Role of structure of C-terminated 4H-SiC(000\overline{1}) surface in growth of graphene layers:
Transmission electron microscopy and density functional theory studies

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The principal structural defects in graphene layers, synthesized on a carbon-terminated face, i.e., the SiC(000\overline{1}) face of a 4H-SiC substrate, are investigated using microscopic methods. Results of high-resolution transmission electron microscopy (HRTEM) reveal their atomic arrangement. The mechanism of such defects’ creation, directly related to the underlying crystallographic structure of the SiC substrate, is proposed. The connection between the 4H-SiC(000\overline{1}) surface morphology, including the presence of the single atomic steps, the sequence of atomic steps, and also the macrosteps, and the corresponding emergence of planar defective structure (discontinuities of carbon layers and wrinkles), is revealed. It is shown that the disappearance of the multistep island leads to the stress-related creation of wrinkles in the graphene layers. The density functional theory (DFT) calculation results show excess carbon atoms convert a topmost carbon layer to the sp2-bonded configuration, liberating Si atoms in the barrierless process. The DFT results show that the diffusion of carbon atoms is essentially impossible at the C-terminated SiC surface. On the contrary, DFT results prove that diffusion of the silicon atoms is possible on the C-terminated SiC surface at a high temperature close to 1600°C. Because, according to TEM studies, at the carbon-terminated SiC surface, the buffer layer is absent, that creates a channel for effective horizontal diffusion of both silicon atoms under the graphene layer. Ultimately the silicon atoms escape could be facilitated by the channels created at the bending layer defects (wrinkles). The sp2-bonded carbon atoms are incorporated into the growing graphene layers, which contribute to stress in the growing layers, detachment from SiC support, and partial contribution to the creation of wrinkles. These results explain the phenomenon of the growth of thick undulated graphene layers by subsequent creation of the new layer underneath the existing graphene cover and also the creation of the principal defects in graphene at the C-terminated SiC(000\overline{1}) surface.

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I. INTRODUCTION

For the last decade, graphene has been a popular research topic due to its unusual electronic properties that are very attractive for potential applications in future sensing and high-speed electronic devices.1 A single carbon atomic layer, characterized by the sp2 bonding of the carbon atoms, distributed on a hexagonal honeycomb lattice, is denoted as graphene. The single carbon layer shows a number of unusual electronic properties, arising from a Dirac-type dispersion relation, confirmed directly by an anomalous magnetic field dependence of integer quantum Hall effect.1–7 The unusual electronic transport properties, related to \(\pi\)-electrons of the carbon atoms, attracted an immense interest of many researchers in graphene.

In the past few years, the notion of graphene was extended from a single layer of carbon to bilayer or many layers of carbon atoms. Such multilayer graphene was synthesized on various substrates: gold, nickel, platinum and ruthenium.8–12 However, a natural and most convenient way to obtain a single layer or a few layers of graphene is to use carbon containing electrically insulating crystals, such as diamond and silicon carbide. Diamond is technologically difficult to process, but silicon carbide thermal decomposition that leads to a loss of more volatile silicon is a natural candidate for graphene technology. It is known that vacuum annealing at a high temperature of 6H-SiC or 4H-SiC in a graphitic form at the surface.13–15 Both polar surfaces, i.e., Si- and C-terminated ones, could be used, but their potential depends on the properties of the synthesized graphene.16–19

Graphene synthesized at a C-terminated SiC surface seems to be relatively weakly attached to the underlying surface. No buffer layer, i.e., covalently bound carbon layer, was detected, and the first graphene layer is located at the distance of about 3.2 Å from the SiC surface, i.e., too far to form covalent bonding between carbon atoms.20 Low-energy electron diffraction (LEED)21–23 and scanning tunneling microscopy (STM)24–26 results indicate a significant degree of rotational disorder in the graphene films. Rotational stacking faults in the graphene layers, which give rise to a moiré pattern, were also observed in transmission electron microscopy (TEM).27

