International Journal of Engineering and Advanced Technology (IJEAT)
ISSN: 2249 – 8958, Volume-9 Issue-1, October 2019

Effect of Annealing on the Crystal Structure of COSI$_2$/SI(100) Formed By MBE, SSE and RE Epitaxy Techniques

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Abstract---The paper reports a number of new original experimental results related to the study of the effect of annealing on the crystal structure of the surface of silicon doped with cobalt ions. The results of studies of the CoSi$_2$/Si(100) epitaxial structures formed by molecular beam epitaxy (MBE), solid state epitaxy (SSE), and other techniques are presented. Relations between morphology, stoichiometry, and growth conditions of CoSi$_2$/ Si structures were established. The ratio of the intensities of the Auger signals of cobalt and silicon in the CoSi$_2$ film, as well as silicon in CoSi$_2$ and the silicon substrate was determined by the Auger profile of the sample. The authors determined that under certain conditions of heat treatment of the radiation on the surface of a single crystal, the so-called epitaxial silicides are formed which can play the role of conductive layers or metal coated. The structural state diagrams of CoSi$_2$ / Si (100) thin-film systems formed by the MBE, SSE and other methods were compiled..

Keywords: impurities, profiles, influences, thermal annealing, depth, concentration distribution, radiation dose, activation temperatures, ion implantation, structure, silicide, film.

I. INTRODUCTION

In the past couple of a couple of years, non-inexhaustible The problem of the formation of thin epitaxial metal layers on semiconductors with high structural perfection is currently attracting close attention of researchers. There is a very limited set of "*metal-semiconductor"* combinations that could be used for epitaxial growth of a metal film on a semiconductor substrate.

The study of CoSi$_2$/ Si epitaxial structures is of great importance for further study of electrophysical processes occurring at the metal-semiconductor interface, since these structures are the only ones for which theoretical expressions for the height of the Schottky barrier can be obtained directly from calculations based on the arrangement of atoms in real structure [1,3].

The issue of practical application of epitaxial silicides in microelectronics is primarily associated with the creation of a silicon high-power transistor with a permeable base, the formation of Schottky barriers, ohmic contacts, and IC interconnects. The possibility of creating a photodiode with a Schottky barrier based on the CoSi$_2$/Si structure seems very attractive.

The relevance of the work is motivated by the existence of a number of unresolved issues both from the point of view of epitaxial growth technology and from the point of view of knowledge of physics of growth of thin films and the effect of structure on the physical properties of silicide films, the use of which opens up new possibilities for developingdevices with unique technical characteristics.

Further development of microelectronics requires new extraordinary materials, that would ensure the increase in the degree of integration of microcircuits and the development of functional electronics. In this regard, silicides appear to be very promising materials.

II. MATERIALS AND METHODS

This paper presents a number of new original experimental results related to the study of the properties of the effect of annealing on the crystal structure of the surface of silicon doped with cobalt ions. The choice of cobalt as a compensating impurity is due to the fact that in a wide temperature range, the state of the impurity atoms in the silicon lattice is quite stable (100-450^{0}C) and, accordingly, the parameters of silicon doped with it are also stable. The technology of alloying silicon with cobalt with specified parameters was developed by authors practically at the industrial level and does not require additional operations (mechanical, chemical, etc.) after diffusion alloying. It is possible to alloy cobalt onto silicon plates of a sufficiently large area, more than 100 cm^2, which is very important for industrial and serial production of temperature converters with reproducible parameters.

III. DISCUSSION

Experimental studies of the concentration profiles of the distribution of cobalt atoms implanted in silicon with an energy of E_0 = 40 keV were carried out with a dose variation in the range of $10^{15} \div 10^{17}$ion/cm^2. Boron doped silicon samples with a specific resistance of ρ = 10 Ohm$\cdot$cm were used as the starting material. The studies were carried out using the methods of secondary ion mass spectrometry, fast electron diffraction by reflection, Rutherford backscattering and Auger electron microscopy.

