Obtaining nanoscale CoSiO/Si/CoSi₂ systems for increasing the range of light ray absorption energy

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Abstract. The morphology, composition and electronic properties of the CoSiO film obtained on the CoSi₂/Si (111) surface by implantation of O₂⁻ ions in combination with annealing were studied. Parameters of energy zones are determined and information about the density of the state of electrons of the valence zone and conductivity zone is obtained. In particular, it is shown that the band gap width of this film is ~2.4 eV. It was ascertained that the CoSiO/Si/CoSi₂ heterosystem is very promising for creating efficient solar energy devices.

1. Introduction

Nano-dimensional structures and films with different band gap widths based on Si can be used to construct various structures such as metal-dielectric-semiconductor and semiconductor-dielectric-semiconductor, ultra-high frequency transistors and diodes, solar energy modules, etc. In particular, to increase the efficiency of solar cells it is necessary to create structures that intensively absorb light radiation in the energy range from 0.3 - 0.4 eV to 3.5 - 4 eV. The width of the forbidden zone of CoSi₂ is 0.5 - 0.7 eV, silicon - 1.1 eV, silicon oxides ≈ 8.5 eV, and silicon nitride - 4.5 eV. By changing the chemical composition of metal silicides it is possible to reduce the width of the prohibited zone to 0.4 - 0.5 eV. Si films provide high efficiency in the energy range from 1.1 to 2 eV. Therefore, there are problems of creation of nanostructures with the band gap width ~2 - 2.5 eV.

It is shown in [1-6] that conducting solid-phase epitaxy of Co on the Si(100)2x1 oxidized surface contributes to the formation of more advanced epitaxial CoSi₂ films. The mechanism of the ongoing processes is disclosed in [6-8], which found that when applying cobalt atoms on the surface of Si(100)2x1, oxidized in situ, the metal atoms penetrate under the oxide layer at room temperature. The result of this effect is the formation of a three-component interface phase Co - Si - O at the interface between the oxide layer and silicon and the subsequent formation of a layer of Co - Si solid solution under it.

However, up to now there have been no scientific studies aimed at producing Co - Si - O type nanofilms, therefore, their stoichiometric composition, crystal and electronic structure have not been studied.

At present, SiO₂/Si heterostructures with various nanostructures serve as the basis for the development of new types of high-frequency transistors, integrated circuits, optical converters, and solar cells [9-13].

In the works shown earlier [14-21] that low-energy ion implantation makes it possible to obtain nanoscale multi-component layers on the surface of films of metals, semiconductors and dielectrics.
Therefore, this paper attempts to obtain three-component Co - Si - O nanofilms by implanting O$_2^+$ ions into CoSi$_2$/Si(111) films in combination with annealing and investigate their morphology, composition and electronic properties.

2. Method
In Ion bombardment, temperature annealing, as well as the study of the composition and structure of the studied samples was carried out in the same experimental device under ultra-high vacuum (P = 10$^{-7}$ Pa). Monocrystalline films CoSi$_2$/Si(111) with thickness of 10 - 50 nm, obtained by molecular beam epitaxy, were used as objects of investigation. The energy of O$_2^+$ ions varied within $E_0 = 1 - 5$ keV. Implantation was carried out to obtain solid films at a dose of $D \geq D_{sat} \approx 4 \cdot 10^{16}$ cm$^{-2}$. The research was carried out using the following methods: Auger Electron Spectroscopy (AES), ultraviolet photoelectron spectroscopy (UPS), characteristic electron energy losses spectroscopy (CEELS), removal of energy dependencies of secondary electron emission factors, scanning electron microscopy (SEM).

3. Results and Discussions
First, the elemental and chemical composition of the surface of CoSi$_2$ films implanted with O$_2^+$ ions with an energy of $E_0 = 1$ keV at a dose of $6 \cdot 10^{16}$ cm$^{-2}$ was studied by Auger electron spectroscopy. During ion implantation, the surface layers were completely disordered, and Co-Si, Co-O, Co-SiO, Si-O compounds, as well as unbound Co, Si, and O atoms were contained in these layers. Post implantation annealing at $T = 900$ K resulted in to the formation of a three-component polycrystalline film with an approximate composition of CoSiO, consisting of individual crystalline blocks with sizes of 20-50 nm (Figure 1). Between the blocks formed nanopores with sizes of 10–20 nm and a depth of 4–5 nm.

![Figure 1. SEM of CoSiO/CoSi$_2$(100) film surface image (111)](image)

From the concentration profiles of the distribution of O, Si, and Co atoms in the CoSiO/CoSi$_2$ system shown in Figure 2, it can be seen that the concentration of these atoms on the surface differs little from
each other (Si ~ 38 at.%; Co ~ 29 at.% and O ~ 33 at.%) and up to 35-40 Å the practical does not change. This fact confirms that in this case, indeed CoSiO compounds are formed. Starting from d ≈ 40 Å to 60 Å, the Co and Si concentrations noticeably increase, while the O concentration sharply decreases. The rate of change in the concentration of these atoms at d > 60 Å slows down and at d ≈ 75-80 Å, the Si concentration stabilizes at 64-66 at.%, Co - 30-35 at.%, O - 1-2 at.%. At a depth of d ≥ 80 at.%, the concentration of these atoms remains practically unchanged, and the stoichiometric composition of CoSi₂ is restored.

