Technical Physics, 2025, Vol. 70, No. 4

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Kinetics of silicide phase formation in the Yb-Si(111) thin-film system

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Received July 25, 2024
Revised November 27, 2024
Accepted December 5, 2024

Formation processes and some physical and chemical properties of ytterbium silicides in the Yb-Si(111) film system have been studied. It is shown that the transition from the metallic ytterbium to silicide films with the Yb_5Si_3, YbSi and $YbSi_{2-x}$ stoicheometry occurs upon annealing at 400, 470, and 600 K, respectively. The latter has the ordered $YbSi_{2-x}$ structure and exists within the range of 600−1000 K. The work function and the valence of Yb atoms are determined for the silicide films. The optimum temperature for the formation of Yb disilicide film of epitaxial quality on the Si(111) surface is established.

Keywords: surface, ytterbium, silicides, Auger electron spectroscopy, work function.

DOI: 10.61011/TP.2025.04.61217.243-24

Introduction

As sizes of components of the electronic and photonic integrated circuits reduce, the studies of new functional materials are becoming increasingly important. They include disilicides of rare-earth metals (REM) as well. They are a specific class of silicides having important physical & chemical properties in terms of practical application — the low formation temperature (≤ 600 K), the very low Schottky barrier height in contact with silicon of the n-type (≤ 0.2 eV), good thermal and electrical conductivity, etc. [1]. Due to the said properties, these compounds are widely applied recently. Thus, based on the $YbSi_{2-x}$ ytterbium disilicide ($x \sim 0.2-0.3$), the Schottky barrier field transistors [2–4] and silicon solar elements without doping layers are created [5].

Another notable feature of some REM disilicides and, in particular, ytterbium disilicide is a capability of epitaxial growth of their films and nanowires on silicon substrates, which in turn makes it possible to comparatively easily integrate these compounds into existing silicon technologies [1,6,7]. Fig. 1 schematically shows the crystal structure of the $YbSi_{2-x}$ disilicide on the Si(111) surface [8]. This film is formed by alternating two-dimensional layer of the atoms of the metal and silicon (the lattice of the AlB_2 type). The key role in its formation belongs to vacancies in the silicon layers [9]. Fig. 1 designates them with unfilled circles. The presence of the vacancies defines not only stoichiometry of a growing film but provides spontaneous (explosive) diffusion of atoms from the silicon crystal into it when reaching the threshold value of the temperature ($\sim 500-600$ K). In this context, there is a question: is it possible to form other silicide phases in the Yb-Si(111) film system at the lower temperatures? If so, what are the mechanism of their formation and the physical & chemical properties? There is almost no such data in the literature. This hinders formation of an adequate model of the Yb-Si(111) film structures within the wide range of temperatures.

The aim of the present work was to study the kinetics of formation of the silicide phase in the Yb-Si(111) system within the wide range of temperatures, starting from the room temperatures to its values, at which there is evapora-

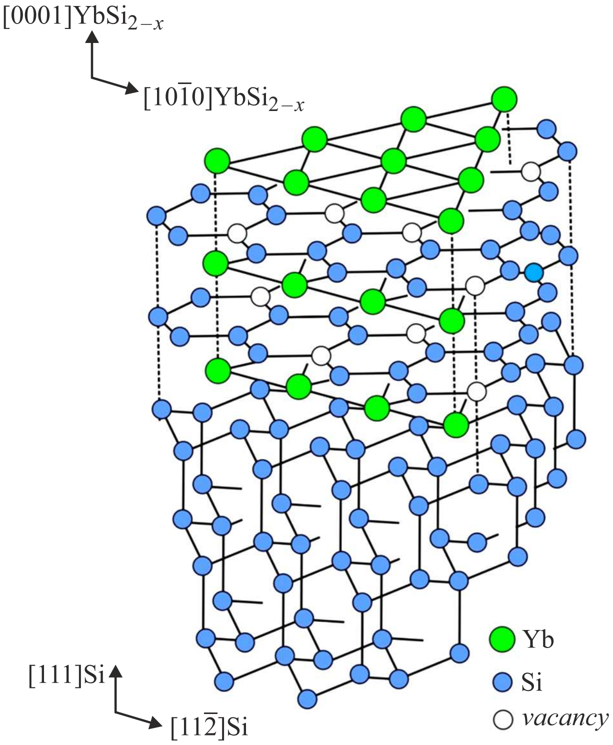

Figure 1. Crystal structure of the $YbSi_{2-x}$ film on the Si(111) surface. The figure is adapted from the paper [8]. The lattice constants of ytterbium disilicide are $a = 3.784$ Å and $c = 4.098$ Å. For silicon, the same magnitudes are — 3.84 and 3.134 Å. The lattice mismatch on the interface is −1.46%.