Revised Manuscript Received on 14 September, 2019.

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The authors used monocrystalline silicon ingots of *n* and *p* type conductivity doped with boron or phosphorus, respectively, with a concentration of $10^{13}$to 10^{18}cm^{-3}, grown by the Czochralski method and crucible-free zone melting. As impurities, elements of the transition group of cobalt were selected. The choice of these impurities was dictated by the fact that, on the one hand, their behavior and properties of silicon doped with these impurities remains to be poorly investigated, and on the other hand, the possibilities of revealing new features associated with the presence of an unfilled 3d-shell in these impurities. The authors used the technique of ion implantation. The implantation of cobalt ions into silicon was carried out on an ILU-3 device at an ion energy of 40 keV along the (100) crystallographic axis. The distribution profile of cobalt in silicon was measured on a LAS-2200 secondary-ion mass spectrometry unit of Riber as well as on the unit described in [2]. The resistivity of the samples was measured by four probe methods.

Figure 1 shows the analytical chamber. The unit includes three growth chambers (1, 2 and 3). In chamber 1, epitaxial growth of silicon, cobalt silicide $CoSi_2$, and calcium fluoride CaF_2 was carried out. Another chamber was equipped with three sources of molecular beams: two electron-beam evaporators 2 and 3, serving as sources of silicon and cobalt, respectively, and an effusive source for the deposition of CaF_2. 4. Sample 5, mounted on a molybdenum holder, was placed inside the chamber on the manipulator 6. The manipulator was equipped with a heater 7 and a thermocouple 8, which made it possible to control the temperature of the sample in the temperature range from room temperature to 1000°C with an accuracy of ± 0.5°C. To ensure uniform heating of the sample and uniform deposition of evaporated materials, rotation of the holder with the sample was provided using an electric motor.

The growth chamber was equipped with a fast electron diffraction meter for reflection, which made it possible to analyze the structure of the crystal surface directly during growth. The diffractometer included an electron gun 9 and a luminescent screen 10.

A quadrupole gas analyzer 11 was used to control the composition of the residual gas atmosphere. In the analytical chamber 3, the grown epitaxial structures were studied by Auger electron spectroscopy and secondary ion mass spectrometry. The vacuum in the system was maintained at 5×10^{-9}bar.

The results of a study of the $CoSi_2$ / Si (100) epitaxial structures formed by MBE, SSE techniques are presented. Cobalt silicide layers were grown on substrates of the Phosphor doped silicon-4.5, Boron-doped silicon-7.5, and Boron-doped silicon -12 type. The films were grown in an ultrahigh-vacuum MBE installation. Before epitaxial growth, the surface of the substrates was subjected to chemical washing and special cleaning in vacuum. A detailed description of the MBE installation and cleaning methods is contained in [2]. The thickness of the deposited cobalt in all cases was 100 Å, and a $CoSi_2$ film with a thickness of about 380 Å was formed. The processes of one-stage and two-stage growth were investigated. With two-stage growth, the film increased in two stages with different growth modes.