Figure 2. Concentration distribution profiles of Si, Co, O atoms by depth of CoSi₂ film obtained after heating at T = 900 K of CoSi₂ film implanted with О₂⁺ ions with E₀ = 1 keV at D = 6·10¹⁶ cm⁻²

Figure 3. Dependencies R(E₀) and δ(E₀) for CoSiO/CoSi₄(111) film with a thickness of 35 - 40 Å
In Figure 3 shows the initial part of the $R(E_p)$ and $\delta(E_p)$ relationships for CoSiO/CoSi(111) film. $R$ - coefficient of elastic reflected electrons; $\delta$ - coefficient of true secondary electrons; $E_p$ - energy of primary electrons. We can see that these dependencies reveal a number of clearly defined features that arise from the excitation of inter-zone electron transitions and plasma vibrations of the valence electrons. There is a connection between the fine structure, dependence curve $R(E_p)$ and the zone structure of semiconductors and dielectrics.

The initial sharp decrease in growth rate $R$ is due to the transition of electrons from the ceiling of the valence zone $E_V$ to the bottom of the conductive zone $E_C$, i.e.,

$$E_{pR} = E_V - E_C = E_g = 2.4 \text{ eV}$$

The $E_{p\delta}$ value corresponds to the transition of electrons from $E_V$ to vacuum level $E_{VC}$.

$$E_{p\delta} = F = E_V = 5.9 \text{ eV}$$

Consequently, at $E_{p\delta}$ there is a sharp initial growth $\delta$ [14]. The value of the affinity to the electron can be estimated by the formula

$$\chi = E_{p\delta} - E_{pR} = 3.5 \text{ eV}$$

The feature observed on the curve of dependence $\delta(E_p)$ under $E_p = E_g$ is explained by excitation of electrons from impurity levels. At energies $E_p = 8.5$ and $13.6$ eV gentle areas are detected, which is explained by the resonant elastic scattering of slow electrons on plasmons [14]. Indeed, taking into account $\chi$ these energies correspond to plasma oscillation excitation in CoSiO film: $\hbar \omega_s = 12 \text{ eV}$ and $\hbar \omega_v = 17 \text{ eV}$.

![Figure 4. Photoelectronic spectra: 1 - Si(100); 2 - CoSi_{2}/Si(111); 3 - CoSiO/CoSi_{2}(111) nanofilms with thickness of 35 - 40 Å](image)
Figure 4 shows the photo electronic spectra for pure Si(111), CoSi₂/Si (111) and CoSiO films with thickness 35 - 40 Å. We can see that \( E_V \) values for Si, CoSi₂ and CoSiO are 5.1, 4.7 and 5.9 eV, respectively. In the case of pure Si, these features are due to the excitation of electrons from the surface states (SS) and \( M_{23}(3p) \), \( M_{23}+M_{1}(3p+3s) \) of the valence electrons state. In the case of CoSi₂ film with \( \theta \approx 120 \) Å (Figure 4 curve 2) three peaks are detected. Based on the results of [9, 10] the presence of these peaks can be explained by hybridization of \( M_1 \), \( M_2 \) and \( M_3 \) states Si with \( M_4 \) and \( M_5 \) states CoSi₂. The curve structure, i.e., the density of the valence electrons state of CoSiO film differs significantly from that of Si and CoSi₂. In the CoSiO spectrum intensive peaks A, B, C are formed at energies \( E_c = -0.2, -1.3, -3.4 \) eV, respectively. We can assume that peak A is formed by hybridization of \( M_3 \) - silicon state, \( M_5 \) - cobalt state and \( L_3 \) oxygen state, and peak B is formed by hybridization of \( M_2 \) - silicon state, \( M_3 \) cobalt state and \( L_3 \) oxygen state, while peak C is formed by hybridization of \( M_1 \) - silicon state, \( M_4 \) - cobalt state and \( M_2 \) - oxygen state.

We determined the composition and parameters of the energy zones CoSi₂ and CoSiO nanofilm (Table 1) based on the analysis of the AES spectra, dependence curves \( \delta(E_p) \) and \( R(E_p) \) (Figure 3) and photon spectra (Figure 4).

The table shows that the \( E_g \) value for CoSiO is \( \sim 2.4 \) eV. Therefore, the CoSiO/Si/CoSi₂ system may have prospects in the development of solar energy devices.

| Films    | Composition, at.% | \( \chi \), eV | \( E_g \), eV |
|----------|-------------------|---------------|--------------|
| CoSi₂    | Co 34 Si 65 O 1   | 4.0           | 0.5          |
| CoSiO    | Co 29 Si 38 O 33  | 3.5           | 2.4          |

4. Conclusions
1. For the first time, the composition, structure and properties of CoSiO/Si/CoSi₂ nanofilm heterostructures were obtained and studied by implanting \( O^+ \) ions into CoSi₂/Si film;
2. Zone energy parameters CoSi₂ and CoSiO were determined;
3. It is shown that the three-layer structure absorbs light rays in the energy range from 0.6 eV to 3 eV.

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