



# Scanning tunneling microscopy study of the early stages of epitaxial growth of CoSi<sub>2</sub> and CoSi films on Si(111) substrate: Surface and interface analysis



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## ARTICLE INFO

### Article history:

Received 2 March 2016

Received in revised form 6 October 2016

Accepted 2 November 2016

Available online 3 November 2016

### Keywords:

Thin films

Cobalt

Silicon(111)

Cobalt silicides

Interface structure

Scanning tunneling microscopy

Density functional theory

## ABSTRACT

We report scanning tunneling microscopy observations of solid-phase epitaxial growth of ultra-thin CoSi<sub>2</sub> and CoSi films at heating temperatures in the range of 350–600 °C using a disordered '(1 × 1)' phase of Co/Si(111) as a pre-existing template. It is found that depending on the growth conditions two types of epitaxial cobalt silicide films can be formed. At coverages below ~2 ML (1 ML = 7.83 × 10<sup>14</sup> atoms/cm<sup>2</sup>) of Co, CoSi<sub>2</sub> phase grows in the form of flat two-layer patches spreading over the surface at elevation of the temperature. It consists of precisely two the completely filled Co layers and four Si layers above the interface. At coverages higher than ~2 ML of Co, the layer-by-layer growth of CoSi phase with the CsCl-type crystal structure also takes place. The CoSi phase consists of one or more Co-Si double layers, which are located on top of the second Si-Co-Si triple layer of CoSi<sub>2</sub>, i.e., it has a coherent double interface CoSi/CoSi<sub>2</sub>/Si(111). According to experimental findings and ab initio total-energy calculations, the structures with the eightfold coordination of interfacial Co atoms and lateral unit cells of the silicide layer and substrate mutually rotated by 180° prove to be the most stable ones.

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## 1. Introduction

Epitaxial cobalt disilicide films have aroused considerable interest in the semiconductor industry because of their low resistivity, thermal stability and good epitaxial alignment with a Si substrate. Growth of ultra-thin CoSi<sub>2</sub> films on Si(111) still involves great difficulties, since formation and surface morphology of these films strongly depend on the various growth conditions. The growth of epitaxial CoSi<sub>2</sub> films have been conducted under two conditions by the use of the 'template technique' [1]. Generally, the first step is done at a low temperature (<500 °C) for maximum nanolayer uniformity and the second step is done at higher temperature (>550 °C) optimized for best crystalline quality. However, we must confess that formation of the thin CoSi film may occur due to the first step, and it will inevitably transform into a CoSi<sub>2</sub> film on the next growth step at higher annealing temperatures. The formation of high quality ultra-thin cobalt silicide films with thickness of a few monolayers is of great importance, as the dimension of devices continues to shrink. On the other hand, the existence of an epitaxial CsCl-type CoSi phase at the top of a CoSi<sub>2</sub> (30–120 Å thick) after annealing at a temperature of 500 °C has been demonstrated [2–4]. It should be stressed that all papers cited above have been showed results focused

on the creation of CoSi layer growing directly on an existing CoSi<sub>2</sub> template, and it does not provide an understanding of layer interface structures at the atomic length scale. It is worth mentioning, that actual structure of CoSi/Si(111) film has not been determined yet.

In this paper, we report the results of a combined study in which the early stages of cobalt silicide growth on Si(111) are reconsidered with scanning tunneling microscopy (STM), low electron energy diffraction (LEED), Auger electron spectroscopy (AES) and ab initio calculations. Here we present concrete evidence showing epitaxial growth of ultra-thin CoSi<sub>2</sub> and CoSi films at moderate temperatures. In attempt to obtain very thin cobalt silicide layers (<10 Å) with homogeneous layer structure and uniform thickness, we have carried out deposition of Co atoms on the '(1 × 1)-RC ('ring cluster') surface consisting of Co-Si clusters on Si(111) [5,6]. Such approach has been applied with much success to the growth of well-ordered Si(111)-√7 R19.1° [7] and Si(111)-√13 R13.9° [8] surface reconstructions (hereafter referred to as √7 and √13, respectively). The STM is used to characterize a surface morphology and the details of the atomic structure of cobalt silicide layers. Theoretical calculations have been employed to find the energetically favorable structures among the possible ones. The experimental data about the absence or presence of an 'additional' Si layers on top of different silicide phases have been obtained by AES. Auger analysis was performed by measuring the peak height ratio of the Co M<sub>2,3</sub>VV (53-eV) and Si LVV (92-eV) lines for relatively homogeneous phases.

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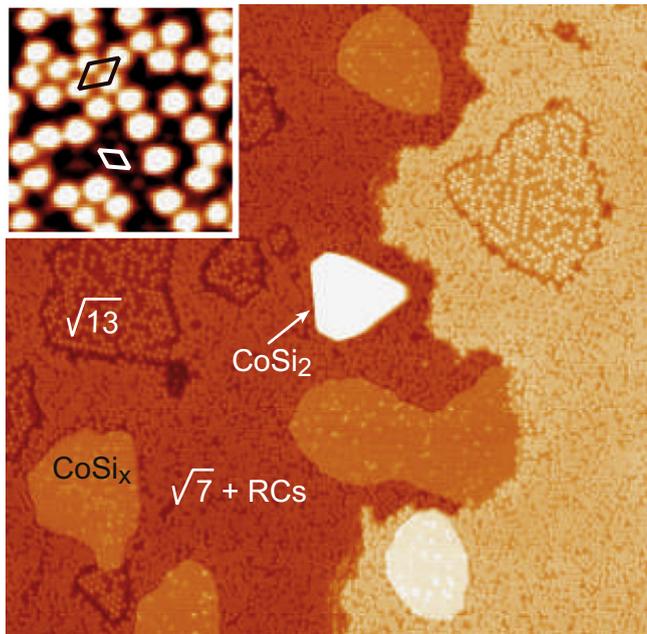
## 2. Experimental

Our experiments were performed with an Omicron STM operating in an ultra-high vacuum ( $\sim 2.6 \times 10^{-8}$  Pa). Atomically-clean Si(111) $7 \times 7$  surface were prepared in situ by flashing to 1280 °C after the sample were first outgassed at  $\sim 650$  °C for several hours. The  $(1 \times 1)$ -RC surface were prepared in saturated conditions by the deposition of Co atoms onto Si(111) $7 \times 7$  surface held at about 810–825 °C for 1 min; after the deposition, the current was turned off and the source shutter was simultaneously closed. Co was deposited from an electron beam evaporator at a rate of  $0.068 \pm 0.008$  ML/min. A monolayer (ML) in this paper corresponds to  $7.8 \times 10^{14}$  atoms/cm<sup>2</sup>. Auger analysis was performed using LEED/AES four grid optics (Omicron). Auger peak height has been measured from peak to peak. STM images were acquired at room temperature in the constant current operating mode.