Systematic investigations of the growth of graphene layers in both orientations have been undertaken quite recently and have brought a limited insight into the processes. Studies over growth on a Si-terminated face have been far more advanced. It is recognized that a graphene growth depends on the temperature, gas pressure, and also the morphology of the SiC(000\overline{1}) surface.28–33 In standard processes, vicinal SiC surfaces are gas etched in the H\(_2\) atmosphere. Depending on the duration of this stage, the partial erosion of the material at the steps occurs, which may lead to the formation of macrosteps28,29 or a significant modification of the step shapes.30
Typically, prepared SiC samples are annealed in a neutral atmosphere at a very high temperature, which leads to graphitization that begins at the steps. The graphitization process proceeds by evaporation of silicon atoms, first at the steps in which Si atoms are more weakly bonded.\textsuperscript{25–34} The details of the process are still disputed, depending on the initial structure of the SiC surface. For vicinal surfaces, it was proposed that surface diffusion is negligible so that three SiC layers constitute a single graphene layer.\textsuperscript{29,30} In some cases, the disintegration of the three steps leads to the formation of trenches, at the portion of the terraces, close to the steps.\textsuperscript{35} In addition, the creation of surface pits is observed.\textsuperscript{29} Most likely, the creation of the pits is related to dislocation or other extended defects in the SiC substrate. At a higher temperature, step instability leads to the formation of fingerlike patterns.\textsuperscript{31} The graphene formation process is two dimensional.

For SiC surfaces transformed to macrosteps, the graphitization scenario is different.\textsuperscript{28,32} It was proposed that the anisotropic process of the growth of graphene layers is supported by C adatom diffusion.\textsuperscript{28} Graphene flakes start to grow at a sidewall of the macrosteps that then continue to extend over a part of the terraces.\textsuperscript{32} It is stipulated that the first graphene layer is created by evaporation through the buffer layer and the subsequent layers emerge due to direct penetration of silicon atoms either by vacancy sites\textsuperscript{35} or grain boundaries.\textsuperscript{35} In order to reach these sites, the liberated silicon atoms diffuse under the conditions in a plane parallel to the carbon atoms. For thicker graphene, the silicon out-diffusion slows down, leading to effective growth termination after the creation of four to five carbon layers.

In a slightly different version, supported by TEM data, the emerging graphene layers are also created at the side of macrosteps.\textsuperscript{33} It is postulated, however, that these layers are anchored at the lower terraces by SiC surface defects, the creation of the structures. The structures have the carbon layers shaped perpendicularly to the SiC surface at the anchoring points. The layers extend over the surface of the upper terrace indefinitely, ultimately to the terrace termination. The new carbon layer originates underneath the previously created carbon layer at the side of the macrosteps.\textsuperscript{33} This model does not apply for disintegration of the terrace or formation of trenches.

Growth on the C-terminated face was studied bringing qualitatively different results.\textsuperscript{36–38} Initial results summarized by Hass et al. indicated that the quality of the graphene layers is exceptionally good.\textsuperscript{36} Further investigation showed a much less optimistic picture: graphene layers contain a number of defects and also the thickness and stacking are difficult to control.\textsuperscript{20,39} These results were confirmed by the results Tedesco et al. indicating that the morphology of graphene layers grown at C-terminated \(4H\)-SiC and \(6H\)-SiC dramatically depends on the temperature and pressure of the argon-mediated growth process.\textsuperscript{37} It was also postulated that the creation of wrinkles is related to stress in growing graphene layers.\textsuperscript{38}

In the present paper only synthesis of the graphene layers at the C-terminated surface is investigated. No results related to the Si-face are presented; so in order to streamline the presentation, the graphene creation at the Si-terminated surface will not be discussed at all. It is well known that the number of graphene layers could be very high, reaching 40 layers, obtained in a single process. In addition, graphene layers are relatively weakly coupled to the SiC surface, located at a distance of about 3.0–3.2 Å.\textsuperscript{20,39} Thus, this space creates a channel for effective horizontal diffusion of liberated Si atoms. This picture is supplemented by the detailed TEM analysis of graphene layers synthesized on this face. These data are confronted with the results of DFT simulations of the energy barriers for diffusion of Si and C atoms on a C-terminated SiC surface. A proposed hypothetical scenario of the graphene synthesis is built using these two sets of data.

