Layer-by-Layer Graphene Growth on β -SiC/Si(001)

Victor Yu. Aristov,^{1,2,} Alexander N. Chaika,^{2,3,*} Olga V. Molodtsova,^{1,4,*} Sergey V. Babenkov,^{1,5} Andrea Locatelli,⁶ Teyfik Onur Menteş,⁶ Alessandro Sala,^{6,7} Dmitrii Potorochin,^{1,4,8} Dmitry Marchenko,⁹ Barry Murphy,³ Brian Walls,³ Kuanysh Zhussupbekov,³ Igor V. Shvets³*

¹Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, D-22607 Hamburg, Germany

²Institute of Solid State Physics of the Russian Academy of Sciences, 2 Academician Ossipyan Street, Chernogolovka, Moscow District, 142432 Russian Federation

³CRANN, School of Physics, Trinity College Dublin, Dublin 2, Ireland

⁴National Research University of Information Technologies, Mechanics and Optics, Kronverksky prospekt 49, 197101 Saint Petersburg, Russian Federation

⁵Institut für Physik, Johannes Gutenberg-Universität, Staudingerweg 7, D-55099 Mainz, Germany

⁶Elettra Sincrotrone Trieste S.C.p.A., S.S. 14 km 163.5 in AREA Science Park, I-34149 Basovizza, Trieste, Italy

⁷Present address: Department of Physics, University of Trieste, via Valerio 2, I-34127 Trieste, and CNR-IOM, S.S. 14 km 163.5 in AREA Science Park, I-34149 Trieste, Italy

⁸Institute of Experimental Physics, TU Bergakademie Freiberg, Leipziger Str. 23, Freiberg, D-09599, Germany

⁹Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Str. 15, D-12489 Berlin, Germany

* Address correspondence to: victor.aristov@gmail.com; chaika@issp.ac.ru;

olga.molodtsova@desy.de

Abstract

The mechanism of few-layer graphene growth on the technologically-relevant cubic-SiC/Si(001) substrate is uncovered using high-resolution core-level and angle-resolved photoelectron spectroscopy, low-energy electron microscopy, and micro-spot low-energy electron diffraction. The thickness of the graphitic overlayer supported on the silicon carbide substrate and related changes in the surface structure are precisely controlled by monitoring the progress of the surface graphitization *in-situ* during high-temperature graphene synthesis, using a combination of micro-spectroscopic techniques. The experimental data reveal gradual changes in the preferential graphene lattice orientations at the initial stages of the few-layer graphene growth on SiC(001) and can act as reference data for controllable growth of single-, double-, and triple-layer graphene on silicon carbide substrates.

KEYWORDS: graphene; nanodomains; β -SiC; ARPES; LEEM; μ -LEED; XPS

The amazing properties of graphene are extremely appealing for both fundamental research and technological applications.^{1,2} Due to the high mobility and large mean free path of the charge carriers,³ graphene may become a competitive alternative to silicon in electronic devices. Graphitization of a silicon carbide surface⁴⁻⁶ allows the fabrication of few-layer graphene supported by a very stable wide-gap semiconductor substrate. Epitaxial few-layer graphene synthesized on hexagonal silicon carbide (α -SiC) substrates in ultra-high vacuum (UHV) and argon atmospheres^{5,6} exhibits almost ideally linear characteristics in the electron spectrum⁷ as well as two-dimensional electron transport properties⁵ similar to those observed in high-quality exfoliated monolayer graphene.¹ However, few-layer graphene on α -SiC is unsuitable for numerous applications because of the small size and high cost of bulk single-crystalline wafers.

Synthesis on (cubic) β -SiC/Si(001) wafers⁸⁻¹⁹ can provide a more viable method for graphene mass-production on low-cost semiconducting substrates, with the advantage of being compatible with existing silicon processing technology. Contrary to graphene grown on hexagonal SiC substrates, which is strongly bonded with the three-fold symmetric substrate, graphene on β -SiC/Si(001) demonstrates the physical properties of quasi-free-standing graphene and is very weakly interacting with the substrate.⁹ Moreover, utilizing vicinal SiC/Si(001) wafers one can synthesize substrate-supported nanoribbon systems with self-aligned domain boundaries.²⁰ The ability to open a sizable energy gap in nanostructured graphene and develop carbon-based electronic devices using nanoribbon structures has been discussed in literature² but few demonstrations of controllable synthesis of self-aligned graphene nanoribbons on technologically relevant substrates have been reported so far. The self-aligned trilayer graphene nanoribbons on β -SiC(001) are known to exhibit useful functionalities such as an energy transport gap on the order of 1 eV,²⁰ large positive in-plane magnetoresistance,²¹ and the

potential to work as a spin filter,²¹ opening realistic opportunities for electronic and spintronic applications. The keys to fabricating useful graphene-based nanostructures are of course the capability to control the lattice and boundary orientations, but the ability to control the layer thickness *in-situ*, during the few-layer graphene synthesis, is also vital. The current work addresses this last challenge for the growth of graphene structures on cubic-SiC.

The thickness of the graphene film grown on SiC substrates is known to simultaneously depend on the vacuum conditions, the temperature during synthesis, and its duration.²² Therefore, it is highly desirable to control the number of the synthesized graphene layers *in-situ*, during the few-layer graphene growth. In this work, we combine high-resolution micro-spot X-ray photoemission spectroscopy (μ -XPS), angle-resolved photoelectron spectroscopy (μ -ARPES), low-energy electron microscopy (LEEM), and micro low-energy electron diffraction (μ -LEED) to show that it is indeed possible to control the thickness of the graphene overlayer on the silicon carbide substrate *in-situ* during the high-temperature UHV synthesis and stop the few-layer graphene growth when the desired number of layers is synthesized. Moreover, the core-level XPS data obtained in these studies can be used as a reference to distinguish between mono-, bi-, and trilayer graphene synthesized on β -SiC surfaces using XPS techniques only. Utilizing the dynamic-XPS synchrotron facilities with real-time control of the C 1s core level spectra shape, working *in-situ* during the sample heating with high energy and time resolution,²³ these data can help to controllably synthesize mono-, bi-, and trilayer graphene without the need to follow a particular recipe (pressure in the vacuum chamber, growth temperature, the temperature *versus* time cycle, *etc.*) or apply a full set of highly sophisticated micro-spectroscopic techniques, enabling a greater range of experimental and industrial processes to be applied to this important material. Importantly, our data reveal the transformations the surface undergoes during the layer-

by-layer graphene growth on β -SiC/Si(001) in UHV at high temperatures. In particular, the results stress the role of the $c(2\times 2)$ reconstruction and linear defects in the formation of nanostructured graphene on β -SiC(001).

