1 surface in [110] \textsuperscript{Si} direction (a) and [100] \textsuperscript{Si} one (b) after deposition of 4.6 ML of Fe at RT and the heating up to 400\degree C.

FIG. 11: The RHEED pattern from the surface shown in Fig. 10(b) at a small glancing angle of \sim 0.3\degree (a), and the theoretical transmission pattern (b) for the \textbeta-FeSi\textsubscript{2} lattice (orthorhombic structure) in [011] \textbeta direction with (100) \textbeta \parallel (001) \textsuperscript{Si}.

of (1/2,1/2) streaks observed in [100] direction (the inset of Fig. 9). The absence of transmission spots from 3D islands observed in AFM image (Fig. 9) is connected with island low density.

We have found that the heating of 4.6 ML of Fe up to 400\degree C (Fig. 10) resulted in more intensive (0,1/2) and (1/2,1/2) streaks than in the case of 4 ML coverage (Fig. 8(b)). We speculate that the simultaneous intensity increase of these streaks with Fe coverage evidences about corresponding growth of area occupied by B-type islands with p(2×2) structure. If surface of islands has c(2×2) structure the island quantity increase would result in the presence of only (1/2,1/2) streaks while (0,1/2) ones would be not observed. Analysis of RHEED pattern obtained at a small glancing angle (Fig. 11(a)) has shown the presence of elongated transmission spots marked by downward arrows. It was established their positions are in accordance with theoretical pattern for \textbeta-FeSi\textsubscript{2} in [011] direction (Fig. 11(b)). The epitaxial relationship for \textbeta-FeSi\textsubscript{2} is (100) \textbeta \parallel (001) \textsuperscript{Si} with [100] \textsuperscript{Si} \parallel [011] \textbeta and [110] \textsuperscript{Si} \parallel [010] \textbeta. The same transmission RHEED pattern was observed by Mahan \textit{et al.} \textsuperscript{[25]} for an epitaxial type-A \textbeta-FeSi\textsubscript{2} film grown on Si(001) (Fig.7(b) in Ref. \textsuperscript{[25]}). Strongly elongated shape of transmission spots in Fig. 11(a) evidences about insignificant height of \textbeta-FeSi\textsubscript{2} islands. We suppose that both \textbeta-FeSi\textsubscript{2} spots and p(2×2) streaks are connected with formation of B-type islands. Subsequent heating of this silicide film from 400 to 800\degree C leads to increase of sharpness and brightness (0, 1/2) streaks as for 4 ML Fe coverage (Fig. 8(c,d)).

It was found that the annealing of Fe layer with thickness of 6.3 ML has resulted in the growth of more large B-type islands. At substrate temperature higher than 500\degree C enlargement of islands begins to occur due to the coalescence of small islands. This process is accompanied by increase of area of Si(001)2×1 regions that becomes free from islands. It is corroborated by appearance of sharp (0,1/2) streaks from Si(001)2×1 surface at 650\degree C (Fig. 8(c)) and following heating up to 800\degree C (Fig. 8(d)).

It is supposed that heating of Fe layer with thickness of 4 or 4.6 ML up to 400\degree C results in preferential formation of B-type islands, which have small lateral size. Strongly elongated shape of (0,1/2), (1/2,1/2) and (1,1) streaks can confirm this assumption (as seen in Fig. 8(b) and Fig. 10). At substrate temperature higher than 500\degree C enlargement of islands begins to occur due to the coalescence of small islands. This process is accompanied by increase of area of Si(001)2×1 regions that becomes free from islands. It is corroborated by appearance of sharp (0,1/2) streaks from Si(001)2×1 surface at 650\degree C (Fig. 8(c)) and following heating up to 800\degree C (Fig. 8(d)).

It was found that the annealing of Fe layer with thickness of 6.3 ML has resulted in the growth of more large B-
type islands with density of \(1.1 \times 10^{10} \text{cm}^{-2}\), respectively.

Obtained results are in accordance with data reported in Ref. [6] where it was shown the formation of flat \(\beta\)-FeSi\(_2\) islands with \(p(2 \times 2)\) structure. From the analysis of LEED pattern and structural analysis of \(\beta\)-FeSi\(_2\) lattice it was concluded about formation of \(p(2 \times 2)\) structure, although STM image have shown \(c(2 \times 2)\) symmetry of island surface structure. In contrast, Nakano et al. [5] have concluded about \(c(2 \times 2)\) surface structure of islands from STM study while the presence of LEED spots with \(p(2 \times 2)\) symmetry have been explained by coexistence of \((0,1/2)\) streaks from free regions of Si(001)2\(p(2 \times 2)\) and \((1/2,1/2)\) streaks from \(c(2 \times 2)\) structure. On the other hand the presence of \((0,1/2)\) structure was corroborated in our work by simultaneous intensity increase of \((0,1/2)\) and \((1/2,1/2)\) streaks with Fe coverage (from 4 to 4.6 ML) as said above. We suppose that our result obtained for iron layer thickness of 4–4.6 ML is in good accordance with data reported by Konuma et al. in Ref. [26]. They found by medium energy ion scattering (MEIS) study that the heating of the Si(001) sample with 4.5 ML of Fe results in formation of continuous FeSi film at first. At following heating up to \(\sim 400^\circ\text{C}\) it converts into \(\beta\)-FeSi\(_2\) film that is no longer continuous and consists of islands covering about 75% of the surface area. It was found by them that \(A\)-orientation \([110^5\text{Si}]\{010\}^3\) is predominant for \(\beta\)-FeSi\(_2\) lattice that agrees with our result.

