

The (2×2) reconstructions on the surface of cobalt silicides: Atomic configuration at the annealed Co/Si(111) interface



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ABSTRACT

We have used scanning tunneling microscopy (STM) and ab initio total-energy calculations to characterize surface and interfacial structure of Co-Si(111) system. It has been found experimentally that two different types of the (2×2) surface structures occur. The coexistence of two phases is demonstrated by the example of STM image of the surface formed at the early stages of cobalt silicide formation under moderate annealing temperatures (500 °C). The measured height difference between the adjacent (2×2) reconstructed patches equal to about 1.0 Å (as determined from the filled-state STM images). In addition, the shift of the atomic rows by half of the row spacing is observed. Two adatom models of the (2×2) surface structures are developed. According to our data, these structures are assigned to CaF₂-type CoSi₂ and CsCl-type CoSi with a (2×2) array of Si adatoms on their surfaces. If the latter is the case, it has a coherent double interface CoSi/CoSi₂/Si(111) with a two-layer CoSi₂. Both of these interfaces are characterized by the eightfold cobalt coordination and incorporate a grown-in stacking fault.

1. Introduction

Epitaxial cobalt disilicide films with a nanoscale structure are of profound importance for modern device technology. Except for its technological applications, the study of the early stages of cobalt silicide formation plays a key part in understanding the structural properties of surfaces, interfaces and thin film growth, in general. It is assumed that, depending on the preparation conditions, the surface of epitaxial CoSi₂ can be either bulk like, i.e., terminated by a Si–Co–Si triple layer (Co-rich structure), or terminated by an ‘additional’ Si bilayer (Si-rich structure) [1]. It is customary to assume that in the former case a (2×2) reconstructed surface is formed during the annealing transition between Co-rich and Si-rich structures [2,3]. On the other hand, in our recent article, we demonstrated the layer-by-layer growth of CoSi phase with a CsCl-type (B2) crystal structure on a two-layer CoSi₂ surface at heating temperatures in the range of 350–550 °C [4]. The CoSi surface appears to be a bulk terminated of CoSi lattice with a Co–Si double layer. In other words, by analogy with CoSi₂ surface, the CoSi surface also has Co-rich structure. One may speculate that the (2×2) reconstruction can also occur on their surface. In addition, there is experimental suggest, using diffraction analysis, that two different (2×2) structures occur, one at low temperatures (~300 °C) and a

second at higher temperatures (~600 °C) [5] (hereafter, type I and II, accordingly). The authors have identified, on scanning tunneling microscopy (STM) observations of the island growth at low temperatures (320 °C), that the (2×2) surface structure corresponds to an ordered array of silicon adatoms on B-type CoSi₂ with 7-fold (111) interface bonding. The idea of using the registry of a (2×2) array of Si adatoms on cobalt silicide with respect to Si adatoms on the surrounding Si(111)-(7×7) surface is not without appeal; however, from theoretical investigation of the annealed Co/Si(111) interface, the stable interface is B8-type one, i.e., the topmost Co atoms are coordinated by eight Si atoms and incorporate a grown-in stacking fault (B-type) [6–8]. It has been found experimentally, using polarization-dependent surface extended x-ray-absorption fine-structure (SEXAFS) [9], medium-energy ion scattering [10] and transmission electron microscopy [11], that Co interface atoms are coordinated with eight Si atoms, as in bulk CoSi₂, with an interface bond length of 2.35 Å. The Si–Si interfacial bonds consistent with a seven-fold coordination of the first Co layer has been reported by Catana and co-workers using high-resolution electron microscopy [12]. It may be questioned, therefore, what is the bonding configuration of Co atoms at interface of cobalt silicides grown on Si(111) substrate. Still, there are a limited number of publications on the subject has been done with STM

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[2,4,5,13–15]. It has been known that STM gives access to the local surface information on the atomic scale, and may be useful for a better understanding of the initial stages of the cobalt silicide growth.

In this paper, we report STM observations of the (2×2) surface reconstructions in Co-Si(111) system. A disordered (1×1) -RC ('ring-cluster' or pseudo- 1×1) phase [16] was selected as a pre-existing template for grow of cobalt silicide layers. It has been applied with much success to the growth of well-ordered surface reconstructions [4,15,17]. The STM was used to characterize a surface morphology and the details of the atomic structure of cobalt silicides. First-principles total-energy calculations within density-functional theory (DFT) were employed to identify possible model structure. We have also performed the registry analysis by using high-resolution empty-state STM image of a two-layer $\text{CoSi}_2(111)-(1 \times 1)$ surface with a (2×2) island bordering with ring cluster on Si(111) substrate.

