13,18

Electron Diffraction Study of transformation the reconstruction $6\sqrt{3}$ on 4H-SiC(0001) in quasi-free-standing epitaxial graphene

© I.S. Kotousova[1], S.P. Lebedev[1], V.V. Antipov[2], A.A. Lebedev[1,¶]

[1] Ioffe Institute,
St. Petersburg, Russia
[2] Saint Petersburg State Institute of Technology (Technical University),
St. Petersburg, Russia
[¶] E-mail: shura.lebe@mail.ioffe.ru

Received August 11, 2022
Revised August 11, 2022
Accepted August 19, 2022

Through the agency of reflection high-energy electron diffraction (RHEED) we have studied the transformation of the reconstruction $6\sqrt{3}$ grown on substrate 4H-SiC in an Ar medium with a short sublimation annealing time in quasi-free-standing epitaxial graphene due to the use of hydrogen intercalation. It was found that grown reconstruction layer was not uniform. The comparison of the results of the structural study of quasi-free-standing graphene and single-layer graphene on buffer layer has been made.

Keywords: SiC, reconstruction, intercalation, graphene, RHEED.

DOI: 10.21883/PSS.2022.12.54401.458

1. Introduction

An important place among the graphene making methods, developed for graphene use in nanoelectronic devices, is held by an approach based on epitaxial synthesis of graphene as a result of thermal decomposition of silicon carbide SiC. Special attention is paid to the making of single-layer graphene with a high crystal structure perfection with the use of the Si-face of carbides 4H-SiC and 6H-SiC.

Thermal destruction of silicon carbide in high vacuum and in argon atmosphere with a rise of annealing temperature leads to sublimation of Si atoms from the silicon carbide surface, and several reconstructions enriched with carbon atoms form on the Si-face at certain annealing stages. As a result, the Si-face at the last stage is fully covered with a carbon layer having a hexagonal lattice; this layer is a reconstruction $6(\sqrt{3} \times \sqrt{3})R30^\circ$ ($6\sqrt{3}$ for shortness), which is related to the substrate by a crystallographic epitaxial correlation [1]. A further increase of annealing temperature causes the growth of single-layer epitaxial graphene film on the surface of reconstruction $6\sqrt{3}$ at first, and then multi-layer film. Thus, reconstruction $6\sqrt{3}$ is an intermediate, buffer layer (BL) between the SiC surface and graphene, however, due to the influence of a strong covalent bond of the BL with Si atoms in the upper substrate layer, which adjoins the BL, deteriorates the transport properties and other characteristics of graphene [2,3]. Hydrogen intercalation allows for eliminating the covalent bonds, as discovered in [4]. Hydrogen intercalation breaks the covalent bond of the buffer layer to the uppermost Si atoms of the substrate and saturation of Si atoms with hydrogen bonds, and the BL becomes the first layer of epitaxial graphene, which was called quasi-free single-layer epitaxial graphene. Studies in the formation of quasi-free epitaxial graphene from a BL grown on SiC both in high vacuum and in Ar medium, followed by BL intercalation with hydrogen, were published later, for instance, papers [5–7].

The present paper is dedicated to a structural study of transformation of reconstruction $6\sqrt{3}$, which forms at a certain stage of sublimation of Si atoms from the 4H-SiC surface under short-time annealing in Ar atmosphere, into an epitaxial monolayer of graphene. A structural study was performed by the method of reflected high-energy electron diffraction (RHEED) in order to obtain additional information about the degree of structure perfection and homogeneity of the formed carbon layers detected earlier [8,9] using the following research methods: Raman scattering spectroscopy, low-energy electron diffraction, atomic force microscopy, including with the use of Kelvin-probe microscopy, and X-ray photoelectron spectroscopy.

2. Samples and measurement procedure

The samples for the structural study were semi-insulating 4H-SiC(0001) substrates with a chemically-mechanical polished (CMP) surface.