RESULTS AND DISCUSSION

UHV-synthesized, few-layer graphene on β -SiC(001) typically exhibits two types of meta-structures on different length scales. The first meta-structure is a family of four nanodomains, each containing a single lattice orientation, with dimensions on the nanometer-scale. This is due to the four different preferential lattice orientations the graphene adopts, which are each rotated by $\pm 13.5^\circ$ relative to the two orthogonal $[110]$ and $[1-10]$ directions of the SiC crystal lattice.⁹⁻¹¹ As discussed in our previous studies,²⁰ this 27° rotation of graphene lattices in the neighboring nanodomains can be related to the formation of a periodic structure along the domain boundaries. Notably, the same rotation angle between the graphene lattices separated by a domain boundary was also observed in electron microscopy studies of polycrystalline monolayer graphene grown on copper foils by chemical vapor deposition.²⁴

The second meta-structure is a pair of micrometer-scale anti-phase domains (APDs), where the underlying β -SiC crystal lattices are rotated by 90° . The graphene nanodomains are connected to one another *via* boundaries aligned either with the $[110]$ or $[1-10]$ directions in the two different types of micrometer-sized APDs, with a single pair of $\pm 13.5^\circ$ -rotated nanodomains present within each APD, generally resulting in four overall orientations.⁹⁻¹¹

Figure 1a shows a typical high-resolution STM image of few-layer graphene on β -SiC(001), measured inside one of the APDs. The nanodomains have widths of several nanometers and their boundaries are aligned with one of the $\langle 110 \rangle$ directions. The graphene layer is randomly rippled inside the nanodomains²⁵ and bent near the boundaries with typical

radii of curvature of the order of several nanometers.²¹ To stress the atomic resolution on this highly corrugated surface, the dz/dx differentiated image is shown in Figure 1b. Although the differentiated image shows two dominating hexagonal lattice orientations rotated relative to one another by 27° (Figures 1c and 1e) in accordance with our earlier works,⁹⁻¹¹ it also reveals a minor fraction of a third graphene lattice orientation (Figure 1d), which has not been discussed in our previous studies of the few-layer graphene/SiC/Si(001) systems. As can be seen from the images presented in Figures 1c-e, the two preferential graphene lattice orientations (Figures 1c and 1e) are approximately symmetrically rotated relative to the third lattice orientation (Figure 1d).

To obtain information about the uniformity of the surface atomic structure on the micro- and millimeter scale we have conducted LEEM and μ -LEED experiments on the same few-layer graphene/SiC/Si(001) sample. μ -LEED data from different surface areas of our sample reveal that a total of six preferential graphene lattice orientations can occur, highlighted by the red, blue, and yellow hexagons in Figures 1g and 1h. According to the μ -LEED studies, three preferential graphene lattice orientations are systematically observed in each individual micrometer-sized APD. For example, the μ -LEED patterns measured from the surface areas labeled (G) and (H) in the dark-field (DF) LEEM image presented in Figure 1f are rotated by 90° (Figures 1g and 1h), featuring two distinct nanodomain families in the APDs (dark and bright areas in the DF LEEM image). From the six preferential orientations, four graphene lattices (red and blue hexagons in Figures 1g and 1h) are rotated by $\pm 13.5^\circ$ relative to the two orthogonal $\langle 110 \rangle$ directions, in accordance with our previous works.⁹⁻¹¹ The other two graphene lattices (yellow hexagons) are aligned with the two $\langle 110 \rangle$ directions of the β -SiC crystal lattice, as can be concluded from the positions of the graphene lattice and substrate spots (marked by dashed

rectangles in Figures 1g and 1h). The origin of these two non-rotated graphene domains on β -SiC(001) will be clarified below using complementary *in-situ* LEEM, μ -LEED, and ARPES measurements conducted during the layer-by-layer graphene growth on β -SiC/Si(001) in UHV. Note that the image shown in Figure 1f was obtained using one of the graphene first-order diffraction spots. However, identical DF LEEM images can be obtained using the other diffraction spots belonging to the same family, suggesting that the individual graphene nanodomains are much smaller than the area probed by μ -LEED (500 nm), which is in agreement with the STM experiments (Figure 1a).

Figure 2 shows μ -LEED, LEEM I - V , ARPES and μ -XPS data obtained from the same region of another β -SiC/Si(001) sample in the course of high-temperature surface graphitization. To illustrate the consecutive surface transformations upon heating in UHV, Figure 2 shows micro-spectroscopic data corresponding to the $c(2\times 2)$ reconstruction (a), mono- (b), bi- (c), and trilayer graphene (d) fabricated consecutively on the β -SiC/Si(001) sample. The experimental data for only one of the APDs are shown in Figure 2, because the other demonstrates identical characteristics. The number of synthesized graphene layers is estimated from the number of peaks in the low energy part of the electron reflectivity curves (I - V) presented in Figures 2b-d (top). In brief, the number of oscillations equals the number of graphene layers.^{26,27} Although it has been shown recently^{28,29} that few-layer graphene films with the bottom layer strongly bonded with the substrate can produce $n-1$ minima on the I - V curve (where n is the number of the graphene layers), we believe that this is not the case for graphene grown on β -SiC(001). As demonstrated in several studies, the graphene overlayer is very weakly bonded with the β -SiC(001) surface and, therefore, reveals the physical properties and electron spectrum typical of quasi-freestanding graphene.⁸⁻¹¹ In this case, the number of oscillations is expected to match the

number of the graphene layers.²⁹ As can be seen from Figures 2b-d, the film thickness gradually increases with increasing annealing temperature and duration of the thermal treatment.

The graphs in Figure 2 (bottom) depict the evolution of the C 1s spectra (acquired in normal emission from a selected circular sample area, $d = 2 \mu\text{m}$) at 325, 330, 400, and 450 eV photon energies for a carbon-terminated $\beta\text{-SiC}(001)\text{-c}(2\times 2)$ surface (a) and graphene monolayer (b), bilayer (c), and trilayer (d). The selected photon energies correspond to different surface sensitivities of the XPS measurements with the highest sensitivity achieved at 325 and 330 eV.

To obtain qualitative information about the $\beta\text{-SiC}(001)$ surface transformations at high temperatures and to independently estimate the change in the graphene film's thickness upon heating, the C 1s spectra were decomposed into individual components corresponding to different carbon atom chemical bonds. The XPS spectra were analyzed with CasaXPS data processing software (version 2.3.16 PR 1.5). Prior to decomposition, the spectra were normalized to the maximum intensity. The multi-peak fitting of the C 1s spectra taken from $\beta\text{-SiC}(001)\text{-c}(2\times 2)$ and graphene/SiC(001) systems was performed using a convolution of either symmetric Gaussian-Lorentzian (GL) lineshapes or asymmetric Doniach-Sunjić (DS) profiles³⁰ and Shirley background.³¹ The symmetric line shapes obtained using a mixed Gaussian and Lorentzian function were utilized for the bulk SiC and surface $\beta\text{-SiC}(001)\text{-c}(2\times 2)$ components in the high-resolution XPS spectra, while the asymmetric line shapes were utilized for graphene contribution. As can be seen from Figure 2 these line profiles reproduce reasonably well the experimental core-level C 1s spectra. The results of the C 1s spectra decomposition are presented in Figure 2 together with the experimental data (black circles) where the red line is the graphene peak (Gr), the blue line is the bulk SiC peak, the brown line is the surface $\beta\text{-SiC}(001)\text{-c}(2\times 2)$ component, the green dashed line is the background and the cyan line is the envelope. During the

multi-peak fitting we kept the position of the bulk SiC peak fixed at 282.9 eV and varied the line widths, energy positions and intensities of the surface components. Tables 1 and 2 summarize the line shape parameters for each component in the C 1s spectra of β -SiC(001)-c(2 $\times$ 2) and graphene/SiC/Si(001) systems, individual peak intensities calculated as areas under the corresponding lines, and full widths at half maximum (FWHM) for each individual component.