2. Experimental

Experiments were carried out in an ultra-high vacuum chamber with a base pressure of 2.0×10^{-11} mbar equipped with Omicron STM. A clean (7×7) -reconstructed Si(111) surface was prepared in situ by flashing to 1280 °C after the sample was first outgassed at ~ 650 °C for several hours. Cobalt was deposited from an electron beam evaporator at a rate of 0.068 ± 0.008 ML/min [15]. A monolayer (ML) in this paper corresponds to 7.83×10^{14} atoms/cm², the surface atomic density on the topmost Si atoms on the unreconstructed Si(111)- (1×1) surface. The pressure during Co deposition was better than $\sim 6.7 \times 10^{-10}$ mbar. The (1×1) -RC surface was prepared in saturated conditions by the deposition of Co atoms onto Si(111)- (7×7) surface held at about 810–825 °C for 1 min [18]; after the deposition, the current was turned off and the source shutter was simultaneously closed. After some cooling, STM observations were carried out to check the surface reconstruction. Cobalt silicide layers were formed by the deposition of Co onto the (1×1) -RC surface at both reaction temperature (500 °C) and room temperature (RT) followed by annealing to 550–570 °C. For STM observations electrochemically etched tungsten probe-tips are employed, and they are thoroughly cleaned by in situ heating prior to use. To find the energetically favorable structures we have performed ab initio total-energy calculations using the Vienna Ab Initio Simulation Package (VASP) [19,20] based on DFT [21,22]. The electronic ground state of the system was calculated using the projector-augmented wave [23,24] potentials as provided in VASP. The generalized gradient approximation within the parameterization of Perdew-Wang for the exchange and correlation functional were employed [25]. The surface was simulated by periodic slab geometry with a (2×2) unit cell containing five silicon atomic layers for all represented reconstructions. Hydrogen atoms saturated the dangling bonds of the bottom slab layer. The hydrogen atoms and the bottom layer silicon atoms were fixed while the rest atoms were free to move. A vacuum gap of approximately 10 Å was incorporated within each periodic unit cell to prevent interaction between adjacent surfaces. All spin-polarized calculations were performed using a \mathbf{k} -point sampling within the Monkhorst-Pack scheme [26] including 18 \mathbf{k} -points in the irreducible wedge of the Brillouin zone and an energy cutoff of 300 eV. The 3d and 5s states of Co were treated as valence states. Total forces after atomic geometry relaxation were less than 5×10^{-3} eV/Å.

3. Results and discussion

Fig. 1a gives an example of STM image of the surface obtained at the early stage of cobalt silicides formation. Apart from the areas occupied by ring like clusters (RCs) and limited-size domains of the Si(111)- $\sqrt{13}$ R13.9° phase (hereafter referred to as $\sqrt{13}$), two types of the flat-top silicide patches are formed both in the middle of substrate terraces (~ 1200 nm) and on lower terraces near the steps changed to an irregular shape. Under such temperature conditions Si atoms

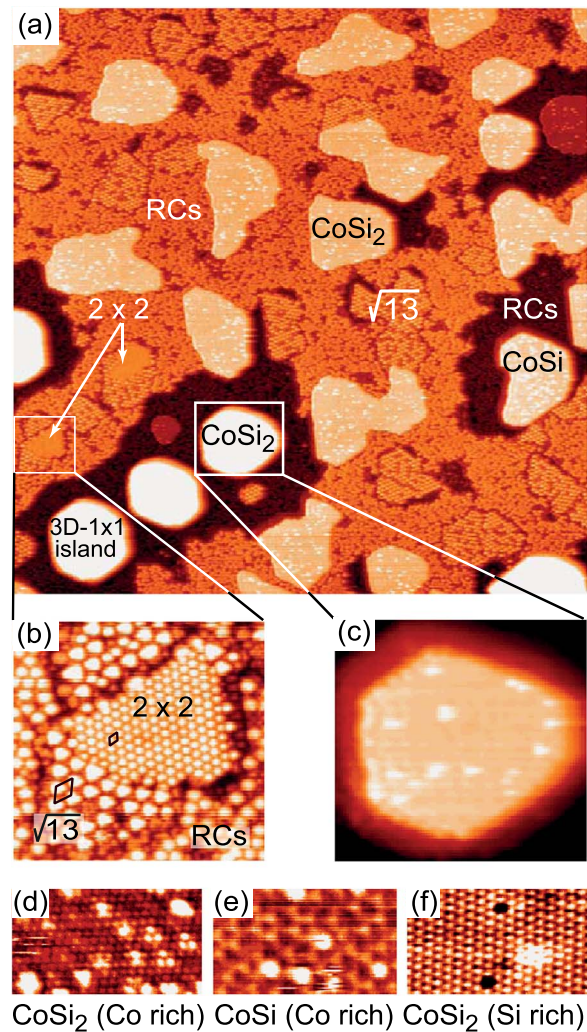


Fig. 1. (a) Filled-state STM image (200×200 nm², -2.0 V, 1 nA) of the surface after depositing of ~ 0.6 ML Co on the (1×1) -RC surface at RT and subsequent annealing at 550 °C. In (b–c), magnified images of rectangles in (a) illustrating small area with a (2×2) reconstruction surrounded by the $\sqrt{13}$ domains or RCs and CoSi_2 island with Co-rich surface, accordingly. The $\sqrt{13} \times \sqrt{13}$ and (2×2) unit cells are indicated. In (d–f), high-resolution characteristic STM images (8×4 nm²) illustrating Co-rich $\text{CoSi}_2(111)-(1 \times 1)$ ($+0.8$ V, 0.7 nA) [4], Co-rich $\text{CoSi}/\text{CoSi}_2(111)$ ($+1.8$ V, 1 nA) [4] and Si-rich $\text{CoSi}_2(111)-(1 \times 1)$ (-0.1 V, 10 nA) [28] surfaces, accordingly.

redistribution at the topmost Si layers in Si(111) substrate is involved in the silicidation process caused by the difference in the top Si atom density in the silicide layers and initial surface. In effect, the original terraces are split into two unequal areas by one Si(111) bilayer apart (3.14 Å) to form upper and lower terrace levels. The Si atoms from the first Si bilayer of Si(111) in RCs areas (as the Co-poor areas) are ejected onto the surrounding silicide regions to react with Co to form silicide patches. At negative tip bias voltages, STM images of the silicide patches appear to be similar to those reported in our recent article [4]. It has been found that the formation of two types of silicide phases, namely, the two-layer CaF_2 -type CoSi_2 and CsCl -type CoSi grown on top of CoSi_2 , are taking place during the silicidation process. A peculiarity of the surface shown in Fig. 1a is that inclusions of the $\sqrt{13}$ domains are observed only at the upper terrace level, while, at lower terrace level, which appears as dark areas, we can see only disordered array of RCs. In addition, the entirely new surface reconstruction can be seen. This is more clearly demonstrated in Fig. 1b, where the high-resolution image reveals the (2×2) reconstructed patches surrounded by the $\sqrt{13}$ domains and RCs. It is remarkable that the highest points of the small areas with the (2×2) reconstructed

