Formation and transport properties of Si(111)/β-FeSi₂/Si nanocluster structures *

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Processes of β-FeSi₂ nanosize islands growth on Si(111)7 × 7 surface and Si(111)-Cr surface phases and silicon growth over β-FeSi₂ nanosize islands have been studied by LEED, in situ electrical measurements and ex situ atomic force microscopy. The close matching of electric parameters of silicon with buried iron disilicide clusters and Si(111)7×7-Cr surface phases proves minimal carrier scattering on these clusters. Thermoelectric measurements of buried β-FeSi₂ islands revealed a very high value of the thermoelectric power coefficient as compared with p-type clean silicon. [DOI: 10.1380/ejssnt.2005.97]

Keywords: Atomic force microscopy; Electrical transport measurements; Epitaxy; Nanocluster materials; Morphology; Fe; Silicides

I. INTRODUCTION

Recently, there has arisen interest to the small group of semiconductor silicides, namely, those whose band gap is direct and narrower than that of silicon. Semiconducting β-FeSi₂ having a direct gap (E_g = 0.85 ~ 0.87 eV [1–7]) has been paid considerable attention as a very attractive material for silicon-based light emitters and detectors as well as for photovoltaic applications. It is known that iron disilicide islands with diameter of 80–100 nm, buried in the p-layer of a silicon p-n junction, demonstrate electroluminescence in the energy range of 0.82~0.84 eV [8–10]. Electroluminescence devices based on such structures can be industrially produced in the near future. As well, systems with buried nanosize iron disilicide clusters are of doubtless interest since they allow realization of quantum size effects.

Continuous films of semiconducting metal silicides have been grown successfully [5–7, 11, 12] however researches on self-organized quantum dots of silicon or silicides are only beginning nowadays (CoSi₂ [13], CrSi₂ [14], β-FeSi₂ [15]).

In this work the LEED and atomic force microscopy (AFM) research and in situ electrical measurements at various temperatures of the self-organizing process of nanosize β-FeSi₂ islands formation on Si(111) substrates and Si(111)-Cr surface phases (SP) followed by silicon overgrowth have been carried out. The influence of buried iron disilicide nanoclusters on electric properties of silicon substrate has been observed.

II. EXPERIMENTAL

Film growth and electrical measurements were performed in the ultra high vacuum chamber with the base pressure of 1 × 10⁻⁹ Torr. It was equipped with LEED optics, in situ Hall unit [16], sublimation sources (Cr, Fe), a manipulator with a sample holder, and a quartz sensor. Silicon overgrowth was carried out by molecular beam epitaxy at 800°С. Silicon cap layer was either 50- or 100 nm-thick, in different experiments. The silicon layers grown atop β-FeSi₂ islands were examined by the LEED method after the growth procedure and cooling

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of the sample. In situ electrical measurements (Hall ($U_h$) and longitudinal ($U_l$) voltage) were performed after each growth procedure, in the temperature range 20–280°C, using automated UHV Hall installation [18]. Conductivity and mobility of majority carriers in the samples were calculated within the one-layer model [19]. Morphology of the samples was investigated ex situ by atomic force microscopy (AFM, Solver P47) in the semi-contact and contact modes. Ex situ thermoelectric measurements were carried out within the temperature range of 30–150°C in the special vacuum cell ($P = 2 \times 10^{-2}$ Torr). The sample temperature during the measurements was controlled by thin copper-constantan thermocouples, mounted inside the copper plate with two small electrical heaters, which ensured the sample heating and temperature gradient (5–10°C). Two tungsten probes, placing straight over the thermocouples, pressed the sample to the copper plate. The sample was isolated from the plate by thin mica layer. The thermoelectric energy was measured by means of tungsten probes. Thermoelectric power coefficient was calculated using the measured thermoelectric power and temperature gradient for each average temperature measured.