One can note that each spectrum displays only two main components. For the β -SiC(001)-c(2 $\times$ 2) reconstruction (Figure 2a and Table 1) two symmetric components with binding energies of 282.9 and 283.95 eV correspond to bulk and surface contributions, respectively. The bulk component was fitted well using a mixed function obtained by a product of (70%) Lorentzian and (30%) Gaussian [GL(70)]. The β -SiC(001)-c(2 $\times$ 2) surface component was fitted well using the mixed (65%) Lorentzian and (35%) Gaussian function [GL(65)]. For the core level C 1s spectra measured from the graphene/SiC/Si(001) systems each spectrum can be decomposed onto symmetric GL and asymmetric DS lines corresponding to the bulk SiC and graphene components, respectively. The asymmetry of the DS graphene lines (given in parentheses in Table 2) varied between 0.026 and 0.032 for the spectra measured at different photon energies and different coverages. The comparison of the C 1s spectra measured from the β -SiC(001) surface before and after single layer graphene synthesis shown in the bottom part of Figure 2a shows that the Gr component is shifted substantially further to higher binding energies compared to the c(2 $\times$ 2) component. Therefore, the start of the graphene growth on the β -SiC/Si(001) wafers can be easily traced using the positions of the surface components in the C 1s XPS spectra. The Gr peak is shifted by $\sim$ 1.65 eV towards higher binding energies relative to the bulk SiC peak located at 282.9 eV. The energy positions of the Gr component varied slightly (within 0.05 eV) with increasing graphene film's thickness from one to three monolayers. The

relative intensity of the graphene component in the XPS spectra increases both with decreasing photon energy and increasing number of graphene layers. The dependence of the relative intensities of the bulk SiC and graphene components on the photon energy corresponds to the energy dependence of the electron mean free path³²⁻³⁴ which is specific for each particular material. Since our XPS data were obtained in the normal emission geometry, the core-level spectra and results of the decomposition shown in Figures 2b-d and Table 2 can be utilized as reference values to distinguish between mono-, bi-, and trilayer graphene synthesized on β -SiC substrates using C 1s XPS spectra measured at these photon energies in normal emission geometry. To some extent, these data can also be used for thickness determination in few-layer graphene synthesized on hexagonal silicon carbide surfaces, because the substrate, graphene, and buffer layer components in C 1s spectra of graphene/ α -SiC surfaces are usually energetically separated by more than 1 eV.

The data presented in Table 2 reveal a slight asymmetry (~ 0.03) of the C 1s spectra measured from the graphene/SiC(001) systems. At the same time, the C 1s spectra taken from the c(2 $\times$ 2) reconstructed surface prior to graphene synthesis could be fitted well using two totally symmetric (bulk and surface) components (Table 1). The slight asymmetry of the C 1s photoemission lines after surface graphitization may be related to an increase in the surface conductivity after the few-layer graphene fabrication. No other components except Gr and bulk SiC were detected in the C 1s spectra of graphene/SiC(001) systems, confirming the absence of strong chemical interactions between the graphene overlayer and β -SiC, which would provide additional components with higher binding energies in the C 1s spectra.^{11,19} The presence of a very strong Gr component in the C 1s spectra taken from the graphene/SiC(001) system that

exhibits one minimum in the I - V curves supports the validity of the method^{26,27} used for graphene thickness determination.

The middle row of images in Figures 2b-d shows the ARPES intensity constant-energy maps taken at $E = E_F - 0.5$ eV and $E = E_F - 1.5$ eV as a function of graphene coverage. The ARPES constant-energy maps taken at 0.5 and 1.5 eV binding energy prove the conical shape of the Fermi surface for all preferential graphene nanodomain lattice orientations at the three coverages hereby considered. This is further illustrated by the constant-energy ARPES intensity maps in Figure 3, showing the electronic structure in the k_x - k_y plane for one of the Dirac cones measured at 1 ML (monolayer) coverage. The conical shape is shown by the maps taken at different binding energies. They reveal an increase in the circle radius with increasing binding energy. The deviation from the circular shape observed in ARPES experiments at $E_B > 1.4$ eV can be related to photoexcitation effects³⁵ or trigonal warping.³⁶

Notably, both μ -LEED and ARPES maps measured for the 1 ML graphene/SiC(001) system reveal almost the same intensities for the features corresponding to the non-rotated and $\pm 13.5^\circ$ -rotated domain lattices. The intensity of the diffraction spots and ARPES features corresponding to the non-rotated domains is systematically suppressed when graphene coverage increases from 1 ML (Figure 2b) to 2 ML (Figure 2c) and then to 3 ML (Figure 2d). It is clear that the two non-rotated graphene lattice orientations (aligned with the orthogonal $\langle 110 \rangle$ β -SiC crystal lattice orientations) are observed only at the beginning of the β -SiC(001) surface graphitization. In contrast, when graphene coverage reaches several monolayers, most of the surface is covered by nanodomains with four preferential graphene lattice orientations, rotated $\pm 13.5^\circ$ relative to the two orthogonal $\langle 110 \rangle$ directions. Even at 3 ML coverage, the intensity of

the non-rotated graphene features is substantially smaller than that of the $\pm 13.5^\circ$ rotated domain variants, as Figure 2d illustrates.

Figure 4 shows (a) LEEM and (b-e) ARPES data obtained from the 1 ML graphene/SiC(001) sample. Figures 4b and 4c show the constant energy ARPES intensity maps measured from different APDs marked as B and C in Figure 4a. The ARPES maps from the APDs are rotated by 90° relative to one another in the same way as μ -LEED patterns shown in Figures 1g and 1h. Figures 4d and 4e show the dispersions obtained by a cut through the experimental data at coordinates which correspond to the dashed lines in Figures 4b and 4c. Eighteen cones showing qualitatively the same linear dispersion are observed both on Figures 4d and 4e, proving that domains with all six preferential lattice orientations at 1 ML graphene coverage exhibit the same electronic spectrum typical of freestanding monolayer graphene.

The prevalence of the μ -LEED and ARPES features associated with the non-rotated graphene domains in the initial phases of the annealing treatment, corresponding to sub-monolayer coverages, is a key factor to understand the mechanism of the graphene growth on the β -SiC/Si(001) wafers. As we will see below, the well-known carbon-terminated β -SiC(001)- $c(2\times 2)$ reconstruction³⁷⁻⁴⁰ can be considered a predecessor of graphene during the sample heating. Aiming at illustrating this concept, Figures 5a-c demonstrate how the non-rotated hexagonal graphene domain lattice with three-fold symmetry can match the β -SiC(001)- $c(2\times 2)$ reconstruction.