We suppose that the formation of epitaxial islands of both \(\varepsilon\)-FeSi and iron disilicide (of \(\alpha\), \(\gamma\) and \(\beta\)-phase) at SPE growth on Si(001) surface depends on size of iron silicide \(\text{Fe}_{1-x}\text{Si}_x\) \((x<0.5)\) clusters which form on the surface after RT deposition of Fe [3]. So, the change of \(\text{Fe}_{1-x}\text{Si}_x\) cluster size with thickness of deposited Fe layer will lead at substrate heating to formation of iron silicides of one kind or another. The presence of such \(\text{Fe}_{1-x}\text{Si}_x\) clusters after RT deposition of Fe and the increase of their size with Fe layer thickness were shown by Park et al. [7] using STM. It is possible that in the case of Fe coverage equal to 0.6 ML the nucleation of \(\varepsilon\)-FeSi islands (Fig. 2) occurs at cluster size less than a critical one. Whereas, the presence of larger \(\text{Fe}_{1-x}\text{Si}_x\) clusters in deposited film leads to nucleation of \(\alpha\)-FeSi\(_2\) islands. Further increase of cluster size after deposition of 2.9 ML of Fe may be responsible for nucleation of islands of \(\gamma\) and \(\beta\)-phases at substrate heating. STM data reported in Ref. [7] evidence about coalescence of clusters on Si(001) surface at increase of Fe layer thickness up to \(\sim 5\) ML. It can be suggested that the coalescence and practically uniform covering of Si surface by \(\text{Fe}_{1-x}\text{Si}_x\) layer involve the formation of \(\beta\)-FeSi\(_2\) islands that is observed in our case for Fe coverage equal to 4.6 ML.

Most likely at the deposition of Fe on hot Si(001) surface the formation of \(\text{Fe}_{1-x}\text{Si}_x\) clusters also occurs and type of silicide islands will be governed by the size of clusters. So, it is possible that small size of \(\text{Fe}_{1-x}\text{Si}_x\) clusters became the reason of predominant growth epitaxial \(\varepsilon\)-FeSi islands at Fe deposition on Si(001) surface at temperature of 800°C observed by Itakura et al. [16]. High chemical activity of Si(001) surface at this temperature leads to nucleation of \(\varepsilon\)-FeSi islands with small size and with high density. In contrast, at the decreasing in growth temperature up to 700 and 600°C the formation of large \(\text{Fe}_{1-x}\text{Si}_x\) clusters on surface occurs that resulted in nucleation and growth of islands of \(\alpha\)-phase at 700°C and \(\beta\)-phase at 600°C in Ref. [16]. In contrast to islands of \(\beta\)-phase, the growth of islands of \(\alpha\)-phase \((\alpha\text{-FeSi}_2(111)\) was also observed by Tanaka et al. [27] at higher substrate temperature.

B. SPE growth of iron silicides on Si(001)4\(\times\)4-B surface

At the deposition of 0.6 ML of Fe on the Si(001)4\(\times\)4-B surface diffuse streaks typical for this structure have still been observed (Fig. 12(a)). At the substrate heating up to \(\sim 300^\circ\text{C}\) the RHEED pattern from the \((4\times4)\)-B structure has not already been observed and at temperature of \(\sim 470^\circ\text{C}\) the intensity of background has increased in addition (Fig. 12(b)). Subsequent heating resulted in appearance of sharp and intensive spots due to transmission diffraction by 3D islands of \(\alpha\text{-FeSi}_2(111)\) and \(\alpha\text{-FeSi}_2(110)\) (upward and downward arrows in Fig. 12(c)). These spots appeared at 600°C rather than at 550°C as for Si(001)2\(\times\)1 surface. Besides, transmission spots from 3D \(\gamma\)-FeSi\(_2\) islands with epitaxial relationships \([111]^{\gamma}\parallel[111]^{\text{Si}}\) and \([110]^{\gamma}\parallel[110]^{\text{Si}}\) were also seen. At temperature above 700°C \(\alpha\)-FeSi\(_2\) transmission spots disappeared whereas \(\gamma\)-FeSi\(_2\) ones marked by downward arrows in Fig. 12(d) retained. The RHEED pattern after annealing at 800°C (Fig. 12(d)) has also shown streaks from flat areas of \((4\times4)\)-B surface in addition to \(\gamma\text{-FeSi}_2\) spots. AFM image of this surface (Fig. 13) reveals the presence of 3D islands with the height of \(\sim 2.2\) nm and the density of \(3.6 \times 10^6\) \text{cm}^{-2}. These islands can mainly be connected with \(\gamma\)-phase whose transmission spots are observed in the RHEED pattern of Figure 12(d). High or elongated islands which formed on Si(001)2\(\times\)1 at Fe coverage of 0.6 ML (Fig. 4) were rarely observed on boron-modified surface. So, the RHEED pattern change during the heating of 0.6 ML of Fe deposited on \(4\times4\)-B surface has practically the same evolution that for Fe coverage of 1.7 (or 2.9 ML) on Si(001)2\(\times\)1 surface. In both cases the annealing results in the formation of 3D islands of \(\gamma\text{-FeSi}_2\). On the other hand, the formation of 2D islands was not observed on the \(4\times4\)-B surface.