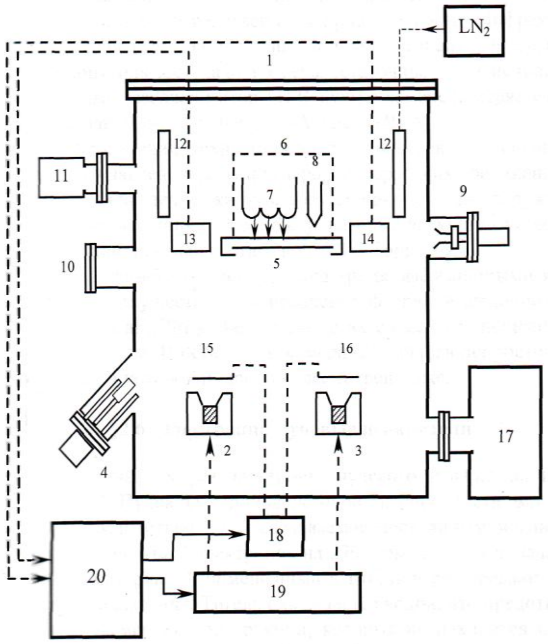

Fig. 1. Analytical growth chamber: 1, 2, 3 — electron beam evaporators; 4-effusion source; 5-sample; 6-manupulator; 7-heater; 8-thermocouple "9-electron gun of a fast electron diffractometer; 10-luminescent screen; 11-quadrupole gas analyzer; 12-cryopanel; 13.14-quartz deposition rate sensors; 15.16-flaps; 17-ion pump; 18-control dampers with thermal actuator; 19-power supplies of electron beam evaporators, 20-computers

IV. RESULT

An analysis of films grown by various methods shows that the morphology and stoichiometry of the films critically depend on the growth conditions. From the point of view of the morphology of $CoSi_2$ / Si films, three main types can be distinguished:

1) continuous $CoSi_2$ films;
2) films with microscopic holes;
3) islet films.

According to the difference in the stoichiometry of $CoSi_2$, two phases are distinguished:

1) $CoSi_2$enriched in silicon ($CoSi_2$-Si);
2) $CoSi_2$ enriched in cobalt ($CoSi_2$-Co).

Establishing a relationship between morphology, stoichiometry and growth conditions of CoSi2 / Si structures is of great importance in the process of developing devices based on epitaxial layers. In most cases, the task is to obtain the most homogeneous layers, however, in a number of applications it is of great interest to form films with submicron-sized holes with controlled morphological characteristics. In [4-7], a technique is proposed for manufacturing a transistor with a permeable base, in which the role of holes in the metal base is played by natural submicron holes in the $CoSi_2$ film. An expression is proposed that relates the current transfer coefficient of the transistor to the coverage coefficient θ in the $CoSi_2$/Si system:

$$\alpha=\frac{\xi}{\gamma+\xi}, \qquad (1)$$

where

$$\gamma=\frac{1-\theta}{\theta}, \qquad (2)$$

$$\varepsilon=\kappa T/e\Delta_0\left[\exp\left(e\Delta_0/kT\right)-1\right] \qquad (3)$$

Here Δ_0 - change in the Schottky barrier in the center of the hole (Δ_0 = $f(x)$; x – average hole diameter). Thus, by changing the growth conditions of the $CoSi_2$ film, it is possible to control the values of x and θ, and therefore, control the current transfer coefficient. The stoichiometry of $CoSi_2$ films affects the electrophysical properties, in particular, the height of the Schottky barrier and resistivity.

The surface structure during growth was controlled by the technique of Reflection high-energy electron diffraction (RHEED). The grown samples were analyzed by the Auger - electron spectroscopy (AES). The surface resistance R_s was measured by the 4-probe method. The intensity ratios of the Auger signals of cobalt and silicon in the $CoSi_2$ film, as well as silicon in $CoSi_2$ and the silicon substrate, were determined from the Auger profile of the sample. Auger profiles of the samples are shown in Fig. 2., Silicide growth modes and analysis results are shown in Table 1.

Based on Auger spectroscopy data, an attempt was made to estimate the coating coefficient of the substrate with a cobalt silicide film. An expression is obtained that relates the intensities of the Auger signals of silicon and cobalt:

$\theta=3(1-I_{Si}/I_{Sisub})I_{Sisub}/I_{Co}$ (4)

whereI_{Co} – cobalt Auger signal intensity in $CoSi_2$ (765 eV); I_{Si} - silicon Auger signal intensity in $CoSi_2$ (91 eV); I_{Sisub} - silicon Auger signal intensity in the substrate (91 eV).

Intensity Ratio Values I_{Co} /I_{Si}иI_{Si} /I_{Sisub}, as well as the value of θ calculated by the formula (4), are given in table 1.1.