As can be seen in Figures 5a and 5c, if the lattice parameters of the $c(2\times 2)$ square unit cell (red square) are doubled, it matches quite well to a slightly distorted square (green lines) connecting carbon atoms of the graphene lattice, which can be laterally translated to cover the entire $c(2\times 2)$ surface by the graphene overlayer. The mismatch of these two quadrilaterals is

below 2%, which is likely sufficient to initiate the growth of the non-rotated graphene monolayer on β -SiC(001)-c(2 $\times$ 2). Such a small mismatch cannot be found for other possible (n $\times$ 2) and (1 $\times$ 1) reconstructions of β -SiC(001).⁴¹⁻⁴⁴ Therefore, we conclude that the β -SiC(001)-c(2 $\times$ 2) reconstruction is a necessary step for enabling successful high-temperature graphene synthesis on β -SiC(001). This is confirmed by our experimental observations showing that the graphene overlayer can be grown only after consecutive fabrication of the well-known β -SiC(001) surface reconstructions with increasing temperature³⁷⁻⁴⁴ but cannot be formed immediately on the carbon-rich (1 $\times$ 1) reconstructed surface. This result is in accordance with previous STM studies of SiC(111),⁴⁵ where the transition from a typical ($\sqrt{3}\times\sqrt{3}$)R30° to an intermediate (3/2 $\times\sqrt{3}$)R30° structure very close to the graphene (2 $\times$ 2) unit cell was observed before the formation of the honeycomb graphene (1 $\times$ 1) overlayer.

Figure 5a suggests that carbon dimers of the c(2 $\times$ 2) reconstruction (dotted black oval in Figure 5a, highlighted as large red spheres in Figures 5a and 5b) may be considered the smallest building blocks of the non-rotated graphene lattice, since the distance between carbon atoms in the dimers (1.31 Å) is reasonably close to that of the graphene honeycomb lattice (1.46 Å). In order for graphene growth to begin, it is clear from Figure 5a that extra carbon atoms must be present on the c(2 $\times$ 2) surface to provide the substantially higher density of carbon atoms in the graphene lattice. Additional carbon atoms are actually observed during STM studies as random bright protrusions or linear <110>-directed atomic chains decorating the β -SiC(001)-c(2 $\times$ 2) reconstruction (Figure 5e). The adatoms form chemical bonds with the dimers of the c(2 $\times$ 2) reconstruction at high temperatures and form the nanodomains with their graphene lattice non-rotated relative to the <110> direction.

These non-rotated domains cannot grow to micrometer scale due to the presence of extra-carbon atoms/clusters and linear defects on the β -SiC(001)-c(2×2) surface (Figure 5e) and the mismatch between the c(2×2) and graphene lattices, which produces strain in the overlayer. However, the reasonably small mismatch of the c(2×2) and the graphene lattice (Figure 5a) leads to the domination of the two non-rotated lattice variants (rotated 90° with respect to one another due to the SiC APDs) in the graphene/SiC(001) system at very small, submonolayer coverages. After the completion of the first graphene monolayer, the next layers presumably grow on top of the first monolayer starting from the defects on the surface (either steps or <110>-directed linear atomic chains), which is supported by the very fast suppression of the non-rotated domain features in the μ -LEED and ARPES maps with increasing graphene coverage (Figure 2). The second and third graphene layers most probably start to grow from the linear defects that define the positions and orientations of the nanodomain boundaries in the few-layer graphene/SiC(001) (Figure 5f). In this case, it is energetically favorable for graphene lattices in neighboring nanodomains to be rotated by 27° relative to one another, as the model in Figure 5d (bottom part) illustrates. The comparison of the atomic resolution STM images of the β -SiC(001)-c(2×2) and trilayer graphene/SiC(001) clearly shows the coincidence of the carbon atomic chain directions in the former structure (Figure 5e) and nanodomain boundary directions in the latter (Figure 5f).

CONCLUSIONS

We have presented a step-by-step *in-situ* study of the UHV synthesis of few-layer graphene on β -SiC/Si(001) wafers performed using complementary high-resolution spectroscopic methods and low energy electron diffraction. ARPES and μ -LEED data demonstrate that graphitization of the β -SiC(001) surface starts from the formation of nanodomains with their graphene lattices aligned relative to the silicon carbide crystal lattice. The growth of such non-rotated graphene domains is

avored by the small mismatch between the β -SiC(001)-c(2 $\times$ 2) and graphene lattices. At sub-monolayer coverages, these non-rotated graphene domains dominate, with the non-rotated and rotated domains coexisting in the first completed monolayer. The following graphene layers start growing from the linear defects of the substrate (steps or carbon atomic chains). The lattices in the top graphene layers are preferentially rotated by $\pm 13.5^\circ$ relative to the two orthogonal $\langle 110 \rangle$ directions of β -SiC. The *in-situ* core-level μ -XPS studies conducted in the course of the few-layer graphene synthesis reveal only two components corresponding to the substrate and the overlayer, demonstrating the very small interaction between the few-layer graphene and β -SiC(001). The results of the C 1s spectra decomposition performed in this work can be used as a reference to distinguish between mono-, bi-, and trilayer graphene using XPS data obtained in the normal emission geometry with 330, 400, and 450 eV photon energies. They can also help to stop the synthesis procedure in fast dynamic-XPS stations with real-time control of the core level spectra shape,²³ when a desirable number of graphene layers (1, 2, or 3 ML) is synthesized.

METHODS

Experiments were performed using the Spectroscopic Photoemission and Low Energy Electron Microscope (SPELEEM) at the Nanospectroscopy beamline of the Elettra synchrotron (Trieste). This microscope offers true multi-method capability for sample characterization within a single vacuum system, thus avoiding exposure of the sample to ambient conditions after preparation or characterization with different techniques. Essentially, the SPELEEM combines low energy electron microscopy with energy-filtered photoemission electron microscopy. Thus, it can either use low energy electrons or soft X-rays to probe solid surfaces, which can be imaged either in real or reciprocal space, after collecting photoelectrons or elastically backscattered electrons.

Micro-spot diffraction (μ -LEED), angle-resolved photoelectron spectroscopy (μ -ARPES), and X-ray photoemission spectroscopy measurements (μ -XPS) are performed after inserting illumination or field limiting apertures within the optical column of the instrument, enabling the selection of suitable areas of interest of micrometer size. The smallest illumination aperture permits the illumination of a region of only 500 nm in diameter, defining the lateral resolution in μ -LEED experiments. The smallest field limiting aperture used in μ -ARPES is 2 μ m. All measurements were carried out at a base pressure of less than 1.0×10^{-10} mbar; the sample temperature was monitored using a W₄Re₉₆/W₂₅Re₇₅ thermocouple.