The buffer layer with the structure of reconstruction $6\sqrt{3}$ was grown on the Si-face of the semi-insulating 4H-SiC substrate using the sublimation epitaxy technology. The buffer layer was grown in argon atmosphere at the temperature for $1590 \pm 20^\circ$C for 1 min. Then the sample was carried in air with the grown buffer layer and moved to another growth chamber for intercalation of the buffer layer in hydrogen flow at 800°C for 40 min. The following was found by the method of Raman scattering spectroscopy [8] in the given conditions of annealing in hydrogen: growth of quasi-free single-layer graphene which occupies approximately 70% of the substrate surface area, with the graphene domain size of

100 nm, while the remaining surface of 4H-SiC is occupied by double-layer epitaxial graphene.

The samples' surface structure was studied by the method of reflected high-energy electron diffraction (RHEED) using an EMR-100 electron diffractometer with the accelerating voltage of 50 kV. Electron diffraction patterns were recorded by means of a digital photo camera through the electron diffractometer sight glass from the fluorescent screen. RHEED patterns of the surface were recorded in the directions of plane (0001) of the substrate SiC$\langle 11\bar{2}0\rangle_{SiC}$ and $\langle 1\bar{1}00\rangle_{SiC}$.

3. Results and discussion

The results of the sample study by RHEED are shown in Fig. 1–3.

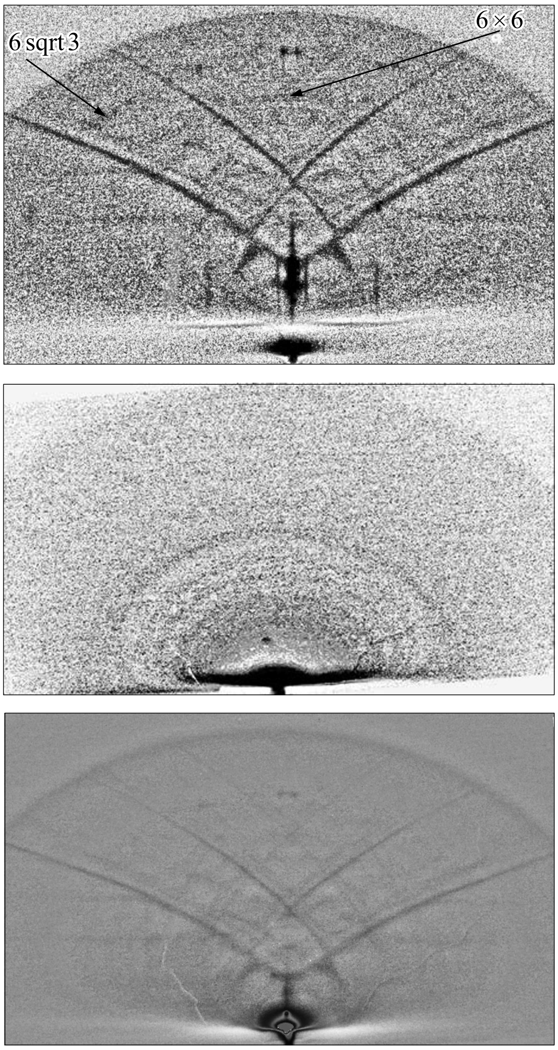

Figure 1. Diffraction patterns recorded in azimuth $[11\bar{2}0]_{SiC}$ at small incidence angles of the grazing electron beam in different regions of the reconstructed SiC surface: *a* — at an angle of about 1° from reconstruction $6\sqrt{3}$ with the first fractional Laue zone and a fragment of the fractional zone of SiC reconstruction (6×6); *b* and *c* — DPs obtained at the beam incidence angle near 0° in two different sample areas from the inclusion of Si oxide.