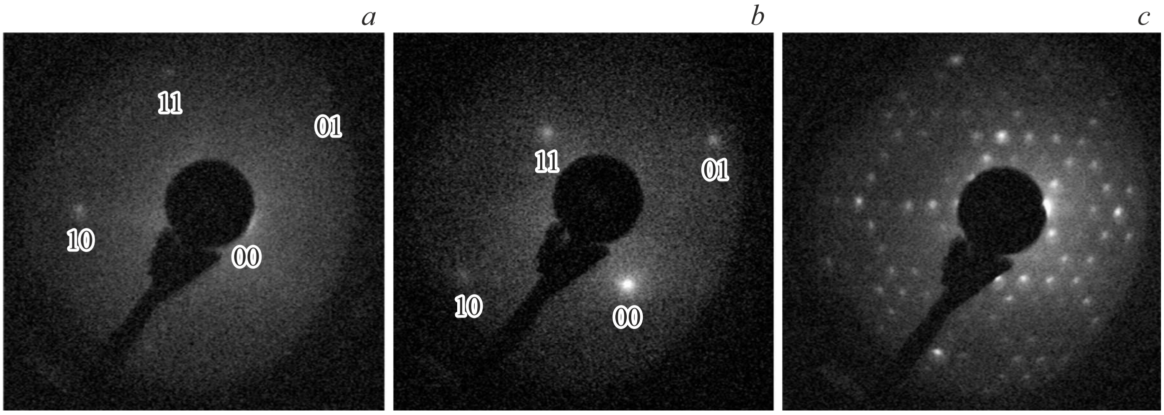

Figure 2. Diffraction patterns obtained after heating the Yb-Si(111) film structure at the various temperatures: *a* — 700, *b* — 800, *c* — 1300 K. The electron energies are 95, 96 and 81 eV, respectively.

tion of ytterbium atoms from the surface. The experiments were performed by a set of procedures including low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and a method of contact potential difference (CPD) for measurement of the work function. The obtained results made it possible not only to specify a composition of the silicide phases, but they also provided information about mechanisms of formation of the silicide films and their structural and electronic properties.

1. Experimental procedure

The studies were carried out *in situ* in an ultrahigh-vacuum system with base pressure lower than $1 \cdot 10^{-10}$ Torr. The substrates were silicon samples of the *n*-type with surface orientation (111), which were doped with phosphorus (the resistivity $7.5\,\Omega\cdot$cm). Their surfaces were cleaned to remove foreign impurities by using a series of short-time heatings at 1530–1550 K. The structure and cleanliness were controlled by applying the AES and LEED methods. The Yb-Si(111) film structures were created using the solid-phase epitaxy method. Ytterbium was deposited to the silicon surface (7×7) at the room temperature (290–300 K). After that the sample was heated at the specified temperature for 45 sec and then the film structures were studied at the room temperature using the above-listed methods. Ytterbium was sputtered from DC-heated tantalum ampules at the pressure in the vacuum chamber $\leq 3 \cdot 10^{-9}$ Torr. The sputtering rate was one monolayer (ML) per minute. The flux was calibrated by appearance of typical features on thermal desorption spectra, diffraction patterns and dependences of the work function on the coverage for the Yb-Si(111) film structures [10,11]. The monolayer coverage of Yb atoms was accepted to be surface concentration $7.84 \cdot 10^{14}\,\mathrm{cm}^{-2}$, which is equal to the atom density on a clean unreconstructed Si(111) facet.

The Auger-spectra were recorded in a differential form dN/dE using an analyzer of the „cylindrical mirror" type. The full energy resolution was ~ 0.7 eV. The work function was determined by the CPD method in the Andersen variant [12]. As known, using this method, it is possible to measure the value of $\Delta\varphi = \varphi - \varphi_0$, where φ_0 —the work function of the clean surface of the substrate (the reference sample) and φ — the work function of this surface after applying adsorbate atoms thereto. The absolute values of the work function were determined by using the value $\varphi_0 = 4.63$ eV for the (7×7) Si surface [13]. The accuracy of measurement of $\Delta\varphi$ was ± 0.03 eV.

2. Results and discussion

The previous studies [11,14] have established that the ytterbium films deposited on Si(111) at the room temperature have a number of important features. First of all, they form a chemically distinct interface with the substrate. There in almost no diffusion of silicon atoms therein. Secondly, they demonstrate very high uniformity along the thickness or low surface roughness. Thirdly, these films have no long-range order. Finally, fourthly, the work function of the Yb-Si(111) structures non-monotonically depends on the film thickness in an abnormally wide range of the values. The changes of the work function terminate only when getting the coverage of 16 ML. Besides, with the coverage, there is termination of all the changes of the values of the Auger signals, which are observed at the earlier stages of system formation. Taking into account the above said, in the present work the value of the thickness of the ytterbium film was accepted to be 16 ML. At this, the film gets features of bulk metal samples of ytterbium. At the same time, the film thickness is optimal for studying the processes of diffusion of atoms out of the silicon crystal.