III. RESULTS AND DISCUSSION

A. Influence of Si(111)-Cr surface phases on $\beta$-FeSi$_2$ island formation

For iron disilicide growth experiments a metal thickness equal to 0.2 nm has been chosen from the condition of high-density iron disilicide islands formation at substrate temperature 475°C [20]. Iron was deposited on different substrates: atomically clean silicon surface Si(111)7 × 7, Si(111) 7 × 7-Cr or Si(111) $\sqrt{3} \times \sqrt{3}$/30°-Cr surface phases. Figure 1(a) shows a typical LEED pattern of Si(111) after cleaning procedure. Deposition of iron on this surface results in disappearance of spots (Fig. 1(b)); that corresponds to absence of crystal order on the top of iron disilicide island and on the free silicon surface.

$\beta$-FeSi$_2$ islands formed on the clean Si(111)7 × 7 surface
have the oblong shape (Fig. 2(a)). They are elongated in some preferential direction (texture), but have no facets; that evidences their disordered structure. The density of clusters is about $5 \times 10^9 \text{ cm}^{-2}$, the lateral sizes are $30\sim40$ nm by $60\sim100$ nm. The island height distribution function (Fig. 2(b)) has two peaks. The first maximum corresponds to the roughness of the surface between the islands. The second peak, with smaller amplitude, is determined by the distribution of island heights. The shift of the second peak with respect to the first peak corresponds to the island height ($12\sim20$ nm). The silicon surface between the islands is not atomically smooth. The erosion of the surface evidences that silicon atoms of the substrate take part in the silicide formation process. It leads to the substrate surface disordering and disappearance of $(1 \times 1)$ spots in the LEED pattern.

After iron deposition onto the Si(111)$7 \times 7$-Cr SP the $(1 \times 1)$ LEED spots of silicon became very weak. Hence, only some small silicon area remained undisturbed but the most part of the surface was occupied with disordered structure.

Analysis of AFM image taken from this surface (Fig. 3(a)) indicates that the island density is about the same as in the previous case ($5 \times 10^9 \text{ cm}^{-2}$). The shape of islands has changed from oval to rectangular, due to their crystallization. Islands have some preferred orientation and the lateral sizes of $50\sim70$ nm by $100\sim130$ nm. Height distribution function has two peaks again (Fig. 3(b)), however the distance between the peaks (8 nm, see Fig. 2(b)) is smaller than that for the case of iron deposition on Si(111)$7 \times 7$. Thus, the average island height has decreased, in comparison with iron deposition on the clean silicon surface; that indicates smaller reorganization of the silicon surface at iron deposition on Si(111)$7 \times 7$-Cr SP.

In the case of iron deposition on Si$(111)\sqrt{3} \times \sqrt{3}/30^\circ$-Cr, preliminary formed on the atomically clean silicon surface Si(111)$7 \times 7$, the silicon substrate LEED (111) spots disappeared. It means absence of order on the iron disilicide island surface and on the silicon substrate surface.

Figures 4(a) and (b) show AFM images for Si$(111)\sqrt{3} \times \sqrt{3}/30^\circ$-Cr SP. It is seen, that the density of the $\beta$-FeSi$_2$
islands is approximately $3 \times 10^9 \text{ cm}^{-2}$ (Fig. 4(a)). They practically do not have facets; that evidences hindering of iron disilicide crystallization on Si(111) $\sqrt{3} \times \sqrt{3}/30^\circ$-Cr SP. There are a number of islands with essentially smaller lateral sizes and heights; their density is about $(1 \sim 1.5) \times 10^9 \text{ cm}^{-2}$ (Fig. 4(a)). The presence of islands with different sizes is the main feature of this sample, in comparison with two previous ones. The tentative explanation of this feature could be as follows.

By STM data, Si(111) $\sqrt{3} \times \sqrt{3}/30^\circ$-Cr surface phase is a flat 2D discontinuous layer, occupying less than 75% of the surface area [21]. It is not stable in the temperature range above 420°C. During $\beta$-FeSi$_2$ islands growth we heated the sample to 475°C [17] resulting in destruction of the surface phase. Chromium from the 2D layer gradually rearranged and CrSi$_2$ islands formed. Coagulation process was accompanied by successive uncovering of the silicon surface and new $\beta$-FeSi$_2$ islands could nucleate on this surface. Re-nucleation took place every time during deposition of iron, therefore we have disilicide islands with various sizes.

