Effect of Deposition of Submonolayer Cs Coatings on the Density of Electronic States and Energy Band Parameters of CoSi$_2$/Si(111)

B.E. Umirzakov, I.R. Bekpulatov*, I.Kh. Turapov, B.D. Igamov

Tashkent State Technical University, Tashkent 100095, Uzbekistan

(Received 07 February 2022; revised manuscript received 21 April 2022; published online 29 April 2022)

Using the methods of ultraviolet photoelectron spectroscopy, light absorption spectroscopy, and true secondary electrons, the effects of deposition of Cs atoms with a thickness of $\theta \leq 1$ monolayer on the density of electronic states in the valence and conduction bands, energy band parameters, and quantum yield of photoelectrons have been studied for the first time. It has been established that when cesium is deposited on the surface of cobalt disilicide with a thickness of $\theta \leq 1$ monolayer, the value of $E_F$ and the positions of the maxima of the density of states of valence electrons practically do not change, the work function of photoelectrons decreases by a factor of 3 or more. After deposition of Cs on the surface of CoSi$_2$/Si (111) with a thickness of $d = 500$ Å, the yield of true secondary electrons into vacuum increases, and the beginning of the spectrum shifts towards lower energies by ~ 2.4 eV, i.e., the potential barrier (electron affinity $\chi$) decreases by 2.4 eV. The decrease in $\Phi$ is mainly due to the decrease in the width of the conduction band $\chi$. In this work, for the first time, the positions of the maxima of the density of free electron states in the conduction band of CoSi$_2$ are experimentally determined. It is shown that the maxima are located at energies of 0.8 and 1.9 eV below the vacuum level.

Keywords: Electronic properties, Auger electron spectroscopy, Ion implantation, Nanophase, Nanolayer, Silicide, Epitaxy, Heterofilm, Heterosystem, Surface morphology.

DOI: 10.21272/jnep.14(2).02026 PACS numbers: 68.55.Ln, 73.40. – c

1. INTRODUCTION

In recent years, a large number of works have been devoted to the preparation and study of the composition, structure, and properties of thin films of silicides, especially CoSi$_2$ [1-8]. This is mainly due to their wide application in the creation of SBS and MDS structures for microwave transistors and integrated circuits, as well as in the creation of microwaves, radiation detectors, and other optical and electronic devices [9-17]. It is known that the deposition of submonolayer coatings of metal and gas atoms (Cs, Rh, Ba, O, H, etc.) on the surface of metals, semiconductors, and dielectrics leads to a significant change in their composition and physicochemical properties [18-21]. In particular, it was shown [18] that during the deposition of barium atoms with a thickness of $\theta \leq 1$ monolayer on the CdTe surface, the work function decreases and the depth of the exit zone of true secondary and photoelectrons increases. In the case of Si, the deposition of Al, Ga, Pd, and Cr atoms led to the formation of a chemical bond of the Me-Si type and a shift in the band gap [19], while in the case of GaAs, the deposition of thin films of metals and gases (Cs, Ca, Se, O and H) led to the stabilization of the position of the Fermi level, regardless of the type of deposited material. However, until now, such studies for CoSi$_2$ films have practically not been carried out.

2. METHODOLOGY

The experiments were carried out in an ultrahigh vacuum device with a three-grid spherical energy analyzer with a retarding field, which makes it possible to study the state of the film surface using the following methods: Auger electron spectroscopy (AES), ultraviolet photoelectron spectroscopy (UPS), true secondary electron spectroscopy (TSES), and light absorption spectroscopy, as well as to carry out various technological operations: thermal heating, electron bombardment, ion etching of the surface, ion implantation. The pressure of residual gases in the device did not exceed $10^{-7}$ Pa. The implantation of ions into silicon was carried out by us at room temperature of the target.

Molecular beam epitaxy (MBE) of CoSi$_2$/Si(111) film with a thickness $d = 500$ Å was used as the object of study. Before Cs deposition, the samples were cleaned by heating to $T \approx 750$ K for 2-3 h at a vacuum of $10^{-7}$ Pa. Target heating, Cs deposition, and the entire study were carried out in the same ultrahigh vacuum instrument. The surface composition was controlled by AES. For one monolayer, the thickness of Cs layer is taken at which the value of the work function has a minimum.

3. RESULTS AND ITS DISCUSSION

Fig. 1 shows the photoelectron spectra of CoSi$_2$/Si (111) film with submonolayer Cs coatings in the range $\theta = 0.2$-1 monolayer. The photon energy $\hbar \nu$ was 10.8 eV. The abscissa shows the binding energy $E_F$ of electrons, measured relative to the level of the top of the valence band $E_V$. Here, on all curves of the energy distribution of photoelectrons, the same vertical scale is used, chosen in such a way that the area under the curve is proportional to the value of the photoelectron quantum yield Y. It can be seen that all curves have a pronounced fine structure.

