Multiple $\pi$-bands and Bernal stacking of multilayer graphene on C-face SiC, revealed by nano-Angle Resolved Photoemission

Leif I. Johansson1, Rickard Armiento1, Jose Avila2, Chao Xia1, Stephan Lorcy2, Igor A. Abrikosov1, Maria C. Asensio2 & Chariya Virojanadara1

1Department of Physics, Chemistry and Biology, Linköping University, SE-58183 Linköping, Sweden, 2Synchrotron SOLEIL, L’Orme des Merisiers, Saint Aubin-BP 48, 9192 Gif sur Yvette Cedex, France.

Graphene-based two-dimensional science has made a major impact on both fundamental and applied condensed matter physics. Epitaxial graphene grown on the basal planes of silicon carbide is considered a most promising route for the development of carbon based nano-electronics. Large-scale epitaxial films with atomic layer defined termination, highly desirable for applications as well as for fundamental and functionalization studies, have been grown on Si-terminated SiC substrates. On the C-terminated SiC(000-1) surface graphene films with similarly large scale uniformity has so far not been possible to produce.

Epitaxial graphene prepared on C-face SiC has moreover been claimed to be fundamentally different compared to Si-face graphene. Whereas Si-face graphene exhibits sharp Low Energy Electron Diffraction (LEED) spots and Bernal (AB) stacking, the macro LEED diffraction pattern published from C-face graphene was smeared out into a strongly modulated diffraction ring. This, together with Surface X-ray diffraction results and moiré patterns observed in STM topographs, was interpreted to indicate that the graphene layers on the C-face stack in such a way that adjacent layers are rotated with respect to each other. This rotational disorder was suggested to explain why epitaxial graphene films, about ten layers thick, in conventional ARPES measurements show single layer electronic properties, i.e. a single linearly dispersing $\pi$-band with the Dirac point located close to the Fermi level. Graphene on the C-face has therefore been called multilayer epitaxial graphene and suggested to order azimuthally in a particular way with alternating rotations of the layers, which results in an electronic band structure of isolated/decoupled graphene layers. This is very different compared to the band structure of Si-face Bernal stacked graphene where only a single graphene layer gives rise to one $\pi$-band cone and linearly dispersing bands close to the K-point. Bi- and tri-layer graphene give rise to two and three cones, respectively, and $\pi$-bands showing a non-linear dispersion close to the K-point.

Because of these reported fundamental differences between C-face and Si-face graphene we have studied graphene samples sublimation grown on nominally on-axis C-face SiC. Low Energy Electron Microscopy (LEEM), X-ray Photo Electron Electron Microscopy (XPEEM), and selected area LEED (micro-LEED) data shows formation of fairly large (some $\mu$m) grains (crystallographic domains) of graphene exhibiting sharp (1 $\times$ 1) spots in micro-LEED, and different azimuthal orientations of adjacent grains. The C-face graphene...
sample utilized in the present ARPES study has these characteristics and grains with a thickness ranging from one to seven layers (see Fig. S1 in Supplementary information). However, only one π-band cone could be resolved at the K-point using conventional ARPES\textsuperscript{13,21} or XPEEM\textsuperscript{7}, i.e. in selected area constant initial energy photoelectron angular distribution patterns, although LEEM showed multilayer graphene on most parts of the sample surface. If the graphene layers are not rotationally disordered more than one π-band should definitely be observed\textsuperscript{19,20} from a multilayer graphene grain having any of the common stacking sequences, Rhombohedral (ABC), Bernal (AB) or simple hexagonal (AA) stacking (see Fig. S2 in Supplementary information). However, conventional ARPES does not have the lateral resolution\textsuperscript{4,12,21} to investigate single grains on C-face graphene samples and in the XPEEM measurements\textsuperscript{8,9} high enough energy and momentum resolutions could not be achieved to resolve if multilayer grains exhibited more than one π-band.

The micro- and nano-ARPES end station at the ANTARES beamline\textsuperscript{22,23} offers a lateral resolution of ca. 90 μm and 120 nm, respectively. At the same time it allows an overall energy and momentum resolution of 5 meV and 0.005 Å\textsuperscript{-1} at 100 eV photon energy in nano-ARPES measurements. Thus, nano-ARPES opens up the possibility to perform detailed studies of the electron band structure from the μm-sized graphene grains typically forming on C-face samples. Micro-, or multigrain-ARPES analysis, on the other hand, can be used to investigate the distribution of azimuthal angles of the grains and determine the dominant azimuthal orientation present. Information about this is also directly visible in macro-LEED patterns, as shown below.