The structural observations made using LEED have shown that the film produced at the room temperature had no long-range order at all. It complies with the earlier results [11]. After heating of the film system, appearance of the reflections on the diffraction pattern is observed at $T = 700$ K (Fig. 2, *a*). They correspond to the structure (1×1). On the figure, near the reflections the numbers denote indices which specify positions of the lattice sites in the reciprocal space. The structure (1×1) appears to indicate formation of ytterbium disilicide of Fig. 1 on the Si(111) surface.

With increase of the temperature, the reflection brightness increases, while the diffraction pattern (1×1) becomes more distinct. Fig. 2, *b* shows the image obtained after heating at 800 K. Analysis of this image indicates further ordering of the disilicide film.

Finally, when getting to $T = 1300$ K, the diffractometer screen rebuilds the pattern (7×7) of the clean surface. It is shown in Fig. 2, *c*. The transition to the structure (7×7) means that the silicide film is fully decomposed. The released ytterbium atoms have evaporated into vacuum, while the silicon atoms are embedded into the substance crystal lattice.

Fig. 3 shows dependences of intensity of the Auger signals of silicon and ytterbium on the heating temperature of the film structures. In case of silicon, the peak $L_{23}VV$ with the energy of 92 eV was used. Its intensity was measured in the „*peak-to-phone*" mode from the minimum value (negative surge of the differential Auger spectrum) to the background level at the side of higher energies. For ytterbium, the line within the energies $\sim 170-180$ eV was used. It is contributed by a number of the Auger transitions (including the Koster-Kronig transitions) due to ionization of the $4d$-shell [15]. More details on the nature of these transitions and a connection of the Auger line form and the electronic state of the Yb atoms will be given at the end of Section 2. As in the case of silicon, the intensity of the ytterbium signal was measured in the „*peak-to-phone*" mode. The values of the Auger peaks were normalized respectively to the values for the clean surface of the metal film at the room temperature. As it is clear in Fig. 3, the entire studied range of temperatures can be conditionally divided into four areas designated by Roman numerals. The lowest-temperature one of them (area I, 300–350 K) the value of the silicon signal is very small, while that of ytterbium is maximal or close to the maximum. It is obvious that this ratio of the signals is caused by screening of the silicon substrate by a clean metal film applied thereto, which has almost no Si atom diffused from the substrate. Some decrease of the ytterbium signal after heating at 350 K draws attention to itself. At first glance, this reduction could be resulted from thermally activated diffusion of silicon into the film. At this, the SI Auger peak must increase. But Fig. 3 shows no such growth. That is why the authors conclude that at 350 K diffusion from the crystal into the film is limited, while decrease of the metal signal is due to reconstruction of its electronic and/or crystal structure.

The area II exhibits significantly more substantial changes of the values of the Auger signals. With increase of the temperatures from 350 to 600 K, the intensity of the silicon peak increases by one order (in 9.5 times), while the intensity of the metal peak is reduced in more than two times. These transformations are due to sharp growth of the number of the Si atoms diffused into the film being formed on the surface. Let us note that the curves in the area II do not have any horizontal parts (plateau). It means that, first of all, this region of temperatures has no formation of any stable compounds from atoms of the metal and the semiconductor, and, secondly, the mixing process is controlled by diffusion from the silicon crystal and depends on the temperature.

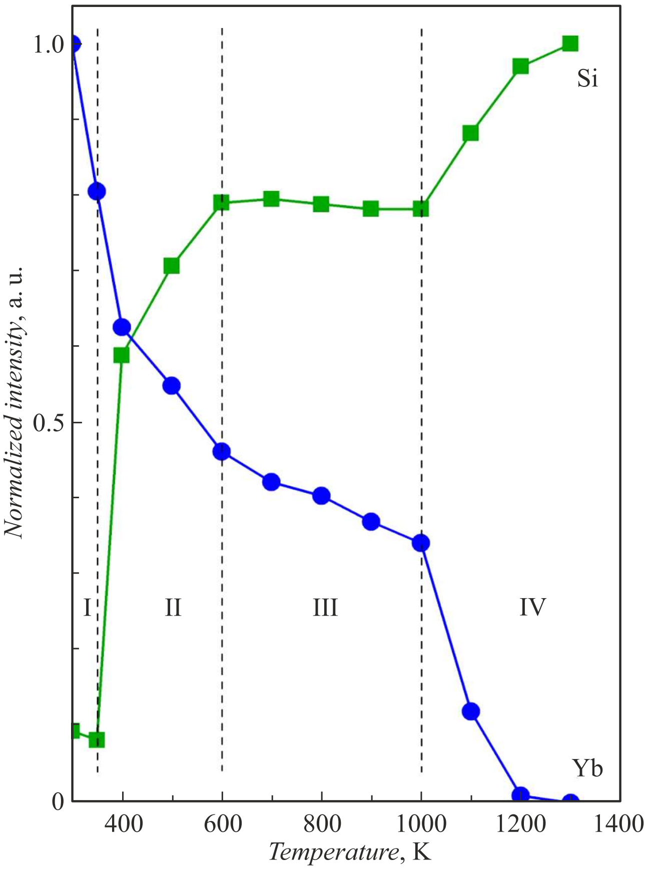

Figure 3. Dependences of the values of the Auger signals of silicon and ytterbium on the sample heating temperature. The dashed lines designate area borders on the temperature scale.