Growth modes, results of an AES analysis of stoichiometry and morphology of surface resistance of $CoSi_2$ / Si (100) films Table 1.1

№	Substrate cond. type	h_{CoSi_2}, Å	Epitaxy	T_s, ^{0}C	T_{anneal}, min	Deposition rate Å/c	I_{co}/I_{Si}	I_{Si}/I_{Si} sub	θ	R_s, μOhm·cm
1	Boron doped silicon-7,5	105 105	RE	633 660	—	2 2	0,52	0,93	0,43	18
2	Boron doped silicon -7,5	210	SSE	575	5	2	0,47	0,88	0,87	25
3	Phosphor doped silicon-4,5	210	SSE	610	7	2	0,54	0,87	0,83	25
4	Phosphor doped silicon -4,5	105 105	RE RE	580 562	—	2 2	0,89	0,78	0,95	8
5	Boron doped silicon -12	210	SSE	630	7	2	0,65	0,94	0,29	23

Designations: h_{CoSi_2} *- the thickness of the cobalt layer deposited on the substrate;* T_s *— substrate temperature during epitaxy;* $t_{annealing}$ *is the structure annealing time during SSE*

It should be noted that formula (4) was obtained on the basis of very rough approximations, in particular, when the stoichiometry is changed, the bulk and surface densities of atoms are not

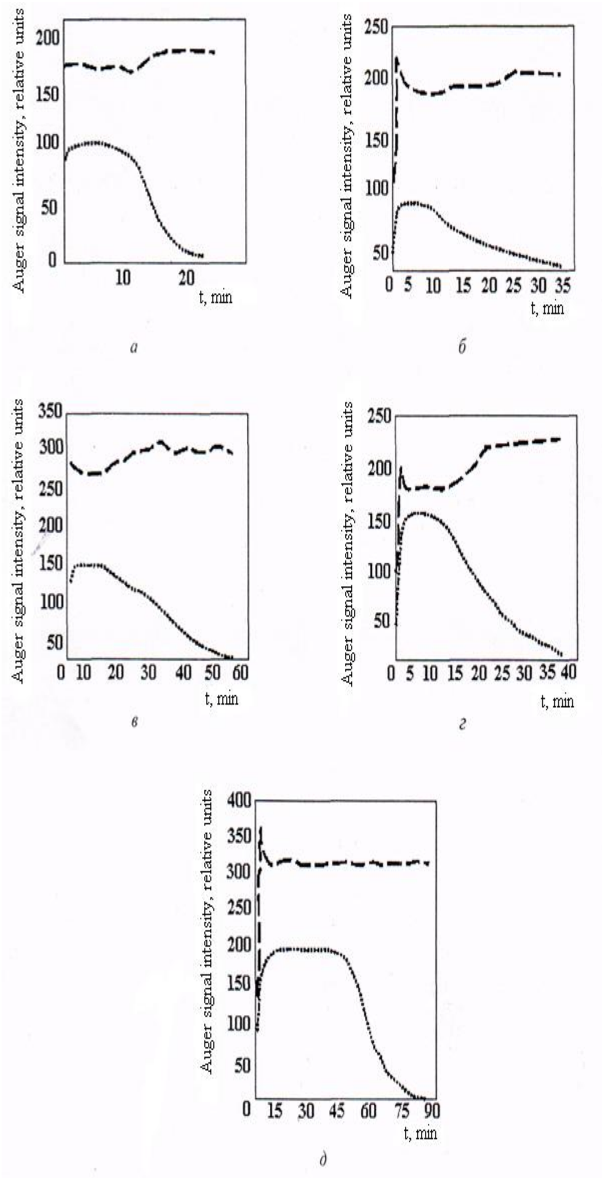

Fig. 2. Growth mode and Auger profiles of $CoSi_2$/Sisamples (sample numbers 1-5 in the table correspond to Auger profiles in Fig. 2.)

breached, that is, when stoichiometry is breached, atoms of the same sort are replaced by others at the nodes of the crystal lattice, the possibility of atoms in the interstices not taken into account. So, in the case of samples *а*and*∂*(4), the formula gives clearly underestimated values of the coverage coefficient.

