In situ Reflection High-Energy Electron Diffraction observation of graphene layer formation on 6*H*-SiC(0001) Substrate

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Evolutions of diffraction patterns of 6*H*-SiC(0001) surface during graphene growth have been studied. Characteristic features of diffraction pattern evolutions during morphological transformations from an initially rough 6*H*-SiC(0001) surface to a step-terraced one with subsequent formation of a buffer carbon layer on it and, finally, epitaxial graphene induced by thermal annealing were determined. Using ex situ atomic force microscopy, scanning electron microscopy and Raman shift spectroscopy methods, morphology, stoichiometric composition and degree of surface perfection of the samples were found to correspond to observed diffraction patterns obtained at the corresponding stages of graphene growth.

Keywords: Graphene, SiC, AFM, Raman spectroscopy, SEM, RHEED.

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1. Introduction

Graphene is a carbon material with a thickness of one atomic layer, the crystal structure of which is a two-dimensional honeycomb lattice. Graphene has good thermal conductivity, flexibility and elasticity, and high mobility of charge carriers, which attracts attention from a fundamental and applied point of view. Many devices have already been developed based on graphene that operate in laboratory conditions [1], including transistors [2]. The cost of manufacturing, the scalability of production, and other factors directly depend on the growth method. However, one of the main difficulties in creating graphene-based electronic devices is obtaining high-quality graphene layers fixed on a substrate. In this regard, the method of thermal decomposition of silicon carbide (SiC) to produce graphene on its surface is promising.

To achieve complete control in the formation of graphene by thermal decomposition, it is necessary to be able to control changes in the stoichiometric composition of the surface layers directly during the annealing process. To date, the possibility of growing perfectly controlled graphene layers on SiC(0001) substrates has been demonstrated using thermal annealing in an inert atmosphere furnace Ar [3]. A number of studies have been devoted to graphitization and the formation of the first graphene layer [4–10], which is formed by the sequential formation of a number of superstructural reconstructions, of which the main ones for controlling the quantity and quality of graphene layers are the structure $(6\sqrt{3} \times 6\sqrt{3})$ R30° (later, $6\sqrt{3}$) of the buffer layer and the structure (1×1) of graphene. It was found in Ref. [11,12] that during annealing at $T = 1200-1400\,^{\circ}\mathrm{C}$ ultrahigh vacuum (UHV) conditions, a buffer layer is first formed with reconstruction $6\sqrt{3}$. This layer consists of carbon atoms, but it does not exhibit the two-dimensional properties of graphene due to the inconsistency of the lattice parameters of graphene and silicon carbide, moreover, it is connected to the substrate by covalent bonds rather than Van der Waals bonds. Next, the buffer layer on the surface of the substrate is transformed into graphene with reconstruction (1×1), and another buffer layer is formed under it.

The authors in the study in Ref. [3] agree that silicon atoms sublimate too quickly from the SiC surface under UHV conditions, which makes it a difficult task to control the formation of graphene layers. Nevertheless, monitoring the formation of superstructures from residual carbon atoms during annealing will allow for better control of each phase of graphene formation even under UHV conditions and at a high rate of Si sublimation. The method of reflection high-energy electron diffraction (RHEED) is a traditional non-destructive *in situ* method of monitoring changes in the surface structure under vacuum conditions. In addition, this method allows tracking the perfection of the crystal structure of the studied materials and the smoothness of the surface, control the uniformity of the formation of materials and other parameters that directly affect the reproducibility of the growth of materials and the basic electronic properties of future devices. This paper is devoted to the study of the crystal structure of the near-surface layer of 6*H*-SiC(0001) substrate using the *in situ* RHEED method and *ex situ* analysis of surface morphology, the presence of nanoscale

defects, and the uniformity of the graphene coating, which directly affect the suitability of the material for devices.

2. Experimental procedure and measurements

Samples with a size of $8.8 \times 1.5 \times 0.33$ mm, cut from a conductive substrate doped with hydrogen-like nitrogen 6*H*-SiC(0001) with a band gap of 3 eV and a resistivity of $0.02-0.1$ Ohm · cm were used in the study. The choice of substrates is determined by the annealing method, which is carried out by passing direct or alternating electric current.