The area III exhibits qualitative changes of the dependence type. In case of silicon, the curve goes to the horizontal plateau, at which the value of the Auger signal does not depend on the temperature. For ytterbium, strictly speaking, no horizontal part on the curve is observed, but the temperature dependence of the Auger signal is very weakly expressed (quasi-saturation). This dependence type is still kept up to $T = 1000$ K. These result indicate formation of the stable compound of the Yb and Si atoms. The composition of the formed film actually does not depend on the temperature. The analysis of intensity of the Auger signals shows that its stoichiometry corresponds to ytterbium disilicide of Fig. 1.

As it is known, the ytterbium-silicon compounds may contain other forms of silicide as well, with less percent content of silicon, i.e. Yb_5Si_3 and YbSi [16]. That is why such quantitative estimates were performed for the area II of Fig. 3 as well. It included determination of the values of the temperatures, at which the film composition corresponds to stoichiometry of the above-said silicides. In accordance with the performed analysis the metal-enriched silicide is matched with the value $T = 400\,\mathrm{K}$, so is the monosilicide with — 470 K. Thus, it follows from the obtained results that the transition from the metal film at the room temperature to the disilicide one at $T \sim 600\,\mathrm{K}$ includes at least two intermediate stages. At $T \sim 400\,\mathrm{K}$, the metastable $\mathrm{Yb_5Si_3}$ phase enriched with ytterbium is formed in the film. With increase of the temperature, the number of silicon atoms diffused into the film increases. It results in formation of the monosilicide phase at $\sim 470\,\mathrm{K}$, in which the percent content of ytterbium decreases. Finally, at $\sim 600\,\mathrm{K}$ the disilicide phase is formed, in which the ytterbium content is the lowest for the films studied in the present work.

Specific explanation shall be given to the mentioned contradiction between the type of the dependences for the metal and silicon in the area III, more specifically, no plateau on one of them. The analysis shows that this contradiction is illusory. For its explanation, let us consider a simple model of the film structure with a reactive interface (Fig. 4). We assume that during deposition of the substance D on the substrate S there is a formed film which consists of atoms of both types and has a homogeneous chemical composition. For convenience, we will believe that the film is of an island type. Consideration can be also extended to the case of solid film with finite roughness. If the height of the islands of Fig. 4 substantially exceeds the depth of electron escape, then the value of the Auger signal D can be written in a simple form $I_D \cong \alpha \cdot I_{D1}$, where α — a portion of the surface covered by the islands, while I_{D1} — the intensity of the Auger signal for the film fully covering the surface (the case $\alpha = 1$). The value of the Auger signal S is somewhat of a more complicated form and can be presented as a sum of two summands: $I_S \cong (1 - \alpha)I_{S0} + \alpha I_{S1}$, where I_{S0} and I_{S1} — the intensities of the signals for the clean surface and the solid film when $\alpha = 1$, respectively. By comparing these expressions, we can understand how the changes of the film morphology affect the magnitudes I_S and I_D. If the difference between I_{S0} and I_{S1} is slight, then when varying the parameter α the intensity I_S will insignificantly vary. At the same time, the changes of I_D will be substantially higher. In the present work $I_{S0} = 1$ and $I_{S1} \cong 0.8$, i.e. these magnitudes are quite close to each other. Apparently, this accounts for the plateau on the temperature dependence of the Auger signal of silicon in the area III of Fig. 3. Absence of the plateau on the similar dependence for ytterbium and weak growth of its Auger signal with the temperature within 600–1000 K can be related to the increased roughness of the disilicide film. More detailed study of its morphology will be performed in the future using scanning tunneling microscopy.

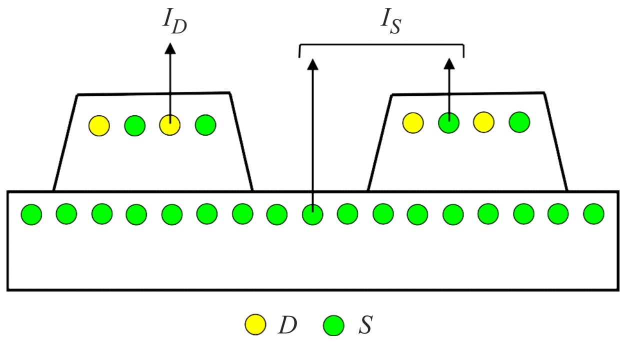

Figure 4. Schematic model of the film structure, in which the film being generated is formed by the substrate atoms (S) and the atoms of the sputtered substance (D). The film consists of islands. The arrows show output of the Auger electrons from this structure into vacuum.