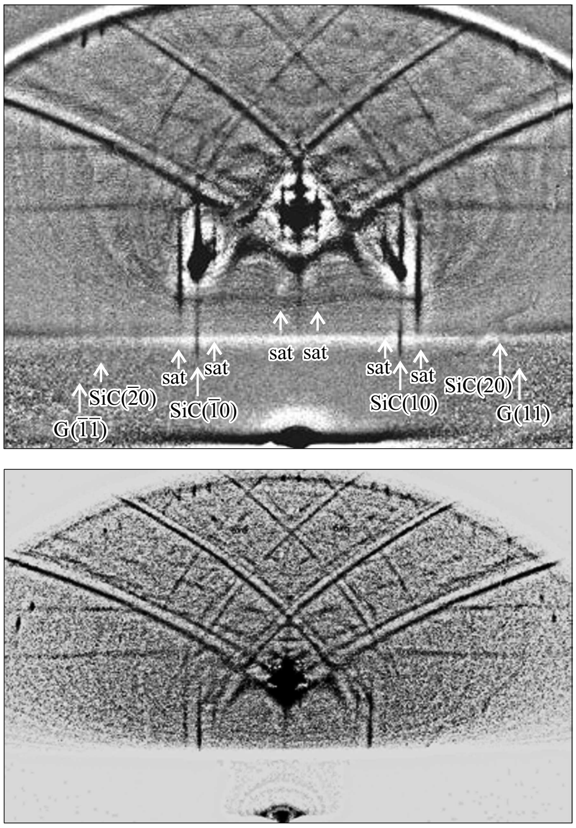

Figure 2. Diffraction patterns obtained from the reconstructed surface at an electron beam incidence angle of about 2.5°, recorded in different sample regions in azimuth $[11\bar{2}0]_{SiC}$: *a* — DP of reconstruction $6\sqrt{3}$ with reflections marked by arrows; *b* — DP from reconstruction $6\sqrt{3}$ and from the rare inclusion of Si oxide in the formed reconstructed layer.

Fig. 1, *a* shows the standard diffraction pattern (DP) recorded at an incidence angle of the incident electron beam about 1° from the SiC surface after short-time annealing in Ar to make a buffer layer. A first-order fractional Laue zone $L_{1/6}$ of reconstruction $6\sqrt{3}$ can be seen well at small beam incidence angles in azimuth $[11\bar{2}0]$. Moreover, the DP has a subtle fragment of a fractional Laue zone which is superfluous for reconstruction $6\sqrt{3}$, which can be attributed to the first-order fractional zone of reconstruction 6×6 forming at a lower SiC annealing temperature (according to [10–11]). The diffraction pattern from $6\sqrt{3}$ in the zero Laue zone L_0 is limited by the rod-like reflections which correspond to (10)SiC, and two satellites near the central reflection.

Scanning of the sample surface at a small electron beam incidence angle has made it possible in some cases to record the diffraction patterns of passage from thin inclusions, protruding above the surface and transparent for electrons, in the reconstructed layer of the SiC surface, which correspond to the finely dispersed Si oxide, mainly with the tridymite structure (Fig. 1, *b–c*).

Fig. 2, *a, b* shows the typical RHEED patterns at angles of electron beam incidence on the reconstructed SiC surface