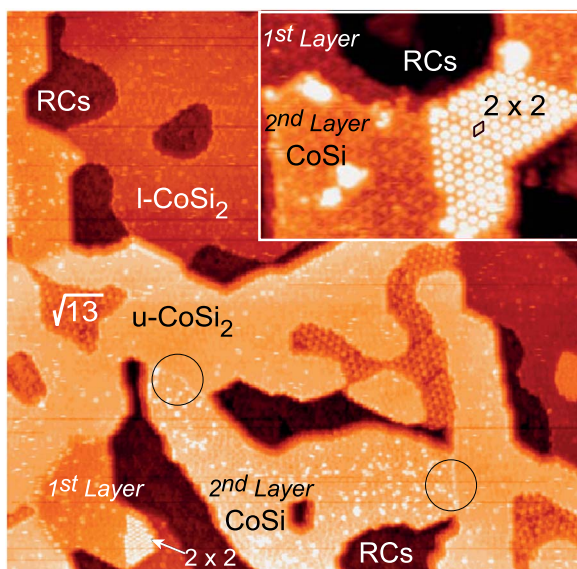


Fig. 2. Typical empty-state STM image ($100 \times 100 \text{ nm}^2$, 1.8 V, 1 nA) illustrating the (2×2) patches on CoSi formed by depositing $\sim 1.8 \text{ ML}$ of Co on the (1×1) -RC surface at RT and subsequent annealing at $\sim 570 \text{ }^\circ\text{C}$. The small (2×2) area on the first layer of CoSi is indicated by arrow. An inset shows high-resolution image ($25 \times 15 \text{ nm}^2$, 1.0 V, 1 nA) of the second layer of CoSi with the (2×2) area. Open circles indicate steps with a height of $0.3\text{--}0.4 \text{ \AA}$.

surface (with type I structure) are nearly the same height as those for $\sqrt{13}$ (or RCs) areas on the upper terrace level. The measured height of the (2×2) patches shown in Fig. 2b raised $\sim 0.15 \pm 0.03 \text{ \AA}$ with respect to the RCs on Si(111) substrate. These patches are consistent with those as reported in the previous study by Bennett with co-workers [5]. If the latter is the case, the island with a (2×2) periodic structure is elevated 1.1 \AA above the 7×7 matrix. One can readily see that the highest points of the small areas with the (2×2) structure and silicide islands in the 7×7 matrix locate almost at the same height.

As it follows from Fig. 1a, in these conditions the growth of flat-top CoSi patches and three-dimensional (3D) CoSi₂ islands becomes dominant. It has been observed in high-resolution STM images that 3D CoSi₂ islands adopt approximately triangular or hexagonal shape and are terminated by well-known (2×2) or (1×1) surface reconstructions [5,6,27,28]. In our case the major 3D CoSi₂ islands have the same surface as two-layer CoSi₂ patches. It is evident that 3D CoSi₂ islands to be bulk-terminated with the completed Si–Co–Si triple layer (TL) at the surface (Co rich structure), i.e., they do not have an ‘additional’ Si bilayer at the top of the upper Si–Co–Si triple layer [29]. Note that annealing in the temperatures range of $600\text{--}700 \text{ }^\circ\text{C}$ is necessary for the formation of the more stable CoSi₂ film with Si rich structure [9,27,28]. It is customary to assume that the high temperature structure of the (2×2) phase (type II) correspond to CoSi₂ with a (2×2) array of Si adatoms. Simultaneous growth of both phases with type I and type II structures will be discussed later.

Referring again to Fig. 1a, it should also be pointed out that there is no clear-cut distinction between the surfaces of CoSi₂ and CoSi patches in filled-state STM image (slight difference between them is in the availability of greater quantities of bright spots on CoSi surface). However, as can be seen in Fig. 1d and e, significant differences between the high-resolution empty-state STM images of cobalt-silicides surfaces are observed. In the former case, the main distinguishing feature of silicide surface is that it has long-range topographic protrusions with (1×1) symmetry. If the latter is the case, the empty states STM images (negative voltage is applied to the tip) of the CoSi layers show up as a disordered structure. Each of these images in turn differs significantly from the image of CoSi₂ surface with Si rich structure shown in Fig. 1f. Such areas are not observed in Fig. 1a, as

they appear at elevated temperature, namely, over and above $\sim 600 \text{ }^\circ\text{C}$ [16,28]. The measured height of the two-layer CoSi₂ patches shown in Fig. 1a raised $\sim 0.8 \text{ \AA}$ with respect to the RCs on Si(111) and in return the two-layer CoSi patches raised $\sim 0.3 \text{ \AA}$ with respect to the CoSi₂ surface.

The (2×2) patches on the CoSi surface are illustrated in Fig. 2. Under such conditions, it is possible that the interaction of cobalt atoms with Si(111) surface may result in the formation of a two-layer CoSi₂ film being on the upper and lower level. In addition, the layer-by-layer growth of CoSi phase also takes place on its surface. Note that a synthesis of a 70 \AA thick CoSi film by the growth on a 10 \AA thick CoSi₂ template on Si(111) have previously been reported [30]. As can be seen in Fig. 2, CoSi₂ and CoSi surfaces are distinguishable from one another in empty-state STM image, even with this large magnification. Each CoSi layer shows up in the STM images as the same and spaced at $1.5 \pm 0.3 \text{ \AA}$ [4,14]. This value coincides with the interlayer spacing for CoSi films with CsCl-type (B2) crystal structure, 1.58 \AA . As it can be seen, the (2×2) periodicity ordered domains are found on both first and second layers of CoSi. Furthermore, we observed the small ‘additional’ steps with a height of $0.3\text{--}0.4 \text{ \AA}$ separated two different types of surfaces similar to those observed previously [14]. These steps are represented the domain boundaries between adjacent regions and are closely related to the silicides structures, discussed later.