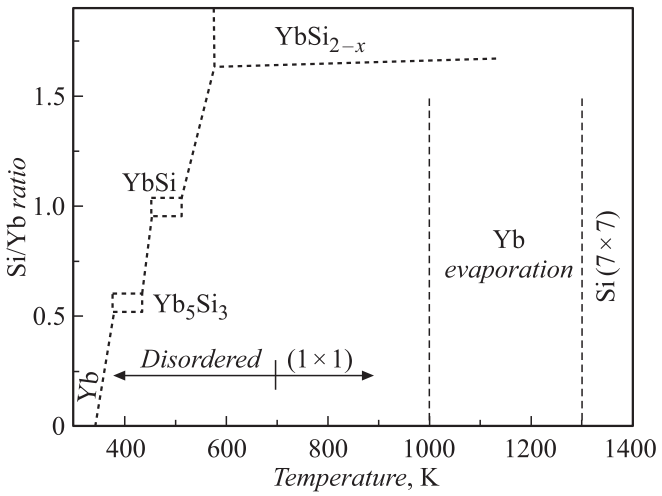

Figure 5. Phase diagram of the Yb-Si(111) system.

Finally, in the highest-temperature area of Fig. 3 (it is designated by the Roman numeral IV) the horizontal parts on both dependences are again replaced by inclined ones: with increase of T the silicon signal noticeably increases, while the ytterbium signal drops. These changes terminate at 1300 K, when the value of the Si signal is unity, while the Yb signal disappears. It means that in the area IV there is intensive evaporation of the metal atoms out of the disilicide film into vacuum. After they are totally removed from the surface at 1300 K, the reconstruction (7×7) is rebuilt thereon (Fig. 2, c).

Fig. 5 shows the main obtained results briefly as the phase diagram of the Yb-Si(111) system. As follows from the diagram, in the area $T \leq 350\,\mathrm{K}$ the silicide phases are not formed in this system. At the higher temperature, due to diffusion of the Si atoms into the ytterbium film its stoichiometric composition monotonically changes towards increase of the percent content of silicon. At 400 K, it corresponds to the $\mathrm{Yb_5Si_3}$ silicide, so does at 470 K to the YbSi silicide. With further growth of the heating temperature, a new phase - ytterbium disilicide is formed. It appears at $T = 600\,\mathrm{K}$ and has a stable structure, which does not depend on the temperature until 1000 K. When $T > 1000$ K, there is noticeable evaporation of the metal atoms out of the disilicide film, which results in its decomposition. When $T = 1300$ K, the silicon surface is fully free of ytterbium and the structure (7×7) is fully rebuilt. The arrows of Fig. 5 mark the areas of the temperatures, in which the film has a long-range order or it is unordered.

In order to obtain additional information about the silicide phases in the Yb-Si(111) system, the temperature dependence of the work function was obtained (Fig. 6). As it is clear, it is of a non-monotonic and quite unsimple nature. At the room temperature, the value $\varphi = 2.89$ eV is expectedly close to the corresponding value for the bulk three-dimensional samples of metal ytterbium [17]. While the temperature increases to 400 K, the work function is almost unchanged. Thus, with the given value of T it is 2.8 eV. It means that the film surface consists of the metal atoms despite diffusion of the Si atoms thereinto when $T > 350$ K.

When the temperature $T = 450$ K, the dependence exhibits the minimum, in which the value of work function φ becomes 2.64 eV. This value is lower than the work function of the ytterbium metal film by 0.25 eV as well as that of the Yb_5Si_3 silicide phase by 0.20 eV. It is natural to assume that the said minimum is related to the phase transition in the film from Yb_5Si_3 to the YbSi monosilicide. It seems that one of the causes of such a low value of φ for the monosilicide film is that there is a double dipole layer on its surface, which is formed by electropositive Yb atoms and electronegative Si atoms. In order to reduce the work function, the „upper“ (i.e., facing to vacuum) part of such a layer shall consist of positively charged atoms (Yb), while its „lower“ (i.e., facing the substrate) part shall consist of the negatively charged (Si).