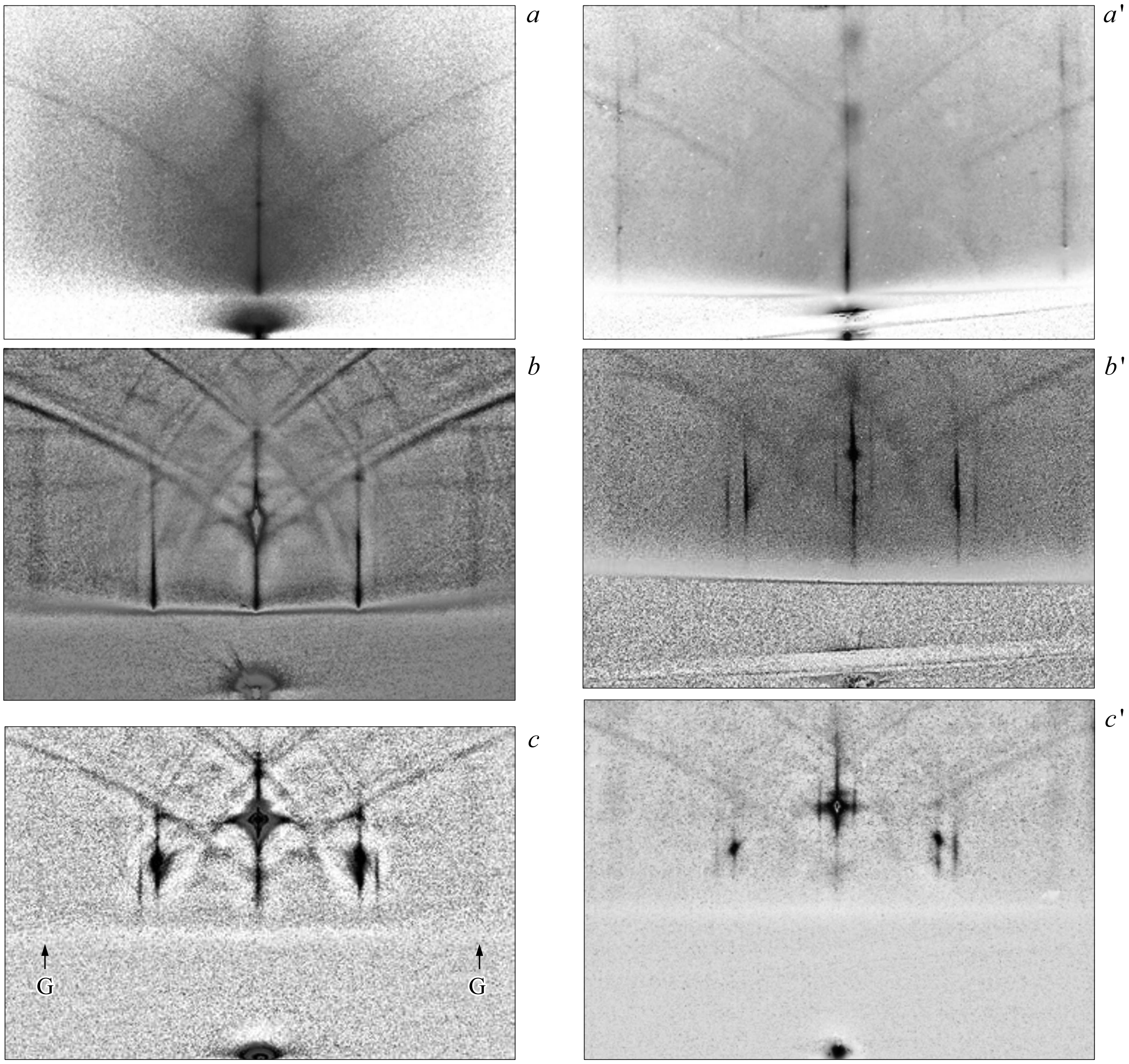

Figure 3. Comparison of RHEED patterns for the surface of the intercalated sample with the sample of single-layer graphene on the barrier layer: a — in azimuth $[11\bar{2}0]_{\text{SiC}}$ at an angle of electron beam incidence of about 1° on the sample after annealing in Ar, a' — in similar recording conditions for the monolayer sample; b — at an incidence angle of about 2° in azimuth $[2\bar{1}\bar{1}0]_{\text{SiC}}$ for the intercalated sample, b' — at an incidence angle of about 2.5° in azimuth $[11\bar{2}0]_{\text{SiC}}$ for the non-intercalated sample; c — in azimuth $[11\bar{2}0]_{\text{SiC}}$ at an incidence angle of about 3.5° on the intercalated sample and c' — at an incidence angle of about 4° on the graphene monolayer with a barrier layer.

near 2.5°. The zero Laue zone in the DP in Fig. 2, a, b is a more developed pattern of reconstruction $6\sqrt{3}$ than in the case of beam incidence of about 1° (Fig. 1, a). The reflections of reconstruction $6\sqrt{3}$ in Fig. 2, a are marked with arrows. It must be noted that the DP from the reconstructed SiC surface shows an increase intensity of reflections with an interplanar distance corresponding to (11)G, in relation to the reflections corresponding to (20)SiC, which is a deviation from the reference diffraction pattern of reconstruction $6\sqrt{3}$, obtained during controlled annealing of the conducting 6H-SiC substrate in high vacuum [10,11].