To find the energetically favorable structures we have performed ab initio total-energy calculations using the Vienna Ab Initio Simulation Package (VASP) [9,10] based on density functional theory (DFT) [11, 12]. The electronic ground state of the system was calculated using the projector-augmented wave [13,14] potentials as provided in VASP. The generalized gradient approximation within the parameterization of Perdew–Wang for the exchange and correlation functional were employed [15]. The surface was simulated by periodic slab geometry with a  $2 \times 2$  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.

## 3. Results and discussion

Deposition of Co atoms onto Si(111) $7 \times 7$  surface by reactive deposition epitaxy (RDE) in the temperature range from 400 to 600 °C leads to the mainly spontaneous growth of three-dimensional CoSi<sub>2</sub> epitaxial islands, and the sample have very rough layer morphology of the

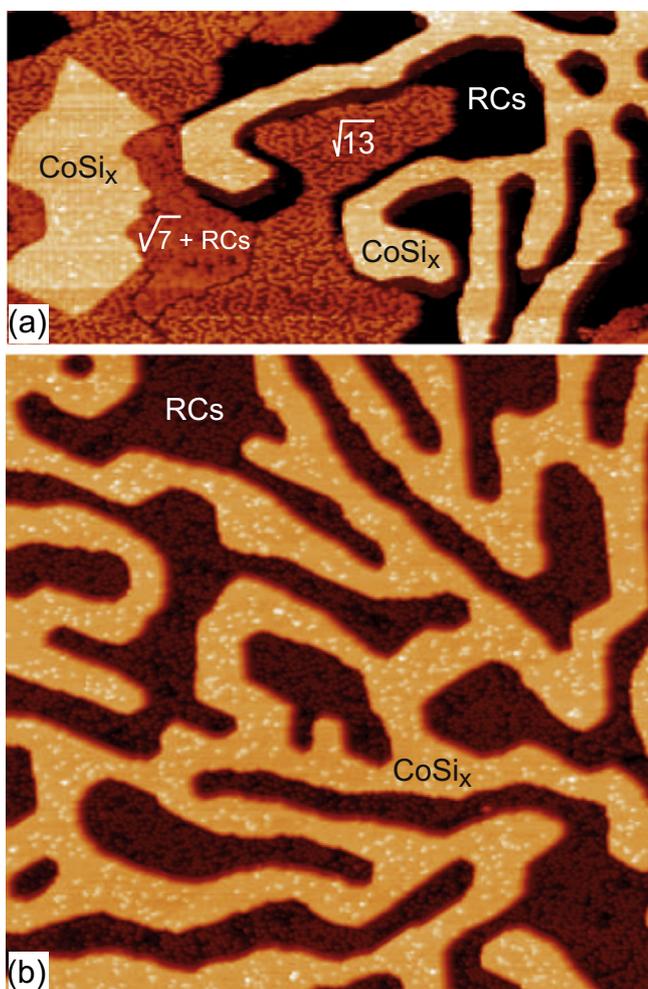


**Fig. 1.** Typical STM topography image ( $150 \times 150$  nm<sup>2</sup>) of the adjacent substrate terraces after depositing  $\sim 0.6$  ML Co on the  $(1 \times 1)$ -RC surface at 500 °C. Image is taken at a negative sample bias of 2 V (filled-state) and a tunneling current of 1.2 nA. The labels are explained in the text. An inset ( $8.5 \times 8.5$  nm<sup>2</sup>) shows high-resolution image of a starting surface with Co coverage of  $\sim 0.08$  ML. The  $\sqrt{7} \times \sqrt{7}$  and  $2 \times 2$  unit cells are indicated.

reacted silicide [16,17]. As can be seen in Fig. 1, in the special case, where the disordered  $(1 \times 1)$ -RC surface formed in the reactive system Co–Si(111) serves as the starting one for experiment, well-ordered surface reconstructions may be grown even at the early stages of cobalt deposition. It seems likely that the formation temperature of  $\sim 500$  °C is too low to induce a significant surface diffusion of cobalt atoms over this surface compared with the Si(111) $7 \times 7$  one. The  $(1 \times 1)$ -RC surface have been established to be built of the same structural elements, ring clusters (RCs), each composed of a single Co atom in a substitutional silicon position under a six Si adatoms ring [5,18]. The  $\sqrt{7}$  phase is an ordered close-packed hexagonal array of RCs with  $1/7$  ML Co coverage [19,20]. Inset at the top of the figure shows high-resolution filled-state STM image of the  $(1 \times 1)$ -RC surface and reveals well-resolved bright round protrusions, which correspond to RCs. Note that, except for RC array, the coexisting regions of  $\sqrt{7} \times \sqrt{7}$  and  $2 \times 2$  surface reconstructions are revealed on its surface. As can be seen from the image in Fig. 1, there are three types of cobalt silicides on the Si(111) substrate: three-dimensional CoSi<sub>2</sub> islands localized only along the steps on a lower terrace, with measured height raised  $\sim 14$ – $17$  Å with respect to the RCs; the  $\sqrt{13}$  periodicity ordered domains, and the flat irregularly shaped patches that are of unknown composition (marked as CoSi<sub>x</sub>) formed both at steps and terraces of the substrate. It has been observed in high-resolution STM images that CoSi<sub>2</sub> islands adopt approximately triangular or hexagonal shape and are terminated by well-known  $2 \times 2$  or  $1 \times 1$  surface reconstructions [21,22]. It is evident that growth of three-dimensional CoSi<sub>2</sub> islands takes place mainly due to accumulating Si atoms from steps, as we can see the step roughening even at  $\sim 0.1$  ML Co coverage. It is worth mentioning that CoSi<sub>x</sub> and  $\sqrt{13}$  phases do not have sharp boundaries, and the measured height of CoSi<sub>x</sub> patches raised  $\sim 0.8$  Å with respect to the RCs on a Si(111) substrate and  $\sim 0.15$  Å with respect to the bright clusters constituting the  $\sqrt{13}$  phase (see Fig. 1).