\section*{II. DFT calculation method}

An \textit{ab initio} simulation of the energy barriers for the diffusional motion of carbon and silicon atoms at polar \{0001\} SiC surfaces used a commercially available Vienna \textit{ab initio} simulation package (VASP), based on a plane-wave basis set.\textsuperscript{40–43} The projector-augmented-wave (PAW) approach was used in its variant available in the VASP package.\textsuperscript{44} For the exchange-correlation functional, the local-spin-density approximation (LSDA) was applied. The plane-wave cutoff energy was set to 500 eV. The Monkhorst-Pack k-point mesh was set to \(7 \times 7 \times 1\). The \(4H\)-SiC\{0001\} superlattice was constructed using eight bilayers of Si-C, which was sufficient to avoid a quantum overlap of the termination and real surface quantum states.\textsuperscript{45} Two top SiC layers were relaxed using the conjugate gradient algorithm.

\section*{III. Experimental}

The graphene layers were grown on the carbon-terminated surface of the \(4H\)-SiC \{0001\} substrate in an Epigress VP508 SiC hot-wall chemical vapor deposition (CVD) reactor, heated by an radio frequency generator.\textsuperscript{20,46} Initially, the SiC substrate was etched in the atmosphere of mixed hydrogen and propane (H\(_2\)-C\(_3\)H\(_8\)) at a temperature close to 1600 °C. Subsequently, the substrate was annealed in the argon atmosphere for about 20 min at a gas pressure of 100 mbar and a temperature of 1600 °C. The annealing led to evaporation of the silicon atoms and the creation of the graphene multilayers by less volatile carbon atoms.

High-resolution (HR) TEM observations of the graphene layers were performed using JEOL JEM 3010 transmission electron microscope operating at 300 kV. Cross-sectional TEM specimens were prepared by a standard method, based on mechanically prethinning of the samples followed by an Ar ion milling procedure.

Atomic force microscopy (AFM) images were recorded using the tapping mode in air at ambient pressure using a Nanoscope IIIa.

\section*{IV. Results}

\subsection*{A. Diffusivity of carbon and silicon atoms at C-terminated SiC surface—DFT study}

The energy surface for the silicon and carbon atoms at the C-terminated face is presented in Fig. 1. As shown in Fig. 1 the energy difference between the maximum, being in the “on top” of the topmost C atoms, and the global minimum is
FIG. 1. (Color online) Atomic structure of silicon carbide C-terminated surface and the energy surface of the adsorbed Si and C atoms derived from DFT results: (a) the atomic structure of an SiC surface, (b) the energy surface of the silicon atom, (c) the energy surface of the carbon atom, at the (000 $\bar{1}$)SiC surface. On the right-hand side (d) and (e), the energy profiles along the black line correspond to the distances shown in the diagrams.

The nature of the unexpected behavior is elucidated by the plot of atomic arrangements of the SiC surfaces, presented in Fig. 2. As it is shown, the presence of a Si adatom at a Si-terminated surface weakly affects the atomic structure of the surface. A completely different scenario was obtained for a C adatom at a C-terminated surface. The carbon atom is strongly bound to the neighboring C atoms, removing a Si atom from the lattice to the adsorbed position. Thus a carbon adatom is replaced by a Si adatom and a portion of the flat C plane, vividly resembling graphene. The position of these C atoms corresponds to the $sp^2$-bonding configuration, indicating on the catalytic influence of carbon adatoms. Thus the nucleation of the graphene layer in the presence of carbon adatoms occurs at SiC terraces, not necessarily at SiC steps. This indicates a possibility of creating a large number of independently growing graphene flakes at the (000 $\bar{1}$) SiC surface, which coalesce incoherently, giving rise to grain boundaries and highly dislocated graphene planes. At large strains, the carbon layers are buckled, giving rise to the creation of wrinkles.