Cubic-SiC thin films with a thickness of ~ 1 μ m grown on on-plane Si(001) wafers were used in the experiments. The samples were prepared as follows. Firstly, a prolonged (12 hours) annealing was carried out in UHV at 400°C to degas the sample and its holder. Subsequently, the sample was transferred to the main measurement chamber equipped with LEEM, μ -LEED, μ -ARPES, μ -XPS techniques. Few-layer graphene was prepared in the main chamber using Si-atom sublimation followed by high-temperature surface graphitization.⁸⁻¹¹ Namely, after the deposition of several monolayers of silicon onto the clean, carbon-rich β -SiC(001)-(1 $\times$ 1) surface, the sample was annealed using electron beam heating. Short (5 seconds) flash heating cycles at gradually increasing temperatures were applied to the sample while monitoring the surface structure constantly by μ -LEED and μ -XPS after each consecutive flash. The pressure in the spectrometer chamber during the sample heating did not exceed 5×10^{-9} mbar. This treatment at temperatures above 1000°C causes the sublimation of Si from the SiC, which manifests as various surface reconstructions. The consecutive formation of the (3 $\times$ 2), c(4 $\times$ 2) and c(2 $\times$ 2) reconstructions³⁶⁻⁴³ was observed by LEED during sample heating in the temperature range of 1000-1200°C. The μ -LEED pattern and C 1s core level spectra taken in bulk- and surface-

sensitive regimes from the β -SiC(001)-c(2 $\times$ 2) reconstruction prepared prior to graphene synthesis are shown in Figure 2a. Finally, the temperature of the β -SiC/Si(001) wafer was increased to 1250°C and graphene spots were observed in the μ -LEED patterns. The first graphene monolayer (Figure 2b) was formed after 10 short flashes at this temperature. For the fabrication of 2 and 3 ML graphene on β -SiC(001) (Figure 2c and 2d), 50 and 100 flash heating cycles, respectively, were applied at 1300°C to the sample. Prior to LEEM, μ -LEED, and μ -XPS characterization, the sample temperature was stabilized to 80°C, which minimized thermal drifts during cool down from synthesis towards room temperature.

Although our LEEM and μ -XPS experiments showed uniform thickness of the graphene coverage on the micrometer-scale, a slight monotonous change of the local thickness could be observed on millimeter-scale surface areas. This was related to variations in the local temperatures during the few-layer graphene synthesis which can hardly be avoided when applying electron beam heating (the sample regions located closer to the electron source are heated to higher temperatures). This effect can be minimized using direct current sample heating. As shown in our earlier LEEM studies,⁹ uniform-coverage, few-layer graphene on the millimeter scale can be synthesized using this approach. Moreover, the few-layer graphene on β -SiC(001) reveals uniform electronic properties on micro- and millimeter-scales, which is very important for potential applications.

As an example, Figure 6 shows uniform contrast in the photoemission electron microscopy (PEEM) images of trilayer graphene prepared using the direct current sample heating (Figure 6a,b). There is only a slight variation in intensity across the sample and no detected variations in the work function, except at the APD boundaries (Figure 6c, green line), where a slight work function reduction of about 50 meV is observed. The PEEM measurements were

done at the Russian-German Laboratory of BESSY II, Berlin, using the Omicron FOCUS IS-PEEM microscope with a retarding energy filter and Hg discharge lamp (4.9 eV photon energy).

The local thickness of the graphene film during the overlayer growth (Figure 2) was determined by measuring its low energy electron reflectivity (I - V curves).²⁶⁻²⁹ For graphene coverages corresponding to one, two, and three monolayers, core-level μ -XPS and ARPES measurements (Figures 2-4) were carried out. To prove the conical spectrum of the synthesized few-layer graphene, ARPES intensity maps were measured using photon energies in the range of 40-50 eV. The undulator was set to produce light polarized in the plane of the synchrotron orbit, *i.e.* (predominantly) p -polarized radiation incident on the sample at 16° grazing incidence from the vertical plane. Energy and momentum resolutions during the ARPES measurements were 300 meV and 0.08 Å⁻¹, respectively. The core-level μ -XPS spectra were measured from micrometer-sized surface areas in normal emission geometry using a wide range of photon energies up to 1000 eV with resolving power up to 4,000 at 400.8 eV. After spectroscopic measurements, the few-layer graphene/SiC/Si(001) sample was *ex-situ* characterized by scanning tunneling microscopy (STM) at room temperature and liquid nitrogen temperature using GPI-300 and Createc microscopes, respectively. Single crystalline W[111] and W[001] tips^{46,47} were utilized in the STM experiments. No drift corrections were applied to the STM images shown in Figure 1.

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgment: This work was partially supported by the Russian Academy of Sciences, the Russian Foundation for Basic Research (Grant Nos. 17-02-01139, 17-02-01291), Science Foundation Ireland (Grant No. 12/IA/1264), Erasmus plus mobility grant (2016-1-IE02-KA107-

000479), and BMBF (Grant No. 05K12KE1). D.P. thanks the Ministry of Education and Science of the Russian Federation (Project 3.3161.2017/4.6). K.Z. would like to acknowledge the support of the Kazakh government under the Bolashak program.

AUTHOR INFORMATION

Corresponding Authors

* victor.aristov@gmail.com; chaika@issp.ac.ru; olga.molodtsova@desy.de

REFERENCES AND NOTES

1. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.
2. Chen, Z.; Lin, Y.-M.; Rooks, M. J.; Avouris, P. Graphene Nano-Ribbon Electronics. *Phys. E Low-dimensional Syst. Nanostructures* **2007**, *40*, 228–232.
3. Castro Neto, A. H.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. The Electronic Properties of Graphene. *Rev. Mod. Phys.* **2009**, *81*, 109–162.
4. Van Bommel, A. J.; Crombeen, J. E.; Van Tooren, A. LEED and Auger Electron Observations of the SiC(0001) Surface. *Surf. Sci.* **1975**, *48*, 463–472.
5. Berger, C.; Song, Z.; Li, T.; Li, X.; Ogbazghi, A. Y.; Feng, R.; Dai, Z.; Marchenkov, A. N.; Conrad, E. H.; First, P. N.; de Heer, W. A. Ultrathin Epitaxial Graphite: 2D Electron Gas Properties and a Route toward Graphene-Based Nanoelectronics. *J. Phys. Chem. B* **2004**, *108*, 19912–19916.
6. Emtsev, K. V.; Bostwick, A.; Horn, K.; Jobst, J.; Kellogg, G. L.; Ley, L.; McChesney, J.