The flat domains with  $\sqrt{13}$  structure of irregular size and shape are visible on the terraces and near step edges. Note that of the surface with a high content of the  $\sqrt{13} \times \sqrt{13}$  ordered domains takes place under a higher annealing temperature ( $\sim 550$  °C) at coverage of about 1.3 ML Co [8]. It has been determined that ‘bright clusters’ constituting the  $\sqrt{13}$  surface reconstruction have essentially the same structure as a CoSi phase with the CsCl-type (B2) crystal structure with two cobalt layers within the silicide, in the sense that it also contains the completed Si–Co–Si triple layer terminated by a Co–Si double layer, but with a non-stoichiometric composition (see also Fig. 8b and e for further detail). This upper double layer consists of a well-ordered array of Co–Si clusters (‘dark clusters’), each of which contains three Co atoms and six Si atoms. The ‘bright clusters’ contain three additional Si atoms on top of the six Si atoms terminating the ‘dark cluster’. Thus, the  $\sqrt{13}$  surface phase incorporates  $16/13$ – $1.23$  ML Co and depending on the quantity of the ‘bright clusters’ from  $33/13$  to  $36/13$  ML Si (it is close to 2.7 ML).

The flat CoSi<sub>x</sub> film with a more uniform structure can be formed by solid-phase epitaxy (SPE) without employing Si deposition in its growth. With lower annealing temperature (350–500 °C) at cobalt coverage range of  $\sim 0.3$ – $1.5$  ML, the flat CoSi<sub>x</sub> patches, each surrounded by RC clusters, are also formed on the surface. Silicide patches start to spread over the surface at elevated temperatures. Fig. 2a and b shows two STM images recorded in the middle of a wide terrace in different positions. As can be seen in Fig. 2a the flat CoSi<sub>x</sub> patches and the flat ramified CoSi<sub>x</sub> layer with irregularly shaped trenches are close together and their surfaces are located at the same level. Note that, the filled- and empty-state STM images of these surfaces are identical (not illustrated). Furthermore, the difference in height between the level of RCs, which are located around CoSi<sub>x</sub> patches, and ones on the bottom of trenches, are 3.14 Å [one Si bilayer of the Si(111)]. The flat ramified CoSi<sub>x</sub> layer, such as seen in Fig. 2b, is observed in the middle of wide terraces ( $\sim 1200$  nm). The formation of the upper (CoSi<sub>x</sub>) and lower (RCs) levels on wide terraces is a direct indication of the Si mass transport. In this case, it is possible to make rough estimation of the composition of



**Fig. 2.** Filled-state STM images ( $-2$  V,  $1$  nA) of the sample formed by depositing  $1.0$  ML Co on the  $(1 \times 1)$ -RC at RT and subsequent annealing at  $\sim 500$  °C. The images recorded in the middle of a wide terrace in different positions. Image sizes are: (a)  $150 \times 100$  nm $^2$ , (b)  $150 \times 150$  nm $^2$ .

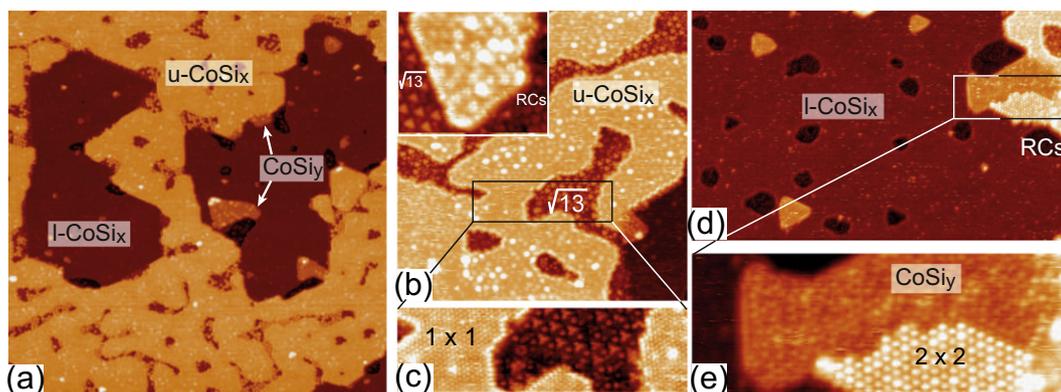
CoSi $_x$  phase on condition that the number of Si and Co atoms in the middle of a wide terrace is kept constant. Note that the Co atom coverage of the surface is in the range of  $1.0$  ML, and the area fraction occupied by the ramified silicide layer is  $0.48 \pm 0.03$ . If taking  $Q_{1 \times 1}$  for the Si atom coverage in the original  $(1 \times 1)$ -RC top layer and  $Q_{\text{CoSi}_x}$  for the

Si atom coverage in the CoSi $_x$  layer on Si(111) surface, as shown in Fig. 2b, one can write.