The samples were annealed in the UHV chamber of a reflective electron microscope [13]. The temperature of the samples was measured using an optical pyrometer. The change in the surface structure of 6*H*-SiC(0001) substrates and the formation of graphene were monitored in the *in situ* mode by the RHEED method. The method is based on the analysis of diffraction patterns (DP) obtained by elastically scattered electrons from the surface under study, which were recorded on a fluorescent screen in the crystallographic directions $[1100]$, $[\bar{1}100]$, $[11\bar{2}0]$ at an angle of incidence of the electron beam relative to the substrate not exceeding 3°.

Atomic force microscopy (AFM, Bruker Multimode 8) was used to further analyze the morphology and the presence of defects in the samples obtained as a result of annealing. To determine the stoichiometric composition of the films obtained on the surface and the quality of their crystal structure, the raman spectrum was measured using a spectrometer (XploRa Plus, Horiba, $\lambda = 532$ nm). A scanning electron microscope (SEM, Hitachi SU8220, accelerating voltage 2 kV) was used to determine areas with different stoichiometric composition.

3. Results and discussion

The formation of high-quality graphene on 6*H*-SiC(0001) substrates can be divided into two stages: obtaining a step-terraced structure of the surface of 6*H*-SiC(0001) substrate, obtaining carbon layers, among which a buffer layer characterized by surface reconstruction of $6\sqrt{3}$ can be singled out separately, and graphene layers with a superstructure of (1×1).

The initial surface of the 6*H*-SiC(0001) SiC substrates is characterized by multiple roughnesses and nano-scratches formed during polishing of SiC plates during their production, with a height difference in the range of $5-10$ nm, as shown in Figure 1, *a*. DP corresponding to the AFM image (Figure 1, *c*) demonstrates vertical rod reflexes in the Laue zero zone and Kikuchi lines, typical for SIC substrates with a hexagonal polytype. The central reflex stands out in particular, which indicates a high degree of perfection of the bulk crystal structure of the substrate. Lateral reflexes, indicated by an arrow in Figure 1, *a*, are wide and have low intensity, which indicates the presence of imperfections and impurities on the original unburned surface, which is noticeable in the AFM image (Figure 1, *a*).

DP changes were observed directly during the annealing process in the *in situ* mode. Figure 1, *d* shows that lateral reflexes after 10 min of annealing have become more intense compared to the DP before annealing at $T = 1250\,^{\circ}$C and the Kikuchi line system has improved, which indicates an improvement in the crystal structure of the surface layer. The improvement of the surface structure is also evidenced by AFM images of the surface after annealing (Figure 1, *b*), which show a step-terraced morphology of the surface with a sharp edge of the boundaries of atomic steps and incomplete filling of narrow terraces with SiC layers $400-500$ nm.

Further annealing leads to the reconstruction of the SiC surface. As can be seen from Figure 1, *e*, short reflexes in the fractional Laue zone with an arc-shaped arrangement were added to the core reflexes in the zero Laue zone corresponding to the SiC crystal structure. The appearance of these reflexes indicates the beginning of the formation of a buffer layer with reconstruction $6\sqrt{3}$ [14]. The formation of the buffer layer can also be determined by the appearance in the Raman spectrum in Figure 1, *f* characteristic lines at frequencies $\approx 1350\,\text{cm}^{-1}$ (D-like band) and $\approx 1580\,\text{cm}^{-1}$ (G-like band), which are indicated in the figure as peaks D and G, respectively. It is important to note that the nature of these buffer layer bands differs from the D and G peaks of graphene associated with defects and optical phonons in the Brillouin zone [15]. The occurrence of a G-like band in the buffer layer is caused by covalent bonding of carbon atoms of the buffer layer with silicon atoms of the SiC(0001) substrate, and the D-like band in the buffer layer is caused by specific structural distortions caused by the mismatch of the permanent lattices of the carbon layer and SiC [16–18]. This discrepancy leads to stresses, bond rupture, and the formation of a superstructure of $6\sqrt{3}$.

Annealing at $T = 1250\,^{\circ}$C a duration of 10 min, it induces significant sublimation of silicon atoms, which in turn leads to a noticeable excess of carbon atoms on the surface and partial coating of the surface with a carbon buffer layer, which is confirmed by the appearance of short reflexes in the fractional zone at DP (Figure 1, *e*) and the occurrence of D-like and G-like bands on the Raman spectrum (Figure 1, *f*). At the same time, the surface of the sample terraces remains incompletely filled with SiC layers, which can be seen in AFM images (Figure 1, *b*) and is expressed by insufficient intensity of lateral reflexes on the DP (Figure 1, *c*). Thus, it is necessary to perform annealing at $T \leq 1250\,^{\circ}$C to form atomically smooth surfaces under UHV conditions.