The application of STM to the study of the early stages of silicide growth under moderate annealing temperatures has allowed us to distinguish two types of the (2×2) phases. Furthermore, it has been found experimentally that both phases can be obtained at the same temperature ($\sim 500 \text{ }^\circ\text{C}$) in the event that sample is heated by passing BC current. This is best illustrated by the example of STM image, such as shown in Fig. 3a, recorded in the middle of a wide terrace ($\sim 1200 \text{ nm}$). It will be recalled that the growth of isolated CoSi₂ islands at steps of the substrate is due to accumulating Si atoms from steps. A large number of above-mentioned type-I domains are developed at the upper terrace level which indicate limited substrate mass transport in the silicide formation. These fact is the distinguishing feature of the type-I domains. Under appropriate conditions two phases coexist in the border areas appearing as relatively dark and bright (2×2) patches on the surface, such as shown in Fig. 3(b–d). As may be seen, the type-II domains are surrounded by a one-bilayer-deep depression, and we have good reason to believe that additional Si atoms from these areas are ejected onto the type-II domain regions to react with Co to form 3D silicide islands. As can be seen from Fig. 3e and f, the measured height difference between type I and type II patches is $0.8 \pm 0.2 \text{ \AA}$. Note that the apparent height can be depend critically on the tunneling voltage, since here electronic effects have an important role. However, our test measurements show that, in the case of filled-state regime, the height difference weakly dependent on the tunneling voltage in the range from -2.0 V up to -0.5 V . Moreover, the white line in Fig. 3b indicates the shift of the atomic rows by half of the row spacing between the adjacent patches. This indicates that two different (2×2) surface structures exist. Although both surfaces in the filled-state STM image appear as bright round protrusions with (2×2) symmetry, they can be clearly distinguished from each other at the early stage of cobalt silicide growth. The main difference is that the STM appearance of type II patches indicates conclusively that they are 3D silicide islands. Another significant difference between them lies in the fact that type I patches grow in the form of flat patches with freeform surfaces spreading over the surface at elevation of the temperature and they formation not to be connected to area with a one-bilayer-deep depression.

Now we would like to supplement STM observations by ab initio total-energy calculations for different interfaces between silicides with the (2×2) surface structure and Si(111), namely, CoSi₂ phase with the CaF₂ (C1) structure and CoSi phase with CsCl (B2) structure at the thickness region of 2, 3 and 4 layers within the silicide. The Co–Si(111) system is represented by four different interface structures: B-type 8-fold, A-type 8-fold, B-type 7-fold, and A-type 7-fold (abbreviated as B8,

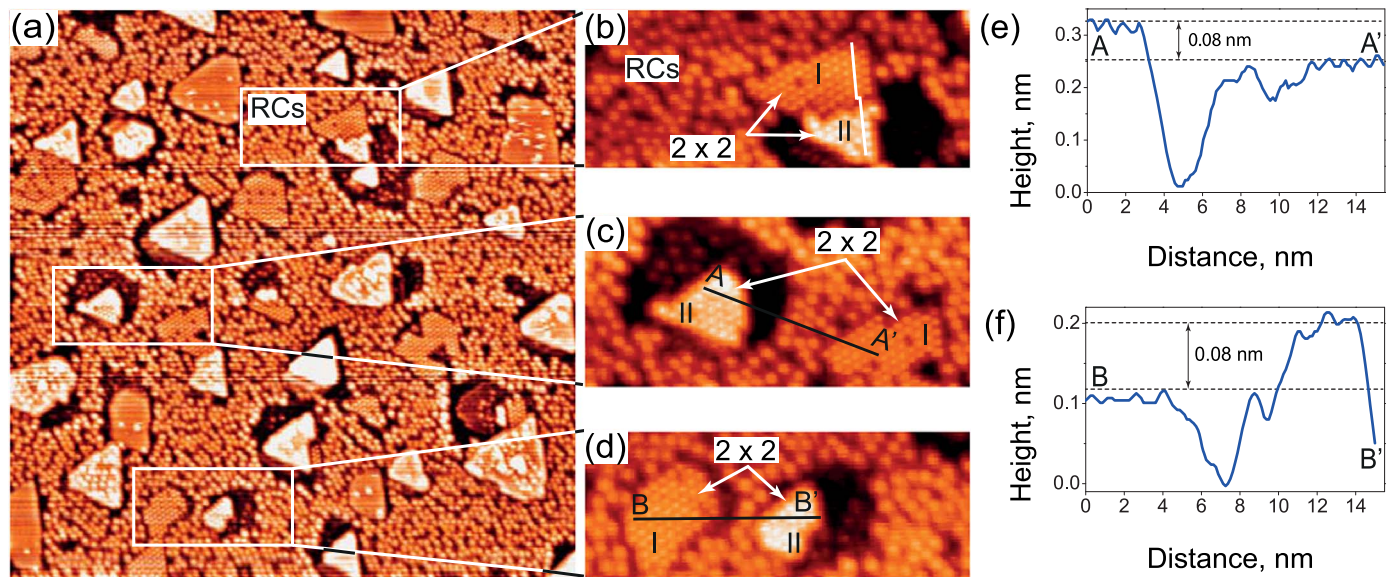


Fig. 3. (a) Typical filled-state STM image ($100 \times 100 \text{ nm}^2$, -2.0 V , 1 nA) of the surface after depositing of $\sim 0.7 \text{ ML}$ Co on the (1×1) -RC surface at $500 \text{ }^\circ\text{C}$ recorded in the middle of a wide terrace ($\sim 1200 \text{ nm}$). In (b–d), STM images of rectangles in (a) showing the surface areas with two types of the (2×2) patches labeled I and II. The white line in (b) indicates the shift of the atomic rows between the adjacent (2×2) patches. (e, f) Line profiles along the solid lines (A–A') and (B–B') in c and d, accordingly.

