13.1;13.2;13.3

Influence of preliminary ion bombardment on the formation of Co and $CoSi_2$ nanofilms on Si surface during solid-phase deposition

© I.Kh. Turapov[1], I.R. Bekpulatov[1], A.K. Tashatov[2], B.E. Umirzakov[1]

[1] Tashkent State Technical University, Tashkent, Uzbekistan
[2] Karshi State University, Karshi, Uzbekistan
E-mail: bekpulatov85@rambler.ru

Received October 1, 2021
Revised October 1, 2021
Accepted December 6, 2021

In this work, to obtain ordered nanophases of Co and $CoSi_2$, nuclei are preliminarily created on the Si surface by bombardment with Ar^+ ions with $E_0 = 0.5$ keV and $D = 8 \cdot 10^{13}$ cm^{-2}. It was found that a narrow band gap ($E_g \approx 0.3$ eV) appears in the band structure at the Co layer thickness of less than 3 ML. The metallic properties of the Co film manifest themselves at a thickness of more than 4–5 ML. Heating the Co/Si(111) system at $T = 900$ K leads to the formation of nanophases and $CoSi_2$ nanofilms. The E_g value is 0.8 eV for the $CoSi_2$ nanophases with $\theta \approx 3$ ML and 0.6 eV for the $CoSi_2$ film.

Keywords: nanophase, epitaxy, low-energy bombardment, surface, single crystal, island growth, ion dose, degree of coverage.

DOI: 10.21883/TPL.2022.03.52877.19043

Multilayer systems based on Si and metal silicides are the primary materials for the up–to–date micro—, nano—, and optoelectronics. For instance, the $MeSi_2$/Si nanostructures are promising for creating UHF transistors, ultra large integrated circuit boards, optical resonant cavities, electronic and magnetic memory devices. Therefore, a large number of papers [1–15] are devoted to studying physical–chemical properties of $MeSi_2$/Si nanophases and nanolayers obtained by molecular beam epitaxy, solid–phase epitaxy and ion implantation. Among metal silicides, the most optimal material for creating multilayer systems semiconductor–dielectric–semiconductor and metal–dielectric–semiconductor is $CoSi_2$ due to its metallic properties (resistivity $\sim 20–30\,\mu\Omega \cdot$ cm) and possibility of its epitaxial growth on Si due to the proximity of lattice parameters. In recent years, ion implantation has been widely used to fabricate nanoscale phases and layers of $CoSi_2$ on the Si surface and in the near–surface region [16,17].

Of especial interest is the task of obtaining regularly arranged structures of equal sizes. Paper [18] showed that during the low–energy ($E_0 = 0.5–1$ keV) bombardment of single–crystal CaF_2 with Ar^+ ions at low fluences $D = (5–6) \cdot 10^{13}$ cm^{-2} ions get into separate surface areas. In the process of depositing atoms of different elements, these areas may become nuclei for atom segregation. In the case of bombardment with Ar^+ ions with energy $E_0 = 0.5–1$ keV, the inter–nucleus distance is $\sim 50–60$ nm. The highest–quality nuclei are formed on smooth atomically clean surfaces of materials.

In this study we made attempts to obtain by solid–phase epitaxy nanoscale phases and films of Co and $CoSi_2$/Si(111) with the aid of preliminary bombardment of Si with ions Ar^+, and also to reveal the dependence of the energy band parameters on dimensions of Co and $CoSi_2$ nanophases.

As substrates, well–polished and processed in hydrofluoric acid single–crystal Si(111) samples KEF-4,5 $10 \times 10 \times 1$ mm in size were used. Prior to depositing the films, the silicon samples were cleaned by heating in ultrahigh vacuum ($P = 10^{-7}$ Pa) at $T = 1100$ K for 4–5 h and short–term heating at $T = 1400$ K. This procedure ensured total removal of oxygen from the surface (within the sensitivity limits of Auger electron spectroscopy), and the low–energy electron diffraction pattern demonstrated a surface structure characteristic of Si(111)-7 × 7. To create the nuclei, the properly cleaned Si(111) surface was bombarded with Ar^+ ions with energy $E_0 = 0.5$ keV and fluence $D = 8 \cdot 10^{13}$ cm^{-2}. After that, cobalt atoms were deposited on this surface at room temperature with the rate of ~ 1 ML/min. When the fluence was increased to $2 \cdot 10^{14}$ cm^{-2}, there was observed an increase in the number of additional centers on the silicon surface to $\sim 30\%$.