On the other hand, the lower value of sample *∂* is confirmed by the RHEED data. On the diffraction pattern, along with reflections from the $CoSi_2$ single crystal surface, reflections corresponding to the reconstructed Si(100)2×1 surface were observed, which indicates a significant area of the silicon substrate not covered by the silicide film. Thus, formula (4) allows us to qualitatively analyze the coverage coefficients obtained under different growth conditions.Auger profiles (Fig. 2.) indicate the formation under certain growth conditions of a thin layer of pure silicon on the surface of cobalt silicide. This effect can be caused either by diffusion of cobalt atoms in the direction from the surface to the depth of the sample, or by diffusion of silicon atoms from the substrate to the surface. The first mechanism seems more likely. In any case, the formation of a silicon layer on the surface of the silicide is potentially advantageous, since the free surface energy of Si is less than that of $CoSi_2$. The formation of a pure silicon layer on $CoSi_2$ can be a useful effect in the case of manufacturing a transistor with a metal base, where it is necessary to grow an epitaxial silicon layer on top of the Co Si_2 / Si structure. It was found that in this case, the presence of a thin silicon buffer layer on the $CoSi_2$ surface improves the crystal perfection of the epitaxial silicon film. As can be seen from the profiles in Fig. 2, a layer of surface silicon is formed only under certain growth conditions. It becomes clear that there is a possibility to manage the process.

Measurements of surface resistance showed that the resistance of the $CoSi_2$ films grown at T> 600°C (sample 4) leads to a three-fold decrease in resistance. AES results indicate that under these conditions, $CoSi_2$ enriched in cobalt — $CoSi_2$-Co — is formed. The predominant formation of $CoSi_2$-Co at lower reaction temperatures was also indicated in [8–10]. The abnormally low value of the specific resistance of $CoSi_2$ (sample 4) indicates that the electrical properties of the $CoSi_2$-Co phase are significantly different from the properties of CoSi2 and $CoSi_2$-S_2.

The classical state diagrams of the Co-Si system are considered in the Hansen handbook. The structural state diagram of $CoSi_2$ / Si (100) thin-film systems formed by the MBE, SSE and RE methods is shown in Fig. 3. and 4.

The structure was identified according to the RHEED data. According to these diagrams, CoSi2, CoSi intermetallic compounds are formed at temperatures above 1000^0C. At the same time, the epitaxial growth of CoSi2 / Si films occurs at relatively low temperatures: Ts = $400 \div 600^0$C.

The discrepancy between the $CoSi_2$/Si epitaxy results and the classical phase diagrams is explained by the following reasons:

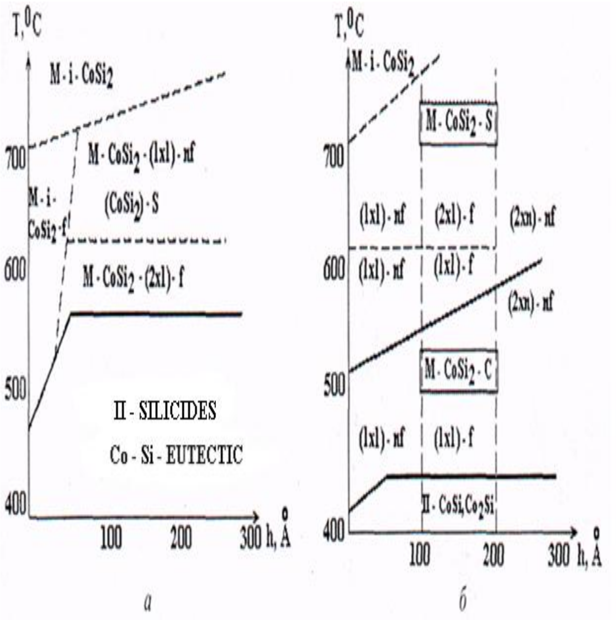

Fig.3. Diagrams of structure MBE (a) and SSE (б) of $CoSi_2$/Si (100)