Table 1

Formation energies (in eV) calculated for different interface configurations of CoSi_2 and CoSi silicides with (2×2) reconstructed surfaces at two adatom positions under unchanged Co coverage (2, 3 and 4 ML) for each one relatively minimal energy as indicated in bold. The abbreviations “TL” and “DL” mean “triple layer” and “double layer”, accordingly. See the text for details.

Silicide with (2×2) adatom termination	Interface configuration and adatom position							
	B8 (ad1)	A8 (ad1)	B8 (ad2)	A8 (ad2)	B7 (ad2)	A7 (ad2)	B7 (ad1)	A7 (ad1)
2 TL CoSi_2 Ref. [28]	0.53	0.6	0	0.04	1.55	1.3	0.6	0.65
3 TL CoSi_2 Ref. [28]	0.66	0.77	0	0.09	1.21	0.93	1.75	1.52
1 DL CoSi on 2 TL CoSi_2	0	0.06	0.58	0.69	1.89	1.65	1.37	1.12
2 DL CoSi on 2 TL CoSi_2	0	0.08	0.47	0.57	1.56	1.39	1.07	0.90

A8, B7, and A7) [31]. There are strong grounds to believe that arranged bright protrusions observed on the (2×2) reconstructed patches correspond to individual silicon adatoms on the top of silicides with Co-rich structure [5,16]. Calculated formation energies for different interface configurations of three- and four-layer cobalt silicides are summarized in Table 1. For comparison, the interface configuration and position of Si adatom for three- and four-layer $\text{CoSi}_2(111)-(2 \times 2)$ are given according to our previous work [4]. As tabulated data demonstrate, two important conclusions are fairly clear: first, that, in either case the B8 configuration represent the most stable one; second, the most favorable adsorption site for the adatom turns out to be the site above the Si atom (ad2) in the second Si layer in the upper Si–Co–Si triple layer for CoSi_2 phase, whereas, for the CoSi phase, they reside directly above the Co atom (ad1) in the upper Co–Si double layer. Note that two models represented $\text{CoSi}_2(111)-(2 \times 2)$ interface structure at B8 and A8 configurations have close energies and are energetically favorable structures.

As an example, the side view models of the annealed $\text{Co/Si}(111)$ interfaces oriented in parallel to the $(\bar{1}\bar{1}0)$ plane is schematically shown in Fig. 4. For reference, the interface configurations of Si adatom on unreconstructed $\text{Si}(111)-(1 \times 1)$ surface, ring cluster [32] and ‘bright cluster’ at the $\sqrt{13}$ surface [15] are enclosed in the same figure (see Fig. 4(a–c), respectively). In line with theoretical calculations, the

energetically favorable two different (2×2) surface structures among the possible ones are presented on Fig. 4d and e, namely, the atomic arrangement in the B8 configuration of the CoSi layer on the top of CoSi_2 (thickness 2 Si–Co–Si triple layers) and $\text{CoSi}_2(111)-(2 \times 2)$ with two or three Co layers, since their surfaces are located at the same level. In the former case, it has a coherent double interface $\text{CoSi/CoSi}_2/\text{Si}(111)$. Note that both phases have the lowest energy for the B8-type interface configuration. Model calculations show that the height of (2×2) CoSi interface (Fig. 4d) calculated from the unreconstructed silicon layer is $1.252 \pm 0.005 \text{ \AA}$ smaller than that for two- or three-layer $\text{CoSi}_2(111)-(2 \times 2)$ interfaces shown in Fig. 4e. As mentioned early, we find experimentally that the height difference between type I and type II islands is equal to about 1.0 \AA . Taking into consideration the electronic effects, the interface arrangement of two different (2×2) surface structures obtained by total-energy calculations is in reasonably good agreement with the experimentally deduced height. These findings are in contradiction with the previous similar research showing that the ‘low temperature’ (2×2) structure (type I) corresponds to Si atoms on B-type $\text{CoSi}_2/\text{Si}(111)$ with a 7-fold interface, i.e., the Co atoms above the interface are coordinated by seven Si atoms [5].

In the following, we consider the local position of the (2×2) arranged adatoms applied registry analysis. For this purpose, the two-layer $\text{CoSi}_2(111)-(1 \times 1)$ surface was chosen [see also Ref. [4]]. In high-resolution filled- and empty-state STM images of the same area, such as shown in Fig. 5a and b, the two-layer $\text{CoSi}_2(111)-(1 \times 1)$ phase occurring in one level appears as array of bright round protrusions, which has (1×1) -symmetry and correspond plausibly to the highest Si atoms in the upper Si–Co–Si triple layer in CoSi_2 . It can be seen that the surface area with the (2×2) reconstructed island exist in the vicinity of the ring cluster. Hence the location of the (2×2) protrusions with respect to the location of Co atom at the centre of the RC, as well as with respect to the location of top Si atoms in the two-layer $\text{CoSi}_2(111) 1 \times 1$, can be fixed. As can be seen from Fig. 5c, the hexagonal grid has been drawn with nodes coinciding with the (1×1) protrusions. By projecting a (1×1) grid on the adatom positions of the (2×2) reconstructed top of the island and the RC area we find the lateral registry shift between different layers. Since the Co atom in ring cluster are known to reside in a substitutional silicon position, which corresponds to a T_1 site, its location can be used as reference point (the mutual location of the main adsorption sites on the bulk-like $\text{Si}(111)$ surface is shown in Fig. 5d). The orientation of the substrate layers was