The Co films were applied on the room–temperature Si surface by heating Co by electron irradiation. The film growth rate was pre–determined by Auger electron spectroscopy jointly with ion etching and appeared to be ~ 2 Å/min. The Co atoms deposition, heating of samples, investigation of their composition and energy band parameters by Auger electron spectroscopy, and measuring the light passing through the sample were performed in ultrahigh vacuum ($P = 10^{-7}$ Pa) using one and the same facility. The surface morphology was studied by scanning electron microscopy (SEM) (Jeol).

Fig. 1 presents intensity I of light passing through the sample versus energy $h\nu$ for Si(111) with Co nanofilms of different thicknesses θ. Here $I = I_{CoSi_2}/I_{Si}$, I_{Si} is the

intensity of light passing through pure Si(111), I_{CoSi_2} is the intensity of light passing through Si(111) with a $CoSi_2$ film. One can see that the $I(h\nu)$ dependence at $\theta = 1$ ML does not differ from that for pure Si(111). A more significant decrease in I is observed only in the $h\nu \approx 0.9-1$ eV range. Apparently, segregation of Co atoms at the nuclei centers does not yet significantly affect the Si optical properties. When $\theta = 3$ ML, intensity I decreases drastically in two $h\nu$ regions: at $h\nu \approx 0.2$ and 0.9 eV. The first decrease is connected with the existence of surface areas covered by Co atoms, the other — with the existence of Si areas free of Co. Extrapolation of the curve left part towards the $h\nu$ axis provides the value of ~ 0.3 eV, i.e., E_g in those regions is ~ 0.3 eV. Using relation

$$Q = 1 - \frac{I_{Co}}{I_{Si}}$$

it is possible to estimate degree Q of the Si surface coverage with Co atoms. In this case, $Q \approx 0.35-0.4$. This approximately agrees with the SEM data (Fig. 2). Taking into account that the distance between the centers of this phase separation is $\sim 50-60$ nm, obtain that their mean surface diameters are $d \simeq 20-25$ nm and approximate nanophase thickness is $\sim 6-8$ ML ($\sim 12-15$ Å). Based on this, we assume that at small thicknesses of the Co nanophase ($\theta \leqslant 3$ ML) quantum−confined effects manifest themselves: in the metal Co phase there arises a narrow band gap characteristic of narrow−bandgap semiconductors. When $\theta \approx 6$ ML, the degree of the Si surface coverage with Co atoms is close to unity and curve $I(h\nu)$ does not exhibit the double drastic decrease in I, i.e., $E_g \approx 0$. When $\theta \approx 8-10$ ML, the surface is fully covered with Co atoms. However, low−intensity light passes through the film with the thickness of up to $\theta \approx 10-12$ ML. Apparently, a very thin Co film is transparent to light. Notice that the Co nanophases and nanofilms were amorphous. The results of Auger electron spectroscopy have shown that no mutual substrate−film diffusion of atoms takes place at room temperature. After heating the Si sample with Co nanophases and films at $T \approx 850-900$ K, nanocrystalline $CoSi_2$ phases and films were formed.

Fig. 3 presents dependences $I(h\nu)$ for Si covered with the $CoSi_2$ films 6 and 10 ML thick (curves *2* and *3*) measured

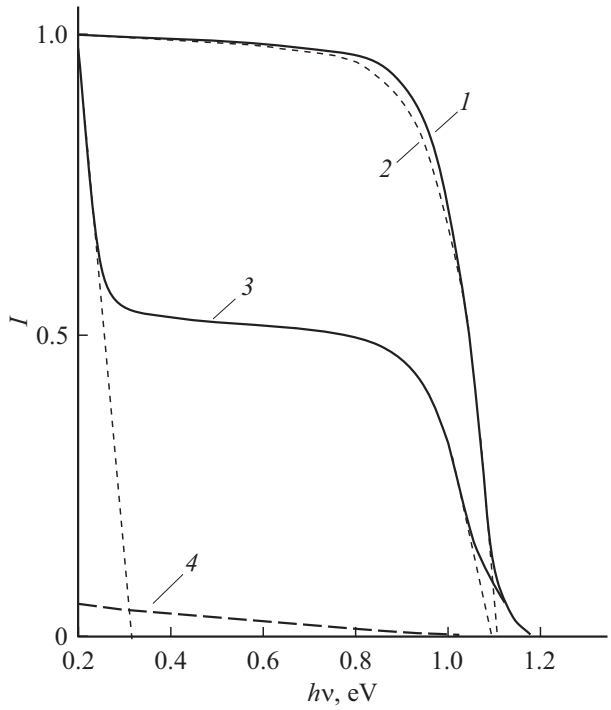

Figure 1. Dependences $I(h\nu)$ for Si(111) with a Co film with the thickness of $\theta = 0$ (pure Si) (*1*) , 1 (*2*), 3 (*3*) and 6 ML (*4*).