A micro-ARPES spectrum of the π-band structure collected at an electron emission angle (θ\textsubscript{e}) that corresponds to probing around the K-point and along one Γ−K−M direction (azimuthal angle φ = 0°), is shown in the inset of Fig. 1. From sets of such spectra recorded at azimuthal angles from 0° to 220° the constant initial energy photoelectron angular distribution patterns, E\textsubscript{i}(k\textsubscript{∥},k\textsubscript{⊥}), displayed in the two semicircular segments in Figs. 1(a) and (b) are extracted, at energies of respectively 0.5 eV and 1.4 eV below the Fermi energy. Three additional K-points at azimuthal angles of around 60°, 120° and 180° are clearly observed in these segments, but also additional features that originate from graphene grains of different orientations. This is even more clearly illustrated in Fig. 1(c), which shows a circular cut through the two first main K-points in Figs. 1(a) and (b). At φ ≈ 0° half a Dirac cone and at φ ≈ 60° a full Dirac cone are clearly observed. These main Dirac cones show linear dispersion close to the K-point, similar to earlier reported conventional ARPES results\textsuperscript{8,13,20}. The bands are quite broad, however, so they may contain contributions from several unresolved bands. Two weaker Dirac cones are also visible at φ around 20° and 40°. These latter cones originate from graphene grains with different azimuthal orientations and correspond to the additional features observed in between the dominant K-points in Figs. 1(a) and (b). The macro-LEED pattern recorded from the sample, see Fig. 2(a), also reveals one dominant and two additional fairly equally favored orientations of the graphene grains. The Fermi surface constructed from the micro-ARPES data is displayed in Fig. 2(b), for comparison. In both pictures the weaker additional diffraction spots/K-points appear elongated which we interpret to indicate a larger spread in the azimuthal orientation of these grains compared to those contributing to the dominant spots/K-points.

For the purpose to distinguish the graphene grains on the sample, using nano-ARPES, the scanning mode of the ANTARES microscope was utilized. The result when setting the analyzer to measure the integrated intensity of photoelectrons, at the K-point at φ = 59° and in 0.5 μm steps over the sample, is shown in Fig. 3(a). Only grains having this dominant azimuthal orientation should give any appreciable intensity and multilayer grains higher intensity than monolayer graphene grains. The four locations labeled B, C, D and E in Fig. 3(a), were among the positions selected to collect nanoARPES spectra from. The resulting spectra, displayed in separate panels, show (b) one, (c) three, (d) four and (e) five π-bands. The color labeling increases from blue-green to orange-red at the four locations labeled B to E. A straightforward conclusion is that the number of π-bands reflects the number of graphene layers in different grains. From the purple/darkest blue areas no π-band contribution is discernable so these areas correspond to locations where the graphene grains have a different azimuthal orientation. The same procedure to map the intensity and select positions to collect nanoARPES spectra from, was repeated at φ = 39°, which correspond to one of the weaker cones in Fig. 1(c). Two spectra are displayed in (f) and (g) and show one and two π-bands, respectively. The azimuthal
angle is obviously almost $1^\circ$ off from the correct $\Gamma - K - \bar{M}$ direction for these grains, since the $\pi$-cones are not cut through their centers so an “apparent" band gap" appears. It deserves to be mentioned that the grains probed in this azimuth shows only one or two $\pi$-bands and clearly a larger spread in the azimuthal orientation of the grains. If one looks carefully in Figs. 3(b)–(e) one can also notice a variation in the location of the $\pi$-band maximum relative to the Fermi level, although smaller, implying a small variation in the orientation of the grains contributing to the dominant cones. This should, however, not affect the band structure within a grain and the goal to determine if more than one $\pi$-band could be resolved from grains of multilayer graphene on C-face SiC. The nano-ARPES spectra displayed in Fig. 3 illustrate clearly that grains are identified and that one can resolve from one and up to five $\pi$-bands. This corresponds well to the LEEM data from this sample, which shows grains with a thickness ranging from one to seven layers of graphene (see Fig. S1 in Supplementary information). The nano-ARPES spectra thus demonstrate unambiguously that also C-face graphene exhibits multiple $\pi$-bands from grains having multiple layers of graphene. The Dirac point is in Figs. 3(b)–(e) seen to be located fairly close to the Fermi level in grains having from one to five layers of graphene. This is noticeably different compared to Si-face graphene where the Fermi level is displaced 0.45 eV above the Dirac point for monolayer graphene, due to electron transfer from the substrate.

The stacking within the graphene grains can be determined from the differences in $\pi$-band dispersions close to the $K$-point for free standing graphene for different stacking sequences (see Figs. S2 and S3 in supplementary information). We find a striking similarity between the experimental results and the theoretical band structure for Bernal stacked graphene shown in Figs. 3(h)–(k), calculated in the framework of the density functional theory (see method section for computational details). Other stacking sequences considered, e.g., rhombohedral and simple hexagonal, can be ruled out as they give qualitatively different band dispersions (see Figs. S2 and S3 in Supplementary information). In the theoretical band structure, the separation between the outermost bands at the $K$-point increases...
somewhat reduced from the value of the Wigner-Seitz radius (for C the radius used is 1.640 Å). For the band structure plot we calculated energy eigenstates at 256 k-points on the high symmetry line through the Gamma point. Each separate segment between two such points is drawn with a line thickness and shade based on the total summed projection onto all angular momentum states for the C atoms on the topmost surface layer. The shading was normalized to full black for the largest summed projection. The intensity and width of the bands thus indicate their relative surface character.

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Author contributions
L.I.J. and C.V. conceived the experiments. L.I.J., C.X., C.V., J.A., S.L. and M.C.A. performed the experiments and the data analysis. R.A. and I.A.A. were responsible for the band structure calculations. L.I.J., C.V. and R.A. wrote the manuscript with input from all other co-authors.

Additional information
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The authors neglected to cite a related study that reports an ARPES experiment indicating the presence of multiple $\pi$ bands in multilayer graphene on C-face SiC. This is given below as Reference 1. In the present Article, nano-ARPES band mappings of individual graphene grains unambiguously show that multilayer C-face graphene exhibits multiple $\pi$-bands.

Reference
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