It was established, that lateral sizes of the bigger clusters are 30~80 nm by 60~100 nm. Again, there are two maximums in the height distribution function (Fig. 4(b)).
FIG. 7: LEED patterns from atomically clean silicon surface Si(111)7×7 (a) and from epitaxial silicon layer (MBE, T = 800°C) deposited over β-FeSi₂ islands, grown on Si(111)7×7-Cr surface phase (b).

FIG. 8: AFM morphology of epitaxial silicon film (50 nm). Si deposition at T = 800°C over β-FeSi₂ islands, grown on Si(111)7×7-Cr surface phase: 3.2 × 3.2 μm² (a) 1.0 × 1.0 μm² (b). Distribution of film roughness (c) along ’x’-coordinate and cross-section (d) of the selected area (marked by dash line and arrow) in the location of a β-FeSi₂ island (b). Coordinates are: ’x – y’ - in plane, and ’z’ - to height (from the right of figures (a, b)).

The first peak is attributed to the surface roughness between the islands. The second maximum is very weak and determined by the height distribution of iron disilicide islands. Its shift corresponds to the island height 8~16 nm. The height of the smaller islands is 3~5 nm so they are not located on the graph (Fig. 4(b)). The silicon surface between the islands is disordered, that results in absence (1×1) LEED points from silicon lattice. Hence, the iron deposition on the hot substrate with Si(111)√3×√3/30°-Cr SP results in formation of non-crystalline β-FeSi₂ islands.

B. Overgrowing with silicon of the β-FeSi₂ islands formed on the Si(111)7×7 and Si(111)-Cr surface phases

Silicon layer (100 nm) was grown over the β-FeSi₂ islands at the substrate temperature of T = 800°C. After β-FeSi₂ islands growth, only the background was observed on LEED pattern. However after deposition of silicon clear (7×7) LEED pattern appeared, although the intensity of the (1×1) spots and (7×7) spots (Fig. 5(b)) was a little bit smaller than for the clean substrate. It confirms epitaxial silicon growth, although does not give
any information about the crystal structure of the buried iron disilicide islands.

Figure 6(a) is the AFM image of the epitaxial film grown over the iron disilicide clusters formed on clean Si(111)7\times 7 surface. It is seen, that the surface consists of equally oriented terraces. Small dots are seen; their density is about $5 \times 10^8 \text{ cm}^{-2}$ and height $4\sim 6 \text{ nm}$. The dots and the rest of the surface are not distinguished by AFM in the lateral force mode; hence, they are of the same material, probably silicon. The silicon film is continuous; practically no pinholes are seen. Some information about the buried β-FeSi$_2$ islands can be obtained from the fine-scale AFM data (Fig. 6(b)). The silicon film surface is smooth and silicon crystallites have sharp borders. There are holes with density up to $2 \times 10^8 \text{ cm}^{-2}$. The main feature of the holes is hexagon-shaped crystallites located at some small depth. These crystallites are β-FeSi$_2$ islands only partially covered with silicon. Taking into account the island density observed on the silicon surface (Fig. 2(a)) before silicon deposition and after it, we could say, that the most part of iron disilicide islands are buried under the silicon film. The curve of height distribution (Fig. 6(c)) evidences that the sample surface is rather smooth and flat. The cross-section (Fig. 6(d)) shows presence of narrow and deep pinholes with $4\sim 6 \text{ nm}$ iron disilicide islands inside (in the selected area marked by arrow). The facets seen evidence the crystalline state of the islands.

After growth of silicon (50 nm) over the iron disilicide islands formed on the Si(111)7\times 7-Cr SP (Fig. 7(a, b)), the silicon film observed was more ordered, it is confirmed by (7\times 7) LEED pattern with intensity similar to the intensity of (1x1) spots for atomically clean silicon surface. Presence of (7\times 7) LEED spots evidences ordering of the silicon film during the growth.