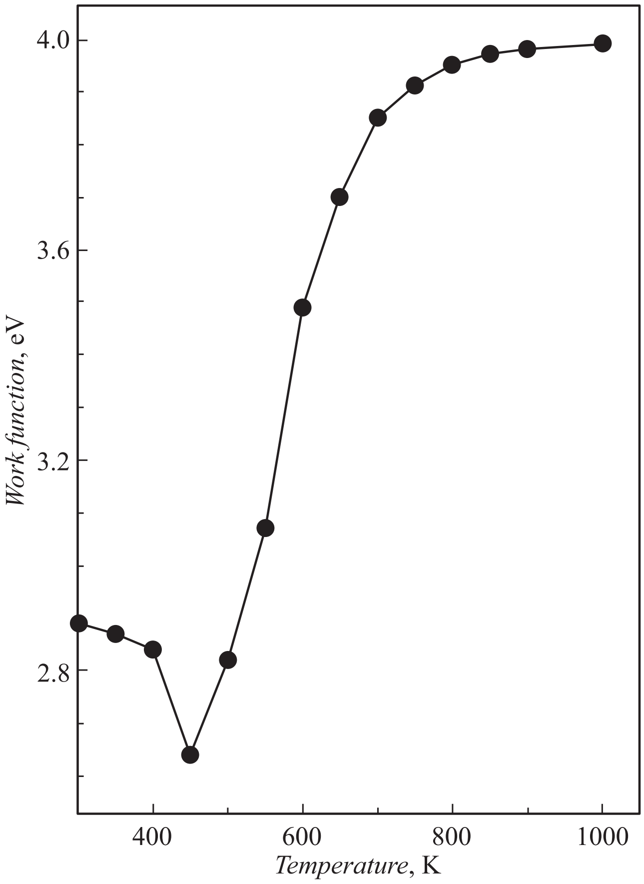

Figure 6. Dependence of the work function of the Yb-Si(111) film structure on the heating temperature.

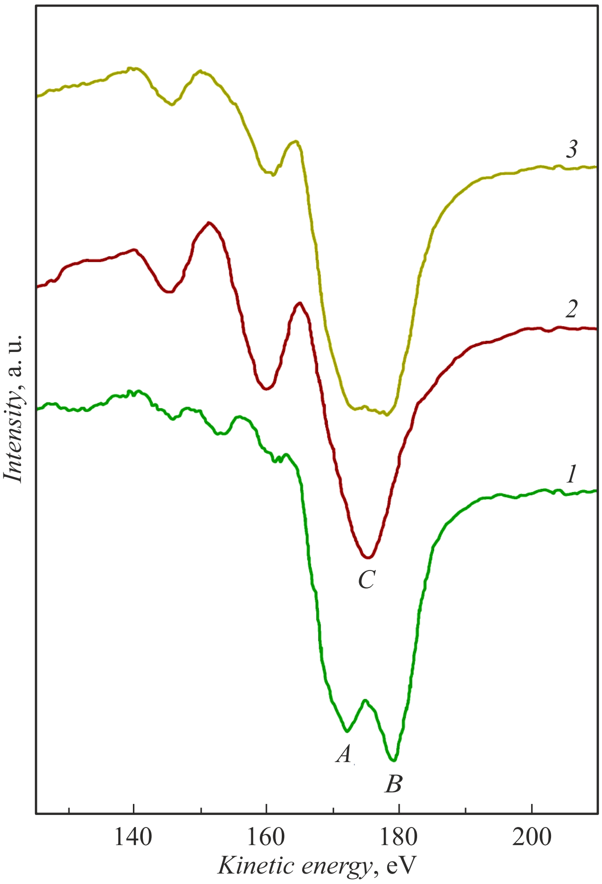

Figure 7. Form of the line of the Auger spectra of ytterbium in various valency states: *1* — 2+, *2* — 3+, *3* — a fractional value of valency, which is equal to 2.4. The spectra *1* and *2* are taken from the work [18]. The spectrum *3* is obtained by superposition of the spectra *1* and *2*.

Within the temperatures 450–650 K, there is observed sharp increase of the work function. On average, it is at least 0.005 eV/K. Finally, when $T = 800$ K the dependence goes to the plateau. As discussed above in detail, at this temperature a well-ordered film of ytterbium disilicide is formed on the sample surface. As per data of Fig. 6, its work function is ~ 4.0 eV. Its value substantially exceeds the work function of metal ytterbium and it is by just ~ 0.6 eV less than the work function of pure silicon. Based on the above said, it can be concluded that the laminar structure of the ytterbium disilicide film faces vacuum with its layer of silicon atoms.