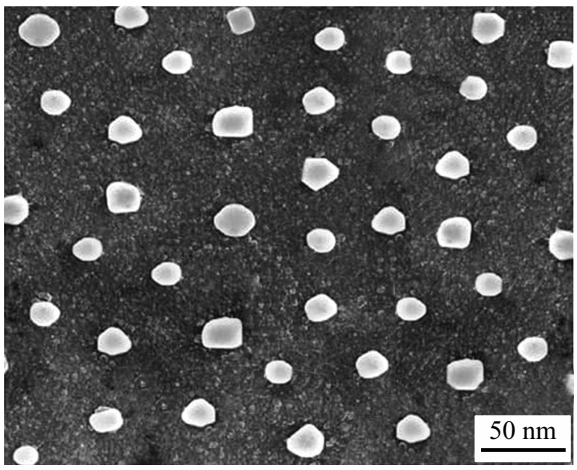

Figure 2. SEM images of the Si(111) surface with the Co film $\theta = 3$ ML thick.

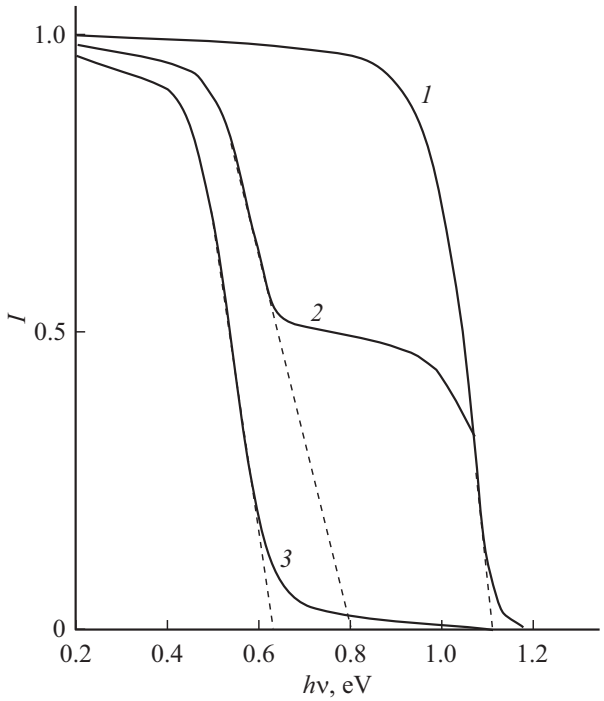

Figure 3. Dependences $I(h\nu)$ for the $CoSi_2$/Si(111) film with the thickness of $\theta = 0$ (pure Si) (*1*) , 6 (*2*) and 10 ML (*3*).

after heating at $T \approx 900$ K for 40 min. Curve *2* shows that, in the case of $CoSi_2$ nanophases with $\theta \approx 6$ ML, the surface coverage degree is 0.5–0.6, $d \simeq 25-30$ nm and $E_g \approx 0.8$ eV. When $\theta_{CoSi_2} \approx 10$ ML, intensity I drops almost to zero in the range $h\nu = 0.45-0.65$ eV. It may be assumed that in this case the Si surface is fully covered by a continuous uniform epitaxial layer of $CoSi_2 \sim 20-25$ ML thick, and E_g of this layer is ~ 0.6 eV which is characteristic of thick epitaxial layers of $CoSi_2$.

Thus, in this work we have obtained by using the Ar^+ ion irradiation regularly arranged centers that serve as nuclei for the growth on the Si surface of Co nanoscale phases and films. Values of E_g for the Co nanofilm and nanophase were determined for the first time. We assume that the nanoscale Co phases with surface diameters of $\leqslant 20-25$ nm possess the properties of narrow–bandgap semiconductors ($E_g \approx 0.3$ eV). The subsequent annealing at $T \approx 900$ K resulted in formation of the nanoepitaxial $CoSi_2$ structure on the Si(111) surface. The studies has shown that, in the case of the $CoSi_2$ nanophases, quantum–confined effects manifest themselves at $d \leqslant 25-30$ nm.