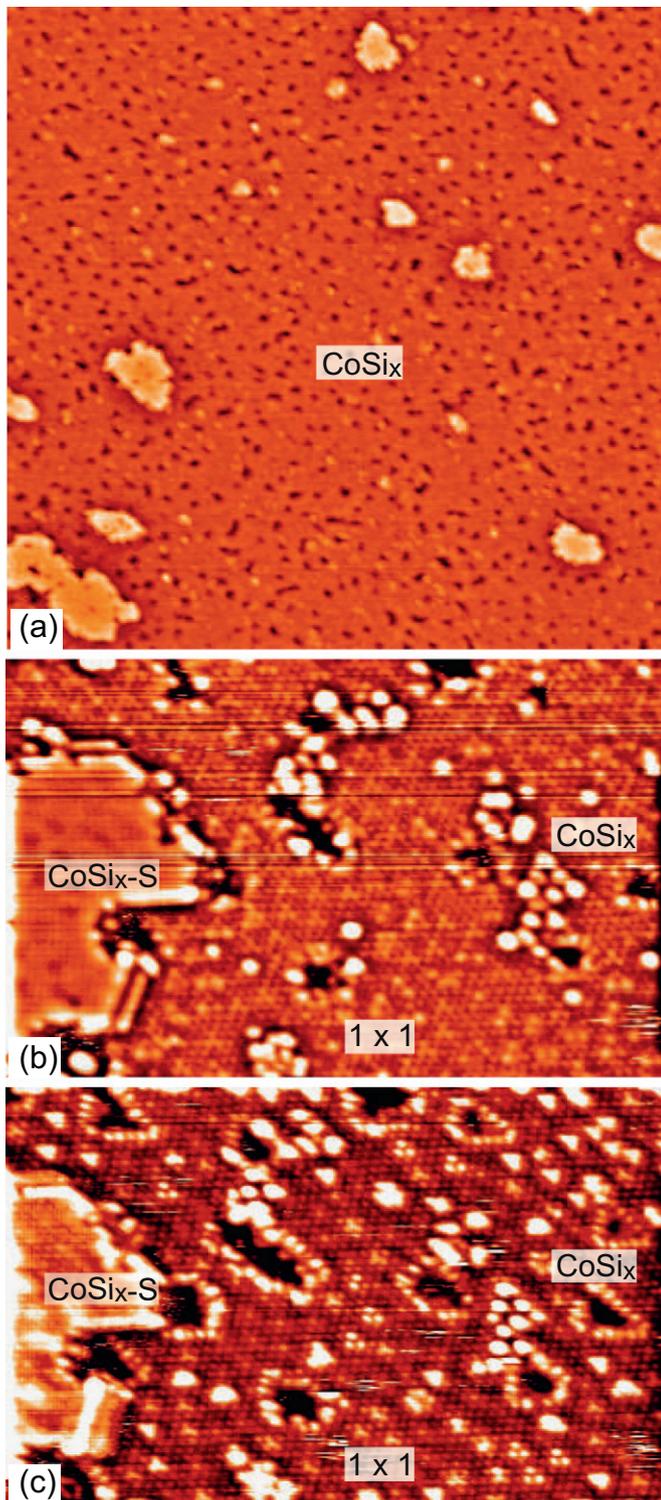
$$Q_{1 \times 1} = S_1(Q_{1 \times 1} - 2) + S_2 Q_{\text{CoSi}_x}, \quad (1)$$

where  $S_1$  and  $S_2$  are the fraction of the areas occupied by the  $(1 \times 1)$ -RC and CoSi $_x$ , respectively. Taking into account that  $S_1 + S_2 = 1$ , Eq. (1) can be rewritten as  $Q_{\text{CoSi}_x} = Q_{1 \times 1} + 2S_1/S_2$ . Note that  $(1 \times 1)$ -RC surface contains  $\sim 0.08$  ML Co and its Si-atom coverage is in between  $2.08$  ML of the original Si(111)  $7 \times 7$  surface and  $2.71$  ML of the completed RC array in the  $\sqrt{7}$  phase [18,20]. We have every reason to believe that CoSi $_x$  phase accumulates  $2$  ML of Co atoms and total number of Si atoms included into the flat CoSi $_x$  layer, equal to  $\sim 4$  ML. This is consistent with a two-layer CoSi $_2$  with the CaF $_2$ -type crystal structure. In our case, nearly half of the first Si bilayer in RC area ( $\sim 1$  ML Si) is ejected onto the surrounding silicide region to react with Co. In line with AES data (as noted below), the silicide layer not terminated by additional Si bilayer, i.e., the deficiency of Si atoms and Co atoms results in the formation of a two trilayer-thickness CoSi $_2$  film with a Co rich structure. It is worth to remember that annealing in the temperatures range of  $600$ – $700$  °C is necessary for the formation of the more stable CoSi $_2$  film with a Si rich structure, and high-resolution STM images of these surfaces are significantly different (see ref. [22]).

In order to obtain an ultra-thin CoSi $_x$  film with homogeneous layer structure, the deposition of Co exceeding  $1.5$  ML on the  $(1 \times 1)$ -RC surface held at RT and subsequent annealing at high temperatures was performed. It turned out that a CoSi $_x$  phase develops as the locally-homogeneous layer only after deposition of Co atoms in an amount of about  $2$  ML while substrate kept at a temperature of  $\sim 600$  °C. A two-level CoSi $_x$  phase by one Si(111) bilayer apart, such as those shown in Fig. 3a, are revealed on STM image ( $150 \times 150$  nm $^2$ ) recorded on a wide terrace. The surface is almost entirely covered by two-level CoSi $_x$  phase ( $>90\%$ ). It has almost smooth surface with small patches of other surface reconstructions. Note that filled-state STM image of the CoSi $_x$  surface, as illustrated in Fig. 3a, is identical with those in Figs. 1 and 2. Furthermore, the step height between the CoSi $_x$  surface at upper level and the Si adatom level of the bright clusters constituting the  $\sqrt{13}$  surface reconstruction is the same as in Fig. 1 (also elevated  $\sim 0.15$  Å). The development of a two levels percolation structure, such as shown in Fig. 3a, indicates that Si atoms redistribution at the topmost Si layers in the initial  $(1 \times 1)$ -RC substrate is involved in the silicidation procedure caused by the difference in the top Si atom density in a silicide layer and  $(1 \times 1)$ -RC. It is worth noting that, at high temperatures, silicon atoms from step-edges can be involved in this process. As illustrated in Fig. 3b and c, the inclusions of a  $\sqrt{13}$  surface reconstruction (or  $\sqrt{13}$ /RCs mixture) were observed only at the upper-level, while, at lower-level, we can see holes with RCs on the bottom (seen as a dark



**Fig. 3.** (a) Filled-state STM image ( $150 \times 150$  nm $^2$ ,  $-2.0$  V,  $1$  nA) of the sample formed by depositing  $1.8$  ML Co on the  $(1 \times 1)$ -RC at RT and subsequent annealing at  $600$  °C. A CoSi $_x$  phase occurring in two levels: (upper, u-CoSi $_x$ ) and (lower, l-CoSi $_x$ ). Arrows indicate second type of patches denoted as CoSi $_y$ . (b) Typical empty-state STM image ( $50 \times 50$  nm $^2$ ,  $1.9$  V,  $1$  nA) showing an upper surface level with small domains of  $\sqrt{13}$  or  $\sqrt{13}$ /RC mixture. Inset shows the image ( $15 \times 12$  nm $^2$ ) of CoSi $_x$  surface taken at sample bias of  $+1.0$  V ( $1$  nA). (c) High-resolution image ( $1.9$  V,  $40$  nA) of CoSi $_x$  surface according to (b). (d) Typical STM image ( $100 \times 65$  nm $^2$ ,  $0.7$  V,  $1$  nA) showing a lower surface level which includes patch of CoSi $_y$ , silicide and holes with RCs on the bottom. (e) The region outlined in (d) shown at a greater magnification.