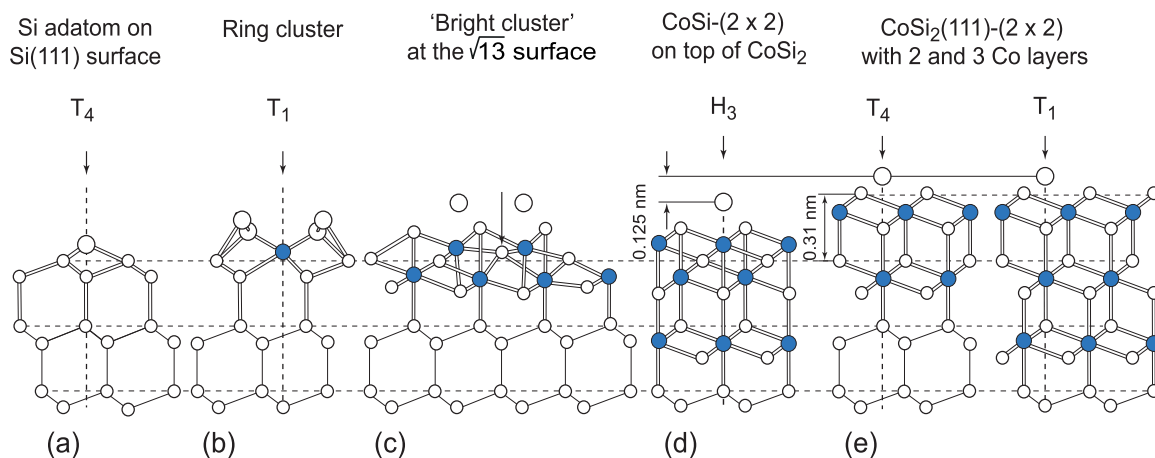


Fig. 4. Schematic side view of models for the annealed Co/Si(111) interface structures: (a) Ring cluster [32]. (b) Adatom Si on the unreconstructed Si(111) surface. (c) The ‘bright cluster’ at the $\sqrt{13}$ surface [15]. A Si atom in the center of the cluster is marked by the arrow. (d) The B8 configuration of the CoSi-(2 \times 2) interface with one Co-Si double layer on the top of two-layer CoSi₂ on Si(111). In (e), the B8 configuration of the CoSi₂(111)-(2 \times 2) interfaces with two and three Co layers. See text for structure details. Open circles represent the silicon atoms, dark circles correspond to the cobalt atoms.

established using the distinction between faulted and unfaulted unit cell halves of the Si(111)-(7 \times 7) reconstructed surface; in the former case the faulted half appears brighter in the filled-state STM images. An assessment of the lateral registry shift between different layers is illustrated by the scheme in Fig. 5e for CoSi₂(111)-(1 \times 1) and CoSi₂(111)-(2 \times 2) phases with two and three cobalt layers within the silicide, accordingly. Note that the height level of three-layer disilicide shown in Fig. 5e is higher by 3.14 Å [one Si bilayer of the Si(111)] than

that shown in Fig. 4e. It can be concluded that adatoms in the (2 \times 2) reconstructed CoSi₂ island are located in the sites corresponding to the H₃ hollow sites in the original Si(111)-(7 \times 7) and, in turn, the highest Si atoms in the upper Si–Co–Si triple layer in the two-layer CoSi₂(111)-(1 \times 1) are located in the site corresponding to T₁ site. These structures are energetically favorable structures among the possible ones. As it can be seen above, the B8-type interface configurations prove to be the most stable one for these two interface structures.