It has to be added that the motion of a C atom, located in the transformed graphite-like configuration, needs to overcome a much higher barrier than 1 eV shown in Fig. 1. The middle part of the diagram corresponds to the repositioning Si atom back in the lattice, which is unlikely as the liberated Si adatom moves away. The analytic continuation of the energy curve from the localized position is very steep indication of very high energy needed to remove carbon from the $sp^2$-bonded lattice. Thus the path shows nonanalytic behavior, being composed of the two different energy surfaces in Fig. 1(e).

FIG. 2. Side view of silicon carbide Si- and C-terminated surfaces, with similar adatoms in the equilibrium positions. The grey and black balls correspond to Si and C atoms, respectively.
FIG. 4. Cross-sectional HRTEM images of graphene layers observed in the [11\overline{2}0] SiC orientation, showing the arrangement of 15 carbon layers (a) and filtered image of a few C layers associated with SiC substrate (b).

presented transformation corresponds to irreversible trapping of carbon in the graphene lattice.

It is well recognized that one of the critical steps of the graphene synthesis by silicon removal from SiC is sublimation of silicon atoms. It is therefore essential to determine the energy barrier for direct detachment of silicon adatoms from the two configurations presented in Fig. 2. The energy barrier was determined by DFT calculations from the energy difference between these configurations and those of the Si atoms that are far away from the surface. It turned out that the energy barrier is very high, equal to 6.13 and 6.15 eV for these two configurations, respectively. Thus direct evaporation of silicon atoms is not an effective channel for Si sublimation. The effective Si evaporation channel involves a more complicated molecular scenario, for both cases alike.

B. Structure of graphene layers grown over vicinal 4\textit{H}-SiC surfaces

A typical multilayer graphene, grown on the SiC(000\overline{1}) surface, measured by an optical microscope, is presented in Fig. 3(a). It is shown that the graphene layers are corrugated, with the number of macrosteps, easily visible even at low magnification. These steps are not affected by the crystal edge, and they are related to the step structure developed during the etching procedure. At higher magnification a dense network of smaller defects is visible in AFM image in Fig. 3(b). The defects—wrinkles, about 2 nm high, are mostly created in the neighborhood of the steps. Structure of the defects in multilayer graphene is very strongly dependent on the initial structure of an annealed surface. It is worth noting that our results closely resemble those in Fig. 2 of Ref. 37.

Relatively perfect regions exist in the areas between surface steps. Such regions, showing a flat multilayer graphene structure, are demonstrated on the TEM image in Fig. 4. Annealing at a temperature of T = 1600 °C for t = 20 min leads to growth of about 15 graphene layers [Fig. 4(a)]. It is shown that the defect-free substrate could be transformed into a multilayer graphene with a large number of graphene layers without any structural defects. The HRTEM image of a few graphene layers deposited on the SiC substrate is shown in Fig. 4(b). From HRTEM image analysis, it follows that the first carbon layer is located about 3.0 ± 0.2 Å above the SiC surface. The next carbon layers are at a distance of 3.3 ± 0.2 Å, typical for the interplanar spacing of hexagonal graphite d_{0002} = 3.35 Å. These results are in agreement with previous observations performed for graphene on a C-terminated face.

The flat graphene areas are surrounded by the defective regions, which are related to the SiC morphology, developed during the etching process. These structures originate at the macrosteps, resulting from coalescence of many atomic steps, present at initially vicinal SiC surfaces. TEM structural and diffraction images of the graphene multilayer about 6 nm thick, containing from 20 (upper) to 25 (lower terrace) layers, are presented in Fig. 5. A number of graphene layers at the upper and lower SiC terrace are different, and new C layers are formed underneath the existing thick graphene cover. Formation of the new C layers, adjacent to the ~5-nm-high step, is shown in Fig. 5(a). The magnified area in Fig. 5(c) (inset) presents the transformation of the (0001)SiC atomic planes into the (0001)C planes. In the [¯1100] SiC orientation, on the defocused TEM images, the disintegrated SiC areas are sometimes mapped with characteristic contrast. Every fourth plane in polytype 4\textit{H} of SiC is imaged with light contrast (dashed lines in the inset). This effect is most likely associated