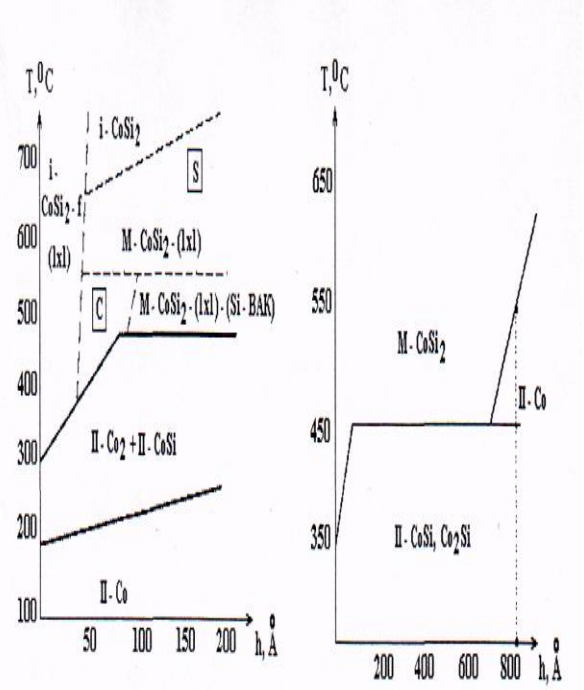

Fig. 4. Diagrams of structure of REЭ-film ofCoSi$_2$/Si (100)

1) the small thickness of Co and CoSi$_2$ films during epitaxy; 2) very clean growth conditions; formation of a clean Si surface, UHV processes; there are no intermediate layers on the reacting surfaces, which reduces the activation energy of the process of silicide formation; 3) the single-crystal nature of the silicon substrate. The results of the studies indicate a strong dependence of the morphological and electrophysical properties of the CoSi$_2$/Si structure on growth conditions. Understanding the patterns of cobalt silicide formation allows us to optimize manufacturing processes for the production of specific instrument structures.

For targeted modification of the properties of ion-doped materials, in many cases the after-implantation annealing is required. As is known, even at low radiation doses, the concentration of electrically active metals in Si is tens of times lower than the concentration of the doped impurity. The after-implantation annealing can contribute to an increase in the concentration of electroactive atoms. Such annealing is especially necessary for samples implanted with high-dose ions. Therefore, at high radiation doses, the surface region is completely amorphized and homogeneous metal compounds are not formed.

The results of investigations showed that upon heating of samples doped with $D \le 10^{15}$/ cm^2 at $T \ge 650$ °C, a sharp increase in the concentration of active atoms in the surface layer is observed. By choosing the temperature and duration of annealing, it is possible to achieve a uniform distribution of impurities in the crystal volume to a certain depth.

During heat treatment at $T \approx 750$ °C, the concentration of electroactive Co atoms increases to $(2\div5)\bullet10^{15}$cm^{-3}, which is 4–5 times more electroactive cobalt atoms than during diffusion doping. A further increase in temperature negatively affected the concentration of electroactive nickel atoms. Starting from a temperature of 1000 C, it was comparable to the concentration of electroactive atoms that is obtained by diffusion doping. For silicon samples implanted with Co, a noticeable increase in the concentration of electroactive atoms occurred at annealing temperatures above 600°C. With an increase in the annealing temperature (600–1250°C), the concentration of electroactive Co atoms increased monotonically within $10^{15}\div6\cdot10^{17}$ cm^{-3}, while the highest concentration of electroactive atoms achieved by diffusion doping increased. The study of distribution profiles showed that for all impurity atoms, activation occurs in a thin surface layer. Moreover, the distribution of the concentration of electroactive atoms in a thin layer is not Gaussian, but decreases monotonically deep into the crystal.