The increased intensity of the reflection (11)G in the DP indicates the formation of a small fraction of epitaxial single-layer graphene, apparently, in the region of the steps of the SiC substrate terraces, since sublimation of Si atoms begins on the terrace ridges [12].

An insignificant disruption of homogeneity of formation of reconstruction $6\sqrt{3}$ also consists in the presence of low-intensity very short reflections in the DP (Fig. 2, a, b) in the zero Laue zone which apparently pertain to an unidentified reconstruction. The unmarked very short extra-reflections correspond to reconstruction 6×6.

Attention is called to the polycrystalline diffraction pattern in Fig. 2, *b*, which corresponds to Si oxide, in addition to the diffraction pattern from $6\sqrt{3}$. The DP in this case is interpreted as an overlap of 2 patterns: for lighting — from the thin oxide inclusion protruding above the surface and for reflection — from the reconstructed surface.

Fig. 3 shows the DPs recorded at the angles of beam incidence on the sample surface from 1 to 4°. The left column of Fig. 3 shows the DPS from the reconstructed SiC surface annealed in H_2 atmosphere. The right column shows the DPs from the surface of the sample of the epitaxial graphene monolayer grown on a 4H-SiC(0001) substrate with a similar pre-epitaxial preparation of the 4H-SiC(0001) substrate in argon medium for 15 min at the temperature of 1855°C without intercalation [13]. The DP in Fig. 3, *a* recorded at about 1° shows extended graphene reflections (11), which proves the transformation of reconstruction $6\sqrt{3}$ into epitaxial graphene. However, the observed blur of reflections (11) (particularly noticeable when compared with the DP in fig. 3, *a*′) on the diffuse background of electron scattering indicates that the buffer layer transformation is accompanied by structural disruptions in the formed epitaxial graphene.

In case of a sliding electron beam close to 1° (Fig. 3, *a*), the DP from the intercalated sample has hardly visible reflections of fractional zone reconstruction $6\sqrt{3}$ above reflections (11)G in the zero Laue zone, which can be plainly seen in the fractional zone in the DP from the graphene monolayer with a buffer layer in Fig. 3, *a*′. It is thereby proved that the epitaxial graphene layer is almost completely quasi-free. Probably, the presence of satellites above (11)G in the DP in Fid. 3, *a* is related to incomplete intercalation of the SiC surface on the interface of the Si oxide inclusions in the reconstructed layer.

Then Fig. 3, *b, b*′ shows the DPs when the beam incidence angle was approximately 2° and about 4° — in Fig. 3, *c, c*′. The DPs in Fig. 3, *b, c* consist of reflections (11)G and (10)SiC accompanied by a satellite on the outside, and the satellites of reconstruction $6\sqrt{3}$ around the central reflection have disappeared, while they can be plainly seen in Fig. 3, *b*′, *c*′. The satellite near reflection (10)SiC must disappear, like the localized satellites around the central reflection after barrier layer intercalation. A satellite near (10)SiC in the DP can appear due to nanostructurization of the SiC surface which is in contact with quasi-free single-layer graphene [14]. It was demonstrated in [14] by studying the hydrogenization process using the methods of inverse photoelectron spectroscopy and Auger-spectroscopy methods that intercalation of the buffer layer with hydrogen above 700°C leads to nanostructurization of the SiC surface which is in contact with quasi-free single-layer graphene. The authors showed the formation of a SiC sub-surface with a reconstruction close to H-$(\sqrt{3}\times\sqrt{3})R30°$ under single-layer graphene.

Fig. 4 shows the RHEED patterns recorded in azimuth $[1\bar{1}00]_{\mathrm{SiC}}$.

Fig. 4, *a* shows the DP from the SiC surface after short-time annealing in Ar. The DP corresponds to reconstruction $6\sqrt{3}$ in the zero Laue zone with a first-order fractional zone.