FIG. 5. Cross-sectional TEM image of the graphene structure on the SiC substrate containing a macrostep. Contact of two thick carbon layers originated from two terraces (a) with diffraction pattern from a flat part of graphene (b). Magnified part of a macrostep (marked by arrow) with inset showing details of transition of the planes from SiC to C (c) and diffraction pattern from area includes the step (d). The magnified areas used in the analysis are shown beside the entire diffraction patterns. Diffraction patterns are negatives. Images are in the [1\overline{1}00] SiC substrate orientation.
with a stress caused by atomic rearrangements, as postulated by Harrison et al.\textsuperscript{38} The diffraction images obtained from the flat area of graphene and area with a step are shown in Figs. 5(b) and 5(d), respectively. There is a superposition of two diffraction patterns: first from the substrate structure of the $[1100]4H$-SiC orientation and the second of the diffraction of the carbon (0002)C planes. Figure 5(b) shows the diffraction pattern obtained from flat graphene on the terrace. The measured interplanar spacing between graphene layers $d_{0002} = 3.4 \text{ Å}$ corresponds to the theoretical interplanar distance in the graphite structure $d_{0002} = 3.35 \text{ Å}$. The diffraction pattern from the area of the step shows streaks along the [0001] direction and the additional pair of maxima, reflected from the graphene, in the vicinity of the (0004)SiC spots [Fig. 5(d)]. The measured interplanar spacings of graphene are equal to $d_{0002C} = 3.4 \text{ Å}$ and $d_{0002EG} = 3.7 \text{ Å}$. The split diffraction spots are located along the same direction, indicating a parallel orientation of the graphene atomic planes. The difference in the distance between graphene layers probably results from the match of carbon planes to the SiC planes in the early stage of the formation of carbon structure.

The SiC surface disintegration at the macrosteps and islands is correlated with the presence of the discontinuities of graphene structure (Fig. 6). As is shown in Fig. 6(a) at the top, such leftover islands are related to the creation of the graphene with bending layers. It is marked by dashed lines in Fig. 6(a). The bending of the graphene multilayer that is located higher results from blocking by the lower one. This arrangement is stable until the graphene layers from two levels of SiC surface are disconnected. In a different situation a flattening and connecting of the top carbon layers is observed.\textsuperscript{33} Such flattening of graphene layers in the vicinity of small steps is visible in the bottom right corner in Fig. 6(b). A connection of graphene discontinuities leads to a stacking of C layers parallel to the edge of the SiC macrostep.

Examples of various arrangements of graphene layers with respect to the SiC planes, observed in TEM, are shown in Fig. 7. In the case of a strong bending of the (0001)C planes, almost perpendicular connections with the SiC stacking sequences are observed [Fig. 7(a)]. For macrosteps, the (0001)C planes are situated parallel to the edge of the steps, and for small steps the C planes are located along the (0001)SiC planes—Figs. 7(b) and 7(c), respectively. These three cases of the graphene arrangement are shown graphically in Fig. 7(d). For cases (1) and (2), the new carbon atoms are added consecutively to the present (0001) graphene planes; it is most likely related to the existing covalent atomic bonds between the substrate and graphene. The third case is proper for the creation of new graphene planes, where C atoms from SiC decomposition are quickly bonded with graphene. On the interface of the SiC substrate and graphene layers, the misfit lattice leads to a formation of dislocations in the (0001) basal plane.

Dissolution of the SiC islands causes the creation of a series of characteristic structures, as shown in Fig. 8. The bending of the graphene multilayers is related to the anchoring of C layers on the SiC steps, and this structure terminates growth of carbon layers on the multistep SiC islands—Figs. 8(a) and 8(b). In the area between islands, the graphene layers are rarely observed.

A close relationship between disappearing multistep islands and the bending graphene structures on both side steps is demonstrated in Fig. 9. The terminating structure is created by the ultimate disappearance of the SiC multistep island.
FIG. 8. TEM images of a pair of graphene multilayers having a different thickness: (a) a general view of the graphene structure on the SiC islands, (b) and (c) magnified parts of the carbon layers located at the edge of the two SiC islands.

and a direct interaction between these bending structures. After coalescence, the graphene multilayers that are located higher have an excess of length in respect to the lower layers—Fig. 9(b). Ultimately these structures will create a network of defects such as wrinkles and delaminations.

