JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **14** No 2, 02026(4pp) (2022)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **14** № 2, 02026(4cc) (2022)

Effect of Deposition of Submonolayer Cs Coatings on the Density of Electronic States and Energy Band Parameters of CoSi₂/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_g and the positions 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. 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 χ) decreases by 2.4 eV. The decrease in Φ is mainly due to the decrease in the width of the conduction band χ. 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 SDS 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, Rb, 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 $T \approx 950$ 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 $h\nu$ was 10.8 eV. The abscissa shows the binding energy E_{sv} 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

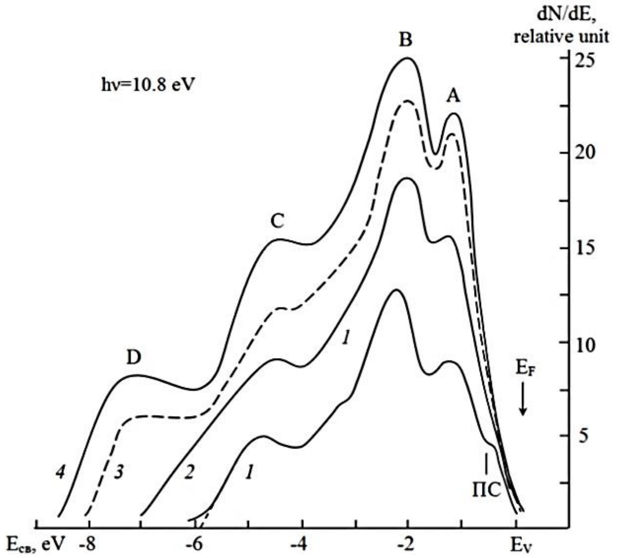

Fig. 1 – Normalized energy distribution of photoelectrons for $CoSi_2/Si$ film with Cs coatings with a thickness (in monolayers): 1 – 0; 2 – 0.2; 3 – 0.6; 4 – 1.0

The spectrum of a pure $CoSi_2$ film shows peaks at $E_{sv} = -0.8$, -2.1, and -4.6 eV, as well as a feature at $E_{sv} \approx -0.4$ 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_{23} state of silicon and the N_1 state of cobalt, and peak B is due to the hybridization of the M_{23} state of silicon and the M_5 state of cobalt, while peak C is formed due to the hybridization of the M_1 state of silicon and the M_4 state of cobalt. The appearance of a feature at $E_{sv} \approx -0.4$ eV is explained by the presence of a surface state (SS). With Cs deposition, with increasing θ in the range $\theta = 0.2$-1 monolayer, the intensity of these peaks increases without a noticeable change in their energy positions, and the feature at $E_{sv} = -0.4$ eV disappears.

In this case, the width of the spectrum ΔE and the area under the energy distribution of photoelectrons increase, i.e., the photoelectronic work function Φ decreases, and the quantum yield of photoelectrons Y increases. At $\theta \geq 0.6$, an intense peak D appears on the energy distribution of the photoelectron monolayer at $E_{sv} = -7.2$ 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 θ 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_g was determined using the method of light absorption spectroscopy.

Fig. 2 shows the light absorption spectra (curves of I_{CoSi2}/I_{Si} versus $h\nu$) for Si (111), $CoSi_2/Si$, and $CoSi_2/Si$ with a Cs monolayer coating. Extrapolation of the right side of the curve I_{CoSi2}/I_{Si} to the $h\nu$ axis (Fig. 2) gives the E_g value of the sample under study.

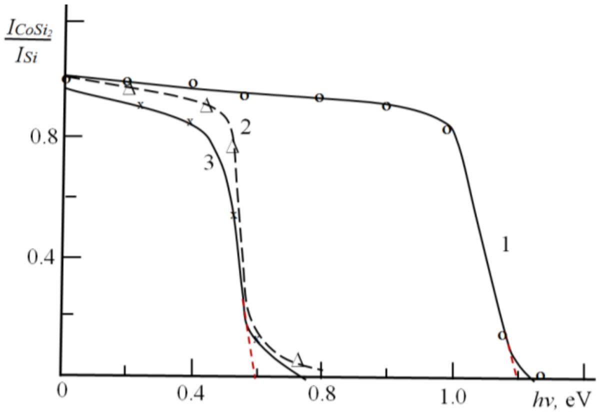

Fig. 2 – Light absorption spectra: 1 – pure Si(111); 2 – $CoSi_2/Si(111)$ films; 3 – $CoSi_2$ with Cs film 1 monolayer thick

Here I_{Si} and I_{CoSi2} are the intensities of light transmitted through Si(111) without and with $CoSi_2$ film, respectively. Fig. 2 shows that the E_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_g practically does not change.