Large and fine scale AFM images of the sample surface are shown in Figs. 8(a) and (b). The film is rather smooth (Fig. 8(a)) but has separate flat hollows. Some dots are seen on the surface of the film; according to the AFM lateral force mode they consist of silicon. The number of iron disilicide islands that are not completely covered by the silicon film is larger than in the previous case. Iron disilicide islands have hexagonal facets, and their density is about $1 \times 10^9 \text{ cm}^{-2}$, i.e. larger than in the case of iron deposition on the atomically clean silicon surface. It can be explained by smaller thickness of the deposited silicon layer (50 nm). For such thickness only 20% of iron disilicide islands are covered by the silicon film. The statistical data on height distribution (Fig. 8(c)) and on the film cross-section (Fig. 8(d)) confirm existence of (2\sim 4 nm)-high steps and smoothness of the surface (in the selected area marked by arrow).

After deposition of a 100 nm-thick silicon cap layer over the iron disilicide islands grown on the Si(111)\sqrt{3} \times \sqrt{3}/30°-Cr SP, (7\times 7) LEED pattern with (1\times 1) and
FIG. 10: Experimental data of Hall \((U_h, \text{triangles})\) and longitudinal \((U_g, \text{squares})\) voltages vs. temperature: clean substrate Si\((111)\)\(7 \times 7\) (a), silicon with \(\beta\)-FeSi\(_2\) islands, grown on Si\((111)\)\(7 \times 7\) (b) and silicon with \(\beta\)-FeSi\(_2\) islands, grown on Si\((111)\)\(7 \times 7\)–Cr (c).

\((7 \times 7)\) spots and rather small background was seen. LEED spots from iron disilicide islands were not observed, like in the previous two cases.

The silicon film was rather flat in the large-scale image (Fig. 9(a)), but the density of hollows and holes was higher (up to \(1.5 \times 10^5\) cm\(^{-2}\)). There were disordered silicon islands with surface concentration of \(7 \times 10^3\) cm\(^{-2}\). On the fine-scale AFM image (Fig. 9(b)) it is seen, that there are some holes on the silicon film surface, but no iron disilicide islands. Hexagonal iron disilicide islands with density up to \(5 \times 10^3\) cm\(^{-2}\) are immersed in the silicon, their top being at the same level as the silicon film surface. The curves of the height distribution (Fig. 9(c)) and the film relief (Fig. 9(d)) show that the surface of the silicon film is rather smooth but has 2 nm-high steps (in the selected area marked by arrow). Thus silicon film grown over substrate surface with iron disilicide islands formed on Si\((111)\) \(\sqrt{3} \times \sqrt{3}\)–30\(^\circ\)-Cr SP has higher hole density in comparison with two previous cases.

C. Electrical properties of silicon with buried \(\beta\)-FeSi\(_2\) clusters

On the basis of the analysis of in situ temperature Hall measurements on silicon, \(\beta\)-FeSi\(_2\) islands and silicon film with buried iron disilicide, influence of the islands have been studied on the processes of carrier scattering and transport in silicon. Hall and longitudinal voltages are been studied on the processes of carrier scattering and transport in silicon. Hall and longitudinal voltages in comparison to the atomically clean silicon surface (Fig. 10 (a)). First of all it is related to the influence of Si\((111)\)\(\sqrt{3} \times \sqrt{3}\)-30\(^\circ\)-Cr SP on the formation and growth of iron disilicide islands, and also on the conductivity of grown system. For all cases, at certain temperature the Hall voltage (Fig. 10 a,b,c) changes the sign.

Calculation of silicon parameters shows (Fig. 11) changes in the conductivity, hole concentration and mobility. After growth of \(\beta\)-FeSi\(_2\) islands, conductivity of the system increases for all temperature range studied. Majority carriers at temperature below 160\(^\circ\)C are holes, like before the film growth. Their concentration increases approximately by the factor of 4 (Fig. 11(c)). Within the range below 130\(^\circ\)C, the hole concentration changes insignificantly but at high temperatures it rises sharply. Similar increase of carrier concentration is observed for atomically clean silicon at temperatures above 150\(^\circ\)C [19].

The above change of the sign of the Hall voltage is related to transition to the intrinsic conductivity. Electron mobility in the silicon is higher than hole’s mobility; hence, at some temperature contribution of electrons in the Hall voltage becomes dominating and the sign of the voltage registered changes to negative. That is why the mobility of carriers also changes its sign (Fig. 11(b)). Since hole concentration in the sample with iron disilicide islands has increased, free holes can appear only due to injection from nanoisland heterojunctions \(\beta\)-FeSi\(_2\)-p/Si-p.