Images showing detachment of the graphene multilayers are presented in Fig. 10. The location of these defects is related to the morphology of the SiC surface, resulting from the etching of the substrate before annealing at high temperature.

A different microstructure of the graphene layer synthesized on a C-terminated SiC surface was evidenced in a number of features, such as a possibility of the growth of a large number of layers, the absence of a buffer layer, a relatively large distance between the SiC topmost layer and the first carbon layer,20 resulting in a very weak van der Waals coupling to the substrate,47 and a possible rotation of the carbon layers.48 From the above results, it can be seen that this structure influences not only the structure but also the formation of the carbon layer, affecting the possible growth mechanism. From the above results, it follows that the wide space between the SiC topmost layer and the carbon layer constitutes a wide channel allowing for the effective planar diffusion of both carbon and silicon atoms. The silicon atoms escape through the channels created by the bending graphene structures. The leftover carbon atoms are incorporated into the topmost carbon layers of SiC, converting it into a sp2-bonded structure increasing the graphene thickness. The process proceeds without any energy barrier. Such a scenario is confirmed by the observed dependence of graphene layers number on the annealing time that strongly indicates that the growth kinetics of graphene is limited by Si evaporation and two-dimensional Si diffusion.49

The Si-terminated SiC surface migration of both Si and C atoms is possible at the temperature close to 1600 °C. Nevertheless, the creation of a buffer layer, covalently bound to the silicon atoms blocks this diffusion channel, thus preventing growth of new graphene layers under the cover of the topmost graphene. Therefore, growth of the graphene layer is terminated after creation of a few carbon layers.

FIG. 9. TEM images of the disappearing SiC islands: (a) a few bending graphene multilayers and (b) coalescence of a pair of bending layers.

FIG. 10. TEM images showing detachment of the multilayer graphene: (a) as a result of disappearance of the SiC island, marked by the arrow, (b) and (c) wrinkles with different sizes of channels on the flat surface, and (d) wrinkle on the islands.

V. CONCLUSIONS

The combined TEM and DFT investigations provide a scenario grasping the basic features and essential differences between the growth of graphene layers on carbon-terminated SiC surfaces. The above-presented DFT data indicate the basic feature of the graphene synthesis on both surfaces of SiC crystals at temperatures about 1600 °C used in the sublimation of a C-terminated SiC substrate to obtain carbon graphene layers.

At a C-terminated SiC(0001) surface, carbon adatoms are incorporated into a graphenelike lattice liberating silicon atoms from the top atomic layer. These silicon adatoms could travel far away across these terraces. The essential fact is that carbon layers are not covalently attached to the (0001)SiC surface, thus silicon atoms diffuse in the channel underneath to find defects, such as wrinkles, which serve as an ultimate outlet of the silicon excess. The carbon atoms do not diffuse at all; they serve as graphene nucleation centers and building matter.

TEM data demonstrates a possibility of a growth of an unlimited number of graphene layers on C-terminated surfaces. The growth is supported by liberation and out-diffusion of silicon atoms from the SiC lattice. The main channel is diffusion of silicon atoms underneath the graphene cover. These data show that wrinkles, arising from the coalescence of independently grown graphene flakes, could additionally facilitate escape of silicon adatoms from the channel underneath the thick graphene layers. The data indicate a large variety of defects present in these layers, which is caused by the independent nucleation of graphene flakes under the thick graphene on the top. Thus the growth of high-quality graphene at a C-terminated SiC surface is problematic.

Direct silicon sublimation from terraces needs to overcome a very high energy barrier, above 6 eV, which renders this channel ineffective. Thus, another escape route has to be identified to create a full, coherent picture of the graphene growth by silicon sublimation at high temperatures.
ROLE OF STRUCTURE OF C-TERMINATED 4H-SiC

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