Based on the data of Fig. 1 and Fig. 2, we determined the main parameters of the energy bands of the $Cs/CoSi_2$ system (see Table 1). Table 1 also shows the values of Y. Here, the value of Φ was determined by the formula $E_v = \Phi = h\nu - \Delta E$, and the value of electron affinity was determined by the formula $\chi = E_v - E_g$. The value of E_v relative to the vacuum level is equal to the photoelectron work function.

It can be seen from the table that the decrease in Φ of the $CoSi_2$ film during the deposition of Cs mainly occurs due to a decrease in the electron affinity χ.

Thus, the spectra of photoelectrons obtained at $h\nu \approx 10$-15 eV reflect well the density of states of valence electrons of the surface layers of the samples under study. However, until now there are no direct methods for estimating the density of electronic states in the conduction band. At the same time, obtaining information about the position of the maxima of the density of electronic states in the conduction band is of great scientific and practical importance.

Table 1 – Band parameters and Y values for $CoSi_2/Si(111)$ with Cs submonolayer coatings

θ_{Cs} in monolayers	Zone parameters, eV			Y (at $h\nu$ = 10.8 eV)
	E_v	E_g	χ	
0	4.9	0.6	4.4	$4 \cdot 10^{-4}$
0.2	3.6	0.6	3.1	–
0.6	2.5	0.6	2	$9 \cdot 10^{-4}$
1	1.9	0.6	1.4	$1.1 \cdot 10^{-3}$

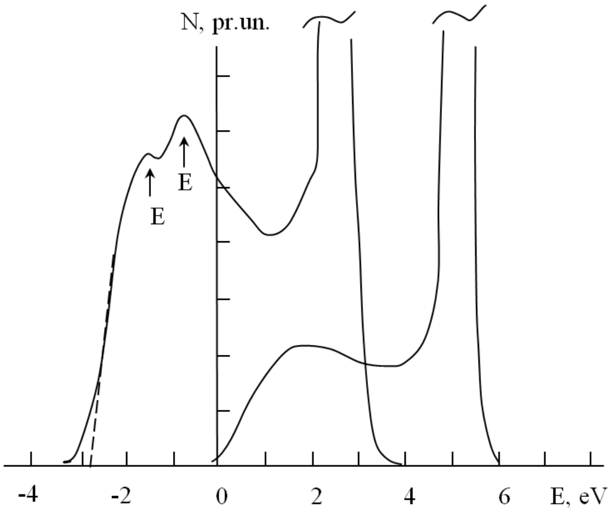

Fig. 3 – TSE spectra of $CoSi_2$ and $CoSi_2$ films coated with Cs with a thickness of $\theta \approx 0.6$ monolayer, measured at $E_p \approx 5$ eV

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 ($\theta \approx 0.6$) 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_g 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