* bekpulatov85@rambler.ru
The spectrum of a pure CoSi$_2$ film shows peaks at $E_{\text{ss}} = -0.8$, $-2.1$, and $-4.6$ eV, as well as a feature at $E_{\text{ss}} \approx -0.4$ eV. An analysis of this spectrum and its comparison with the spectra of Si and Co suggests that peak A is formed due to the hybridization of the $M_{53}$ state of silicon and the $N_{1}$ state of cobalt, and peak B is due to the hybridization of the $M_{53}$ state of silicon and the $M_{1}$ state of cobalt. The appearance of a feature at $E_{\text{ss}} \approx -0.4$ eV is explained by the presence of a surface state (SS). With Cs deposition, with increasing $\theta$ in the range $\theta = 0.2\text{–}1$ monolayer, the intensity of these peaks increases without a noticeable change in their energy positions, and the feature at $E_{\text{ss}} = -0.4$ eV disappears.

In this case, the width of the spectrum $\Delta E$ and the area under the energy distribution of photoelectrons increase, i.e., the photoelectronic work function $\Phi$ decreases, and the quantum yield of photoelectrons $Y$ increases. At $\theta > 0.6$, an intense peak D appears on the energy distribution of the photoelectron monolayer at $E_{\text{ss}} = -7.2$ eV, apparently associated with the excitation of electrons from the $M_{1}$ state of silicon. The greatest change in the spectrum is observed at $\theta \approx 1$ monolayer. A further increase in $\theta$ leads to some increase in the work function (energy distribution of photoelectrons taken at $\theta > 1$ monolayer is not given here). The value of $E_{\text{ss}}$ was determined using the method of light absorption spectroscopy.

Here $I_{\text{Si}}$ and $I_{\text{CoSi}}$ are the intensities of light transmitted through Si(111) without and with CoSi$_2$ film, respectively. Fig. 2 shows that the $E_{\text{g}}$ of pure Si is 1.1 eV, while that of CoSi$_2$ is 0.6 eV. Upon deposition of Cs with a thickness of 1 monolayer, the intensity of the transmitted light slightly decreases in the entire investigated region $h\nu$, while the value of $E_{\text{g}}$ practically does not change.

Table 1 – Band parameters and $Y$ values for CoSi$_2$/Si(111) with Cs submonolayer coatings

<table>
<thead>
<tr>
<th>$\theta_{\text{Cs}}$ in monolayers</th>
<th>Zone parameters, eV</th>
<th>$Y$ (at $h\nu = 10.8$ eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{\text{vs}}$</td>
<td>$E_{\text{g}}$</td>
</tr>
<tr>
<td>0</td>
<td>4.9</td>
<td>0.6</td>
</tr>
<tr>
<td>0.2</td>
<td>3.6</td>
<td>0.6</td>
</tr>
<tr>
<td>0.6</td>
<td>2.5</td>
<td>0.6</td>
</tr>
<tr>
<td>1</td>
<td>1.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>


**Fig. 3** – TSE spectra of CoSi$_2$ and CoSi$_2$ films coated with Cs with a thickness of $\theta = 0.6$ monolayer, measured at $E_p = 5$ eV

Experimentally, this can be done by recording the energy spectra of TSE $N(E_2)$ at low energies of primary electrons $E_p$ of the material, reducing the work function of its surface in a controlled way.

Fig. 3 shows the TSE spectra $N(E_2)$ taken at $E_p = 5$ eV for pure CoSi$_2$ and CoSi$_2$ with a submonolayer ($\theta = 0.6$) Cs film. $E_2$ is the energy of secondary electrons. Zero on the $E_2$ axis corresponds to the vacuum level of the CoSi$_2$ film.

### 4. CONCLUSIONS

It is shown that when Cs is deposited on a CoSi$_2$ surface with a thickness of $\theta \leq 1$ monolayer, the value of $E_p$ and the position of the maxima of the density of states of valence electrons practically do not change, the work function of photoelectrons decreases to 3 eV, and the quantum yield of photoelectrons increases by a factor of 3 or more. At $\theta \geq 0.6$, a monolayer appears in the spectrum with a new maximum at $E_b = -7.2$ eV, which is characteristic of silicon.

The positions of the density maxima of free electron states in the conduction band of CoSi$_2$ are experimentally determined for the first time. These maxima are located at energies of 0.8 and 1.9 eV below the vacuum level.

### REFERENCES

ронах зменшується на 2,4 еВ. Зменшення Е відбувається переважно за рахунок зменшення ширини зони провідності χ. У роботі вперше експериментально визначені положення максимумів густини ста- нів вільних електронів у зоні провідності CoSi{sub}2. Показано, що максимуми розташовані при енергіях 0,8 та 1,9 еВ нижче рівня вакууму.

Ключові слова: Електронні властивості, Оже-електронна спектроскопія, Іонна імплантація, Наношар, Силіцид, Гетеросистема.