**Fig. 4.** (a) Filled-state STM image ( $150 \times 150 \text{ nm}^2$ ,  $-2 \text{ V}$ ,  $1 \text{ nA}$ ) of the  $\text{CoSi}_x$  surface formed by sequential depositing of  $2.0 \text{ ML Co}$  and  $1.2 \text{ ML Si}$  onto the  $(1 \times 1)$ -RC at RT followed by annealing at  $580 \text{ }^\circ\text{C}$ . High-resolution (b) filled- and (c) empty-state STM images ( $25 \times 15 \text{ nm}^2$ ,  $\pm 0.7 \text{ V}$ ,  $1 \text{ nA}$ ) of the same area. The labels are explained in the text.

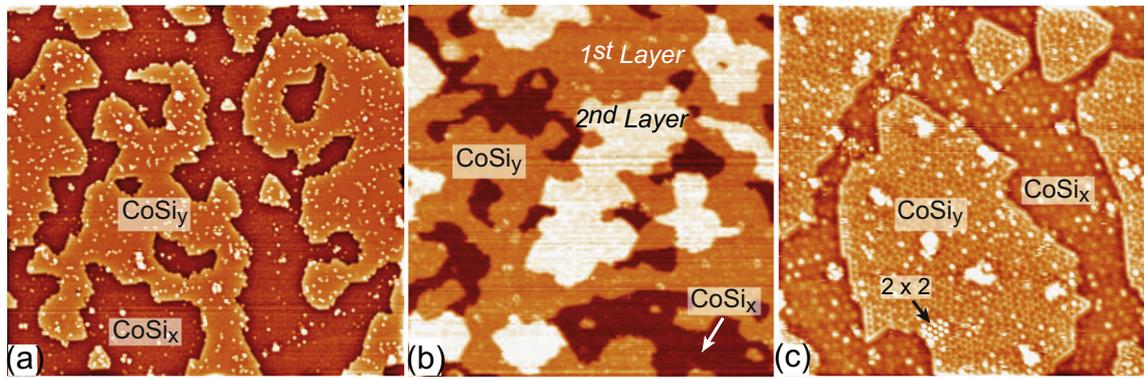
areas in Fig. 3d). Note that the  $\text{CoSi}_x$  surface is typically seen in filled-state STM image as a smooth surface, but (as illustrate in Fig. 3c) it shows up in empty-state STM image as bright round protrusions with  $1 \times 1$  symmetry. The STM images of the surfaces shown in Fig. 3a and d revealed the simultaneous presence of two types of silicide phases. The regions immediately adjacent to steps or imbedded in  $\text{CoSi}_x$  phase on lower level are represented a new silicide phase (denote as  $\text{CoSi}_y$ ).

In the empty states STM images (negative voltage is applied to the tip),  $\text{CoSi}_y$  layer shows up as a disordered structure. One can see in Fig. 3e that small region with a  $2 \times 2$  surface reconstruction can be detected on  $\text{CoSi}_y$  surface. Experimentally, at slightly higher Co coverage than  $\sim 2 \text{ ML}$ , the different silicide phases are fully covered the surface, one,  $\text{CoSi}_x$  phase, and second,  $\text{CoSi}_y$  phase. Simultaneous growth of both silicides over the whole surface area will be discussed latter.

Now we briefly consider the results obtained by means of another common technique which is being used for growth of the epitaxial silicides. A series of experiments have been carried out by a sequential deposition of  $\sim 2.0 \text{ ML Co}$  and about  $1\text{--}3 \text{ ML Si}$  on the  $(1 \times 1)$ -RC surface at RT followed by annealing to  $350\text{--}600 \text{ }^\circ\text{C}$ . It is found that the deposition of  $2.00 \pm 0.24 \text{ ML Co}$  and  $1.20 \pm 0.18 \text{ ML Si}$  at temperature  $\sim 580 \text{ }^\circ\text{C}$  yields an ultra-thin epitaxial  $\text{CoSi}_x$  film that covered almost the entire surface of the sample. As illustrated in Fig. 4, pinhole defects were observed in the flat  $\text{CoSi}_x$  surface. Three important features are quite visible in these images. First, the  $\text{CoSi}_x$  phase occurring in one level is formed under appropriate conditions, as compared with those using RDE or SPE growth, without employing Si deposition in its growth. In high-resolution filled and empty-state STM images of the same area (Fig. 4b and c, respectively), the  $\text{CoSi}_x$  surface appears as bright round protrusions with  $1 \times 1$  symmetry, which correspond plausibly to the highest Si atoms in the upper layer of silicide. Second, a larger number of randomly distributed pinholes appear in the sample as dark patches. This means that a silicide formation involves Si mass transport in the top Si layers from a pinhole area to film and, as a result, the absence of silicide layer is observed in the areas mentioned. The measured depth of the pinholes with respect to the  $\text{CoSi}_x$  surface in filled-state image showing in Fig. 4b is  $\sim 3.6 \text{ \AA}$ . Third, the individual crystallographically oriented islands with atomically flat surface are formed onto the Si(111) substrate. The empty-state STM image in Fig. 4c shows that the surface of these islands has  $(1 \times 1)$  structure. The apparent height of the islands ranges from  $3.5 \text{ \AA}$  (at  $-0.8 \text{ V}$ ) to  $2.5 \text{ \AA}$  (at  $+0.8 \text{ V}$ ) higher than the  $\text{CoSi}_x$  surface; that is both surfaces have different surface structures. We suggest that the small islands have another type of surface reconstruction and this structure has been assigned to the  $\text{CoSi}_2\text{-Si}$  (Si rich) structure [22]. Note that these silicide islands contain the small pinholes too.