All the studied samples passed through the step-terraced surface formation stage. Figure 2, *a* and 3, *a* show surface profiles measured along dotted lines, indicating that a stepped-terraced surface was formed on the samples. The measured step height of the studied samples at 0.75 nm is equal to half of the lattice constant 6*H*-SiC in the [0001]

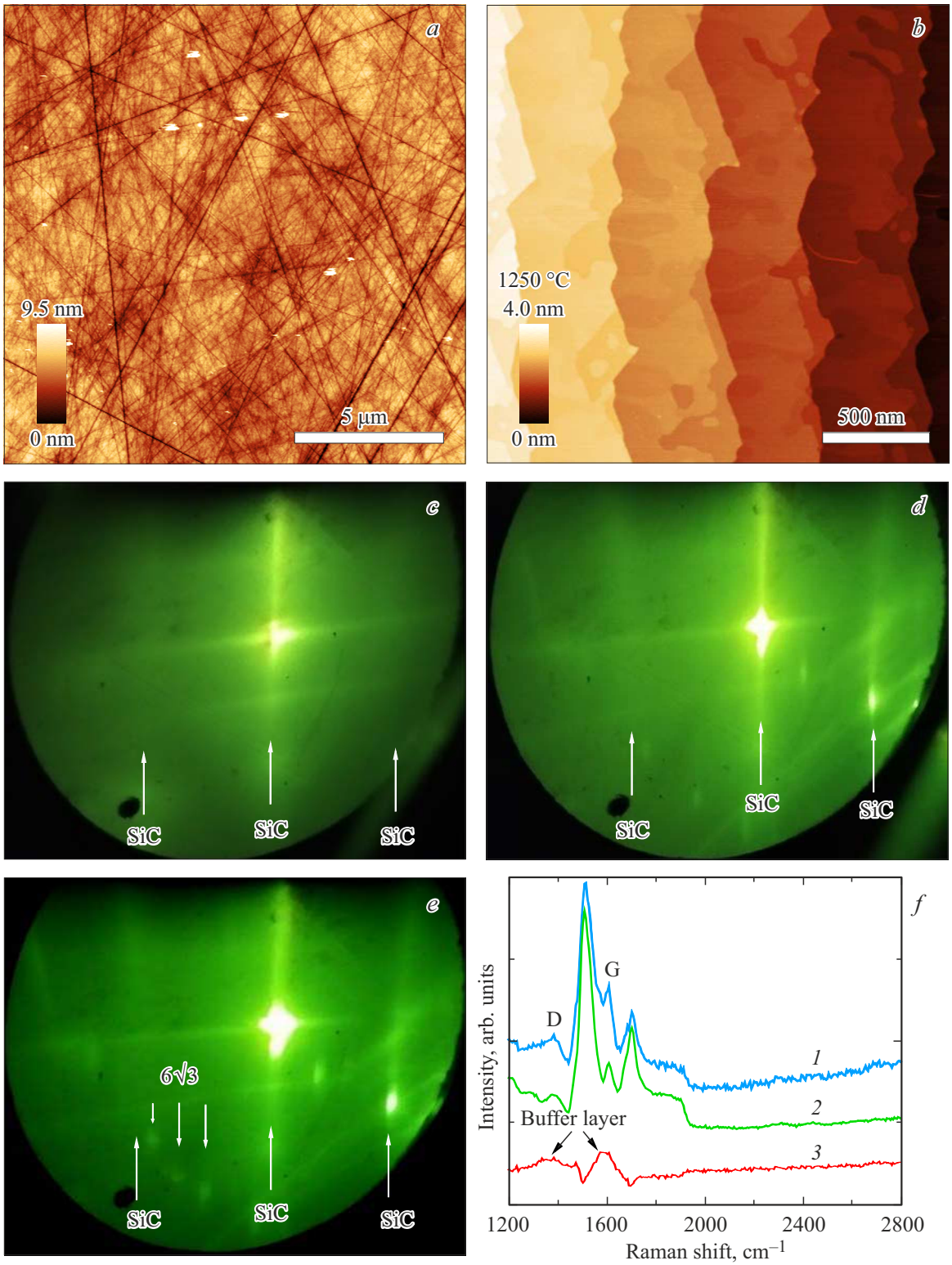

Figure 1. Study of the first stage of epitaxial graphene formation on substrates 6*H*-SiC(0001): *a* — AFM image of the sample surface before annealing; *b* — AFM image of the sample surface after annealing at $T = 1250\,^{\circ}\mathrm{C}$; *c* — DP to annealing; *d* — DP after 10 min annealing at $T = 1250\,^{\circ}\mathrm{C}$; *e* — DP after 20 min annealing at $T = 1250\,^{\circ}\mathrm{C}$; *f* — Raman spectra after annealing $t = 20$ min at $T = 1250\,^{\circ}\mathrm{C}$ — curve *1*, before annealing — *2*, difference in spectra before and after annealing — *3*. The DP are obtained along the direction [1100] and correspond to the AFM images.