Conflict of interests

The authors declare that they have no conflict of interests.

References

[1] J.S. Pan, R.S. Liu, Z. Zhang, S.W. Poon, W.J. Ong, E.S. Tok, Surf. Sci., **600** (6), 1308 (2006). DOI: 10.1016/j.susc.2006.01.029

[2] S.P. Dash, D. Goll, H.D. Carstanjen, Appl. Phys. Lett., **90** (13), 132109 (2007). DOI: 10.1063/1.2717525

[3] J.S. Tsay, C.S. Yang, Y. Liou, Y.D. Yao, J. Appl. Phys., **85** (8), 4967 (1999). DOI: 10.1063/1.370060

[4] H.W. Chang, J.S. Tsay, Y.C. Hung, F.T. Yuan, W.Y. Chan, W.B. Su, C.S. Chang, Y.D. Yao, J. Appl. Phys., **101** (9), 09D124 (2007). DOI: 10.1063/1.2712532

[5] M.V. Gomoyunova, G.S. Grebenyuk, I.I. Pronin, Tech. Phys., **56** (6), 865 (2011). DOI: 10.1134/S1063784211060077.

[6] K.O. Hara, Ch.T. Trinh, K. Arimoto, J. Yamanaka, K. Nakagawa, Y. Kurokawa, T. Suemasu, N. Usami, in *IEEE 43rd Photovoltaic Specialists Conf.* (PVSC) (IEEE, 2016), p. 25. DOI: 10.1109/PVSC.2016.7750159

[7] T. Nemoto, S. Matsuno, T. Sato, K. Gotoh, M. Mesuda, H. Kuramochi, K. Toko, N. Usami, T. Suemasu, Jpn. J. Appl. Phys., **59** (SF), SFFA06 (2020). DOI: 10.35848/1347-4065/ab69dc

[8] V.L. Dubov, D.V. Fomin, Uspekhi prikl. fiziki, **4** (6), 599 (2016). https://www.advance.orion-ir.ru/UPF-16/6/UPF-4-6-599.pdf (in Russian)

[9] B.E. Umirzakov, D.A. Tashmukhamedova, A. Dzhurakhalov, E.U. Boltaev, Mater. Sci. Eng., **101** (1), 124 (2003). DOI: 10.1016/S0921-5107(02)00677-3

[10] A.S. Rysbaev, A.K. Tashatov, Sh.X. Dzhuraev, Zh.B. Khuzhaniyazov, G. Arzikulov, S.S. Nasriddinov, J. Synch. Investig., **5** (6), 1193 (2011). DOI: 10.1134/S1027451011100193.

[11] A.A. Alekseev, D.A. Olyanich, T.V. Utas, V.G. Kotlyar, A.V. Zotov, A.A. Saranin, Tech. Phys., **60** (10), 1508 (2015). DOI: 10.1134/S1063784215100023.

[12] [Y.S. Ergashov, D.A. Tashmukhamedova, B.E. Umirzakov, J. Synch. Investig., **11** (2), 480 (2017). DOI: 10.1134/S1027451017020252.

[13] Y.S. Ergashov, B.E. Umirzakov, Tech. Phys., **63** (12), 1820 (2018). DOI: 10.1134/S1063784218120058.

[14] V.I. Rudakov, Yu.I. Denisenko, V.V. Naumov, S.G. Simakin, Tech. Phys. Lett., **37** (2), 112 (2011). DOI: 10.1134/S106378501102012X.

[15] V.S. Vavilov, Sov. Phys. Usp., **28** (2), 196 (1985). DOI: 10.1070/PU1985v028n02ABEH003854.

[16] R. Ayache, M. Sidoumou, A. Kolitsch, Int. J. Thin Films Sci. Technol., **4** (3), 211 (2015). DOI: 10.12785/ijtfst/040309

[17] N.N. Gerasimenko, Ros. khim. zhurn., **46** (5), 30 (2002). http://www.chemnet.ru/rus/journals /jvho/2002-5/30.pdf (in Russian)

[18] B.E. Umirzakov, S.B. Donaev, J. Synch. Investig., **11** (4), 746 (2017). DOI: 10.1134/S1027451017040139.