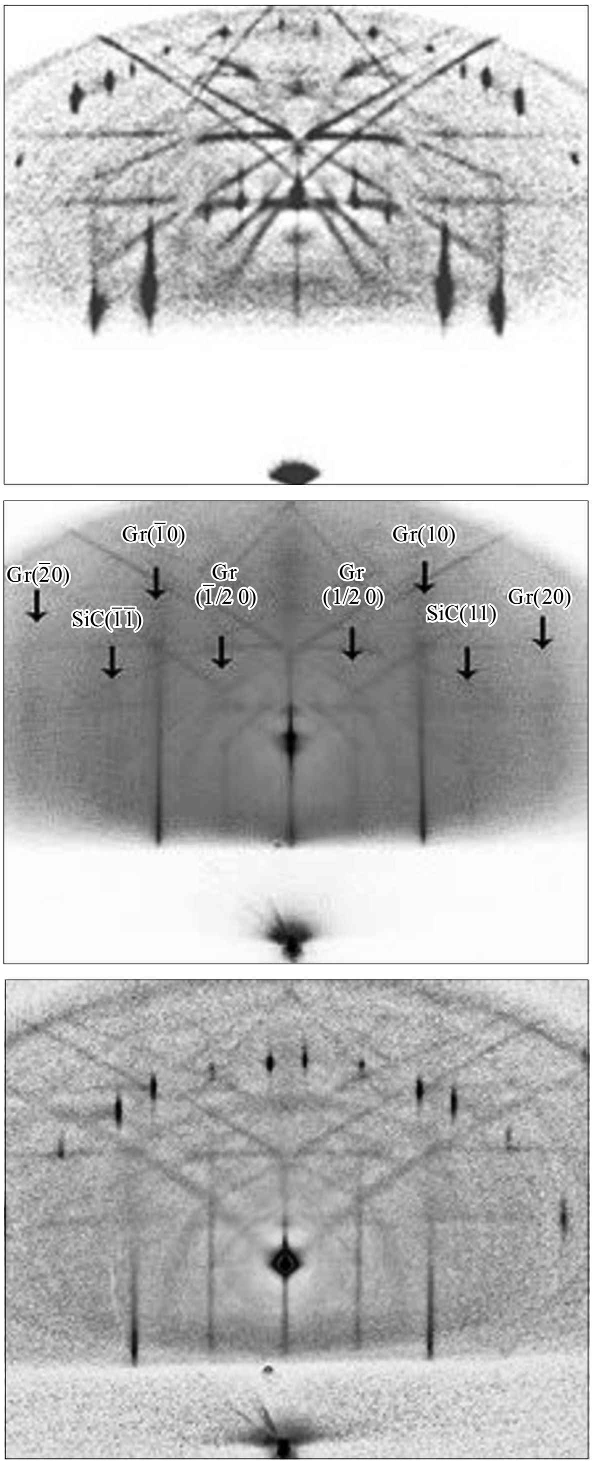

Figure 4. DPs recorded in azimuth $[1\bar{1}00]_{\mathrm{SiC}}$: *a* — from the SiC surface with annealing in argon medium, *b* — from the SiC surface after annealing, followed by intercalation, *c* — from the SiC surface with grown single-layer epitaxial graphene on the barrier layer.

Fig. 4, *b* shows the DP from the SiC surface after short-time annealing, followed by intercalation. The DP consists of graphene reflections with complete absence of reflections-satellites and a fractional zone of reconstruction $6\sqrt{3}$.

The DP in Fig. 4, c was obtained from the substrate surface with grown single-layer epitaxial graphene on a barrier layer without intercalation and is a diffraction pattern from graphene with a fractional zone of reconstruction $6\sqrt{3}$.

A comparison of DPs in Fig. 4, $a{-}c$ confirms the conclusion about barrier layer transformation into epitaxial quasi-free graphene.

4. Conclusion

The following has been established after the study of two samples of the 4H-SiC(0001) substrate by the RHEED method with one-minute annealing in argon atmosphere and with subsequent intercalation of the annealed sample in hydrogen flow.