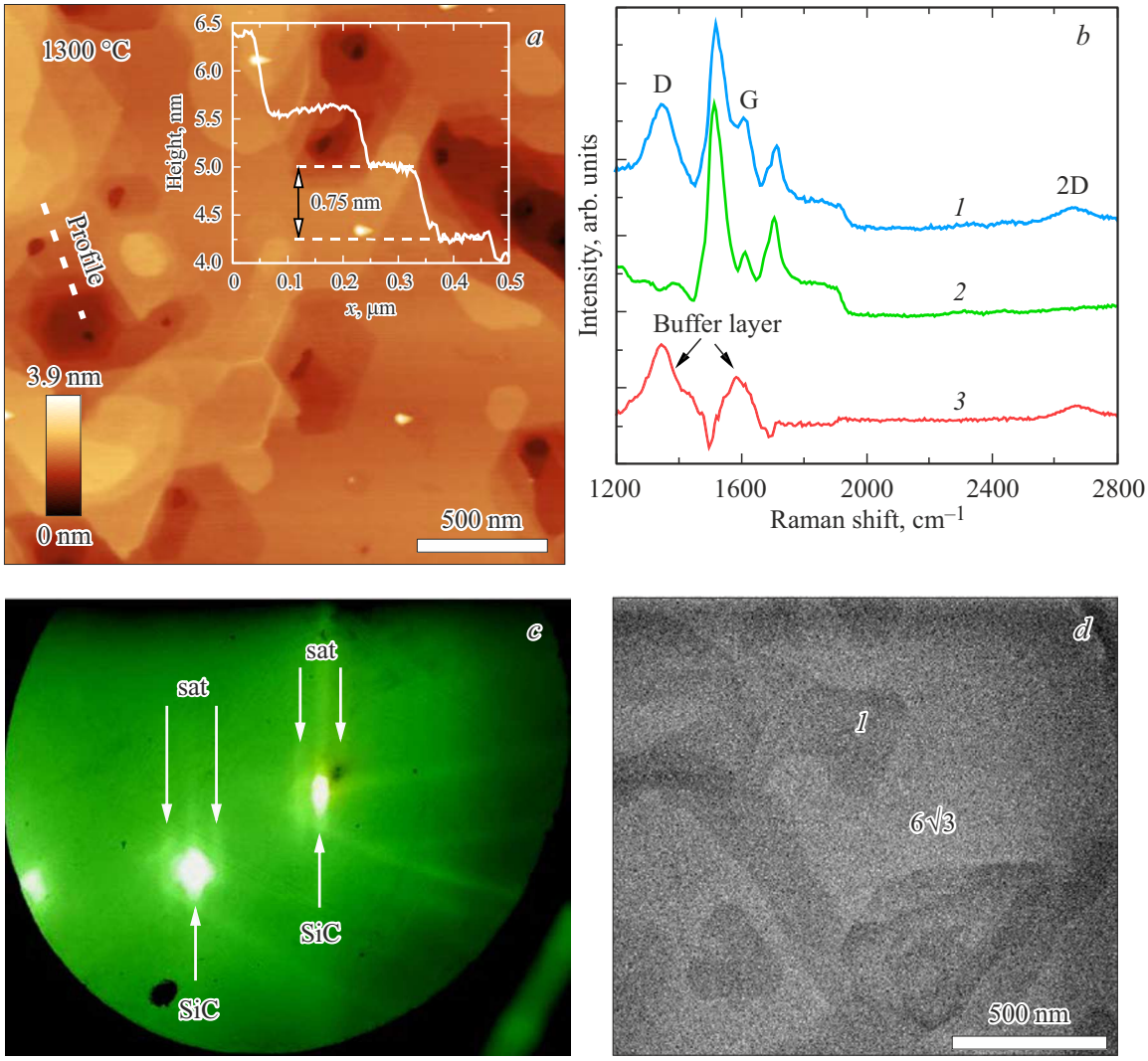

Figure 2. Study of the formation of a carbon buffer layer on substrates 6*H*-SiC(0001): *a* — AFM image of the sample surface after $t = 5$ min of annealing at $T = 1300\,^{\circ}$C, the surface profile measured along the dotted line is shown in the insert; *b* — Raman spectra after $t = 5$ min of annealing at $T = 1300\,^{\circ}$C — curve *1*, before annealing — *2*, spectrum difference before and after annealing — *3*; *c* — DP observed along the direction $[11\bar{2}0]$ during annealing at $T = 1300\,^{\circ}$C; *d* — SEM image of surface layers in the mode of detecting backscattered electrons after $t = 5$ min of annealing at $T = 1300\,^{\circ}$C, the labels „$6\sqrt{3}$“, „1“ indicate the regions corresponding to the coating of the sample surface with a buffer layer and one graphene layer.

direction, which corresponds to the height of the 6*H*-SiC steps formed during low-temperature annealing.

The next stage after obtaining a high-quality step-terraced surface is the stage of formation of carbon layers, accompanied by surface superstructural transitions observed at DP. The DP obtained along the direction of [1100] from terraces partially covered with a buffer layer is shown in Figure 1, *e*. The partial coating of the sample surface with a buffer layer is indicated by a weakly pronounced D-like band in Figure 1, *f*. To proceed to the next stage of graphene production, it is necessary to completely cover the surface of the sample under study with a buffer layer. For this purpose, samples with a previously formed terraced surface were subsequently annealed at $T = 1300\,^{\circ}$C. Figure 2, *c* shows the DP along the direction $[11\bar{2}0]$ obtained after 5-minute annealing, during which the rod-shaped reflexes corresponding to the SiC structure began to be complemented by two satellites corresponding to the reconstruction $6\sqrt{3}$, on both sides of the core reflexes. The presence of a buffer layer is confirmed by the presence of pronounced D-like and G-like bands on the Raman spectrum (Figure 2, *b*), which are indicated in the figure as D and G, respectively, the intensity of which is several times more than Figure 1, *f*. There is also a low-intensity and wide line in the Raman spectrum at a frequency of $\approx 2700\,\text{cm}^{-1}$, called the 2D peak, which indicates a low surface coverage of the studied samples with crystalline graphene. Up to 5 nm deep large pits are present on the sample surface (Figure 2, *a*), in which graphene layers are formed, formed from excess carbon atoms on the surface as a result of the sublimation of silicon atoms