1. A.A. Alekseev, D.A. Olyanich, T.V. Utas, V.G. Kotlyar, A.V. Zotov, A.A. Saranin, *JTF* **85** No 10, 94 (2015) [In Russian].
2. K.J. Kim, T.P. Kang, K.W. Kim, I.J. Shin, B. Kim, *Appl. Surf. Sci.* **161**, 268 (2000).
3. U. Starke, J. Schardt, W. Weib, G. Rangelav, T.H. Fauster, K. Heinz, *Surf. Rev. Lett.* **5**, 139 (1998).
4. M.V. Gomoyunova, I.I. Pronin, N.R. Gall, S.L. Molodtsov, D.V. Vyalykh, *Phys. Solid State* **45**, 1596 (2003).
5. J.P. Colinge, *Mater. Res. Soc. Proc.* 35, 653 (1985).
6. V.I. Rudakov, Yu.I. Denisenko, V.V. Naumov, S.G. Simakin, Tech. Phys. Lett. **37**, 112 (2011).
7. B.E. Umirzakov, D.A. Tashmukhamedova, A.K. Tashatov, N.M. Mustafoeva, *J. Tech. Phys.* No 5, 759 (2019).
8. B.E. Umirzakov, D.A. Tashmukhamedova, E.U. Boltaev, A.A. Dzhurakhalov, *Mater. Sci. Eng. B* **101**, 124 (2003).
9. A.S. Rysbaev, J.B. Khujaniyozov, I.R. Bekpulatov, A.M. Rakhimov, O.R. Pardaev, *J. Synch. Investig.* **11** No 2, 474 (2017).
10. A.S. Risbaev, J.B. Khujaniyazov, I.R. Bekpulatov, A.M. Rakhimov, *J. Synch. Investig.* **11** No 5, 994 (2017).
11. A. Seubert, J. Schardt, W. Weiss, U. Starke, K. Heinz, T. Fauster, *Appl. Phys. Lett.* **76**, 727 (2000).
12. W. Weiss, U. Starke, K. Heinz, G. Rangelov, T. Fauster, G. Castro, *Surf. Sci.* **347**, 117 (1996).
13. G. Masini, L. Colace, G. Assanto, *Mater. Sci. Eng. B* **89**, 2 (2002).
14. L. Pavesi, *J. Phys.: Cond. Mat.* **15** No 26, R1169 (2003).
15. A.A. Druzhinin, I.P. Ostrovsky, Yu.N. Khoverko, S.I. Nichkalo, R.N. Koretsky, *Tech. Des. Electron. Equipment* **5**, 19 (2021).
16. T.S. Kamilov, A.S. Rysbaev, V.V. Klechkovskaya, A.S. Orekhov, B.D. Igamov, I.R. Bekpulatov, *Appl. Sol. Eng.* **55** No 6, 380 (2019).
17. Yu.B. Bolkhovityanov, A.S. Deryabin, A.K. Gutakovski, L.V. Sokolov, *J. Crystal Growth.* **483**, 265 (2018).
18. B.E. Umirzakov, D.A. Tashmukhamedova, M.A. Tursunov, Y.S. Ergashov, G.Kh. Allayarova, *J. Tech. Phys.* **89** No 7, 1115 (2019).
19. A. Franciosi, I.N. Weaver, D.G. O'Neill, *J. Vac. Sci. Technol.* **21**, 624 (1982).
20. R.K. Yafarov, *Phys. Technol. Semicond.* **49** No 3, 329 (2015).
21. Yu. Kudryavtsev, R. Asomoza, M. Mansurova, L.A. Perez, V.M. Korol, *J. Tech. Phys.* **83** No 5, 115 (2013).

Вплив осадження субмоношарових покриттів Cs на щільність електронних станів та параметри енергетичної зони $CoSi_2/Si(111)$

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

Tashkent State Technical University, Tashkent 100095, Uzbekistan

За допомогою методів ультрафіолетової фотоелектронної спектроскопії, спектроскопії поглинання світла та вторинних електронів було вперше досліджено вплив осадження атомів Cs товщиною $\theta \leq 1$ моношар на густину електронних станів у валентній зоні та зоні провідності, параметри енергетичної зони та квантовий вихід фотоелектронів. Встановлено, що при осадженні цезію на поверхню дисиліциду кобальту товщиною $\theta \leq 1$ моношар, значення E_g і положення максимумів густини станів валентних електронів практично не змінюються, робота виходу фотоелектронів зменшується до 3 еВ, а квантовий вихід фотоелектронів збільшується в 3 і більше разів. Після осадження Cs на поверхню $CoSi_2/Si(111)$ товщиною $d = 500$ Å вихід вторинних електронів у вакуум збільшується, а початок спектру зміщується в бік менших енергій на ~ 2,4 еВ, тобто потенціальний бар'єр (спорідненість до електронів χ) зменшується на 2,4 еВ. Зменшення Φ відбувається переважно за рахунок зменшення ширини зони провідності χ. У роботі вперше експериментально визначені положення максимумів густини станів вільних електронів у зоні провідності $CoSi_2$. 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.