With small angles of incidence of a sliding electron beam on the reconstructed surface of 4H-SiC(0001) after annealing in Ar medium, the diffraction patterns show a distinct fractional first-order Laue zone of reconstruction $6\sqrt{3}$ and a small fragment of a hardly visible fractional zone of reconstruction 6×6, which indicates the formation of an incomplete carbon coating of the substrate when a barrier layer is created.

With an increase of the beam incidence angle, the RHEED patterns demonstrate a well-developed structure of reconstruction $6\sqrt{3}$ in the barrier layer. An analysis of the reconstruction pattern shown a small intensification of the reflection corresponding to (11)G, which indicates the formation of a certain fraction of epitaxial graphene even in the conditions of short-time annealing of SiC at 1590°C.

A certain inclusion of finely dispersed silicon oxide in the BL was found.

After annealing of the reconstructed SiC surface (the surface with a buffer layer) in hydrogen, the RHEED-patterns of the sample showed a transformation of the buffer layer into quasi-free epitaxial graphene, but with a lower degree of perfection of the graphene single-crystal structure as compared to the structure of single-layer graphene on the buffer layer.

We assumed the formation of a SiC subsurface with a reconstruction close to H-$(\sqrt{3} \times \sqrt{3})R30^\circ$, under the epitaxial graphene as a result of sample intercalation with annealing in argon medium.

Acknowledgments

The work was partially supported by the Ministry of Science and Higher Education of the Russian Federation (agreement 075-15-2021-1349).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A.J. Van Bommel, J.E. Crombeen, A. Van Tooren. Surf. Sci. **48**, *2*, 463 (1975).
[2] K.V. Emtsev, F. Speck, Th. Seyller, L. Ley, J.D. Riley. Phys. Rev. B **77**, *15*, 155303 (2008).
[3] J. Jobst, D. Waldmann, F. Speck, R. Hirner, D.K. Maude, T. Seyller, H.B. Weber. Phys. Rev. B **81**, *19*, 195434 (2010).
[4] C. Riedl, C. Coletti, T. Iwasaki, A.A. Zakharov, U. Starke. Phys. Rev. Lett. **103**, *24*, 246804 (2009).
[5] E. Pallecchi, F. Lafont, V. Cavaliere, F. Schopfer, D. Mailly, W. Poirier, A. Ouerghi. Sci. Rep. **4**, *1*, 1 (2014).
[6] F. Speck, J. Jobst, F. Fromm, M. Ostler, D. Waldmann, M. Hundhausen, H.B. Weber, Th. Seyller. Appl. Phys. Lett. **99**, 122106 (2011).
[7] S. Tanabe, M. Takamura, Y. Harada, H. Kageshima, H. Hibino. Jpn. J. Appl. Phys. **53**, 04EN01 (2014).
[8] I.A. Eliseyev, A.N. Smirnov, S.P. Lebedev, V.N. Panteleev, P.A. Dementev, J. Pezoldt, G. Hartung, J. Kroger, A.V. Zubov, A.A. Lebedev. Fuller. Nanotub. Carbon Nanostruct., **28**, *4*, 316 (2020).
[9] S.P. Lebedev, I.A. Eliseyev, V.N. Panteleev, P.A. Dementev, V.V. Shnitov, M.K. Rabchinskii, D.A. Smirnov, A.V. Zubov, A.A. Lebedev. Semiconductors **54**, 1657 (2020).
[10] X.N. Xie, H.Q. Wang, A.T.S. Wee, K.P. Loh. Surf. Sci. **478**, *1–2*, 57 (2001).
[11] X.N. Xie, K.P. Loh. Appl. Phys. Lett. **77**, 3361 (2000).
[12] M.L. Bolen, R. Colby, E.A. Stach, M.A. Capano. J. Appl. Phys. **110**, 074307 (2011).
[13] I.S. Kotousova, S.P. Lebedev, A.A. Lebedev, P.V. Bulat. FTT **61**, *10*, 1978 (2019).
[14] Y.-P. Lin, Y. Ksari, J.-M. Themlin. Nano Res. **8**, 839 (2015).