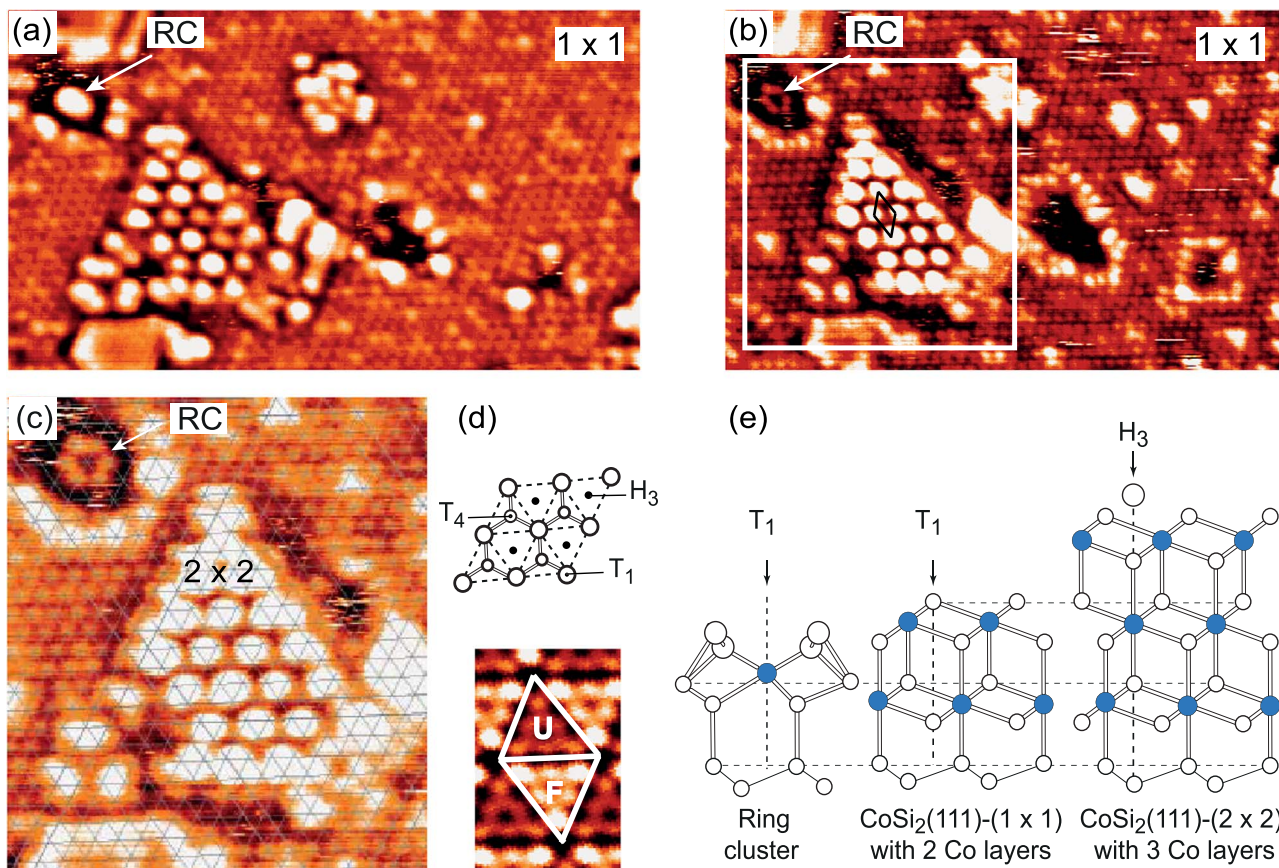


Fig. 5. High-resolution filled- (a) and empty-state (b) STM images (25 \times 15 nm², \pm 0.7 V, 1 nA) of a two-layer CoSi₂ film on Si(111) recorded at the same surface area [see also Fig. 4 in Ref. [4]]. The surface contains island with a (2 \times 2) surface structure and RC. The (2 \times 2) unit cell is indicated. (c) Magnified images of the region outlined in (b). The superimposed hexagonal grid drawn through the (1 \times 1) protrusions depicts the registry shift between (2 \times 2) adatoms and the cluster center. (d) Schematic diagram illustrating the mutual location of the main adsorption sites on bulk-like Si(111) surface. The (7 \times 7) unit cell is indicated. (e) Schematic side view of ring cluster, two-layer CoSi₂ and the (2 \times 2) reconstructed island with three-layer CoSi₂ in accordance with the (2 \times 2) adatom registry. The registry shifts are indicated.

4. Conclusion

In summary, the structure of the (2×2) phases in Co-Si(111) system has been the subject of our investigation. Our research is based on accurate calibration of the Co evaporator and a review of the early stages of cobalt silicides formation on Si(111) supported by relevant theoretical calculations. At moderate annealing temperature (450–550 °C), Si atoms redistribution at the topmost Si layers in the initial substrate is involved in the silicidation procedure. In consequence of this, at cobalt coverage range of 0.5–2.0 ML, the formation of a two-layer CoSi₂ phase with CsCl crystal structure or the layer-by-layer growth of a CoSi phase with CsCl crystal structure on its surface is taking place. It has been found that under the experimental condition employed, both surfaces can be terminated by well order (2×2) adatom structure; the latter silicide has a coherent double interface CoSi/CoSi₂/Si(111). According to experimental findings and ab initio total-energy calculations, both the CoSi₂ and the CoSi structures with the B8-type interface prove to be the most stable ones. For (2×2) reconstruction on the CoSi₂(111) surface, Si adatoms occupy positions over bottom Si atoms in the top Si–Co–Si triple layer while, for (2×2) reconstruction on the CoSi surface, they occupy positions over the top Co atoms in the top Co–Si double layer. It has been determined that the (2×2) arranged adatoms on the three-layer silicide island are located in the sites corresponding to H₃ hollow sites in (7×7) reconstruction, while the upper Si atoms in the two-layer CoSi₂(111)–(1×1) surface are localized in the sites corresponding to T₁ sites. Thus, the results of this study add considerable support for CoSi₂/Si(111) and CoSi/CoSi₂ interface structures, which are characterized by eightfold coordination of interfacial Co atoms and a grown-in stacking fault.

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Appendix A. Supporting information