- L.; Ohta, T.; Reshanov, S. A.; Röhrl, J.; Rotenberg, E.; Schmid, A. K.; Waldmann, D.; Weber, H. B.; Seyller, T. Towards Wafer-Size Graphene Layers by Atmospheric Pressure Graphitization of Silicon Carbide. *Nat. Mater.* **2009**, *8*, 203–207.
7. Sprinkle, M.; Siegel, D.; Hu, Y.; Hicks, J.; Tejeda, A.; Taleb-Ibrahimi, A.; Le Fèvre, P.; Bertran, F.; Vizzini, S.; Enriquez, H.; Chiang, S.; Soukiassian, P.; Berger, C.; de Heer, W. A.; Lanzara, A.; Conrad, E. H. First Direct Observation of a Nearly Ideal Graphene Band Structure. *Phys. Rev. Lett.* **2009**, *103*, 226803.
 8. Aristov, V. Y.; Urbanik, G.; Kummer, K.; Vyalikh, D. V.; Molodtsova, O. V.; Preobrajenski, A. B.; Zakharov, A. A.; Hess, C.; Hänke, T.; Büchner, B.; Vobornik, I.; Fujii, J.; Panaccione, G.; Ossipyan, Y. A.; Knupfer, M. Graphene Synthesis on Cubic SiC/Si Wafers. Perspectives for Mass Production of Graphene-Based Electronic Devices. *Nano Lett.* **2010**, *10*, 992–995.
 9. Chaika, A. N.; Molodtsova, O. V.; Zakharov, A. A.; Marchenko, D.; Sánchez-Barriga, J.; Varykhalov, A.; Shvets, I. V.; Aristov, V. Y. Continuous Wafer-Scale Graphene on Cubic-SiC(001). *Nano Res.* **2013**, *6*, 562–570.
 10. Chaika, A. N.; Molodtsova, O. V.; Zakharov, A. A.; Marchenko, D.; Sánchez-Barriga, J.; Varykhalov, A.; Babenkov, S. V.; Portail, M.; Zielinski, M.; Murphy, B. E.; Krasnikov, S. A.; Lübben, O.; Shvets, I. V.; Aristov, V. Y. Rotated Domain Network in Graphene on Cubic-SiC(001). *Nanotechnology* **2014**, *25*, 135605.
 11. Chaika, A. N.; Aristov, V. Y.; Molodtsova, O. V. Graphene on Cubic-SiC. *Prog. Mater. Sci.* **2017**, *89*, 1–30.
 12. Ouerghi, A.; Ridene, M.; Balan, A.; Belkhou, R.; Barbier, A.; Gogneau, N.; Portail, M.; Michon, A.; Latil, S.; Jegou, P.; Shukla, A. Sharp Interface in Epitaxial Graphene Layers

- on 3C-SiC(100)/Si(100) Wafers. *Phys. Rev. B* **2011**, *83*, 205429.
13. Gogneau, N.; Balan, A.; Ridene, M.; Shukla, A.; Ouerghi, A. Control of the Degree of Surface Graphitization on 3C-SiC(100)/Si(100). *Surf. Sci.* **2012**, *606*, 217–220.
 14. Ouerghi, A.; Balan, A.; Castelli, C.; Picher, M.; Belkhou, R.; Eddrief, M.; Silly, M. G.; Marangolo, M.; Shukla, A.; Sirotti, F. Epitaxial Graphene on Single Domain 3C-SiC(100) Thin Films Grown on off-Axis Si(100). *Appl. Phys. Lett.* **2012**, *101*, 21603.
 15. Abe, S.; Handa, H.; Takahashi, R.; Imaizumi, K.; Fukidome, H.; Suemitsu, M. Temperature-Programmed Desorption Observation of Graphene-on-Silicon Process. *Jpn. J. Appl. Phys.* **2011**, *50*, 70102.
 16. Velez-Fort, E.; Silly, M. G.; Belkhou, R.; Shukla, A.; Sirotti, F.; Ouerghi, A. Edge State in Epitaxial Nanographene on 3C-SiC(100)/Si(100) Substrate. *Appl. Phys. Lett.* **2013**, *103*, 83101.
 17. Gogneau, N.; Ben Gouider Trabelsi, A.; Silly, M. G.; Ridene, M.; Portail, M.; Michon, A.; Oueslati, M.; Belkhou, R.; Sirotti, F.; Ouerghi, A. Investigation of Structural and Electronic Properties of Epitaxial Graphene on 3C-SiC(100)/Si(100) Substrates. *Nanotechnol. Sci. Appl.* **2014**, *7*, 85–95.
 18. Hens, P.; Zakharov, A. A.; Iakimov, T.; Syväjärvi, M.; Yakimova, R. Large Area Buffer-Free Graphene on Non-Polar (0 0 1) Cubic Silicon Carbide. *Carbon N. Y.* **2014**, *80*, 823–829.
 19. Suemitsu, M.; Jiao, S.; Fukidome, H.; Tateno, Y.; Makabe, I.; Nakabayashi, T. Epitaxial Graphene Formation on 3C-SiC/Si Thin Films. *J. Phys. D. Appl. Phys.* **2014**, *47*, 94016.
 20. Wu, H.-C.; Chaika, A. N.; Huang, T.-W.; Syrlybekov, A.; Abid, Mourad; Aristov, V. Y.; Molodtsova, O. V.; Babenkov, S. V.; Marchenko, D.; Sánchez-Barriga, J.; Mandal, P. S.;

- Varykhalov, A. Y.; Niu, Y.; Murphy, B. E.; Krasnikov, S. A.; Lübben, O.; Wang, J. J.; Liu, H.; Yang, L.; Zhang, H. et al. Transport Gap Opening and High On–Off Current Ratio in Trilayer Graphene with Self-Aligned Nanodomain Boundaries. *ACS Nano* **2015**, *9*, 8967–8975.
21. Wu, H.-C.; Chaika, A. N.; Hsu, M.-C.; Huang, T.-W.; Abid, Mourad; Abid, Mohamed; Aristov, V. Y.; Molodtsova, O. V.; Babenkov, S. V.; Niu, Y.; Murphy, B. E.; Krasnikov, S. A.; Lübben, O.; Liu, H.; Chun, B. S.; Janabi, Y. T.; Molotkov, S. N.; Shvets, I. V.; Lichtenstein, A. I.; Katsnelson, M. I. et al. Large Positive in-Plane Magnetoresistance Induced by Localized States at Nanodomain Boundaries in Graphene. *Nat. Commun.* **2017**, *8*, 14453.
 22. Gupta, B.; Notarianni, M.; Mishra, N.; Shafiei, M.; Iacopi, F.; Motta, N. Evolution of Epitaxial Graphene Layers on 3C SiC/Si(111) as a Function of Annealing Temperature in UHV. *Carbon* **2014**, *68*, 563–572.
 23. Babenkov, S. V.; Aristov, V. Y.; Molodtsova, O. V.; Winkler, K.; Glaser, L.; Shevchuk, I.; Scholz, F.; Seltmann, J.; Viefhaus, J. A New Dynamic-XPS End-Station for Beamline P04 at PETRA III/DESY. *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.* **2015**, *777*, 189–193.
 24. Huang, P. Y.; Ruiz-Vargas, C. S.; van der Zande, A. M.; Whitney, W. S.; Levendorf, M. P.; Kevek, J. W.; Garg, S.; Alden, J. S.; Hustedt, C. J.; Zhu, Y.; Park, J.; McEuen, P. L.; Muller, D. A. Grains and Grain Boundaries in Single-Layer Graphene Atomic Patchwork Quilts. *Nature* **2011**, *469*, 389–392.
 25. Fasolino, A.; Los, J. H.; Katsnelson, M. I. Intrinsic Ripples in Graphene. *Nat. Mater.* **2007**, *6*, 858–861.