The simultaneous growth of two types of epitaxial cobalt silicide phases usually takes place at moderate annealing temperatures ( $450\text{--}550 \text{ }^\circ\text{C}$ ) at initial Co coverages more than  $2 \text{ ML}$ . It is clearly seen in Fig. 5a and b that only two distinctly different surface phases are seen at the whole surface area. The close inspection of numerous STM images, such as shown in Fig. 5b, has revealed the layer-by-layer growth of a  $\text{CoSi}_y$  film at insignificantly increasing of Co coverage. The layer distance between the upper and lower layers of  $\text{CoSi}_y$  film shown in Fig. 5b is  $1.5 \pm 0.3 \text{ \AA}$  (not illustrated). The area fraction occupied by the  $\text{CoSi}_x$  phase decreases with increase of initial Co coverage. The empty-state image shown in Fig. 5c makes it clear that a small domain with the  $2 \times 2$  periodic structure develops on the surface of the second silicide phase ( $\text{CoSi}_y$ ). It should be noted that the formation of similar structure has been also reported for co-deposited films of  $\text{CoSi}_2$  [17,21,23].

As can be seen in Fig. 6a, the sequential deposition of Co and Si atoms on Si(111) substrate at RT followed by annealing to  $500 \text{ }^\circ\text{C}$  also makes it possible to growth of an ultra-thin  $\text{CoSi}_y$  film. In the case that the coverages of the as-deposited sample are  $3.4 \pm 0.3 \text{ ML Co}$  and  $2.4 \pm 0.2 \text{ ML Si}$ , nearly the entire surface is covered by  $\text{CoSi}_y$  phase. A large number of small holes ( $\sim 5 \times 10^6 \text{ cm}^{-2}$ ) were formed on the SPE-grown film. In addition, the empty-state STM image in Fig. 6a reveals the existence of a  $\text{CoSi}_x$  phase at the bottom of each holes. The surfaces of each level of the  $\text{CoSi}_y$  phase has the same surface structure, and empty- and filled-state STM images of these surfaces identical with those shown in Fig. 3a and e, accordingly. Line profiles of the  $\text{CoSi}_y$  film drawn across the surface according to STM image (A–A' and B–B' in Fig. 6b and c) demonstrate that distance between neighboring layers in the three-layer silicide is about  $1.5 \pm 0.3 \text{ \AA}$ . This value coincides with the



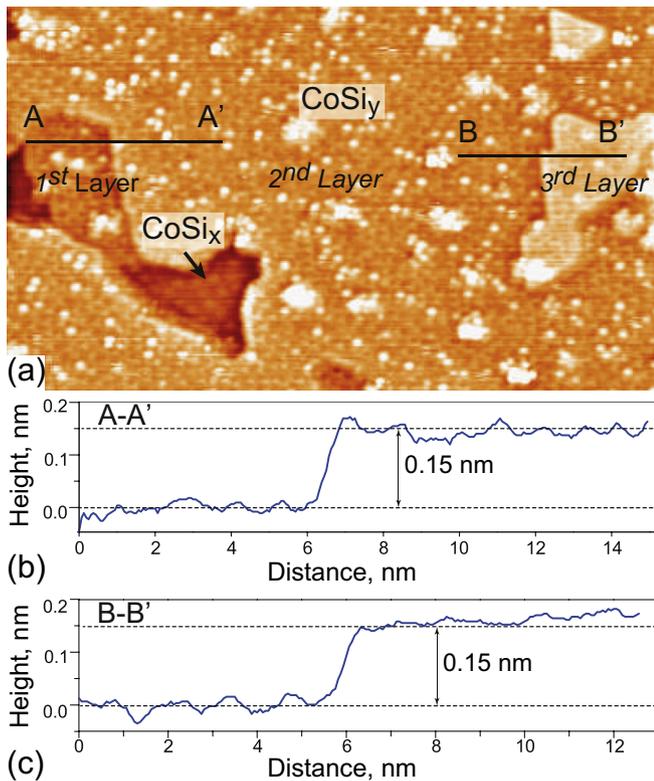
**Fig. 5.** STM images showing morphology of the surface consisted of two phases over the whole surface area. (a) Filled-state STM image ( $100 \times 100 \text{ nm}^2$ ,  $-2.0 \text{ V}$ ,  $1 \text{ nA}$ ) of the sample formed by depositing  $\sim 2.4 \text{ ML}$  Co on the  $(1 \times 1)$ -RC at RT and subsequent annealing at  $550 \text{ }^\circ\text{C}$ . (b) Filled-state STM image ( $100 \times 100 \text{ nm}^2$ ,  $-2.0 \text{ V}$ ,  $1 \text{ nA}$ ) in the case of the deposition of  $\sim 3.2 \text{ ML}$  Co. Two different levels of the  $\text{CoSi}_y$  phase are indicated. (c) Same as (a), but at a greater magnification ( $50 \times 50 \text{ nm}^2$ ,  $1.8 \text{ V}$ ,  $1 \text{ nA}$ ) showing distinctions between different surfaces in empty-state STM image. The small area with  $2 \times 2$  surface reconstruction is indicated by arrow.

interlayer spacing for  $\text{CoSi}$  film with the CsCl-type (B2) crystal structure,  $1.58 \text{ \AA}$  [16]. Since  $\text{CoSi}_x$  layer previously have been identified as  $\text{CoSi}_2$  layer, we believe that the upper layers shown in Fig. 6a are  $\text{CoSi}$  layers with the CsCl-type (B2) crystal structure growing on top of a two-layer  $\text{CoSi}_2$  film. Remind that such coherent double interface  $\text{CoSi}/\text{CoSi}_2/\text{Si}(111)$  has been observed on thicker  $\text{CoSi}_2$  films [2–4].