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References

- [1] L. Haderbache, P. Wetzel, C. Pirri, J.C. Peruchetti, D. Bolmont, G. Gewinner, Identification of three distinct CoSi₂(111)(1×1) surface structures, *Appl. Surf. Sci.* 41–42 (1990) 257–261.
- [2] R. Stalder, N. Onda, H. Sirringhaus, H. von Känel, C.W.T. Bulle-Lieuwma, Surface and interface structure of epitaxial CoSi₂ films on Si(111), *J. Vac. Sci. Technol. B* 9 (1991) 2307–2311.
- [3] P.A. Bennett, S.A. Parikh, D.G. Cahill, Scanning tunneling microscopy studies of nucleation and growth in a reactive, epitaxial system: Co/Si(111), *J. Vac. Sci. Technol. A* 11 (1993) 1680–1685.
- [4] V.G. Kotlyar, A.A. Alekseev, D.A. Olyanich, T.V. Utas, A.V. Zotov, A.A. Saranin, Scanning tunneling microscopy studies of the early stages of epitaxial growth of CoSi₂ and CoSi films on Si(111) substrate: Surface and interface analysis, *Thin Solid Films* 619 (2016) 153–159.
- [5] P.A. Bennett, S.A. Parikh, M.Y. Lee, D.G. Cahill, Atomic structure of cobalt silicide islands formed by reactive epitaxy, *Surf. Sci.* 312 (1994) 377–386.
- [6] F. Hellman, R.T. Tung, Surface structure of thin epitaxial CoSi₂ grown on Si(111), *Phys. Rev. B* 37 (1988) 10786–10794.
- [7] A. Seubert, J. Schardt, W. Weiß, U. Starke, K. Heinz, Th Fauster, Interface structure of ultrathin CoSi₂ films epitaxially grown on Si(111), *Appl. Phys. Lett.* 76 (2000) 727–729.
- [8] A.P. Horsfield, H. Fujitani, Density functional study of the initial stage of the anneal of a thin Co film on Si, *Phys. Rev. B* 63 (2001) 235303(6).
- [9] G. Rossi, X. Jin, A. Santaniello, P. DePadova, D. Chandresris, Evidence of eightfold coordination for Co atoms at the CoSi₂/Si(111) interface, *Phys. Rev. Lett.* 62 (1989) 191–194.
- [10] J. Vrijmoeth, S. Zaima, E. Vlieg, J.W.M. Frenken, CoSi₂/Si(111) interface: Determination of the interfacial metal coordination number, *Phys. Rev. B* 45 (1992) 6700–6708.
- [11] C.W.T. Bulle-Lieuwma, Epitaxial growth of CoSi₂/Si structures, *Appl. Surf. Sci.* 68 (1993) 1–18.
- [12] A. Catana, P.E. Schmid, S. Rieubland, F. Levy, P.J. Stadelmann, Evidence for sevenfold cobalt coordination at the CoSi₂/Si(111) interface, *J. Phys.: Condens. Matter* 1 (1989) 3999–4004.
- [13] R. Stalder, H. Sirringhaus, N. Onda, H. von Känel, Strain-induced (2×1) reconstruction on epitaxial CoSi₂/Si(111) observed by scanning tunneling microscopy: structure model and electrical properties, *Surf. Sci.* 258 (1991) 153–165.
- [14] B. Ilge, G. Palasantzas, J. de Nijs, L.J. Geerlings, The temperature evolution of ultrathin films in solid-phase reaction of Co with Si(111) studied by scanning tunneling microscopy, *Surf. Sci.* 414 (1998) 279–289.
- [15] D.A. Olyanich, T.V. Utas, A.A. Alekseev, V.G. Kotlyar, A.V. Zotov, A.A. Saranin, Structure of the Co/Si(111)√13×√13 surface revisited, *Surf. Sci.* 625 (2014) 57–63.
- [16] P.A. Bennett, M. Copel, D. Cahill, J. Falta, R.M. Tromp, Ring clusters in transition-metal-silicon surface structures, *Phys. Rev. Lett.* 69 (1992) 1224–1227.
- [17] D.A. Olyanich, T.V. Utas, V.G. Kotlyar, A.V. Zotov, A.A. Saranin, L.N. Romashev, N.I. Solin, V.V. Ustinov, C60 layer growth on the Co/Si(111)√7×√7 surface, *Appl. Surf. Sci.* 292 (2014) 954–257.
- [18] R.J. Phaneuf, P.A. Bennett, M. Marsi, S. Günther, L. Gregoratti, L. Casalis, M. Kiskinova, Equilibration of ring-cluster surfaces and silicide islands for Co adsorbed on Si(111), *Surf. Sci.* 431 (1999) 232–241.
- [19] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total energy calculations using a plane-wave basis set, *Phys. Rev. B* 54 (1996) 11169–11186.
- [20] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.* 6 (1996) 15–50.
- [21] P. Hohenberg, W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* 136 (1964) B864–B871.
- [22] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* 140 (1965) A1133–A1138.
- [23] P.E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* 50 (1994) 17953–17979.
- [24] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* 59 (1999) 1758–1775.
- [25] J.P. Perdew, Y. Wang, Accurate and simple analytic representation of the electron-gas correlation energy, *Phys. Rev. B* 45 (1992) 13244–13249.
- [26] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B* 13 (1976) 5188–5192.
- [27] M.A.K. Zilani, L. Liu, H. Xu, Y.P. Feng, X.-S. Wang, A.T.S. Wee, Nucleation of cobalt silicide islands on Si(111)√7×√7, *J. Phys.: Condens. Matter* 18 (2006) 6987–6995.
- [28] A.A. Alekseev, D.A. Olyanich, T.V. Utas, V.G. Kotlyar, A.V. Zotov, A.A. Saranin, Scanning tunneling microscopy observation of ultrathin epitaxial CoSi₂(111) films grown at a high temperature, *Tech. Phys.* 60 (2015) 1508–1514.
- [29] U. Starke, J. Schardt, W. Weiß, G. Rangelov, T.H. Fauster, K. Heinz, Structure of epitaxial CoSi₂ films on Si(111) studied with low-energy electron diffraction (LEED), *Surf. Rev. Lett.* 5 (1998) 139–144.
- [30] H. von Känel, C. Schwarz, S. Goncalves-Conto, E. Muller, L. Miglio, F. Tavazza, G. Malegori, New epitaxially stabilized CoSi phase with the CsCl structure, *Phys. Rev. Lett.* 74 (1995) 1163–1166.
- [31] S. Walter, F. Blobner, M. Krause, S. Müller, K. Heinz, U. Starke, Interface structure and stabilization of metastable B2-FeSi/Si(111) studied with low-energy electron diffraction and density functional theory, *J. Phys.: Condens. Matter* 15 (2003) 5207–5220.
- [32] M.-H. Tsai, J.D. Dow, P.A. Bennett, D.G. Cahill, Electronic structure and stability of ring clusters in the Si(111)-(√7×√7)Co surface, *Phys. Rev. B* 48 (1993) 2486–2492.