In the final part of the present work we consider the data concerning the electronic state of the ytterbium atoms in the silicide film. It is obvious that the process of its formation includes changes of a chemical environment and of a nature of bonds of these atoms. They can be traced by analysis of the form of the Auger spectra of ytterbium that are studied in the present work. These spectra are due to emission of electrons from the valence band and from the $4f$-level of the atoms. The typical form of the Auger line for the divalent ytterbium (the electronic configuration $4f^{14}6s^2$) is shown in Fig. 7 (the spectrum *1*). It is contributed by a number of the transitions ($N_{45}N_{67}N_{67}$, $N_{45}N_{67}V$ and $N_{45}VV$) [18]. This determines the type of the Yb^{2+} spectrum with the typical features *A* and *B* at the energies 172 and 179 eV, respectively. In the trivalency state (the electronic configuration $4f^{13}5d^1 6s^2$) the important role for the Auger line is played by appearance of a hole on the $4f$-shell of the Yb^{3+} atom. It enables the transition of the $4d$-electron to the $4f$-level (the so-called „giant resonance"), which is induced by irradiation of the sample by primary electrons. As a result, the Yb^{3+} atom goes into the unstable excited state $4d^9 4f^{14}$ with the ionized $4d$-shell, which quickly relaxes into the ground one by reverse recombination $4f \rightarrow 4d$ with subsequent emission of the $4f$-electron into vacuum. The scheme of this process can be written as follows: $4d^9 4f^{14} \rightarrow 4d^{10} 4f^{12} +$ the Auger electron. The entire chain of the said transitions (the giant resonance → the reverse recombination → the output of the Auger electron) results in appearance of the peak *C* in the spectrum of trivalent ytterbium (the curve *2*, Fig. 7). It is important that their probability is very high since the levels participating in the transitions have the same principal quantum number ($n = 4$). This makes the peak *C* a dominant feature. Besides, compounds are known for ytterbium in which its atoms have the fractional (intermediate) valency between the values 2+ and 3+ [19]. In this case, the Auger spectrum is superposition of the curves *1* and *2* (Fig. 7).

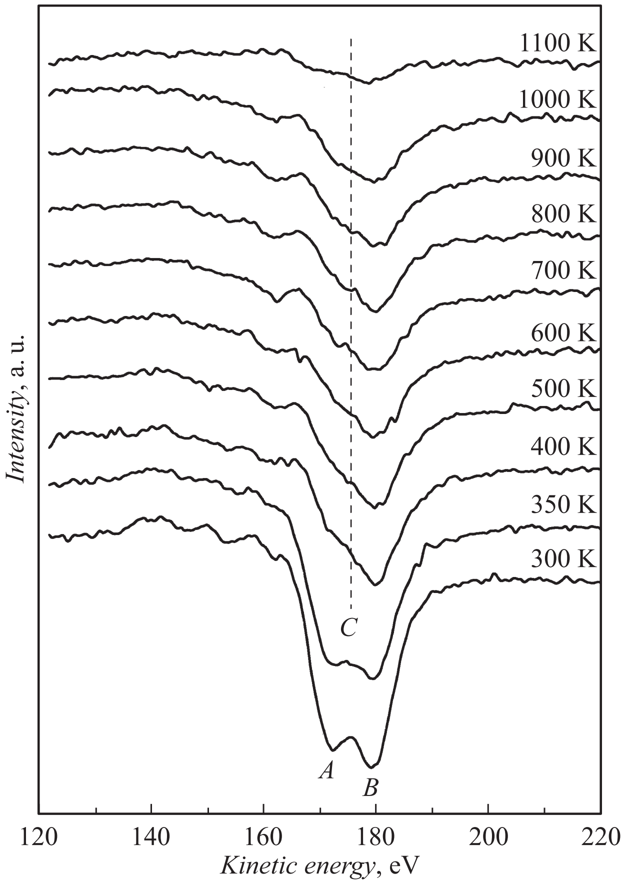

Figure 8. Evolution of the form of the line of the Auger spectra of ytterbium for the Yb-Si(111) structures with increase of the heating temperature. The dashed line designates the position of the feature *C*.

Based on the above-said, let us analyze the form of the Auger spectra of the Yb-Si(111) structures produced at the different temperatures. They are shown in Fig. 8. As it is clear, the spectrum for the unheated structure has the form typical for the bivalent metal. At the qualitative level, the similar form of the line is kept for the structure heated at 350 K, although in this case the features *A* and *B* are expressed more weakly than at the room temperature. When $T \geq 400$ K, the form of the spectra is somewhat transformed. It is related to transition from the metal ytterbium to its compounds with silicon. Comparison of the figures 7 and 8 shows that at these temperatures ytterbium has the intermediate valency between the values 2+ and 3+, while the spectra are contributed by all three features — *A*, *B* and *C*. The spectrum *3* of Fig. 7 is obtained by superposition of the spectra *1* and *2* for the case when ytterbium has the valency of +2.4. Generally, its form well agrees to the form of the experimental spectra of Fig. 8 when $T \geq 400$ K. The main difference is that in the last ones the feature *B* is expressed somewhat more distinctly than the features *A* and *C*. It should be also noted that when $T \geq 400$ K the form of the Auger spectra negligibly depends on the temperature. It means that the values of the valencies of the ytterbium atoms in the various silicide phases are close to each other. It is planned to get more detailed information in the future about the valency states of the ytterbium atoms in the silicide films using X-ray photoelectron spectroscopy.