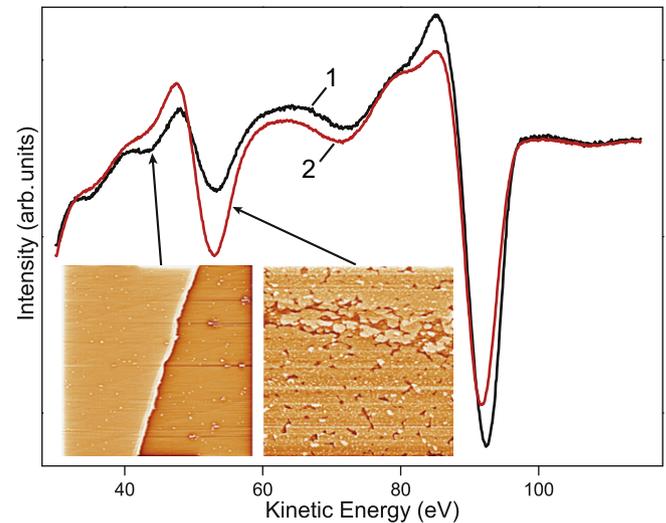
It is well known that  $\text{CoSi}_2$  surface can be made to have a different termination (with Si rich or Co rich structures) [24]. The main difference between them is the presence or absence of Si bilayer on top of the upper Si-Co-Si triple layer [25]. The CsCl-type crystal structure of  $\text{CoSi}$  is terminated by a Co-Si double layer, i.e., by analogy with a  $\text{CoSi}_2$  surface, the  $\text{CoSi}$  surface has the Co rich structure too. Therefore, an additional Si bilayer also may occur on its surface. To solve that problem,

we have used an AES analysis technique by measuring the peak height ratio of the Co  $M_{2,3}VV$  ( $53\text{-eV}$ ) and Si  $LVV$  ( $92\text{-eV}$ ) lines. Auger spectra from cobalt silicide films on  $\text{Si}(111)$  in range  $30 \text{ eV}$  to  $115 \text{ eV}$  is shown in Fig. 7. The surface of four-layer  $\text{CoSi}_2$  film with homogeneous and uniform thickness (see Fig. 4 in ref. [14]) shows a peak height ratio near  $0.17$  (curve 1). This  $\text{CoSi}_2$  film with  $\text{CoSi}_2\text{-S}$  (Si rich) structure contains additional silicon bilayer on top of four completed Si-Co-Si triple layers. In the case of the relatively homogeneous  $\text{CoSi}_y$  phase as shown in Fig. 6a, this ratio is higher by a factor of  $\sim 0.49$  (curve 2). In the latter case, as illustrated in Fig. 7, the flat islands are observed along the step on a lower terrace. In our view, it is possible to assign the island structure with above-mentioned  $\text{CoSi}_2\text{-Si}$  structure. The area occupied by the islands does not exceed  $5\%$ , and it has little effect on the peak height ratio. The surface illustrated in Fig. 3a, where  $\text{CoSi}_x$  phase occupies  $\sim 90\%$  of total area of the surface, also has similar a peak height ratio (about  $0.45$ ). Thus, it may be conclude that  $\text{CoSi}_x$  surface in Fig. 3a and  $\text{CoSi}_y$  surface in Fig. 6a have Co rich structure, i.e., they do not have an ‘additional’ Si bilayer at the top of the films.

Next, we consider the results of DFT calculations of the interface between cobalt silicides and  $\text{Si}(111)$  substrate, namely,  $\text{CoSi}_2$  phase with the  $\text{CaF}_2$ -type (C1) structure and  $\text{CoSi}$  phase with CsCl-type (B2) structure at the thickness region of 1–3 Co layers. Note, that both silicides



**Fig. 6.** (a) Empty-state STM image ( $50 \times 25 \text{ nm}^2$ ,  $1.8 \text{ V}$ ,  $1 \text{ nA}$ ) of the surface in the middle of a wide terrace formed by depositing  $3.4 \text{ ML}$  Co and  $2.4 \text{ ML}$  Si on the  $(1 \times 1)$ -RC at RT and subsequent annealing at  $500 \text{ }^\circ\text{C}$ . The number of each  $\text{CoSi}_y$  levels is indicated. (b, c) Line profiles along the solid lines (A-A') and (B-B') according to STM image. The measured step heights are multiple of  $1.5 \pm 0.3 \text{ \AA}$ .



**Fig. 7.** Auger spectra from epitaxial cobalt silicide films on  $\text{Si}(111)$  substrate: 1 – the four-layer  $\text{CoSi}_2$  film with  $\text{CoSi}_2\text{-S}$  (Si rich) structure formed by depositing  $4 \text{ ML}$  Co and  $7.3 \text{ ML}$  Si onto the  $(1 \times 1)$ -RC at RT and subsequent annealing at  $680 \text{ }^\circ\text{C}$  for  $1 \text{ min}$  [22]; 2 – the  $\text{CoSi}_y$  film, which is the same as in Fig. 6a. Image sizes are  $400 \times 400 \text{ nm}^2$ . The energy of the incident electron beam was  $1500 \text{ eV}$ , the amplitude of the modulating signal was  $5 \text{ V}$ .

**Table 1**

Formation energies (in eV) calculated for CoSi<sub>2</sub> and CoSi layers with Co rich structure on Si(111) substrate under unchanged Co coverage for each one relatively minimal energy as indicated in bold.

Co coverage (ML)	Interface	Interface configuration			
		B8	A8	B7	A7
1	CoSi/Si(111)	0.02	<b>0.00</b>	0.47	0.43
2		<b>0.00</b>	0.15	0.18	0.18
3		0.07	0.16	<b>0.00</b>	0.01
2	CoSi <sub>2</sub> /Si(111)	<b>0.00</b>	0.02	0.34	0.25
	CoSi/Si(111)	0.72	0.87	0.90	0.90
3	CoSi <sub>2</sub> /Si(111)	<b>0.00</b>	0.03	0.23	0.18
	CoSi/Si(111)	1.09	1.29	1.02	1.03
3	CoSi/Si(111)	0.60	0.70	0.54	0.54
	CoSi/CoSi <sub>2</sub> /Si(111)	0.02	<b>0.00</b>	0.47	0.43