V. CONCLUSION

The results of studies of the distribution profiles of impurities with deep levels in silicon after various heat treatments showed that by choosing the temperature and duration of annealing for each radiation dose, it is possible to achieve a uniform distribution of impurities in the crystal volume to a certain depth, followed by a relatively sharp decrease in concentration. A comparative analysis of the distribution profiles of impurities showed that such a sharp decrease in concentration cannot be achieved by diffusion alloying due to the formation of various silicides. The concentration of impurities in a uniform section increases in proportion to the radiation dose and at a dose of 10^{17}ion/cm^{2}was 2-3 orders of magnitude higher than the equilibrium concentration of impurities during diffusion doping.

It is proved that under certain conditions of heat treatment and radiation dose, so-called epitaxial silicides form on the crystal structure, which can play the role of conducting layers or metal coatings.

The optimal conditions for the preparation of silicon ion-implanted Co have been determined, allowing to preserve the initial parameters of the samples, both during ion implantation and during heat treatment in the temperature range 300÷1200 ^{0}C. It was established that upon heating of samples doped with a dose of 10^{15}ion/cm^2, the activation is observed at a temperature of 650°C. For example, in the process of heat treatment at T = 750^{0}C, the concentration of electroactive cobalt atoms in Si increases to $(2\div5)\cdot10^{15}$cm^{-3}, which is 4-5 times higher than with diffusion doping. An increase in the annealing temperature above 1200°C led to a sharp decrease in the concentration of electroactive impurities.

It has been revealed that on a rough surface after alloying with ion bombardment at an annealing temperature above 800°C, edged regions characteristic of single crystals are formed.

It was found that structural changes depend on the radiation dose and annealing temperature. For example, for cobalt with an irradiation dose of 10^{17}ion/cm^2, after annealing at a temperature of 950^{0}C, a layer of the form of a single crystal with a large number of defects is formed on the surface. A further increase in temperature to 1100°C leads to the formation of an amorphous layer on the surface.

It was established that under certain growth conditions, a CoSi (100) (2×n) reconstruction occurs on the surface of the CoSi film (the exact nature of the reconstruction has not been established). During MBE growth of CC- (2×n), it occurs at high deposition rates of R_d~2 Å/c and not very high temperatures, T_s>600 ^{0}C. Superstructural rearrangements were not detected in the RE films; Under any growth conditions, a $CoSi_2$(100)-(1×1)surface is formed. TEF layers have SS (2×n) at $h_{CoSi_2} > 200$ Å. In thin films with $h_{CoSi_2} < 100$ Å, SS (2×n) is not observed. In films with a thickness of 105 Å, superstructural rearrangement (2 × n) occurs at T_s>615 ^{0}C. RE films have a single facet at $h_{CoSi_2} \leq 50$ Å; films with a thickness of more than 100Å do not show faceting. In MBE, faceted films are formed at T_S=540÷570 ^{0}C; at T_S>600 ^{0}C, there is no faceting. Faceting disappears during post-growth annealing of MBE structures to T ~ 800 ° C. In TFE films of CoSi2 / Si (100) with $h_{CoSi_2} > 200$ Å, faceting is absent under any growth conditions. It was established by the OES method that there are two surface phases of CoSi2 / Si (100) enriched in cobalt $CoSi_2$-$C_O$and silicon - $CoSi_2$-Si, which are formed at T>600 ^{0}C. *SSE* $CoSi_2$/Si(100) occurs at T_S=450 ^{0}C.

It was shown that the electrical resistivity ρ of thin $CoSi_2$/Si(100) films depends on the formation temperature and post-growth annealing temperature T=500÷650 ^{0}C. In this temperature range, уменьшение decreases due to an improvement in the crystalline perfection of the $CoSi_2$ film, and at T>750 ^{0}C a sharp increase in resistance is observed, which is apparently associated with the formation of an island film.

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