26. Hibino, H.; Kageshima, H.; Maeda, F.; Nagase, M.; Kobayashi, Y.; Yamaguchi, H. Microscopic Thickness Determination of Thin Graphite Films Formed on SiC from Quantized Oscillation in Reflectivity of Low-Energy Electrons. *Phys. Rev. B* **2008**, *77*, 75413.
27. Riedl, C.; Coletti, C.; Iwasaki, T.; Zakharov, A. A.; Starke, U. Quasi-Free-Standing Epitaxial Graphene on SiC Obtained by Hydrogen Intercalation. *Phys. Rev. Lett.* **2009**, *103*, 246804.
28. Srivastava, N.; He, G.; Luxmi; Feenstra, R. M. Interface Structure of Graphene on SiC(0001). *Phys. Rev. B* **2012**, *85*, 41404.
29. Feenstra, R. M.; Srivastava, N.; Gao, Q.; Widom, M.; Diaconescu, B.; Ohta, T.; Kellogg, G. L.; Robinson, J. T.; Vlassiouk, I. V. Low-Energy Electron Reflectivity from Graphene. *Phys. Rev. B* **2013**, *87*, 41406.
30. Doniach, S.; Sunjic M. Many-Electron Singularity in X-ray Photoemission and X-ray Line Spectra from Metals. *J. Phys. C: Solid State Phys.* **1970**, *3*, 285-291.
31. Shirley, D. A. High-Resolution X-Ray Photoemission Spectrum of the Valence Band of Gold. *Phys. Rev.* **1972**, *55*, 4709-4714.
32. Powell, C. J. The Quest for Universal Curves to Describe the Surface Sensitivity of Electron Spectroscopies. *J. Electron Spectros. Relat. Phenomena* **1988**, *47*, 197–214.
33. Krawczyk, M.; Zommer, L.; Kosiński, A.; Sobczak, J. W.; Jablonski, A. Measured Electron IMFPs for SiC. *Surf. Interface Anal.* **2006**, *38*, 644–647.
34. Tanuma, S.; Powell, C. J.; Penn, D. R. Calculations of Electron Inelastic Mean Free Paths. IX. Data for 41 Elemental Solids over the 50 eV to 30 keV Range. *Surf. Interface Anal.* **2011**, *43*, 689-713.

35. Shirley, E. L.; Terminello, L. J.; Santoni, A.; Himpsel, F. J. Brillouin-Zone-Selection Effects in Graphite Photoelectron Angular Distributions. *Phys. Rev. B* **1995**, *51*, 13614–13622.
36. Rusponi, S.; Papagno, M.; Moras, P.; Vlaic, S.; Etzkorn, M.; Sheverdyayeva, P. M.; Pacile', D.; Brune, H.; Carbone, C. Highly Anisotropic Dirac Cones in Epitaxial Graphene Modulated by an Island Superlattice. *Phys. Rev. Lett.* **2010**, *105*, 246803.
37. Derycke, V.; Soukiassian, P.; Mayne, A.; Dujardin, G.; Gautier, J. Carbon Atomic Chain Formation on the β -SiC(100) Surface by Controlled $sp \rightarrow sp^3$ Transformation. *Phys. Rev. Lett.* **1998**, *81*, 5868–5871.
38. Derycke, V.; Soukiassian, P.; Mayne, A.; Dujardin, G. Scanning Tunneling Microscopy Investigation of the C-Terminated β -SiC(100) $c(2 \times 2)$ Surface Reconstruction: Dimer Orientation, Defects and Antiphase Boundaries. *Surf. Sci.* **2000**, *446*, L101–L107.
39. Aristov, V. Y. β -SiC(100) Surface: Atomic Structures and Electronic Properties. *Physics-Uspekhi* **2001**, *44*, 761–783.
40. Soukiassian, P. G.; Enriquez, H. B. Atomic Scale Control and Understanding of Cubic Silicon Carbide Surface Reconstructions, Nanostructures and Nanochemistry. *J. Phys. Cond Matt.* **2004**, *16*, S1611-S1658.
41. Semond, F.; Soukiassian, P.; Mayne, A.; Dujardin, G.; Douillard, L.; Jaussaud, C. Atomic Structure of the β -SiC(100)- (3×2) Surface. *Phys. Rev. Lett.* **1996**, *77*, 2013–2016.
42. Soukiassian, P.; Semond, F.; Douillard, L.; Mayne, A.; Dujardin, G.; Pizzagalli, L.; Joachim, C. Direct Observation of a β -SiC(100)- $c(4 \times 2)$ Surface Reconstruction. *Phys. Rev. Lett.* **1997**, *78*, 907–910.
43. Aristov, V. Y.; Douillard, L.; Fauchoux, O.; Soukiassian, P. Temperature-Induced

- Semiconducting $c(4\times 2) \Leftrightarrow$ Metallic (2×1) Reversible Phase Transition on the β -SiC(100) Surface. *Phys. Rev. Lett.* **1997**, *79*, 3700–3703.
44. Douillard, L.; Fauchoux, O.; Aristov, V.; Soukiassian, P. Scanning Tunneling Microscopy Evidence of Background Contamination-Induced 2×1 Ordering of the β -SiC(100) $c(4\times 2)$ Surface. *Appl. Surf. Sci.* **2000**, *166*, 220–223.
 45. Gupta, B.; Placidi, E.; Hogan, C.; Mishra, N.; Iacopi, F.; Motta, N. The Transition from 3C-SiC(111) to Graphene Captured by Ultra High Vacuum Scanning Tunneling Microscopy. *Carbon* **2015**, *91*, 378–385.
 46. Chaika, A. N.; Nazin, S. S.; Semenov, V. N.; Bozhko, S. I.; Lübben, O.; Krasnikov, S. A.; Radican, K.; Shvets, I. V. Selecting the Tip Electron Orbital for Scanning Tunneling Microscopy Imaging with Sub-Ångström Lateral Resolution. *Europhysics Lett.* **2010**, *92*, 46003.
 47. Chaika, A. N.; Orlova, N. N.; Semenov, V. N.; Postnova, E. Y.; Krasnikov, S. A.; Lazarev, M. G.; Chekmazov, S. V.; Aristov, V. Y.; Glebovsky, V. G.; Bozhko, S. I.; Shvets, I. V. Fabrication of [001]-Oriented Tungsten Tips for High Resolution Scanning Tunneling Microscopy. *Sci. Rep.* **2014**, *4*, 3742.