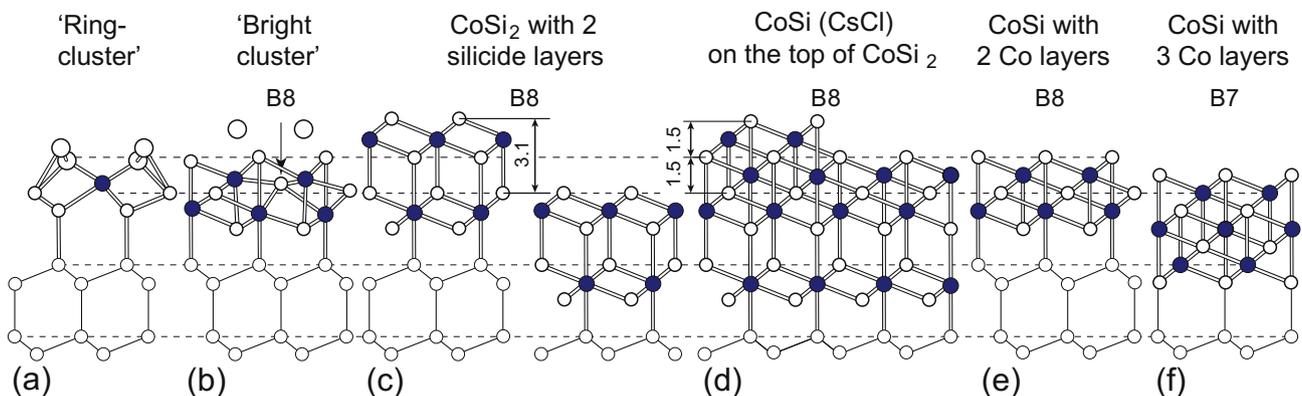
have the similar local structure, since CsCl lattice can be constructed from CaF<sub>2</sub> lattice by the addition of cobalt layer to latter between each of Si-Co-Si triple layers in the [111] direction. According to AES findings, we shall only deal with CoSi<sub>2</sub> and CoSi surface phases with Co rich structure that make up bulklike structures terminated by a Si-Co-Si triple layer or Co-Si double layer, respectively. Calculated formation energies are summarized in Table 1 for one-, two-, and three-layer cobalt silicide models. Depending on the coordination number of Co interface atoms and the stacking sequence of silicide layers relative to the substrate, both A- and B-type interfaces and seven-, and eightfold coordination for the CoSi<sub>2</sub>/Si(111) and CoSi/Si(111) interfaces were taken into consideration [26]. 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, A8, B7, and A7) [26,27]. As tabulated data demonstrate, two important conclusions for CoSi/Si(111) interface at the thickness region of 1–3 Co layers within the silicide are fairly clear: first, that the B8 interface structure have been found to represent the most stable configuration in case of a CoSi(111) film has thickness equal of two Co layers within the silicide; second, that, with increasing film thickness up to three Co layers, a structural transition from CoSi at B8 interface structure to CoSi at B7 (or A7) interface structure should be occurred. In the latter case, two models represented CoSi/Si(111) interface structure at B7 and A7 configurations have close energies and are energetically favorable structures.

The comparison of calculated formation energies for CoSi/Si(111) and CoSi<sub>2</sub>/Si(111) interfaces both at two and three cobalt layers show that eightfold coordinated CoSi<sub>2</sub>/Si(111) interface structure is the most energetically favorable structure, than any one of several different

CoSi/Si(111) interfaces. The B8 model represents the lowest-energy interface configuration, but the A8 model is less stable by only 0.2–0.3 eV per 1 × 1 cell and cannot be conclusively ruled out. The side view models for different Co-Si interface structures oriented in parallel to the (110) plane is schematically shown in Fig. 8. For reference, the atomic arrangement of the ‘ring cluster’ interface [5] and the ‘bright cluster’ interface (constituting the √13 phases) [8], are shown in Fig. 8a and b, respectively. The B8 configuration of the two-layer CoSi<sub>2</sub>/Si(111) interface in two different levels is shown in Fig. 8c. The results of calculations for different silicide interfaces with 3 Co layers are shown at the end of the table. It was found that the latter interface turn out to be the most stable one, 0.54 eV lower in energy than the CoSi/Si(111) interface. Note that all Co interface atoms entered into the composition of these layers are coordinated with eight Si atoms, and CoSi<sub>2</sub>/Si(111) interface being of B-type. The side view models for one- and two-layer CsCl-type CoSi on top of two-layer CoSi<sub>2</sub>, which are formed a coherent double CoSi/CoSi<sub>2</sub>/Si(111) interface, schematically shown in Fig. 8d. Models for two-, and a three-layer CoSi/Si(111) interface structures that have received special attention are energetically unfavorable ones are shown in Fig. 8e and f, respectively, for the illustration purposes only.

#### 4. Conclusion

In summary, we have reconsidered the early stages of cobalt silicide formation within the heating temperature range of 350–600 °C using a disordered ‘(1 × 1)’ surface. It appears the most promising approach to grow well-ordered surface reconstructions in Co/Si(111) system, and may also be useful to investigate other transition metal systems. The structure and morphology of cobalt silicide phases at the thickness region of 2–4 Co layers strongly depend on both temperature and coverage of Co atoms. Our STM observations support formation of two types of silicide phases. It has been determined that CoSi<sub>2</sub> phase consists of two Co layers and four Si layers above the interface, and interfacial Co atoms are coordinated to eight Si atoms. It is remarkable that CoSi phase has a coherent double interface CoSi/CoSi<sub>2</sub>/Si(111). In this case, the first Co-Si double layer (which is CoSi layer) being on top of the second Si-Co-Si triple layer (which are CoSi<sub>2</sub> layer). It seems reasonable to say that the formation of CoSi phase on Si(111) substrate takes place only at CoSi/CoSi<sub>2</sub> interface. The interface arrangement of both phases obtained by total-energy calculations is in good agreement with experiment. It is reasonable to expect that CoSi layers on top of a two-layer CoSi<sub>2</sub> film developed as homogeneous layer may be used as a suitable template for epitaxial growth of thick uniform CoSi<sub>2</sub> films on Si(111).



**Fig. 8.** Schematic side view of models for Co/Si(111) interface structures: (a) ‘ring cluster’ (RC) [5]. (b) The central part of the ‘bright cluster’ located inside a  $\sqrt{13} \times \sqrt{13}$  unit cell [8]. A Si atom in the center of the cluster is marked by the arrow. (c) 8-fold B-type of a two-layer CoSi<sub>2</sub> phase occurring in two levels. (d) 8-fold B-type of CoSi with 1 and 2 Co-Si double layers with a CsCl structure on CoSi<sub>2</sub>. (e) 8-fold B-type of two-layer CoSi. (f) 7-fold B-type three-layer CoSi. Silicide structures showing in (e) and (f) are energetically unfavorable. See the text for structure details. Open circles represent silicon atoms, dark circles correspond to cobalt.

## Acknowledgements

The work was supported in part by the RAS “Far East” Program grant no. 0262-2015-0005 and NSH-6889.2016.2.

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