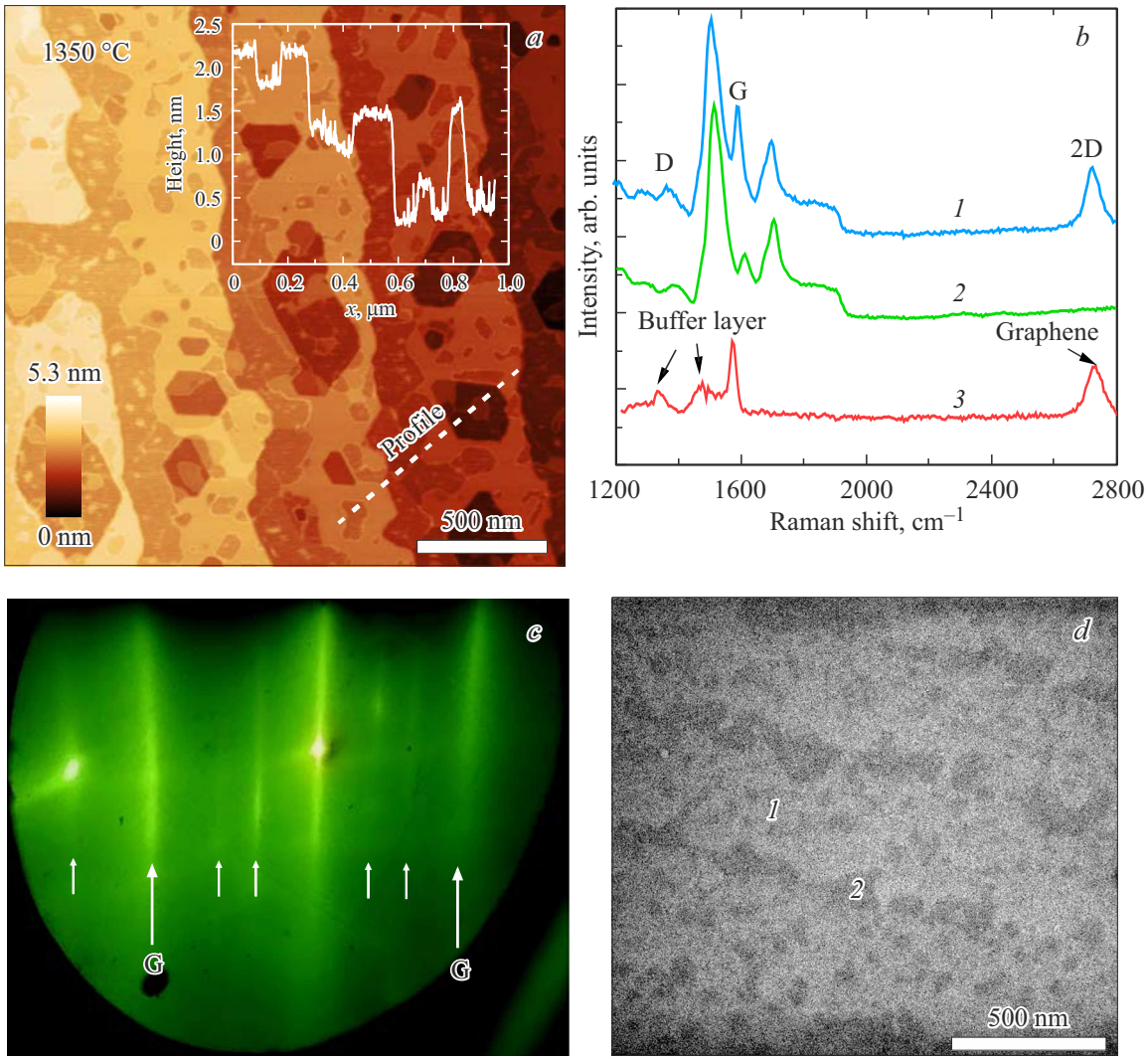

Figure 3. Study of the formation of a carbon buffer layer on substrates 6*H*-SiC(0001): *a* — ACM-image of the sample surface after annealing for $t = 4$ min at $T = 1350\,^{\circ}$C, the image shows the surface profile measured along the dotted line; *b* — Raman spectra after annealing for $t = 4$ min at $T = 1350\,^{\circ}$C — curve *1*, before annealing — *2*, spectrum difference before and after annealing — *3*; *c* — DP, observed along the direction $[\bar{1}100]$ during annealing at $T = 1350\,^{\circ}$C, the arrows without symbols indicate reflexes from the buffer layer with reconstruction $6\sqrt{3}$; *d* — SEM image of surface layers in the mode of detecting backscattered electrons after annealing for $t = 4$ min at $T = 1350\,^{\circ}$C, labeled „1“, „2“ areas corresponding to coating the sample surface with one graphene layer and two graphene layers.

from near-surface layers. The complete buffering of the surface of the sample under study and the filling of the pits with graphene are confirmed by the SEM images of the surface taken in the backscattered electron detection mode, since they are sensitive to the elemental composition of the substrate surface. The regions corresponding to the coating of the sample surface with a buffer layer and one graphene layer are marked by tags „$6\sqrt{3}$“, „1“ in the SEM image in Figure 2, *d*. The contrast *Z* indicates a difference in the composition of the surface, a higher concentration of atoms with a higher atomic number corresponds to a brighter contrast. In our case, the near-surface layers that do not have graphene clusters have a higher concentration of silicon, i. e., a higher atomic number, which means they correspond to areas with a lighter contrast in the SEM image. The buffer layer with reconstruction $6\sqrt{3}$ occupies 70,% of the surface, the remaining surface area is occupied by graphene in pits. The occurrence of graphene clusters visible in the SEM image and the Raman spectrum is explained by the high rate of sublimation and the need for a gradual decrease in the annealing temperature of the samples due to different coefficients of thermal expansion of the carbon layers and the substrate, which increases the annealing time. Thus, monitoring the formation of the buffer layer using the *in situ* RHEED method does not allow to see the formation of graphene clusters if the degree of coverage with crystalline graphene is $< 30\,\%$ of the area.