The hole mobility decrease tentatively could be explained by scattering on imperfections of the silicon lattice around islands or on the holes in the region of space charge induced under the islands. The indirect evidence of this is the significant reduction of electron mobility at high temperatures (160–280\(^\circ\)C) in the sample with iron disilicide islands on silicon surface (Fig. 11(b)).

Calculations have shown rather small reduction of carrier mobility for the sample with iron disilicide islands on Si\((111)\)\(7 \times 7\)-Cr SP (Fig. 12) in comparison with the case of the island growth on atomically clean silicon surface. It is related to improvement of crystal quality of iron disilicide islands and their interface with sil-
FIG. 11: Calculated data of conductivity (a), carrier mobility (b) and carrier concentration (c) vs. temperature for the silicon with atomically clean surface Si(111)7 × 7 (yellow rhomb) and the silicon with β-FeSi₂ islands grown on Si(111)7 × 7 (blue squares).

FIG. 12: Temperature dependencies of conductivity (a), carrier mobility (b) and carrier concentration (c) in silicon with atomically clean surface (yellow rhomb), in silicon with Si(111)7 × 7-Cr surface phase (open squares), in silicon with β-FeSi₂ islands grown on Si(111)7 × 7-Cr SP (triangles) and in the structure with buried islands (circles).
FIG. 13: Temperature dependences of thermoelectric power coefficient, registered for bare silicon substrate (orange circles); buried $\beta$-FeSi$_2$ islands formed on Si(111)7 × 7-Cr surface phase (pink squares), buried $\beta$-FeSi$_2$ islands formed on Si(111)$\sqrt{3} \times \sqrt{3}$/30$^\circ$-Cr SP (blue rhomb) and buried $\beta$-FeSi$_2$ islands formed on clean Si(111) (yellow triangles).

part of $\beta$-FeSi$_2$ islands preserve inside the silicon matrix. Since the TPC is negative for the samples with buried islands, injection of electrons into the silicon matrix could be assumed. For now, we cannot explain such a behavior. The influence of enhanced phonon scattering at the $\beta$-FeSi$_2$ island/Si interface on the electron injection process could be taken in consideration too.

IV. CONCLUSIONS

Influence of Si(111)-Cr surface phases on the formation, structure, density and the sizes of iron disilicide islands have been investigated. It has been established, that Si(111)7 × 7-Cr surface phase has influence on iron disilicide island growth. Island density does not change, in comparison with the growth on atomically clean silicon surface, but they became lower and wider. It is shown, that Si(111)$\sqrt{3} \times \sqrt{3}$/30$^\circ$-Cr SP reduces the iron disilicide island density and influences their re-nucleation; that evidences strong morphological changes of the substrate after formation of this surface phase. The epitaxial growth of silicon over the iron disilicide islands, formed on various chromium surface phases on silicon has been investigated. It was shown, that silicon thickness of 0.1 $\mu$m is not enough for complete burying of iron disilicide islands in silicon. The influence of buried iron disilicide islands on the conductivity, carrier concentration and mobility in silicon has been investigated at various temperatures. Iron disilicide islands, grown on Si(111)7 × 7-Cr surface phase, reveal the minimal influence on the hole mobility and hole concentration in the silicon substrate and epitaxial silicon layer in comparison with their growth on Si(111)$\sqrt{3} \times \sqrt{3}$/30$^\circ$-Cr SP and atomically clean silicon surface. Similarity of electric parameters of silicon with buried iron disilicide islands and atomically clean silicon evidences that the scattering carrier on these islands is small; we assume their epitaxial burying in the silicon crystal lattice. Thermoelectric measurements of the samples with buried $\beta$-FeSi$_2$ islands revealed a prominent value of the thermoelectric power coefficient: for the samples with the surface phases Si(111)7 × 7-Cr and Si(111)$\sqrt{3} \times \sqrt{3}$/30$^\circ$-Cr it is 10~150 times higher than for the clean p-type silicon.

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