FIGURES AND CAPTIONS

Figure 1| STM and LEEM characterization of few-layer graphene synthesized on SiC(001)| (a) STM image of few-layer graphene on SiC(001) demonstrating the nanostructured overlayer. The image was measured at $U = -1.5$ V and $I = 45$ pA. (b) The same STM image after dz/dx differentiation showing atomic resolution. (c-e) Zooms of the STM image taken from the areas C, D, and E on panel (b). The images illustrate three preferential orientations of graphene lattices in the nanodomains. These three preferential lattice orientations are responsible for the eighteen diffraction spots indicated by colored hexagons in the μ -LEED patterns taken from one of the APDs (g or h). (f) DF-LEEM taken from few-layer graphene on SiC(001). Field of view is $10 \mu\text{m}$. Bright and dark areas correspond to APDs of cubic-SiC. (g and h) μ -LEED patterns taken from the surface areas indicated by G and H on panel (f). Each pattern reveals four substrate spots indicated by dashed rectangles and eighteen graphene spots (marked by blue, red, and yellow hexagons) corresponding to three preferential orientations of graphene lattices in each APD.

Figure 2| *In-situ* LEEM, μ -LEED, ARPES, and XPS showing control over the SiC(001) surface graphitization during heating in UHV. (a) μ -LEED (top) and μ -XPS data (bottom) obtained from the SiC(001)-c(2 $\times$ 2) reconstruction. To illustrate the principal difference between the c(2 $\times$ 2) and graphene spectra, the C 1s spectrum from the 1 ML graphene/SiC(001) system is presented on the same panel (bottom line). (b-d) μ -LEED, LEEM I - V reflectivity spectra, ARPES constant energy maps, and μ -XPS data obtained from one of APDs of the graphene/SiC(001) system at approximately 1 ML (b), 2 ML (c), and 3 ML (d) coverage. Top row: μ -LEED taken from a circular sample area ($d = 0.5 \mu\text{m}$) using a 44 eV electron beam (left) and LEEM I - V curves demonstrating one (b), two (c), and three (d) minima (indicated by arrows) corresponding to the number of the synthesized graphene layers (right). Middle row: Photoemission angular distribution maps taken at 0.5 eV (left) and 1.5 eV (right) binding energies, measured using a 47 eV photon energy. Bottom row: Experimental XPS C 1s spectra (black circles) obtained with 330, 400 and 450 eV photon beams for 1, 2 and 3 ML from selected circular sample areas ($d = 2 \mu\text{m}$) and results of the spectra decomposition (red, blue, green and cyan lines).

Figure 3| ARPES constant energy maps near the Fermi level measured for one of the Dirac cones. (a-h) Constant energy ARPES intensity maps taken near one of the K points at binding energies (E_B) from 0 to 2.0 eV, showing the electronic structure in the k_x - k_y plane ($h\nu = 47$ eV). **(i)** Schematic diagram of the $E(k)$ dispersions near six corners of the Brillouin zone.

Figure 4| LEEM and ARPES characterization of the nanostructured monolayer graphene. (a) DF-LEEM taken from the 1ML graphene/SiC(001) system. (b and c) Corresponding photoemission patterns taken for domains B and C in panel (a) at $E - E_F = 0.5\text{eV}$, measured with $h\nu = 47\text{eV}$ from a circular sample area ($d = 2\ \mu\text{m}$). (d and e) Dispersion of the Dirac cones obtained by a cut through the data at coordinates which correspond to the dashed lines in patterns (b) and (c).

Figure 5| Model of few-layer graphene growth on β -SiC(001). (a) A schematic model showing the non-rotated graphene lattice on top of the SiC(001)-c(2 $\times$ 2) surface reconstruction. Carbon and silicon atoms are shown as grey and yellow spheres, respectively, with c(2 $\times$ 2) carbon dimers highlighted by red spheres. The distances between neighboring carbon atoms of the c(2 $\times$ 2) reconstruction are shown by a blue distorted hexagon. The red square indicates the c(2 $\times$ 2) unit cell, the green square shows the distorted coincidence quadrilateral resembling a doubled c(2 $\times$ 2) unit cell. (b) Quasi-3D view of the SiC(001)-c(2 $\times$ 2) reconstruction. (c) A model of the graphene honeycomb lattice with the quadrilaterals showing the surface and overlayer cells with a small mismatch. (d) A schematic model of the few-layer graphene growth on SiC(001): At the beginning of the surface graphitization, domains with a non-rotated honeycomb lattice nucleate in accordance with panel (a), then $\pm 13.5^\circ$ -rotated lattices start to grow from the linear defects, which become the nanodomain boundaries in the nanostructured graphene overlayer. (e,f) Atomically resolved STM images of the SiC(001)-c(2 $\times$ 2) surface (e) and trilayer graphene synthesized on a SiC/Si(001) wafer (f).

Figure 6. Photoemission electron microscopy of trilayer graphene/SiC(001). (a,b) PEEM images at two magnifications and (c) photoemission spectra measured with Hg-lamp excitation averaged over different sample areas marked at (b).

TABLES

Table 1. Parameters of deconvolution for the C 1s spectra measured from the β -SiC(001)-c(2 $\times$ 2) reconstructed surface at different photon energies (Figure 2a). The percentage of the Lorentzian function in the mixed Gaussian-Lorentzian (GL) profiles is shown in parentheses. The intensities of the bulk and surface components are given as areas under the corresponding lines.

	hν = 325 eV				hν = 400 eV			
	Shape	FWHM (eV)	Area (a.u.)	Area (%)	Shape	FWHM (eV)	Area (a.u.)	Area (%)
SiC bulk component	GL(70)	0.71	1	35.77	GL(70)	0.73	1	63.91
SiC(001)-c(2$\times$2) surface comp.	GL(65)	0.97	1.80	64.23	GL(65)	1.03	0.57	36.09

Table 2. Parameters of deconvolution for the C 1s spectra of single- (1ML), double- (2ML), and triple-layer graphene (3ML) synthesized on the β -SiC/Si(001) sample (Figures 2b-d). The percentage of the Lorentzian function in the symmetric Gaussian-Lorentzian (GL) lines corresponding to bulk SiC component is shown in parentheses. Graphene lines were fitted by asymmetric Doniach-Sunjc (DS) lines with the asymmetry parameter as indicated. The intensities of the bulk SiC and graphene components are given as areas under the corresponding lines.

		hν = 330 eV				hν = 400 eV				hν = 450 eV			
		Shape	FWHM (eV)	Area (a.u.)	Area (%)	Shape	FWHM (eV)	Area (a.u.)	Area (%)	Shape	FWHM (eV)	Area (a.u.)	Area (%)
1 ML	SiC bulk	GL(45)	0.91	1	11.36	GL(50)	0.90	1	20.46	GL(50)	0.90	1	27.03
	Graphene	DS(0.029)	0.59	7.80	88.64	DS(0.026)	0.65	3.89	79.54	DS(0.029)	0.68	2.70	72.97
2 ML	SiC bulk	GL(45)	0.93	1	4.31	GL(50)	0.93	1	10.59	GL(50)	0.91	1	16.37
	Graphene	DS(0.030)	0.59	22.20	95.69	DS(0.028)	0.64	8.45	89.41	DS(0.032)	0.70	5.11	83.63
3 ML	SiC bulk	GL(50)	0.93	1	1.85	GL(50)	0.89	1	5.24	GL(50)	0.88	1	8.71
	Graphene	DS(0.028)	0.55	53.14	98.15	DS(0.032)	0.62	18.07	94.76	DS(0.029)	0.63	10.48	91.29