Conclusion

Using the LEED, AES and CPD methods, the kinetics of formation of the silicide phases in the film system Yb-Si(111) has been studied, so have their structure and electronic properties. The phase diagram is proposed based on the obtained results. It is shown that when $T \leq 350$ K diffusion of the atoms from the silicon substrate into the film of metal ytterbium is limited and the silicides are not formed. With increase of the temperature, diffusion of silicon into the film increases. When $T \cong 400$ and 470 K, the stoichiometry of the film corresponds to the Yb_5Si_3 and YbSi silicide phases, whereas their work function is 2.84 and 2.64 eV, respectively. When getting to the temperature of 600 K, the $YbSi_{2-x}$ disilicide phase is formed in the surface of the silicon crystal. The surface of this film is formed by the silicon atoms and the work function is 4.0 eV. In all the listed silicide phases, ytterbium has the fractional valency between the values 2+ and 3+. The film of ytterbium disilicide is preserved on the surface until the temperature is ~ 1000 K. When its values are higher, disilicide is decomposed and the metal atoms are removed from the substrate surface into vacuum. At last, at 1300 K the silicon structure (7×7) is rebuilt. The optimal temperature for formation of the $YbSi_{2-x}$ film on the Si(111) surface is 800 K. After heating at this temperature, the film has the well-ordered structure (1×1).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] F.P. Netzer. J. Phys.: Condens. Matter., **7**, 991 (1995).

[2] S. Zhu, J. Chen, M.-F. Li, S.J. Lee, J. Singh, C.X. Zhu, A. Du, C.H. Tung, A. Chin, D.L. Kwong. IEEE Electron Device Lett., **25** (8), 565 (2004). DOI: 10.1109/LED.2004.831582

[3] D. Connelly, C. Faulkner, P.A. Clifton, D.E. Grupp. Appl. Phys. Lett., **88**, 012105 (2006). DOI: 10.1063/1.2159096

[4] K.-H. Shen, S.-H. Chen, W.-T. Liu, B.-H. Wu, L.-J. Chen. Mater. Design, **114**, 220. DOI: 10.1016/j.matdes.2016.11.084

[5] J. Cho, H.S. Radhakrishnan, M.R. Payo, M. Debucquoy, A. van der Heide, I. Gordon, J. Szlufcik, J. Poortmans. ACS Appl. Energy Mater., **3** (4), 3826 (2020). DOI: 10.1021/acsaem.0c00256

[6] J.H.G. Owen, K. Miki, D.R. Bowler. J. Mater. Sci., **41**, 4568 (2006). DOI: 10.1007/s10853-006-0246-x

[7] S. Appelfeller, S. Kuls, M. Dähne. Surf. Sci., **641**, 180 (2015). DOI: 10.1016/j.susc.2015.07.001

[8] G. Rossi. Surf. Sci. Rep., **7** (1–2), 1 (1987).

[9] K.S. Chi, W.C. Tsai, L.J. Chen. J. Appl. Phys., **93**, 153 (2003). DOI: 10.1063/1.1525064

[10] T.V. Krachino, M.V. Kuz'min, M.V. Loginov, M.A. Mittsev. FTT, **39** (2), 256 (1997). (in Russian)

[11] M.V. Kuz'min, M.A. Mittsev, FTT, **65** (6), 1082 (2023). (in Russian) DOI: 10.21883/FTT.2023.06.55670.48

[12] D. Woodruff, T. Delchar. *Sovremennye metody issledovaniya poverkhnosti* (Mir, M., 1989) (in Russian)

[13] M. Balkanski (ed.). *Optical properties of semiconductors. V. 2. Handbook on semiconductors* (Elsevier, Amsterdam, 1994)

[14] M.V. Kuz'min, M.A. Mittsev, ZhTF, **90** (8), 1359 (2020). (in Russian) DOI: 10.21883/JTF.2020.08.49548.81-20

[15] J.C. Riviere, F.P. Netzer, G. Rosina, G. Strasser, J.A.D. Matthew. J. Electron Spectr. Rel. Phen., **36**, 331 (1985).

[16] A. Palenzona, P. Manfrinetti, S. Brutti, G. Balducci. J. Alloys Compounds, **348**, 100 (2003).

[17] E.M. Savitskii, V.F. Terekhova.*Metallovedenie redkozemel'nykh metallov* (Nauka, M., 1975) (in Russian)

[18] M.V. Kuz'min, M.A. Mittsev, FTT, **53** (3), 569 (2011). (in Russian)

[19] D.I. Khomskii. UFN, **129** (3), 443 (1979). (in Russian)

Translated by M.Shevelev