The formation of a buffer layer on SiC dramatically reduces the rate of silicon sublimation due to passivation of the surface. Since the formation of a graphene layer requires

the destruction of a stable buffer layer, the annealing time for graphene formation increases by orders of magnitude compared to the time of formation of the buffer layer, therefore, to obtain graphene, the annealing temperature increased to 1350 °C. It was not possible to observe a diffraction pattern at a low sliding angle, combined with a faintly noticeable system of Kikuchi lines, this indicates the presence of microrelief on the surface, i. e., a violation of the perfection of the structure in the surface layer of the annealed sample. This is confirmed by the AFM images obtained subsequently. Figure 3, *a* shows the division of terraces into strips along the steps, as well as a large number of pits in the form of polygons up to 1 nm high, as can be seen in the inset. The presence of graphene layers is confirmed by the analysis of Raman spectra (Figure 3, *b*), which show a significant decrease in the intensity of the D-like peak responsible for the buffer layer, as well as a noticeable increase in intensity and a decrease in the half-width of the peak 2D. The SEM image (Figure 3, *d*) shows *Z*-contrast, indicating the formation of one graphene layer (light area) and two graphene layers (dark area) on the surface, which are designated „1“ and „2“ respectively. Nevertheless, based on the obtained AFM images (Figure 3, *a*), the SEM image (Figure 3, *d*) and the Raman spectrum (Figure 3, *b*), it can be argued that the band corresponding to the darker contrast does not consist of two graphene layers, but simply has an excessive amount of carbon, since silicon sublimation from 2–3 SiC layers is necessary to form a graphene layer, which is not visible from the measured the surface profile in the insert to Figure 3, *a*.

The DP shown in Figure 3, *c* along the direction $[\bar{1}100]$ corresponds to the above description and was observed during 4-minute annealing at $T = 1350\,^{\circ}\mathrm{C}$ at the angle of incidence of the electron beam in 2–3 °. With this angle of incidence of the electron beam on the DP, two surface layers can be judged, therefore, it is possible to monitor both the formation of the buffer layer and the quality of the formation of graphene layers. The DP obtained from the annealed sample at $T = 1350\,^{\circ}\mathrm{C}$ has similar features to DP from the step-terraced surface of the SiC substrate in Figure 1, *d*. Both surfaces have a reconstruction (1×1) and have rod reflexes on the DP, showing a hexagonal structure. In addition to the fact that the rod-shaped reflexes related to graphene (Figure 3, *c*) have a bright contrast and uniformity along their entire length, the lateral reflexes are continuous along their entire length, which indicates the formation of two-dimensional graphene clusters. However, reflexes are present in the Laue zero zone in DP (Figure 3, *c*), indicated by a white arrow without a signature, indicating the presence of a buffer carbon layer [19]. The presence of these reflexes also confirms that the sample does not have a second graphene layer on its surface. But it is necessary either to reduce the annealing temperature or to reduce the annealing time at a constant temperature to form high-quality graphene, and it is necessary to be guided by the occurrence of reflexes on the DP corresponding to graphene, so that no excess carbon remains on the surface after silicon sublimation. Thus, for the formation of a single-layer graphene, it is necessary to monitor the DP in the form of a superposition of reflexes from graphene and the buffer layer during annealing and complete the annealing process before these reflexes disappear, which would indicate that the surface is completely filled with a second layer of graphene [20].

4. Conclusion

The evolution of DP from the surface of SiC substrates during resistive annealing under UHV conditions was studied in this paper. The annealing duration required for the formation of step-terraced surfaces of SiC, buffer layer, and single-layer graphene was determined using the *in situ* RHEED method. The optimal temperature conditions for annealing were determined in conjunction with *ex situ* AFM, SEM, and RS analysis of samples obtained as a result of annealing. The formation of step-terraced surfaces in high-temperature conditions requires annealing of the substrate at $T = 1250\,^{\circ}\mathrm{C}$ for 20 min, and annealing at $T = 1300\,^{\circ}\mathrm{C}$ is sufficient for the controlled formation of carbon layers under UHV conditions. It has been established that formation of one graphene layer requires stopping annealing before the diffraction reflections corresponding to the carbon buffer layer begin to disappear.

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Conflict of interest

The authors declare that they have no conflict of interest.

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