Analysis of AFM and RHEED data (Fig. 14) shows...
The RHEED pattern did not show any spots from 3D is-
surface after annealing of 2.9 ML of Fe.

The density of 3D

clusters with less density than at the Fe deposition on
the 2×1 surface. So, Park et al. [7] have shown that
the passivation of Si dangling bonds by Sb atoms leads to
growth of more large islands at the RT and their density
decreases compare with the 2×1 surface.

We suppose that the RT deposition of 0.6 ML of Fe on
Si(001)4×4-B surface also gives rise to the formation of
rather large Fe$_{1-x}$Si$_x$ islands with less density than at the
Fe deposition on the Si(001)2×1 surface. Because of this,
the annealing at 800°C results in growth of 3D γ-FeSi$_2$
structures at Fe coverage of 0.6 ML while on the Si(001)2×1
surface they form at a coverage higher than 1 ML. The
fact that the density of γ-FeSi$_2$ islands (3.6×10$^9$cm$^{-2}$)
for the 4×4-B surface (Fig. 13) is more than the total density
of ε-FeSi and α-FeSi$_2$ islands (2×10$^9$cm$^{-2}$) on 2×1 surface
(Fig. 4) can be connected with less active coalescence
process of γ-FeSi$_2$ islands at the substrate heating up to
800°C.

The formation of β-phase on the 4×4-B surface at Fe
coverage of 6.3 ML, and not at coverage of 4.6 ML as for
the 2×1 surface, can also be explained by less density of
Fe$_{1-x}$Si$_x$ islands on the 4×4-B surface after the RT Fe
deposition. As it was concluded above, the coalescence
of Fe$_{1-x}$Si$_x$ islands at the RT Fe deposition can be the
reason of the formation of flat epitaxial β-FeSi$_2$ islands at
the heating. However, at low density of formed Fe$_{1-x}$Si$_x$
clusters with less density than at the Fe deposition on
the 2×1 surface the distance between islands
will large and, respectively, the coalescence will occur not
at 4.6 ML, but at 6.3 ML.

We have found the annealing of Fe film with the thick-
ness of 11.3 ML has revealed the same evolution of
structural-phase composition for both 4×4-B surface and
2×1 one. The heating of the Fe film up to 350-400°C leads
to the formation of ε-FeSi polycrystalline film. At
the substrate temperature of 550°C we observed in the
RHEED pattern the diffraction rings from β-FeSi$_2$
polycrystalline film. The composition of the film preserved
the same after the annealing at 800°C for 5 minutes. Such evolution of film composition is in accordance with
data of phase diagrams for Si(001)/Fe system reported in
Ref. [4,5]. Tanaka et al. [30] have also observed in the
RHEED pattern the transition from diffraction rings of
ε-FeSi to ones of β-phase at the heating of thick Fe layer
(6.3 nm).

IV. CONCLUSION

The morphology and structure of iron silicide films
SPE grown on Si(001)2×1 surface and the boron-
modified Si(001)4×4-B one were investigated by AFM
and RHEED. It was found the annealing of iron film
with thickness of less than 1 ML at 800°C resulted in the growth of 3D islands of ε-FeSi and α-FeSi2 on the 2×1 surface. It was established that at further increasing of the Fe coverage the transition to growth of 3D γ-FeSi2 and 2D β-FeSi2 islands occurs. In contrast to growth on the clean Si(001)2×1 surface γ-FeSi2 islands began to form on the Si(001)4×4-B surface at Fe coverage of less than 1 ML. For the Si(001)2×1 surface the complete transition to growth of β-FeSi2 islands occurred at the Fe coverage of 4.6 ML, while for the Si(001)4×4-B one at 6.3 ML. The thickness dependence of the phase composition of epitaxial iron silicide islands was proposed to explain by the size change of Fe1−xSi2 (x<0.5) islands which form after the Fe deposition at RT. It was assumed that Fe deposition on the boron-modified surface at RT results in formation of larger Fe1−xSi2 islands than on the Si(001)2×1 one. As a result of this the SPE growth of islands of γ- and β-phases on the Si(001)4×4-B surface takes place at another Fe coverage compared to 2×1 surface.

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